PowerPlant Chemistry Contents 1999-2000 (Volume 1 and 2)

Issue	Author(s)	Title	Key Words
1999, 1(4)	Joseph B. Conlin, Donald Vinnicombe	Periodic Oxygen Treatment for Drum Boilers	Boiler Water Treatment, Oxygenated Treatment
	Kevin J. Shields Barry Dooley Thomas H. McCloskey Barry C. Syrett John Tsou	Copper Transport in Fossil Plant Units	Copper Transport, Copper Deposition, Plant Cycle Chemistry
	Andrew G. Howell	Mitigation of Copper Deposition in High Pressure Turbines of Utility Drum Boilers	Copper Transport, Copper Deposition, Plant Cycle Chemistry
	Karol Daucik	Strategy of Ion Exchange Demineralisation at ELSAM	Makeup Water Treatment, Ion Exchange
	Michael A. Sadler Barry Dooley	Possible Methods of Reducing the Cost of Condensate Polishing on Fossil Fired Power Stations	Condensate Polishing, Off-Site Regeneration, Ammonium Form Operation, Design Cost
	Eduard Noks Anton Olkis Roland Kleinstück Donald A. Johnson	The Use of Ozone as Microbiocide in Cooling Water Treatment - Experiences with an "All-Organic" Program	Cooling Water, Phosphonate, Ozone

Issue	Author(s)	Title	Key Words
1999, 1(5)	Donald A. Palmer Simon L. Marshall J. Michael Simonson M. S. Gruszkiewicz	The Partitioning of Acetic, Formic, and Phosphoric Acids Between Liquid Water and Steam	Thermodynamics, Partitioning, Acetic Acid, Formic Acid, Phosphoric Acid
	Chung-Hsien Liang Yu-Ting Ting-Chin Cheng Hsien-Cheng Wang	Root Cause of High Differential Pressure Across Condensate Polisher During Plant Startup	BWR, Condensate Polishing, Crud, Pressure Drop
	Albert Bursik	State of the Art in Fossil Plant Cycle Chemistry on the Threshold of the Next Millennium	Fossil Plant Cycle Chemistry Review
	ABB Alstom Power	Water Chemistry of Combined Cycle Power Plants - Standard Specifications	Combined Cycles, HRSG, Guidelines
	Søren Kiil Jan E. Johnsson Kim Dam-Johansen	Modelling of Limestone Dissolution in Wet FGD Systems: The Importance of an Accurate Particle Size Distribution	Flue Gas Desulfurization, Modeling, Limestone Dissolution

Issue	Author(s)	Title	Key Words
1999, 1(6)	Barry Dooley	Fossil Plant Cycle Chemistry and Steam	Fossil Plant Cycle Chemistry Review, Steam Chemistry
	Serguei Lvov N.N. Anikiev A.V. Bandura Fabio Sigon Giorgio Perboni	MULTISYS: Computer Code for Calculating Multicomponent Equilibria in High-Temperature Subcritical and Supercritical Aqueous Systems	Thermodynamics, Modeling, High-Temperature Equilibria
	Frank McCarthy Jason E. Bane Gerard O'Connor	Oxygenated Treatment in a 300 MW Drum Type Boiler	Boiler Water Treatment, Oxygenated Treatment
	Rudolph Blum Ole Hede Larsen Niels Henriksen	Superheater Failures in Ultra Supercritical Boilers - Cases from Fynsværket, Vestkraft, and Skærbækværket Power Plants	Ultra Supercritical Units, Boiler Tube Failures
	Siemens KWU	Steam purity Target Values for Main and Auxiliary Steam Condensate; HMN and GuD Series Turbines	Steam Chemistry Guidelines

Issue	Author(s)	Title	Key Words
2000, 2(1)	Serguei N. Lvov Xinagyang Y. Zhou Sergey M. Ulyanov Digby D. Macdonald	Potentiometric Measurements of Association Constants and pH in High Temperature HCl(aq) Solutions	Thermodynamics, pH Measurements at High Temperatures
	Jan Stodola Peter Tremaine Violet Binette L. Trevani	Volatility of Copper Corrosion Products in a Power Generation Cycle	Copper Transport, Copper Deposition, Copper Volatility
	Milan Zmítko Tomáš Grygar Václav Štengl Jan Šubrt Adriana Kláriková	Hydrothermal Reactions of Corrosion Products in Reactor Primary Conditions	PWR Primary Cycle, Spinels, Zinc Addition
	Shane Filer Vicki Alison	Temperature Compensation and Reference Electrode Considerations for Power Plant High Purity Water pH	Monitoring, pH Measurements
	Till Wacker Michael Rziha	Method for Determination of Traces of Short-Chain Organic Acids in Plant Cycles	Ion Chromatography, Organic Acids

Issue	Author(s)	Title	Key Words
2000, 2(2)	Gernot Repphun Andreas Hiltpold	Corrosion Potential and Contamination in BWR	BWR Chemistry, Corrosion Potential
	Robert Svoboda Harald Sandmann Frank Gabrielli	Steam/Water Cycle Chemistry: Current Developments and Challenges in the Future	Combined Cycles, HRSG, Boiler Water Treatment, Failures
	Karol Daucik Niels Henriksen Jørgen Peter Jensen	Supercritical Steam Oxidation of Steel Surfaces	Ultra Supercritical Units, Boiler Tube Failures, Hydrogen Monitoring
		VGB Conference „Chemistry in Power Plants 1999"	Conference Abstracts
		Sixth International Conference on Cycle Chemistry in Fossil Plants	Conference Agenda
	Michael Luckas Bernd Heiting	Simulation of the Flue Gas Desulfurization Process for FGD Scrubbers in Power Plants	Flue Gas Desulfurization, Modeling, Adipic Acid

Issue	Author(s)	Title	Key Words
2000, 2(3)	Digby D. Macdonald Jing Pang Peter J. Millett	The Hydrolysis of Metal Salt Solutions at Elevated Temperatures	Thermodynamics, High-Temperature pH Measurements, Modeling
	Anwer Puthawala Norbert Henzel	Hydrogenation of Reactor Water in BWR Plants by On-Line Membrane Electrolyzers	BWR Chemistry, Hydrogen Dosing, On-Line Membrane Electrolyzers
	Elton W. Floyd J. C. Carpenter Robert Svoboda Ronnie Jones	On-Line Chemical Cleaning of a Water-Cooled Generator Stator	Water-Cooled Generator Stator, Chemical Cleaning
	Hiroshi Takaku	Plant Cycles with Heat Recovery Steam Generators: Water Quality Guidelines (Japan)	Combined Cycles, HRSG, Cycle Chemistry Guidelines
	Albert Bursik	Cycle Chemistry Monitoring in Combined Cycle Units and in Units with Heat Recovery Steam Generators	Combined Cycles, HRSG, Cycle Chemistry Monitoring

Issue	Author(s)	Title	Key Words
2000, 2(4)	Barry Dooley Peter S. Chang	The Current State of Boiler Tube Failures in Fossil Plants	Boiler Tube Failures, Review
	Oleg A. Povarov Valery N. Semenov Alexander N. Troitsky Barry Dooley	Effect of Chemistries and Steam Purity on Moisture Generation and Formation of Liquid Films in Turbine Stages	Steam Chemistry, Moisture Generation, Liquid Films
	Andrew Howell Ken Weisser	Loss of Copper Sampled from Main Steam	Sampling, Monitoring
	Hans-Hermann Neuburg Ladislav Bursik	Corrosion and Efficiency Control by Continuous Cleaning of Condenser Tubing	Condenser Tubing, Continuous Mechanical Cleaning
	Eric V. Maughan Gerhard Gericke Graham Roscoe	The Measurement of TOC in the Cycle Fluid of Modern Power Plants and Correct Selection of Monitoring Equipment	Monitoring, TOC
		Conference: Membranes in Drinking and Industrial Water Production	Conference Program

Issue	Author(s)	Title	Key Words
2000, 2(5)	Donald A. Palmer Pascale Bénézeth David J. Wesolowski	Boric Acid Hydrolysis: A New Look at the Available Data	Thermodynamics, Boric Acid Hydrolysis
	Dietmar Nieder Bernhard Stellwag Richard Ruf Jürgen Haag Micael Jürgensen	Zinc Injection in the Primary Coolant of PWR for Dose Rate Reduction - Experience from Biblis and Obrigheim	PWR Primary Coolant Chemistry, Zinc Injection, Dose Rates
	Hans-Curt Flemming	Membranes and Microorganisms - Love at First Sight and the Consequences	Membrane Processes, Biofilms, Biofilms Prevention
	Tamara I. Petrova Oleg A. Povarov Valery N. Semenov Valery I. Kashinsky Andrei Yu. Petrov	Effect of Different Chemistries on the Concentration of Impurities in the Liquid Film: Experimental Turbine Tests	Steam Chemistry, Liquid Films
		Reverse Osmosis Cleaning, Sanitizing, and Storage	Reverse Osmosis, Cleaning, Sanitizing, Storage

Issue	Author(s)	Title	Key Words
2000, 2(6)	Bo Yang	Advances in Localized Corrosion Control in Cooling Water Systems	Cooling Water, Localized Corrosion, Corrosion Monitoring
	Geoff Spowart	Cooling Water Contamination - The People Issues	Cooling Water, Biological Contamination, *Legionella*, *Naegleria fowleri*
	Geoff J. Bignold	Chemistry in Combined Cycle Units - The National Power Experience	Combined Cycle Units, Cycle Chemistry Review
	Siu-Kuen Hui Chun-Pang Yuen	The Development of the Equilibrium Phosphate Treatment of the HRSG	Combined Cycle Chemistry, HRSG, Equilibrium Phosphate Treatment
	Andre G.L. Zeijseink R. Heijboer	Experience with Different Water/Steam Treatments in Combined Cycle Units in the Netherlands	Combined Cycle Chemistry, HRSG, Failures, Organics
		EPRI Sixth International Conference on Cycle Chemistry in Fossil Plants	Conference Abstracts

Issue	Author(s)	Title	Key Words
2000, 2(7)	R. Barry Dooley Douglas E. Hubbard	Latest Development in Fossil Plant Cycle Chemistry	Fossil Plant Cycle Chemistry and Steam Chemistry Review
	Folmer Fogh	Spray Dray Absorption Product - An Efficient Absorbent for Wet Desulfurization	Flue Gas Desulfurization
	Geoff Banks	The Environmental and Process Advantages of Membrane Technology for the Production of Demineralized Water in Environmentally Sensitive Areas	Membrane Processes, Reverse Osmosis, Gas Transfer Membranes, Elektrodeionization
	Stephen Kerr	TRIPOL® Condensate Polishing at Stanwell Power Station: Six Years of Operational Experience	Condensate Polishing, Tripol® System
	Mark Wyburn	Economics of the Eraring Power Station Water Reclamation Plant	Water Reclamation, Use of Secondary Effluents
	Colin Gwynne Shane Shipperley	Should I Chemically Clean My Boiler? - An Australian Case Study	Boiler Tube Failures, Chemical Cleaning, Cleaning Criteria

Issue	Author(s)	Title	Key Words
2000, 2(8)	Arvind D. Belapurkar Narendra M. Gupta	A Hydrophobic Catalyst for Recombining H_2/D_2 and O_2 in Nuclear Reactors	Recombination of Hydrogen and Oxygen at Room Temperature, Pt/PE Catalyst
		VGB Conference "Power Plant Chemistry 2000"	Conference Program
	Des McInnes Ray Sutton	Oxygen Treatment, Australia Wide	Oxygenated Treatment Application Review
	Karol Daucik	Is Countercurrent Regeneration an Option for Condensate Polishing?	Condensate Polishing, Separate Beds, Countercurrent Regeneration, Kinetics,
	Jean-Claude Calay Coralie Goffin	The Use of EDI to Reduce the Ammonia Concentration in Steam Generator Blowdown of PWR Nuclear Power Plants	PWR, Steam Generator Blowdown, Electrodeionization, Ammonia Removal
	Alan Whitehead R. Grant Rowe	Water and Steam Use in Gas Turbines in GE Combined Cycle Plants	Gas Turbines, Water and Steam Quality Requirements
		Eskom International Conference on Power Plant Chemistry	Call for Papers
	Dirk J. Hanekom	Cooling Water Chemistry Limitations and the Method of Evaluating the Best Value for Money Options	Cooling Water, Zero Effluent Discharge, Anion-Free Flocculant, Lime Softening

Issue	Author(s)	Title	Key Words
2000, 2(9)	Donald A. Palmer Pascale Bénézeth David J. Wesolowski Scott A. Wood Caibin Xiao	The Solubility of Metal Oxides and Hydroxides at High Temperatures: Results and Implications of Recent ORNL Measurements	Thermodynamics, High-Temperature Solubility, Review
	Andrzej Anderko Malgorzata M. Lencka	Modeling Transport Properties of Electrolyte Solutions in Wide Concentration and Temperature Ranges	Thermodynamics, Transport Properties, Modeling
	Robert Svoboda Maurice Bodmer Harald Sandmann	Impact of Organic Impurities on Steam Turbine Operation	Steam Chemistry, Organics, Turbine Failures
	Joseph Lyons Jason E. Bane	Characterization of Organic Matter and a Field Study of Its Role in Turbine Corrosion	Organics, Turbine Failures
	Geoff J. Bignold	Sources of Corrosive Conditions in Low Pressure Steam Turbines	Steam Chemistry, Turbine Failures, Turbine Deposits
	Miroslav Šťastný Miroslav Šejna	Analysis of Heterohomogeneous Condensation of the Steam Flowing in a Turbine Cascade by Numerical Two-Population Model	Modeling, Heterohomogeneous Condensation

Issue	Author(s)	Title	Key Words
2000, 2(10)	Valil S. Sathyaseelan S. Velmurugan Appadurai L. Rufus et al.	Analysis of Constituents of a Decontamination Formulation Containing Complexing Agents and Transition Metal Ions	Decontamination, Analytics
	Václav Petr Michal Kolovratník	Heterogeneous Effects in the Droplet Nucleation Process	Modeling, Heterogeneous Nucleation
	Ivo Jiříček	Organics in Water/Steam Cycle - Three Case Studies	Behavior of Organics in Plant Cycles
	Albert Bursik	Chemistry in Cycles with Heat Recovery Steam Generators - a Problem and Challenge	Combined Cycle Units, HRSG; Cycle Chemistry selection
	Tamara I. Petrova Valery I. Kashinsky Andrei A. Zonov Evgeny P. Trishin	Alternative Treatments: Removal of Deposits from the Turbine Flowpath at Sakhalinskaya Power Plant Using a Filming Amine	Turbine Deposits, Chemical Cleaning, Octadecylamine
	Wilfried Kelm Hans-Dieter Kranz Detlef Vrhel	Alternative Treatments: Boilout of Drum-Type Boilers with HELAMIN®	Boilout of Drum Boilers, Application of Polyamines and Polyacrylates
		VGB Conference „Chemistry in Power Plants"	Conference Abstracts

Issue	Author(s)	Title	Key Words
2000, 2(11)	Amaladoss A.M. Prince Amaladoss M. Remona S. Velmurugan et al.	Dissolution Behaviour of Mixed Ferrites and Chromites in Aqueous Solutions Containing Chelating Agents	Decontamination, Magnetite, Substituted Magnetite, Chromites
	Pongalam Ananthan Gopala Venkateswaran	Influence of Carbon Steel and Other Structural Materials on the Dissolution of Hematite	Decontamination, Hematite, Regenerative Dilute Chemical Decontamination
	Erhard Liebig Robert Svoboda Herbert Hehs Harald Sandmann	Combined Cycle Plants: New Concepts - New Solutions	Combined Cycles, HRSG, New Concepts
	Manuel de Martín Mas Marta Solloa Sáiz Elías Rodríguez Martín Alberto Hervías Gómez	Cycle Chemistry in Iberdrola's Velilla Power Plant (Unit 2)	Drum Boilers, AVT without Hydrazine Application
	Risto Sonninen	Experiences from Oxygenated Water Treatment at Kymijarvi Power Station	Once-Through Boiler, Oxygenated Treatment

Issue	Author(s)	Title	Key Words
2000, 2(12)	Barry Dooley Warren P. McNaughton	Recent Developments in Understanding of the Phase Transition Zone in the Low Pressure Steam Turbine	Steam Chemistry Review
	M. Lasch U. Krumpholz G. Klessen C. Scheuerer	The Application of Ozone for the Purification of Waters in Nuclear Power Plants	Nuclear Power Plants, Spent Fuel Pool, Clarification, Ozone
	W. Hater B. Mayer M. Schweinsberg	Development of Environmentally Benign Scale Inhibitors for Industrial Applications	Cooling Water, Scaling, Scale Inhibitors
	Jürgen Koppe D. Mielke D. Polster	Catalytic Disinfection of Circulation Cooling Water in Cooling Towers	Cooling Water, Disinfection, Catalytic Process
	Hong Xu	Alternative Treatments: Improvement of Flushing Procedure in Chemical Cleaning	Chemical Cleaning, Oxygen Scavenger

PowerPlant Chemistry Contents 2001 (Volume 3)

Issue	Author(s)	Title	Key Words
2001, 3(1)	William T. Lindsay, Jr.	Partitioning of Volatile Solutes in Steam Generating Apparatus	Thermodynamics, Volatility, Partitioning
	J. Dennis Aspden Ken J. Galt	Key Factors for a Successful Cycle Chemistry Programme	Cycle Chemistry Management, Cycle Chemistry Indicators
	Kamal Kishore Puspalata Rajesh Ghasi R. Dey Ashok G. Kumbhar	A Dilute Chemical Decontaminant Formulation Containing Gallic Acid as a Reductant	Decontamination, CANDU Reactors
	Thomas Klasen Klaus Görner	The Influence of Furnace Geometry and Wall Materials on the Combustion Process and the Prediction of Problem Areas in Waste Incinerators	Waste Incineration, Gas Side Corrosion, Fouling, Slagging, Modeling
	Hartmut Grupp	Monitoring of Used Oils and Fire-Resistant Fluids in Turbine Installations	Monitoring, Turbine Oil, Fire-Resistant Fluids
	Eric Maughan	Demineralisation of Water and the Elimination of TOC	Makeup Water Treatment, Organics, Monitoring

Issue	Author(s)	Title	Key Words
2001, 3(2)	Hans D. Pflug Eric V. Maughan George Mueller Gottfried Betz	Central Control Unit for On-Line Power Plant Chemistry, Part 1: Data Acquisition and Processing for On-Line Monitoring and Cycle Operation	Monitoring, Data Acquisition, Expert Systems
	Joachim Wasel-Nielen	The Treatment of Recirculated Cooling Water with Ozone	Cooling Water, Ozonation
	Jayappa Manjanna Gopala Venkateswaran Bailure S. Sherigara Peruduru V. Nayak	Reductive Dissolution of Chromium Substituted Hematites in V(II)-EDTA Formulation	Decontamination, BWR
	Klaus Knecht Richard Stark Karl Habeck	In-Core Sipping at BWR Plants in Only 16 Hours	BWR, Sipping
	Tomáš Prošek Pavel Novák	Irregular Corrosion of Austenitic Stainless Steel under Heat Transfer Conditions	Austenites, Corrosion, Heat Transfer
	Herbert Prenzel	Development of Ion Chromatography in Power Plant Chemistry	Ion Chromatography, Flue Gas Desulfurization, DeNOx Systems, Wastewater

Issue	Author(s)	Title	Key Words
2001, 3(3)	Barry Dooley Warren P. McNaughton	Appropriate Controls for Phosphate Boiler Water Treatments to Avoid Acid Phosphate Corrosion	Boiler Tube Failures, Acid Phosphate Corrosion, Hydrogen Damage, Equilibrium Phosphate Treatment
	Albert Bursik Ulrich W. Staudt	Carbon is Not Equal to Carbon – Comments on TOC Discussions	Cycle Chemistry Guidelines, Organics
	Tamara I. Petrova Andrei Yu. Petrov Julia V. Zhgenti Barry Dooley	Behavior of Acetate and Formate in Liquid Film in Steam Turbines	Cycle Chemistry, Partitioning, Steam Turbines
	Margareta Bugajski Bruno Wilhelmi Markus Horn	Refractory Non-Basic Mixes and Systems for Applications in Waste Incineration Units	Waste Incineration, Refractory Mixes
	Heinz-Peter Borchardt Carsten Holst Thomas Peters	Special Features of the Chemical Cleaning of HRSGs with Horizontal Evaporator Tubing	Chemical Cleaning, Heat Recovery Steam Generators
	Hans D. Pflug Eric V. Maughan Georg Mueller Gottfried Betz	Central Control Unit for On-Line Power Plant Chemistry, Part 2: Programmed Control of Cycle Chemistry and Other Areas of Power Plant Chemistry	Monitoring, Data Acquisition, Expert Systems

Issue	Author(s)	Title	Key Words
2001, 3(4)		Survey on Topics to Be Covered in Our Journal	Survey Reults
	Stephen E. Ziemniak	Solubility Behavior and Phase Stability of Transition Metal Oxides in Alkaline Hydrothermal Environments	Thermodynamics, Solubility, Transition Metal Oxides
	James A. Mathews	Cost of Chemical Excursions	Cycle Chemistry Management, Economics
	Francis Nordmann Michel Dijoux Agnès Stutzmann	EdF Approach for Fouling Mitigation	PWR, Secondary Cycle Chemistry, Fouling, Fouling Mitigation
		Eskom International Conference on Power Plant Chemistry and Process Water Treatment	Abstracts
	Neil B. Caris	On-Line Condensate Polishing Plant Resin Kinetic Challenge	Condensate Polishing, Kinetics, Kinetic Testing

Issue	Author(s)	Title	Key Words
2001, 3(5)	Neville F. Rieger R. Barry Dooley	The Influence of Electrostatic Charge in the Phase Transition Zone of a Steam Turbine	Steam Chemistry, Phase Transition Zone, Electrostatic Charging
	Sharon P. Mellor Felix W.R. Matthee	Operating Experience Gained During the Copper Oxide Plugging Incident in Koeberg Unit 1 Generator Stator	Generators, Water-Cooled Stators, Fouling, Cleaning
	Danny Traksel Donald A. Vinnicombe	Recent Advances of Ultraviolet Light Technologies in Water Treatment	Water Treatment, UV Oxidation,
	Nicholas C. Woodhouse	Factors Affecting Leachate Production at Lethabo Power Station Ash Dump	Ash Disposal, Leaching
	Karol Daucik	Accumulation of Ionic Impurities in the Plant Cycle	Plant Cycle Chemistry, Deposition, Concentration Processes
	Frances M. Cutler	Causes of and Cures for Chloride Leakage out of Condensate Polishers	Condensate Polishing, Chloride Leakage

Issue	Author(s)	Title	Key Words
2001, 3(6)	Otakar Jonas Lee Machemer Barry Dooley	EPRI ChemExpert: A Cycle Chemistry Advisor for Fossil Power Plants	Expert Systems
	Jo Savelkoul Peter Janssen Hans Verhoef	Monitoring of First Condensate Corrosion (FCC) in Industrial Steam Systems	Industrial Steam Generation, First Condensate, Corrosion, Monitoring
	Peter Wuhrmann	Automatic Quality Assurance in Power Cycle Monitoring	Monitoring, Quality Assurance
	Hans Duve Gregor Sudhoff	Measuring the Conductivity after UV Oxidation: A Reliable and Evaluated Method for the Detection of Organics in Boiler Feedwater and Condensate Returns	Monitoring, Organics, UV Oxidation
	David M. Gray	Advances in Cycle Chemistry Conductivity Measurement	Monitoring, Conductivity
	Ebbe Höffner	The On-Line Measurement of pH in High-Purity Water	Monitoring, Oxygen

Issue	Author(s)	Title	Key Words
2001, 3(7)	R. (Vis) Viswanathan W. T. Bakker	Materials for Ultra Supercritical Coal Power Plants – Part 1: Boiler Materials	Materials, Ultra Supercritical Cycles, Boilers
	Maarten C.M. Bruijs Lars P. Venhuis Henk A. Jenner George J. Licina David Daniels	Biocide Optimization Using an On-Line Biofilm Monitor	Cooling Water, Biofouling, Monitoring
	Ebbe Höffner	The On-Line Measurement of Low Level Dissolved Oxygen	Monitoring, Oxygen
	C.J. Brouckaert Dirk Hanekom C. Woodhouse C.A. Buckley	Optimal Location of a Membrane Treatment Plant in a Power Station	Membrane Techniques, Water Reuse, Modeling
	Mike van der Walt Abrie Wessels	Saving on Natural Resources with SRO – Desalination of Industrial Waste Water for Reuse at ESKOM Tutuka (Two Years Operating Experience)	Membrane Techniques, Water Reuse

Issue	Author(s)	Title	Key Words
2001, 3(8)	R. (Vis) Viswanathan W. T. Bakker	Materials for Ultra Supercritical Coal Power Plants – Part 2: Turbine Materials	Materials, Ultra Supercritical Cycles, Turbines
	Mrinal R. Pai Salil Varma Arvind D. Belapurkar Narendra M. Gupta	Development of Catalysts for Mitigation of Hydrogen in Water Cooled Nuclear Power Reactors – Part 1: Preparation, Characterization, and Activity Measurements	Nuclear Reactors, Hydrogen Mitigation, Catalysts
	Albert Bursik	Boiler Tube Failures in Industrial Drum-Type Steam Generators – Part 1: Feedwater Treatment and Under-Deposit Corrosion Failures	Industrial Power Generation, Boiler Tube Failures, Feedwater Treatment
	Herman J. Quakkelsteijn	Helium Leak Detection in Condenser Systems During Operation	Condensers, Leak Detection, Cooling Water Ingress, Air Inleakage
	Jørgen P. Jensen Lars D. Fenger Niels Henriksen	Cold-End Corrosion in Biomass and Waste Incineration Plants	Gas Side Corrosion
	Michael Hocquel Sven Unterberger Klaus R. G. Hein	Understanding Mercury Behavior – A Contribution to Higher Removal Efficiencies	Fossil Power Generation, Mercury Emissions

Issue	Author(s)	Title	Key Words
2001, 3(9)	Yujirou Uchino Osamu Yoshikawa Takashi Morimoto Senichi Tsubakizaki	Study on the Practical Application of a Method for Corrosion Potential Measurement in a Water Quality Monitoring System Used During Combined Water Treatment	Oxidation-Reduction Potential, Corrosion Potential, Monitoring
	Mrinal R. Pai Salil Varma Arvind D. Belapurkar Narenda M. Gupta	Development of Catalysts for the Mitigation of Hydrogen in Water Cooled Nuclear Power Reactors – Part 2: Poisoning Characteristics	Nuclear Reactors, Hydrogen Mitigation, Catalysts, Catalyst Poisoning
	Ashok S. Kerkar Mrinal R. Pai Salil Varma Narenda M. Gupta	Development of Catalysts for the Mitigation of Hydrogen in Water Cooled Nuclear Power Reactors – Part 3: A Prototype Recombiner Device	Nuclear Reactors, Hydrogen Mitigation, Catalytic Recombination
	François de Dardel Brian J. Hoffman	New Ion Exchange Resins for Condensate Polishing	Ion Exchange, Condensate Polishing
	Philip Fatula Stefan Hilger Fred Muir Paul Gross Darin Cunningham	The Cost of Producing Demineralized Water in the Gulf Coast with Upflow "Packed Beds"	Ion Exchange, Makeup Water Treatment, Economics
	Frances M. Cutler	Maintaining Healthy Resin – Appropriate Resin Specifications, Testing, Treatment, and Storage	Ion Exchange, Ion Exchange Resin Performance

Issue	Author(s)	Title	Key Words
2001, 3(10)	Miroslaw Gruszkiewicz David B. Joyce Simon L. Marshall Donald A. Palmer John M. Simonson	The Partitioning of Acetate, Formate, and Phosphates around the Water/Steam Cycle	Cycle Chemistry, Partitioning, Thermodynamics
	Otakar Jonas William Steltz Barry Dooley	Steam Turbine Efficiency and Corrosion: Effects of Surface Finish, Deposits, and Moisture	Turbines, Steam Chemistry, Efficiency, Corrosion
	Karl-Franz Hahn Hans-Günter Seipp	Layup Measures during Shutdowns for Turbogenerator Sets and Water/Steam Cycles in Large Utility Plants	Layup
	Michael A. Sadler	Ammonium Form Operation of Condensate Polishing Plants – Position and Possible Developments	Condensate Polishing, Ammonium Form Operation
		Press Release for IAPWS Annual Meeting in Gaithersburg, MD, USA, September 2001	Press Release
	Jayappa Manjanna Gopala Venkateswaran	Preparation and Dissolution of La-, Ce- and Zr-Containing Magnetites in Citric Acid-EDTA-Ascorbic Acid Mixtures	Decontamination
		VGB Conference "Chemistry in Power Plants 2001"	Abstracts

Issue	Author(s)	Title	Key Words
2001, 3(11)	Bruce A. Larkin Francis M. Cutler	Off-Site Regeneration of Condensate Polishing Resins	Ion Exchange, Condensate Polishing
	David C. Shallcross Phil Renouf	Modeling Radial Flow Ion Exchange Performance for Condensate Polisher Conditions	Ion Exchange, Condensate Polishing
	Irma Dedekind Denis Aspden Ken J. Galt Dave Dalgetty	Oxygenated Feedwater Treatment at the World's Largest Fossil Fired Power Plant	Plant Cycle Chemistry, Oxagenated Treatment
	Des McInnes Javier Cabrera David Ryan	Tarong Energy's Experience with Unit Cycle Copper Transport and Deposition	Plant Cycle Chemistry, Copper Transport, Copper Deposition
	Peter A. Zhdan James E. Castle	Copper Pick-up from Admiralty Brass in Ultra Pure Water	Plant Cycle Chemistry, Copper Transport
	Miroslav Šťastný	Effect of Copper Deposition on the Steam Turbine Efficiency and Capacity	Plant Cycle Chemistry, Copper deposition
	Albert Bursik	PowerPlant Chemistry's Survey on Layup Practices in Fossil-Fired Power Plants	Layup
		International Conference on "Boiler Tube Failures, HRSG Tube Failures, and Inspections"	Abstracts

Issue	Author(s)	Title	Key Words
2001, 3(12)	Barry Dooley Richard Tilley	Tube Failures in Conventional Fossil Plants and in HRSGs	Boiler Tube Failures, Fossil Plants, Heat Recovery Steam Generators
	Barry Dooley Todd Kuntz Warren McNaughton Steve Paterson Michael Pearson Kevin J. Shields	EPRI's Heat Recovery Steam Generator Tube Failure Manual	Boiler Tube Failures, Heat Recovery Steam Generators
	Richard R. Harries Michael J. Willet	Flow Accelerated Corrosion in HRSGs: Interdependence of Cycle Chemistry and Design	Boiler Tube Failures, Heat Recovery Steam Generators
	Matthias Meirer Sigrid Harmgart	Fouling and Slagging Phenomena in Hard Coal-Fired Steam Generators	Coal-Fired Boilers, Fouling, Slagging
	Norbert Eimer Matthias Meierer	Optimization of Chemical Process Engineering of Flue Gas Desulfurization Systems	Flue Gas Desulfurization, System Optimization
		10th Annual International Chemistry On-Line Process Instrumentation Seminar	Seminar Evaluation

2002's Scientific and Technical Contributions
Papers in English

Author(s)	Title	Abstract	PPChem
Oleg A. Povarov Tamara I. Petrova Valeri N. Semenov Valeri I. Kashinski Alexander N. Troitskii Andrei Yu. Petrov R. Barry Dooley	Study of the Electrochemical Properties of Liquid Films Formed on Turbine Stages	Loss of efficiency and corrosion failures of blades and disks of turbine stages operating in the phase transition region persist as one of the important problem areas in the utility industry. In recent years many countries have been dealing with this problem, but so far electrochemistry phenomena occurring inside the turbines have been poorly studied. The oxidation-reduction potential is one of the basic parameters which control the conditions for the formation of protective films on the surface of construction materials; the metal potential may be used to estimate the occurrence of corrosion processes. The conductivity of the early liquid films formed on metal surfaces of the turbine flow path is one of the factors which largely influence the rate of electrochemical corrosion. Previous tests have shown that liquid films generated on the surface of the turbine flow path may contain large amounts of corrosive impurities. This problem is also related to recent EPRI research aimed at modifying the moisture condensation process and improving unit efficiency and capacity. The paper presents the results of a study on the oxidation-reduction potential, metal potential, and conductivity of liquid films performed under an EPRI research program at the Moscow Power Institute.	2002, 4(1), 5–11
Valeri N. Semenov Alexander N. Troitskii Roman V. Agapov Konstantin O. Povarov R. Barry Dooley	Measurement of the Conductivity of Liquid Films in the Turbine Flow Path	This paper describes a new technique of liquid film conductivity measurement on the surfaces of the turbine flow path. In addition, it contains the results of a study on the effect of different chemistries with controlled addition of impurities on the liquid film conductivity on the turbine surface and a study on the dependence of the conductivity level in liquid films on the initial wetness of steam at the inlet on the test channel. The information presented is based on experimental results produced on a test turbine with an attached test channel at the Moscow Power Institute.	2002, 4(1), 13–17
Albert Bursik	Chemistry On-line Instrumentation – What Will Be the Needs of the Power Plants of Tomorrow?	In the last decade, the power industry has undergone important changes. The most important changes have been privatization and/or the breaking up of large state-owned utilities, deregulation of the power market in many countries, the appearance of new independent power producers on the power market, and the introduction of heat recovery steam generators and combined cycles in the power industry. These changes markedly influence conditions on what optimum power plant chemistry can be realized. The most serious consequences for power plant chemistry are the reductions in staff and the reduced willingness to spend money on a seemingly unproductive power plant area – power plant chemistry. Under these conditions, it is very important to take advantage of and to exhaust all the features of the modern chemistry on-line instrumentation. Here, some deficiencies are clear, particularly deficiencies in the communication between the respective instruments, the central process control unit, and the remote users of the produced data. In addition, many of the on-line instruments available on the market require extensive calibration and validation. The contribution focuses on these aspects and tries to specify the future needs of the power industry with respect to the chemistry on-line instrumentation.	2002, 4(1), 18–21
Walter Wied Christoph Randt	Possibilities for Avoiding Deposits and Fouling in River Water-Cooled Condensers and Heat Exchangers	For the last 30 years or so, BASF Aktiengesellschaft has operated separate pipeline and drainage systems for cooling water and wastewater at its Ludwigshafen works. Waste water is disposed of via the works' own treatment plant; cooling water is fed back untreated into the Rhine. Because the quality of the river water has steadily improved in recent years, mussels and microorganisms (biofilms) tend to multiply in the works' once-through cooling systems, significantly reducing the efficiency of heat exchangers. Various possibilities exist for preventing blockages in heat exchangers, for example,	2002, 4(1), 23–27

		back flushing and filtration, with automatic wedge-wire filters having proved very successful. Biofilms can be efficiently countered with biocides. Even small concentrations are very effective, so that the legally prescribed limits are readily and reliably observed.	
Michael Rziha	General Instructions for Unit Layup	These instructions summarize the most important general layup actions. When applying these instructions, as a rule, the individual plant-specific issues have to be considered. Important aspects are, e.g., the planned mode of operation and the type of readiness for startup. For this reason, individual instructions have to be tailored to each individual plant cycle.	2002, 4(1), 31–33
Martin Mineur Manfred Rotermund	Deposits of Ammonium Chloride at Heat Exchanger Tubes of a Flue Gas Cleaning System	Deposits in flue gas apparatus and channels belong to the everyday annoyances of many operator teams. In the sewage sludge combustion plant VERA in Hamburg (Germany) first intense investigations and extensive experiments led to a valid explanation and to the solution of a problem in the countercurrent heat exchanger of the flue gas cleaning system.	2002, 4(1), 34–38
Helmut Nopper Wolfgang Metzner	A Tool for Cross-System Calculation of Water Chemistry Parameters in Power Plants	The WaChem water chemistry analysis program was developed for the calculation of cross-system water chemistry parameters in power plants. The PC program has a graphical user interface for modeling a plant heat flow diagram and performs an iterative cycle calculation of water chemistry parameters. The calculation results are presented graphically and can be output in diagrams and tables. WaChem can be used to analyze the existing power plant chemistry and to optimize it with case studies. The program can also be used as a knowledge base for on-line monitoring.	2002, 4(2), 69–71
Michael Rziha Bernd Senger Stephen Merry Alistair Greig	Chemical Operation Experience with the CCPP Cottam	The heat recovery steam generator in the combined cycle power plant Cottam is a new development in that it incorporates both drum type and once-through evaporators, the low pressure evaporator being a conventional drum type and the intermediate and high pressure evaporators having a once-through configuration. Both once-through and drum boilers are fed from the same condensate source. Flow through parallel, vertical evaporator tubes in this horizontal heat recovery steam generator is only upward, as in a natural-circulation boiler with horizontal gas pass. In contrast to standard once-through evaporators, a special fluid dynamics design results in a higher mass flow rate in tubes with increased heat absorption. This system requires different chemistries to be applied to the LP and the HP/IP evaporator water/steam circuits in order to minimize: • corrosion of the plant, • transport of corrosion products around the water/steam cycle, and • deposition of impurities within the water/steam cycle. Insufficient control of the water/steam cycle chemistry can result in dissolution of metal from the tubes and can cause them to weaken or fail. Several factors affect the process of corrosion in a boiler system. These include the type of metal used for construction, the dissolved gases and ions present in the water, and the temperature in the boiler and tubes. A boiler can outlast the economic life of the plant if the water chemistry and passivation are controlled to limit the type of corrosion to general surface corrosion. Experience gained during the commissioning and operating phase of the combined cycle power plant Cottam regarding cycle chemistry is outlined.	2002, 4(2), 73–79
Ladislav Bursik	Once-through Boiler as an Autoclave for Testing an Organic Cycle Treatment Chemical	An early condensate sampler supplied by Alstom Switzerland AG was employed to investigate the early condensate pH and the concentration of organic anions on Unit IV of the Munich South power station of SWM Munich. A mixture containing a low-volatile film-forming polyamine and volatile neutralizing and alkalizing amines was used for cycle chemistry treatment. Despite the unavoidable partial decomposition of the tested chemical, the pH of the early condensate is more alkaline than the main unit condensate.	2002, 4(2), 81–85

Karol Daucik	Layup Practice at ELSAM	This paper discusses the layup procedures for large power utility units. As almost all large units at ELSAM are once-through boiler units, the discussion is limited to these installations.	2002, 4(2), 91–92
Harry J. G. Polman Henk A. Jenner	Pulse-Chlorination®, the Best Available Technique in Macrofouling Mitigation Using Chlorine	In 1998, KEMA developed a new chlorination method called Pulse-Chlorination®. It enables optimal antifouling treatment with a minimum use of chlorine. This technology is based on the principle that in general mussels and clams have a recovery period after exposure to chlorination before opening fully and restarting filtration. The method takes advantage of this recovery time by using short successive periods of chlorination, alternating with periods without chlorine. The tests undertaken between 1998 and 2001 resulted in chlorine savings up to 50 % on a yearly basis, compared to regimes applied in earlier years. Results on site after one year with Pulse-Chlorination® show improved control of macrofouling and a better overall performance of the cooling water system. This in turn allows longer intervals between planned outages, thus spreading the running costs over three years rather than two years. There are additional advantages for power plants that use electrochlorination plants to produce hypochlorite. As the Pulse-Chlorination® reduces the hypochlorite dosage up to 50 %, only part of the installed equipment is used at any one time allowing maintenance of the unused electrochlorination plants. Because less hypochlorite is dosed, there is a reduction in chlorination by-products discharged and thus less environmental impact.	2002, 4(2), 93–97
John Murrer Steve Latter	Reducing the Costs of Ultrapure Water Production – A Case Study	The 380 MW combined cycle gas turbine power station in Peterborough changed its water supply from town mains to high purity reverse osmosis permeate in October 2000. The high purity water is produced from secondary treated sewage effluent using advanced membrane technology. Alpheus Environmental and British Gas staff have recently completed a study on the power station's demineralization plant to identify the differences in operating costs associated with the change in feedwater. The results show that the ultrapure water produced after the change to a high purity feed is of improved quality and that the demineralization plant regeneration operating costs have been reduced by over 90 %. The demineralization plant availability has increased from 78 to 98 % enabling almost 20 % more ultrapure water to be produced. The change in feedwater has also improved the local environment by significantly reducing the amount of waste chemicals discharged from the site.	2002, 4(2), 101–102
Brad Buecker	The Impact of Steam Condenser Performance upon Power Plant Efficiency	Efficient operation of steam-generating plants is of primary importance in these times of concern about environmental protection and rising energy costs. A steam generator has many features that improve efficiency, yet often they are taken for granted by plant personnel. These include the steam reheater, regenerative feedwater heaters, and the condenser. This article examines the basic thermodynamics of these systems, and illustrates why they improve efficiency. The forecast growth in world population will continue to increase electricity demand, which will require efficient design and operation of power plants around the world.	2002, 4(2), 103–105
Howard Ocken Sean Bushart	Radiation Exposure Management Update December 2001	Nuclear utilities are obligated to implement technology to protect plant personnel from the adverse effects of ionizing radiation. EPRI's Radiation Exposure Management Program supports two main activities to address this issue: [i] radiation control technology reduces shutdown radiation fields and [ii] radiation protection technology optimizes worker safety and productivity. This paper summarizes recent EPRI successes, which have helped U.S. nuclear utilities reach historic low levels of collective exposure.	2002, 4(3), 133–137
Ian A. McLure Andrei Yu. Petrov Duncan H. Gordon Malcolm Ball R. Barry Dooley	Interfacial Behavior at Above-Ambient Temperatures of Ionic and Non-Ionic Aqueous Solutions Important in Boiler Water Chemical Conditioning	The reliability and efficiency losses in steam turbines have been one of the major problems faced by the utility industry worldwide. The size of droplets in the last low pressure stages of the turbine is one of the most important factors affecting these losses. One method of controlling the droplet size might be by changing the surface tension in the turbine environment.	2002, 4(3), 139–146

		The paper presents results of EPRI sponsored research on the surface tension of various substances which might be present in or added to the power plant cycle as conditioning chemicals (inorganic salts, ammonium and amine compounds) and discusses whether they can exert a significant effect on surface tension in amounts typical for power plant operation.	
Frank Gabrielli Stephen Goodstine Thomas Mastronarde	Cold-End Corrosion in HRSGs	Many of the processes for increasing the efficiency of combined cycle plants can result in lower flue gas temperatures exiting the heat recovery steam generators and/or increased flue gas moisture content. These conditions can as a consequence increase the potential for corrosion of the low temperature gas-path components. The attack of these surfaces is generally referred to as cold-end corrosion. There are various aspects and components of cold-end corrosion, of which the most significant is dew point corrosion. The paper discusses these corrosion mechanisms of major significance to heat recovery steam generators as well as presents results from field and laboratory test programs.	2002, 4(3), 148–153
Pierre J. Ploumen	Avoiding HRSG-Tube Failures	Based on long-standing experience with the analysis of boiler tube failures, KEMA has expertise in the aspects that are crucial to avoiding tube failures. In particular, KEMA has gathered experience with heat recovery steam generator tubes over a period of 25 years. The crucial aspects concern the design of the boiler, the choice of design values, heat flux, and the water treatment. An overview of failures in heat recovery steam generators in the Netherlands is presented, including an explanation of the cause of the failure. Design aspects of heat recovery steam generators are also discussed, especially the necessity of achieving an equal flue gas flow distribution and water distribution. Furthermore, the influence of an unequal flow distribution on the tubes in a horizontal LP evaporator, resulting in increased heat flux, changes in steam quality and void fractions are discussed. The results are based on two-phase flow calculations of an LP evaporator with its own computer programs. Guidelines for water treatment are given to avoid tube failures.	2002, 4(3), 157–161
Albert Bursik	Boiler Tube Failures in Industrial Drum-Type Steam Generators – Part 2: Boiler Water Treatment	Boiler tube failures in industrial drum-type steam generators are very frequent. The root causes of the most serious boiler tube failure mechanisms occurring in industrial boilers are related to plant cycle chemistry. Unfortunately, the internationally accepted fossil cycle chemistry guidelines drawn up and published by VGB and EPRI do not reflect conditions typical in industrial steam generating installations. Part 1 of this paper dealt with the major differences between steam generation in utility boilers and in industrial steam boilers and other steam generating apparatus (e.g., differences in design, material selection, and cycle contaminants) and treated some site-specific issues influencing cycle chemistry. The applicability of VGB or EPRI feedwater guidelines was evaluated and discussed. This paper (Part 2 of a planned 4-part publication) deals with the applicability of internationally accepted boiler water treatments and with their influence on the occurrence of boiler tube failures.	2002, 4(3), 169–172
Stuart R. Holdsworth	Prediction and Prevention of Stress Corrosion and Corrosion Fatigue Cracking in LP Steam Turbines	The current ability to predict and prevent stress corrosion and corrosion fatigue cracking in LP steam turbines has developed from the knowledge base accumulated during the past 30 years from unilateral and collaborative R&D activities, in particular in Europe, Japan and the US, and from service experience. The two environmental cracking mechanisms are due to the combined influences of (i) material condition, (ii) environment and (iii) applied stress (static or cyclic). The influence of these factors on the material parameters used to predict stress corrosion and corrosion fatigue behavior is reviewed in the paper. The appropriate control of these factors and an understanding of the underlying damage mechanisms provide the basis for preventing stress corrosion and corrosion fatigue cracking in turbine components.	2002, 4(4), 197–208

Thomas McCloskey	Troubleshooting Turbine Steam Path Damage	Steam path damage, particularly of rotating and stationary blading, has long been recognized as a leading cause of steam turbine unavailability for large fossil fuel plants worldwide. Turbine problems cost the utility industry as much as one billion dollars per year. Failures of blades, discs, and rotors in both fossil and nuclear steam turbines represent a serious economic loss of availability and reliability for electric power generation suppliers and other energy supplies worldwide. Turbine problems such as deposition and erosion of blades can result in severe efficiency losses, resulting in significant economic penalties. The primary objective of this paper is to provide a methodology to identify the underlying damage or failure mechanisms, determine the root cause, and choose immediate and long-term actions to lessen or prevent recurrence of the problem.	2002, 4(4), 209–219
Kevin J. Shields Ewa Labuda	Operational Tube Failures in Heat Recovery Steam Generators: Metallurgical and Water Chemistry Perspectives	Operators of combined cycles with heat recovery steam generators are reporting an increasing extent of boiler tube failures. The most important failure mechanisms include flow-accelerated corrosion in low pressure evaporators and under-deposit corrosion in high pressure evaporators. Careful examination of the failed tubes and the cycle chemistry applied is essential for identifying the actual failure mechanism and for determining or confirming the actual failure root cause. The failure appearance and other likely microscopic and metallurgic features as well as the failure location help to identify the possible failure mechanisms. Determining the root cause includes, among other things, evaluation of possible environmental factors (e.g., cycle chemistry in the case of water-touched tubes). This paper describes the troubleshooting procedure and approach applied in two tube failure cases, in the low pressure evaporator of a dual pressure unit and in the high pressure evaporators of two dual pressure units.	2002, 4(4), 221–228
Fred V. Ellis	Root Cause Failure Assessment of Waterwall Tubing	An in-depth study of the waterwall tubing failures at Unit 1 of the Newington Station was performed. The service related damage/failure mechanisms were hydrogen damage, oxygen pitting, and corrosion fatigue. The tubing failure history showed a significant increase in the failure rate from approximately four tube failures per year for the years prior to the middle of 1991, to failure rates from approximately seven to twenty failures per year for the years after the third quarter of 1993. The cycle chemistry data analysis showed that the principal reason for the increased failure rate is ingress of contaminants, primarily chlorides and oxygen. The chloride ingress was due to both minor and major condenser leaks. The condenser problems are the direct result of wiring the cathodic protection system in reverse polarity, the significant corrosion activity due to this error, and the failure of remedial measures (application of plastic coating) to stop the leaks. The oxygen ingress was attributed to possible leaks at the deaerator and unit layup procedures. The stress ranking, environment parameter, and equivalent operating hours information were used in determining the probable root cause of failure for the corrosion fatigue failures. For the locations with the higher stress ranks of B and C (burner corners/attachments, buckstay and economizer door attachments), the major root cause of failure influence is excessive stresses/strains. Corrective action requires redesign and modifications to alleviate the applied stresses/strains. For the locations with the lowest stress rank of D, the major root cause of failure is the environmental factors of poor water chemistry and boiler layup. Corrective actions are to rehabilitate and/or replace the condenser tubing, utilize the nitrogen blanket system during unit shutdown, and to inspect the deaerator for possible leak paths and repair as required.	2002, 4(4), 229–234
Andrei Yu. Petrov Abdolreza Zaltash D. Tom Rizy Solomon D. Labinov	Study of Flue Gas Emissions of Gas Microturbine-Based CHP System	The number of distributed energy resources such as gas microturbines and combined cooling, heating and power systems has increased markedly over the last several years. Environmental issues (i.e., emissions, noise) are among the most important aspects of operating these systems. This paper presents the results of an emissions study of the Combined Cooling, Heating and Power Integration Test Facility (microturbine-based with heat recovery) located at the ORNL.	2002, 4(4), 235–239

Howard Ocken Keith Fruzzetti Paul Frattini Christopher J. Wood	Recent Developments in PWR Zinc Injection	This paper reviews the status of zinc injection in PWRs. Initial field applications have been undertaken to mitigate degradation of Ni-base structural alloys by primary water stress corrosion cracking. The first U.S. demonstration was at Farley 2 in 1994; zinc injection was later initiated at Farley 1 and Diablo Canyon 1 and 2. Reactor water zinc levels are in the 30–40 $\mu g \cdot kg^{-1}$ range, since laboratory results have shown that this concentration is needed to mitigate primary water stress corrosion cracking. Zinc injection at low levels (~ 5 $\mu g \cdot kg^{-1}$) has been started at three Siemens-designed PWRs and at Palisades, where the aim is to lower shutdown radiation fields. All U.S. PWRs injecting zinc have seen significant decreases in shutdown dose rates. Available data suggests it is premature to conclude if zinc mitigates primary water stress corrosion cracking.	2002, 4(5), 261–265
Francis Nordmann Agnes Stutzmann Jean-Luc Bretelle	Overview of PWR Chemistry Options	This paper describes the main options for the primary and secondary water chemistry of PWRs. After having focused on corrosion mitigation in the past, the options now emphasize cost saving, ease and reliability of operation, low activities, and limitation wastes. For the primary coolant, the main options concern ways to get the optimum pH (lithium increase or enriched boric acid use), zinc addition, fuel axial offset anomaly limitation, and the best shutdown procedure to save time and efficiently eliminate radioactive elements. For the steam-water system, the main options concern mitigation of Alloy 600 MA stress corrosion cracking of steam generator tubing, flow-accelerated corrosion of carbon steel and the control of steam generator fouling by selection of the most appropriate secondary water treatment (pH, amine, hydrazine concentration, dispersant addition).	2000, 2(5), 269–276
Luis Carvalho Rosa Crovetto Gerry W. Sauve Paul Sehl	Cation Conductivity and Power Plant Reliability: A 20-Plant Survey	The purity of steam and boiler feedwater is one of the most important criteria for ensuring component availability and reliability in power plants. Steam turbine manufacturers are tying increasingly stringent steam purity requirements to warranty clauses of their machinery. Cation conductivity, with its many limitations, is the most prominent control parameter for steam purity enforced by turbine manufacturers. Low molecular weight aliphatic organic acids, carbon dioxide, and inorganic anions affect cation conductivity. According to the literature, specific corrosion effects of organic acids are inconclusive and deserve more research. Independent power producers (IPP), unlike most utility generating stations, operate with minimal staff. IPP owners, in trying to comply with the tighter steam purity requirements, incur higher capital and operating expenditures with sophisticated water treatment equipment and more complex monitoring instrumentation. Additional on-site laboratory complexity and meaningful interpretation of all the collected data also burden the typical high-efficiency IPP operation. This paper reports on a survey of twenty operating plants (mostly power plants) across Canada ranging in pressure from 6.2 to 19.65 MPa. The paper presents data collected during the survey. Organic acid concentration, cation conductivity, and selected inorganic anions showed no correlation to system reliability in any of the plants surveyed.	2002, 4(5), 281–284
R. K. Singh Raman	Thermal Scaling in the Context of Life Assessment and Microstructural Degradation of Weldments Steels in Steam Generation Systems	The paper discusses the estimation of remnant creep life and determination of crack velocity using thickness of oxide scales that are generally present on the in-service steam generating systems. The prevalence of in-service failures in the welds of Cr-Mo ferritic steels causes great concern in steam generating/handling systems of power plants. This paper discusses the non-uniform scaling behavior across microstructural gradients in weldments of pressure vessel steels. The necessity for developing a global model for life assessment by relating oxide scale thickness with the time-temperature history of in-service welded components is also discussed. The paper also presents evidence of steam corrosion-assisted deterioration in microstructure that can profoundly affect the creep life.	2002, 4(5), 285–289

Andrei Yu. Petrov Caibin Xiao Donald A. Palmer D. Whitney King	Chemiluminescence Method for the Determination of Sub-$\mu g \cdot kg^{-1}$ Copper Concentrations	Copper deposition in high-pressure steam turbines represents a significant source of performance and reliability loss to fossil power plants with mixed-metallurgy feedwater systems. Provisions for reliable and prompt monitoring of low concentrations of copper compounds at power plants as specified by recent copper guidelines have become more crucial. This paper presents the chemiluminescence method for the determination of low ($\mu g \cdot kg^{-1}$ and sub-$\mu g \cdot kg^{-1}$) copper concentrations and provides a comparison with ion chromatography and graphite furnace atomic absorption.	2002, 4(5), 293–295
Beverly Newton	Use of Ion Chromatography for Measuring Ions in Water to Protect the New Generation Gas-Fired, Combined Cycle Power Plants	The use of ion chromatography for monitoring corrosive ions in water has been implemented at several new combined cycle, gas fired power plants in the U.S. Due to stringent requirements for clean water to prevent corrosion and plugging of turbine components, this methodology is predicted to have a significant impact in extending useful operating lifetimes and to measurably increase the availability of components in contact with water. Ion chromatography, due to its ability to identify individual anion and cation species, to achieve parts-per-trillion detection limits, and to operate on-line, has played a central role in the effectiveness of these water chemistry monitoring programs. Ion chromatography has provided the capability to distinguish between corrosive and non-corrosive ionic intrusions, identify and eliminate sources of corrosive ingress, optimize and extend the lifetime of demineralizer resins, measure hideout return, determine mass balances, and maintain neutral anion-to-cation balances. Cost savings due to chemistry monitoring programs using ion chromatography have been estimated to be in the millions of dollars per year. This paper provides an overview of the applications and justification (using case studies) for using ion chromatography for the analysis of water in these new generation power plants.	2002, 4(5), 297–299
Anton E. Cattaert	Major Reliability and Lubricant Consumption Savings at Tutuka Power Station	The proper selection and management of lubricants is very important for both improvement of equipment reliability and reduction of operating cost. The paper briefly describes actions undertaken as part of the establishing and optimizing of a basic lubricant condition-monitoring program. These efforts have resulted in considerable cost savings.	2002, 4(5), 301–303
Barry Dooley	The Relationship between Cycle Chemistry and Performance of Fossil Plants	Cycle chemistry influenced failures and performance losses have increased recently on fossil plants worldwide. These directly affect the overall performance and cost the industry enormous amounts of money in availability loss and replacement power. For instance, the number of hydrogen damage incidences is at an all-time high, and the percentage of organizations experiencing each of the major chemically influenced boiler tube failures has increased drastically since 1997. The paper analyzes this situation in a number of ways. Firstly, the case is made that cycle chemistry is the major business in a fossil plant, and to be successful an organization needs to address the performance gaps associated with day-to-day operation, as well as the introduction of new technology and new ways of doing business. Secondly, a benchmarking process is introduced that has been applied to around 100 fossil plant organizations/plants/units. Deeper analysis of the areas "behind" the benchmarks illustrates how organizations need to link together all aspects of cycle chemistry around the plant, and that dealing with only one or two items is not sufficient and will lead to an increasing number of chemically influenced activities. Finally, analysis of all the results from this large number of organizations/units/plants leads to an indication of the most reliable chemistry treatment/plant system/materials combination. Thus, the way is clear for any organization that desires to improve or build in reliability and performance either in a new unit or as retrofit.	2002, 4(6), 320–327
Digby D. Macdonald	The Electrochemistry of IGSCC Mitigation	A brief review is presented of the electrochemical mitigation of intergranular stress corrosion cracking (IGSCC) in water-cooled reactor heat transport circuit structural materials. Electrochemical control and mitigation is possible because of the existence of a critical potential for intergranular stress corrosion cracking and due to the feasibility of modifying the	2002, 4(6), 329–335

		environment to displace the corrosion potential to a value that is more negative than the critical value. However, even in cases where the corrosion potential cannot be displaced sufficiently in the negative direction to become more negative than the critical potential, considerable advantage is accrued, because of the roughly exponential dependence of the crack growth rate on potential. The most important parameters in affecting electrochemical control over the corrosion potential and crack growth rate are the kinetic parameters (exchange current densities and Tafel constants) for the redox reactions involving the principal radiolysis products of water (O_2, H_2, H_2O_2), external solution composition (concentrations of O_2, H_2O_2, and H_2), flow velocity, and the conductivity of the bulk environment. The kinetic parameters for the redox reactions essentially determine the charge transfer impedance of the steel surface, which is shown to be one of the key parameters in affecting the magnitude of the coupling current and hence the crack growth rate. The exchange current densities, in particular, are amenable to control by catalysis or inhibition, with the result that surface modification techniques are highly effective in controlling and mitigating intergranular stress corrosion cracking in reactor coolant circuit materials.	
Andy Rudge Phil Turner Ajit Ghosh Wolfgang Clary David R. Tice	Chemical Cleaning of UK AGR Boilers	For the first time in their operational lives, UK AGR once-through boilers have been chemically cleaned. Chemical cleaning was necessary to avoid lost output resulting from boiler pressure drops, which had been increasing for a number of years. Chemical cleaning of these boilers presents a number of unique difficulties. These include lack of access to the boilers, highly sensitised 316H superheater sections that cannot be excluded from the cleaning flow path, relatively thin boiler tube walls and an intolerance to boiler tube failure because of the role of the boilers in nuclear decay heat removal. The difficulties were overcome by implementing the clean in a staged manner, starting with an extensive materials testwork programme to select and then to substantiate the cleaning process. The selected process was based on ammoniated citric acid plus formic acid for the principal acid cleaning stage. Materials testwork was followed by an in-plant trial clean of six boiler tubes, further materials testwork and the clean of a boiler tube in a full-scale test rig. An overview is presented of the work that was carried out to demonstrate that the clean could be carried out safely, effectively and without leading to unacceptable corrosion losses. Full-scale chemical cleaning was implemented by using as much of the existing plant as possible. Careful control and monitoring was employed to ensure that the cleaning was implemented according to the specified design, thus ensuring that a safe and effective clean was carried out. Full-scale cleaning has resulted in significant boiler pressure drop recovery, even though the iron burden was relatively low and cleaning was completed in a short time.	2002, 4(6), 339–346
Keiko Kudo Masako Yasutomi Hirohisa Kubota	Thermally Stable Anion Exchange Resin and Postulated Effect by Application in Condensate Polishing System	A strongly basic anion exchange resin which has a butylene spacer between the ion exchange group (trimethylammonium group) and the benzene ring has been found to have higher thermal stability than conventional anion exchange resin, which places the trimethylammonium group in the benzyl position. Thus it is now possible to operate anion exchange resin at higher temperatures than was previously acceptable. Elevated temperatures decompose the chemical structure of anion exchange resin at the anion exchange site. The rate of thermal decomposition is much higher with conventional anion exchange resin as compared to thermally stable anion exchange resin. In addition, it is known that in condensate polishing systems polystyrenesulfonic acid leaches out of cation exchanger. These polystyrenesulfonic acid species can be adsorbed at anion exchange sites of anion exchange resin. Thus, thermally stable anion exchange resin exhibits a higher adsorption capability for polystyrenesulfonic acid than does conventional anion exchanger, especially when they are utilized at elevated temperatures. In condensate polishing systems, the requirement for anion exchange resin with higher sulfate capability at elevated temperatures has been increasing in order to generate higher power levels for longer periods and to maintain the reliability of the power plant.	2002, 4(6), 349–353

Tony C.-T. Lam Robert P. Dewey	Probabilistic Analysis of Turbine Disc Stress Corrosion Cracking Incubation and Propagation	Stress corrosion cracking (SCC) is a common problem found on aging low pressure turbine rotors that operate in a wet/dry stream environment. While much has been published on the growth rate of SCC in turbine rotor disk materials, incubation time is rarely addressed. Since no effective way has been demonstrated to prevent disk rim SCC from occurring other than to replace the damaged rim with a weld repair of higher chromium content, a better understanding of incubation time could provide operators with a means to treat SCC before cracks are large enough to start to grow. This paper discusses the critical mechanisms involved in the SCC incubation process and describes a probabilistic approach to make meaningful assessments of incubation time. Data published for General Electric turbine rotors is used to test the model.	2002, 4(6), 357–362
Thomas C. Ruppel Alfred N. Mann Leo E. Makovsky	What Have We Learned in Seven Conferences on Unburned Carbon on Utility Fly Ash? – A Review of Past Conferences	The information presented in the previous seven Conferences on Unburned Carbon (UBC) on Utility Fly Ash, dating from 1995 to 2001, is reviewed. The objectives of the conferences have been (1) to provide a forum for ash associations, boiler manufacturers, entrepreneurial companies, federal and state government agencies, research personnel and utilities to discuss technical, regulatory and economic issues associated with UBC, and (2) to facilitate progress toward mitigating the problem. Past conference subjects have consisted of regulatory updates, experiences and observations, predictive performance tools, processing and utilization of high-UBC fly ash, high-UBC fly ash characterization, effects on specifications and resultant sales, and economics. The impact of the conferences towards understanding and mitigating the problem of UBC on fly ash is analyzed.	2002, 4(6), 365–375
Mirna Urquidi-Macdonald Stefany Lyn Jacesko Digby D. Macdonald Monica Salter-Williams	Importance of ECP in the Prediction of Radiation Fields in PWR and VVER Primary Circuits	A model has been developed for predicting mass and activity transport in the primary coolant circuits of PWRs and VVERs with the objective of demonstrating and quantifying the importance of the electrochemical corrosion potential (ECP) in determining the impact of both processes on reactor operation. The model initially employs a radiolysis/mixed potential code to calculate the ECP at four locations (core, hot leg, steam generator, cold leg) and the ECP is then used to estimate the local magnetite solubility. The solubility is then averaged around the loop to yield the "background" solubility. Comparison of the background solubility with the local solubility determines whether precipitation or dissolution will occur at any given point in the circuit under any given set of conditions. It is further assumed that the concentration of ^{59}Co in the coolant is given by the isotopic fraction of this species compared with iron averaged over all materials and weighted by the respective wetted areas. Activation of ^{59}Co to ^{60}Co is assumed to occur in the coolant phase by fast, epithermal, and thermal neutron capture. The calculated activity is then used to train an artificial neural network to establish relationships between activity at any given location and the operating properties of the reactor, including coolant pH, ECP, temperature, power level, etc. The model predicts that during shutdown, magnetite (and hence ^{59}Co) migrates to the core, where it is irradiated and activated, particularly during subsequent startup. During startup, the magnetite (and hence ^{60}Co) migrates from the core to out-of-core surfaces, where it establishes the radiation fields.	2002, 4(7), 384–390
Craig Torville	Power Station Chemists – Recent Past, Present Life and Visions of the Future	Challenges and key result indicators for power station chemists are economic, technical, and managerial. What should we carry from the past, to manage the present and meet future economic, technical, and managerial challenges? The results of an Australia-wide survey are presented in an attempt to develop a view of future impacts on the power station chemist's role.	2002, 4(7), 393–399
Sallie Fisher	My Dream Plant	A chemist with over 50 years experience in systems design for and monitoring the performance of high purity water production systems puts together pieces for primary treatment and condensate polishing for a future power plant with emphasis on reliable performance rather than capital cost.	2002, 4(7), 401–405
Sallie Fisher	Spotlight on the Cation Resin	A review of the overall dependence of sulfonic acid resin performance on divinylbenzene content shows that resin selection based on a single property is probably unwise.	2002, 4(7), 407–410

Geoff Spowart	Legionella – An Appendix to the Saga	This paper deals with the issues facing power stations attempting to manage Legionella in large scale cooling water systems. Australian power stations are keen to minimise Legionella levels and therefore are seeking to establish a standard suitable for the industry without the prescriptive requirements of the existing air conditioning standard. The issues surrounding metallurgy, environmental discharges, system complexity and makeup water quality and quantity are examined. The work that has been done over the past two years is detailed.	2002, 4(7), 411–412
David Knights	Reducing the Volume of Water in Tarong Power Station's Ash Dam	Tarong Power Station, a major supplier to Queensland's electricity grid, recently faced a potentially severe operational problem. A prolonged drought in the first half of the 1990s significantly depleted supplies of raw water. Water conservation measures were implemented, but required cooling tower blowdown to be stored in the on-site ash dam. Consequently, rising water levels in the ash dam posed a significant environmental risk. Several methods of water removal were considered, but a novel approach, using installed plant, was eventually chosen, with a very successful outcome. This paper traces the problem and its eventual solution.	2002, 4(7), 413–417
Graeme E. Batley Kenneth W. Riley	Power Stations and the ANZECC/ARMCANZ Water Quality Guidelines	The release of waters from coal-fired power stations may be of environmental concern in some environments. The management of large volumes of ash dam water can be particularly difficult. "Dry" landfill sites may also release trace elements where groundwater or rainwater comes into contact with the ash residue. A number of these elements are toxic or accumulate in organisms to an extent that biological function is impaired. The biological activity of the leached elements is a function of factors such as speciation (including organic complexation), pH and water hardness. Simple limits of water release based on concentration alone are often used in the licensing of power stations but are an inadequate parameter with which to manage water quality. The Australian and New Zealand Environment Conservation Council Water Quality Guidelines provide broad holistic guidance on discharge limits as well as detailed advice on the monitoring and assessment of environmental impact.	2002, 4(7), 419–423
David Addison Keith Hopkins Brad White	Oxygenated Treatment at Huntly Power Station Unit 2: Preliminary Results from Steady State and 2-Shifting Operation	Concerns over flow-accelerated corrosion (FAC) damage in the feed systems of the four Huntly Power Station 250 MW units and the corresponding risk to personnel and plant led to a decision in 1995 to eliminate the use of an oxygen scavenger (hydrazine) on all units and in February 2000 to a decision to go ahead with a trial of oxygenated treatment (OT) on Huntly Power Station Unit 2. The injection system, designed in-house, incorporates a single oxygen injection point between the condensate polisher and LP heater 1, injecting to a concentration of 50 $\mu g \cdot kg^{-1}$ dissolved oxygen based on condensate flow. Oxygen injection on Unit 2 commenced in October 2001. During oxygen injection, the deaerator is operated with the vent to condenser shut. Soluble and insoluble iron and copper measurements are made at the economiser inlet, boiler downcomer and main steam primary sample points. Problems have been experienced with the injection system control, passing valves in the deaerator leading to oxygen loss, air inleakage at the chemical analyser wet racks and analytical issues with dissolved oxygen and oxidation reduction potential measurements. Immediate changes in oxide layer morphology were observed during an internal inspection after two weeks of OT operation with previous FAC-damaged areas now showing the growth of a hematite dominated layer, giving an early favourable result for OT operation. Preliminary results from corrosion product sampling have indicated that no copper migration in the steam to the turbine has occurred and there is a decrease in insoluble iron levels during steady state operation. 2-shifting operation has led to a slight increase in the insoluble iron levels being detected above steady state values.	2002, 4(8), 449–455

Charles Emslander Alan Waddingham	Intergranular Corrosion in a Stainless Steel Reheater	Stainless steel has been used in power boilers for over 40 years in the hottest sections of the superheater and reheater. One of the most common alloys used in these sections is SA 213 TP304H. It provides a good balance of mechanical properties and corrosion resistance to minimize the effects from coal ash corrosion, high temperature oxidation and long term creep mechanisms. However, recurring failures in a stainless steel reheater prompted a root cause analysis and the development of an eddy current testing method.	2002, 4(8), 457–465
Michael A. Sadler	The Resin on Resin Technique for Minimising Sodium Levels in Water from CP Mixed Beds	The mechanisms by which traces of impurities can escape being removed by the ion exchange resins used in condensate polishing plants are generally well known. They can still be a problem when attempting to prepare very high quality water such as when using condensate polishing to purify condensate. Some of these mechanisms can be controlled by attention to the design and operation so that the effect known as equilibrium leakage often becomes the predominant mechanism controlling the leakage of ionic impurities in the treated condensate. Equilibrium leakage can itself be controlled by reducing the levels of ionic impurities remaining on resins after regeneration and so a considerable amount of effort has been directed at improving regeneration processes. When regenerating mixed beds it is essential to achieve as complete separation as possible, but although improvements can be made, some resin cross-contamination inevitably occurs. Several proprietary processes exist that seek to correct this problem and some have proved very effective. A simple non-proprietary technique, "Resin on Resin", represents a different approach to reducing the trace leakage of sodium that result from a small quantity of cation resin being entrained in the anion resin and so becoming sodium contaminated. The paper discusses the application of "Resin on Resin", the possible theoretical basis for its action and the results that have been reported by power stations that have adopted its use.	2002, 4(8), 467–472
S. Ian Garbutt Robin Walker	Quantitative Air Ingress Leak Detection in Power Plant Turbine Condensers	Power plant main turbine condensers often suffer from degradation in back pressure resulting in reduced output. When this is due to increased air ingress, it is not necessarily a function of ineffective detection, but had more to do with the fact that the source of the air ingress is often difficult to locate. Current methods of detection are either qualitative or quantitative in terms of the overall air ingress into the system. This, however, presents the problem to plant engineers of establishing the largest source(s) of air ingress. By their very nature, power plant vacuum systems are extensive and have remote/tortuously linked connections with the condenser, thereby providing a multitude of potential air ingress sites. Working on the 80/20 rule, the ability to quickly locate, from a few measurements, the largest sources of air ingress would represent a powerful tool and one of significant financial benefit. A technique developed over several years by QuantiFlo and used successfully in UK power plants is that of "Quantitative Air Ingress Measurement". Using strategically located tappings, the technique enables the plant engineer to rapidly focus on areas of high air ingress rather than spend valuable time finding "in-leakage" that when sealed, produces little or no change in condenser back pressure. Two case studies have been conducted within British Energy power plants. The first reduced the average condenser back pressure by 2.3 kPa (approximately 13 MW electrical) and highlighted areas for further potential gain. The second reduced the total air ingress from 0.0374 $kg \cdot s^{-1}$ (0.0288 $m^3 \cdot s^{-1}$) to 0.0160 $kg \cdot s^{-1}$ (0.0123 $m^3 \cdot s^{-1}$).	2002, 4(8), 475–481
Michael Thompson Anthony Dal-Corobbo Bassam Zaid	Cooling Tower Experience at Osborne Cogeneration	Cooling water for the 180 MW Osborne Cogeneration plant is sourced from a saltwater river. To comply with the local Environmental Protection Authority licensing requirements for the cooling water discharge temperature and concentration, a cooling tower and dilution water system are employed. The tower is a five-cell, counter flow, induced draught type. Biocides are dosed intermittently with no cooling tower blowdown and recirculated until measured chemical residuals decrease below detectable limits before blowdown is reinstated.	2002, 4(8), 483–486

		To date, the adopted cooling water system chemical dosing and operational regime is providing good scale control and biological activity has been confined to the cooling tower proper with no reported drop in performance of the single main condenser. Slime growth is problematic and ongoing below the tower fill, particularly on the outer structure. Bacteria testing of slime samples indicates vibrio strains are the main species present. Biocide dosing automation is being pursued and alternative biological control programs investigated for the effective control of this slime growth.	
Keith Fruzzetti Paul Frattini Phil Robbins Alan D. Miller Robert D. Varrin Marc Kreider	Dispersant Trial at ANO-2: Results from a Short-Term Trial Prior to SG Replacement	Corrosion products that make their way to the secondary side of pressurized water reactor (PWR) steam generators (SGs) via the feedwater can deposit on the SG tubes. These deposits can form an occluded region which inhibits heat transfer, leads to thermal hydraulic instabilities through blockage of tube supports and creates regions where corrosive species can concentrate along tubes and tube to tube support plate crevices. The performance of the SG is compromised not only by formation of an insulating scale, but by the removal of tubes from service due to corrosion. A promising new method for significantly reducing corrosion product deposition on the secondary side of recirculating steam generators is the use of online dispersant addition to help prevent the corrosion products from adhering to the steam generator surfaces. By inhibiting the deposition of the corrosion products, they are more effectively removed from the steam generator via blowdown. After completion of a significant and comprehensive qualification program, a short-term dispersant trial was performed at Arkansas Nuclear One Unit 2 (ANO-2) in Winter/Spring 2000, lasting approximately 3 months. A high purity, high molecular weight polyacrylic acid (PAA) dispersant produced by BetzDearborn was injected at low concentrations ($0.5\ \mu g \cdot kg^{-1}$ to $12\ \mu g \cdot kg^{-1}$) into the final feedwater. The blowdown iron removal efficiency was observed to increase by an order of magnitude and more with use of PAA. Normal chemistry parameters, such as blowdown cation conductivity and TOC/TIC, were unaffected by PAA application. The results and conclusions from the trial are presented and discussed.	2002, 4(9), 513–520
David G. Daniels	HRSG Waterside Failure Mechanisms	Heat recovery steam generators (HRSGs) are responsible for more and more of the steam generating capacity of many utilities. Unfortunately, they are also increasingly responsible for the number of tube failures in the system. Corrosion that leads to failures often begins before commissioning and is exacerbated by cycling operation. This article reviews common waterside failure mechanisms in HRSGs, where they occur, and what can be done to prevent failures in the future.	2002, 4(9), 521–526
Joseph W. Harpster	Reducing Dissolved Oxygen under Conditions of High Air Ingress	Recent considerations of steam and air mixture dynamics in operating condensers have led to a more thorough understanding of how condenser performance is affected by air in-leakage. Results of this model-based theoretical description, which are in agreement with measurement data from operating condensers, are reviewed and used to propose beneficial design features for new and re-tubed condenser assemblies. It is anticipated from this work that condensers can be designed which significantly reduce the amount of dissolved oxygen in condensate from locations of free air ingress above the hotwell level. This reduction also applies to other undesirable noncondensables that enter condensate driven by the same mechanism contributing to dissolved oxygen. When air in-leakage becomes sufficiently high, it contributes to excess back pressure on the turbine. In this region of high air in-leakage, the amount of dissolved oxygen can become very high. The design, therefore, minimizes or eliminates the corrosive effects of air in-leakage, both high and low, which is particularly important during periods of high demand when load must be maintained.	2002, 4(9), 535–541

K. Anthony Selby	Closed Cooling and Heating Systems in Power Plants	Closed recirculating systems are used for cooling and heating tasks in power plants. In the power plant environment, these "balance of plant" systems often do not receive the same attention as the steam generating/turbine cycle. Nonetheless, closed recirculating systems play an important role in the consistent and safe operation of the plant. Closed recirculating systems experience problems of corrosion, microbiological growth, and fouling. These problems can be minimized through appropriate chemical and physical treatment. Closed systems must be adequately monitored to determine treatment needs, control treatment programs and detect problems.	2002, 4(9), 543–547
Ken Natesan Ankur Purohit David L. Rink	Fireside Corrosion of Alloys for Combustion Power Plants	A program on fireside corrosion is being conducted at Argonne National Laboratory to evaluate the performance of several structural alloys in the presence of mixtures of synthetic coal ash, alkali sulfates, and alkali chlorides. Candidate alloys are also exposed in a small-scale coal-fired combustor at the National Energy Technology Laboratory in Pittsburgh. Experiments in the present program, which addresses the effects of deposit chemistry, temperature, and alloy chemistry on the corrosion response of alloys, were conducted at temperatures in the range of 575 °C – 800 °C for time periods up to ≈ 1850 h. Alloys selected for the study included HR3C, 310TaN, HR120, SAVE25, NF709, modified 800, 347HFG, and HCM12A. In addition, 800H clad with Alloy 671 was included in several of the exposures. Data were obtained on weight change, scale thickness, internal penetration, microstructural characteristics of corrosion products, mechanical integrity, and cracking of scales. Results showed that the relationship of corrosion rates to temperature followed a bell-shaped curve, with peak rates at ≈ 725 °C, but the rate itself was dependent on the alloy chemistry. Several alloys showed acceptable rates in the sulfate-containing coal-ash environment; but NaCl in the deposit led to catastrophic corrosion at 650 and 800 °C.	2002, 4(9), 549–555
H. Vasken Aposhian	Elemental, Mercuric and Organic Mercury: Biological Interactions and Dilemmas	The greatest exposure of the general population to mercury appears to be from the elemental mercury emitted by dental amalgams. The next greatest exposure is from methylmercury in seafood. One of the major sources of this methylmercury is from mercury emitted by power plants burning fossil fuel. After the mercury enters the atmosphere, some of it will be deposited in lakes, rivers, bays, seas and oceans. In an aquatic environment, inorganic mercury is converted to methylmercury by bacteria. Once in the methylmercury form, it is bioaccumulated up the food chain. The bacteria are consumed by other unicellular organisms that are eaten by small fish; small fish are eaten by bigger fish; then bigger fish are eaten by other animals and humans. Methylmercury and elemental mercury are efficiently absorbed by humans and are transported rapidly to and deposited in the brain. In the brain, methylmercury is converted very slowly to mercuric mercury while the elemental mercury is converted very quickly. Methylmercury and elemental mercury are extremely toxic to the developing central nervous system. Those at greatest risk are fetuses, very young children, women of childbearing age and pregnant women. There are no safe or reliable methods to remove these two forms of mercury and their biotransformant mercuric mercury from the human brain. The chelating agents DMPS (sodium dimercaptopropanesulfonate) and DMSA (dimercaptosuccinic acid) decrease the body's burden of mercury but not the brain's. Because of the toxicity of methylmercury, the major source of mercury emissions, namely, emissions from power plants, needs to be curtailed.	2002, 4(9), 557–561
Jack Bionda	Flue Gas SO_3 Determination – Importance of Accurate Measurements in Light of Recent SCR Market Growth	This paper presents background information on SO_3 formation, SCR operation, as well as a discussion of the inter-related nature of SCR performance and SO_3, and how each can affect balance of plant operation. A detailed discussion of applicable EPA, ASTM and instrument test methods for the determination of sulfuric acid mist is also presented. Testing challenges associated with flue gas sampling downstream of wet scrubbers is also discussed, as well as the limitations of each of the relevant test methods.	2002, 4(10), 582–589

John W. H. Price Brian Kerezsi	Thermal Shock Cracking in Carbon Steel Boiler Pressure Equipment – Guidelines for Initiation and Growth	Thermal shock cracking is an important damage mechanism for many pressurised components. The growth of thermal shock cracks is influenced by a combination of several factors including geometry, the severity of the thermal shocks, the applied mechanical loads and the environment. In the work reported here it is shown that thermal shock cracks will arrest if these factors are below certain limits. In other cases, the cracking can progress and eventually cause failure or other operational problems. This work seeks to determine the relevant levels of these factors. This paper presents an analysis of the crack growth mechanisms involved, including an assessment of the environmental effects. Proposals are presented as to the guidelines which might be used for design and operation of vessels to prevent the initiation of thermal shock cracking. The guidelines presented here are much more flexible than the highly restrictive guidelines published by EPRI in 1989 for economiser headers. The work also includes a study of the nature of the growth of the cracking. Most of the cracks are found to grow in conditions leading to arrest. This presents the possibility of fitness for purpose assessment of the cracking when it is found in service.	2002, 4(10), 590–596
Albert Bursik	Cation Conductivity – What Are We Talking About?	Cation conductivity monitoring in a plant cycle is the basic surveillance tool for detecting the ingress of contaminants in the cycle. Unfortunately, cation conductivity of a sample is a non-specific parameter. The kind of substances contributing to or causing a cation conductivity increase are not known. For this reason, evaluating the value measured is not easy or is hardly possible. The results of calculations performed show that more precise information about the cycle contamination during periods with slightly or markedly increased cation conductivity is required. Whereas a steam contamination with chlorides, sulfates, and formates is dangerous even at very low contaminant concentrations, the presence of acetates and in particular of carbon dioxide appears to be relatively harmless. Further evaluation for cycles using amines as alkalizing agents and additional or improved surveillance techniques for interpreting the cation conductivity values measured are required. The focus should be on contaminants that may to initiate or take part in local environment-related turbine damage mechanisms.	2002, 4(10), 597–603
Barry N. Taylor	Conversion Factors	This publication gives factors for converting values of quantities expressed in various units – predominantly units outside the International System of Units (SI) that are unacceptable for use with it – to values expressed either in (a) SI units, (b) units that are accepted for use with the SI (especially units that better reflect the nature of the unconverted units), (c) units formed from such acceptable units and SI units, or (d) decimal multiples or submultiples of the units of (a) to (c) that yield numerical values of convenient magnitudes. The factors for units are listed by kind of quantity or field of science.	2002, 4(10), 605–620
Darryl A. Rosario S. S. (Stan) Tang Peter C. Riccardella David W. Gandy Ramaswamy (Vis) Viswanathan	Evaluation of LP Rotor Rim-Attachment Cracking Using LPRimLife	Stress corrosion cracking (SCC) in the blade attachment region of low-pressure (LP) turbine rotors has emerged as one of the most significant problems affecting both nuclear and fossil steam turbines today. To assist turbine operators in evaluating the remaining life of LP rotors with known or suspected cracking, an easy-to-use PC-based computer program, LPRimLife, was developed for EPRI by Structural Integrity Associates. The first phase of development, incorporating the methodology for evaluating cracking in General Electric (GE) dovetail (straddle-mount) attachments, was completed in 1999 [1]. The second phase, which included evaluation of cracking in Westinghouse axial-entry (steeple) attachments, was completed in 2000 [2]. The third phase, to address cracking in GE multi-pin-finger attachments, is currently under way. Since initial development, the LPRimLife computer code has been successfully employed at nuclear and fossil plants, providing the basis for deferring or eliminating major	002, 4(11), 641–649

		unscheduled and costly repairs, such as "pressure plating," which would have significantly extended the outages. Deferring unscheduled repairs for even one more fuel cycle allows for advance planning to evaluate and select the most-effective repair/replacement option and lead time needed for procurement of appropriate materials/services. In today's competitive marketplace with ever-tightening outage schedules, timely application of LPRimLife has resulted in significant cost savings to utilities. This paper provides a summary of the LPRimLife program methodology, software features and recent utility applications.	
Jørgen Peter Jensen Karol Daucik	Solubility of Sodium Chloride in Superheated Steam	The solubility of sodium chloride in superheated steam was investigated in laboratory-scale experiments up to 20 MPa and 475 °C. These experiments were carried out using a dynamic method where deionized steam was passed through a packed bed of salt crystals in a 500 mL Hastelloy autoclave. The residence time of the steam in the salt bed was sufficient to saturate the steam with the salt. The steam samples were cooled and analyzed by ion chromatography. Correlations based on temperature and density were selected to describe the solubility of sodium chloride in superheated steam. The density dependence is much stronger than the temperature dependence. By using these correlations, it is possible to estimate the solubility of salt in steam at lower densities than those used in the experiments. Enthalpy-entropy diagrams are given that show the steam expansion line in turbines, including curves for constant concentration of sodium chloride solubility in steam. These can be used to analyze where in the steam cycle this salt may deposit.	2002, 4(11), 653–659
Vitaly A. Prisyazhniuk	Condensation of Steam	An equation for nucleation kinetics in steam condensation has been derived, the equation taking into account the concurrent and independent functioning of two nucleation mechanisms: the homogeneous one and the heterogeneous one. The equation is a most general-purpose one and includes all the previously known condensation models as special cases. It is shown how the equation can be used in analyzing the process of steam condensation in the condenser of an industrial steam-turbine plant, and in working out new ways of raising the efficiency of the condenser, as well as of the steam-turbine plant as a whole.	2002, 4(11), 665–668
Kevin J. Shields R. Barry Dooley	Chemical Cleaning's Role in Tube Failure Prevention and Correction	Properly applied, chemical cleaning is a valuable tool used to prevent tube failures involving overheating and corrosion due to waterside deposits. In many cases, however, cleaning becomes yet an additional cost associated with correction of tube failure incidents. Discussion is focused on approaches taken to appraise tube waterside cleanliness and determine the need to clean, as typically practiced in conventional fossil plants. Also presented is an assessment of the suitability and limitations of these approaches to plants with heat recovery steam generator units.	2002, 4(11), 671–683
George J. Verib	Sodium to Phosphate Ratios	Phosphate chemistry is widely used in fossil-fired utility boilers and many of these phosphate programs use the sodium to phosphate ratio as the controlling parameter. This paper steps through the fundamental chemical analyses to determine a systems Na/PO_4 ratio. A mathematical equation is introduced to simply calculate the ratio using the pH and phosphate concentration. This equation is also used to build graphs to chart the boiler's phosphate chemistry. By looking at the dynamic nature of the chemistry, boiler health can be determined.	2002, 4(11), 687–690
Ernest Beinrohr Walter Labhart Eric V. Maughan	Heavy Metal Discharge from Coal-Fired Power Plants – How Does This Affect the Environment and Cost-Effective Production of Electric Power?	Although heavy metals are naturally occurring elements, there are rather draconian laws, imposed by global authorities and institutions, which forbid their discharge from industry into the environment. Most of these elements have limits of concentration which are not readily measured by standard laboratory techniques. Even if measurable, how may these contaminants be adequately dealt with? Fossil-fired power plants without a dry-ashing facility suffer the risk of accidental discharge of undesired heavy metals leached from the disposed ash via the wet-ashing disposal system.	2002, 4(11), 693–696

		This paper investigates: • a continuous method of rapid identification and measurement of heavy metals and • an economical method for the safe removal and disposal of these contaminants.	
Pascale Bénézeth Donald A. Palmer David J. Wesolowski	Dissociation Quotients of Aqueous Dimethyl-ammonium Ion	The acid dissociation equilibria involving aqueous dimethyl-ammonium ion in the reaction $(CH_3)_2NH_2^+ \rightleftharpoons (CH_3)_2NH + H^+$ were measured potentiometrically with a hydrogen-electrode concentration cell from 0 °C to 290 °C in sodium trifluoro-methanesulfonate (NaTr) solutions at ionic strengths of 0.1, 0.3 and 1 molal. The molal dissociation quotients and selected literature data at infinite dilution were fitted by an empirical equation involving six adjustable parameters involving functions of temperature, solvent density and ionic strength. This treatment yielded the following thermodynamic quantities at 25 °C and infinite dilution: $\log K_d = -10.77 \pm 0.02$, $\Delta H_d = (50.8 \pm 0.7)\ kJ \cdot mol^{-1}$, $\Delta S_d = (-35.8 \pm 2.5)\ J \cdot K^{-1} \cdot mol^{-1}$, $\Delta C_{pd} = (116 \pm 11)\ J \cdot K^{-1} \cdot mol^{-1}$, and $\Delta V_d = (-4.3 \pm 2.5)\ cm^3 \cdot mol^{-1}$.	2002, 4(12), 707–711
George Lai	Performance of Automatic GMAW Overlays for Water-wall Protection in Coal Fired Boilers	The paper reviews the performance history of modern weld overlays applied by the automatic gas-metal-arc welding (GMAW) process in mitigating the severe wastage problems encountered for the waterwalls of coal-fired boilers. Commonly used overlay alloys of Type 309 stainless steel, Alloy 625 and Alloy 622 are discussed. Many boilers with overlaid water walls have accumulated service experience approaching 10 years with great success. Approximately 100 boilers with about 21 000 m^2 (227 000 ft^2) of total waterwall area have been overlaid with the three overlay alloys. The weld overlay has been considered by the boiler owners/operators to be the most viable waterwall protection method for mitigating the severe waterwall wastage problems. Nevertheless, a couple of boilers of one boiler design have been found to show circumferential cracking for the 625 overlay. It has been found that this circumferential cracking was the result of preferential sulfidation attack due to overheating of the overlay surface layer to possibly 593 °C (1100 °F). Metallurgical issues on the overlay alloys are discussed. An alternate alloy for mitigating the preferential sulfidation attack due to overheating is recommended.	2002, 4(12), 712–719
Michael H. Dorsey George J. Licina Brian J. Saldanha Richard C. Ebersole	Monitoring for Corrosion and Microbiological Activity in a Cooling Water System	Corrosion of heat exchanger tubes and carbon steel piping at a chemical processing plant had been attributed to a high level of microbiological activity in the cooling water. Two electrochemical biofilm activity sensors with integrated data acquisition and data analysis capabilities were installed in the plant's cooling system to augment the coupon-based corrosion monitoring activity. Those sensors provided the plant with an on-line measurement and early detection of biofilm activity on metallic surfaces. Sensor response was correlated with coupon examinations, determinations of biocide residuals, and determination of the numbers and types of microorganisms. Results from the plant monitoring activity are described. These results emphasize the necessity to integrate the various types of field and laboratory data to monitor and effectively control microbiologically influenced corrosion.	2002, 4(12), 721–731
Jørgen Peter Jensen Karol Daucik	Solubility of Sodium Sulfate and Sodium Hydroxide in Superheated Steam	The solubility of sodium sulfate in superheated steam was investigated in laboratory-scale experiments up to 25 MPa and 600 °C. These experiments were carried out using a dynamic method where deionized steam was passed through a packed bed of salt crystals in a 500 mL Hastelloy autoclave. The residence time of the steam in the salt bed was sufficient to saturate the steam with the salt. The steam samples were cooled and analyzed by ion chromatography. A "density" model was selected to correlate the experimental data of the solubility of sodium sulfate in superheated steam. The density dependence is much stronger than the temperature dependence. By using this type of correlation, it is possible to estimate the solubility of salt in steam at lower densities than those used in the experiments.	2002, 4(12), 735–740

		Enthalpy-entropy diagrams are given that show the steam expansion line in turbines, including curves for constant concentration of sodium sulfate and sodium hydroxide solubility in steam. These can be used to analyze where in the steam cycle sodium sulfate and sodium hydroxide may deposit.	
Albert Bursik	Boiler Tube Failures in Industrial Drum-Type Steam Generators – Part 3: Alternative Cycle Chemistry Treatments	Part 1 of this paper dealt with the major differences between steam generation in utility boilers and in industrial steam boilers and other steam generating apparatus (e.g., differences in design, material selection, and cycle contaminants) and treated some site-specific issues influencing cycle chemistry. Part 2 dealt with the applicability of internationally accepted boiler water treatments and with their influence on the occurrence of boiler tube failures. This part (the third part of a four-part publication) discusses the applicability of amine-based plant cycle treatments which are covered neither by the VGB Guideline for Boiler Feedwater, Boiler Water, and Steam of Steam Generators with a Permissible Operating Pressure of > 6.8 MPa nor by the set of EPRI Cycle Chemistry Guidelines for Fossil Plants.	2002, 4(12), 743–746

2003's Scientific and Technical Contributions: Papers in English

Barry Dooley
Digby Macdonald
Barry C. Syrett

ORP – The Real Story for Fossil Plants

Oxidation/reduction potential (ORP) measurements are now used extensively to monitor the feedwater conditions in fossil power plants. These measurements are typically made at ambient temperature, using platinum as the indicator electrode and a saturated silver/silver chloride [Ag/AgCl, KCl(sat)] reference electrode. However, some confusion exists about the physical meaning of ORP in these systems. So the purpose of the present paper is to comment upon the interpretation of measured data in terms of modern electrochemical and corrosion concepts, in particular in terms of the mixed potential model (MPM), and to indicate how the monitoring protocols should evolve so as to maximize the extent of information transferred to the plant operator or chemist. As such, it then becomes clear that ORP reflects a balance between the amounts of dissolved oxygen and the reducing agent in the feedwater. ORP is a function of the system pH, the partial pressures of oxygen and hydrogen, the mass transport properties, the flow rate and the materials in the cycle.

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Stefan Ritter
Hans-Peter Seifert

Strain Induced Corrosion Cracking of Low-Alloy Reactor Pressure Vessel Steels under BWR Conditions

In this paper results of slow rising load and low-frequency corrosion fatigue (LFCF) experiments with three different low-alloy reactor pressure vessel (RPV) steels and with a RPV weld material at temperatures of 288, 250, 200 and 150 °C are presented. To characterize and quantify the strain-induced corrosion cracking (SICC) and LFCF crack growth behavior under transient boiling water reactor/normal water chemistry conditions, modern high-temperature water loops, on-line crack growth monitoring and fractographical analysis by scanning electron microscopy were used.

Under highly oxidizing conditions, electrochemical corrosion potential (ECP) > 100 mV (SHE), a maximum in SICC susceptibility was observed in all investigated materials at intermediate temperatures (≈ 200–250 °C) and slow strain rates. The SICC growth rates were very similar for all materials, increasing with increasing strain rate and increasing temperature, with a possible maximum/plateau at/above 250 °C.

The cycle-based LFCF crack growth rates Da/DN increased with decreasing frequency and increasing temperature. The LFCF growth behavior of low- and high-sulfur steels and of the weld material was comparable over a wide range of loading conditions. Under low-flow and highly oxidizing (ECP > 100 mV (SHE)) conditions, the ASME XI "wet" reference crack growth curve could be significantly exceeded by cyclic fatigue loading at low frequencies (< 10^{-3} Hz), at high and low load ratios R, and by ripple loading near fatigue thresholds ΔK_{th}. Sustained environmentally-assisted crack growth could be maintained down to low frequencies of 10^{-5} Hz. The environmentally-assisted crack growth rates were bounded by the low- and high-sulfur line of the General Electric model.

PPChem 2003, 5(1), 17–29

Supatpong Mattaraj
James E. Kilduff

Using Reverse Osmosis to Remove Natural Organic Matter from Power Plant Makeup Water

A field-scale reverse osmosis (RO) system was used to remove salts and natural organic matter (NOM) from a surface water source. The RO membrane exhibited an NOM solution hydraulic permeability of 8.33 x 10^{-9} $m \cdot s^{-1} \cdot kPa^{-1}$, about 6 % less than the clean water value, over pressures ranging from 414 to 1 000 kPa (60 to145 psi). The rejection of salt and NOM were greater than 98 % and 99 %, respectively. Under controlled laboratory conditions, greater than 99 % mass recovery of NOM could be obtained. A small fraction of NOM was not recovered using hydrodynamic cleaning but could be recovered with chemical cleaning (NaOH wash solution). The mass recovered in the NaOH solution increased from < 1 % to > 6 % with increasing transmembrane pressures from 414 kPa to 1 000 kPa, respectively. This is consistent with fouling that results from an increase in solution flux, and a concomitant decrease in tangential crossflow velocity.

PPChem 2003, 5(1), 31–35

Wolfgang Hater
Birgit Glüsen
Ulrich Pegelow
Matthias Schweinsberg

Comparative Assessment of Dispersant Programs for Cooling Water

The prevention of mineral scales and sludge presents a major challenge for cooling tower management throughout a wide variety of industrial processes. The universal application of dispersants has proven itself to be a cost-effective solution to prevent the precipitation of mineral particles contained in feeding waters for industrial cooling systems.

In this paper, an integrated approach to the development and application of new ecologically friendly dispersant systems for cooling water is presented as an example for such processes. A variety of static as well as dynamic monitoring techniques for dispersant performance is presented, ranging from fast on-site testing methods such as turbidity monitoring to sophisticated laboratory techniques such as light scattering and zeta potential measurements. This coherent framework of testing procedures yields comprehensive information ranging from sedimentation mechanisms to optimum concentration balances as a function of key process parameters (temperature, flow rates, water quality) under practical conditions. This enables the development of new chemical formulations and the tailored adaptation of treatment programs to the customer, directly translating into mutual benefits ranging from faster response times to optimized cost-effective solutions for a wide variety of dispersing tasks. This is demonstrated by a case study of the cooling water treatment at a nuclear power plant.

PPChem 2003, 5(1), 37–41 and 58

Stephen E. Ziemniak
Harmon M. Tunison

Hydrothermal Synthesis of Maricite via Iron Oxide Decomposition in Sodium Phosphate Solutions

Aqueous sodium phosphate solutions having Na:P atom ratios between 1.6 and 2.0 are shown to transform iron oxide ($Fe_3O_4/Fe(OH)_2$) into either of two sodium-iron-phosphate minerals: maricite ($NaFePO_4$) or a member of the alluaudite group. Microchemical, infrared and Mössbauer spectroscopic analyses indicate that the latter compound has the approximate (single-phase) composition $NaFePO_4 \cdot 4\ NaFe(OH)PO_4$. Maricite formation was promoted by the imposition of dissolved hydrogen gas, which likely stabilizes a layer of hydrous iron(II) oxide on the magnetite surface:

$$1/3\ Fe_3O_4(s) + 1/3\ H_2(g) + 2/3\ H_2O \longrightarrow Fe(OH)_2(s)$$

On the basis of observed reaction threshold sodium phosphate concentration and temperature values for maricite synthesis via:

$$Fe(OH)_2(s) + Na^+ + H_2PO_4^- \longrightarrow NaFePO_4(s) + 2H_2O$$

the standard entropy (S°) and free energy of formation (ΔGf^o) for maricite were calculated to be 157.3 $J \cdot mol^{-1} \cdot K^{-1}$ and –1419.4 $kJ \cdot mol^{-1}$, respectively.

PPChem 2003, 5(2), 69–74

Jan Stodola

Fifteen Years of Equilibrium Phosphate Treatment (Correct Use of Phosphates in Drum Boilers)

This paper explores differences between the Ontario Power Generation Inc. (formerly Ontario Hydro) and the EPRI concepts of equilibrium phosphate treatment (EPT). After a brief developmental history of the EPT method, the paper addresses the actual differences in the areas of boiler water alkalinity control and control of contaminants. In addition, the paper also discusses the fundamental behavior of sodium phosphates in pure solutions and in operating boilers to offer alternatives to the EPRI interpretation of the root causes of phosphate induced corrosion and hydrogen damage. The purpose is to rationalize safe chemistry control practices in boilers using sodium phosphates.

PPChem 2003, 5(2), 75–84

Peter Angell

Use of Microbial Kinetics to Control MIC in the Nuclear Industry

In common with many other industries that use large quantities of water, nuclear power utilities have experienced piping degradation attributable to microbially influenced corrosion (MIC). The effects of MIC are generally associated with fire protection and cooling

water systems, which may use large quantities of untreated water. Failure of these systems could lead to a forced shutdown of a nuclear power plant. Existing countermeasures, which are often expensive and have a negative environmental impact, are not always adequate; however, lessons can be learned when MIC does occur.

This paper reviews a number of MIC failures discovered in nuclear power plants, as well as the associated failure mechanisms. Based on an understanding of the microbial kinetics involved in the failure, design and operational remedial measures are then explored. It is shown that a fundamental understanding of microbial growth kinetics can be applied to mitigate many MIC problems without the use of expensive and potentially environmentally damaging biocides.

PPChem 2003, 5(2), 85–88

Michael A. Sadler

Condensate Polishing for Fossil Power Stations: A Review of Recent Work Aimed at Reducing Costs

EPRI has for many years encouraged fossil power stations to use condensate polishing, as its use not only allows them to use more effective forms of water treatment, but also protects steam/water cycles. Many stations, however, still do not use condensate polishing and the reasons for this are believed to be the capital and operating costs involved. EPRI, therefore, initiated an "Innovative Condensate Polishing Program" aimed at identifying methods of reducing the capital and/or operating costs of polishing. The small team of specialists involved have now studied and prepared a guideline document on "Ammonium Form Operation". Appropriately used, this procedure can reduce operating costs of deep bed plants by 80–90 %. They have also prepared a guideline document on the use of "Off-Site Regeneration of Condensate Polisher Resins" as in some new plant situations this can result in a 20–30 % reduction in capital costs. Attention has been paid to reducing the cost of service vessels and in particular to the use of radial flow vessels, as computer studies have shown that their use can offer both cost and space savings. Other interesting innovative ideas are also being pursued and, as part of the program, a training course for station staff on condensate polishing has been developed and instruction is being given.

PPChem 2003, 5(2), 91–95

Robert D. Bartholomew
David A. Cline, Jr.
Gary H. Roberts

Renovation or Replacement of Existing Makeup Water Treatment Systems

The renovation or replacement of existing makeup water treatment systems at power plants should consider both old and new treatment technologies, water usage, wastewater production, and the choice of permanent or leased equipment. These considerations are extensively discussed in EPRI's Revised Guidelines for Makeup Water Treatment. In this progress report, case studies are presented as examples of system selection for facilities with a zero liquid discharge requirement and makeup water supply limitations.

PPChem 2003, 5(2), 96–104

Hans Blöchl
Norbert Staub
Joachim Fahlke

20 Years of Reverse Osmosis at Grosskraftwerk Mannheim – Operating Experience

For makeup water production in Mannheim Power Station two makeup water treatment plants with integrated reverse osmosis are operated. The older system was commissioned in 1982 and the newer system was commissioned in 1996. These plants produce makeup water with electric conductivities below 0.2 $\mu S \cdot cm^{-1}$ (at 25 °C). The production varies between 75 $m^3 \cdot h^{-1}$ and occasionally even 350 $m^3 \cdot h^{-1}$. For both systems, the raw water is the Rhine River bank filtrate. The overall raw water quality is very good. The level of organics is low with an average TOC below 1 $mg \cdot L^{-1}$.

Besides a description of the treatment technique, the paper gives a short overview of the different types of reverse osmosis membranes which have been used in both plants since the beginning of operation until today, and the operating experience that has been made with these membranes so far. In addition, there is a short description of a problem with a catalytic ion exchanger in one of the plants.

PPChem2003, 5(3), 133–136

Andrew G. Howell
Sandra J. Lucero

Copper Deposition in Superheater Tubing

Copper deposits have frequently been observed in power station superheater tubing. Deposit density measurements were made on superheater specimens from a number of boilers of varying drum pressure, with results ranging from less than 0.1 to 215 $g \cdot m^{-2}$ (< 0.01 to < 20 g/ft^2). The heaviest deposition was found in the primary section of the superheater. Microstructural observation indicates that the deposition is crystalline in form, consistent with a deposition mechanism from steam on an atomic growth basis, rather than with physical transport of solid particulates. Microanalysis demonstrated that the surface of some copper deposits were in oxide form, whereas others were metallic; the oxidation state of copper likely has significance regarding the extent of transport of superheater copper deposits to the high pressure turbine.

PPChem 2003, 5(3), 137–147

Ladislav Bursik
Albert Bursik

Inhibited Hydrofluoric Acid – An Effective Chemical Cleaning Solvent

Inhibited hydrofluoric acid has been used in Europe for 35 years for the preoperational and operational chemical cleaning of water- and steam-touched surfaces of steam generators and cycle components. The scientific studies on the dissolution of iron oxides in different acids were begun already in the 1950s; the most significant results, especially for hydrofluoric acid, were achieved in the 1960s.

Chemical cleaning with hydrofluoric acid has proven very successful in combination with the open circuit (OC) technique for supercritical once-through boilers. The advantages of the OC technique together with inhibited hydrofluoric acid are the fast dissolution of iron oxides, short application time, low temperatures (50 °C – 80 °C), and the relatively easy handling of wastewater.

The OC technique combined with the use of inhibited hydrofluoric acid is also used for parts of drum-type boilers and heat recovery steam generators.

PPChem 2003, 5(3), 149–153

Luda Nasri
Paul Leinonen
Frank V. Puzzuoli
Dev Swami

OPG Operational Experience with Stator Conductor Bar Fouling

Over the last three years, Ontario Power Generation (OPG) Pickering Nuclear has experienced fouling of the stator conductor bar cooling water channels on two units. To address the associated stator bar temperature rises, chemical cleaning was undertaken three times on one unit and once on the other.

These events were the subject of two formal investigations and a single rigorous chemistry assessment. The investigations were conducted using a formalized root-cause protocol.

The assessment involved a system chemistry review over a 10-year period and a critical evaluation of dissolved oxygen control.
This paper describes:

- the internal investigations undertaken by OPG to better understand and resolve the problem,
- OPG's cleaning strategy and different cleaning options performed on affected units,
- the remedial actions undertaken by OPG, and
- the interim actions following the final post-cleaning inspections.

PPChem 2003, 5(3), 155–162

EPRI Publishes Revision 1 of the Cycle Chemistry Guidelines for Fossil Plants: All-Volatile Treatment

This contribution is a short review of the Revision 1 of the *Cycle Chemistry Guidelines for Fossil Plants: All-Volatile Treatment*, which was published in November 2002. This Revision is evaluated as a very important guide for all fossil utilities operating units on all-volatile treatment. Some of the attachments to the Revision are also valuable for operators using other cycle chemistry treatments.

In publishing this Revision, EPRI has clearly demonstrated its leadership in the field of fossil plant cycle chemistry and chemistry of water and steam in general.

PPChem 2003, 5(3), 163–167

Steam Turbines – Steam Purity – A New Technical Specification Issued by the IEC

This paper is a short review of the IEC technical specification IEC/TS 61370, *Steam Turbines – Steam Purity*, issued in June 2002. The review focuses on a comparison between the new technical specification and the classic EPRI and VGB plant cycle chemistry guidelines.

PPChem 2003, 5(3), 171–173

Ivan D. Dobrevski
Neli N. Zaharieva
Katia F. Minkova
Radka A. Ivanova

The Concentration of the Coolant ^{7}Li in Kozloduy Nuclear Power Plant Operating with Potassium Hydroxide as an Alkalizing Reagent (Possible Impact on the Occurrence of Axial Offset Anomaly)

The phenomenon of axial offset anomaly (AOA) has occurred in a number of pressurized water reactors (PWRs) operating with extended fuel cycles and high boiling duty cores. Up to now AOA has been observed in PWRs operating with lithium hydroxide as the alkalizing reagent used for pH adjustment in boric acid water solutions. Since AOA is connected with the $LiBO_2$ precipitation in porous corrosion product deposits on the fuel cladding surfaces, we could presume that the replacement of lithium hydroxide with potassium hydroxide will avoid AOA.

Nowadays there is a lack of observed AOA in VVERs (Soviet/Russian Federation designation for pressurized water reactors), i.e., a lack of formation of lithium metaborate ($LiBO_2$) deposits on the fuel element surfaces by coolant alkalization with potassium hydroxide. Nevertheless, the concentrations of ^{7}Li appear in the coolant, as a product of the neutron reaction with boron:

$$^{10}B\ (n, \alpha) \longrightarrow {}^{7}Li\ (n, \alpha)$$

As a consequence the possibility is not excluded of $LiBO_2$ formation in VVERs with potassium hydroxide water chemistry.

The aim of this study is to inform the reader about the development of the concentration of the coolant lithium concentration during the fuel cycles of VVERs and to discuss the possibility of $LiBO_2$ formation under VVER operation conditions.

PPChem 2003, 5(4), 197–202

Jean-Louis Drommi
Frédérique Mesnage

How to Prevent Hollow Conductor Plugging: EDF's Solution for Aerated Systems

Between the early 1980s and 1995, Electricité de France (EDF) faced several plugging problems on its aerated water-cooled generators causing significant production losses due to reduced load operation and unscheduled outages for off-line cleaning: up to 150 days per year. As an ultimate solution, several stators were rewound.

In 1995, research and metallurgical investigations led to a better understanding of the plugging phenomenon and allowed EDF to design and implement a soft on-line treatment: cationic purification.

Since 1995, on-line cationic purification has enabled 100 % availability of the generator cooling function. As a proactive policy to prevent hollow conductor plugging, EDF has undertaken, on 95 % of its 58 pressurized water reactors, significant modifications of the generator winding cooling system so that the water chemistry parameters avoid the buildup of cupric oxide (CuO).

PPChem 2003, 5(4), 203–205

Robert Svoboda
Claudio Picech
Herbert Hehs

Experience with Stainless Steel Hollow Conductors for Generator Stator Water Cooling

Copper is a traditional material for hollow conductors. As a future tendency, stainless steel is a proven alternative as a hollow conductor material. In our almost 30 years of experience we have not encountered any failures related to cooling water chemistry with this material. We recommend the use of high purity water with no restriction on oxygen content.

PPChem 2003, 5(4), 211–215

Albert Bursik

AVT Guidelines for Drum Boilers and the pH at Temperature

pH values measured at 25 °C are used for controlling the boiler water treatment. The question arises as to whether this practice is correct. The paper shows that the difference between the actual pH and the neutral pH, both at the boiler water temperature, decreases extremely with increasing temperature in boilers operated on all-volatile treatment. Even slight anionic contamination may cause the pH(t) to move into the dangerous acidic region. In this connection, the VGB guideline AVT limit for the cation conductivity of the boiler water (< 3 $\mu S \cdot cm^{-1}$) seems to be too high. Many examples demonstrate this fact.

PPChem 2003, 5(4), 225–232

Pascale Bénézeth
Donald A. Palmer
David J. Wesolowski
Caibin Xiao

The Solubility of Zinc Oxide to 350 °C

The solubility of crystalline zincite (ZnO) has been re-evaluated in noncomplexing solutions over a wide range of pH to 350 °C at pressures ranging from slightly above saturation vapor pressure to significantly higher pressures in NaOH, NH_3, F_3CSO_3H/F_3CSO_3Na (HTr/NaTr), $CH_3COOH/NaOH$, and F_3CSO_3H/NH_3 solutions using a hydrogen-electrode concentration cell and a flow-through cell with downstream acid injection. Recent new results, coupled with our earlier data at 75–100 °C, indicate that the solubility of zinc oxide is higher in near neutral solutions than we reported previously, but substantially lower than previous estimates available in the scientific literature. The solubility of ZnO versus pH profile has a broad minimum in near neutral solutions. This is also the range of operation of the primary circuit of a pressurized water reactor, where zinc injection is being carried out in some plants to mitigate stress corrosion cracking. Therefore, a precise knowledge of the solubility in this pH region at all temperatures is required to permit significant doping with zinc(II) while not exceeding the solubility limits of ZnO.

PPChem 2003, 5(5), 260–265

Robert Svoboda
Hans-Dieter Pflug
Thomas Warnecke

Investigations into the Composition of the Early Condensate in Steam

This paper reports on investigations into concentration effects in the first condensate. The equipment and the analytical techniques used do not markedly differ from those applied in previous measuring campaigns. During these investigations, however, small amounts of various contaminants (e.g., NaCl) were injected into the cycle. In this way, the accuracy of the analytical techniques was improved. Care was taken to maintain the cation conductivity within the VGB guideline specifications. In comparison to the previous measurements, the extent of the analytical parameters measured was broadened.

Apart from inaccuracy in analytics and problems in sampling at very low steam moistures, the following conclusions could be drawn:

- for strong electrolytes such as salts of sodium, potassium and calcium, the concentration is a reciprocal linear function of the steam moisture,
- volatility of inorganic and organic acids affects the concentration dependence of the steam moisture,
- for ammonia and carbon dioxide, any concentration dependence on steam moisture could not be recognized.

The experiment results may contribute to better assessing of possible steam turbine damage due to carbon dioxide and organic acids.

PPChem 2003, 5(5), 273–280

Vitaly A. Prisyazhniuk

Ways of Raising the Thermodynamic Efficiency of Steam Power Plants

An equation for estimating the thermodynamic efficiency of the Rankine cycle is proposed which includes the thermophysical characteristics of the working medium and the condensation completeness coefficient. Three alternative ways of raising the thermodynamic efficiency of the cycle are discussed:

– by using, as a working medium, some chemical agent having "optimal" thermophysical characteristics,

– by using a "composite" working medium, that is a solution with "optimal" thermophysical characteristics, and

– by changing the thermophysical characteristics of a conventional liquid by way of restructuring the liquid with an active electrical or magnetic field, for instance, by employing the magneto-hydrodynamic (MHD) resonance method.

Some examples of actual cases of change in the thermophysical characteristics of a liquid by the MHD resonance method are given.

PPChem 2003, 5(5), 281–288

Hans-Günter Seipp

Corrosion as a Result of Unsatisfactory Attemperator Water Quality

In fossil power plants and particularly in industrial power plants, the superheated steam temperature is widely reduced via injection (attemperation) of water. Corrosion damage has been repeatedly observed in equipment downstream of the water injection point. For this reason, the technical codes of practice were checked for preventive explanations. Two case studies make the hardly surveyable coherences evident.

PPChem 2003, 5(5), 289–297

Stefan A. Huber

Sources and Behavior of Organics, in Particular Polysaccharides, in Boiler Feedwater Preparation and in Water-Steam Cycles

There are many different ways in which organic matter (OM) may get into water-steam cycles. One important pathway is OM brought into the system via the makeup water under standard operation conditions. This is particularly true for sites where a surface water source is treated conventionally without reverse osmosis. Here, it has to be taken into account that high amounts of high-molecular weight organic matter, in particular polysaccharides, are brought into the water-steam cycle. Under hydrothermal conditions, polysaccharides are broken up into – among other things – organic acids, in particular acetic acid. The different sources of polysaccharides in the different natural water systems are briefly discussed.

The results of a previously published and well-documented autoclave test are briefly discussed. The test supports another issue, the propensity of OM to mask halogens, in particular chlorine. Such organochlorine compounds are not necessarily amenable to trihalomethane or activated carbon organic-bound halogen analysis.

The impact of condensate polishers is briefly discussed.

Three case studies are described. At all sites, surface water was treated without reverse osmosis. In parallel, at all sites corrosion was observed in areas of the turbine or the boiler and organic acids were made responsible for this.

The paper finishes with some water treatment considerations: How can we remove polysaccharides effectively?

PPChem 2003, 5(5), 302–309

Phillip Smurthwaite

Optimizing Condenser Ball-Cleaning Performance by $\mu g \cdot kg^{-1}$ Transition-Metal Analysis

The ball cleaning of condensers has proved to be an effective method of maintaining the heat transfer characteristics of tube surfaces by minimizing deposition and removing scale. In the case of cupro-nickel tubes, ferrous sulphate dosing is then required to protect the tubes against seawater corrosion following ball cleaning. There is therefore a balance to be struck between condenser protection and heat transfer efficiency.

By monitoring the pick-up of dissolved copper in the cooling water across the condenser and maintaining levels between 0 and 10 $\mu g \cdot kg^{-1}$, condenser performance may be optimized. It can be shown that chelation ion chromatography of cooling water samples taken at the inlet and outlet of cupro-nickel condensers can accurately determine the concentrations of copper necessary to ensure optimization.

Of the three condensers controlled using $\mu g \cdot kg^{-1}$ transition metal analysis, all surpassed three years base load operation without on-load failures and net efficiencies rose by 0.9 % following introduction of ball cleaning and monitoring.

PPChem 2003, 5(6), 340–343

Nicolas Dobrowitch

The Use of Titanium for Condenser Tube Bundles

In a power plant, the condenser is a strategic heat exchanger with regards to the efficiency of the steam turbine, and its reliability guarantees the performance and continuous operation of the plant.

Until the early 1980s, copper alloys were routinely used in condenser tubes, thanks to their high heat transfer rates. Yet, numerous problems arose from the use of this material, such as stress corrosion cracking, ammoniacal corrosion, fouling, erosion, dezincification, abrasion, erosion-corrosion, etc. and lately the problem of the inadequacy of copper with nuclear steam generators.

The trend was then to consider new tube materials, such as stainless steel and titanium, at first for particular operating conditions and now for most of the projects, with several objectives, such as:

- improving reliability (titanium in particular can bring major improvements including higher water velocities promoting better heat transfer coefficients, and excellent resistance to abrasion, erosion and corrosion, thereby improving resistance to fouling);
- finding more cost-effective solutions. The first investment is higher but money is saved on maintenance costs and on time reliability of the material.

PPChem 2003, 5(6), 351–357

Søren Birk Rasmussen
Stefan U. Hagen
Stephen G. Masters
Anke Hagen
Kenny Ståhl
K. Michael Eriksen
Peter Simonsen
Jørgen Nørklit Jensen
Mogens Berg
Rasmus Fehrmann
Ib Chorkendorff

Catalytic and Chemical Properties of Boiler Deposits from Orimulsion™ Fuel

Bulk and surface analyses have been conducted for selected deposit samples from an Orimulsion™ fired boiler unit at the Asnaes power plant in Kalundborg, Denmark.

Analyses of the composition show that the deposits on the boiler tubes contain significant quantities of vanadium, calcium, nickel and sulfur. Furthermore the SO_2 oxidation activity of the collected samples has been measured as a function of oxygen and SO_2 content in the flue gas and of the gas temperature. The results show a significant SO_2 oxidation capability in the temperature range 530–670 °C. The catalytic oxidation reaction on the deposits is found to be a gas-solid, heterogeneously catalyzed reaction. The catalytically active species have been determined as surface oxo vanadium compounds with vanadium in a formal oxidation state between +IV and +V.

PPChem 2003, 5(6), 360–369

Albert Bursik
Pierre Bezzoli
Anton Graf

Cycle Chemistry in Cycles with Drum Boilers: Is There a Niche for the Use of Alternative Organic Chemicals in the Continuum of Treatments?

Organic cycle additives, particularly amines, have been used for many years in both industrial steam and power generation. The extent of the application of amine treatments in classic fossil utility power plants is steadily increasing. The use of amines is reported even from relatively new combined cycles, too. So far, none of the acknowledged plant cycle chemistry guidelines have included or discussed this type of cycle treatment. This means that neither the current nor the potential users have adequate guidance on hand. For this reason, in addition to good and approved organic cycle additives, some inadequate products are still on the market.

This paper discusses the behavior of organics in the plant cycle in general and focuses on the possible application of amines for the cycle treatment. The pros and cons of their application are considered. The possibility of including the amine treatment in the continuum of treatments is discussed.

PPChem 2003, 5(6), 373–378

Václav Petr
Michal Kolovratník
Vilém Hanzal

Instrumentation and Tests on Droplet Nucleation in LP Steam Turbines

The aim of this paper is to provide a contribution to the droplet nucleation discussion by presenting the results obtained from new tests on 1 000 MW nuclear and 210 MW fossil steam turbines. The turbine tests consisted of prediction of the droplet size spectra and electrostatic charge of droplets in the steam. Measurement was carried out by means of a combined extinction–charge probe.

An additional aim of this paper is to provide information on the expansion chamber, which can be used for experimental prediction of the initial size and number of impurities present in expanding steam.

PPChem 2003, 5(7), 389–395

Richard R. Harries
Paul G. McCann

The Degradation and Distribution of Organics in Steam/Water Cycles of Drum Boilers

An investigation was undertaken into the distribution of total organic carbon, acetate and formate between the steam and water phases of a number of power plants with drum boilers. The boiler types included high pressure coal-fired and multi-pressure heat recovery systems. The key conclusions are:

- A high percentage of the organic matter in the steam/water cycle remains as non-reactive organic carbon and does not degrade to acetate, formate or carbon dioxide.
- Acetate is normally the dominant organic acid anion in the steam/water cycle.
- Retrofitting of reverse osmosis to a makeup water treatment plant changed the dominant organic anion in the steam/water cycle to formate.
- Boiler water with solid alkali dosing has a lower partition coefficient for acetate, formate and non-reactive organic carbon into the steam phase compared with AVT chemistry.

In multi-pressure heat recovery boilers, the most effective way to reduce organic contaminants from the steam/water cycle is to preferentially blow down from solid alkali dosed LP drum water.

PPChem 2003, 5(7), 397–405

Eric Maughan
Hans-Dieter Pflug

Design and Operation of a Sampling and Analysis System to Meet the Needs of On-Line Monitoring of Cycle Chemistry in Modern Power Plants

The face of sampling and on-line monitoring has changed considerably since the 1970s. Initially the power plant was overpopulated with on-line analysers for the monitoring of the cycle chemistry. As the power industry began to economise, especially with respect to the labour force, many of these analysers fell into disuse and today only the minimum equipment is installed. However, standards and specifications with respect to the sampling and on-line monitoring of chemical variables have been compiled and are of great assistance to the end user in the selection of equipment. Additional criteria for selection include

- ease of operation
- reliability
- minimum maintenance

This presentation explores the dilemma of maintaining steam purity specifications whilst taking into account the economic operation of the plant versus the financial implications of poor cycle chemistry monitoring. The value of quality assurance and control as well as data logging and on-line diagnostics is also presented.

PPChem 2003, 5(7), 409–413

Ulrich Schirmer
Wolfgang Spiegel
Wolfgang Müller

Phosphine Formation in Grate-Firing Systems

Last year, in several German waste incineration plants phosphine was occasionally detected in slag-handling areas (e.g., at slag extraction, transport, and storage sites). In some cases, the phosphine concentrations determined were higher than the maximum allowable workplace concentration.

For this reason, VGB PowerTech e.V. has initiated a VGB research project "Investigations into the Formation of Phosphides/Phosphine in Various German Waste-to-Energy Plants." This paper reports on the most important results of this research project. It focuses, among other things, on phosphine formation and properties, the half-life of phosphine, and the dynamics of phosphine release.

Consequences for the operator from the industrial safety point of view are discussed and adequate measures are proposed.

PPChem 2003, 5(7), 421–429

Brad Buecker
Paul Dyer

Flue Gas Desulfurization Systems for the Future

In large fossil-fired power plants worldwide, flue gas desulfurization (FGD) systems are becoming more and more a standard. The limestone-based and lime-based technologies are used in the majority of units in operation and are intended even for many new power plant sites. This paper gives an overview of the typical limestone-based wet and lime-based dry FGD systems.

Since sulfur dioxide control is not the only power plant air pollution issue, the development of multi-pollutant control technologies capable of simultaneous removal of SO_2, NO_x and mercury is very attractive. Two recently developed technologies, which are in large-scale testing, Powerspan's Electro-Catalytic Oxidation (ECO®) process and the BOC Group's LoTOx™ process using ozone, are briefly introduced.

PPChem 2003, 5(7), 435–439

John P. Dimmer
R. Barry Dooley
Lewis J. Rubin

EPRI's BTFR/CCI Program Provides Tremendous Benefits to Utilities

EPRI's Boiler Tube Failure Reduction/Cycle Chemistry Improvement (BTFR/CCI) Program began in 1985. Over the last six years more than 65 organizations around the world have implemented and/or received training in this program. The organizations range in size from single plants to 40 000 MW systems. Tremendous benefits have resulted for utilities that have implemented the program for two years or more. Cost savings have ranged as high as $60,000,000/year. This paper briefly describes the program implementation strategy, methodologies used to benchmark participating utility performance in both BTFR and CCI, and the results from five utilities, ranging in size from 1 200 to 34 000 MW, that have implemented the program for two years or more.

PPChem 2003, 5(8), 453–462

Greg Bartley
Rob Taylor

Off-Site Condensate Resin Regeneration by Service Contract – An Operating Experience Update

Operating experiences from off-site condensate polishing resin regeneration at four fossil stations are shared. Employing this service improved cycle chemistry, lowered and improved management of treatment costs, eliminated lost generation from acid and caustic ingress, and eliminated hazardous regenerant chemicals from the sites. The overall operating cost for this service ranged between $812 and $1024 per m^3 ($23 and $29 per cubic foot) for 2001 and 2002. Off-site regeneration also provides the unique capability to adjust resin ratios at each regeneration to optimize polisher performance based on cycle chemistry.

PPChem 2003, 5(8), 463–469

Daniel E. Meils

Power Plant Chemistry QA/QC – A Practical Application

Fossil power plant laboratory chemistry Quality Assurance/Quality Control (QA/QC) programs have historically been a low priority for many end-users. A trained chemistry staff, it was thought, should be able to determine when things were going wrong, and plant design margins allowed a lot of forgiveness when upset conditions occurred. However, in today's downsized, competitive, reliability-driven workplace, QA/QC takes on new importance. Downsizing initiatives have reduced the number of experienced personnel and new plant designs are not as forgiving. As the industry adapts to the new paradigm, some plants are relying more on installed on-line instruments and using fewer skilled workers to perform chemistry analysis. At some plants, on-line instruments provide real-time information to data acquisition systems and expert advisor systems in an attempt to replace qualified personnel. At other plants, untrained operators make their rounds recording chemistry data from outdated instruments that may not have been calibrated in years. In any case, it is imperative to have confidence in the data used to make operational decisions. Under our new operating paradigm, practical power plant chemistry QA/QC programs become an essential part of everyday operation.

PPChem 2003, 5(8), 485–490

Branko Stanisa
Loreta Pomenić

Stress Corrosion Cracking in a 664 MW Low-Pressure Turbine – A Case Study

The most significant crack growth mechanism in low-pressure shrunk-on disk keyway cracking has been identified as stress corrosion cracking. This is one of the most dangerous kinds of corrosion processes which may occur during the operation of steam condensing turbines with shrunk-on disks on the turbine shaft. Stress corrosion of the turbine shrunk-on disks may cause disk fracturing and severe turbine damage. In this paper the basic technical data, a description of a 664 MW steam turbine in a nuclear power plant and the causes of stress corrosion crack growth in the turbine shrunk-on disks are presented. The relation between the crack propagation of the longest stress corrosion crack found in the keyway of the second disk in the low-pressure turbine LP1 (generator side) and the turbine operating hours is presented.

PPChem 2003, 5(8), 491–497

Katia S. Verheyden
Roger A. M. Ertryckx
Marc De Wispelaere
Nancy Poelemans

Belgian Experience with Film-Forming and Neutralizing Amines

This report gives an overview of experience gained in Belgium with the use of a commercial mixture containing film-forming and neutralizing amines as a conditioning product for the water/steam cycle. The first application concerns the conditioning of two fossil-fueled drum type boilers with an operating pressure of 12.8 MPa; the second application concerns the conditioning of two waste incinerators with an operating pressure of 4.0 MPa. Data are given on the iron and copper concentrations in the water/steam cycle and the impact on the conductivities in the water/steam cycle.

Metallographic examination of a boiler tube extracted from one of the boilers revealed the presence of a very thin magnetite layer between 5 and 10 µm.

The most positive effect of this type of treatment is the gain in startup time after a short stop of the units. The required steam and boiler water quality is reached remarkably quicker than with the conventional ammonia treatment.

PPChem 2003, 5(9), 516–522

Michael A. Sadler
Frances M. Cutler
Eli Salem
Kevin J. Shields

Regeneration of Condensate Polishing Resins for Fossil Power Stations: Utility Requirements and Comments on Possible Regeneration Procedures

The regeneration of ion exchange resins used in deep bed condensate polishing plants on fossil power stations is normally performed on-site by power station personnel. The use of specialist contractors to perform similar functions on other water treatment plants has in recent years become more widespread. Electric Power Research Institute is interested in the use of off-site regeneration of polisher resins as it could reduce the capital cost of condensate polishing plants and may possibly have other benefits for some fossil power stations. One large utility in the USA has already adopted the approach and others are showing interest. In this paper consideration is given to the necessary quality to which resins should be regenerated by specialist contractors so as to ensure satisfactory performance when in service. It is recognized that the two commonly used modes of operation of condensate polishing, the conventional H-OH mode and ammonium form operation, have different requirements. The suggested limits for the ionic impurity content of the resins, i.e., for sodium, chloride and sulfate, therefore cover both modes of operation. Possible procedures that supplement conventional regeneration processes are also described and discussed.

PPChem 2003, 5(9), 523–533

John Babinec

Copper Ion Treatment for Zebra Mussel Mitigation in House Service Water Systems

We Energies utilizes copper ion technology to control zebra mussel infestation of its Oak Creek Power Plant service water system. The Oak Creek Power Plant, located in southeast Wisconsin along the western shore of Lake Michigan, first observed zebra mussels in plant raw water components in 1991. The mussels began to show up in quantity in 1992. Present infestation levels in the intake forebay are > 60 000 zebra mussels per square meter.

The Oak Creek Power Plant is a four unit, coal-fired plant totaling 1 140 MW. The plant has a once-through circulating water system with a common forebay, from which it draws both main condenser circulating and house service water. System design prohibits thermal treatment strategies and obtaining environmental permitting for molluscicidal treatments is difficult at best. Initial treatment strategies revolved around chlorination, using sodium hypochlorite, which proved to be marginally successful, or chlorine dioxide, which raised safety concerns.

MacroTech's ZM-15 copper ion generator was installed and started up in the spring of 1998 to treat the service water system. The copper ion generator controls zebra mussel macrofouling through the controlled dissolution of copper and aluminum anodes. The copper toxicity, at target levels of 10 ppb, causes mortality in mussel veligers and inhibits adult mussel settlement. The aluminum creates a flocculent which smothers veligers and discourages biofilm from forming, reducing microbe induced corrosion, and further inhibiting adult mussel settlement.

This paper discusses plant design, treatment history, environmental permitting issues, design and installation of a copper ion generator, problems encountered and solutions, operating and maintenance requirements, and results to date of copper ion technology at We Energies' Oak Creek Power Plant.

PPChem 2003, 5(9), 539–547

Miroslav Šťastný
Olga Bláhová
Dalibor Šimůnek

Copper Deposition on and Surface Structure of Steam Turbine Blades

On the observed 200 MW turbine, thick deposits of copper oxides with a maximum thickness of 2.2 mm were found on the stages of HP part blades. The growth time of the deposits was 54 647 operational hours, without a turbine washing. The morphology of the deposits indicates that the deposits probably originated from the mechanical carryover, or from condensate used in the boiler for steam temperature control. Measurement of the blade surface structure with deposits was performed by means of a portable device. The evaluation of the measurements was done in agreement with the methodology of geometrical product specifications (GPS). Thick deposits on the convex sides of nozzle blades have the greatest roughness. Thick deposits on the convex sides of moving blades have a slightly lower roughness. Surface profiles of thick deposits are remarkable, with a large mean width of the elements of the roughness profiles. Thin deposits on the control stage and also on the concave parts of blades of other stages have a comparatively low roughness. The surface profiles of thin deposits are marked by a low mean width of roughness profile elements.

PPChem 2003, 5(9), 548–552

Svend-Erik Therkildsen

Water Chemistry Control and Monitoring Concept for Avoiding Chemistry-Related Failures in Small Combined Heat and Power Plants

The number of boiler tube failures and breakdowns in power plants, and especially in the relatively new combined cycle plants with heat recovery steam generators, has been increasing since the middle of the 1990s. Some of the factors are staff reductions and too little focus on water chemistry and new constructions (e.g., multi-pressure units, combined drum and once-through boilers, conversion of hot-water boilers to steam boilers), which may demand a specific individual adjustment in water chemistry. In Denmark we have also seen many new small-scale combined heat and power plants (CHP plants) in the last 15 years. The co-generation makes it possible to increase the efficiency to 85–95 % of the fired quantity of fuel. Many Danish small-scale CHP plants are located in small towns, primarily for the purpose of providing the local area with district heating. The consequences are for most of the plants 150 to 250 startups/shutdowns a year, even though heat accumulator tanks are used, because the high efficiency is only achieved at full-load operation. Typically, there is neither a laboratory in the plants nor staff with expertise in chemistry.

Wishing that our operating experience may be helpful to others, this contribution describes how Kyndby Power Station controls and maintains ENERGI E2's 11 small-scale CHP plants, in particular how the 6 staff members at the Kyndby Power Station labora-

tory monitor and control water chemistry conditions at Kyndby Power Station, the above-mentioned 11 small-scale CHP plants, 7 external waste-fired combined heat and power plants (waste incineration plants) and approximately 37 district heating systems. Even with the recommended water chemistry, we have seen 3 cases of failures in the water/steam cycle, which have necessitated repairs (2 failures in an ENERGI E2 plant and 1 failure in a waste incineration plant). All 3 failures were due to hidden design faults. 2 of the failures are being compensated by adjusting the water chemistry, while one design fault has been corrected.

PPChem 2003, 5(9), 553–560

Rolf E. Graf
Aleš Seitz
Xia Fan Gao

Advanced Large-Capacity Commercial Technology for Multi-Pollutant Control – Operating Experience in Europe and China with Single-Module Dry Flue Gas Desulfurization Systems for Coal-Fired Power Plant Boilers with Capacities between 100 and 300 MW

The presentation describes the application in commercial installations in Europe and China of circulating fluid bed (CFB) scrubbers of advanced GRAF/WULFF technology design, retrofitted to coal-fired steam boilers.

Details are presented of design and operating experience with installations of CFB scrubbers that efficiently remove diverse pollutants down to and below the required and permitted levels. The paper describes successful solutions to substantial operating problems encountered at a CFB scrubbing plant.

The described flue gas scrubbing plants of this simple system design clean the flue gases from boilers comprising units of a capacity of 100 to 300 MW using a single-train scrubbing system arrangement. Specifically, the simultaneous high rates of removal of multi-pollutants are, e.g., SO_2 > 98 %, SO_3 > 99 %, HF > 99 %, HCl > 98 %, mercury > 95%, and particulate matter > 99.99 %. These pollutants are removed in a single scrubber module in combination, downstream, with baghouse or electrostatic precipitator means of dedusting.

Information is given on rates and design of a single-module, 660 MW system as would be applied to a coal-fired power plant facility.

PPChem 2003, 5(9), 565–571

Robert Svoboda
Josef Denk
Carlo Maggi

Influence of Carbon Dioxide on Corrosion in Steam Turbines

Earlier investigations have shown that low pH conditions caused by carbon dioxide enhance aqueous corrosion of steels.

The goal of the present investigation was the clarification of whether carbon dioxide in steam promotes stress corrosion cracking of turbine steels by a mechanism other than the pH effect. For this, sensitized turbine steel was subjected to a NaCl solution, with and without carbon dioxide, at constant pH conditions. The time to fracture and the morphology of the fracture surface were used as distinguishing criteria for assessing the influence of carbon dioxide. Although the sensitized turbine steel and NaCl solution may only be partly representative of the actual conditions in a steam turbine, the examination is nevertheless indicative of the influence of corrosion promoting factors.

The present investigation indicates that besides the pH effect, carbon dioxide does not specifically attack turbine steels. It is, however, unlikely that carbon dioxide causes low pH in the liquid film in steam turbines, provided that the cycle pH is controlled adequately.

These results indicate that under normal plant operating conditions carbon dioxide in steam is tolerable as long as a sufficient alkalization of the steam/water cycle is provided. Such tolerance would be consistent with Alstom's steam turbine performance history.

PPChem 2003, 5(10), 581–586

Organic acids, however, for example acetate, may not be so benign.

Masamichi Miyajima
Yasuhiro Nishino
Masayoshi Hirano
Satoshi Itaba

Evaluation of the Oxygenated Feedwater Treatment at Chubu Electric Power's Plants

The Chubu Electric Power Company started research on the oxygen treatment method (combined water treatment, CWT) in 1992, about 10 years prior to other electric power companies in Japan. As a result, we have obtained good results, such as a suppressed increase in boiler differential pressure, reduced boiler feed pump power consumption and extended intervals between chemical cleanings of boilers; at the same time, we have detected no particular damage or negative influence on corrosion.

Based on these good results, CWT has been introduced to 14 units/10 400 MW, including Unit 1 at Chita Daini Power Station. In this paper we summarize these attempts and provide data on, among other things, the effects of small amounts of foreign matter on turbine materials and research on chemical cleaning criteria for boilers using CWT.

PPChem 2003, 5(10), 597–615

Albert Bursik

Selecting Cycle Chemistry – This Time in a Different Way

It is standard practice that when selecting the cycle chemistry for a particular unit or a steam generating system, the type of boiler (once-through or circulation steam generator) and the cycle metallurgy are the two most decisive parameters. In this paper, many other factors affecting the selection are focused on.

These additional factors are important in particular for units (also combined cycle units) erected for and operated by inexperienced independent power producers and for all steam and power generating systems besides the classic fossil utility power plants (in the industry, e.g., chemical industry, refineries, sugar and paper mills, in municipal incinerators, and cogeneration units).

Dealing with the factors of influence shows that many "non-optimum" cycles have to be operated in the very right open end of the funnel of the continuum of treatments. The fact that alternative cycle chemistry treatments may probably represent a promising alternative for this area is dealt with in another conference paper.

PPChem 2003, 5(10), 619–623

Matthias Koebel
Robert Svoboda

Investigations on the Temporal Stability of Ultrapure Water Samples by Means of Ion Chromatography

As part of the VGB research project # 182 "Chemistry of the Phase Transition in Steam Turbines" we have carried out an analytical study employing state of the art $\mu g \cdot kg^{-1}$ ion chromatography to investigate the long-term storage stability of ultrapure water samples in PP (polypropylene) and FEP (fluorinated poly-ethylene-propylene) storage media. In the case of chloride, sulfate, sodium, and potassium, over a period of 28 days we found no evidence of interactions with the storage media. This is reflected in the excellent temporal stability of blank water samples (no dissolution of ionic compounds from the polymer material) and diluted ionic cocktails (no adsorption or exchange reaction between sample and storage container). After 28 days, we found a 10 % decrease in ammonium. We therefore recommend analyzing samples for their ammonium content within 14 days. FEP bottles are ill suited for the analysis of fluorides due to their release of such ions; in polypropylene, however, no such effects on fluorides could be observed. Over all, the additional efforts connected with the use of FEP bottles in addition to PP bottles cannot be justified. Depending on the sample composition ("cocktail" or "blank"), we found decomposition as well as formation of the low molecular carboxylates acetate and formate within a few days. Based on this work it is possible to ship ultrapure water samples from anywhere in the world to a given analytical laboratory, confident that a measurement will yield a representative result of its ionic contents.

PPChem 2003, 5(11), 653–659

Ruedi Germann

Automation of Analytical Systems

The paper explains the possibilities and limitations of automation of analytic systems used for cycle chemistry surveillance in fossil and nuclear power plants. The most important interrelations among sample input conditions, actual analytical devices and output information are discussed. Among other things, the author presents some examples

PPChem 2003, 5(11), 671–675

of verification of values measured, a cation conductivity measurement with integrated automated quality assurance, and automated quality assurance systems.

Walter Guhl
Wolfgang Hater
Thomas Hörtinger

The Environmental Behaviour of Water Treatment Products in Cooling Water Systems

Water treatment products must be technically and economically effective; in addition, they have to be environmentally compatible, because they are generally discharged directly into the receiving water. Teamwork between product development, application technology and ecology from the beginning of the development of water treatment products leads to economically and ecologically optimised products, specially tailored for use in cooling systems. The ecological profile of a hardness stabiliser with long-term effectiveness (P3-ferrofos 8444) shows that the product degrades slowly after use in the receiving water, but due to its nontoxicity to water organisms, the environment will not be affected. A hardness stabiliser for shock dosage (P3-ferrofos 8413-3) is nontoxic, too, but is additionally rapidly biodegradable. When using the biocide for shock dosage, the product is destroyed in the environment by hydrolysis within a few minutes to some hours, so that a negative influence on the environment can be excluded. To reduce the biocide quantity, a biocide activator and dispersant (P3-ferrofos 8460) with a very low toxicity to water organisms is used.

PPChem 2003, 5(11), 677–685

Stephen W. Najmy

Ion Exchange Resin Analysis: What It Means and How It Helps

Sampling and analyzing ion exchange resin is a key part of ensuring long-term performance of the resin system in regard to product water quality and operational cost efficiency. This paper presents laboratory evaluation test methods essential for characterizing the mixed bed ion exchange resin used in steam cycle condensate polishing.

PPChem 2003, 5(11), 689–694

Ken McGrath

Independent Review of Operational Chemistry Practices at Power Plants

Management at both the local and corporate levels need an assurance that their power plants are being operated by best practice and to internationally recognised standards. A review of operational chemistry practices can provide a level of this assurance through an assessment of the quality and status of the chemistry of the power cycle. In this paper the author describes the review process he adopts and recommends. It is stressed that a review should involve the services of an experienced independent practitioner. The resulting benefits of a review are identified, as are some of the potential pitfalls.

PPChem 2003, 5(11), 695–698

Mirna Urquidi-Macdonald

The Impact of the G-Values and the Set of Water Radiolysis Reactions in the Calculation of the ECP on Normal Operation PWR Conditions

A chemistry/radiolysis/mixed potential model has been developed to calculate radiolytic species concentrations and the corrosion potential at closely spaced points around the primary coolant circuit of a pressurized water reactor (PWR). The pH(T) (pH as a function of the temperature) of the coolant is calculated at each point of the primary loop. The program has the ability to calculate the transient reactor response; however, in this paper, only the reactor steady state condition (normal operation) is discussed. The radiolysis model is a modified version of the code that was previously developed to model the radiochemistry and corrosion properties of boiling water reactor (BWR) primary coolant circuits. The modifications include the inclusion of additional species and reactions taken from other models that have been developed by others (e.g., Christensen) for describing the radiolysis of water; the model offers the possibility of choosing a different set of reactions while calculating the water radiolysis. The radiolytic yields (G-values) for the primary species, up to 14 species (e^-, H, OH, H_2O_2, HO_2, HO_2^-, O_2, O_2^-, H_2, O^-, O, O_2^{2-}, OH^-, H^+), can be modified depending on the set adopted. Finally, the Mixed Potential Model (MPM), which we previously developed to calculate the corrosion potential (ECP) around the primary heat transport circuit of a BWR, is used to calculate the ECP in the PWR primary coolant circuit. Because electrochemical

kinetic data is available only for the hydrogen electrode reaction (HER, H_2/H^+), the oxygen electrode reaction (OER, O_2/H_2O), and the hydrogen peroxide electrode reaction (HPER, H_2O_2/H_2O), only H_2, O_2, and H_2O_2 can be considered as the redox species in the MPM. Furthermore, we currently have electrochemical kinetic data for these species only on Type 304 SS, so that only this substrate could be modeled with respect to the ECP. However, it is believed that Type 304 SS serves as a good analog for other stainless steels and, perhaps, also for nickel-based alloys, such as Alloys 600 and 718. This is based on the observation that all of these chromium-containing alloys form passive films that are essentially Cr_2O_3 and that have the same thickness at any given potential. Because the exchange current density of a redox species is determined by resonant tunneling of charge carriers across the passive film, the exchange current densities for any given redox reaction on a wide variety of Fe-Cr-Ni alloys are expected to be similar. Furthermore, the electrooxidation current densities for various Fe-Cr-Ni alloys in the same solutions and under the same conditions are also similar, again reflecting the essentially similar natures of the passive films. Accordingly, the electrochemical potential (ECP), which reflects a balance between the partial currents for the anodic reactions (substrate oxidation and hydrogen oxidation) and the cathodic reactions (reduction of oxygen and hydrogen peroxide) that occur on the substrate surface, should be similar. No electrochemical data is available for Zircaloy, so that the ECP of this substrate could not be modeled. However, the code has been written so that appropriate values are readily inserted when they become available.

The importance of rate constant sets and radiolytic species yield in the calculations of the ECP on a hypothetic PWR was simulated. Six different types of rate constant sets and four types of radiolytic yields were explored. Among the explored sets, we used the set used by Macdonald to simulate a BWR. We modified the present model to simulate a hypothetic BWR, and we calculated the ECP along the reactor core. The results of the BWR calculations using the present model agreed with the ECP results published by Macdonald (results are not presented here). Once the present model was "benchmarked" against other existing models, the model was used to calculate the ECP in PWR conditions and its variations if different sets of reactions or G values were considered. The ECP, in the PWR, was calculated along the primary loop. The impact of the rate constants and yields on the results of the ECP calculations for a part of the core, steam generator, and the residual heat removal system (RHRS) is presented; all calculations are based on normal operation conditions.

The ECP, when different sets of radiation yields are considered, shows a wide range of variation, with differences – depending on where the ECP is measured – ranging from 200 mV (SHE) in the core regions to about 250 mV (SHE) in the low temperature regions of the steam generator. ECP variations on the order of 50 mV (SHE) in the core and 100 mV (SHE) in the RHRS are found for a given set of radiolytic yield values if we choose different sets of reactions.

Surprisingly – or perhaps expectedly – the large variation of the calculated ECP strongly depends on the set of radiolytic species chosen and the G-values assigned to the species considered on the reaction set [24]. These results point out the importance of carrying out additional experiments to more accurately determine i) the set of radiolysis species, and ii) G-values for the species considered.

PPChem 2003, 5(12), 708–720

Barry R. Dooley
Steve R. Paterson
J. Michael Pearson

HRSG Dependability

Heat recovery steam generator (HRSG) dependability relates strongly to the original design, thermal transients experienced, and the cycle chemistry regimes chosen. The leading HRSG tube failures (HTFs) are: corrosion fatigue in economizers and evaporators, thermal fatigue in economizers, superheaters and reheaters, flow-accelerated corrosion (FAC) in low pressure evaporators, and underdeposit corrosion (hydrogen damage, acid phosphate corrosion, and caustic gouging) in high pressure evaporators. The first two relate to inadequate decisions during the conceptual stages of the HRSG, and to poor designs which don't account for thermal transients. Corrosion fatigue is heavily influenced by nonoptimum chemistry, especially where large pH changes are allowed to occur during peak induced strain periods. Both single-phase and two-phase FAC oc-

curs and can be addressed by adequate cycle chemistry. The underdeposit corrosion mechanisms are driven by poor chemistry choices, and adventitiously or purposely added control chemicals. EPRI has developed a comprehensive understanding of all HTFs in terms of the mechanisms and possible root causes. This understanding has now been taken one step further to develop a set of lifetime actions (design, fabrication, commissioning and operation), which when applied will assist in alleviating HTFs. The paper will review some of the most important HTF mechanisms, the optimum approach to choosing the chemistry for each pressure cycle, and the key thermal transient issues and solutions.

PPChem 2003, 5(12), 727–739

Albert Bursik

The 1988 VGB Guideline for Boiler Feedwater, Boiler Water, and Steam of Steam Generators with a Permissible Operating Pressure of > 68 bar – Is This Guideline Still Up-to-Date?

Since 1951, the VGB Guideline for Boiler Feedwater, Boiler Water, and Steam of Steam Generators has been the most acknowledged European fossil plant cycle chemistry guideline. The current edition is from 1988. Fifteen years is a long period when looking at developments in the power and related industries. Naturally, such developments markedly influence tasks and solutions in the field of plant cycle chemistry. For this reason, the question *Is this guideline still up-to-date?* is asked.

An evaluation of any guideline requires consideration of the historical development of the guideline and the guideline-issuing organization. This is particularly important for overseas readers who are not familiar with either the VGB organization or the VGB Guideline for Boiler Feedwater, Boiler Water, and Steam of Steam Generators. Therefore, a brief historic overview precedes the actual evaluation.

Of the many possible evaluation criteria, the applicability of the guideline in utility units with all-ferrous and mixed metallurgy, in units with drum boilers, and in typical "non-utility" (industrial) steam-generating installations is considered. In addition, the appropriateness of the guideline for combined cycles with multipressure heat recovery steam generators (and for a combination of once-through and drum boilers in one combined cycle unit), the utilization of state-of-the-art knowledge of power cycle and steam chemistry, and the suitability for advanced training of chemistry and operation staff in power plants are also subjects of this assessment.

The evaluation reaches the conclusion that a reediting of this guideline is urgently required to ensure that the VGB organization remains a serious worldwide player in the fossil cycle chemistry field.

PPChem 2003, 5(12), 740–748

Robert F. Rathbone
Russ K. Majors

Techniques for Measuring Ammonia in Fly Ash, Mortar, and Concrete

The presence of ammonia in fly ash that is to be used in mortar and concrete is of increasing concern in the U.S., mainly due to the installation of selective catalytic reduction (SCR) DeNOx systems. When the SCR catalyst is new, contamination of the fly ash with ammonia is generally not a concern. However, as the catalyst in the SCR ages and becomes less efficient, the ammonia slip increases and results in a greater amount of ammonium salt being precipitated on the fly ash. The increase in ammonia concentration is compounded by variability that can occur on a day-to-day basis. When marketing ammonia-laden fly ash for use in mortar and concrete it is imperative that the concentration of ammonia is known. However, there currently is no widely accepted or "standard" method for ammonia measurement in fly ash. This paper describes two methods that have been developed and used by the University of Kentucky Center for Applied Energy Research and Boral Material Technologies, Inc. One of the methods uses gas detection tubes and can provide an accurate determination within five to ten minutes. Thus it is suitable as a rapid field technique. The other method employs a gas-sensing electrode and requires a longer period of time to complete the measurement. However, this second method can also be used to determine the quantity of ammonia in fresh mortar and concrete.

PPChem 2003, 5(12), 757–761

2004's Scientific and Technical Contributions: Papers in English

Robert Svoboda
Hans-Günter Seipp

PPChem 2004, 6(1), 7–15

Flow Restrictions in Water-Cooled Generator Stator Coils – Prevention, Diagnosis and Removal
Part 1: Behaviour of Copper in Water-Cooled Generator Coils

Flow restrictions in the stator bar cooling channels are commonly caused by copper oxide deposits. The paper discusses the mechanisms of such flow restrictions: formation, release, migration and transport of copper oxides. These parameters can be controlled by water chemistry. Of the 1,600 water-cooled stators world-wide (excluding Russia, China and Japan), about half operate under high-oxygen chemistry, the other half under low-oxygen conditions. Alkaline treatment and "cationic purification" are promising options.

Hariharan Subramanian
Madapuzi P. Srinivasan
Tulasi V. Krishna Mohan
Yadavalli V. Harinath
Valil S. Sathyaseelan
Sankaralingam Velmurugan
Sevilmedu V. Narasimhan

PPChem 2004, 6(1), 17–25

On-Line Measurement of Chemistry Parameters in a Simulated Reactor Coolant System

Structural materials interact with coolant water at high temperatures even though alkaline chemistry is prevalent in reactor circuits. The properties of oxide films formed on construction materials change with the regime of water chemistry. Proper understanding of the effect of the ingress of impurities and consequent changes in water chemistry on the integrity of power plant heat transport system structural materials is essential. On-line water chemistry monitoring helps in achieving this goal in an effective and comprehensive manner. The primary side water chemistry in pressurized heavy water reactors was simulated in a high temperature high pressure loop. Various water chemistry parameters, such as high temperature pH, conductivity, redox and open circuit potential of various structural materials, were monitored under normal as well as off-normal operating conditions simulated in the recirculating loop. All the potential measurements were referenced against an external pressure balanced reference electrode with Ag/AgCl as the active element. The reliability and sensitivity of on-line measurements were investigated.

Anthony C. Bevilacqua
Eric Maughan
Marc St. Germain

PPChem 2004, 6(1), 29–33

Is the Measurement of TOC in the Steam-Water Circuit of Power Plants Really Necessary?

Total organic carbon (TOC) has evolved as an important measurement in power/steam generation over the past decade. Different measurement technologies are required as compared to the monitoring of TOC in wastewaters. The significance of TOC measurement in the pure water circuits such as found in power/steam generation is discussed. Different technologies are described which are available for the monitoring of TOC in pure water circuits. The advantages and shortcomings of each method are presented. An alternative technology to those currently in use is described.

Albert Bursik

PPChem 2004, 6(1), 38–42

Power Plant Chemistry Practice – Cation Conductivity

In 1999 and 2000, some useful diagrams appeared in the PowerPlant Chemistry® journal. They shared the caption *Power Plant Chemistry Practice*.

Over the last few months, the PowerPlant Chemistry® editorial office has received many requests asking us to publish data useful in everyday power plant chemistry practice, e.g., basic diagrams which help in the interpretation of on-line analysis results and in controlling the most important cycle chemistry parameters.

For this reason, we are presenting a new series of diagrams starting in this issue. This month's topic is cation conductivity. Cation conductivity monitoring in a plant cycle is the basic surveillance tool for detecting the ingress of contaminants in the cycle. Unfortunately, the cation conductivity of a sample is a non-specific parameter. The kinds of substances contributing to or causing a cation conductivity increase are not known. For this reason, it is not easy or is sometimes hardly possible to evaluate the value measured]. The eight diagrams presented will help the user in evaluating the on-line monitoring results.

PPChem 2004, 6(1), 43–59

2003' Scientific and Technical Contributions – Papers in English

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Robert Svoboda
Russell Chetwynd

PPChem 2004, 6(2), 71–79

Flow Restrictions in Water-Cooled Generator Stator Coils – Prevention, Diagnosis and Removal
Part 2: Detection of Flow Restrictions in Water-Cooled Generator Stator Coils

Useful methods for detecting flow restrictions in stator bar cooling channels are the review of operating parameters and history vs. original design, of generator cooling water chemistry, of strainer and filter clogging history and of results from diagnostic chemical cleaning, as well as monitoring of stator water flow vs. pressure drop, individual stator bar water flow measurements, monitoring of on-line stator temperatures, visual inspections, and DC Hipot testing. A combination of these methods can be selected under consideration of plant specific hardware features and the cost-to-benefit relation.
A proactive approach to detecting flow restrictions is recommended in order to permit advanced planning of corrective action, thus reducing the risk of unplanned maintenance downtime, or even component failure. Managing flow restrictions at an early stage reduces the risk of severe plugging of conductors, which may be very difficult to remove later on.

Donald A. Palmer
Pascale Bénézeth
John M. Simonson

PPChem 2004, 6(2), 81–88

The Solubility of Copper Oxides around the Water/Steam Cycle

This paper summarizes an extensive laboratory scale experimental study of the solubility of cupric and cuprous oxides in water over a wide range of temperature (25–350 °C) and pH in the presence of various chemical agents (NaOH, NH_3, $B(OH)_3$, H_3PO_4, $(OHCH_2)_3CNH_2$, $(OHCH_2)_3CN(OHCH_2CH_3)_2$, HF_3CSO_3, HNO_3 and mixtures thereof), and in steam to 400 °C as a function of pressure. The results of this study show large discrepancies exist in previous data in the literature, especially at high temperatures for cuprous oxide, where the current solubilities are orders of magnitude lower. The solubilities of both oxides in water under power plant operating conditions are highly pH dependent, particularly above 100 °C, but are pH independent in steam, where the dependence on temperature is slight and the effect of pressure is only significant above 300 °C. The effect of temperature (i.e., during startup) on solubility at constant $pH_{25\,°C}$ is surprisingly large and varied. The effects of the added chemicals are discussed, particularly those due to ammonia in the case of cuprous oxide. Finally, the role of oxygen is mentioned, including its effect on the solubility of copper metal.

Des McInnes

PPChem 2004, 6(2), 91–96

Tarong Energy's Experience of Copper Mobilisation through a Drum Unit Cycle

Comprehensive preparation of the unit's water and steam cycles was completed prior to the implementation of oxygenated treatment on the 4 x 350 MW drum units at Tarong Power Station. Despite the completion of chemical cleans on the HP feedwater systems, boiler water walls and pendant superheaters prior to conversion, significant loss of turbine capacity and efficiency occurred. Tarong Energy and EPRI entered into a collaborative investigation into the capacity and efficiency losses, causes and source of the problems. The project utilised EPRI and Tarong Energy resources as well as independent contractors. This paper describes the symptoms and investigations, including on-line measurement, sampling, steam path auditing, turbine inspection and other indicative methods, used to positively identify the source and mobilisation of rogue copper.

Geoff J. Bignold
Graham P. Quirk

PPChem 2004, 6(2), 99–109

Corrosion Monitoring of LP Blade Materials in a 500 MW Steam Turbine

Steam turbine blade and disc failures have occurred from time to time throughout the world. Although they are rare events, the implications for safety, for repair costs and for loss of availability are severe. Current operational and maintenance practices for any particular turbine design may be based on many years of satisfactory service. However, recent deregulation of the power industry in the UK and forthcoming deregulation in the USA may have an effect on operational and reliability issues, as changing operational demands are placed upon power generators through economic forces.

In the UK in the 1990s with deregulation and privatisation of power generation, the introduction of high efficiency gas-fired stations transformed the profile of the industry. The nuclear stations (which can only operate safely and economically under base load conditions), the gas-fired stations, and those coal-fired stations that have been fitted with flue gas desulphurisation (FGD) systems, accounted for the majority of base load supply. The remaining coal-fired stations were, therefore, forced towards operating for peak demand rather than base load. They have had to develop operating procedures that enable them to provide power flexibly and economically with rapid response to variable demand. One of these procedures covers running up the unit to stable conditions before power is produced.

This paper gives an account of the research carried out over 7 months to confirm the risks of turbine damage, which was essentially due to corrosion during the startup sequence. On-line corrosion monitoring with the electrochemical noise technique was used with probes installed directly within the low pressure (LP) section of an operating 500 MW turbine. Pitting corrosion at the turbine blade root had been found to be the primary factor in the onset of stress corrosion cracking (SCC), which eventually caused the failure of a turbine blade with very serious consequences for the unit. Determining the causes and reducing the occurrences of pitting activity would mitigate the risk of blade failure due to SCC.

The early results showed that the corrosion in this unit did indeed occur predominantly during the startup sequence, coinciding with the presence of chloride contamination in the condensate, which was sprayed onto the final stage for blade cooling. After the Phase 1 monitoring programme, engineering modifications were completed on the spray system to eliminate the risk of spraying with contaminated condensate. The corrosion monitoring then continued for a further 4 months and demonstrated that the rate of the corrosion had been very significantly reduced. This quantitative demonstration of reduction of corrosion activity enabled rescheduling of ultrasonic inspections of the blade roots, with a consequent increase in station availability.

Hans-Peter Seifert
Stefan Ritter
John Hickling

PPChem 2004, 6(2), 111–123

Research and Service Experience with Environmentally Assisted Cracking of Low-Alloy Steel Pressure-Boundary Components under LWR Conditions

Environmentally assisted cracking (EAC) of carbon and low-alloy steels has been identified as a possible degradation mechanism for pressure vessels and piping in nuclear power plants. Selected aspects of research and service experience with EAC of these materials in high-temperature water are reviewed, with special emphasis on the primary pressure-boundary components of boiling water reactors (BWRs). The main factors controlling EAC susceptibility under light water reactor conditions are discussed with regard to both crack initiation and crack growth. The adequacy and conservatism of the current "BWRVIP-60 SCC disposition lines" and "ASME Section XI reference fatigue crack growth curves" are evaluated in the context of recent research results, e.g., on the effect of so-called "ripple loading", or of water chemistry transients. Finally, the relevant operating experience is summarized and compared with the background knowledge which has been accumulated in laboratory experiments over the last 30 years.

Robert Svoboda
Christoph Liehr
Hans-Günter Seipp

PPChem 2004, 6(3), 135–144

Flow Restrictions in Water-Cooled Generator Stator Coils – Prevention, Diagnosis and Removal
Part 3: Removal of Flow Restrictions in Water-Cooled Generator Stator Coils

The removal of flow restrictions in generator stator bars can be achieved either by mechanical or by chemical cleaning, or by a combination of both. Experience has shown that mechanical cleaning on its own is not thorough, and chemical cleaning is not capable of removing very severe plugging, as found in completely plugged conductors. The choice of method or combination of methods thus will depend on the specific case, as well as on its impact on generator availability. Mechanical cleaning can be done by backflushing or by localized manual cleaning. The latter is very effective but possible only within a limited range of accessibility. Chemical cleaning can be done by acids or by complexants. It is important that chemical cleaning be done in at least some stages under oxidizing conditions. A post-cleaning surface treatment may be required under certain circumstances. Managing flow restrictions at an early stage is recommended in order to reduce the risk of severe plugging of conductors that may be very difficult to remove later on.

Daniel Zinemanas

PPChem 2004, 6(3), 145–150

A Simple Model for Studying the Effect of Condenser Cooling Water Leakage on Cycle Water Chemistry

In this paper, a dynamic simulation of the main cycle chemical variables in a generation unit under condenser leakage conditions is performed by means of a simple numerical model of the main water/steam cycle. The results of this simulation are compared to the values measured online in an operating unit under similar conditions, and a close correspondence between them is found. This close agreement between the model predictions and the real data indicates that the model, although simple, is robust enough to provide good insight into and understanding of the water/steam cycle behavior under the conditions studied. However, in spite of the good predictions achieved, further improvement and validation of the model are desirable and will follow in future work.

R. Barry Dooley
Kevin Shields

PPChem 2004, 6(3), 153–166

Cycle Chemistry for Conventional Fossil Plants and Combined Cycle/HRSGs

To become or to remain World Class in cycle chemistry, an organization must be continually assessing its total treatment philosophy. Not least here is that the guidelines to which it operates its units must be on the cutting edge of science and technology. In this regard, EPRI's research over the last 10 years into steam, the phase transition zone, partitioning/volatility, copper corrosion and transport, and boiler water corrosion/deposition has provided the ability to make the previous guidelines and understanding obsolescent.
Over the last two years, most of the suite of EPRI treatment guidelines have been revised. In addition to all-volatile treatment (AVT) and caustic treatment (CT), the new phosphate continuum (PC) has been introduced. This supplements the recently introduced concepts of oxidizing AVT (AVT(O)) and reducing AVT (AVT(R)). More importantly, these guidelines now contain a new methodology, which decouples the derivation of the boiler water guidelines from the steam guidelines, and provides unique limits to protect the boiler and turbine individually. The discussion in the paper focuses on the application of these guidelines to conventional and combined cycle plants, illustrating how they have been designed to address the major chemically influenced problems in both types of plant.

Syuichi Gotou
Yuichi Abe
Takashi Morimoto
Kenji Mawatari
Senichi Tsubakizaki

PPChem 2004, 6(3), 167–176

Experience of Phosphate Treatment by Disodium Phosphate Application in Sakata Kyodo Power Station

Most commercial drum boiler units with an operation pressure higher than 10 MPa in Japan generally use sodium phosphate at a Na-to-PO_4 molar ratio of 2.5–2.8, although there are some cases of industrial boiler units that must be controlled at Na-to-PO_4 molar ratios of 3.0 or greater because of the occurrence of the sodium phosphate hideout phenomenon, or in order to deal with the lowering of pH by organic components in the makeup water (these are decomposed within the boiler and generate organic acids). This paper reports on the experiences at Unit 1 of the Sakata Kyodo Thermal Power Station under conditions of application of disodium phosphate in the phosphate treatment.

Miroslaw Gruszkiewicz
Albert Bursik

PPChem 2004, 6(3), 177–184

Degassed Conductivity – Comments on an Interesting and Reasonable Plant Cycle Chemistry Monitoring Technique
Part 1: Degassing of Low-Molecular-Weight Organic Acids in Technical Degassed Cation Conductivity Monitors

Degassed cation conductivity monitoring is not as common as specific and cation conductivity monitoring even though this technique offers some very interesting features. This technique can help to distinguish between plant cycle contamination with inorganic and/or organic acids and/or their salts and that caused by carbon dioxide. This may be important, e.g., during startup of a unit. Two issues are often discussed in connection with degassed conductivity monitoring: the behavior of formic and acetic acid during degassing and the correct conversion of values measured at nearly 100 °C to standard temperature (25 °C). This first part of a two-part publication focuses on the first issue. A rigorous thermodynamic approach was chosen for the evaluation of conditions in the degassing part of the monitoring system. The results of calculations clearly show that the actual loss of formic and acetic acid in a technical atmospheric degassing

system via system vents is so low that it can be disregarded. In contrast, the concentration of formic and acetic acid in the sample exiting the technical atmospheric degassing system is somewhat higher than that in the original sample. The actual increase in concentration is based on the volatility behavior of both acids and depends additionally on the evaporation rate of the system.

Robert Svoboda
Christoph Liehr
Hans-Günter Seipp

PPChem 2004, 6(4), 197–202

Flow Restrictions in Water-Cooled Generator Stator Coils – Prevention, Diagnosis and Removal
Part 4: Chemical Cleaning of Water-Cooled Generator Stator Coils by the Cuproplex® Method

The Cuproplex process for removing copper oxides from generator cooling systems is characterized by the coordinated use of complexants, oxidants and auxiliary chemicals. The process can be performed off-line, as well as on-line with the generator in operation.

Off-line cleaning is usually done by injecting the dilute chemicals into the running pure-water system, sequentially over several cycles. On-line cleaning employs the continuous injection of chemicals at a sufficiently dilute concentration to keep conductivity below maximum allowed limits. On-line cleaning does not interfere with generator availability and provides real-time monitoring of the cleaning effects. However, on-line cleaning takes longer. The reagent and the dissolved copper are absorbed in the ion exchanger that is part of the system and disposed of as solid waste. The process thus offers the possibility of zero-liquid discharge.

Hugh P. Fallon

PPChem 2004, 6(4), 203–222

A Performance-Based Approach to Cooling Water Chemistry Control

Cooling water treatment programs traditionally rely on the application of chemical products to design-based residuals, with the use of external – typically reactive – analysis and monitoring techniques to maintain system performance. Such programs can be inherently inefficient, using too much or too little chemical at the wrong times. Decision-making is often based on how the system was behaving in the past, not how it is performing currently, or how it may perform in days or weeks to come.

The Otahuhu B Power Station is a modern 380 MW single-shaft combined cycle facility, incorporating a low-cycle, estuarine water, evaporative hybrid cooling tower. A comprehensive control and instrumentation project is underway to modernise the cooling water treatment program. The ultimate goal of this project is to move from a passive control system with very little monitoring to one based around real-time, on-line, semi-predictive performance monitoring techniques that proactively manage the application of varying residuals according to actual system requirements. Control programs are being designed to assess the known system parameters and the plant performance, and to dose chemical on the basis of that performance according to rules-based logic. Work to date has already resulted in a more efficient dosing regime, significantly reducing chemical treatment costs, while simultaneously improving the overall plant monitoring and helping to minimise the environmental impact of discharged effluent.

Geoff Spowart

PPChem 2004, 6(4), 224–228

Implementing the Power Station Cooling Water Standard AS 5059-2003

The new Australian standard "Power Station Cooling Tower Systems – Management of Legionnaires' Disease Health Risk" (AS 5059-2003) was released in September 2003 following several years of work by a large number of chemists in the power industry. The standard uses a risk based methodology to allow power stations to develop plans to minimise *Legionella* levels in cooling water systems.

This paper addresses the issues that stations are likely to encounter in meeting the requirements of the standard. The paper discusses the impacts of the:
- cooling system design,
- operating and maintenance philosophies,
- characteristics of the makeup water,
- biocide treatment program,
- alternative treatment program,
- monitoring requirements and reporting requirements.

Abdolreza Zaltash
Andrei Petrov
D. Tom Rizy
Rick Langley
Eric Hubbard

PPChem 2004, 6(4), 229–236

Emissions Levels of Various Gas Microturbines

The variety of new distributed generation (DG) technologies, such as gas microturbine generators, as well as of integrated energy systems (IESs) has increased markedly over the last several years. Oak Ridge National Laboratory and EPRI PEAC have worked collaboratively to test various DG machines, including 30 to 80 kW microturbine generators (MTGs). Environmental issues are among the most important aspects of operating these DG systems. This paper addresses the emissions from MTGs of various makes and sizes. The two basic emissions components – carbon monoxide (CO) and nitrogen oxides (NO_x) – were given close attention. For each MTG, emissions at steady-state operation were measured at different power output levels. For transient tests the emissions were measured as the MTG power output varied during startup, shutdown and during power dispatch (as the power varied from one setting to another). Evaluation of the various emissions levels for the different MTGs was performed as well as of compliance with existing environmental regulations (U.S. and Europe) and manufacturer's data.

PPChem 2004, 6(4), 237–248

Down Under – The ESAA's Conference "Power Station Chemistry 2004"

In March 2004, the Energy Supply Association of Australia Limited (ESAA) in conjunction with Connell Wagner PPI held its "Power Station Chemistry 2004" conference in New South Wales, Australia. In this paper, the ESAA and the conference venue are briefly introduced and some details illustrating the flair of the conference are presented. The conference organizers succeeded in making possible an extended exchange of experience in a nice and informal atmosphere with more than thirty high-level technical papers.

Valérie Larbalestrier
Simon Gare

PPChem 2004, 6(5), 261–264

Combined Chemical and Physical Oxygen Removal Strategies for the Power Industry

Over the last 25 years Ecolochem has gained knowledge and experience providing short term and emergency solutions to power industries worldwide. In 2001, the organisation began providing both short term and emergency services in Australia. This paper describes two techniques used for the removal of oxygen to meet the requirements of power stations, and finally reviews the combination of these two techniques.

Garry Craig
Steve Wheeler

PPChem 2004, 6(5), 269–272

Low Load Operation – Effect on Cycle Corrosion

Market forces require intermediate loaded power stations (such as Eraring) to operate at low loads at times when prices are low. Lack of operational experience at these low loads has led to some operational problems, such as control of dissolved oxygen in the condensate. At lower loads dissolved oxygen levels are elevated due to both dilution effects (less flow) and the fact that equipment normally under pressure is placed under vacuum.

These higher dissolved oxygen levels in conjunction with sub-cooling of the condenser at these low loads leads to high levels of ammonia in areas outside the air extraction zone. The air extraction zone is protected by the use of 90/10 copper/nickel tubes. Tubes outside the air extraction zone are aluminium brass. Grooving of the condenser tubes can then occur when the condensate pools at a tube support plate (or sag plate) with these high levels of ammonia and dissolved oxygen.

Eraring Power Station has experienced many more condenser tube failures whilst operating at loads below 230 MW (below 35 % of unit capacity). Minimum load for units has now been pegged to this load following trials at 210 MW and as low as 180 MW.

This paper explores the failures experienced at Eraring and suggests some methods that may improve the situation at loads lower than 230 MW.

David J. Knights

PPChem 2004, 6(5), 273–278

Water Reform, Droughts, Fish and the Community: Tarong's Approach to Water Supply Issues and Risks

Tarong Energy operates and maintains the 1 400 MW Tarong Power Station in Queensland's South Burnett region. The station is a major water user, drawing water from two major catchments in southeast Queensland.

Council of Australian Governments water reforms and Queensland's Water Resource Plans will leave a lasting impression on water users. The reforms and the resulting operating rules for water resources are important issues for large water users like Tarong Energy.

Droughts, the reliability of water supply, community and environmental concerns are some of the major issues confronting Tarong's past and future operations. This paper describes Tarong's approach to and options for dealing with the water supply risks, which have been numerous and complex.

Miroslaw Gruszkiewicz
Albert Bursik

PPChem 2004, 6(5), 279–289

Degassed Conductivity – Comments on an Interesting and Reasonable Plant Cycle Chemistry Monitoring Technique
Part 2: Degassing of Carbon Dioxide in Technical Degassed Cation Conductivity Monitors and Temperature Conversion of the Cation Conductivity Measured at Nearly 100 °C to 25 °C

The efficiency of degassing carbon dioxide in vented reboiling systems is discussed on the basis of thermodynamic equilibrium calculations. Even though the vapor containing carbon dioxide is continuously removed instead of remaining in contact with the liquid, it is believed that the thermodynamic model provides a realistic approximation of the actual process. The essential parameter of the model, the fraction of the solution evaporated, corresponds to the actual rate of evaporation before any possible reflux. The analysis of a number of examples indicates that the efficiency of carbon dioxide removal depends strongly on the rate of evaporation, and therefore, taking into account the construction and operation of typical degassed conductivity monitors, is expected to often be far from complete. The presence of impurity anions lowers the pH of the solution leaving the cation exchange column, suppressing the dissociation of carbon dioxide, and thus increasing its volatility. However, this effect is small at the levels of impurities that meet the usual requirements for high-pressure power plant cycles, and, additionally, the resultant decrease in conductivity can be at least partially masked by the increased concentration of non-volatile impurities. The problem of conversion of the conductivities of mixtures of unknown composition measured near the normal boiling point of water to ambient temperature (25 °C) cannot be solved due to non-trivial variations in ionic association and equivalent conductances between different electrolytes. The conversion equation proposed here is based on an empirical approach minimizing the probable error. The necessary ionic mobility data are based on a semi-empirical predictive method for the estimation of ionic mobilities as a function of temperature.

Richard T. Wilburn
Thomas L. Wright

PPChem 2004, 6(5), 295–304

SCR Ammonia Slip Distribution in Coal Plant Effluents and Dependence upon SO_3

The selective catalytic reduction (SCR) of nitrogen oxides by ammonia has become a common control technology for European and Japanese stationary combustion sources. It is becoming an increasingly more prevalent technology in the United States, yet has not reached the level of maturity as in overseas applications. As such, there are many differences in the fuel quality and other plant operating conditions that require special consideration, such as high sulfur bituminous coal and the effect of sulfur trioxide (SO_3) evolution and mitigation at the SCR catalyst. This paper addresses the formation of the ammonium deposits and the distribution of ammonia slip in plant waste streams as a function of SO_3 concentrations and other parameters. Many plant situations can expect some ammonia related plugging of air heaters and contamination of wastewater streams; however, in the case of burning high sulfur coal and the implementation of a SO_3 removal process, expected ammonia distributions can shift dramatically from air heater and electrostatic precipitator deposits to the absorption of ammonia directly into flue gas desulfurization process water.

Stephen E. Ziemniak
Edward P. Opalka

PPChem 2004, 6(6), 325–332

Phase Stability of Chromium(III) Oxide Hydroxide in Alkaline Sodium Phosphate Solutions

Grimaldiite (α-CrOOH) is shown to transform to a sodium chromium(III) hydroxyphosphate compound (SCrHP) in alkaline sodium phosphate solutions at elevated temperatures via

$$CrOOH(s) + 4Na^+ + 2HPO_4^{2-} = Na_4Cr(OH)(PO_4)_2(s) + H_2O$$

X-ray diffraction analyses indicate that SCrHP possesses an orthorhombic lattice having the same space group symmetry (Ibam, #72) as sodium ferric hydroxyphosphate. The thermodynamic equilibrium for the above reaction has been defined in the system Na_2O-P_2O_5-Cr_2O_3-H_2O for Na/P molar ratios between 2.0 and 2.4. On the basis of observed reaction threshold values for sodium phosphate concentration and temperature, the standard molar entropy (S^0) and free energy of formation (ΔG_f^0) for SCrHP has been calculated to be 815.4 and –3 497.01 kJ · mol^{-1}, respectively.

Santhanam Ranganathan
Madapuzi P. Srinivasan
Sevilmedu V. Narasimhan
Pandalgudi S. Raghavan
Raghavachary Gopalan

PPChem 2004, 6(6), 333–342

Kinetics of Dissolution of α-Fe_2O_3 and γ-Fe_2O_3 in EDTA and NTA-Based Formulations

The dissolution studies were carried out on haematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) in two different formulations of ethylenediaminetetraacetic acid (EDTA) and nitrilotriaceticacid (NTA). The rate constants were calculated using the "inverse cubic rate law." The leaching of the metal ions from the oxide is controlled partly by the Fe(II)-L_n (L is a complexing ligand and n is the number of ligands attached to Fe^{2+}), a dissolution product arising from the oxides having Fe^{2+} in the lattice. The addition of Fe(II)-L_n along with the formulation greatly increased the initial rate of dissolution. The effect of the addition of Fe(II)-L as a reductant on the dissolution of α-Fe_2O_3 was not the same as in the case of γ-Fe_2O_3. The rate constants (k_{obs}) for the dissolution of α-Fe_2O_3 and γ-Fe_2O_3 in the presence of ascorbic acid were less in the EDTA formulation than in the NTA formulation. The studies using Fe(II)-NTA and Fe(II)-EDTA with varying compositions of citric acid and ascorbic acid revealed that a minimum quantity of the chelant is sufficient to initiate the dissolution process, which can be further controlled by the reductants and weaker chelants such as citric acid.

Nigel J. Drew

PPChem 2004, 6(6), 343–349

Evaluation of Degassed After-Cation-Exchange Conductivity Techniques

After-cation-exchange conductivity (ACC) systems are the universally used method for rapid detection of anionic impurity ingress into the steam/water circuit of power plant. In some utilities, ACC is measured after degassing the sample. It is generally considered that carbon dioxide is the least aggressive contaminant of feedwater that is normally present and causes elevation of the measured ACC. The elevation of ACC by carbon dioxide can be particularly noticeable when the oxygen scavenger is carbohydrazide, or the water contains dosed amines or neutral organic compounds in the make-up water. Ingress of carbon dioxide could be considerable in the case of tube leakage in some parts of the boilers of gas-cooled nuclear stations. The elevated ACC then delays unit start-up. There are two widely used techniques for degassed ACC systems: gas stripping with nitrogen and heating to near boiling. Membrane gas-exchange systems are now also beginning to appear on the market. British Nuclear Fuels Plc. and British Energy arranged for an evaluation of these three types of system to determine if they would be sufficiently effective for use in their power stations. The results of the evaluation are summarised here and measured values are compared with theoretical calculations for ACC and degassed ACC.

Geoffrey Frost

PPChem 2004, 6(6), 351–357

The Use of Mobile Water Treatment Equipment to Supply Supplemental High Purity Water during Commissioning at Millmerran

Large volumes of high purity water are required during power station commissioning for the critical tasks of boiler hydrotesting, chemical cleaning and steam blows. As with most new stations, the permanent water treatment plant at Millmerran was sized for normal operating conditions and could not supply the quantity of high purity water required for the commissioning program. To resolve this situation a mobile water treatment plant, provided by Ecolochem, produced a supplemental flow of up to 30 m^3 · h^{-1} of high purity water on a continuous basis over a period of six months from March to September 2002. The conductivity of the supply water to the mobile plant ranged from 1 700 to 2 700 µS · cm^{-1} and it was a major challenge to achieve the final treated water quality targets of 0.1 µS · cm^{-1}, 10 µg · L^{-1} SiO_2 and 100 µg · L^{-1} total organic carbon. This paper discusses the design and operation of the mobile water treatment plant used at Millmerran and how various operational problems were overcome during the project.

Jenny Lindsay

PPChem 2004, 6(6), 361–365

Loy Yang Power – Cooling Tower Chemical Dosing Implementation: Practical Findings

From early 2001, GE Betz were given the opportunity to treat the Loy Yang Power Station cooling water systems to control microbiological activity and corrosion of the copper-based metallurgy in those systems.
After commencing with continuous dosing of sodium hypochlorite as the biocide and the traditional tolyltriazole (TTA) as the copper corrosion inhibitor, the treatment program was optimised over the next year of operation. Sodium hypochlorite efficiency was determined by monitoring of both *Legionella* and total bacteria to determine the effectiveness of the biocide program and by using oxidation reducing potential to measure on-line the activity of the biocide. Copper corrosion inhibitor efficiency was determined using the on-line linear polarisation resistance technique (Corrator), corrosion coupons and by measuring copper concentrations in the recirculating cooling water.
The optimisation process concluded that to meet the key performance indicators for control of microbiological activity the most cost effective water treatment program was to use intermittent dosing of sodium hypochlorite. Further optimisation of the sodium hypochlorite consumption was achieved by proactively adjusting the dosage rate by taking into account the historical microbiological activity results. This proactive altering of the dosage rate of the sodium hypochlorite resulted in extra dosage occurring when the ambient temperature increased, i.e., in the hotter summer months, and a reduced dosage being required in the cooler winter months.
The traditionally used copper corrosion inhibitor, TTA, was found to be unable to control corrosion to meet the key performance indicators at cost effective dosage rates when the higher levels of sodium hypochlorite dosage were being applied, which resulted in the introduction of the halogen resistant azole (HRA) as an alternative to TTA. HRA provided an immediate improvement in copper corrosion and whilst there is still a requirement to adjust the HRA dosage as the level of sodium hypochlorite is increased, this optimisation process has shown the HRA to be a more effective copper corrosion inhibitor than TTA.

Albert Bursik

PPChem 2004, 6(6), 373–377

Utility Management vs. Power Plant Chemistry – A Defense Counsel's Summation

Over the last two decades, the number of power plant chemists in fossil utilities – not to mention industrial steam and power generation – has dramatically decreased. In this paper, an attempt is made to find out the reasons why utilities in general underestimate the role of plant cycle chemistry. It seems that shortsighted economic evaluations disregarding the long-term aspects entice the utility management to decide against plant cycle chemistry with respect to manpower and costs.
It is felt that chemists in utilities play a part in their not very high valuation. Some examples are given demonstrating how a chemist may contribute to his poor appraisal. To improve the chemist's position in a utility, benchmarking of cycle chemistry and chemistry's function in an organization on a regular basis is advantageous.
For utilities, it is shown that being concerned with plant cycle chemistry and establishing conditions which make achieving or maintaining the "World Class" category in plant cycle chemistry possible pays. For this reason, providing utility chemists with adequate funds and carrying out regular cycle chemistry audits, peer reviews, or benchmarking actions helps in ensuring optimum plant cycle chemistry and optimum operation and maintenance costs.

Santhanam Ranganathan
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Raghavachary Gopalan
Madapuzi P. Srinivasan
Sevilmedu V. Narasimhan

PPChem 2004, 6(7), 389–399

The Dissolution Kinetics of Magnetite under Regenerative Conditions

Dissolution studies of magnetite were carried out under regenerative conditions in dilute chemical decontamination formulations. During regeneration of the formulation, the H^+ from the strong acid cation exchange resin gets released and the metal is absorbed on the resin. The efficiency of the regenerative process depends on the stability constants of the complexes involved and the selectivity on the ion exchange column. The regenerative condition helps to maintain a constant chelating agent concentration and pH during the dissolution experiment. Such a condition is ideal for obtaining data on the dissolution behaviour of the corrosion products with special application to actual reactor decontamination. The ethylenediaminetetraacetic acid (EDTA) based formulation

used was found to be ineffective due to the high stability constant of Fe(III)-EDTA complex, which is not easily removed by the cation exchange resin. Hence, knowledge of the kinetics of magnetite dissolution under regenerative condition is of primary importance. The 2,6-pyridinedicarboxylic acid formulation is found to be better for the dissolution of Fe_3O_4 in both static and regenerative modes in the presence of reductants than nitrilotriacetic acid and EDTA.

Kenneth Tittle

PPChem 2004, 6(7), 401–406

The Continuous Measurement of Total Carbon Dioxide in Water/Steam Circuits

The paper describes a robust monitor for the continuous measurement of carbon dioxide in water/steam circuits based on a gas permeable membrane system. Samples to be analysed are acidified to pH 3.4–3.6 to convert all the contained carbon dioxide species into 'free' carbon dioxide/carbonic acid. A fraction of this carbon dioxide is then diffused through a membrane into a stream of high purity water generating an increase in conductivity. This change in conductivity is used as a measure of the total carbon dioxide content of the original sample.
The paper describes the design, operation and calibration procedures used. The monitor can be used to measure carbon dioxide concentrations ranging from a few $\mu g \cdot kg^{-1}$ up to $mg \cdot kg^{-1}$ carbon dioxide.
The effects of sample temperature and flow rate are discussed together with possible interference from other species present in acidified samples. Some results of plant monitoring tests are also included.

Stuart Day

PPChem 2004, 6(7), 407–413

Oxygen Conversion of Collie No 1: Results from Operation at Predominantly Base Load with Overnight Load Reduction

This paper describes the conversion of a 300 MW unit with a drum-type natural circulation boiler from a hybrid treatment (all-volatile treatment from the condenser up to the deaerator inlet, reducing all-volatile treatment using hydrazine from the deaerator outlet to the boiler and the turbine) to the oxygenated all-volatile treatment. The reasons for the conversion were the occurrence of flow-accelerated corrosion, high iron levels in the feedwater and extended magnetite deposition in some parts of the cycle. Since the conversion, no iron levels less than 2 $\mu g \cdot kg^{-1}$ have been measured, hence it seems that flow-accelerated corrosion is still active in some parts of the condensate and feedwater system. One of the interesting issues is the fact that in this unit the oxygenated treatment is practicable even with a Tripol condensate polishing plant which is operated in ammonia cycle.

Mike Caravaggio

PPChem 2004, 6(7), 417–424

Lambton Generating Station's Experience with HP Turbine Copper Deposition

This paper covers the understanding developed from, as well as the timeline and techniques that were used to address, rapid, dramatic HP turbine performance losses associated with copper deposition on two of four 500 MW coal-fired drum units at Ontario Power Generation's (OPG's) Lambton Generating Station (GS) over the last three years. The two affected units both had greater than 20 MW de-rates caused by copper deposition and 5–10 % losses in HP cylinder efficiency during the period. On one unit the HP cylinder was being replaced by a dense pack HP turbine (decision made prior to identifying the copper deposition issue), and on the other unit a physical clean of the turbine was opted for, with additional study being conducted for possible chemical cleans in the future. This paper outlines Lambton's current understanding of the copper transport cycle through a drum type boiler (based on industry literature and OPG/Lambton GS operating experience), as well as Lambton's experiences to date with the solutions chosen for addressing HP turbine copper deposition.

Albert Bursik

PPChem 2004, 6(7), 425–430

EN 12952-12:2003, Water-Tube Boilers and Auxiliary Installations – Part 12: Requirements for Boiler Feedwater and Boiler Water Quality – A European Standard Put to the Test –

In December 2003, Part 12 (Requirements for Boiler Feedwater and Boiler Water Quality) of the European Standard "Water-Tube Boilers and Auxiliary Installations" appeared. According to the Pressure Equipment Directive of the European Commission, this standard should ensure that the hazards associated with the operation of water-tube boilers

are reduced to a minimum and that adequate protection is provided to contain the hazards that still prevail when the water-tube boiler is put into service. The standard is compulsory. Power plant chemists should keep in mind that noncompliance with this standard may have serious (legal) consequences.

This contribution considers whether this standard actually addresses all safety-related parameters and whether it abstains from setting parameters that are not related to equipment and personnel safety. According to the Pressure Equipment Directive demands, parameters important for economics, availability and steam quality as well as those relevant to the operation of other cycle components should not be dealt with in this standard.

Brad Buecker

PPChem 2004, 6(7), 431–436

Wet Limestone FGD Solids Analysis by Thermogravimetry

Wet limestone scrubbing is once again becoming a popular technology for removal of sulfur dioxide (SO_2) from power plant emissions. Critical to the operation of wet limestone flue gas desulfurization (FGD) systems is accurate chemical analysis of scrubber solids. The analytical technique of thermogravimetry is ideal for this application, as the instrument can give precise readings of the principal scrubber solids components, calcium sulfite/sulfate hemihydrate, calcium sulfate dihydrate (gypsum), and unused calcium carbonate. The data provides plant chemists, engineers, and operators with information needed to fine-tune scrubber operation and detect process upsets.

Kevin J. Shields
Keith Fruzzetti
Michael A. Sadler

PPChem 2004, 6(8), 452–457

Condensate Polishing in Fossil and Nuclear Steam/Water Cycles

Impurity levels in the water supplied to the high pressure steam raising plants used for power production must be maintained at as low a level as reasonably possible in order to minimise corrosion and deposition in their steam/water circuits. This has led to the Electrical Power Research Institute strongly supporting the continuous purification of condensate on fossil and nuclear power stations by the use of ion exchange and filtration. It has sponsored the testing and investigation of new processes and currently is exploring innovative approaches aimed at meeting the perceived future requirements of the power industry. This paper briefly reviews the work already carried out in this field and stresses the need to reduce both the capital and operating costs of condensate polishing plants on fossil fired power stations. It also suggests possible developments.

Alan D. Miller
Keith Fruzzetti

PPChem 2004, 6(8), 461–464

Optimization of Ion Exchange in Polishers at PWRs

Blowdown polishers are indispensable components in the secondary systems of pressurized water reactors. The application of advanced amines to reduce iron levels in final steam generator feedwater influences the resin selection for and operation of condensate polishers. There are many opportunities to optimize blowdown polisher performance. This paper summarizes the work currently underway to optimally use resin properties such as ion selectivity and capacity and operational parameters to maximize water quality while minimizing cost. It is shown that the best amine for a given power plant is a complex function of amine properties, ion exchange resin choice, purification systems and other plant design and operational parameters.

Claudia Lacher
Matthias Franzreb
Wolfgang H. Höll

PPChem 2004, 6(8), 465–471

Improving the Efficiency of Electrodeionization by Means of Magnetic Ion Exchange Resins

Magnetic micro ion exchangers have been used in an electrodeionization cell within a magnetic field to prevent demixing of the ion exchange filling in the diluate chamber. Initial studies showed that the electrical resistance is an appropriate parameter to characterize the homogeneity of the mixed bed. In order to describe the effect of the magnetic field on magnetic ion exchangers, the electrical resistance of the cell has been determined prior to electrodeionization experiments. Experiments were conducted within and outside a magnetic field to evaluate the improvements.

Stuart Harrison
Brendan Poots
Geoff Grellman

PPChem 2004, 6(8), 475–481

An Evaluation of MIEX® for DOC Removal from Power Station Water Supplies

A revolutionary process for the removal of dissolved organic carbon (DOC) has been developed in Australia by Orica Advanced Water Technologies in conjunction with the South Australia Water Corporation and the Commonwealths Science and Industrial Research Organisation. The MIEX® resin process is a continuous ion exchange process, employing a unique strong base anion resin, designed for the removal of DOC from water supplies.

In the first stage of the process, the MIEX® resin is mixed with the water to be treated and its small size encourages rapid removal of DOC. The resin beads also contain a magnetic component responsible for their rapid agglomeration and very efficient removal by sedimentation in the second stage of the process. Flexibility in the process is achieved by recycling approximately 90 % of the recovered resin and adding the remaining 10 %, required for maintaining the resin concentration, as fresh (regenerated) resin. The remaining 10 % of the recovered (used) resin is sent to a regeneration system where it is regenerated and returned to the system for use. The high capacity and unique structure of the resin guarantees minimal attrition, a long performance life and makes the process very cost effective.

The MIEX® resin process differs significantly from conventional ion exchange processes in that the overall ion exchange capacity within the process is continuously maintained. That is, it does not drop off with time as ion exchange capacity is progressively exhausted, as is the case for conventional ion exchange processes. As a consequence, the product water from this process is of consistent quality with DOC controlled at a predetermined level. The process is capable of handling significant fluctuations in raw water quality.

The MIEX® process was evaluated to determine how it might be best implemented for DOC removal at Delta Electricity's Wallerawang Power Station in New South Wales, Australia. DOC in the raw water supply to Delta Electricity's steam generation demineralisation pre-treatment plant was compromising the efficiency of the overall process. The DOC was fouling the demineralisation plant resulting in the production of poorer quality water, repeated cleaning and increased maintenance requirements. Batch and pilot plant studies were conducted to evaluate the MIEX® resin performance when it was applied to treat raw water before the existing demineralisation pre-treatment facility. The demineralisation plant is currently used to supply water to the steam generation plant. Measurements of DOC and ultraviolet absorbance at 254 nm were made to characterise DOC removal. In addition, the impact of this MIEX® treatment on the existing treatment regime together with potential improvements in operational efficiency of the plant were also evaluated.

This paper provides an assessment of the MIEX® treatment process for DOC removal in power station applications. Data on process performance, the impact of operating conditions, point of application, resin concentrations and potential alternative applications of this technology in power stations are presented and discussed.

Frank McCarthy
Gerry O'Connor

PPChem 2004, 6(8), 483–496

Ammonia Form Operation of Condensate Polishing Plant for Long Periods in High pH Systems at Moneypoint Power Station

This paper details ammonium form operation experience of the condensate polishing system at Moneypoint Power Station, a 3 x 300 MW coal fired station operated by the Electricity Supply Board (ESB) of Ireland.
Ammonium form operation is part of the normal operation of the condensate system since June 1988. Regeneration procedures using a conventional two vessel regeneration system have been developed using both two bed and three bed resin systems to achieve very low levels of cross contamination of resins necessary to allow ammonium form operation whilst still maintaining a very high level of polished condensate quality. Sodium levels of about 0.3 $\mu g \cdot kg^{-1}$ are being achieved without the aid of high efficiency separation/regeneration plant by the adoption of optimum resin particle sizes and densities and the use of a double resin movement technique. Bed run lengths of up to 200 days are being obtained at pHs as high as 9.6.

Padma S.Kumar
Puspalata Rajesh
Sumathi Suresh
Sinu Chandran
Sankaralingam Velmurugan
Sevilmedu V. Narasimhan

PPChem 2004, 6(8), 497–507

Studies on the Process Aspects Related to Chemical Decontamination of Chromium-Containing Alloys with Redox Processes

Presence of chromium in the oxide layer makes oxidative pre-treatment with oxidizing agents such as potassium permanganate ($KMnO_4$) a must for the decontamination of stainless steels and other chromium containing alloys. The effectiveness of pre-treatment with oxidizing reagent varies with the conditions of treatment such as temperature, concentration and whether the medium is acidic or alkaline. A comparative study of the two acidic oxidizing agents, i.e., nitric acid-permanganate and permanganic acid was made. The dissolution behavior of copper and its oxide in permanganic acid was found to be comparable to that of chromium oxide. Citric acid and ascorbic acid were investigated as alternatives to oxalic acid for the reduction/decomposition of permanganate left over after the oxidizing pre-treatment step. It has been established that the reduction of chromate by citric acid is instantaneous only in presence of Mn^{2+} ions. It has also been established that reduction of residual permanganate can be achieved with ascorbic acid and with minimum chemical requirement. The capabilities of nitrilotriacetic acid (NTA)-ascorbic acid mixture for the dissolution of hematite have been explored. This study would help to choose the suitable oxidizing agent, the reducing agent used for decomposition of permanganate and to optimize the concentration of reducing formulation so that the process of decontamination is achieved with a minimum requirement of chemicals. The generation of radioactive ion exchange resin as waste is therefore held at a minimum. Ion exchange studies with metal ion complexes of relevance to decontamination were carried out with a view to choose a suitable type of ion exchanger. It has been established that treatment of the ion exchange resin with brine solution can solve the problem of leaching out of non-ionic organics from the resin.

Brian J. Handy
John C. Greene

PPChem 2004, 6(9), 517–522

Predicting the Operating Performance of Condensate Polishing Plant Using a Mathematical Kinetic Model

NNC Limited provides an Ion Exchange Resin Technology Facility, which includes a resin testing service. A range of ion exchange resin properties is measured and this includes ion exchange capacity, resin bead particle sizes and anion kinetic performance in terms of mass transfer coefficients. It has long been considered by the authors that the experimental data for resins taken from operating condensate polishing plant (CPP) could be used to predict the expected plant performance. This has now been realised with the development of a mathematical model which predicts CPP behaviour using appropriate experimentally derived parameters and plant design data.
Modelling methods for the separate anion and cation components of a mixed bed were initially developed before the mixed bed as a whole was addressed. Initially, an analytical approach was adopted, which proved successful for simple cases. For more complex examples a numerical approach was developed and found to be more suitable. The paper describes the development of anion and cation bed models, and a mixed bed model. In the latter model, the anion and cation components modelled earlier are combined, and used to model simultaneously typical concentrations of ammonia, sodium, chloride and sulphate. Examples of operation are given, and observations and points of interest are discussed with respect to the calculated concentration profiles.
The experimental behaviour of a number of resin samples taken from operating plant was examined in a purpose-built ultrapure water recirculation loop equipped with a range of analytical instruments. This has permitted the observed experimental results to be compared with model predictions. The next stage of the model development is to identify plants suitable for testing the model against real plant performance and the authors are now seeking to identify plant managers interested in collaborating in this venture.

Allen Apblett
Satish I. Kuriyavar
Gary L. Foutch
Phung Tran

PPChem 2004, 6(9), 523–528

The ETA Fouling Mechanism of Mixed Bed Ion Exchange Resin

Pressurized water reactor (PWR) nuclear power plants use amine pH control agents in the secondary steam cycle to reduce corrosion potential induced by hydronium ions. Ethanolamine (ETA) is a popular pH control agent currently used in many plants. However, some plants have reported fouling of the anion resin with ETA resulting in reduced service life. This paper presents preliminary analyses of the interaction chemistry of current fouling/degradation problems associated with the use of ETA on ion exchange resins used in PWRs.

Masayoshi Hirano
Satoshi Itaba
Toshio Sakurada
Yukio Imaizumi
Takao Minami
Li-Bin Niu
Hiroshi Takaku

PPChem 2004, 6(9), 529–541

Effects of Minor Amounts of Corrosive Chemicals on Corrosion Behavior of Low-Pressure Steam Turbine Materials for Fossil Power Plants under Alternating Dry and Wet Conditions

The materials of the attachment near the last stage of low-pressure steam turbines in power plants are exposed to severe corrosion conditions due to the concentration of corrosive chemicals during alternating dry and wet phases, a phenomenon caused by the frequent shutdowns and load changes in power plants. The stress corrosion cracking (SCC) behavior of typical low-pressure steam turbine materials has been evaluated by SCC tests under the dry and wet conditions and the electrochemical corrosion method. For both materials tested (3.5NiCrMoV and 12Cr steels) under alternating dry and wet conditions, the ion which induced the most severe SCC sensitivity was sulfate (SO_4^{2-}), which concentrated greatly in crevices; the next most severe ion was chloride (Cl^-), while sodium (Na^+) caused almost no SCC sensitivity. The co-occurrence of crevices and stress considerably increased the SCC sensitivity of the 3.5NiCrMoV steel tested. The maximum corrosion pit depth became greater as the dissolved oxygen content in water increased, and it rose significantly when a crevice was present. A consideration of the SCC sensitivity and the characteristics of the corrosion film has shown that the chromium content in the materials controls the SCC sensitivity and also the corrosion potential. This may be due to the formation of the passive Cr_2O_3 film.

Albert Bursik

PPChem 2004, 6(9), 549–555

Polyamine/Amine Treatment – A Reasonable Alternative for Conditioning High Pressure Cycles with Drum Boilers

The polyamine/amine treatment is applied in hundreds and hundreds of fossil plant cycles, particularly in the industry. Over the last decade, the extent of its application in utilities has been increasing. This paper focuses on the polyamine/amine regime in cycles with drum boilers, although one case study is presented which reports on application of this treatment in units with once-through steam generators. The major hindrance with respect to the use of this treatment in utilities is the fact that the cation conductivity of steam increases slightly when this treatment is applied.

Operation experience in industrial power and steam generation and in utilities demonstrates that a slight cation conductivity increase in the steam does not cause any turbine-related problems, assuming that the pH is correctly set by low-molecular volatile amines being a part of the polyamine/amine formulation. Steam cation conductivity-related studies for establishing the actual interaction of slightly contaminated steam and turbine materials in the presence of an adequate alkalizing agent (a low-molecular amine with a favorable distribution behavior), i.e., when the early condensate is adequately alkaline, are suggested.

Terry L. Maddox
Kal Farooq

PPChem 2004, 6(9), 557–561

Control of Copper Transport during Boiler Startup Using High Flow, High Efficiency Condensate Filtration

Copper deposition on turbine blades, resulting in a significant loss of power generation capacity, is a fairly common occurrence, especially in plants using high drum pressures (17.9 MPa (2 600 psi) and higher), copper alloy condensers, and LP and HP feedwater heaters with copper alloy tubes. The primary source of the copper deposition on turbines is the copper oxide that forms during the layup on metal surfaces where oxygen and water are in prolonged contact with the metal. This copper oxide along with other metal oxides and silica is dislodged and transported during plant startup. These solids settle out or circulate in the system and turn into dissolved contaminants under appropriate conditions of temperature, pressure and alkalinity. Solid contaminants, therefore, serve as a primary source reservoir in the formation of dissolved contaminants, making their control beneficial for the reduction of dissolved metals and the resulting problem of copper plating. Besides copper, significant amounts of iron are also present, causing underdeposit corrosion of tubes, as well as silica deposits on the IP and LP sections of the turbine and on boiler tubes.

Startup is the most appropriate time to capture the solid contaminant since temperatures are low and most of the particles are in suspension due to thermal expansion, vibration, and fluid drag associated with startup. Utilities that monitor copper levels in the boiler feedwater and steam report copper levels during startup that are as much as

1 000 times higher than the levels seen during normal operation. To date, utilities have employed several methods to reduce solid particulate transport. Improved layup practices are helping minimize oxidation of metallic surfaces and better operational procedures on startup help to reduce particulate in the feedwater and condensate. Examples of these practices are feedwater heater shell side blowdown and wide open boiler blowdown during the first few hours of startup.

Additional work at the Ottumwa plant has shown that the installation of an inline condensate filtration system will substantially reduce the transport of solid particulate and consequently reduce the amount of dissolved metal found in the boiler. Mitigating the transformation of particulate metal to dissolved metal, particularly copper, has the beneficial effect of reducing boiler tube deposits and copper deposition on turbine blades. Boiler tube deposits contribute to underdeposit corrosion and ultimately forced outages due to tube failure. Copper deposits reduce turbine efficiency and increase required corrective maintenance during outages. Both of the above have a negative impact on plant revenue. The implementation of Pall Ultipleat High Flow filters, specifically designed for application in the condensate system, will provide an effective and economical control of copper, iron, silica, and all other solids for drum and turbine protection.

Santhanam Ranganathan
Madapuzi P. Srinivasan
Pandalgudi S. Raghavan
Sevilmedu V. Narasimhan
Raghavachary Gopalan

PPChem 2004, 6(9), 562–570

Dissolution Studies on Nickel Ferrite in Dilute Chemical Decontamination Formulations

Nickel ferrite is one of the important corrosion products in the pipeline surfaces of water-cooled nuclear reactors. The dissolution of the nickel ferrite by chelating agents is very sensitive to the nature of the chelant, the nature of the reductant used in the formulation and the temperature at which the dissolution studies are performed. The dissolution is mainly controlled by the reductive dissolution of the ferrite particles, but complexing agents also play a significant role in the dissolution process. This study deals with the leaching of iron and nickel from nickel ferrite prepared by the solid-state method. The dissolution studies are performed in pyridine-2,6-dicarboxylic acid (PDCA), nitrilotriacetic acid (NTA), and ethylenediaminetetraacetic acid (EDTA) formulations containing organic reductants like ascorbic acid and low oxidation state transition metal ion reductants like Fe(II)-L (where L = PDCA, NTA, EDTA) at 85 °C. The dissolution of nickel ferrite in PDCA, NTA and EDTA formulations is influenced by the presence of reductants in the formulations. The addition of Fe(II)-L in the formulation greatly enhances the dissolution of nickel ferrite. The preferential leaching of nickel over iron during the dissolution of nickel ferrite was observed in all the formulations.

R. Barry Dooley
Kevin J. Shields

PPChem 2004, 6(10), 581–589

Alleviation of Copper Problems in Fossil Plants

Research sponsored by EPRI has now led to a clear understanding of both the science of copper corrosion, transport and deposition, and the transport processes through the feedwater, boiler water and steam in a fossil plant.

Brian J. Handy
John C. Greene
Kenneth Tittle

PPChem 2004, 6(10), 591–600

The Estimation of Degassed Acid Conductivity of Steam/Water Samples in Power Plant

The present paper proposes a method of estimating the degassed acid conductivity (DK_H) from the measured acid conductivity (K_H) and the total carbon dioxide content of a sample. The acid conductivity of a sample is a summation of contributions from a number of anion-hydrogen ion pairs having a range of equivalent conductance values. In the first part of the paper a single "mean" equivalent conductance is selected and used to estimate the total hydrogen ion concentration, $[H^+]$, in the acid conductivity sample. The $[H^+]$ value is then used to estimate the fraction of the total carbon dioxide concentration in the sample that is present as bicarbonate ion, HCO_3^-. This allows the contribution to the acid conductivity due to the HCO_3^-/H^+ ion pair, (K_{H/HCO_3}), to be calculated. The "degassed" acid conductivity, (DK_H), is then given by

$$DK_H = K_H - K_{H/HCO_3}$$

The procedure is applied to the range of possible steam/water samples, illustrating the comparison between the "estimated" and calculated degassed acid conductivities. This

procedure takes no account of the changes in the contributions to the total conductivity from other weak electrolytes present in the acid conductivity sample (e.g., water, acetic acid).

The second part of the paper describes a more sophisticated method using measured carbon dioxide and conductivity values and known thermodynamic and electrochemical data to calculate the degassed after cation conductivity. "Mean" equivalent conductances are selected for the anions present both before and after degassing. A series of equations is written for the dissociation constants for the acids that may be present in terms of the concentration of ionic species and hydrogen ion concentration. These equations are coupled with the mass balance and charge balance equations and expressions are derived for concentrations of all species. The conductivity of the solution can then be calculated before and after degassing. Comparisons are made in cases with low, intermediate and high carbon dioxide concentrations and in cases where conductivities are dominated by (a) mineral acids, and (b) organic acids. Optimum values of "mean" equivalent conductance are presented for several types of secondary water.

Jeffrey S. Rohrer
Edward Kaiser
Beverly Newton
Kannan Srinivasan
Rong Lin
Dennis Libby
Edward Riley

PPChem 2004, 6(10), 605–609

Ion Chromatography for Anion Analysis of Borated Waters

Borated waters are commonly used in power plants to control thermonuclear reactions. Contaminant anions, such as chloride and sulfate, in borated waters are known to cause corrosion in power plant components. A reliable method is needed to measure these anionic contaminants in this borate matrix. Ion chromatography with a tetraborate eluent has been used to monitor contaminant anions. However, this technique requires manually prepared eluents that can yield inconsistent results. A new method using eluent generation with a boric acid eluent allowed us to reliably determine fluoride, chloride, and sulfate to low $\mu g \cdot L^{-1}$ (ppb) levels in waters with 2 000 $mg \cdot L^{-1}$ (ppm) boron.

Santhanam Ranganathan
Madapuzi P. Srinivasan
Pandalgudi S. Raghavan
Raghavachary Gopalan
Sevilmedu V. Narasimhan

PPChem 2004, 6(10), 613–619

Role of Reductants in Dilute Chemical Decontamination Formulations

Iron(III) oxides are the major corrosion products formed in boiling water reactors. The iron(III) oxides are of two types, namely hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3). The dissolution of these oxides is in no way simple because of the labile nature of the Fe(III)-O bond towards the chelants. The leaching of metal ions is partially controlled by reductive dissolution. In order to understand the role of the reductant, it is essential to study the dissolution behaviour of a system like Fe_2O_3, which does not contain any Fe^{2+} in the crystal lattice. The present study was carried out with γ-Fe_2O_3 and dilute chemical decontamination (DCD) formulations containing ascorbic acid and citric acid with the addition of Fe(II)-L as a reductant. The chelants used for the dissolution process were nitrilotriacetic acid, 2,6-pyridinedicorboxylic acid and ethylenediaminetetraacetic acid. The γ-Fe_2O_3 was chosen since the earlier studies revealed that the dissolution kinetics of α-Fe_2O_3 is slow and it is difficult to dissolve even by strong complexing agents, whereas γ-Fe_2O_3 dissolution is comparatively easier. This is due to the structural difference between these two oxides. The studies also revealed that the dissolution was partly influenced by the nature of the chelating agents but mainly controlled by the power of the reductants used in the formulation. The dissolution behaviour of γ-Fe_2O_3 under various experimental conditions is discussed and compared with that of magnetite in order to arrive at a suitable mechanism for the dissolution of iron oxides and emphasize the role of reductants in DCD formulations.

Phillip Smurthwaite
Colin Harrison

PPChem 2004, 6(10), 621–625

Investigation of a Superheater Multiple Tube Failure Incident at a CCGT Power Plant

An investigation was carried out into the failure of 30 of 33 HP superheater tubes that occurred during a single incident at a modern combined cycle gas turbine power plant. Metallurgical examination of a failed tube uncovered a multi-layered corrosion product that once cleaned revealed significant wall thinning of the sample tube. Analysis of the corrosion product revealed a grey inner layer containing the elements Na, Fe, P and O, possibly indicating the presence of maricite ($NaFePO_4$), covered by a dark outer layer probably of magnetite (Fe_3O_4). It is proposed that the tubes failed as a result of an acid phosphate corrosion mechanism caused by excessive liquid and contaminant carry-over from the HP steam drum. A liquid entrainment test was carried out during the

course of the investigation that revealed a carry-over of approximately 2–3 %. Contributing factors to the failures included a minimal level of control instrumentation and substandard condition of the drum water/steam separation equipment.

PPChem 2004, 6(10), 626–630

VGB PowerTech e.V. Conference "Chemistry in Power Plants 2004"

This year's VGB PowerTech e.V. Conference "Chemistry in Power Plants 2004" took place in Essen, Germany, on October 27–28, 2004. Here we present abstracts of all the papers presented at this conference.

George R. Engelhardt
Digby D. Macdonald
Yancheng Zhang
R. Barry Dooley

PPChem 2004, 6(11), 647–661

Deterministic Prediction of Corrosion Damage in Low Pressure Steam Turbines

In this paper, the foundations of the deterministic prediction of damage due to localized corrosion in low pressure steam turbines are outlined, including the theoretical basis for predicting a complete cycle of damage development: the nucleation, growth, and death of individual events (pits/cracks) and the evolution of damage as an ensemble of events occurring in a progressive manner. The application of damage function analysis is illustrated with reference to the prediction of localized corrosion damage in low pressure steam turbines and it is predicted that deaeration of the turbine during shutdown may dramatically reduce the probability of failure at long operational times.

Robin L. Jones

PPChem 2004, 6(11), 663–669

Mitigating Corrosion Problems in LWRs via Chemistry Changes

Corrosion experience in U.S. light water reactor nuclear power plants is reviewed with emphasis on mitigation strategies based on water chemistry changes. While many components have suffered corrosion problems, the most costly issues to date have been stress corrosion cracking of stainless steel piping in boiling water reactors and corrosion damage to steam generator tubes in pressurized water reactors. Through industry-wide R&D programs, these early-developing problems are now understood, and cost-effective countermeasures have been developed and deployed. Corrosion-related problems of current concern are briefly reviewed for both reactor types, and opportunities for chemistry-based mitigation methods are identified. It is concluded that, while tremendous progress has been made in controlling corrosion, minimizing its impact on plant operations will present a continuing challenge throughout the remaining service lives of the current fleet of U.S. nuclear power plants.

Robert Svoboda
Maurice Bodmer

PPChem 2004, 6(11), 673–680

Investigations into the Composition of the Water Phase in Steam Turbines

Experimental techniques to sample the early condensate in steam turbines include direct sampling, in-line sensors (e.g., conductivity), and simulating the early condensate in nozzles or in external condensation devices. The Alstom early condensate sampler is an external condensation device based on injection cooling of superheat steam. An overview of these techniques and their results indicate impurity concentrations in the range of some tens of $\mu g \cdot kg^{-1}$ to some tens of $mg \cdot kg^{-1}$, but not the highly concentrated solutions that are predicted. Visual inspections, however, deliver "footprints" of such concentrated solutions.

Albert Bursik
Miroslaw Gruszkiewicz

PPChem 2004, 6(11), 683–688

Drum Boilers on All-Volatile Treatment – The pH Pitfall

Hydrogen damage remains one of the major causes of boiler tube failures in fossil units with drum boilers. This is surprising since this kind of damage and its causes are adequately known. It seems that misunderstanding of the high temperature ionization behavior of ammonia and misinterpretation of the pH monitored at room temperature are the possible reasons for the high number of boilers operated on all-volatile treatment which have experienced damage. This paper discusses the impact of contaminants on the boiler water pH at the actual boiler temperature and shows adequate measures for avoiding hydrogen damage failures in units operated on all-volatile treatment.

Horst Kutzenberger
Günter Kuhnle
Gerhard Mohr
Jörg Strohhäcker

Experience with Damage to Highly Alloyed Superheater Tubes

The efficiency of steam power stations fired by fossil fuels can be improved by increasing the steam temperature and the steam pressure. With live steam temperatures of up to 600 °C, it is no longer possible to use the previously usual tube materials. Highly

PPChem 2004, 6(11), 693–699

alloyed ferritic and austenitic steel materials are employed for these applications. The scaling behavior is demonstrated by means of investigations of tubes which have been taken, after different operating periods, from the superheater and reheater regions.

R. Barry Dooley
Richard Tilley

PPChem 2004, 6(12), 708–719

Tube Failures in Conventional Fossil Fired Boilers and in Combined Cycle/HRSGs

Boiler tube failures (BTFs) in conventional fossil plants can be beaten by a comprehensive management-supported Boiler Tube Failure Reduction Program/Cycle Chemistry Improvement Program. Case study results are included to illustrate the superb results that have emanated from six organizations. HRSG tube failures (HTFs) are also the leading cause of availability loss in combined cycle units. The primary failure mechanisms are thermal- and creep-fatigue, and flow-accelerated corrosion (FAC). In the HRSG there is an opportunity to avoid these HTFs by incorporating the known avoidance factors in the design, and by conducting thermal and chemical monitoring early in the life of the HRSG. For both BTF and HTF, the optimum approaches to alleviation are included.

PPChem 2004, 6(12), 720–728

International Conference
Boiler Tube and HRSG Tube Failures and Inspections

Boiler tube failures (BTFs) in conventional fossil plants can be beaten by a comprehensive management-supported Boiler Tube Failure Reduction Program/Cycle Chemistry Improvement Program. Case study results are included to illustrate the superb results that have emanated from six organizations. HRSG tube failures (HTFs) are also the leading cause of availability loss in combined cycle units. The primary failure mechanisms are thermal- and creep-fatigue, and flow-accelerated corrosion (FAC). In the HRSG there is an opportunity to avoid these HTFs by incorporating the known avoidance factors in the design, and by conducting thermal and chemical monitoring early in the life of the HRSG. For both BTF and HTF, the optimum approaches to alleviation are included.

Digby D. Macdonald

PPChem 2004, 6(12), 731–747

Stress Corrosion Cracking in Reactor Coolant Circuits – An Electrochemist's Viewpoint

Extensive work over the past hundred years has shown that the stress corrosion cracking of metals and alloys in aqueous environments is primarily an electrochemical phenomenon falling within the realm of the differential aeration hypothesis. An important feature of the differential aeration hypothesis is that the local anode and the local cathode are spatially separated, with the former existing within the crack enclave (on the crack flanks and at the crack tip) and the latter existing on the bold, external surfaces. Because of the need to compensate the positive charge being deposited into the crack enclave from metal dissolution, anions (e.g., Cl^-) are transported into the crack, a process that is manifest as a positive current flowing from the crack to the external surfaces, where it is consumed by hydrogen ion, water, and/or oxygen reduction. Thus, strong electrochemical coupling exists between the crack internal and external surfaces and this coupling has been observed in stress corrosion cracking in a variety of systems, including intergranular stress corrosion cracking (IGSCC) in sensitized Type 304 SS in simulated boiling water reactor coolant environments at 288 °C, IGSCC in the same sensitized alloy in thiosulfate solutions at ambient temperature, and caustic cracking in AISI 4340 high strength steel at 70 °C. Examination of this "coupling current," which is easily measured experimentally using a sensitive zero resistance ammeter, shows that it contains "structured" noise superimposed upon a mean. In the case of the sensitized stainless steel in the high temperature aqueous environment, the mean current is found to be linearly related to the crack propagation rate and, indeed, the measurement of the coupling current may provide a sensitive method of measuring crack growth rate. Furthermore, the noise in the current is found to yield a wealth of information on the fracture events that occur at the crack tip, including their frequency, temporal relationship with other events, and size. This information has provided a clearer view of the fracture mechanisms, which in all three cases (IGSCC in sensitized stainless steel in BWR environments and in thiosulfate solution and caustic cracking in AISI 4340) appear to involve brittle microfracture events of a few micrometers to a few tens of micrometers in size. These data are more consistent with hydrogen-induced fracture than

they are with a slip/dissolution mechanism, even when the external environment is oxidizing in nature. Finally, this improved understanding of IGSCC in high temperature aqueous systems has led to a more complete assessment of the viability of various electrochemical methods for controlling and mitigating IGSCC in sensitized Type 304 SS in the primary coolant circuits of boiling water reactors.

Stefan Ritter
Hans-Peter Seifert

PPChem 2004, 6(12), 748–760

The Effect of Chloride and Sulfate Transients on the Stress Corrosion Cracking Behavior of Low-Alloy Reactor Pressure Vessel Steels under Simulated BWR Environment

The adequacy and conservative character of the Boiling Water Reactor (BWR) Vessel and Internals Project (BWRVIP-60) stress corrosion cracking (SCC) Disposition Lines during and after water chemistry transients were evaluated and assessed in the context of the current Electric Power Research Institute (EPRI) BWR water chemistry guidelines. For this purpose, the SCC behavior of three nuclear grade low-alloy reactor pressure vessel steels during and after sulfate and chloride transients was investigated under simulated BWR power operation conditions by tests with periodical partial unloading (PPU) and experiments under constant load. Modern high-temperature water loops, on-line crack growth monitoring with direct current electrical potential drop measurement and fractographical analysis by scanning electron microscope were used to quantify the cracking response.

In oxygenated, high-temperature water (T = 288 °C, 8 $mg \cdot kg^{-1}$ dissolved oxygen), the addition of 370 $\mu g \cdot kg^{-1}$ sulfate (> EPRI Action Level 3) did not result in acceleration of crack growth under PPU and constant load in all materials, and the SCC crack growth rates (CGRs) under constant load during sulfate transients were conservatively covered by the BWRVIP-60 Disposition Line 2. The addition of 10 $\mu g \cdot kg^{-1}$ (≥ EPRI Action Level 1) to 50 $\mu g \cdot kg^{-1}$ chloride (≥ EPRI Action Level 2) resulted in acceleration of the SCC CGRs in all investigated materials by at least one order of magnitude and in fast, stationary SCC under constant load in the investigated stress intensity factor range K_I from 32 to 62 $MPa \cdot m^{1/2}$ with CGRs significantly above the BWRVIP-60 Disposition Line 2. In some cases stable, stationary SCC with CGRs above the BWRVIP-60 Disposition Line 2 could be sustained after severe (≥ EPRI Action Level 2) and prolonged chloride transients for much longer periods (> 1 000 h) than the 100 h interval suggested by BWRVIP-60.

Matthias Meierer
Norbert Eimer

PPChem 2004, 6(12), 761–767

Corrosion Damage on the Stack of Unit 4/Boiler 15 of Grosskraftwerk Mannheim AG

The subject matter of this report is unexpected corrosion damage which was detected on the double-shell steel stack of Unit 4 of the Grosskraftwerk Mannheim AG power plant. Unit 4 is a hard-coal-fired supercritical cogeneration unit with an output of 220 MW. The flue-gas cleaning system consists of an electrostatic precipitator, a wet flue-gas desulfurization system (limestone/gypsum process), and an SCR DeNOx system in a tail-end arrangement. Unit 4 went online in 1970. The FGD and DeNOx systems were retrofitted in 1988.

The unexpected corrosion damage and its causes are described in detail. The basic options for rehabilitating the stack are presented, compared, and evaluated. The rehabilitation measures performed on the facility are described. The aspects of time frame, operational conditions, rehabilitation work on the inner and outer tubes, statics and construction, installation and quality control are explained in detail.

2005's Scientific and Technical Contributions

John Hickling
Hans-Peter Seifert
Stefan Ritter

PPChem 2005, 7(1), 4–15

Research and Service Experience with Environmentally Assisted Cracking of Low-Alloy Steel

Environmentally assisted cracking (EAC) of carbon and low-alloy steels has been identified as a possible degradation mechanism for pressure vessels and piping in nuclear power plants. Selected aspects of research and service experience with cracking of these materials in high-temperature water are reviewed, with special emphasis on the primary pressure boundary in boiling water reactors. The main factors controlling EAC susceptibility under reactor conditions are discussed with regard to both crack initiation and crack growth. The adequacy and conservatism of the relevant engineering criteria for component design and disposition of detected or postulated flaws are evaluated in the context of recent research results, e.g., on the effects of so-called "ripple loading" or of water chemistry transients. Finally, the relevant operating experience over the last 30 years is briefly summarized and compared with the background knowledge which has been accumulated in more recent laboratory experiments. Some of the insights gained in this work may also be of value in improving understanding and prediction of the EAC behavior of carbon and low-alloy steels in certain fossil plant components, if appropriate allowances are made for differences in temperature and water chemistry.

Masayoshi Hirano
Satoshi Itaba
Takao Minami
Li-Bin Niu
Hiroshi Takaku

PPChem 2005, 7(1), 16–20

Corrosion Behavior of Boiler Materials during Long-Term Layup of a Fossil Unit

The applicability of the electrochemical corrosion potential (ECP) method as an online corrosion monitoring technique for boiler equipment during long-term layup in fossil units was experimentally investigated for boiler equipment materials. It was found that the ECPs of all materials tested show stable values for a few hundred hours after the test, and that oxide films formed under AVT (all-volatile treatment) conditions show a good stability in the subsequent ECP measurements. Under conditions of the presence of hydrazine, the corrosion potential of STB410 carbon steel shifts to the noble side, showing high corrosion resistance. The results obtained by the ECP method are in good agreement with those of the corrosion immersion test. The temporary decrease in the corrosion potential due to the addition of hydrazine to the water may result from effects of both the reducing reaction of oxide films and the decomposition of hydrazine. The results in this work suggest that the ECP method may be effective for the corrosion monitoring of boiler equipment materials. Based on the fundamental results obtained, it is expected that the corrosion of boiler equipment during the layup period can be detected by the ECP method.

Siegfried Köhler
Mechthild Müller

PPChem 2005, 7(1), 25–30

Corrosion Behaviour of and Damage to Copper Alloy Power Cycle Components

At temperatures > 60 °C, the corrosion behaviour of copper alloys is determined above all by the oxygen content and the temperature of the medium. The prevailing corrosion mechanisms include dezincification, pitting corrosion, stress corrosion cracking, ammonia grooving, and sulphide-induced corrosion. In addition, intergranular corrosion may occur in aluminium brass.

Subrata Dutta
Shantanu Das
Arun R. Kandalgaonkar
P. I. Suryanarayanan
Bibhuranjan Basudev Biswas
Vadakke Kodakara
Prabharakan Unny

PPChem 2005, 7(1), 35–39

Modeling of Diffusion Phenomenon of Liquid Poison in Shutdown System #2 of PHWRs

The diffusion phenomenon of poison solution (gadolinium nitrate) in connection with the secondary shutdown system of pressurized heavy water reactors is studied with a simple approach of one-dimensional macro-modeling and application of the experimental results to arrive at actual power plant operational specifications. The results obtained by mass balance macro-dynamics and simple laboratory experiments tally with the power plant operational requirements. Obtaining Fick's constant from the results confirms the validity of the model. A new interpretation of Fick's constant is given for better understanding of the diffusion process.

Brad Buecker

PPChem 2005, 7(1), 40–43

Condenser Performance – A Critical Issue for Plant Chemists

Along with the boiler, the steam condenser is one of the two largest heat exchangers in a steam generating power plant. Waterside scaling or fouling, or excess air in-leakage on the steam side, will seriously impair heat transfer, which in turn increases fuel requirements and costs. Power plant chemists must keep track of condenser performance, especially as it relates to cooling water chemical treatment. Failure or poor operation of chemical feed systems will initiate fouling that often can only be removed by a unit shutdown and mechanical cleaning. Prompt detection of air in-leakage upsets is also important to maintain proper condenser efficiency. This article outlines a practical method for condenser performance monitoring that the author has used with excellent success.

PPChem 2005, 7(1), 44–62

2004' Scientific and Technical Contributions – Papers in English

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

R. Barry Dooley
Neville F. Rieger
Farhang Bakhtar

PPChem 2005, 7(2), 69–80

Studies of Electrostatic Charge Effects Relating to Power Output from Steam Turbines

This paper summarizes the work done in several recent studies concerning the effects of electrostatic charge imposed on the steam flow in a turbine exhaust environment. The purpose of these studies was to determine whether an electrostatic charge imposed on the turbine exhaust steam could increase turbine power output in a commercially useful manner.

Certain studies carried out in the Ukraine on this topic using a 50 MW utility turbine are considered first. The results of these studies indicated that electrostatic charging of steam could lead to a small but commercially useful increase in power output. Basic work was subsequently undertaken in the USA to study the influence of an electric field on wet steam in a laboratory chamber. A full-scale test program was also undertaken in the USA, in which electric charge was imposed on the steam flowing through the exhaust hood of a large (425 MW) utility turbine. Several grids of wire electrodes strung within the exhaust hood of the turbine were used in this test. These wires carried a high voltage of sub-corona potential.

In a separate program the electrostatic effects associated with a nucleating flow of steam within a two-dimensional cascade were examined. The measurements are of the electrical charges generated on first nucleation and of the effect of electrical charge on nucleation of steam droplets.

The paper describes the work undertaken in these programs, and it summarizes the results achieved to date. Conclusions drawn from the results are presented, with discussion.

Paul B. Desch
James J. Dillon
Steef H. M. Vrijhoeven

PPChem 2005, 7(2), 82–94

Case Histories of Stress-Assisted Corrosion in Boilers

Stress-assisted corrosion refers to attack at locations where applied and/or residual stresses are imparted to the metal. Case histories are presented from a variety of different boiler systems that illustrate the effects of stress-assisted corrosion, including environmental conditions that may promote attack. Methods that may be used to control stress-assisted corrosion are also outlined.

Bernhard Stellwag
Ulrich Staudt

PPChem 2005, 7(2), 95–102

Water Chemistry Practice at German BWR Plants

As visual examinations carried out in 1994 detected cracks in a German boiling water reactor (BWR) plant due to intergranular stress corrosion cracking in core shroud components manufactured from Nb-stabilized CrNi steel 1.4550, safety-related assessments and in-service inspections were subsequently performed for the other six German BWRs. No cracks were found in the core shrouds of these plants.

The second major event in the early 1990s was the detection of cracks at various German BWRs in piping systems made of Ti-stabilized CrNi steel 1.4541 caused by thermal sen-

sitization in the heat-affected zone of welds. Comprehensive investigations resulted in a number of remedial measures (repair, replacement) implemented at piping in contact with reactor coolant of temperatures above 200 °C.

Thanks to the remedial measures and according to the analyses performed, cracking in the components in question due to the considered damage mechanisms need not be expected. German operators have therefore continued operating their BWR plants on normal water chemistry with an oxidizing environment. As a precaution, more stringent reactor coolant quality requirements have been specified and the limiting values of VGB Guideline R 401 J revised. This paper gives an overview of the trends in chemistry parameters at German BWR plants in the past 10 years. In addition, other relevant experience gained from the German BWR plants operating under normal water chemistry conditions is outlined: dose rates and collective doses, fuel performance, and results of periodic in-service inspections of major components of the reactor system. In the nearly 10 years of plant operation since implementation of the remedial measures, no cracks or other indications have been detected in any of the systems and components concerned.

Peter J. Millett

PPChem 2005, 7(2), 107–111

Advances in High Temperature Water Chemistry and Future Issues

This paper traces the development of advances in high temperature water chemistry with emphasis in the field of nuclear power. Many of the water chemistry technologies used in plants throughout the world today would not have been possible without the underlying scientific advances made in this field. In recent years, optimization of water chemistry has been accomplished by the availability of high temperature water chemistry codes such as MULTEQ. These tools have made the science of high temperature chemistry readily accessible for engineering purposes. The paper closes with a discussion of what additional scientific data and insights must be pursued in order to support the further development of water chemistry technologies for the nuclear industry.

Sung Chul Cha
Michael Spiegel

PPChem 2005, 7(2), 112–118

Studies on the Local Reactions of Alkali Chloride Particles on Metal Surfaces

During biomass combustion alkali chloride particles are formed, depositing on the metallic surface or on the already formed oxide layer. Subsequently, they react with the metal or the oxide layer and accelerate the oxidation process. To investigate these reactions equipment for particle deposition by impactor and thermophoresis was installed and optimized for homogeneous deposition. After deposition of KCl, iron samples were exposed to 800 $mL \cdot L^{-1}$ N_2-200 $mL \cdot L^{-1}$ O_2 and 799.5 $mL \cdot L^{-1}$ N_2-200 $mL \cdot L^{-1}$ O_2-0.5 $mL \cdot L^{-1}$ HCl atmospheres for short times at 300 °C. In 800 $mL \cdot L^{-1}$ N_2-200 $mL \cdot L^{-1}$ O_2, some deformation and local spreading of the particles were observed, probably by melt formation in contact with the metal. Oxidation with HCl addition led to a significant increase of chlorine and oxygen contents on the KCl deposited sample surfaces. Finally, thermogravimetric tests were conducted on deposits formed on iron at temperatures from 300 °C to 400 °C in 950 $mL \cdot L^{-1}$ Ar-50 $mL \cdot L^{-1}$ O_2 atmospheres with and without addition of 0.5 $mL \cdot L^{-1}$ HCl. In the case of HCl addition, mass gains increased rapidly in the beginning of oxidation. The iron chloride or chlorine-rich layer was formed directly at the metal scale and under the oxide layer.

K. G. Subramanian
Abhiraman Suriyanarayanan
Natarajan Thirunavukarasu
Vanal Ramachari Naganathan
Bhabani Shankar Panigrahi
Dwadasantham Jambunathan

PPChem 2005, 7(2), 119–125

Online Monitoring of Steam/Water Chemistry of a Fast Breeder Test Reactor

Operating experience with the once-through steam generator of a fast breeder test reactor (FBTR) has shown that an efficient water chemistry control played a major role in minimizing corrosion related failures of steam generator tubes and ensuring steam generator tube integrity. In order to meet the stringent feedwater and steam quality specifications, use of fast and sensitive online monitors to detect impurity levels is highly desirable. Online monitoring techniques have helped in achieving feedwater of an exceptional degree of purity. Experience in operating the online monitors in the steam/water system of a FBTR is discussed in detail in this paper. In addition, the effect of excess hydrazine in the feedwater on the steam generator leak detection system and the need for a hydrazine online meter are also discussed.

Milan Zmítko
Jan Kysela

PPChem 2005, 7(3), 133–139

Coolant Technology and Experience in VVER Units

The primary coolant technology approaches currently used in VVER units are reviewed and compared with those used in PWR units. Standard and modified water chemistries differing in boron/potassium control are discussed. Preparation of the VVER Primary Water Chemistry Guidelines in the Czech Republic is noted. Operational experience of some VVER units operated in the Czech Republic and Slovakia in the areas of the primary water chemistry and radioactivity transport and build-up are presented. In the Mochovce and Temelín units, a surface preconditioning (passivation) procedure has been applied during hot functional tests. The main principles of the controlled primary water chemistry applied during the hot functional tests are reviewed and the importance of the water chemistry, technological and other relevant parameters is stressed in regard to the quality of the passive layer formed on the primary system surfaces. The first operational experience obtained in the course of the commissioning of these units is presented, mainly with respect to the corrosion product level in the coolant and surface activities of the corrosion products. The effect of the initial passivation performed during hot functional tests and the primary water chemistry on the radioactivity level and radiation situation of corrosion products is discussed.

Ewa M. Labuda
Robert D. Bartholomew

PPChem 2005, 7(3), 145–153

Stress-Assisted Corrosion: Case Histories

Three case studies involving waterwall and economizer tubes from a conventional type boiler and a high pressure primary superheater header removed from a heat recovery steam generator are presented. In each case, results of visual examination, scanning electron microscopy/energy dispersive X-ray spectroscopy, and optical metallography are provided. Corrosive environments and possible stresses that led to failures are discussed.

Preet M. Singh
Jorge J. Perdomo
Jamshad Mahmood
Pablo Conde

PPChem 2005, 7(3), 155–161

Stress-Assisted Corrosion Simulation in the Laboratory

Stress-assisted corrosion (SAC) of boiler tubes and economizer tubes from the waterside is one of the major problems in availability loss and safety of power plants and industrial boilers. Use of carbon steel for the service of high temperature water applications strongly depends upon the formation and stability of the protective magnetite oxide film, Fe_3O_4, on the waterside surface of boiler tubes. Failure mechanisms involved in waterside SAC surely include film damage as an important step. To understand SAC, a recirculation-loop autoclave facility for high temperature water testing was set up. The autoclave is designed for tests under industrial boiling water conditions. The maximum operational temperature is 350 °C, with test pressures of up to 24.1 MPa (3 500 psi) and flow rates of up to 10 $L \cdot h^{-1}$. Boiler water chemistry can be changed during the tests and the dissolved oxygen can be controlled within the range of 10 $\mu g \cdot kg^{-1}$ to 32 $mg \cdot kg^{-1}$. Initial tests were conducted to develop magnetite film on carbon steel tube samples at different temperatures.

Keezhanatham S. Seshadri
Muthiah Pushpa
Pradeep Kumar Sinha
Kamal Behari Lal

PPChem 2005, 7(3), 163–167

Wet Oxidation of EDTA Using Metal-Doped MCM-41 as Catalyst

Decontaminants like ethylenediaminetetraacetic acid (EDTA), ascorbic acid, and citric acid are widely used in the radioactive decontamination of reactor components. The complexants interfere in the treatment of radioactive effluent and hence it is imperative to oxidatively destroy the complexant to enable easy treatment of radioactive effluent. An attempt has been made to oxidatively destroy EDTA using hydrogen peroxide as oxidant in the presence of metal-doped MCM-41 as catalyst. The reason for using metal-doped MCM-41 as catalyst for the oxidative degradation is because of its larger surface area (~ 1 000 $m^2 \cdot g^{-1}$) with small pore size (20–100 Å). Also the metal used has variable valency, which helps in undergoing electron transfer reactions. Metal-doped MCM-41 was synthesized. Results indicate that among the metals chosen for doping MCM-41, the catalytic efficiency in the oxidative degradation decreased in the following order: molybdenum > vanadium > titanium.

Albert Bursik

PPChem 2005, 7(3), 169–175

Power Plant Cycle Chemistry – A Currently Neglected Power Plant Chemistry Discipline

Power plant cycle chemistry seems to be a stepchild at both utilities and universities and research organizations. It is felt that other power plant chemistry disciplines are more important. The last International Power Cycle Chemistry Conference in Prague may be cited as an example. A critical reviewof the papers presented at this conference seems to confirm the abovementioned statements.

This situation is very unsatisfactory and has led to an increasing number of component failures and instances of damage to major cycle components. Optimization of cycle chemistry in fossil power plants undoubtedly results in clear benefits and savings with respect to operating costs. It should be kept in mind that many seemingly important chemistry-related issues lose their importance during forced outages of units practicing faulty plant cycle chemistry.

Eric V. Maughan

PPChem 2005, 7(3), 181–187

pH – A Simple Measurement Most Frequently Done Incorrectly

pH is the most popular analytical process measurement. Despite this, it is also very often misinterpreted. This paper will attempt to explain the measurement of pH, the pitfalls and the influences which other variables have on this analytical method.

Hans-Günter Seipp
Frank-Udo Leidich

PPChem 2005, 7(4), 197–207

Damage in Water/Steam Cycles – Often a Matter of Solubility

Water and steam, the working fluids in the water/steam cycles of power plants, nowadays are characterized by a high degree of purity. Nevertheless, from time to time, damage is detected on plant components that is attributable to a substantial localized accumulation of "contaminants." This report presents a number of examples where typical damage was found, but the effects of the process-dependent varying solubility of substances had not fully been taken into consideration.

David M. Gray

PPChem 2005, 7(4), 214–218

pH and CO_2 Determinations Based on Power Plant Conductivity Measurements

Previous work has focused on major improvements in the accuracy of conductivity measurements and on the development and benefit of multi-parameter on-line analytical instrumentation. This background as well as continuing work now provide additional parameters that can be derived from accurate specific, cation (acid) and degassed cation (acid) conductivity measurements.

Masahiko Kurashina
Hideo Uzawa
Koya Utagawa
Hiroshi Takaku

PPChem 2005, 7(4), 219–223

On-Line Analysis of ETA and Organic Acids in Secondary Systems of PWR Plants

To reduce the iron concentration in the secondary water of plants with pressurized water reactors (PWRs), ethanolamine (ETA) is used as an alkalizing agent in the secondary cycle. An on-line ion chromatography (IC) monitoring system for monitoring concentrations of ETA and anions of organic acids was developed, its performance was evaluated, and verification tests were conducted at an actual PWR plant. It was demonstrated that the concentration of both ETA and anions of organic acids may be successfully monitored by IC in PWR secondary cycle streams alkalized by ETA.

Albert Bursik

PPChem 2005, 7(4), 224–230

Is Pittsburgh (PA) Worth a Trip for a Power Plant Chemist?

In this paper, power plant chemistry-related papers presented at the 65th International Water Conference® held in Pittsburgh (PA) last year are reviewed. The review of these papers results in a recommendation to attend the conference this year again (Orlando, FL, October 9–13).

Pavel Kolat
Dagmar Juchelková
Anna Nezhodová

PPChem 2005, 7(4), 231–242

Energy Utilization of Biofuels Based on Sludge and Lignite

Energy utilization of alternative fuels is one of the main tasks in the development of renewable sources in the European Community and the Czech Republic. The topics of the research consist of combustion tests in an experimental pilot plant with an atmospheric fluidized bed located at the Technical University, Dresden, Germany, for the lignite and sewage sludge, and thermo-analytical studies of biofuels. Recommendations for the suitability of thermal disposal of wastes in the atmospheric fluidized bed are presented

with respect to minimizing the harmful emissions. It may be assumed from results that combustion with a content of 15 % biofuels is applicable in the large fluidized bed boilers installed in the Czech Republic.

Eric V. Maughan

PPChem 2005, 7(4), 247–251

The Conductivity Cell and the Determination of Cell Constant in Pure Water Systems

There are many manufacturers of conductivity measurement systems for pure water, all of which work on the same physical principles. However, what is often confusing is the range of conductivity measurement cells or sensors and how to select the most appropriate cell constant for a particular application. This paper covers the theory of conductivity measurement and the determination of cell constants.

Ulf Ilg

PPChem 2005, 7(5), 261–270

Failure Analysis of Austenitic Stainless Steel Piping in Boiling Water Reactors – Root Cause and Remedies

In stainless steel piping DN 150–250 mm (DN, diameter nominal, metric equivalent to NPS, nominal pipe size) of German boiling water reactors, intergranular cracks in the heat affected zones of titanium-stabilized material have been detected. The piping systems are connected with the reactor pressure vessel and characterized by permanent reactor water flow at 288 °C.

Crack susceptibility is based on local sensitization. The present sensitization mechanism is due to a sequence generating free carbon caused by dissolution of Ti carbides followed by precipitation of chromium-rich carbides at the grain boundaries. This occurred during formerly used manufacturing processes about 20 years ago.

All affected piping systems were replaced by an optimized niobium-stabilized austenitic steel with low-carbon content and a high niobium to carbon ratio. Well controlled manufacturing and welding procedures with a good root weld quality were realized. In addition to this, reactor water chemistry was improved.

In the measures above, the total number of stainless steel welds DN > 50 mm within the containment was drastically reduced from about 450 to about 100. All nondestructive tests performed with the piping lines under discussion confirmed a condition without indications.

Kevin J. Shields
Michael A. Sadler

PPChem 2005, 7(5), 271–277

Power Industry Application of Condensate Polishing Technology

Condensate polishing was originally valued in power cycles as it offered protection against the impurities that entered the steam/water circuits. Its use also shortened the time necessary to start up the units. In addition, polishing permits fossil units to use more effective methods of cycle chemistry treatment. This is now recognized as a very important advantage. There are now various condensate polishing plant configurations in use around the world, but these have not changed significantly for some time. EPRI has initiated an investigation of innovative polishing techniques that may lower capital and operating costs and simplify operation so that future polishing systems are suitable for use on fossil (conventional or combined cycle) plants.

Miroslaw Gruszkiewicz
Albert Bursik

PPChem 2005, 7(5), 289–296

Degassed Conductivity – Comments on an Interesting and Reasonable Plant Cycle Chemistry Monitoring Technique

Part 3: Degassing of Strong Inorganic Acids and a Final Assessment

This is the third part of a three-part publication focusing on the behavior of typical plant cycle contaminants during degassing in a typical degassed cation conductivity system. A rigorous thermodynamic approach was chosen for the evaluation of conditions in the degassing part of the system. As shown in Part 1, low-molecular acids are not removed during the degassing; carbon dioxide, however, is nearly completely removed (Part 2). In this part of the series, it is demonstrated that the relevant strong inorganic acids are not lost in the degassing device.

Degassed cation conductivity monitoring is not as common as specific and cation conductivity monitoring even though this technique offers some very interesting features. As shown in the case studies discussed, this technique can help to distinguish between

plant cycle contamination due to inorganic and/or organic acids and/or their salts and that caused by carbon dioxide. This may be important, e.g., during startup of a unit.

Luis Carvalho

PPChem 2005, 7(5), 297–304

Avoiding Costly Water Treatment Mistakes in Combined Cycle Power Plant Projects

In a typical power plant, water treatment is a relatively small slice of the operating budget, generally less than 2 % of the total cost of operation. However, its impact on the plant heat rate, net capacity factor and ultimate profitability can range from significant to disproportionately high. One area of particular concern is the high-purity water requirement in various areas of an increasingly complex power plant cycle. This ranges from several boiler feedwater loops to combustion turbine NOx control and combustion air-cooling.

Plant owners, developers, owners' engineers, and engineering/constructor firms often fail to understand the multitude, interaction and complexity of water treatment technologies (both equipment and chemical based) available in the market place today and how best to incorporate them at the design phase of the project. Equipment selection is also often made with complete disregard to the alternate use of more technically feasible and cost-effective chemical-based treatment options. The end result is plant designs unable or barely capable of meeting the performance specifications of critical equipment such as steam and gas turbines even during the start-up phase, leading to start-up delays and legal disputes, and later translating into high water treatment operating costs, plant downtime and potential expensive plant modifications.

This paper discusses water treatment technologies such as membrane separation (e.g., reverse osmosis), electrodialysis and electrodeionisation, and the fading yet unique role that ion exchange can play. It also addresses the critical role that well-qualified chemical water treatment companies can play in avoiding costly mistakes during power plant design, how to best fit chemical treatment options, and what can go severely wrong when the raw water to the plant is not critically evaluated.

Eric Maughan

PPChem 2005, 7(5), 305–308

Developments in On-Line Instrumentation

In this paper, some useful advice and answers to frequently asked questions are presented with respect to common problems occurring in the on-line monitoring of fossil plant cycle chemistry. Focus is on monitoring of the three most important cycle chemistry parameters, conductivity, oxygen content, and pH.

Klaus Weigl
Christopher C. Ayers
Ludwig Gockner
Josef Tauschitz

PPChem 2005, 7(5), 309–313

On-Site SCR Catalyst Rejuvenation Process as Part of a Catalyst Management Plan

The on-site catalyst rejuvenation process is a highly efficient tool to reduce operating and maintenance costs for lifetime extension of catalysts for selective catalytic reduction (SCR) of NOx compared to catalyst exchange and/or additional catalyst installation. Depending on the type of deactivation, the process is fit to the requirements based on our experience. Thus the tailor-made process can handle deactivation types like pluggage, alkali and earth alkaline depositions, and more. One of the important constraints is to perform the rejuvenation on-site within the given outage of the boiler to reduce any additional costs and risks. New results from rejuvenations performed on SCR catalysts from coal and oil fired units are presented. A cost analysis compared to the additional catalyst installation is given as part of a catalyst management plan.

Digby D. Macdonald

PPChem 2005, 7(6), 324–338

Fact and Fiction in ECP Measurement and Control in Boiling Water Reactor Primary Coolant Circuits

A review is presented of various electrochemical potentials, including the electrochemical corrosion potential (ECP), that are used in the mitigation of stress corrosion cracking in the primary coolant circuits of boiling water reactors (BWRs). Attention is paid to carefully defining each potential in terms of fundamental electrochemical concepts, so as to counter the confusion that has arisen due to the misuse of previously accepted terminology. A brief discussion is also included of reference electrodes and it is shown on the basis of experimental data that the use of a platinum redox sensor as a reference elec-

trode in the monitoring of ECP in BWR primary coolant circuits is inappropriate and should be discouraged. If platinum is used as a reference electrode, because of extenuating circumstances (e.g., potential measurements in high dose regions in a reactor core), the onus must be placed on the user to demonstrate quantitatively that the electrode behaves as an equilibrium electrode under the specified conditions and/or that its potential is invariant with changes in the independent variables of the system. Preferably, a means should also be demonstrated of transferring the measured potential to the standard hydrogen electrode (SHE) scale.

Beverly Newton
Mike Doyle
Luis Carvalho
Ian Scarth
Peet Lindau

PPChem 2005, 7(6), 339–345

Fear and Loathing at a Combined Cycle Power Plant – Ion Chromatography in a Box

The use of ion chromatography for monitoring corrosive ions in water has been implemented at several new combined cycle gas-fired power plants. Due to stringent requirements for clean water to prevent corrosion and plugging of turbine components, this methodology is predicted to have a significant impact in extending useful operating lifetimes and to measurably increase the availability of components in contact with water. Ion chromatography, due to its ability to identify individual anion and cation species, to achieve parts-per-trillion detection limits, and to operate on-line, has played a central role in the effectiveness of these water chemistry monitoring programs.

Combined cycle power plants are faced with tough choices for water monitoring. The lack of trained chemists to run low level analyses results in uncertainty as to the quality of the water used for steam going to the turbine and in some cases to the generator. This paper presents a report on a recent study of a low cost, hands-off ion chromatography solution to provide on-line monitoring at the water panel for chloride and sulfate ions at 1 part per billion or below.

Wilfried Rühle
Harry Neder
Günter Holz
Volker Schneider

PPChem 2005, 7(6), 355–363

Oxygen Injection into Reheating Steam of Moisture Separator Reheaters

The steam/water cycles of the nuclear power plants Philippsburg 2 (KKP-2), Isar 2 (KKI-2) and Biblis A/B (KWB-A/B) operate under high-AVT-chemistry conditions (pH at 25 °C ≥ 9.8 in final feedwater). After many years of excellent operating performance, flow-accelerated corrosion (FAC) in the carbon steel heater tubes of the moisture separator reheaters (MSRs) was observed. In order to counteract the flow-accelerated corrosion it was decided to inject oxygen into the reheating steam line upstream moisture separators. As is known, more stable protective oxide layers are formed in oxygen-containing steam condensate. However, reducing conditions in the recirculating water of the steam generators also had to be ensured after the implementation of oxygen injection at the plants to definitely exclude conditions under which localized corrosion could occur. Visual and eddy current inspections performed after four cycles of operation confirmed that FAC in the MSRs in KKP-2 and KWB-A/B could be stopped without negative side effects on the steam generators.

This paper describes the influence of the oxygen injection on the water chemistry parameters and system performance at KKP-2, KKI-2 and KWB-A/B.

Geoff Spowart

PPChem 2005, 7(6), 365–367

Hypochlorite and the pH in Cooling Water

This paper looks at the issues surrounding the relationship between pH and chlorine effectiveness in power station cooling water. In particular, the impact of changes to cooling water chemistry on Legionella counts is highlighted along with some strategies for optimizing biocide dosing and the pH set point.

K. Anthony Selby

PPChem 2005, 7(6), 369–372

The 25th Annual University of Illinois Electric Utility Chemistry Workshop – Extending the Life and Reliability of Power Plant Equipment through Improved Chemical Control

In May this year, the 25th Annual University of Illinois Electric Utility Chemistry Workshop took place in Champaign, IL, U.S.A. The abstracts of the papers presented at this event are compiled in this paper.

Eric V. Maughan

PPChem 2005, 7(6), 375–378

On-Line Calibrator for Verifying Sodium Ion Transmitters

The question of calibration and verification of on-line instrumentation at the concentration of interest is often raised. This paper describes a method using a conductivity measurement to calibrate and verify sodium ion analyzers, as well as pH and conductivity sensors.

Jean Belles-Baumann

PPChem 2005, 7(7), 388–396

Production of Makeup Water with Ion Exchange Resins

The use of ion exchange resins for purifying makeup water is the on-going state-of-the-art technology for this application. Water treatment with ion exchange resins is for the majority of sites the method of choice because of the high flexibility of this technology. In this paper, basic principles of ion exchange are explained, and the different ion exchange systems and technologies, including operating conditions, are reviewed and compared. Furthermore, the important role of proper pretreatment and operating temperature is discussed. Some principles of ion exchange plant design and plant monitoring are described in detail. Finally, technical hints are given for maintenance and protection of ion exchange resin plants during operation and shutdown periods.

Geoff Bignold
Robert Svoboda

PPChem 2005, 7(7), 411–414

Meetings of the IAPWS Working Group "Power Cycle Chemistry" in Santorini, Greece, July 3–8, 2005

In July 2005, the 2005 Annual Meeting of the International Association for the Properties of Water and Steam (IAPWS) took place in Santorini, Greece. This paper reports on the sessions of the IAPWS Working Group "Power Cycle Chemistry" and other power plant chemistry-related activities of the IAPWS. Included are a review of the current priority list (a list of areas considered by the working group members to need basic research), a summary of the conclusions of the 2004 international collaboration project initiated by the Working Group, summaries of the research presentations given during the meeting, a list of the presentations made during the focused topic discussions, a summary of the Working Group's plans for the coming year, and a list of the presentations made at the IAPWS Symposium on Applied Water Treatment Processes for Power Plant Cycles.

Karol Daucik

PPChem 2005, 7(7), 417–421

Sampling of Particulates in the Water/Steam Cycle

Analysis of particulate components in the water/steam cycle is an important issue in the chemical control of fossil and nuclear power plants. Sampling is the most difficult part of this issue. In this paper significant parameters affecting the quality of the sample are discussed and their importance is demonstrated by field investigations. The author emphasizes the importance of turbulence through the sample line during isokinetic sampling. Well-designed sampling devices and sampling procedures are prerequisites for reliable sampling of particulates.

Kazuo Marugame
Li-Bin Niu
Hiroshi Takaku

PPChem 2005, 7(7), 422–428

Development of a Gluconate Ion Selective Electrode for Gluconate Measurement in the Boiler Water

To develop a gluconate ion selective electrode for the measurement of the gluconate ion concentration, sensitive liquid ion exchangers were incorporated into a polyvinyl chloride membrane to form a gluconate ion selective electrode. The newly developed electrode showed a linear response to the gluconate ion activity between 10^0 mol · dm^{-3} and 10^{-4} mol · dm^{-3}, and the average potential change in this concentration region was –51 mV, when tridodecylmethylammonium gluconate was used as the ion exchanger. The selectivity coefficients of the electrode for various anions were determined with the mixed solution method. The electrode showed a constant potential in the pH range of 4 to 10, and also exhibited a steady potential within 3–10 s after a gluconate concentration change of $10 \cdot 10^{-3}$ mol · dm^{-3} to $5.5 \cdot 10^{-3}$ mol · dm^{-3} in an aqueous solution.

Eric V. Maughan

PPChem 2005, 7(7), 429–433

On-Line Chemistry Analysis of Stator Coolant Systems

Water-cooled generator stator systems with copper conductors suffer from plugging with corrosion products, which invariably leads to localized overheating. To avoid plugging, the correct chemistry and subsequent monitoring of the core parameters must be carried out. This paper focuses on the in-line measurement of essential chemical variables in the stator coolant water.

Vitaly A. Prisyazhniuk

PPChem 2005, 7(7), 435–442

The Langelier Saturation Index: Further Development

A simplified technique has been worked out to calculate the Langelier saturation index as an index of the corrosive and scale-forming properties of water. To perform the calculations it is necessary to know the total alkalinity of the water, its electrical conductivity, and pH. A method is presented for making semi-quantitative estimation of the water scaling capacity based on the thickness of the deposits formed. To calculate the thickness of the scale layer it is necessary to know the conductivity of the water at room temperature and the "operative" temperature of the surface on which scale formation is expected.

Miroslav Šťastný
Miroslav Šejna

PPChem 2005, 7(8), 455–462

The Effects of Steam Chemistry on the Condensation Process

A two-population numerical model of hetero-homogeneous condensation is used for the calculation of the wet steam flow with condensation in convergent-divergent nozzles. This computational model applies governing equations of the wet steam flow and equations of spontaneous nucleation. Parallel heterogeneous nucleation is evaluated on the assumption that heterogeneous water droplets originate by nucleation on chemical impurities (for instance sodium chloride) in the salt solution zone close above the steam saturation line. The calculation results of the flow in the nozzles with mean expansion rates of 4 500 s^{-1} and 1 000 s^{-1} in divergent nozzle parts are described and the effects of heterogeneous and/or spontaneous nucleation and condensation are discussed and compared with experiments. The concentrations of heterogeneous droplets were found by fitting of calculation results to experimental ones. A possible dynamic gradual origin of heterogeneous droplets during expansion was observed.

Robert Svoboda
Albert Bursik

PPChem 2005, 7(8), 472–480

Carbon Dioxide and Feedwater Chemistry

In this paper, the influence of carbon dioxide contamination on the pH of condensate/feedwater at temperature in fossil plant cycles is investigated. It is shown that in particular at temperatures below 200 °C, automatic feedwater pH control (ammonia dosing) has to be adapted to the overall cycle conditions (e.g. to a carbon dioxide ingress into the cycle. While at higher temperatures the presence of carbon dioxide has nearly negligible influence on pH (at cation conductivity $\leq 2\ \mu S \cdot cm^{-1}$), at temperatures lower than 200 °C, the pH at temperature may significantly decrease. Disregarding adequate pH (25 °C) control during periods with increased carbon dioxide content (increased cation conductivity) may create dangerous environmental conditions that favor flow-accelerated corrosion.

Francis Nordmann

PPChem 2005, 7(8), 481–488

Optimization of Chemistry in PWR and VVER Nuclear Power Plants

This paper, based on international feedback and studies, proposes potential improvements for PWR and VVER operation:

- pH optimization in the primary coolant in order to minimize corrosion product transport/deposition and associated radiation exposure, crud induced power shifts (previously called axial offset anomaly), and fuel failure;
- use of enriched boron acid (enriched with ^{10}B) to easily optimize the above described pH, particularly with the increased use of higher fuel enrichments;
- zinc addition in the reactor cooling system;
- establishment of secondary water chemistry specifications which take into consideration the steam generator tubing materials and design to minimize corrosion risk while keeping sufficient plant availability and decreasing environmental impact;
- amine selection for the secondary system aimed at mitigating steam generator tube fouling, power loss and maintenance costs as well as corrosion risks;
- overall operating chemistry options designed to minimize environmental impact, such as elimination of condensate polishers and optimum ion exchange resin use.

J. Barry Hughes

PPChem 2005, 7(8), 489–493

Automated Control of Chemistry Whilst under Cycling Regime at Teesside Power Station

Today a large number of power plants are run under cycling regimes. This calls for detailed control of the chemistry using automatic analysis and process control. The best determinant for analytical control has to be one that is directly measurable and control-

lable. A number of processes on the overall plant cycle at Teesside Power Station will be discussed and the reason for each determinant will be shown.

Muthiah Puspha
Keezhanatham S. Seshadri
Pradeep Kumar Sinha
Kamal Bihari Lal

PPChem 2005, 7(8), 494–499

A Comparative Account of the Wet Oxidation of Cation Exchange Resin with Hydrogen Peroxide Using Titanium, Vanadium, and Molybdenum Doped MCM-41 as Catalysts

Ion exchange resins are widely used in the nuclear industry for treatment of radioactive waste as well as for the upgrading of heavy water used in the primary heat transport system and moderator system. Repeated usage of the resins calls for replacement and treatment before disposal. The present work involves the application of metal-doped MCM-41 material as a catalyst for the wet oxidation of cation exchange resins using hydrogen peroxide as an oxidizing agent. The sulfate produced from the exchangeable group of the resin reflects the extent of decomposition and the carbonate produced reflects the extent of oxidation of the ion exchange resin. Results indicate that the percentage decomposition and oxidation increase with the weight of the catalyst and the volume of the oxidant, i.e., hydrogen peroxide. As much as 0.5 g of the resin could be decomposed by 12 mL of 30 % hydrogen peroxide to 98.7 % and oxidized to 99.25 % using molybdenum doped MCM-41. Vanadium doped and titanium doped MCM-41 required 14 to 16 mL for complete decomposition and 18 to 20 mL for complete oxidation of the ion exchange resin..

Eric Maughan

PPChem 2005, 7(8), 500–507

The Measurement of Dissolved Oxygen in Condensate and Feedwater Circuits

Questions often arise about the calibration, verification, and maintenance of oxygen sensors. This paper offers an overview of the available systems and gives advice with respect to troubleshooting related to the on-line measurement of oxygen and to the storage of oxygen sensors.

Frederick J. Pocock, Jr.
Jack W. Stewart

PPChem 2005, 7(9), 517–531

The Solubility of Copper and Its Oxides in Supercritical Steam

This paper contains a study of the solubility of copper and its oxides in supercritical steam which was undertaken because of difficulties experienced with copper deposition in the high-pressure turbine of the Ohio Power Company's Philo 6 supercritical steam-generating cycle. This study shows that copper has appreciable solubility in superheated supercritical steam. The extent of solubility is apparently a function of the oxidation state of the metal, with the highest state of oxidation (CuO) showing the greatest solubility. A slightly increased solubility was effected by increasing pH values from 7.5 to 9.5 with ammonia. It is also shown that copper solubility is principally a function of pressure over the narrow temperature range tested (900 °F to 1 150 °F) probably because this parameter has the greatest effect on specific volume.

Brian R. Ohler
Jasbir S. Gill

PPChem 2005, 7(9), 534–538

Improving the Performance of ZLD Cooling Water System through Innovation in Chemistry and Control

An innovation in chemistry and control technology was deployed at Deseret power station to control corrosion, scale, and biofouling. A low phosphate molecule containing no heavy metals was used for both scale and corrosion control. The monitoring and control is based on several fluorescence-based probes to determine the optimum dose and monitor the treatment performance for scale, bio, and corrosion control. The new treatment in combination with the on-line 24/7 monitoring, control, and the ability to communicate performance via web or modem resulted in optimum performance and cost. The study was deemed successful and is currently deployed as a commercial technology.

Peter L. Andresen

PPChem 2005, 7(9), 541–560

Critical Processes to Model in Predicting Stress Corrosion Response in Hot Water

Structural materials have a fundamental susceptibility to stress corrosion cracking (SCC) in high temperature water, and extensive efforts have been made to quantify their specific response as a function of material and condition, water chemistry, temperature, stress, etc. There are many primary variables, and dozens of important factors, all of which are inter-dependent in establishing SCC response. The only comprehensive way

of tackling this problem is to identify the underlying processes that control SCC, which provides a fundamental framework for understanding the myriad of interdependent factors. This paper discusses the processes that must be understood and modeled, and compares various approaches in this quest.

R. Barry Dooley
James E. Castle
Peter A. Zhdan

PPChem 2005, 7(9), 561–567

Minimizing Copper Pickup from Copper Alloys in the Feed Train by Control of pH and ORP: New Operating Limits

This paper reviews recent research, sponsored by EPRI, by which the amount of copper release from the copper alloys commonly found in the feed train of power stations has been determined. The investigations have been undertaken under carefully controlled laboratory conditions to simulate feedwater. Release rates are given for pure water as a function of the pH value and the oxidation-reduction potential (ORP). The ORP responds directly to the level of dissolved oxygen and is a sensitive indicator of whether the feedwater is oxidizing or reducing with respect to copper. For all conditions of exposure, the copper alloy surfaces have been characterized in terms of the morphology and composition of the surface oxides. The mechanism of release is discussed on the basis of the surface characteristics.

Measurements relevant to the LP heaters were made using a standard test temperature of 95 °C (203 °F). Under reducing conditions (defined by an ORP of –300 mV) the minimum release is found, for admiralty brass, 90/10 cupronickel and aluminum brass, to be close to a pH value of 9.5. Under fully oxidizing conditions (an ORP of +100 mV), the minimum is shifted to a lower pH value, in the range 7–8. Copper release decreases on reduction of oxygen concentration, but evidence is found for very high release rates in the ORP range –50mV to +50 mV, associated with the transition between Cu_2O and CuO as the thermodynamically stable surface phase. In this region of instability, approximately between 0.1 and 1 $mg \cdot kg^{-1}$ O_2 or –50 to +50 mV ORP, very high release rates may be found. It should be considered unsafe to operate in this range. Transitions through the range in either direction must be made promptly in order to minimize copper pick up by the feedwater. Measurements relevant to HP heaters were made using test temperatures up to 350 °C (660 °F). Release from 70/30 cupronickel followed a similar pattern to that observed for the LP train.

Based on these measurements, a new set of operating limits for these alloys under typical fossil fueled plant conditions has been incorporated into the latest revisions of the EPRI Guidelines for AVT, Phosphate Continuum and Caustic Treatment. These limits minimize copper pickup from copper alloy and mixed-metal feedwater systems.

Masahiko Kurashina
Hideo Uzawa
Toshiaki Aoki
Li-Bin Niu
Hiroshi Takaku

PPChem 2005, 7(9), 569–573

Development of Electric Cation Exchanger for Measurement of High pH Secondary Water Quality in PWR Plants

High pH operation is applied to the secondary water treatment of Japanese pressurized water reactor (PWR) plants. To reduce the maintenance frequency to as low as possible, an electric cation exchanger used with electric dialysis film as a substitute for the cation exchange resin was developed. Some tests conducted at an actual PWR plant as well as at our laboratory have confirmed that the performance of the developed electric cation exchanger may be promising for actual use.

R. Barry Dooley
Albert Bursik

PPChem 2005, 7(10), 581–585

International Conference on "The Interaction of Organics and Organic Cycle Treatment Chemicals with Water, Steam, and Materials" – Conference Discussion Groups and Summary

At the beginning of the conference, Dooley and Bursik had presented five key topics in the world of organics in power generation cycle chemistry for which they thought knowledge was deficient. Following the working group summaries, the conference chairmen came back to the same points and provided the following summary.

The conference provided a great cross-section of the science, applications and results in all aspects of organics in the energy cycle chemistry cycle. The science appears to be improving. The number of applications is also increasing. But quantitative assessments remain weak and thus raise more questions than they provide answers. Particularly,

answers will be needed in the first five areas before any quantitative guidelines can be derived:
- Effect on cycle materials
- Properties of organics in the cycle
- Organics as treatment chemicals
- Shutdown/layup protection
- Role of organics in efficiency/performance improvement
- Economics

Albert Bursik
R. Barry Dooley

PPChem 2005, 7(10), 593–598

Organics: A Retrospective Look at Fossil Plant Cycle Chemistry and the Possible Requirements for the Future

The current suite of EPRI fossil plant cycle chemistry guidelines for all-volatile treatment (AVT), oxygenated treatment (OT), phosphate continuum (PC), and caustic treatment (CT) have established themselves as the treatments of choice around the world. These guidelines contain little information on the presence of organics in the cycle nor do they advocate the use of organic additives during either operation or shutdown. This paper, and indeed the conference *Interaction of Organics and Organic Cycle Treatment Chemicals with Water, Steam, and Materials*, has been assembled to review the status of all aspects of organics in a fossil plant cycle. The two main thrusts are to thoroughly review the science and application and to recognize the main areas of deficiency in that knowledge so that a structured research program can be developed. Interest is focused not only on the adventitious ingress of organics through the makeup and cooling water systems, but also on the purposeful addition of organics to the cycle as treatment chemicals or preservatives.

Peter J. Millett
Keith Fruzzetti

PPChem 2005, 7(10), 599–603

Status of Application of Amines in US PWRs

Prior to 1990, the majority of US units with pressurized water reactors (PWRs) were using ammonia as the primary pH control agent in secondary systems. Morpholine was used in one plant that did not employ condensate polishers. With the introduction of ethanolamine and other advanced amines in 1992, US PWRs could now get the benefit of improved pH control and still operate condensate polishers in the H-OH form. In this paper, the current practice with amines in US PWRs is reviewed with consideration for the optimization of pH control in secondary systems.

Kazuo Marugame
Li-Bin Niu
Hiroshi Takaku

PPChem 2005, 7(10), 605–610

Corrosion Behavior of Magnetite Grown from Amine-Carboxylate and Amine Aqueous Solutions

A unique boiler water treatment using amine-carboxylate and amine for the application in the temperature range of 150–364 °C and at pressures from 0.5–20 MPa has been developed. The size of the magnetite formed by this method is very fine 0.3–1.5 µm, while that of magnetite formed by the conventional boiler feedwater treatment is 20–40 µm. Laboratory test results have shown that the specimens treated with this magnetite have good corrosion resistance in both severe acidic and caustic environments, while those formed by the conventional boiler feedwater treatment experience severe general and pitting corrosion. Results from an actual power plant test show the same corrosion behavior as in the laboratory tests. The formation of this fine and tight magnetite on the boiler tube inner surface is very effective for corrosion suppression.

Melanie Montgomery
Ole Hede Larsen

PPChem 2005, 7(10), 611–622

Field Investigation of Various Weld Overlays in a Waste Incineration Plant

A test waterwall was fabricated so that alternatives to alloy 625 could be exposed in the first pass of the waste incineration plant Haderslev. The difference between application method was also a parameter, such that manual welding, machine welding and arc spray coating of alloy 625 were compared. In addition to the test waterwall exposure, the chemical environment from the waste incineration was also monitored by analyzing deposits and corrosion products from various locations in the boiler. These were analyzed with respect to morphology and composition using electron microscopy with energy dispersive spectrometry. Based on these results it was detected that the aggressive environment had changed during the exposure period, which made direct comparison difficult between alloys that had been exposed the first year and those exposed for

the second year. However, all candidate alloys could be compared with alloy 625, which was present in every test panel. It was observed that all the weld overlay test sections behaved similarly to machined alloy 625 in that there was general corrosion and pitting corrosion. In addition, alloy 622 also exhibited preferential corrosion with respect to its dendrite structure.

Raúl B. Rebak

PPChem 2005, 7(10), 623–631

Environmentally Assisted Cracking of Commercial Ni-Cr-Mo Alloys – A Review

Nickel-Chromium-Molybdenum alloys (Ni-Cr-Mo) are highly resistant to general corrosion, localized corrosion and environmentally assisted cracking (EAC). Chromium acts as a beneficial element under oxidizing acidic conditions and molybdenum under reducing conditions. All three elements (Ni, Cr and Mo) act synergistically to provide resistance to EAC in environments such as hot concentrated chloride solutions. Ni-Cr-Mo alloys may suffer EAC in environments such as hot caustic solutions, hot wet hydrofluoric acid solutions and in supercritical water oxidation applications. Not all the Ni-Cr-Mo alloys have the same susceptibility to cracking in the mentioned environments. Most of the available data regarding EAC is for the oldest Ni-Cr-Mo alloys such as N10276 and N06625.

Miroslaw S. Gruszkiewicz
Donald A. Palmer

PPChem 2005, 7(11), 644–655

Modeling the Behavior of Formate, Acetate, and Carbon Dioxide in Water/Steam Cycles

Organic substances persist in high-temperature aqueous environments for varying periods of time depending on temperature, pH, contact with solid surfaces, and other factors. Since carboxylic acids and CO_2 affect the pH and can potentially play specific roles in the promotion or inhibition of turbine corrosion, it is important to be able to predict the amounts of these substances that are transferred to steam and the composition of the early condensate as a function of condensation ratio for various boiler chemistries. Such predictions can only be made using a speciated model including all the solutes. Example calculations for AVT and OT chemistry show complex relationships between early condensate enrichment ratios and boiler pressure, boiler water composition, and condensation ratio. Even small amounts of sodium and chloride below 0.1 $\mu g \cdot kg^{-1}$ in the steam are relevant to early condensate pH and carboxylic acid concentration. The calculations show that the enrichment of the early condensate relative to steam is typically 10 times greater for formate than for acetate.

Ursula Hollwedel

PPChem 2005, 7(11), 656–664

Secondary Side Chemical Cleaning of Steam Generators of Pressurized Water Reactors

Chemical cleaning (CC) is a qualified, efficient method to remove not only sludge piles from the tube sheets of steam generators (SGs) but in addition scales from the heat transfer tubing. A major component of SG deposits is magnetite, which is dissolved using an organic chelating agent, usually ethylenediaminetetraacetic acid, in an alkaline, reducing environment. If copper is present in the SGs, it is removed in a separate step using organic chelants under oxidizing conditions. There are two well-known processes on the market for magnetite and copper removal, the EPRI/SGOG developed chemical cleaning process open for application by all interested companies and the Siemens/KWU developed and patented High Temperature Steam Generator Chemical Cleaning (HT-SGCC) process. The characteristic features of both processes are compared and the application and results of the latest HT-SGCCs performed with respect to the amount of deposits removed and application time are summarized.

Walter Guhl
Wolfgang Hater

PPChem 2005, 7(11), 667–673

Snails and Mussels in Cooling Systems

Foreign matter in cooling systems may seriously deteriorate the effectiveness of the cooling cycle, especially if this matter reduces the regular flow of the cooling water by blocking the condenser tubes. Often, these foreign bodies are mussels and snails, which may be present in large numbers and whose shells may block the flow through the tubes. The most important species living in cooling systems are presented and their behaviour in cooling systems is described. Comprehensive studies have shown that the biocides P3-ferrocid 8591 or P3-ferrocid 8580 in combination with the biodispersant P3-ferrofos 8460 are excellent for controlling mussels and snails. This procedure is more effective if a partial stream filtration is also used at the same time.

Ashok G. Kumbhar
Arvind D. Belapurkar
Gopala Venkateswaran
Kamal Kishore

PPChem 2005, 7(11), 674–679

Impact of Different Metal Turbidities on Radiolytic Hydrogen Generation in Nuclear Power Plants

Radiolytic hydrogen generation on gamma irradiation of turbid solutions containing metal turbidities such as titanium, nickel, iron, chromium, copper, indium, and aluminium was studied. It is suggested that the chemical reactivity of the metal in the turbid solution with radicals produced by radiolysis of water interferes with the recombination reactions which destroy hydrogen and hydrogen peroxide, thus leading to higher yield of hydrogen. The rate of generation of hydrogen and the radiolytic yield of hydrogen is related to the reactivity of the metal ion/hydroxylated species with the free radicals.

Steef H. M. Vrijhoeven,
Paul B. Desch
James J. Dillon

PPChem 2005, 7(11), 680–693

Case Histories of Unusual Boiler Failures

Case histories are presented that describe atypical failures in boiler systems that are related to nonstandard or improper design, installation, materials specification, and operating practice. Some cases demonstrate how residual stresses in boiler components combine with unexpected environmental conditions to produce damage. The specific circumstances that promoted the failures are described and corrective actions are discussed.

Václav Roubíček
Pavel Kolat
Bohumír Čech
Dagmar Juchelková
Zdeněk Kadlec

PPChem 2005, 7(11), 695–702

Utilization of Alternative Fuels in Fluidized-Bed Boilers

The energy utilization of alternative fuels is one of the main topics for future development of recoverable resources in the European Union and in the Czech Republic. The subject of the research is combustion tests in a fluidized-bed boiler located at Štětí, Czech Republic. The experiments were carried out using Czech brown coal, wood, sewage sludge and wastes. Analyses and recommendations for optimal thermal utilization and minimization of harmful emissions were developed. The second step was thermal analyses of coal and the alternative fuels wood pellets and sewage sludge from treatment plants. From the results of the experiments and thermal modeling it is clear that 15 % alternative fuels can be used in the large fluidized-bed boilers located in the Czech Republic.

Andrew G. Howell
George E. Saxon, Jr.

PPChem 2005, 7(12), 708–716

Condenser Tube Fouling and Failures: Cause and Mitigation

The two most common condenser tube problems faced by chemists are internal tube fouling and tube failure. Fouling can have a major impact on power station generating efficiency and/or capacity, and tube leaks can seriously impact unit availability and reliability. Fundamental understanding of the root cause(s) of these issues and their mitigation is essential to resolving these problems and/or preventing their occurrence.

Ruedi Germann

PPChem 2005, 7(12), 718–720

Process Monitoring: What Really Matters

This paper focuses on an increasingly important topic: problems with bidding procedures for process monitoring instrumentation. The recent calls for bids are exclusively focussed on prices and do not take into account the kind of application and the specific requirements with respect to instrument maintenance and quality assurance. As a rule, the cheapest instrument selected does not in the majority of cases represent the best solution, in particular for cycle chemistry monitoring in power plants.

David M. Gray

PPChem 2005, 7(12), 729–731

Measurement of Organics in Power Plant Makeup Water Treatment

Most efforts at producing pure water have focused on removing minerals, with processes that do not necessarily remove organic compounds. There is increasing awareness of the problems that organics can cause in the power plant cycle and this can drive changes in water treatment methods. A key to confirming and trouble-shooting organics removal processes is a reliable TOC (total organic carbon) measurement. Presented here is a particularly applicable and economical instrumentation approach for rapidly detecting organic contamination in various stages of pure water treatment systems. The instrument platform uses a separate TOC sensor and transmitter which enable simultaneous measurements of conductivity, pH, dissolved oxygen and flowrate, in addition to TOC, on the same transmitter.

Jo Savelkoul
Roy van Lier

PPChem 2005, 7(12), 733–739

Operational Experience with Organics in Industrial Steam Generation

In the chemical process industry, the steam cycle is of secondary importance: the (petro)chemical process comes first. High heat flux designs and – generally unavoidable – water quality problems make industrial boilers susceptible to corrosion.

The selected steam cycle treatment has to be tolerant towards (in)organic contaminants. Conventional programs are not always suitable to meet the specific challenges of individual plant steam cycles. Moreover, degradation products of classic organic alkalizing agents like morpholine may worsen the situation in some respect.

A polyamine program can be a worthwhile alternative. Our experience with polyamines so far has been very positive and has made us confident enough to now consider these products for 12.5 MPa steam systems.

Dennis P. Raught
Gary L. Foutch
Allen Apblett

PPChem 2005, 7(12), 741–747

Ion Exchange Resin Fouling by Organic Amines in Secondary Systems at U.S. Nuclear Power Plants

Organic amines added to power plant feedwater to control iron concentrations have an impact on ion exchange resin performance. Several theories attempt to explain the cause. One such theory is that cation resin reacts with the amine, cleaving fragments, which then deposit on the anion resin. The deposition blocks pores or permanently utilizes exchange capacity on the anion resin, resulting in reduced exchange of impurities. Nuclear industry operators have recognized this phenomenon and are working with researchers to apply laboratory experience to improving plant performance.

Matthias Meierer

PPChem 2005, 7(12), 753–762

Studies on the Issue of Fine Dust Based on the Example of Grosskraftwerk Mannheim AG

Recently, the issue of fine dust has come to the fore in the public interest because of repeated incidents where the maximum permissible levels for ambient pollution (immissions) were violated significantly. A recent EU directive has defined new limit values, which have already been integrated into German law through an ordinance under the Federal Immission Control Act. The new limit values came into effect in January 2005. This report provides some background information regarding the sources and mechanisms of fine dust formation, as well as the transfer and the separation of fine dust. Specific measuring and analytical methods are capable of identifying the concentration of both fine dust emissions and immissions (ambient pollution levels).

Over the past decades, effective technical measures have helped to significantly reduce dust emissions from power plants and industrial facilities in Germany. The current situation of ambient pollution in Germany is characterized by great regional differences. In particular, traffic has a share in limit value violations. The report describes other types of emission sources as well. The share of fine dust pollution specifically attributable to fossil-fired power plants is very low in Germany. This has been confirmed for the local pollution scenario in the Mannheim area by an examination of the dust ratios emitted from the Grosskraftwerk Mannheim AG plant using propagation calculations.

2006's Scientific and Technical Contributions

Eric Maughan

PPChem 2006, 8(1), 6–7

Summary of the Eskom International Chemistry Conference "Power Plant Chemistry and Process Water Treatment"

This paper is a very brief summary of the recent traditional and as always very successful Eskom International Chemistry Conference, which took place in Mabalingwe, South Africa, on November 9–11, 2005.

Karol Daucik

PPChem 2006, 8(1), 10–12

Decomposition of Chlorinated Hydrocarbons in the Water/Steam Cycle of a Power Plant

By mistake, a small amount of trichlorethane was injected into the condensate of a power plant unit with a once-through boiler. The gradual decomposition of the contaminant could be observed by measuring acid conductivity at different places along the feedwater and steam path. The ion chromatographic analysis showed that the increase in acid conductivity was attributable to chloride. The observations give a basis for simplified evaluation of the kinetics of thermal decomposition of trichlorethane in water.

Andy Rudge
Gary Cook
Ian Woolsey

PPChem 2006, 8(1), 13–19

The Potential Use of Amines in High Temperature Once-Through Nuclear Power Plant Boilers

A project to implement amine dosing to the steam/water circuit in two of British Energy's nuclear power plants is underway, which, it is hoped, will arrest increases in boiler pressure drop. This paper summarises the reasoning behind the decision to go forward with amine dosing, the amine selection process, and progress to-date with the implementation project. Evidence from boiler rig testing is presented, which shows that amine dosing should be effective at arresting increases in boiler pressure loss. Results from a short plant trial with dimethylamine dosing are also presented, which show that amine decomposition under plant operating conditions is low.

Dietrich Frahne
Thomas Blum

PPChem 2006, 8(1), 21–30

Formation of Polyamine Films on Iron Surfaces under Power Plant Conditions – Laboratory Investigations

Polyamines have been used for more than two decades and are currently being applied to an increasing extent for successful conditioning of low, medium and high pressure boiler and steam/water cycles, this despite the fact that amines in general are comparatively reactive and in some cases less thermally stable. In some high temperature applications, polyamines and amines are repeatedly alleged in the literature to degrade into volatile organic acids, especially to form the very stable and corrosive acetic acid, in addition to dreaded sticky degradation products on metal surfaces.

In order to find a suitable response to these risky and long debated topics and to provide laboratory evidence to support the numerous practical successes and performance achievements obtained over more than 20 years, we have performed some laboratory experiments that address the origin of volatile acids, the question of stability of decomposition products and the film forming features of polyamines and their protection of metal surfaces. The estimation of low or residual concentrations of polyamines as typically encountered in practice is also discussed. These experiments were partly performed in open vessels at atmospheric pressure. Experiments involving polyamine stabilities were conducted in an autoclave at 175 °C and 400 up to 520 °C. Although laboratory experiments under such simple conditions are not always comparable to practical conditions, the results obtained still offer acceptable confirmation of the many positive practical observations and applications of polyamines in industry.

Kevin J. Shields
Dennis A. Frey
Robert D. Bartholomew
Gary H. Roberts

PPChem 2006, 8(1), 33–42

Chemical Cleaning of Fossil Steam Generators with Organic Solvents: North American Experience

Use of organic-based solvents as an alternative to inorganic solvents has been practiced in North America since the 1960s. Solvents in use include hydroxyacetic-formic acid, citric acid, and ethylenediaminetetraacetic acid. Initial applications were in the cleaning of waterwalls of conventional fossil fueled boilers, including drum-type boilers and once-through subcritical and supercritical steam generators, and subsequently in the cleaning of superheaters and reheaters. Most recently, organic solvents have been used in the preoperational cleaning of heat recovery steam generators of combined cycle units.

The organic solvents offer certain advantages as well as some limitations and these aspects must be considered during the selection process. Various characteristics and features of these organic solvents are considered and comparisons to commonly used inorganic solvents are made. Case studies based on field application of the organic solvents for specific purposes are presented to demonstrate the possible uses of these solvents and the required process conditions.

PPChem 2006, 8(1), 43–58

2005's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Geoff J. Bignold

PPChem 2006, 8(2), 68–73

The Behaviour of Ammonia, Amines, Carbon Dioxide and Organic Anions during Condensation in an Air Cooled Condenser

Air cooled condensers are being used increasingly frequently in new plants, not only in arid locations where supplies of large quantities of cooling water are absent, but also in many places where restrictions are being imposed on the issue of licences for abstraction of water for cooling applications. It is economically important to achieve the lowest practicable steam temperature and pressure in order to maximise the efficiency of the steam turbine. Heat transfer from the condensing steam to air, with only a small temperature difference, requires an air cooled condenser (ACC) with very large areas of finned tubing, which is normally made of carbon steel. Even with very modest corrosion rates, the very large area of steel can contribute a significant amount of iron to the condensate, and this can be a major source of iron rich deposits accumulating in the boiler plant.

The corrosion processes occurring in a steel air cooled condenser will inevitably be influenced by the chemistry of the condensate, which changes as the condensation process proceeds.

In a circuit where alkalinity is provided by the presence of ammonia, the early stages of condensation in the ACC will have a relatively low ammonia concentration in the liquid phase and correspondingly low pH. Any organic anions such as acetate or formate found in the steam will suppress the pH further. Carbon dioxide will also have this effect. Thus it is the upstream ends of the ACC tubes that will be expected to contribute most to the iron level in condensate. As steam passes further along the condenser tubes, the pH in the condensate rises, so that any dissolved iron may become supersaturated and some particulate iron is produced.

If the steam contains an amine with a distribution coefficient that favours the water phase, then the water in the early stages of condensation may have an appreciably higher pH and the loss of iron from steel surfaces may be suppressed. However, the interactions are complex. Amine decomposition elsewhere in the circuit is likely to cause the concentrations of carbon dioxide and organic anions in the steam to rise, and these will be less volatile in the condenser and consequently more difficult to expel from the circuit. An initial approach to understanding these interactions is set out in this paper.

S. Ronnie Pate
Sam J. McChesney
Randy C. Turner

PPChem 2006, 8(2), 74–81

Southern Company's Approach to Cycle Chemistry

The Southern Company has long sought to develop water chemistry treatment philosophies and out-of-specification actions that ensure long-term operations and availability of the fossil-fueled steam units. This has been accomplished by utilizing the best known science from world class chemists, both academic and from original equipment manufacturers, and from organizations such as the Electric Power Research Institute (EPRI), as well as the personal experience of the chemistry practitioners. This paper explains the results sought and basic steps on how to achieve these ends. Some of the concepts covered include minimum qualifications for plant chemists, chemistry control philosophies, and annual peer reviews, including EPRI Benchmarking of each unit's chemistry program.

Jørgen P. Jensen
Katrine Nielsen
Christian N. Ottesen

PPChem 2006, 8(2), 82–88

Water Chemistry Control of an Ultra-Supercritical Boiler – Avedøre Unit 2

Avedøre Unit 2 is an ultra-supercritical boiler with an integrated steam cycle that includes a biomass boiler and two heat recovery steam generators. The unit is only equipped with a condensate polishing capacity of 14 % at full load. This results in chemical excursions during startup of the boiler, when salt deposits are washed off the turbine. Initiatives are being taken to eliminate a high content of impurities in the condensate and feedwater at startup.

Michael A. Sadler
Kevin J. Shields

PPChem 2006, 8(2), 95–104

Minimizing Levels of Volatile Organic Acids and Carbon Dioxide in Steam/Water Circuits

Low concentrations of weak organic acids such as acetic and formic acids are commonly found in water sampled from the steam/water circuits of boilers and steam generators. The debate concerning their influence on corrosion in these circuits continues, but there is agreement that their presence is a nuisance and if reasonably possible levels of these impurities in steam/water should be minimized. The main origin of these volatile organic acids has been shown to be traces of more complex organic impurities present in makeup water. Improved techniques of deionization such as the use of reverse osmosis will significantly reduce the organic contaminant levels in makeup water. There is clear evidence that levels of weak organic acids can be effectively removed from the steam/water circuit by the use of condensate polishing operating in its conventional H-OH mode. Polishers operating in the economical ammonium form will in most cases also successfully control these impurities, but, in some circumstances, difficulties could arise, so care in monitoring their performance is recommended.

Stefan A. Huber

PPChem 2006, 8(2), 105–116

The Behaviour of Natural Organic Matter in Water Treatment and the Water/Steam Cycle: Deeper Insights

The paper focuses on specific components of natural organic matter (NOM) whose molecular charge densities are too low to allow efficient removal by ion exchange. This fraction of NOM is mainly polysaccharidic in nature. It does not contribute much to conductivity in the makeup water, but in the water/steam cycle the reaction products are decomposed to organic acids (pathway: polysaccharides → monosaccharides → organic acids). In the past, non-ionic NOM was largely overlooked because it was not accessible to analytical techniques. Only recently has a new technique, called LC-OCD (liquid chromatography – organic carbon detection), allowed rapid identification and quantification. The paper describes in detail the behaviour of polysaccharides during pre-treatment, demineralization and in the water/steam cycle. Strategies on how to remove polysaccharides in the makeup water are also presented.

Volker Ender
Björn Kettner
Thomas Schumann
Sigrun Hajdamowicz

PPChem 2006, 8(2), 117–125

The Influence of Temperature on the Removal of Organics from Natural Waters by Ion Exchange – Laboratory and Pilot Plant Experiments

In laboratory and pilot plant experiments we investigated the influence of temperature on the removal of organics from natural waters by ion exchange resins and three types of scavenger resins. The temperature was varied during the loading phase as well as during the regeneration process (20 °C, 30 °C, and 40 °C in the laboratory experiments;

30 °C, 40 °C, and 50 °C in the pilot plant). The water quality was analysed using the liquid chromatography – organic carbon detection (LC-OCD) method.

The following main results were found:

- Neither the variation in the loading temperature nor the variation in the regeneration temperature could influence the removal of total organic carbon (TOC) before the breakthrough point. The reaction enthalpy of the removal of TOC from natural waters by ion exchange resins is therefore about zero.
- A higher loading temperature leads to a later TOC breakthrough point. Higher regeneration temperatures give better TOC regeneration rates.
- The most important potential for the improvement of the retention of organic matter by ion exchange resins is a better understanding of the relation between TOC ion exchange and the adsorption mechanisms regarding their individual fractions. This seems to be valid especially for the hydrophobics fraction.

Pascale Bénézeth
David J. Wesolowski
Donald A. Palmer
Moira K. Ridley
Caibin Xiao

PPChem 2006, 8(3), 132–136

Effect of Amines on the Surface Charge Properties of Iron Oxides

Large-scale, flow-through experiments were conducted at Chalk River Laboratories [1,2] in which the deposition rate of suspended magnetite (Fe_3O_4) particles onto Inconel boiler tube walls was determined in water at 270 °C with the pH controlled nominally at 6.2 (at 270 °C) by the use of potassium hydroxide and various amine buffers (morpholine (MOR), dimethylamine (DMA), ethanolamine (ETA), and ammonia). Relative to the deposition rates in KOH solutions as the control, MOR was found to result in the highest magnetite deposition rates among the various amines, and DMA the lowest. A hypothesis was developed from this work that sorption of the protonated form of the amine onto negatively charged magnetite surfaces might enhance the deposition rate by reducing electrostatic repulsion between the magnetite particles and the boiler tube walls. This paper summarizes results of potentiometric titrations performed in 0.03 molal NaTr to determine whether MOR (200 and 250 °C) and DMA (150 and 200 °C) or their protonated cations significantly alter the proton-induced surface charge of magnetite over the range of pHs of interest in PWR secondary cycles [3]. However, in order to measure these effects, it was deemed necessary to first establish the hydrolysis constants of MOR and DMA over the entire range of experimental conditions of the magnetite surface titrations, and in the same ionic medium.

Anton Banweg

PPChem 2006, 8(3), 137–140

Organic Treatment Chemicals in Steam Generating Systems – Using the Right Tool in the Right Application

Nalco has developed organic treatment chemistries for many applications in steam generating systems to provide better performance than the traditional alternatives. Several specific applications are discussed: fluorescent organic materials for monitoring and diagnostic applications, all-polymer internal boiler water treatment for deposit inhibition, hydrazine alternatives, and engineered multiple amine products for optimal condensate system corrosion protection.

Wayne Micheletti

PPChem 2006, 8(3), 141–150

Atmospheric Emissions from Power Plant Cooling Towers

Power plant recirculated cooling systems (cooling towers) are not typically thought of as potential sources of air pollution. However, atmospheric emissions can be important considerations that may influence cooling tower design and operation. This paper discusses relevant U.S. environmental regulations for potential atmospheric pollutants from power plant cooling towers, and various methods for estimating and controlling these emissions.

Nestor van Eeden
Ken J. Galt

PPChem 2006, 8(3), 159–168

Corrosion Product Sampling at Koeberg Nuclear Power Station

Corrosion and corrosion product transport have a negative impact on the performance and reliability of secondary cycle systems and components. Taking a grab sample, acidifying it and measuring the iron and copper concentrations is not an effective method to measure corrosion products as the sample is not representative and results are limited to the detection level of the analytical technique employed. Koeberg has installed fixed corrosion product sampling equipment at several strategic points in the secondary system. The technique involves accumulation of the insoluble material on a filter paper over a period of time and then analysis of the deposit. A cation resin impregnated filter collects the soluble ionic material which is analysed separately. The filter papers are digested with acids and chemical analysis is performed to determine insoluble and soluble iron and copper concentrations by flame and graphite furnace atomic absorption spectrophotometry.

The sampling equipment, sample collection, analysis method, operating experience and some further developments are discussed.

Neil B. Caris

PPChem 2006, 8(3), 169–174

The Changing Role of Chemistry in the Power Industry

Corrosion costs the U.S. electricity industry between five and ten billion dollars a year. In steam generating plants it is estimated that over half the forced outages are caused by corrosion, and in the U.S. industry, corrosion increases the cost of electricity more than it increases the cost of any other product, adding over 10 % to its price. The total cost of corrosion to U.S. industry is in excess of $276 billion annually, of which more than 30 % could be prevented through the use of optimum corrosion management practices [1].

In order to effectively deal with these issues it will require a coordinated approach throughout the industry, in which chemistry has a major role to play. Chemistry has effectively moved from being a problem to being a solution for materials and corrosion issues, and judging by the current advances and initiatives, will continue to do so. The window of opportunity to positively influence the entire industry is here. This will be especially challenging for us as chemists in Eskom, with an ageing fleet and lack of excess generating capacity. The spin-off of taking up this challenge to "get our chemistry right" and take a quantum step forward would be a significant positive effect on the unit capability factor (UCF) and the forced loss rate (UCLF) for the Generation Division. This could, in turn, influence issues as far reaching as the cost of electricity for the South African consumer and when the construction of new generating plant is scheduled.

Zbyszek Szeliga
Dagmar Juchelková
Bohumír Čech
Franz Winter

PPChem 2006, 8(3), 180–189

The Potential of Alternative Sorbents for Desulphurization – From Laboratory Tests to the Real Combustion Unit

At present, natural limestone is used for the desulphurization of waste gases from the combustion of fossil fuels. However, it is important to save all primary resources for the future, and this applies for limestone as well. The research discussed in this paper focused on finding potential alternative sorbents for the purpose of desulphurization using the dry additive method. The article primarily describes desulphurization tests of selected substances, starting from tests in the laboratory and in pilot scale units, through tests in real combustion facilities.

Rob Heijboer
Marga H. van Deelen-Bremer
Leo M. Butter
André G. L. Zeijseink

PPChem 2006, 8(4), 197–202

The Behavior of Organics in a Makeup Water Plant

It is well known that organic compounds are decomposed in the water/steam cycle and affect the cation conductivity of the steam. KEMA and others have demonstrated that acid decomposition products like acetate and formate are enriched in the early condensate. KEMA has found strong indications that these organics played a role in a low

pressure turbine blade failure. As a measure to prevent future damage, the Dutch power industry asked KEMA to carry out research to assess the behavior of organics in makeup water plants based on ion exchange resins. A survey has been conducted of the raw water sources used by the Dutch power industry. It appears that not only the concentration of the organics (total organic carbon, TOC) is different but also the composition. Because most of the TOC could be classified as natural organic material (NOM) the seasonal influence on the TOC composition has also been addressed.

The performance of a demineralization plant is influenced by the quality of the raw water, the composition of the TOC playing a very important role. The research revealed a seasonal influence on the TOC concentration and composition in the makeup water after mixed bed. With the results it is now much easier to predict the possibility of operational disturbances and/or decreased makeup water quality and to implement the technical alternatives to prevent these.

Masato Matsubara
Satoshi Itaba
Masamichi Miyajima

PPChem 2006, 8(4), 203–207

The Results of Chemical Cleaning by Organic Chemicals of Boiler Tubes of a Plant Operated on OT

In December 2003, Unit 1 of the Chita Second Thermal Power Plant underwent chemical cleaning; the first time our company has chemically cleaned a plant operated on oxygenated treatment (OT). The cleaning resulted in the complete removal of scale using the procedure typically applied in units operated on all-volatile treatment (AVT), and there was no corrosion caused by excessive cleaning. However, we discovered that the acid cleaning process requires more time than in plants operated on AVT, and consequently this must be reflected in future chemical cleaning processes of units operated on OT.

Hans-Günter Seipp
Frank-Udo Leidich
Christoph Liehr

PPChem 2006, 8(4), 208–214

Aspects of the Distribution of Volatile Amines in LP Turbines

Minor amounts of acids have frequently been identified in various areas of LP turbines that are exposed to initial condensation processes. To avoid the general use of highly corrosion-resistant materials in such areas, an optimal precautionary measure is to provide for sufficient alkalization of the initial condensates. The effectiveness of the alkalization in preventing corrosive attack by contaminants is dependent on a number of factors. Several related problems are discussed.

Eric V. Maughan
Ulrich Staudt

PPChem 2006, 8(4), 224–233

TOC: The Contaminant Seldom Looked for in Feedwater Makeup and Other Sources of Organic Contamination in the Power Plant

All life forms, their wastes and their decomposition products fall into the category of naturally occurring organic matter (NOM). Furthermore, man also contributes to the overall load with synthetic organic compounds such as plastics, organic solvents, pesticides, organic coatings and polymers, which do not occur in nature.

At face value the majority of organic compounds appear to be insoluble due to their non-polar nature and are therefore considered to be immiscible in water. Nevertheless, water as the universal solvent will retain certain fractions, whether as trace soluble compounds or due to electrostatic forces, e.g., van der Waals.

NOM and man-made organics are difficult to detect by conventional means, e.g., by conductivity or pH measurements, and specialised equipment is required. Once a contaminant is identified as such, steps must be taken for effective removal before it enters the power plant cycle. However subsequent contamination within the plant cycle should not be overlooked.

This presentation explores:

- The nature of organic matter found in water supplies
- Identifying whether contamination by organic matter is taking place in the pre-treatment plant as well as the power plant cycle

– Measurement of organic matter, i.e., different methods
– Effects of organic matter on the plant cycle chemistry
– Effective measures to attempt to counteract any detrimental effects
– Case studies
– Organic contaminants which might be introduced into the plant cycle

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Guy W. Hutchinson
Keith Garbett
Nigel J. Drew

PPChem 2006, 8(4), 234–243

Concentrations of Total Organic Carbon and Trihalomethanes in Feedwater of a Nuclear Power Plant

A UK Magnox coastal power station was found to experience organic fouling of the condensate polishing plant resins, leading to impaired anion resin kinetics. After 25 years of operation it also began to experience some on-load corrosion boiler tube leaks from a source of halide. Dry primary coolant of carbon dioxide has to be maintained, and each boiler tube leak requires that power must be reduced to plug the leaking tube. Sources of the organic materials were investigated and trihalomethanes (THMs) were identified in the station 'Town's Main' water supply. Seasonal variations and the change in concentration through the make-up water treatment plant and in the steam/water circuit were investigated. Approximately 4 % of the total organic carbon (TOC) and 80 % of the THMs passed through the water treatment plant (WTP) with some of the remaining THMs breaking down in the once-through boiler, in this case releasing halide into the boiler. This required palliative measures for boiler alkalisation and an upgrade to the WTP.

Robert Svoboda

PPChem 2006, 8(4), 244–248

Down Under – The ESAA's Conference "Power Station Chemistry 2006"

This paper reports about the last Power Station Chemistry Conference organized biannually by the Energy Supply Association of Australia. This year, thirty technical papers were presented to 121 participants from 9 countries. In addition, two interesting training courses were offered to the conference participants. The topics of the conference, especially the advanced considerations on water resource management, are of worldwide relevance.

Robert Svoboda

PPChem 2006, 8(5), 270–276

Chemistry in Steam Turbines

The local chemical environment in steam turbines is governed by the solubility and the volatility of substances in the steam. Both are influenced by steam expansion and condensation. Nowadays there is sufficient knowledge to predict, quantify and experimentally verify these effects. Basic data and experimental results as well as their practical application are discussed.

Shunsuke Uchida

PPChem 2006, 8(5), 282–292

Latest Experience with Water Chemistry in Nuclear Power Plants in Japan

Water chemistry control in nuclear power plants (NPPs) is principally based on experience with such control in fossil power plants (FPPs). However, the much more severe targets for integrities of fuel assemblies and structural materials, accumulation of radioactive species involved in the primary cooling water and irradiation-induced degradation of component materials cause major differences in the control of the two plant types.

In this article, major cooling systems of NPPs are compared with those of FPPs and then the latest experiences with water chemistry in NPPs, especially evaluation and control of radiolytic species for mitigating corrosion damage of structural materials in primary cooling water of boiling water reactors, are summarized. Procedures of radioactive corrosion product control for moderating shutdown radiation levels and radwaste source reduction are also introduced.

David J. Cahalane
Danial Quigley

PPChem 2006, 8(5), 293–297

A New Generation of Automated Water and Steam Sampling

Flow control of water and steam samples is important to help assure the quality of the samples and repeatability of the analytical results. Constant velocity in the sample line maintains the integrity of the sample even with the entrapment and/or release of both soluble and insoluble species deposited within the system piping.

Sample inlet temperature and flow are easily controlled under constant conditions. Since sample pressures typically fluctuate, specifically at the time of startup and shutdown or at peaking power plants, maintaining a representative sample can be difficult and labor intensive. The traditional manual sample conditioning system requires constant adjustment during startup or as plant conditions change. With plants continually operating with limited maintenance and operational resources, an automated sample conditioning system is essential. Previously available flow sensing and automated sample conditioning technologies required maintenance on sample lines with high levels of crud. A new automated sample conditioning system continually adjusts a pressure-reducing valve in order to maintain a constant sample flow rate. By automatically maintaining the sample flow rate, unattended representative sampling is achieved. Automatic startup including a controlled blowdown sequence can be initiated from sample conditions or remote commands. Additional features and benefits of an automated sample conditioning system are discussed. System operation, instrument diagrams and results from field trials are presented.

Des McInnes

PPChem 2006, 8(5), 298–302

Stator Cooling Water Deoxygenation Control at Tarong Power Station

Large electrical generators are normally cooled by circulating deionised water through hollow strands in the stator bars. Corrosion of the copper strands can lead to restriction of the cooling water flow through the strands, resulting in reduced cooling and consequently reduced output, or in the worst case catastrophic failure due to local overheating. Two key chemical parameters which can be managed to minimise the risk of flow restriction due to deposition of corrosion products are the dissolved oxygen concentration and the pH of the cooling water.

Tarong Power Station has four 350 MW Hitachi generators and is currently completing generator stator rewinds on all units. In conjunction with the rewind, Tarong has installed a deoxygenation system to provide low oxygen make-up water to the stator cooling systems. The stator cooling water systems have operated for twenty years under low oxygen neutral pH conditions, however the make-up water has always had up to 8 $mg \cdot kg^{-1}$ of dissolved oxygen.

This paper briefly discusses the corrosion issues and provides an overview of the modified make-up system at Tarong.

Massalha Loay
Aharon Grabli

PPChem 2006, 8(5), 303–305

Experience with Organic Treatment at American Israeli Paper Mills (AIPM)

The nature of a paper mill, generally, creates a challenge for the water cycle treatment, which must be based on different considerations. An illustration of these considerations is provided and discussed briefly throughout the presentation of American Israeli Paper Mills' experience with amine treatment. Encouraging as well discouraging results of such a treatment are described. Moreover, it is shown that the VGB range values for the water cycle parameters are achievable even in a paper mill.

Eric V. Maughan
David Dalgetty

PPChem 2006, 8(5), 306–310

The On-Line Measurement of Silica in the Power Plant (Part One)

The measurement of silica has always been a core measurement in the plant cycle. However, owing to the perceived complexity of the measurement and the maintenance requirements, many of these on-line analysers have fallen into disuse. The purpose of this paper (in two parts) is an attempt to dispell these notions. A review of the principles of measurement, calibration and troubleshooting is presented in this two-part paper.

David Addison

PPChem 2006, 8(6), 332–343

Improving Chemical Planning Aspects of New Generation Plant – Huntly e3p Project Experience

Modern Engineer, Procure and Construct (EPC) contracts can, at times, lack suitable thermal power station chemistry expertise, resulting in less than best practice design choices being made. It is the responsibility of thermal power station chemists within organisations that are the clients of EPC contracts to ensure that thermal power station chemistry knowledge and good practice is utilised for new projects. This approach has been followed with Genesis Energy's new "Energy, Efficiency, Enhancement" 385 MW combined cycle gas turbine (CCGT) plant (e3p), located at its Huntly Power Station site in New Zealand. This project has also shown that the inclusion of condensate polishing for CCGT units is economically viable with significant long term benefits in terms of lower plant operating costs and improved plant reliability.

Wolfgang Leye
Eric Maughan

PPChem 2006, 8(6), 349–352

The Removal of Magnetite to Protect On-Line Analysis Equipment

The transport of corrosion products through the steam-water circuit is of major importance to the power plant chemist. Several devices are commercially available to perform on-line sampling of corrosion products with subsequent analysis in the laboratory. However, the bulk of the corrosion product (mainly iron oxides) found in the sampling lines for on-line analysis is transported to the chemical analysers, resulting in deposition and blinding of the sensors. This results in additional maintenance.

This paper describes a device for the removal of iron oxide (magnetite) in the sample lines prior to on-line analysis.

David J. Knights

PPChem 2006, 8(6), 353–360

Water for Power Generation in Australia – Now & into the Future

Australia is the driest inhabited continent on earth. This paper summarises the current water usage for electricity generation in Australia and explores the future alternatives for water resources. Many power stations use large volumes of good quality water for cooling, most of which is simply evaporated into the atmosphere. The author examines the community's awareness of the volume of water used for electricity generation and attempts to determine the value of this lost water.

As water resources in Australia are stretched to their limit and the urban and rural users compete for the resource, power generators will need to look for water savings, alternative water supplies, improvements in generating efficiency and other forms of cooling in an attempt to save water. Whilst generators have made water savings, many of the alternative cooling processes and water saving alternatives result in a net increase in carbon emissions, or have other environmental impacts.

The author highlights the issues associated with making water savings, and discusses the water options available in the future for electricity generators.

Dumitra Lucan

PPChem 2006, 8(6), 361–369

Behaviour of Steam Generator Tubing in the Presence of Silicon Compounds

The chemical reactions that take place between the components of concentrated solutions generate an aggressive environment. The presence of this environment and of the tubesheet crevices lead to localized corrosion and the affected tubes cannot ensure effective heat transfer between the fluids of the primary and secondary circuits. Thus, it becomes necessary to understand the corrosion process that occurs on the CANDU steam generator secondary side. The purpose of this paper is the assessment of the corrosion behaviour of the tube material Incoloy 800 at the normal secondary circuit parameters (temperature = 260 °C, pressure = 5.1 MPa). The testing environment was demineralized water containing silicon compounds, at a pH = 9.5 regulated with morpholine and cyclohexylamine. The paper presents the results of metallographic, electronic microscopy and X-ray diffraction examinations, as well as the results of electrochemical measurements.

Eric V. Maughan
David Dalgetty

PPChem 2006, 8(6), 370–373

The On-Line Measurement of Silica in the Power Plant (Part Two)

In Part 1 of this paper, the rationale for the measurement of silica, on-line methods and troubleshooting were presented. In this second part more detail is given on the theory of measurement, the chemistry of the reaction and the calibration of on-line analysers.

Carolina Acuña-Caro
Harald Thorwarth
Günter Scheffknecht

PPChem 2006, 8(6), 374–381

A Thermodynamic Study on the Effects of Individual Flue Gas Components on Mercury Speciation

Thermodynamic equilibrium calculations have been carried out to investigate the effect of common flue gas components on mercury behaviour under oxidising conditions in coal-fired power plants. The calculations were implemented based on the free Gibbs energy minimisation method. Considering homogeneous and heterogeneous reactions the shares of the different elements/compounds were varied over a wide range. The coal mercury content does not show any impact on its own speciation along the temperatures under study. The weak influence of O_2 (g) on the oxidation of elemental mercury, the importance of the coal chlorine content as well as the inhibiting effect of H_2O (g) in the conversion of Hg^0 (g) to $HgCl_2$ (g) have been found to be the major flue gas influencing factors.

Josef Denk
Robert Svoboda

PPChem 2006, 8(7), 401–408

Stress Corrosion Cracking due to Carbon Dioxide and Organic Impurities in the Steam/Water Cycle

Carbon dioxide and organic species such as formates or acetates are present in many steam cycles of power plants. However, there is only limited knowledge available concerning their effect on stress corrosion cracking of turbine steels. In the case of CO_2 these data are often controversially discussed. Based on the known mechanisms of stress corrosion cracking of low pressure rotor steels, literature results, company-imternal investigations and service experience, the effects of carbon dioxide and organics are discussed.

It is known that both types of impurities can reduce the pH of the condensed steam if this is not compensated by a proper water treatment and may enhance most types of aqueous corrosion of steels, including stress corrosion cracking. The scope of the present investigation was the identification of specific corrosion effects, other than the pH effect. There are some indications of such ion-specific effects, especially for acetate, under very specific test conditions. However, the relevance for real service conditions seems to be limited.

Plant experience feedback indicates that the pH effect of organics has caused some failures in steam turbines, but specific corrosion effects could not be identified unambiguously. It is therefore concluded that specific corrosion effects of these substances are not of prime importance. The priority for protecting the steam turbine against corrosion by carbon dioxide and organics is therefore maintaining a sufficient local pH value.

Amaladoss A. M. Prince
Sankaralingam Velmurugan
Sevilimedu V. Narasimhan
Pandalgudi S. Raghavan
Raghavachary Gopalan

PPChem 2006, 8(7), 409–414

The Role of Metal Complexes in Nuclear Reactor Decontamination

Chemical decontamination is the process of removal of radioactivity from corrosion products formed on structural materials in the nuclear reactors. These corrosion products cause problems for the operation and maintenance of the plants. Removal of the radioactive contaminants can be achieved by dissolving the oxide from the system surface using organic complexing agents in low concentrations known as dilute chemical decontamination (DCD) formulations. These organic complexing agents attack the oxide surface and form metal complexes, which further accelerate the dissolution process. The stability of the complexes plays an important role in dissolving the radioactive contaminated oxides. In addition, the DCD process is operated through ion exchange resins for the removal of the dissolved metal ions and radioactive nuclides. In the present study, the kinetics of dissolution of various model corrosion products such as magnetite (Fe_3O_4), hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) have been studied in the presence of complexing agents such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), hydroxyethylethylenediaminepentaacetic acid (HEEDTA), and 2,6 pyridinedicarboxylic acid (PDCA). The reductive roles of metal complexes and organic reducing agents are discussed.

Troy Walker
Les Lloyd

PPChem 2006, 8(7), 415–420

Alternative Water Sources for Industry

Australia's record-breaking drought has placed increasing emphasis on the importance of the security of water supplies for both domestic use and industry.

The decrease in the availability of water that has traditionally been seen as easy to treat is driving some users to investigate alternative sources of water. Developments in water treatment technology have enabled the use of a range of processes to produce this water reliably at ever decreasing costs. This increasing acceptance of new technologies has seen recycling of plant waste streams, municipal wastewater re-use and seawater desalination, among others, become commonplace.

This paper surveys the trends in water treatment for industry both in Australia and internationally with a review of technologies and case studies of operating plants.

Tamara I. Petrova
Valery I. Kashinsky
Viktor A. Rogovoy
Aleksander E. Chub
Aleksander A. Kryuchkov

PPChem 2006, 8(7), 421–424

The Effect of Temperature on the Contamination of Condensate with Organic Impurities

The results of tests on the effect of condensate temperature on the washing out of organic and inorganic impurities from anion resins used in condensate polishing units at fossil power plants are presented. It is shown that elevated condensate temperature results in increased washing out of these impurities.

Boris Michailovich Larin
Anatoli Stepanovich Sedlov

PPChem 2006, 8(7), 425–429

An Investigation of the Sorption/Desorption of Organics from Natural Waters by Solid Adsorbents and Anion Exchangers

The results of laboratory and operational tests at thermal and nuclear power stations on anion exchangers and solid adsorbents of makeup water treatment plants with regard to the sorption/desorption of organic substances in natural water and condensate are presented. The resins Amberlite™[1] IRA-67, IRA-900, IRA-958Cl, Purolite®[2] A-500P, Dowex™[3] Marathon, and others were tested. Retention of up to 60–80 % of the "organic" material on the anion exchangers and organic absorbers installed at different places in the technological scheme of the water processing unit was attained. The possibility of a partial "poisoning" of the resins and the degradation of the working characteristics over the first year of operation are discussed.

[1] Amberlite is a trademark of the Rohm and Haas Company.
[2] Purolite is a registered mark of the Purolite International Ltd.
[3] Dowex is a trademark of the Dow Chemical Company.

Tomáš Blejchař
Rostislav Malý
Pavel Kolat
Martin Dluhoš

PPChem 2006, 8(7), 438–445

Plasma Systems in Power Engineering

Plasma technology is currently being investigated as an alternative to heavy fuel oil and gas in the process of ignition of pulverized-coal/air mixtures at the start-up of pulverized-coal boilers and in the stabilization of combustion. Low-temperature plasma generators have been successfully tested at a Czech power plant and have now been handed over to the operator for further application. The process of ignition with plasma technology is described, as well as the results of the on-site tests. The development and application of mathematical modelling of the flow in the design of the generators is discussed.

PPChem 2006, 8(8), 452–459

Eighth International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators

June 20–22, 2006, Calgary, Alberta, Canada

The EPRI International Conferences on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators are the most important conferences dealing exclusively with fossil plant cycle-related topics worldwide. This contribution is a compilation of the abstracts of all the papers presented at this year's conference in Calgary, Alberta, Canada.

Brian Hoffman
J. Denis Aspden

PPChem 2006, 8(8), 460–468

Critical Aspects of Ion Exchange Resin Performance in High Temperature Condensate Polishing Applications

As more fossil-fired power stations are constructed in hot and dry regions, there is an increasing desire to practice condensate polishing at temperatures which approach and exceed 60 °C. In some cases, the condensate temperatures are even reaching the limits which are set by allowable back pressure on the steam turbine. This paper discusses the fundamental behavior of ion exchange resins in condensate polishers at high temperatures. The critical degradation mechanisms for both anion and cation exchangers are examined in terms of both resin life and, more importantly, their effect on overall process performance. The critical issues of silica, sulfate, and resin kinetic performance are discussed. Although routine operation of ion exchange resins above 60 °C is very stressful, suggestions are made for optimizing polisher performance and minimizing risks. By selecting the correct resins and applying good process design and operating practices, deep bed condensate polishing has been successfully practiced for many years at elevated condensate temperatures in fossil-fired generating plants.

David M. Gray

PPChem 2006, 8(8), 470–478

A Multiparameter Instrumentation Approach to Makeup and Cycle Chemistry Measurements

With fewer personnel to operate today's generating stations, on-line chemistry instrumentation becomes more critical. A practical approach to improving installed reliability and accuracy is the use of a high-performance multiparameter instrument platform. Its commonality of installation, functions, calibration and maintenance plus the availability of on-line computed parameters can have far-reaching benefits. Parameters of specific, cation and degassed cation conductivity, pH, dissolved oxygen, oxidation reduction potential and total organic carbon as well as the benefits of having them available within a common instrument platform are discussed. Also addressed are good sampling practices and appropriate sensor design, installation and maintenance.

Michael Sheedy

PPChem 2006, 8(8), 482–488

Short Bed Ion Exchange Technology Produces Ultrapure Water without Using a Mixed Bed

Conventional practice when producing water with a conductivity of less than 0.1 $\mu S \cdot cm^{-1}$ is to use a mixed bed ion exchange unit. This paper describes a novel short bed ion exchange technology that produces water of this quality using separate columns of cation and anion resin. The principle features of this technology include the use of compressively packed beds only 7.6 cm to 15.2 cm (3 in to 6 in) in depth, fine mesh resins that improve exchange kinetics, countercurrent regeneration, and low exchanger loadings. This results in a system that is much smaller and less complex than an installation with a regenerated mixed bed unit. Case studies are presented that describe operation of this technology for the treatment of a surface water source, a municipally treated water source, and reverse osmosis permeate.

Stephen Kerr
Brett Connor

PPChem 2006, 8(8), 489–499

Life without Mud – The Installation of Clarification Pre-treatment for Fitzroy River Water Make-up to Stanwell Power Station Cooling Water Systems

The design and operation of a new clarified raw water plant at an Australian power station using a proprietary Actiflo clarification arrangement are discussed with respect to plant priorities of water conservation, cooling efficiency, microbiological control efficacy and operational costs. Plant experiences with achieving a low suspended solids regime and new challenges and opportunities for this plant are presented.

Robert Svoboda
Frank Gabrielli
Herbert Hehs
Hans-Günter Seipp
Frank-Udo Leidich
Bruce Roberts

PPChem 2006, 8(8), 502–509

Organic Impurities and Organic Conditioning Agents in the Steam/Water Cycle: A Power Plant Manufacturer's Point of View

Power plants are designed to run with pure water and steam. For simple cycles (no export steam) no other products should be necessary. If organic additives are used, the possible side effects have to be carefully addressed.

Possible side effects include corrosive degradation products, interference with monitoring cation conductivity, influence on boiling and on condensation, and fouling. Examples from boiler and turbine operation are given.

Organic amines produce volatile acidic degradation products, but the amine provides cations for pH counterbalance.

In contrast, organic oxygen scavengers, dispersants, chelants as well as organic impurities generally produce volatile acidic degradation products, but with no cation for counterbalance. For this reason, such products must be considered as potentially corrosive.

From a power plant manufacturer's point of view, any organic matter in the steam/water cycle brings the risk of detrimental side effects. The general use of organic additives should thus be avoided and restricted to specific needs and situations, as for example in certain process steam systems.

Andrew G. Howell
Robert Pritekel

PPChem 2006, 8(9), 516–525

Turbine Deposition: Two Cases

Two coal-fired drum boiler units of similar vintage experienced both similarities and differences in turbine deposition patterns. Deposits containing copper, sodium, phosphate, sulfate, iron, chloride and silica resulted in damage and performance problems of varying extent for the two units. Root-cause problem evaluation, actions taken, and recommendations for further actions to address causative issues are discussed.

Emory H. Hull
Robert D. Bartholomew

PPChem 2006, 8(9), 526–535

Rigorous Calculation of Sodium-to-Phosphate Mole Ratios for Phosphate Treatment Programs

The sodium-to-phosphate ($Na:PO_4$) mole ratio and/or free caustic concentration is the primary control parameter for most phosphate-based treatment programs. Traditionally, these have been determined by comparison with graphs of pH versus phosphate for various sodium phosphate solutions. Approximate methods of estimation have also been used. This paper presents a more rigorous calculation method of the $Na:PO_4$ mole ratio and free caustic concentration (which has been used for about a decade by Sheppard T. Powell Associates LLC and some of our clients). Calculated $Na:PO_4$ mole ratios and free caustic concentrations based on the method presented in this paper are then compared to those calculated using the approximate method published by Verib.

Volker Ender
Thomas Schumann
Susanne Sachs
Gert Bernhard

PPChem 2006, 8(9), 541–549

On the Uptake Mechanisms of Organics from Natural Water – Investigations with Strong and Weak Base Ion Exchangers and Their Corresponding Copolymers

In laboratory column experiments, ion exchange resins and the corresponding non-functionalized copolymers were compared in order to investigate the uptake mechanisms of organics during the water demineralization process. To improve the detection limit, ^{14}C-labeled model substances (β-alanine, starch, synthetic humic acid type M42) were used. These compounds are supposed to represent the TOC fractions of neutrals/amphiphilics, polysaccharides and humics following the LC-OCD method. The uptake was investigated depending on the salinity and pH, the concentration of the organics, and the loading temperature. The main results are:

- At neutral pH, a near 100 % removal of β-alanine and starch by ion exchange and/or adsorption was observed, whereas humic acid was taken up by ion exchange to an extent of about 10 %.
- In acidic conditions, β-alanine and starch were completely removed up to the breakthrough point of the sulfate ions. These elute the organics. Humic acid will be removed owing to precipitation.
- The last mechanism allows the removal of humic acid by the copolymers too. These are inefficient in regard to the uptake of β-alanine and starch.
- The variation in the concentration of the organics as well as that in the loading temperature have only a subordinate influence on the uptake.

Pavel Hübner

PPChem 2006, 8(9), 551–557

The Fate of Organics in the Water-Steam Cycle

The behaviour of organic matter in power plants has been examined. The samples were taken from water treatment plants producing make-up water for boilers as well as from water-steam cycles and cooling cycles. The power plants examined were Czech power plants, both fossil and nuclear, and one Slovakian nuclear plant.

The tests were performed by the liquid chromatography – organic carbon detection (LC-OCD) method at a subcontractor lab. This method enables distinguishing between different groups of organic matter and from experience the effectiveness of water treatment technologies and the possible influence on the water-steam cycle of the power plant can be estimated.

It has been confirmed that by using appropriate flocculation the problems in water treatment plants diminish and the VGB limit for total organic carbon (TOC) concentration of 200 $\mu g \cdot L^{-1}$ in boiler feedwater may be reached. The lower limit following EPRI recommendations of 100 $\mu g \cdot L^{-1}$ is hardly achievable using existing water treatment technology. This provides an open field for reverse osmosis technology that is able to remove organics completely.

Hao-Feng Zhang
Li-Bin Niu
Shuji Oishi
Hiroshi Takaku
Kunio Shiokawa
Mitsuo Yamashita
Yoshihiro Sakai

PPChem 2006, 8(9), 558–564

Influence of Chloride and Carbon Dioxide on General and Crevice Corrosion of Steam Turbine Materials for Geothermal Power Plants

The influence of chloride and CO_2 on general and crevice corrosion of steam turbine materials for geothermal power plants was investigated in two simulated geothermal waters. The general corrosion rates of the rotor steels with a lower Cr content were accelerated due to the CO_2 in the water, while the corrosion rates of the blade steels with a higher Cr content were controlled mainly by the chloride concentration in the waters. Concerning the crevice corrosion behavior, the galvanic corrosion effects in each of the waters were confirmed for the rotor steels with lower corrosion potentials than those of the blade materials, and almost no difference in corrosion behavior was observed between the two waters tested. Regarding general and crevice corrosion in the two simulated geothermal waters, it was determined that a newly developed rotor material and also an improved heat-treated blade material are promising for actual usage in geothermal power plants.

Bradley Buecker

PPChem 2006, 8(9), 570–573

Water Pre-Treatment with Membranes: A Developing Technique for the Power Industry

The paper describes the successful application of new microfiltration technology for suspended solids removal in a U.S. power plant in lieu of clarification/sand filtration. The process, results and problems encountered are discussed.

PPChem 2006, 8(10), 580–587

A Look Back at the International Conference "Instrumentation for Power Plant Chemistry"

On September 19–21, 2006 the PowerPlant Chemistry International Conference "Instrumentation for Power Plant Chemistry" was held in Zurich, Switzerland. This paper gives an overview of the conference, with abstracts of the 27 technical presentations, brief reports on the panel and breakout sessions, and a review of the conference exhibition of manufacturers of power plant chemistry-related instrumentation.

Daniel E. Meils
Joseph A. Mastroianni

PPChem 2006, 8(10), 596–602

On-Line Instrument QA/QC Standard Practices

This paper has been written to assist nuclear power plant laboratories in establishing a laboratory quality management system (QMS) to assure that the accuracy and precision of analytical data produced meets operational needs. Without such a QMS, data produced in a laboratory may not have the sufficient accuracy and precision, leading to inappropriate operational decisions being made. The paper addresses all the necessary requirements a nuclear power plant laboratory needs to fulfill to be able to establish a successful QMS, provide adequate analytical procedures, demonstrate adequate instrument capability, demonstrate laboratory capabilities, and demonstrate individual analyst capabilities.

Frank A. Dunand
Nicolas Ledermann
Serge Hediger

PPChem 2006, 8(10), 603–608

Luminescent Oxygen Sensor to Monitor Power Plant Water and Steam Cycles

The majority of existing dissolved oxygen analyzers use polarographic sensors. These are well recognized for their accuracy and reliability, but maintenance complexity and frequency, as well as flow dependence and calibration needs are among the issues encountered by users. A new oxygen sensor has been developed based on luminescent technology. The main advantages of luminescent technology over electro-chemical cells are the operator independence of the calibration, the low flow requirement, the absence of flow dependence, and of course the drastic reduction of the maintenance activities. The application of luminescent technology to accurately measure low ppb oxygen concentrations is demonstrated based on laboratory and field experience in both all-volatile treatment (AVT) and oxygenated treatment (OT) environments.

Richard A. Breckenridge
L. Joseph Hancock
Robert L. Bryant
John W. Clark

PPChem 2006, 8(10), 609–615

A Method for Continuously Monitoring and Selectively Sampling Plant Cycle Water for Metal Oxide Transport Analyses

Results from analytical methods for monitoring iron and copper transport through the plant cycle water may include dissolved species, but more typically detect insoluble compounds of metal oxides [1]. Since the presence of these insoluble particulates can be indicative of serious system problems, the methods provide useful quality control and troubleshooting information. However, the data is "averaged" over some time period, e.g., one day or one week. This is better than a single "grab sample," but these methods do not necessarily enable plant operators to identify when large "spikes" occur or what causes them. If information could be available, corrective or preventive actions could possibly be taken at the time of the incident.

An instrument that continuously samples plant cycle waters, detects very low levels ($< 2\ \mu g \cdot kg^{-1}$) of particulate metal oxides and automatically obtains a sample for laboratory analysis when the reading exceeds a preset threshold has proven to be very helpful in operating and maintaining reliability of steam generation systems.

Robert Svoboda
Geoff Bignold

PPChem 2006, 8(10), 624–627

Meetings of the IAPWS Working Group 'Power Cycle Chemistry' in Witney, UK, September 3–8, 2006

This paper reports on the sessions of the IAPWS working group "Power Cycle Chemistry" at the 2006 Annual Meeting of the International Association for the Properties of Water and Steam (IAPWS) in Witney, United Kingdom, September 3–8, 2006. It discusses, among other things, the 2006 working group Priority List of areas in need of basic research, the proposals for IAPWS Certified Research Needs developed from the priority list, a proposal for international collaboration, and presentations made at the meeting.

Miroslav Šťastný
Olga Bláhová
Ivo Jiříček
Bohumil Lorenc

PPChem 2006, 8(10), 629–634

Effects of Steam Chemistry on the Turbine Blades in the Phase Transition Zone

This paper discusses the relationship between the concentration of corrosive anions in the steam and the occurrence of stress corrosion cracking of LP turbine moving blades. Although the titanium alloy (Ti6Al4V) proved stress corrosion resistant in the phase transition zone even with non-optimum chemistry, optimization of cycle chemistry and improvement in the quality of steam create conditions under which steel moving blades may also be applied in the phase transition zone without risk of stress corrosion cracking.

The deposits on the LP turbine blades in the phase transition zone significantly increase the surface roughness and lead to energy losses.

Philippe Dudouit
Pierre Guillou
Eva L'Hostis

PPChem 2006, 8(11), 645–650

Sodium Monitoring in the Water and Steam Cycle of Power Plants

Today sodium concentration has become one of the most important indexes for quality control of water and steam at power plants; however, measurement of this parameter can be difficult in practice. The use of ion selective electrodes means that analyzers are sensitive to pH shifts, and constant exposure to very low concentrations of sodium ions in ultrapure water conditions can lead to electrode desensitization. In addition, there is

a need to address drift through regular calibration. This paper discusses the technical challenges in low level sodium analysis and the required features for a practical and accurate analyzer to provide trouble free, sub $\mu g \cdot kg^{-1}$ (sub ppb) measurement.

Beverly J. Newton
Detlef Jensen

PPChem 2006, 8(11), 652–657

Advances in Ion Chromatography for Power Plant Operations

Ion chromatography is used in the power industry to monitor and minimize corrosive ions in the steam generator, turbines, steam and feedwater piping, and protect against cooling water impurity ingress. This paper includes a review of the recent advances in the science of ion chromatography which are aimed at improving trace analysis of corrosive ions in power plant waters and chemicals. An overview of hardware and column advances for these applications is presented. Included are details on lowering detection limits through the use of automated eluent generation and specialty columns. The emphasis is on advances in the science which will help extend the operating life of steam generators, secondary systems and turbines. Examples of the use of ion chromatography for troubleshooting corrosion problems in power plants are given.

Heini Maurer

PPChem 2006, 8(11), 658–664

Cation Conductivity: Facts and Fiction

Cation exchangers are of paramount importance to reliable conductivity readings. They come in all shapes and sizes and each and every type has its advocates. The purpose of the paper is to separate facts from fiction and shed light on such issues as rinse down, temperature effects and response time.

Frank I. H. M. Oesterholt
Jo Savelkoul
Antoine I. van Hoorn
Lambèr L. M. J. Paping
Johan W. G. van Mourik

PPChem 2006, 8(11), 666–673

Dutch Approach to *Legionella* Control in Cooling Water Systems: History and Perspectives

Cooling systems with recirculating open cooling towers represent a considerable *Legionella* risk. The Dutch Policy Rule 4.87 forces employers to carry out a risk assessment and establish a control plan for their cooling towers. This legislation only gives general descriptions and no standards. However, to provide employers with more detailed information on how to control and maintain their system, the Information Report AI-32 was written as a Dutch Code of Practice. The biggest problem for cooling tower owners is obtaining accurate data on *Legionella* concentrations in their cooling systems. The results of different methods in use to quantify *Legionella* differ to such an extent that it is very difficult to make a realistic estimate of the risk of *Legionella* infection to employees and the environment, and to adequately decide on corrective actions to be taken. More and more industries and laboratories are affected by the same lack of a reproducible analytical technique. It has become clear that the existing methods were developed primarily for relatively clean water systems with a limited lifetime, like potable waters, and not for industrial cooling systems. Especially for these industrial waters, which are re-used many times, the same analytical method cannot consistently deliver the necessary degree of reproducibility. Two cases at Corus and Dow in their industrial water systems demonstrate that there are differences in accuracy between laboratories using the same analytical method as well as between analytical methods themselves. Future work should result primarily in a new analytical method which is faster, more reliable and better reproducible compared to the current methods. Secondly there is a need for a protocol on the method for obtaining a representative sample from a complex cooling system.

Albert Bursik

PPChem 2006, 8(11), 679–690

Some Questions and Answers on All-Volatile Treatment

PowerPlant Chemistry has received a multitude of questions regarding currently used feedwater and boiler water treatments. This contribution addresses many of the inquiries about all-volatile treatment, giving general information on the subject and providing references where the questioners and readers of this paper can find more detailed information on the topics discussed.

Richard Woodward

PPChem 2006, 8(11), 694–698

Online Coal Analyzers Bring Benefits to the Utility Industry

Online coal analyzers have been in commercial use for more than two decades now, with coal producers accounting for most of the units purchased. In the past three years or so, coal-fired power plants have shown an increasing share of the analyzers bought. This article explains the most common applications of analyzers at power plants, ranging from boiler optimization to compliance with emission regulations. The article also provides a brief overview of different analyzer types, their principles of operation, and typical performance achieved.

Steven West
Xiaowen Wen
Charles Baer

PPChem 2006, 8(12), 709–712

Methods for Verification of Low Parts-per-Trillion Sodium Determination by On-Line ISE-Based Sodium Monitors

As needs and capabilities for the production of ultrapure water advance, the analysis technology for determining contaminant levels is continuously challenged to keep pace. In water used for steam generation, maintaining the lowest possible levels of sodium ion is of great importance for the prevention of damage to turbine blades. Today, sodium levels in water and steam are being pushed lower and lower, making validation of readings from on-line analyzers increasingly difficult. In this paper, we compare two methods of validating on-line, ion-selective electrode-based analyzer performance at low $ng \cdot kg^{-1}$ (low parts-per-trillion, ppt) sodium concentrations. Dynamic dilution and recovery and grab sample analysis by inductively coupled plasma mass spectrometry are applied to analyses by a recently introduced sodium monitor and to an existing monitor provided by another manufacturer. Verification studies in the range of 1 000 $ng \cdot kg^{-1}$ down to less than 10 $ng \cdot kg^{-1}$ are described. Results of this study and discussion of analyzer design features that enable such low-level analysis are presented, and techniques available to plant operators for on-site verification of low-level chemical analyzers are discussed.

George J. Licina

PPChem 2006, 8(12), 718–726

Monitoring Biofilms in Real Time for Control of MIC and Heat Exchanger Fouling

Microbiologically influenced corrosion (MIC) of piping and heat exchanger materials in power plant cooling waters can cause expensive unplanned outages, the need for local repairs, and, in some cases, the need for complete system replacement. Biofouling of heat exchanger tubes also decreases overall plant efficiency and power output. The biocide additions necessary to mitigate biofouling and MIC increase costs, raise concerns over effluents, and can even increase corrosion.

In this paper, an electrochemical biofilm sensor with integrated data acquisition and data analysis capabilities for monitoring biofilm activity on metallic surfaces is presented. Power plant and other industrial experience with this tool, including biocide optimization projects in plants, is described.

Thomas Kappes

PPChem 2006, 8(12), 727–731

State of the Art in Flue Gas Analysis Technology for Emission Monitoring and Combustion Control

The continuous monitoring of gaseous emissions of power plants is gaining more and more importance worldwide, not only in industrialized countries, due to stringent environmental legislation and the need for efficient use of resources. An outline of modern exhaust gas analysis instrumentation is given together with applications for emission monitoring as well as for the optimization of combustion and exhaust gas treatment processes in fossil- and biomass-fueled power plants. Further, an overview of the amendment to the German federal immission control regulations for large combustion plants and gas turbines is presented.

Xueyong Guan
Ting Zhu
Digby D. Macdonald

PPChem 2006, 8(12), 732–741

Application of Electrochemical Noise Analysis in High Subcritical and Supercritical Aqueous Systems

In this study, electrochemical noise analysis (ENA) is used to identify corrosion mechanisms and to analyze the effect of pressure on corrosion reactions in high subcritical and supercritical aqueous systems. Two corrosion mechanisms, "chemical oxidation"

(CO) and "electrochemical oxidation" (EO), are used to describe the corrosion reactions in supercritical aqueous systems, depending upon the density and dielectric constant of the fluid. ENA is used to differentiate the two corrosion mechanisms by postulating that only the electrochemical mechanism gives rise to spontaneous fluctuations in current and potential. A rugged electrochemical noise sensor has been developed to monitor the fluctuations in the coupling current between two identical specimens. Experiments show that the electrochemical mechanism is the dominant corrosion process when the temperature is less than 350 °C and that it becomes of progressively lower importance as the temperature increases above the critical temperature (T_c = 374.15 °C). ENA is also used to explore the effect of pressure on the rate of corrosion of metals at supercritical temperatures. As predicted by the pressure-effect model, the experimental data demonstrate that the electrochemical corrosion rate increases with increasing pressure in low-density supercritical systems, corresponding to an increase in the density and the dielectric constant.

Troels Mathiesen
Torben S. Nielsen
Jan Elkjær Frantsen
John Kold
Anne R. Boye-Moeller

PPChem 2006, 8(12), 742–750

Influence of Various Surface Conditions on Pitting Corrosion Resistance of Stainless Steel Tubes of Type EN 1.4404

The pitting resistance of pickled, ground and electropolished surfaces of EN 1.4404 (AISI 316L) tubes was tested using cyclic polarization and ASTM G150 for determination of the pitting potential and critical pitting temperature, respectively. The materials were tested in chloride-containing solutions with 0.05 to 5.0 % chloride. Crevice corrosion was avoided using a flushed port cell with a specially cast gasket. A ground finish with low surface roughness shows no improvement over the coarse pickled finish, while an electropolished finish provides considerably higher resistance but at the same time scattered results. The two testing techniques give almost identical critical pitting temperatures that show only little dependence on chloride concentration. The variation in pitting resistance has been correlated to the surface morphology of the different surface conditions.

Charles Laire
Raymond De Graeve
Yves Comptdaer
Philippe Gilbert

PPChem 2006, 8(12), 756–762

Experience with Titanium Condensers in Belgian Nuclear Power Plants

In Belgium, five nuclear power plants are equipped with titanium condensers of different designs. At the Doel sites, where the cooling water is very corrosive, full titanium condensers have replaced the original condensers. The cooling water is brackish water; a cooling tower is installed for two units.

At Tihange, one unit is equipped with a replaced condenser in titanium, although the cooling water is less aggressive compared to Doel.

At some units, small leaks have occurred during service and the causes of these leaks could be related to the following mechanisms:

- Steam droplet erosion at the tube outer surface; inspections with eddy current and a visual inspection have drastically reduced the occurrence of small leaks at the Tihange 1 unit.
- Mechanical wear due to foreign objects blocking the tube entrance on the raw water side. Small debris coming from the cooling tower has generated wear and this type of degradation has resulted in the installation of protective short sleeves at one unit (Doel 4). After 8 years of operation with these sleeves, the absence of degradation was verified on pulled tubes. Despite the aggressive water, no corrosion under the sleeves has occurred, and erosion behind the sleeves – possibly due to local turbulence – has not been observed. This experience confirms the excellent corrosion resistance of titanium.

The paper summarizes the results of the different inspections and investigations on pulled tubes.

2007's Scientific and Technical Contributions

Francis Nordmann

PPChem 2007, 9(1), 4–10

Efficient, Sustainable, and Economical Plant Operation

Nuclear power plant operation has to be improved in regard to its environmental impact and economical performances.

Chemistry may bring its own contribution to such improvements through several approaches:

- corrosion minimization, which always brings improved safety and availability of the nuclear power plant (NPP),
- a chemistry specifications update which takes into account the development of new designs and materials,
- shorter shutdown duration thanks to optimized processes,
- costs and maintenance reduction through better operating modes.

This paper describes the most important approaches to achieve the above objectives. The first one deals with the integrity of the fuel and the mitigation of crud-induced power shifts (CIPSs). Primary water chemistry purification and shutdown process improvement, particularly hydrogen elimination, is a way of decreasing dose rates and increasing availability.

The secondary water chemistry specifications should be modified to achieve the progressive elimination of sensitive materials, particularly Alloy 600 MA, from steam generators in order to increase flexibility in operation and particularly to decrease costs and environmental impact.

Condensate polishers should be used only when this appears necessary, thus decreasing pollution risks by regeneration reagents and resin fines, operating costs and wastes, and consequently environmental impact.

The secondary water chemistry may, under certain circumstances, allow a better recycling and a longer ion exchange resin duration. The best all-volatile treatment (AVT) selection is beneficial for reducing the maintenance costs of sludge lancing and of chemical cleaning and for maintaining a sufficient thermal heat transfer, which is the main issue with resistant materials and proper chemistry.

Finally, material and design development also allows a reduction in the monitoring analyses program, and thus costs reduction.

The paper reviews the main useful trends observed from a 58 unit French fleet and worldwide experience.

Terry M. Williams

PPChem 2007, 9(1), 14–22

The Mechanism of Action of Isothiazolone Biocides

Isothiazolone biocides have proven efficacy and performance for microbial control in a variety of industrial water treatment applications. Understanding the mechanism of action of industrial biocides is important in optimizing their use and combating resistance if encountered. Isothiazolones utilize a two-step mechanism involving rapid inhibition (minutes) of growth and metabolism, followed by irreversible cell damage resulting in loss of viability (hours). Cells are inhibited by disruption of the metabolic pathways involving dehydrogenase enzymes. Critical physiological functions are rapidly inhibited in microbes, including growth, respiration (oxygen consumption), and energy generation (adenosine triphosphate synthesis). Cell death results from the destruction of protein thiols and production of free radicals. The rate and extent of killing may be enhanced by various adjuvants including surfactants. This unique mechanism results in a broad spectrum of activity, low use levels, and difficulty in attaining resistance.

Fred Böttcher
Wilfried Rühle

PPChem 2007, 9(1), 23–27

Mandatory and Desirable Instrumentation in PWR and BWR Units

In national and international guidelines, chemical parameters are described that are important for safe and reliable plant operation. Modern light water reactors are equipped with online analysers for those chemical parameters which directly indicate operational or technical incidents. Chemical parameters that represent technical specifications should also be monitored by online analysers. More chemical parameters exceeding the routine surveillance programme are important for long-time integrity of the systems and components or are necessary for design-based peculiarities.

Sheikh Akbar
Prabir Dutta

PPChem 2007, 9(1), 28–33

Development and Application of Gas Sensing Technologies for Combustion Processes

Identifying gas species and their quantification is important for optimization of many industrial applications involving high temperatures, including combustion processes. CISM (Center for Industrial Sensors and Measurements) at the Ohio State University has developed CO, O_2, NO_x, and CO_2 sensors based on TiO2 semiconducting oxides, zirconia and lithium phosphate based electrochemical sensors and sensor arrays for high-temperature emission control. The underlying theme in our sensor development has been the use of materials science and chemistry to promote high-temperature performance with selectivity. This article presents key results of our studies on CO, NO_x, CO_2 and O_2 sensors.

Padma Sasikumar
K. Shivakamy
Appadurai L. Rufus
Vinit K. Mittal
Santanu Bera
Sankaralingam Velmurugan
Sevilimedu V. Narasimhan

PPChem 2007, 9(1), 34–40

Stability of Gadolinium in Aqueous Solutions in the Presence of Impurities

Gadolinium (Gd^{3+}) in the concentration range of 0.05–20 $mg \cdot kg^{-1}$ is used as a soluble neutron absorber in the moderator systems of many pressurized heavy water reactors. A pH_{ap} range of 5–5.5 is specified for the moderator heavy water as Gd^{3+} is in solution only in acidic pH conditions. This paper presents studies on the removal of gadolinium from solution at pH values less than 5.5 by the trace level impurities in the water. Studies carried out in normal water (H_2O) and heavy water (D_2O) indicated that gadolinium can be removed from solution by colloidal non-reactive silica. The colloidal non-reactive silica, which consists of aluminosilicates, picks up the gadolinium even at pH 4.5. The results of the absorption experiments and X-ray photoelectron spectroscopic analysis of the residue collected after adsorption are presented in this paper.

PPChem 2007, 9(1), 41–58

2006's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Stephen Lower

PPChem 2007, 9(2), 68–76

A Gentle Introduction to the Structure of Water

Basic chemical theory predicts that a substance whose molecules are made up of just three lightweight atoms could not possibly exist as a liquid under ordinary conditions. This is just one of the "anomalous" properties that the structural unit H_2O confers on the liquid we know as water, and which enable this remarkable substance to play a central role in shaping both our planet and the living organisms on it.

This article attempts to show how the nature of water-the-molecule leads to higher-level structural elements that give water-the-substance its unique properties. The essential role of water in the human body has caused some science-naive seekers-of-health to stray into the realm of pseudoscience; sales of miracle water-treatment devices, homeopathic remedies and various fictional "structured" waters are now a thriving industry.

Larry Paul
Gregg Clark
Michael Eckhardt

PPChem 2007, 9(2), 81–88

Laboratory and Field Corrosion Performance of a High Chromium Alloy for Protection of Waterwall Tubes from Corrosion in Low NOx Coal-Fired Boilers

Corrosion-resistant weld overlays are now commonly used to reduce corrosion of boiler tubes in low NOx coal-fired boilers. Alloys with higher chromium contents are the most resistant to corrosion in this type of service. A new alloy with high chromium has recently been introduced and has shown excellent resistance to corrosion in low NOx coal-fired environments. The new material is Alloy 33 (UNS R20033) and contains approximately 33 % chromium, 32 % iron and 31 % nickel. The improved corrosion resistance of Alloy 33 should result in longer life of the weld overlay used to protect boiler tubes. Alloy 33 should also better resist circumferential cracking than the Mo-containing alloys now being used (such as Alloys 622 and 625); recent studies show that Mo segregation in weld overlays may be part of the circumferential cracking mechanism. After an 18-month field test in a low NOx coal-fired boiler, an Alloy 33 weld overlay has demonstrated that it resists both corrosion and cracking.

Guenter Schmitt
Mirdash Bakalli

PPChem 2007, 9(2), 89–106

A Critical Review of Measuring Techniques for Corrosion Rates under Flow Conditions

The rotated disc, rotated cylinder, rotated cage, jet impingement, pipes and channels are frequently used to study the corrosion performance of materials in flowing media. All these corrosion investigation and test tools are discussed critically with respect to beneficial aspects and inherent shortcomings. A clear distinction is made between corrosion experiments and electrochemical measurements in order to clarify the depth of information and the limits of application of both approaches. This is important especially for reliable estimation of threshold conditions for the initiation of flow-induced localized corrosion (FILC). For all experimental tools the preferential range of flow regime, the known power laws for mass transport relationships with their range of validity, the equations to quantify wall shear stresses and the equations relating diffusion limited current densities (specifically from microelectrodes) to specific data of the flow system are given. The paper aims to help in extracting as much information from flow experiments as possible.

Eric Maughan

PPChem 2007, 9(2), 107–123

Calibration of On-Line Analysers in the Steam–Water Circuit of Power Plant

Analysers used for continuous surveillance of chemical variables in the plant cycle are often neglected with respect to calibration and basic maintenance. This presentation discusses the basics of calibration, validation and verification of on-line analysers. Techniques are presented to simplify the task of calibration with the objective of improving the quality of the measured results with minimum effort.

Jane Kucera

PPChem 2007, 9(3), 132–137

Troubleshooting Reverse Osmosis

The use of reverse osmosis (RO) has grown tremendously over the last 10 years, as advancements in technology continue to lead to economic justification of RO, and as more operators and plant managers gain familiarity with RO. To keep RO systems operating optimally, operators need to understand how an RO system works, including how to inspect or "troubleshoot" a system. The ability to troubleshoot and correctly diagnose a problem with an RO system is critical to keeping the system on line. This paper describes RO troubleshooting techniques to prevent system problems and to identify mechanisms of system failures that, when managed, ultimately lead to improved RO performance.

Shunsuke Uchida
Masanori Naitoh
Yasushi Uehara
Hidetoshi Okada
Koji Hotta
Ryoko Ichikawa
Seiichi Koshizuka

PPChem 2007, 9(3), 143–156

Evaluation Method of Corrosive Conditions in Cooling Systems of Nuclear Power Plants by Combined Analyses of Flow Dynamics and Corrosion

Problems in major components and structural materials in nuclear power plants have often been caused by flow induced vibration, corrosion and their overlapping effects. In order to establish safe and reliable plant operation, it is necessary to predict future problems for structural materials based on combined analyses of flow dynamics and corrosion and to mitigate them before they become serious issues for plant operation.

The analysis models are divided into two types.

1. Prediction models for future problems with structural materials
   Distributions of oxidant concentrations along flow paths are obtained by solving water radiolysis reactions in the boiling water reactor (BWR) primary cooling water and hydrazine–oxygen reactions in the pressurized water reactor (PWR) secondary cooling water. Then, the electrochemical corrosion potential (ECP) at the point of interest is also obtained by the mixed potential model using oxidant concentration. Higher ECP enhances the possibility of intergranular stress corrosion cracking (IGSCC) in the BWR primary system, while lower ECP enhances flow accelerated corrosion (FAC) in the PWR secondary system.

2. Evaluation models of wall thinning caused by flow accelerated corrosion
   The degree of wall thinning is evaluated at a location with a higher possibility of FAC occurrence, and lifetime is estimated for preventive maintenance.

General features of models are reviewed in this paper and the prediction models for oxidant concentrations are briefly introduced.

Shun'an Cao
Jing Hu
Qing Zhu

PPChem 2007, 9(3), 157–160

Determination of Low-Molecular-Weight Organic Acids and Inorganic Anions by Gradient Elution Chromatography

Conditions of the separation and detection of organic and inorganic anions by gradient ion chromatography and suppressed conductivity detection were studied, and the procedure of gradient elution was optimized. A detection limit of $1 \cdot 10^{-3}$ $\mu g \cdot L^{-1}$ was obtained using the pre-concentrated column and most relative standard deviations obtained in the determination of seven organic and inorganic anions were below 5 %. This method was proved to be simple, rapid and accurate for the separation and determination of low-molecular-weight organic acids and inorganic anions and could be applied in the analysis of the samples from water and steam systems of thermal power plants with satisfactory results.

Martin Herberg
Heinz-Peter Borchardt

PPChem 2007, 9(3), 162–167

Oil Removal from a Closed Secondary Cooling System during Operation

This paper describes a novel cleaning technique for removal of oil contamination in a closed cooling system during operation. This technique includes among other things the application of ceramic ultrafiltration membranes during the cleaning process. Information is given about the successful removal of oil from a cooling system in a cogeneration combined cycle unit.

Stephen J. Shulder

PPChem 2007, 9(3), 172–178

Experience and Use of Oxidation Reduction Potential Measurements in Power Plant Applications

Oxidation reduction potential (ORP) measurements may be used in a variety of power plant processes including boiler cycle feedwater treatment, cooling water treatment, make-up water treatment, and wastewater treatment. These measurements are typically performed using a platinum measuring electrode and a silver/silver chloride reference electrode containing a potassium chloride solution. ORP is influenced by the amount of dissolved oxygen, and oxidizing and reducing agents in a water sample. In addition, pH, partial pressure of hydrogen and oxygen, and the materials also influence ORP in the system where the measurement is made. ORP measurements can be an effective control method for maintaining an oxidizing, neutral, or reducing environment. This presentation provides some examples of how ORP is used to control plant processes and some of the pitfalls to avoid.

Albert Bursik

PPChem 2007, 9(3), 179–183

Oxygenated Treatment for Units with Once-through Steam Generators – Some Questions and Answers

PowerPlant Chemistry has received a multitude of questions regarding currently used feedwater and boiler water treatments in fossil-fired plants. This contribution addresses many of the inquiries regarding oxygenated treatment applied in units with once-through steam generators, giving general information on the subject and providing references where the questioners and readers of this paper can find more detailed information on the topics discussed.

Suat Odar
Volker Schneider
Thomas Schwarz
Rainhard Bouecke

PPChem 2007, 9(4), 196–203

Cleanliness Criteria to Improve Steam Generator Performance

High steam generator performance is a prerequisite for high plant availability and for possible lifetime extension. The major obstacle to this is corrosion and fouling of the heating tubes. Such steam generator degradation problems arise from the continuous ingress of non-volatile contaminants, i.e., corrosion products and salt impurities which accumulate in the steam generators. These impurities have their origin in the secondary side systems. The corrosion products generally accumulate in the steam generators and not only form deposits in the flow restricted areas, such as on top of tube sheet and in tube support structures, but also build scales on the steam generator heating tubes. Whereas the deposits on top of tube sheet and in tube support structure crevices are responsible for the corrosion phenomena, the tube scales in general affect the steam generator thermal performance, which ultimately causes a reduction in power output. The most effective ways of counteracting all these degradation problems and thus of improving the steam generator performance is to keep them in clean condition or, if necessary, to plan cleaning measures such as mechanical tube sheet lancing or chemical cleaning. This paper presents a methodology of how to assess the cleanliness condition of a steam generator by evaluating all available operational and inspection data together, such as thermal performance and water chemistry data. By means of this all-inclusive approach the cleanliness condition is quantified in terms of a fouling index. The fouling index enables monitoring of the condition of a specific steam generator, allows comparison with other plants and, finally, can serve as a criterion for cleaning measures such as chemical cleaning. The application of the cleanliness criteria and some field results achieved with respect to improvements in steam generator performance are presented in this paper.

Hartmut Venz

PPChem 2007, 9(4), 206–207

Cost Savings in Power Plant Chemistry?

Against the background of the reduction of greenhouse gases, the steadily increasing energy demand, and the main objective of supplying electricity at the lowest possible costs, the paper focuses on the function of chemistry today and in future power plants. The title question is answered with a strong NO. Cutbacks in power plant chemistry do not pay off. Cost benefits may be achieved with the aid of power plant chemistry, not by savings in power plant chemistry.

Keith Fruzzetti
Christopher J. Wood

PPChem 2007, 9(4), 209–215

Developments in Nuclear Power Plant Water Chemistry

This paper reviews the changes in light water reactor water chemistry management that have occurred in recent years. Performance of nuclear power plants in most countries, measured by achieved capacity factors or other indicators (e.g., World Association of Nuclear Operators, WANO, indicators) has improved markedly, and advances in water chemistry have played an important role. No longer seen as the cause of materials degradation and fuel failures, water chemistry advances now represent the most effective methods for mitigating materials and fuel performance concerns. After a brief review of historical developments, this paper focuses on recent advances and inferences for continuing developments in the future.

Recent moves to increase plant output have brought about a new set of challenges, placing renewed emphasis on the need to optimize water chemistry between the sometimes conflicting requirements of materials and fuel, while maintaining the trend towards lower radiation fields. Mitigation of stress corrosion cracking of materials has been demon-

strated (for example, zinc injection in pressurized water reactors, PWRs, and noble metal addition in boiling water reactors, BWRs), but the potential side-effects must continue to be evaluated. Fuel is being driven harder, with longer operating cycles, increased burn-up and increased duty, which has tended to reduce margins. As a result, water chemistries that were satisfactory a few years ago may no longer provide sufficient mitigation of fuel performance degradation and possibly fuel failures.

This paper illustrates the changing role of water chemistry in current operation of nuclear power plants. Water chemistry was sometimes perceived as the cause of materials problems, such as denting in PWR steam generators and intergranular stress corrosion cracking in BWRs. However, starting in the last decade, new chemistry options have been introduced to mitigate stress corrosion cracking and reduce fuel performance concerns.

In BWRs and PWRs alike, water chemistry has evolved to successfully mitigate many problems as they have developed. The increasing complexity of the chemistry alternatives, coupled with the pressures to increase output and reduce costs, have demonstrated the need for new approaches to managing plant chemistry, which are addressed in the final part of this paper.

Ivan D. Dobrevski
Neli N. Zaharieva

PPChem 2007, 9(4), 216–222

The Impact of Boiling on the Chemical Environment of Heating Surfaces in Nuclear Power Plants

Possible consequences of boiling on the heating surfaces resulting in changes in chemical environment characteristics are evaluated for two surface conditions: with and without corrosion product deposits. The changes in chemical environment characteristics determine the corrosion attack on heating surfaces and finally eventually influence their performance.

Special attention is paid to the impact of boiling on the chemical environment of fuel claddings, including the synergetic influence of water radiolysis. The reason is the development of advanced operation concepts to achieve higher burnup and better fuel utilization, connected with increases in cladding temperature and a real possibility for the occurrence of sub-cooled nucleate boiling on fuel element cladding surfaces of pressurized water reactors.

Lewis R. Douglas
Joseph E. Schroeder

PPChem 2007, 9(4), 223–228

Designing HRSGs for Cycling

With U.S. combined-cycle plants increasingly being cycled rather than being run continuously, as they were designed to do, owner/operators worry that units expected to last two or three decades may survive only a few years without an expensive overhaul. Cycling takes as much of a toll on heat recovery steam generators (HRSGs) as it does on gas turbines. Whether you are procuring a new HRSG or adapting an existing one for cycling service, robust design features should be considered.

Phillip Smurthwaite
Britt-Marie Tureson
Romel Makdessi

PPChem 2007, 9(4), 229–237

Investigation of a Persistent Episode of Drum pH Depression Experienced at Händelö Combined Heat and Power Plant

An investigation was undertaken into an episode of persistent pH depression that occurred at Händelö combined heat and power plant in Norrköping, Sweden. Chemical analysis undertaken during the incident revealed the presence of boron throughout the water/steam cycle, which is believed to contribute to pH depression as a result of boric acid ionisation.

Raw water for the process is obtained by the condensation of moisture released during combustion using a heat exchanger situated inside the flue gas stream. Prior to appropriate treatment, the flue gas condensate is heavily contaminated with trace species from various fuel streams. While the plant also fires coal, rubber, biomass, and industrial and municipal waste, it appears possible that boron was introduced into the raw water from construction wood waste fuel, which as a raw material is treated with boron-based compounds for fire protection. Chemical analysis demonstrates that the installed water treatment plant does not appear to be capable of removing boron from the raw water supply under normal operation.

Stéphanie D. M. Marais
Eric V. Maughan

PPChem 2007, 9(4), 240–244

Eskom's Contribution to Good Chemistry Practice in the Generation of Electrical Power

Eskom, the largest electrical power producer in Africa, has always been serious about the quality of chemistry practiced at its power plants. To maintain this high level of power plant chemistry, Eskom has introduced an excellent management and performance control system, which includes, among other things, a definitive set of uniform analytical methods and compulsory standards, measurement and review of performance, education and effective pre-emptive chemistry control. In this paper, the authors give an overview of Eskom's system and share some of the reasons for its success.

Martin R. Godfrey

PPChem 2007, 9(5), 260–267

Use of an Inert Fluorescent Tracer for Diagnostics in Utility Boilers

Case histories of the use of disodium naphthalene disulfonic acid as an inert fluorescent tracer in electric utility boilers are presented. The tracer has proven to be thermally stable in utility cycles at drum pressures as high as 17.9 MPa (2 600 psi) and at saturation temperature of about 357 °C. The non-volatile tracer was used to measure a variety of hydraulic parameters in both conventional coal-fired units and heat recovery steam generators. Diagnostic measurements performed include determination of the mass of liquid water in operating boilers, the rate of loss of concentrated boiler water and the consumption of phosphate internal treatment chemistry. On-line measurement of the fluorescent tracer concentration in drum water was used to automatically control the injection of a traced phosphate internal treatment formulation using simple deadband control.

Andrew G. Howell
Robert J. Pritekel
R. Barry Dooley

PPChem 2007, 9(5), 270–275

Steam Cycle Chemistry and Air-Cooled Condensers

Recently, an increased number of failures in air-cooled condensers have been reported. This paper presents brief information about flow-accelerated corrosion in these large cycle components. In particular, exhaust steam ducts and any high-velocity piping may be subject to flow-accelerated corrosion as well as areas of high turbulences and two-phase flow. The most important options for mitigating flow-accelerated corrosion and in this way for reducing flow-accelerated corrosion induced iron transport are suggested.

Harry Neder
Michael Jürgensen
Dieter Wolter
Ulrich Staudt
Suat Odar
Volker Schneider

PPChem 2007, 9(5), 276–283

VGB Primary and Secondary Side Water Chemistry Guidelines for PWR Plants

The recent revision of the VGB Water Chemistry Guidelines was issued in 2005 and published in the second half of 2006. These guidelines are based on the primary and secondary side operating chemistry experience with all Siemens designed pressurized water reactors gained since the beginning of the 1980s. These guidelines cover

- For the primary side chemistry
  - Modified lithium boron chemistry
  - Zinc chemistry for dose rate reduction
  - Enriched boric acid (EBA) chemistry for high duty core design
- For the secondary side chemistry
  - High all-volatile treatment (AVT) chemistry (high pH operation)
  - Oxygen injection in the secondary side

Especially for the secondary side chemistry, compared with the water chemistry guidelines of other organizations worldwide, these Guidelines are less stringent, providing more operational flexibility to the plant operation, and can be applied for all new designs of steam generators with egg-crates or broached hole tube supports and with I 690TT or I 800 tubing materials.

This paper gives an overview of the 2006 revision of the VGB Water Chemistry Guidelines for PWR plants and describes the fundamental goals of water chemistry operation strategies. In addition, the reasons for the selected control parameters and action levels, to achieve an adequate plant performance, are presented based on the operating experience.

Kevin J. Shields

PPChem 2007, 9(5), 284–293

Condenser Tube Failure Prevention in Fossil Plants

Cycle chemistry personnel frequently identify condenser tube leaks as an area of significant concern in the fossil plants for which they are responsible. This concern is reflected in the fact that contamination due to cooling water ingress from leaking condenser tubes is a root cause of some well-understood yet all too frequently experienced chemistry-related damage mechanisms. Investigation indicated that there were deficiencies in approaches taken by organizations to understand and minimize the impacts of condenser tube leaks on fossil unit availability and performance. To address these needs, the Electric Power Research Institute (EPRI) initiated work on a comprehensive manual dealing with the subject of condenser tube failures (CTFs) in 2004. This report provides member organizations with needed technical background on condensers and the science involved in the various forms of CTF which may be encountered. In addition, it outlines the culture and managerial approach needed to minimize the impact of tube failures on unit availability. Development of the manual confirmed that there is an overwhelming body of information pertaining to damage in condenser tubes and related condenser components such as tubesheets and waterboxes. Further, although the technical understanding of damage mechanisms is generally good, past efforts were collectively deficient in that they did not emphasize the practical, action-oriented steps needed to effectively deal with the various forms of damage. The EPRI CTF manual identifies all known damage mechanisms that affect condenser tubes. For each major damage type, there is a discussion of the features of damage, susceptible materials, susceptible environments, most common locations, mechanism, root causes, methods of determining the extent of damage, actions needed to prevent or mitigate repeat failures, and possible ramifications to the unit. It also provides supporting technical information that will help users implement recommended actions.

Matthias Roßkamp
Norbert Albrecht
Ulf Ilg
Harry Neder
Uve Reitzner
Bernd Riedmüller
Dittmar Rutschow

PPChem 2007, 9(5), 296–300

VGB Water Chemistry Guidelines for BWR Plants: Principles and Recommended Goals

This paper gives an overview of the 2006 revision of the VGB Water Chemistry Guidelines for boiler water reactor (BWR) plants. The guidelines specify "classic" normal water chemistry (NWC) operation with an oxidizing environment. Fundamental goals of water chemistry operation strategies are described. Underlying assumptions and criteria for NWC operation of BWR plants are outlined and recommended goals and action levels of the VGB Water Chemistry Guidelines are described.

Peter D. Hicks

PPChem 2007, 9(5), 301–312

Redox Stress Control Using @T ORP™

The protection and life extension of boiler assets should be primary drivers for water chemistry control in these hot water systems. This includes complicated boiler feedwater and condensate systems. Low-temperature oxidation-reduction potential (ORP) measurements have now become fairly common in many utility boiler systems. Some systems have struggled to maintain recommended room temperature ORP values, and these low-temperature ORP systems often do not detect the true reduction/oxidation stress that is found under operating temperatures in these utility feedwater systems.

Using ORP technologies for high-temperature and -pressure evaluations, as compared to low-temperature ORP solutions, provides a much better technical solution to managing redox stress in boiler systems. The reasons for these enhancements are presented in this paper. Examples are given of why this at-temperature (@T) ORP technology can be used to understand, monitor and control redox (reduction/oxidation) stress events.

Peter D. Hicks
David A. Grattan
Phil M. White
Kurt M. Bayburt

PPChem 2007, 9(6), 324–336

Feedwater Redox Stress Management: A Detailed @T ORP™ Study at a Coal-Fired Electric Utility

Arizona Electric Power Cooperative Inc. (AEPCO), located in Cochise, Arizona, has several coal-fired electric power boilers. The boiler systems have copper-based feedwater heaters. The plant feeds carbohydrazide (ELIMIN-OX®) as its oxygen scavenger and metal passivator.

AEPCO is constantly looking for ways to improve their boiler operation and protect their capital investment. In 2006, AEPCO began an evaluation of Nalco Company's new, innovative @T ORP™ sensor technology. This technology has the ability to measure the oxidation-reduction potential of feedwater at system operating temperatures and pressures.

Monitoring and controlling the feedwater oxidation-reduction potential at system temperature and pressure was successfully demonstrated at AEPCO. A quantum improvement (paradigm shift) in redox (reduction/oxidation) stress management was achieved after the plant switched to controlled feed of carbohydrazide based on the at-temperature (@T) ORP signal. The sensitivity, responsiveness and reliability of this technology were shown during the yearlong evaluation. At-temperature ORP (ORP(T)) showed excellent sensitivity in picking up even small changes in redox stress, providing early detection of a corrosive situation and a means of correcting it. Room temperature (RT) ORP probes were found to be relatively ineffective in picking up these feedwater (FW) redox excursions as compared to ORP(T) probes.

Matthew R. Freije

PPChem 2007, 9(6), 340–341

Around the *Legionella* World in 20 Minutes

This paper provides a brief update on *Legionella* guidelines, risk reduction strategies, legal issues, and domestic water disinfection, with recommendations for facility operators and water treatment specialists.

Akira Morita
Takaya Hisamatsu
Takahiko Uchida

PPChem 2007, 9(6), 342–347

Recent Status of *Legionella* Issues in Japan

The "Japanese Guideline for the Prevention of Legionellosis" is introduced and the status of *Legionella* inhibition in cooling water systems in Japan is reviewed. About 9,000 sampling data on *Legionella* in cooling water systems are discussed. A seasonal trend has been observed based on cooling water sample numbers and positive *Legionella* findings. Moreover, the percentage of positive findings with a registered chemical treatment program at the Japanese Association of Air Conditioning Water Treatment Chemicals for *Legionella* is about half that without chemical treatment. It is concluded that the registered chemical treatment program is successful in Japan.

George Licina

PPChem 2007, 9(6), 348–357

Corrosion of Service Water Piping in Nuclear Systems

Service water systems are a critical part of the infrastructure of nuclear plants. Corrosion has been shown to be the predominant degradation mechanism for service water piping. Because of the diversity of water sources (seawater, brackish water, and various fresh waters), piping materials (bare carbon steel, coated or lined carbon steel, stainless steels, and non-ferrous metals), and service water system designs, a guideline for service water piping requires a set of concise rules, rather than a prescriptive chemical "recipe," for the system to achieve its design life.

Albert Bursik

PPChem 2007, 9(6), 358–363

Organic Plant Cycle Treatment Is Becoming More Attractive

On May 22–23, 2007 the PowerPlant Chemistry Seminar "Organic Cycle Treatment Chemicals" was held in Heidelberg, Germany. This paper gives a short review of the seminar with brief summaries of the individual seminar contributions.

Daniel Zinemanas
Amiel Herszage

PPChem 2007, 9(7), 388–395

Single-Phase Flow-Accelerated Corrosion in Bifurcations

Flow-accelerated corrosion (FAC) is a corrosion mechanism that is induced by a combination of various chemical, physical and hydrodynamic factors. Among these factors, the flow has, through its coupled relation to the mass transport, a dominant role. Prediction and mitigation of this phenomenon thus requires a deep understanding of these two phenomena, and in particular, of the local nature of their interactions. As shown in this paper through a comparison between the numerical analysis of the flow in two types of bifurcations and the actual outcome of two FAC failures, these interactions are not simple and do not behave as in straight pipes. In the bifurcations studied here it is found that the highest local wall wear rate cannot always be directly correlated to the mean flow or to

the highest flow near the wall. Interestingly, in one case the region of the highest wear rate is in a zone where the local velocities are low. In this region, however, the mass transport near the wall is predicted to be the highest.

Yancheng Zhang
Digby D. Macdonald
Mirna Urquidi-Macdonald
George R. Engelhardt
R. Barry Dooley

PPChem 2007, 9(7), 401–408

Prediction of Pitting Corrosion of AISI Type 403 Stainless Steel in Chloride-Containing Borate Buffer Solution

The prediction of pitting corrosion damage on low-pressure steam turbine (LPST) blade surfaces has been investigated experimentally and the results have been interpreted in terms of the Point Defect Model (PDM) for passivity breakdown and the nucleation of pits. Experimental relationships between the critical breakdown potential (V_c) and the chloride activity a_{Cl^-} and pH have demonstrated the applicability of the PDM for describing passivity breakdown on AISI Type 403 stainless steel (SS), a commonly employed blade alloy in LPSTs, in chloride-containing borate buffer solutions. The model parameter values, as determined by optimization of the PDM on passivity breakdown data, may be used to predict the nucleation and accumulation of pitting damage on LPST blades under simulated turbine shutdown conditions. In order to evaluate the predictions, integral damage functions (IDFs) and extreme value distributions in pit depth have been measured on samples taken from failed blades recovered from the field (Texas Genco). These data are being used to test the predictions of Damage Function Analysis (DFA), which is based on the PDM and on deterministic models for pit growth and delayed repassivation. However, the success of this analysis critically depends on our ability to define the corrosion evolutionary path.

Tamara I. Petrova
Valery I. Kashinsky
Valery N. Semenov
Andrei E. Verkhovsky
Vladimir V. Mokrushin
R. Barry Dooley

PPChem 2007, 9(7), 409–419

Effect of Heat Flux on Deposition Rate of Iron Corrosion Products in Boiler Tubes

The reliability of operation of heating surfaces of modern boilers is mostly determined by the deposition rate on heat exchange surfaces. Due to the increased purity of feedwater for both drum-type and once-through boilers, deposits on the inner surfaces of steam generating tubes mainly consist of corrosion products of construction materials, i.e., iron and copper oxides. The aim of this EPRI-sponsored research was to study the effect of (a) water chemistry, (b) heat flux, (c) iron concentration in water, and (d) copper concentration in water on the deposition rate of iron corrosion products in drum-type boiler tubes. The results have indicated that (a) the amount of deposits with AVT was higher than that with OT chemistry; (b) an increase in high flux resulted in a higher amount of deposits with both AVT and OT chemistries; and (c) the presence of copper corrosion products had a slight effect on the deposition rate of iron corrosion products.

Albert Bursik

PPChem 2007, 9(7), 420–424

Chemistry-Related Instrumentation in Fossil Plant Cycles

The paper discusses the required extent of chemistry-related instrumentation for control of chemistry in plant cycles. The focus is on comparison of EPRI and European guidelines specifying the parameters to be monitored. Particularly in non-standard utility and industrial cycles, tailoring of the extent of instrumentation is required for identification and control of contaminant ingress and possibly emerging problems or chemistry upsets.

E. D. Beaton

PPChem 2007, 9(7), 426–431

Understanding Microbially Induced Corrosion in Process Water Systems: Recent Findings on Its Control

Corrosion of cooling water systems has been evaluated in terms of parameters that may control microbially induced corrosion (MIC) in these systems. Results from tests on parameters such as flow and dead leg geometry suggest that mass transfer throughout a system determines whether MIC bacteria are more or less active. The preconditioning of the steel surface also appears to affect MIC by the sulfate reducing bacteria. These results aid in identifying locations where MIC would be prevalent in process water systems and may also provide a justification for selecting locations for corrosion monitoring.

Amaladoss A. M. Prince
Amaladoss M. Remona
Sankaralingam Velmurugan
Santanu Bera
Chakravarthy Amirthavalli
Pandalgudi S. Raghavan
Sevilimedu V. Narasimhan

PPChem 2007, 9(7), 432–440

Characterization of Ferrites and Chromites Prepared by Solid-State Methods: XRD, XPS and Mössbauer Study

Corrosion of structural materials of the coolant system in nuclear reactors leads to the formation of oxides like ferrites and chromites, which are contaminated with radioactivity. This causes radiation field build-up in the out-of-core surfaces and must be removed by the dilute chemical decontamination (DCD) process. Understanding of the contamination process and development of a suitable decontamination formulation require knowledge about the nature of these corrosion products formed on the surface. In this study an attempt has been made to synthesize ferrites and chromites by solid-state reaction in the temperature range 900 °C – 1 400 °C. The synthesized spinels are characterized by powder X-ray diffraction. The chemical state of the metal ions present in the ferrites and chromites is investigated by the X-ray photoelectron spectroscopy technique. In addition, the elemental composition at the oxide surface is determined using the $2p_{3/2}$ photoelectron peaks. The metal ion distribution in the tetrahedral and octahedral sites is studied by Mössbauer spectroscopy and the results are discussed.

George R. Engelhardt
Digby D. Macdonald
R. Barry Dooley

PPChem 2007, 9(8), 454–462

The Prediction of Blade and Disc Failures in Low Pressure Steam Turbines

This paper provides a review of the latest analytical methods that are being explored for predicting the failure probability for low pressure steam turbine discs and blades. Two deterministic methods are explored. The first method is Damage Function Analysis (DFA), which posits that damage can be described in terms of a damage function (DF) for a large ensemble of events (pits and/or cracks), and which provides a measure of the total damage (area under the DF) and of the time at which the deepest event exceeds in length the critical dimension. However, in many situations, the population of pits is not sufficiently large to effectively define the damage function and systems often fail by a single event. In these cases, failure is better described by a Monte Carlo method that retains the deterministic nature of the nucleation, growth, and death of individual events, but in which the sites of pit nucleation are statistically distributed and in which the fate of, and interaction between, individual pits may be followed in detail. The two approaches yield the same results if a sufficiently large ensemble is available, but the "deterministic" Monte Carlo method has significant advantages in describing the repassivation of events and in accounting for failure in terms of "rare events". DFA and the Monte Carlo method are used in this paper to calculate the failure probability of low pressure turbine discs in terms of the concentrations of oxygen and chloride ion in, and the pH of, the thin electrolyte film that exists on turbine surfaces upon shutdown over 219 cycles, each of 600 h duration (100 h shutdown, 500 h operating). These modeling studies suggest practical strategies for decreasing the probability of turbine blade and disc failure due to stress corrosion cracking and corrosion fatigue.

Rosa Crovetto
William J. Beer

PPChem 2007, 9(8), 463–471

New Organic Closed Loop Corrosion Inhibitor

GE Water & Process Technologies (GE) developed a new organic-based mild steel corrosion inhibitor for use in closed recirculating cooling systems to effectively replace benchmark molybdate/nitrite treatments. Laboratory data comparing the corrosion inhibition obtained with the new product with the benchmark and with other organic mild steel inhibitors used for closed cooling loops are presented. The corrosion inhibition efficacy in the laboratory was established by standard electrochemical tests, linear polarization, and under heat transfer conditions with an apparatus that simulates a closed loop recirculating system. In the apparatus corrosion is monitored by coupon weight loss measurement, corrosion rate meters, and the visual appearance of a heat exchanger tube.

Hypothetical mechanisms by which the new product inhibits corrosion of mild steel are also discussed.

Frances M. Cutler
Kevin J. Shields
George J. Verib

PPChem 2007, 9(8), 472–480

EPRI Resin Tester Field Trials at Bruce Mansfield Plant

Under work sponsored by the Electric Power Research Institute (EPRI), the concept of a portable resin tester device for assessment of resin kinetics and other properties was envisioned. Ensuing work included design of the instrument and fabrication of a prototype version. Initial testing of the EPRI Resin Tester was performed at the LabComp, Inc. manufacturing facility in California and the FirstEnergy Corp. Bruce Mansfield Plant in Pennsylvania. These tests demonstrated both the simplicity of instrument operation and the feasibility of using the resin tester for rapidly determining anion and/or cation exchange kinetics. The tests also provided recommendations for optimizing instrument design and operation. Additional field tests at the Bruce Mansfield Plant were performed to determine the exchange kinetics of condensate polisher resin collected from a number of company plants and to compare resin tester results with plant performance results. This paper reports on the outcome of the field tests and discusses the correlation between laboratory analyses and the field trial results.

Walter Guhl
Wolfgang Hater
Stefan Stumpe

PPChem 2007, 9(8), 481–489

Biocide Efficiency against *Legionellae* and Amoebae in Cooling Towers – The Necessity to Control the Risk of Legionnaires' Disease

Legionella, known to be the causative agent of Legionnaires' disease, is a wide-spread bacteria occurring naturally in water. Favorable growing conditions in man-made systems can lead to massive growth and thus to a considerable risk for human beings. Evaporative cooling towers provide good living conditions due to their operational conditions. As a consequence, the growth of *Legionella* in these systems has to be controlled. Amongst other measures biocides are dosed to control the growth of the microbiological population and thus the possible risk of an infection by legionellae. However, *Legionella* preferably lives in biofilms and/or amoebae, which strongly shelter this microbe. Furthermore, amoebae by themselves can be harmful to humans as well. Therefore, a biocide treatment should control *Legionella* (planktonic in water and in biofilms/amoebae) as well as the amoebae.

This paper shows that an adapted biocide treatment can increase the efficiency of a biocide against legionellae and amoebae und therefore minimize the risk of an infection by *Legionella*.

Hao-Feng Zhang
Li-Bin Niu
Shuji Oishi
Hiroshi Takaku
Kunio Shiokawa
Mitsuo Yamashita
Yoshihiro Sakai

PPChem 2007, 9(8), 490–498

Electrochemical Corrosion Behavior of Steam Turbine Materials for Geothermal Power Plants in Simulated Geothermal Waters

In order to evaluate the influence of chloride, sulfate and carbon dioxide in water on the electrochemical corrosion behavior of geothermal steam turbine materials, measurements of the anodic polarization and the pitting corrosion potential were conducted in simulated geothermal waters.

The corrosion resistance of all materials tested was lowered by an increasing carbon dioxide content in the simulated geothermal waters. Higher chloride concentrations in the waters induced lower corrosion resistance and also lower pitting corrosion potentials for materials with higher chromium contents, suggesting the corrosion behavior was mainly controlled by the chromium content of the materials. The corrosion resistance of 9CrMoV and 13Cr steels was also influenced by the concentration of sulfate in the water. The improved heat-treated 16Cr-4Ni material for turbine blades showed excellent corrosion resistance. In the presence of sulfate, the corrosion reactions are mitigated due to a decreasing concentration of chloride (due to the presence of sulfate) in corrosion pits.

Thomas Vogt
Gerhard Besl
Manfred Stecklina

PPChem 2007, 9(8), 500–508

Change in Plant Cycle Chemistry from Hydrazine/Phosphate to Amine/Polyamine Treatment in an Industrial Power Station

In an industrial power station with several natural circulation boilers (permissible operation pressure 13.6 MPa), raw water treatment via demineralization, condensate polishing and thermal feedwater degasification, the cycle chemistry was changed from hydrazine/phosphate to amine/polyamine treatment.

The modification was supervised by TÜV SÜD with several water chemical analyses of the water/steam circuit. No problematic water conditions were found during the investigations. Fewer condensate impurities and a reduced amount of boiler blowdown can be stated as positive results of the transition to the polyamine treatment.

Frank A. Dunand
Nicolas Ledermann
Serge Hediger
Max Haller
Christoph Weber

PPChem 2007, 9(9), 518–522

Luminescent Oxygen Sensor for Monitoring of Nuclear Primary Water Cycles

When we introduced a luminescent sensor to measure dissolved oxygen in water and steam cycles at the end of last year, a number of questions regarding its use in nuclear power plant applications remained open. The issues to be investigated were the behavior in the presence of hydrogen and the effect of radiation on the luminescent sensor. In collaboration with the Mühleberg Nuclear Power Plant in Switzerland a series of tests on the reactor water and the feedwater were performed to demonstrate the performance of the sensor in typical nuclear applications. In addition the system was exposed to high radiation intensities to validate the robustness of the sensor in a nuclear power plant environment.

Eric V. Maughan

PPChem 2007, 9(9), 529–533

The Annual Meeting of the International Association for the Properties of Water and Steam (IAPWS), Lucerne, Switzerland, August 26–31, 2007

Each year the International Association for the Properties of Water and Steam (IAPWS) organizes a meeting of the Executive Committee and the four Working Groups (WG), viz. Thermophysical Properties of Water and Steam (TPWS), Industrial Requirements and Solutions (IRS), Physical Chemistry of Aqueous Solutions (PCAS) and Power Cycle Chemistry (PCC). The 2007 meeting was held in Lucerne, Switzerland, August 26–31. The IAPWS is an international association of scientists and engineers and serves as a forum where persons from the power industry and academics may share problems and formulate solutions. This paper presents a brief overview of the activities of the Power Plant Chemistry Working Group at the 2007 meeting.

Victor Marcu
Alexander Averbach
Daniel Zinemanas
Shmuel Lev

PPChem 2007, 9(9), 534–540

Implementation of Oxygenated Treatment in Drum Boiler Units at the Israel Electrical Corporation

Two drum boiler units at the Israel Electric Corporation's Orot Rabin power plant were recently converted to oxygenated treatment after having been operated on an equilibrium phosphate treatment for about 10 years. The decision followed some concerns regarding boiler phosphate carryover and early signs of flow-accelerated corrosion in the tubes of an economizer header. After more than one year in operation, the basic goal of feedwater iron concentration reduction has clearly been achieved. In this contribution the conversion process and its results are described and discussed.

Gopala Venkateswaran
Ashok Ganpati Kumbhar
Bushan Kishor Gokhale
Vadivelu Balaji
Nirmal Kumar Sarangi
Anil Kumar Sinha
Motichand Doodhnath Prasad Gupta
Suresh Bhaskar Jawale
Kasalanati Harikrishna
Nagaraj Nayak
Venkata Rao
Thachattu Sunil Kumar
Anjali Choudhari

PPChem 2007, 9(9), 541–550

Iron Turbidity Removal from the Active Process Water System of the Kaiga Generating Station Unit #1 Using an Electrochemical Filter

Iron turbidity is observed in the intermediate cooling circuit of the active process water system (APWS) of Kaiga Generating Station (KGS). Deposition of hydrous/hydrated oxides of iron on the plate type heat exchanger, which is employed to transfer heat from the APWS to the active process cooling water system (APCWS), can in turn result in higher moderator D_2O temperatures due to reduced heat transfer. Characterization of turbidity showed that the major component is γ-FeOOH. An in-house designed and fabricated electrochemical filter (ECF) containing an alternate array of 33 pairs of cathode and anode graphite felts was successfully tested for the removal of iron turbidity from the APWS of Kaiga Generating Station Unit #1 (KGS #1). A total volume of 52.5 m^3 water was processed using the filter. At an average inlet turbidity of 5.6 nephelometric turbidity units (NTU), the outlet turbidity observed from the ECF was 1.6 NTU. A maximum flow rate ($10\ L \cdot min^{-1}$) and applied potential of 18.0–20.0 V was found to yield an average turbidity-removal efficiency of ~75 %. When the experiment was terminated, a throughput of $> 2.08 \cdot 10^5$ NTU-liters was realized without any reduction in the removal efficiency. Removal of the internals of the filter showed that only the bottom 11 pairs of felts had brownish deposits, while the remaining felts looked clean and unused.

Albert Bursik
Hans-Günter Seipp

PPChem 2007, 9(9), 552–558

Condenser Tube Failures in Water-Cooled Condensers with Copper-Based Alloys

Integrity of the condenser is one of the most important prerequisites for optimum availability, reliability and performance of fossil and nuclear units. For many decades, copper-based alloys exclusively were used for condenser tubing. Recently, generic 300 Series stainless steels, proprietary austenitic and ferritic stainless steels, and titanium seem to have completely displaced the traditional copper-based alloys. However, arsenical admiralty brass, arsenical aluminum brass, and 70-30 copper-nickel alloy have been successfully applied in countless applications in units with once-through and circulating cooling tower systems. It is believed that also in the future copper-based alloys will maintain their important position among the condenser tube materials. This contribution focuses on operation experience and the most important types of tube failures in water-cooled condensers with copper-based alloys.

Irene Mailand
Hartmut Venz

PPChem 2007, 9(9), 562–570

Optimized Shutdown Chemistry Instead of Decontamination to Reduce the Dose Rate during Outages

The Nuclear Power Plant Beznau (NPP Beznau) comprises two identical 380 MW PWR units with two loops each, commissioned in 1969 and 1971. Because of increasing dose rates many different countermeasures have been introduced, including special shutdown chemistry, the replacement of fuel grids, and improvements in the coolant chemistry, which have led to a reduction in dose rates of about 50 %.

Shutdown chemistry was introduced in Beznau at the beginning of the eighties and repeatedly improved. In 2005 the shutdown chemistry was optimized regarding better separation of the acid-reducing condition phase from the acid-oxidizing condition phase. The influence of the shutdown chemistry on the dose rate is considerable. During shutdown, corrosion products are mobilized as a result of changes in pressure, temperature and water chemistry. This process is supported by the dosage of hydrogen peroxide. The strict adherence to the conditions of both phases of the shutdown chemistry is crucial for the successful optimal removal of nickel and ^{58}Co as well as iron and ^{60}Co.

This report refers to the special conditions of the primary component materials of the NPP Beznau and explains in detail the formation of protective layers and water chemistry. Special attention has been paid to the different behaviour of the two cobalt nuclides, in comparison to nickel and iron. Further optimization is challenging in respect to the reduction of dose rate.

The introduction of annual shutdown chemistry is more advantageous than decontamination after several cycles. It enables selective release of cobalt nuclides and a gentle treatment of the surfaces of the primary components, which results in better integrity of the primary materials as well as in a reduced amount of radioactive waste.

Miroslav Šťastný
Miroslav Šejna

PPChem 2007, 9(10), 582–586

Condensation of Flowing Steam with Nucleation in the Salt Solution Zone

The effects of chemistry on nucleation in flowing steam are particularly unclear. An approach is used in the paper which is based on binary nucleation of the main impurity, NaCl, and water. Physical and mathematical models are described and applied on the steam flow with condensation in a convergent-divergent nozzle. A binary nucleation numerical model is applied for the calculation of the flow with condensation in the nozzle, with an expansion rate in the divergent nozzle part of $\dot{P} = 4\,500\ s^{-1}$. The flow in the nozzle is smooth and it is possible to observe only a small delay in the pressure and a small temperature shock downstream of the nozzle throat.

Digby D. Macdonald
Shoufeng Yang

PPChem 2007, 9(10), 596–607

Oxyanion Inhibition of Passivity Breakdown and the Nucleation of Pits on Type 316L Stainless Steel

Passivity breakdown of Type 316L SS (UNS S31603) in the presence of aggressive Cl^- and inhibitive NO_3^- anions has been experimentally studied and the results have been interpreted in terms of the point defect model (PDM). By expanding the PDM to include competitive adsorption of Cl^- and NO_3^- into surface oxygen vacancies at the passive film/solution interface, the critical breakdown potential, V_c, has been predicted to vary

linearly with log [Cl^-] and with log ([Cl^-]/[NO_3^-]), which is found experimentally. The slope of V_c vs. log [Cl^-] is found to be unaffected by NO_3^-, thereby yielding the same values for the polarizability of the film/solution interface, regardless of the nitrate concentration. The critical breakdown potential increases weakly with increasing nitrate concentration at low [NO_3^-] but, at a concentration of 0.06 M, V_c increases sharply and pitting attack is no longer observed. The viability of the PDM for accounting for passivity breakdown on Type 316 SS is explored by measuring the voltage scan rate dependence of the critical breakdown potential, from which the critical areal (two-dimensional) concentration of condensed vacancies at the metal/barrier layer interface can be derived. Good agreement between the value obtained from experiment and those calculated from structural arguments demonstrate the validity of the PDM.

Luis Carvalho
Thomas James
William E. Hunter

PPChem 2007, 9(10), 608–612

Is Cation Conductivity Monitoring Relevant For Today's Combined Cycle Power Plant? Yet Another Case Study Says It Is Not

Cation (or acid) conductivity is the main control parameter in the cycle chemistry of many combined-cycle power plants today. However, hundreds of these systems consistently fail to achieve cation conductivity values that are required to meet the strict steam turbine original equipment manufacturer (OEM) specifications.

This paper describes the cycle history of a combined cycle cogeneration plant in the U.S. Southwest and relates it to plant asset integrity. Commissioned in the late 1980s, this 120 MW (1x1x1, combined cycle, GE 7EA x Zurn HRSG x GE steam turbine) plant was designed for and operated in base-load mode for 15 years before converting to two-shift cycling approximately two years ago. Plant records show that during its entire operating life, cation conductivity readings throughout the cycle (condensate, feedwater, steam) ranged between 2–5 $\mu S \cdot cm^{-1}$. This is more than an order of magnitude higher than the maximum allowable values in recent turbine OEM specifications. Organic matter and other contaminants also consistently exceeded recommended industry guidelines. However, several major turbine inspections reveal a turbine in excellent condition. In more than 17 years of plant operating life, past problems have been limited to a few expansion-related failures in the feedwater economizer and high-pressure superheater drain during the first year of operation.

The paper describes other key cycle chemistry data, including internal treatment and condensate treatment regimes, and proposes alternative monitoring techniques to cation conductivity.

Piti Srisukvatananan
Derek H. Lister
Robert Svoboda
Karol Daucik

PPChem 2007, 9(10), 613–626

Assessment of the State of the Art of Sampling of Corrosion Products from Water/Steam Cycles

A properly designed sampling system and a suitable sampling procedure are required to obtain representative samples from water/steam cycles and general coolant water systems in power plants because operating decisions often rely on water chemistry information. Several factors must be taken into consideration, such as material selection, system design, proper procedures to maintain the integrity of the sample prior to analysis, etc. This report reviews and summarizes key points and sampling problems experienced in real situations. Theoretical considerations are discussed to some extent to provide more comprehensive views of phenomena in sampling systems. In addition, based on available literature, the report briefly explains sampling techniques and studies pertinent to operating power plants.

Albert Bursik
Hans-Günter Seipp

PPChem 2007, 9(10), 627–631

Condenser Tube Failures in Water-Cooled Condensers with Stainless Steel and Titanium Tubes

Integrity of the condenser is one of the most important prerequisites for optimum availability, reliability and performance of fossil and nuclear units. Recently, generic 300 Series stainless steels, proprietary austenitic and ferritic stainless steels, and titanium seem to have completely displaced the traditional copper-based alloys. After publishing a paper dealing with condenser tube failures in water-cooled condensers with copper-based

alloys in the last issue of the journal, this contribution focuses on operational experience and the most important types of tube failures encountered in stainless steel and titanium condenser tubing.

Michael Rziha
Peter Wuhrmann

PPChem 2007, 9(11), 644–648

Cation Conductivity Monitoring during Startup

In recent years, the requirements on startup time durations of combined cycle units with heat recovery steam generators have become extreme. In this context, measures taken in the area of monitoring of the key cycle chemistry parameters towards reducing the time necessary to obtain correct and representative analysis values are very important. This paper describes some recent developments and clearly demonstrates that the response time of the instrumentation may be reduced by more than half. In this way, the bypass operation time may be markedly reduced, yielding significant benefits.

Eric V. Maughan
Alexander Hörig
Karl-Heinz Leleux
Wolfgang Leye

PPChem 2007, 9(11), 658–662

Fast Sampling under Process Conditions and after New Start-up in the Steam-Water Cycle of Power Plant

Acid ("cation") conductivity is used throughout the power industry by manufacturers of steam-driven plants, utility operators and supporting organisations (e.g. the VGB) in specifications, guidelines and standards to quantify steam quality.

Although this measured quantity is non-specific and cannot identify any single contaminant, it remains nevertheless a good indication of the steam quality being fed to the turbine.

Since the acid conductivity is measured after a strong cation resin exchanger, any changes in flow can upset the measured result, even if flow is discontinued for a short period of time. In addition the presence of dissolved carbon dioxide, found mainly under start-up conditions, will strongly influence the measurement and mask the presence of more harmful ionic contaminants, which have been implicated in the corrosion of materials of construction in the plant cycle.

This presentation describes a method to maintain the integrity of the cation exchanger resin even under upset flow conditions and a device for the rapid removal of dissolved carbon dioxide (degassed acid conductivity) to eliminate this nuisance contaminant, which would otherwise unnecessarily delay the return of the steam turbine to service, owing to elevated acid conductivity values.

In addition a device to remove transported corrosion products (particularly present during start-up conditions), thus preventing "blinding" of on-line sensors and contamination of the analysers, is also presented.

Hiroshi Takaku

PPChem 2007, 9(11), 663–667

Essentials of the Revised Guideline "Water Conditioning for Boiler Feedwater and Boiler Water" in Japan (JIS B 8223:2006)

This paper summarizes the revised parts of the Japanese Industrial Standards for "Water Conditioning for Boiler Feedwater and Boiler Water" (JIS B 8223: 2006). The major changes regard the following subjects: the quality of the boiler feedwater and boiler water for heat recovery steam generators (HRSGs) in combined cycle power plants, and the boiler feedwater quality at plant start-up for oxygenated water treatment (OT) of once-through boilers (new additions to JIS B 8223). In particular, the latter focuses on the water quality at plant start-up and on short-term plant outage/lay-up under OT conditions. The main topics to be reviewed and discussed during the next revision of this guideline will be hydrazine for oxygen removal, steam quality, and sodium hydroxide treatment for drum-type boilers.

Albert Bursik

PPChem 2007, 9(11), 680–687

To Shut Down, or Not to Shut Down, That Is the Question

Faced with the data from their monitoring instruments, personnel at a power plant may be required to make a quick decision – to shut down or not to shut down a drum boiler. The major cycle guidelines give lower limits of 8.0 or 8.5 for the boiler water pH.

However, calculations reported on in this paper indicate that these limits are not sufficient to ensure alkaline conditions in the entire temperature range in which drum-type boilers are operated. It is concluded that the boiler water shutdown limits in the guidelines should be re-evaluated, a pressure-dependent shutdown pH limit may be safer and more economical, and a pressure-dependent minimum sodium level for ensuring alkaline conditions at temperature may be advisable.

Eric V. Maughan
Alexander Hörig
Karl-Heinz Leleux
Wolfgang Leye

PPChem 2007, 9(12), 708–715

The Dr. Leye DAC Spinning Disk Reactor – A Different Approach to the Measurement of Degassed Acid Conductivity

This paper describes innovative technology for the rapid and accurate measurement of degassed acid conductivity (DAC) which is the culmination of 21 years of scientific research into the measurement of dissolved carbon dioxide and its removal from the sample to speed up the return to service of the turbine after an outage.

William H. Stroman

PPChem 2007, 9(12), 721–728

Declining Pressure Method for Boiler Storage and Boiler Cleanliness Assessment by Ultrasonic Technique

During the 1980s, a utility was concerned about the lack of boiler corrosion protection during idle periods when cycling for economic reasons. This led to a search for better ways to protect the boiler waterside and still meet the needs of the load dispatch control center. With system load requirements dictating short periods of shutdown for some units, a challenging dilemma for the boiler water chemistry program developed due to the reluctance on the part of those involved with operations to call the economic shutdowns "storage outages." The duration of the economic shutdowns often varied between overnight to 40 days and seasonally could be as long as 6 months. Wet storage treatment was not considered until the boiler had been off-line for seven days.

The declining pressure method of storage utilizes the residual boiler temperature and pressure of ~1.38 MPa (~200 psi) to thermally mix a low level storage dosage that is injected with the existing boiler water chemical feed system. The effectiveness of the boiler storage program has been evaluated over the past 20 years when determining the need to chemically clean the boiler. One of the tools investigated was the use of the ultrasonic technique to measure the waterwall oxide thickness in high heat areas. Confirmation by tube specimen deposit analyses yielded mixed results although the ultrasonic testing did prove to be helpful in selecting the tube with the highest potential for the most deposition. A recent study found that the Kyushu ultrasonic testing method could provide accurate oxide thickness measurements of tube oxides [1].

Mike Caravaggio

PPChem 2007, 9(12), 729–737

Lay-up and Return to Service Practices at Ontario Power Generation

Ontario Power Generation (OPG; formerly Ontario Hydro) is a provincially owned Canadian utility that has provided better than 80 % of the province's electricity for the past 100 years. OPG's current mix of assets includes several peaking fossil fuel plants (primarily coal-fired drum units). This paper reviews the current practices for short- and medium-term lay-up of these peaking units. It includes the key return to service parameters and practices used at OPG, and reviews the relative performance of the units following these practices. The paper focuses on the water chemistry aspects of the lay-up and return to service, in particular on chemical parameter monitoring and chemical dosing practices in addition to the use of chemical control equipment such as condensate polishers. The paper focuses on two-shifting, weekend outage turnarounds and planned maintenance outage turnarounds, but it also covers indefinite length non-maintenance outages which can last up to several months.

Ashok Ganpati Kumbhar
Sangeeta D. Kumar
Devidas Beerappa Naik
Gopala Venkateswaran
Kamal Kishore
Kandala Satyanarayana Krishna Rao

PPChem 2007, 9(12), 738–743

Dissolved Oxygen Removal from Primary Heat Transport Systems of Indian PHWRs under Nitrogen Atmosphere

A reduction in the dissolved oxygen concentration level of the primary heat transport (PHT) system was observed after a changeover from helium to nitrogen in the cover gas of the D_2O storage tanks of PHT systems of Indian pressurized heavy water nuclear reactors (PHWRs). Radiolysis of the dissolved nitrogen to form atomic nitrogen and its reaction with water and OH radicals leads to the formation of NO and NH_3, which results in scavenging of the dissolved oxygen. However, the concentration of corrosive nitrate formed in this process needs to be minimized. Enhancing the coolant purification flow for the removal of nitrate imposes a heat loss penalty, resulting in a reduction in power generation. On the other hand, hydrogen injection to the system, which suppresses the concentration of corrosive nitrate species, seems advantageous. Thus, a combination of nitrogen as a cover gas in the PHT heavy water storage tank with continued hydrogen injection is recommended to suppress the corrosive effects due to dissolved oxygen and nitrate while retaining the benefits due to the substitution of helium with nitrogen.

Pradeep Jain
Umesh Chand Bhakta

PPChem 2007, 9(12), 746–752

Improvement of Boiler Efficiency and Availability by Post-Operational Chemical Cleaning – A Case Study

Oxides and deposits on the internal surfaces of boiler tubes reduce heat transfer and increase corrosion in waterwall tubes and creep in superheater tubes. To improve the heat transfer, boiler efficiency and availability, chemical cleaning of boilers is regularly carried out by interconnecting the waterwall and economizer tubes in circuit and applying adequate solvents. We have carried out the chemical cleaning of more than 15 boilers of the National Thermal Power Corporation and other utilities in India. The chemical cleaning was carried out mainly by hydrochloric acid along with other chemicals. Single stage, double stage or multi stage chemical cleaning was carried out depending upon the quantity, type and quality of internal deposit in water wall tubes.

Recently, two old boilers (100 MW and 200 MW) were cleaned by two-stage and multi-stage cleaning in one of the stations of the National Thermal Power Corporation. Improvement in the unit heat rate ranging from 135–220 $kcal \cdot kW^{-1} \cdot h^{-1}$ was observed after the overhaul and chemical cleaning of the boilers, and the boiler efficiency was increased in the range of 1.3–2.3 %.

This paper discusses the reasons for the increase in internal deposits in boiler tubes, sampling and internal deposit quantity measurement, criteria for post-operational chemical cleaning, solvent selection, and efficiency measurement and its advantages.

Taro Ichihara
Kenji Mawatari
Takashi Morimoto
Tomohiro Sozuyama
Kazuhide Namikawa

PPChem 2007, 9(12), 754–766

Simplification of Chemical Cleaning Steps during Thermal Power Plant Construction by Mitsubishi Heavy Industries

Newly constructed thermal power plants have typically been subjected to chemical cleaning before the start of operations in order to remove oily substances and metal oxidation scale which may have accumulated during the manufacturing process. In this paper steps taken to save time and costs in regard to this phase of commissioning by Mitsubishi Heavy Industries, Ltd. are presented. These include quality control improvements during construction/manufacturing and the proprietary "Single Stage Chemical Cleaning Method". The results of investigations are discussed which show these developments to be very successful in the simplification of chemical cleaning steps during plant construction. In some cases chemical cleaning is no longer considered necessary at all.

2008's Scientific and Technical Contributions

Jason Fues
ane Kucera

PPChem 2008, 10(1), 4–11

High-Efficiency Filtration for Membrane Pretreatment

Reverse osmosis (RO) has become a common method to demineralize water. A successful RO system requires not only a good design but also appropriate pretreatment to minimize fouling of the membranes with suspended solids. We investigated using high-efficiency filters as pretreatment to RO systems to remove suspended solids and minimize fouling of the RO membranes. These filters have the ability to remove particles down to 0.25 µm in size. This report describes various aspects and specific applications of this technology.

Tom Pike
Douglas Dewitt-Dick

PPChem 2008, 10(1), 19–25

A Novel Approach to Storing and Returning Feedwater Heater Shells to Service

Feedwater heater shells are frequently left unprotected during unit shutdowns and outages. Even though means are generally available during outages to protect these critical areas, many plants either fail to protect the heater shells or, in some cases, opt to leave the shells exposed to damaging environments. Failure to protect heater shells, even during short outages, can exacerbate problems with metal oxide transport when returning the heaters to service – particularly if the heaters contain copper-bearing tubes. This paper investigates a novel approach used by one utility to circumvent problems with oxide transport due to inadequate heater shell storage. It discusses structural modifications incorporated by the plant to improve the storage process. It also details the proper chemistry and testing procedures necessary for shell protection under various conditions. Equally important, this paper outlines critical controls for minimizing copper oxide transport during subsequent unit startup.

Frank Udo Leidich
Hans-Günter Seipp

PPChem 2008, 10(1), 34–41

40th Anniversary of 'ALSTOM Power Plant Chemistry' in Mannheim

The power plant chemistry department of Alstom in Mannheim was founded in 1967. The presentation summarizes our contributions to the development of new power plant technologies over the past four decades. In addition, an overview of the future activities of our department is presented. In the retrospective the following examples are mentioned: nuclear power, combined cycles, supercritical steam generators and the contributions of Alstom's power plant chemistry department to, for example, the VGB guidelines. The outlook includes the expected contribution of power plant chemistry to solving challenges in connection with 700 °C technology steam power plants, oxyfuel processes and carbon capture.

Ladislav Bursik
Albert Bursik

PPChem 2008, 10(1), 42–45

Is Fossil Cycle Chemistry the Cinderella of Power Plant Chemistry?

A survey of the topics addressed at three major European power plant chemistry conferences has revealed that fossil cycle chemistry, like the neglected stepsister Cinderella, is not getting the attention it deserves. Boiler tube failures are the leading cause of forced outages in the conventional fossil plant utility industry, and heat recovery steam generator tube failures are the major cause of damage in the multiple-pressure combined-cycle plants. While other topics are surely important, more honest and open discussion of chemistry-related problems in fossil cycles is imperative to achieving operational benefits like higher reliability, availability, and efficiency.

PPChem 2008, 10(1), 47–64

2007's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

R. Barry Dooley

PPChem 2008, 10(2), 68–89

Flow-Accelerated Corrosion in Fossil and Combined Cycle/HRSG Plants

Flow-accelerated corrosion (FAC) has been researched for over 40 years at many locations around the world, and scientifically all the major influences are well recognized. However, the application of this science and understanding to fossil and combined cycle/HRSG plants has not been entirely satisfactory. Major failures are still occurring and the locations involved are basically the same as they were in the 1980s and 1990s. This paper reviews the mechanism of FAC with particular emphasis on fossil and combined cycle/HRSG plants. It includes discussion on a) typical locations of FAC, b) the single- and two-phase variants by describing their typical appearances in plant, c) oxides which grow in the areas of interest, d) the cycle chemistry alternatives and particularly the effect of potential (ORP) on the oxide forms, and e) the major influences on FAC of turbulence, geometry, mass transfer, and materials. Different approaches are needed within fossil and HRSG plants and these are delineated. The important differences between all-ferrous and mixed-metallurgy feedwater systems are emphasized. Overall, organizations should consolidate their inspection, predictive, and chemistry approaches into a company-wide, coordinated, multi-disciplinary FAC program.

Barbara Moriarty
Joan Chao
Dan Cicero
Craig Myers
F. Philip Yu

PPChem 2008, 10(2), 92–100

Closed Cooling System Treatment: Using Phosphinosuccinate Oligomers (PSO) as an Alternative to Molybdate

Recently, there has been much interest in greener alternatives to molybdate to control corrosion in closed cooling water systems. Driving forces such as environmental restrictions and the cost of molybdate have made the use of molybdate less desirable. This paper discusses the use of phosphinosuccinate oligomers (PSO) in closed cooling water systems. The use of PSO and factors affecting the use of PSO are described, based on laboratory work and field studies.

Robert L. Bryant

PPChem 2008, 10(2), 102–114

Using Particle Counters for Pretreatment Optimization, Iron Transport Monitoring, Condenser Leak Detection, and Carryover Monitoring – A Synopsis of Experiences

Steam generating systems all require clean water. The effects of particulate material in the steam/water cycle on metal corrosion, erosion, cracking, and deposition are frequently observed. However, the physical/chemical mechanisms are often difficult to correlate with a specific plant event, since the periodic "grab" samples from various areas of the water/steam process which are generally conducted do not allow real time continuous on-line particulate monitoring and data collection. This paper introduces the concept of using particulate measuring instruments to monitor the steam generation cycle, and presents case histories of real world plant situations where on-line particulate measurement using particle counters and particle monitors has defined the source of a problem, quantified the severity of a problem, and provided a solution to a problem.

James C. Bellows

PPChem 2008, 10(2), 118-122

Mass Transfer and Deposition of Impurities in Steam Turbines

Mass transfer is a critical part of the process of deposition of impurities in turbines. Metal surfaces have numerous atomic level irregularities that can act as nucleation sites. Once a deposit crystal is nucleated, the growth is limited by the rate at which material can be brought to the surface. This rate is a function of the steam properties and the properties of the molecule being deposited. The important molecular properties are the diffusivity and the solubility in steam. Absolute deposition rates can be calculated with no adjustable parameters.

Silica is relatively soluble in steam. Its deposition rate and redissolution are presented. The implications for deposition patterns and turbine efficiency are explored. Deposition rates are compared with studies in surface roughness to estimate the rate at which efficiency may be lost.

Sodium chloride is much less soluble in steam than is silica. In most cases, once the sodium chloride is deposited, it will remain on the turbine until it is washed off. The quantities of salt actually deposited will be examined. The corrosion implications of the sodium chloride deposition are examined.

Andrew Kern *Peter Ten Eyck* *George Peabody* PPChem 2008, 10(3), 132–142	**Nuclear Power Plant Cooling System Performance Improvement through Real-Time Monitoring, Diagnostics and Control** The nuclear power industry meets 20 % of the North American electricity demand with a high degree of reliability. The fleet of U.S. nuclear plants works to maximize generation and environmental performance while reducing their total cost of operation. Managing the impact of large open cooling water systems can be a challenge. Factors complicating the successful treatment of recirculating cooling water systems include variable makeup water quality, ever-tightening environmental discharge regulations, inadequate program monitoring capability and poor feed control of water treatment chemicals. Scale, corrosion and microbial growth in cooling water systems adversely effect nuclear plant performance by reducing heat transfer and plant efficiency, limiting plant generating capacity (unit derating), restricting flow in critical safety-related systems and increasing maintenance costs.
William Stroman PPChem 2008, 10(3), 144–148	**Southport Power Plant Pretreatment Particulate Monitoring Evaluation** After experiencing severe fouling of cartridge filter elements and reverse osmosis (RO) membranes due to problems with the well water pretreatment system, the Primary Energy Southport Power Plant conducted a study on the continuous monitoring of the well supply and the filtrate quality using a particle counter and a particle monitor. The results, which indicate that such devices may certainly be useful for alarming operations personnel to undesirable well water conditions, are discussed in this paper.
Karol Daucik PPChem 2008, 10(3), 149–153	**Is Countercurrent Regeneration an Option for Condensate Polishing? Yes, It Is.** This paper presents a brief report on operation experience with a three-train separate bed condensate polisher in countercurrent operation/regeneration mode installed at a 400 MW ultra supercritical unit. Operation data show that the quality of the polished condensate is superior to that of the previously used standard (cation–mixed bed) condensate polisher, and it has been possible to almost completely eliminate sodium sulfate-related deposition problems in the plant cycle experienced when operating with that standard design unit.
Eric V. Maughan *Karl Heinz Leleux* PPChem 2008, 10(3), 154–157	**On-Line Multi-parameter Measurements for Water Not Directly Associated with the Steam/Water Cycle of Power Plant** On-line analysis of chemistry variables enjoys a high priority in the monitoring of modern power plant, particularly in the steam/water cycle. However other water circuits and systems do not appear to enjoy the same status. This paper presents a multi-parameter, multi-channel on-line monitor for a wide range of chemical variables.
Shun'an Cao *Rui Li* *Kai Sheng* PPChem 2008, 10(3), 168–173	**Prediction of the Breakdown Voltage of Transformer Oil Based on a Backpropagation Network** Prediction of the breakdown voltage of transformer oil facilitates the early fault diagnosis of transformers, and provides a scientific basis for the prevention of faults in transformer oil. In this paper, based on the correlation between performance parameters of transformer oil, along with the excellent fault-tolerant ability, prominent non-linear approximation capability and self-learning capacity of backpropagation (BP) networks, a BP network with a BP algorithm and a BP network with an improved BP algorithm are developed to simulate the correlation between breakdown voltage and four relevant parameters, using the monitoring data of transformer oil. The results show that the latter algorithm gives more accurate predicted values, which proves to be of high application value.
Albert Bursik PPChem 2008, 10(3), 179–182	**Sodium Hydroxide Treatment for Boiler Water – Some Questions and Answers** PowerPlant Chemistry has received a multitude of questions regarding currently used feedwater and boiler water treatments. This contribution addresses many of the inquiries about sodium hydroxide treatment, giving general information on the subject and providing references where the inquirers and readers of this paper can find more detailed information on the topics discussed.

Sam R. Owens
Rick H. Maxey

PPChem 2008, 10(4), 196–199

Achieving Zero Blowdown for Cooling Towers

A new chemistry approach provides water savings in hard, alkaline cooling waters. Hardness and silica are removed as a semi-viscous fluid. This economical treatment program reclaims over 95 % of open circulation cooling tower water blowdown. Significantly reduced make-up and wastewater treatment costs often make this the preferred treatment program.

Edward C. Hill

PPChem 2008, 10(4), 202–209

Microbiological Problems in Turbine Oils – Detection On-Site, Anti-microbial Strategies

Some microbes can gain access to wet turbine oil systems, and if they find the chemical and physical environment conducive, they will proliferate wherever there is free water. This infected water can be considered as the factory which produces these slimy, sticky, corrosive organisms; their surfactancy allows them to spread into the oil causing operational problems and to colonize other niches. Many will die when they are in dry or hot oil, but they still have the ability to cause fouling. A variety of anti-microbial strategies can be deployed to minimize the risk of operational problems. Considerable care must be used when implementing them, particularly the use of biocides. It is much easier to kill a few microbes than many microbes, and it is sensible to do this before operational problems occur. On-site microbiological test kits are now being used by power station chemists to monitor turbine oils and detect early growth, and to check the efficacy of any remedial measures implemented.

Andrew Howell

PPChem 2008, 10(4), 212–217

Basics of Integrated Steam Cycle Metals Sampling.

Corrosion and transport of metals in the high-purity steam cycles of power plants can cause very costly problems with station components. Metals sampling in these systems provides useful data for evaluating corrosion and corrosion product transport. Collection of both particulate and dissolved metals can inform the plant about the performance of chemistry treatment and monitoring programs, and the effect of program changes on corrosion and metals transport. One mode of sampling is to collect metals from a known volume of water over an extended period of time (integrated sampling), and then analyze the result to determine what is essentially an average metals transport value over that time frame. Consistent procedures and processes carried out over an extended period result in data that reasonably represents the long-term metals corrosion and transport characteristics of plant systems. This paper describes some of the basic factors involved in integrated metals sampling, and demonstrates the value of the technique with actual plant data for several situations.

Daniel E. Meils
Joseph A. Mastroianni

PPChem 2008, 10(4), 218–222

The Development of a Standard for a Power Plant Analytical Chemistry Quality Management System

This paper reports on the changes that have taken place since 2004 in the development of a Standard that defines those objectives that must be met in order for a power plant laboratory to demonstrate it operates a technically competent quality management system and is capable of producing technically competent results. The Standard for a Power Plant Analytical Chemistry Quality Management System was produced by the Power Plant Chemistry QA/QC Advisory Group and includes those practices required to meet the stated objectives.

William A. Shaw

PPChem 2008, 10(4), 232–241

Treatment of Wastewaters from Coal-Fired Power Plants

The largest volume of water in most power plants is used for cooling. Pulverized coal (PC) plants use water for the steam cycle, wet flue gas desulfurization plant, ash transport, demineralizer plant regeneration, and boiler cleaning. As gasification technologies advance, new integrated gasification combined cycle (IGCC) plants will use water for quenching and gas scrubbing. In all coal-fired power plants the current and future trends are water conservation and minimizing the quantity of effluents discharged from the plant.

Using examples from operating plants, this paper describes the various types of effluent streams generated in both PC and IGCC plants, typical pollutants they contain, and the treatment technologies and systems most commonly used to meet regulated discharge limits. It also describes methods of minimizing water usage and discharge, including achieving zero liquid discharge.

Stefan Murza
Norbert Henkel

PPChem 2008, 10(5), 260–265

Operational Flexibility Enhancements of Combined Cycle Power Plants

High operational flexibility is an essential precondition to ensure economic success in a liberalized market. It is imperative that a plant have the ability to start and adjust load quickly and predictably to meet market requirements. Plants that were originally built as base load are being forced to operate as peak load or as cycling plants with daily start-ups because of current market conditions and increasing fuel costs. Plants running in this manner can install upgrades designed for combined cycle power plants (CCPP) in order to reduce start-up times and increase operational flexibility.

Some of the major factors limiting the load output of an existing CCPP are the pressure and temperature transients of the steam turbine and heat recovery steam generator (HRSG), the wait times to establish required steam chemistry conditions, and warm-up times for the balance of plant and main piping systems, thus delaying fast start capability when compared to a simple cycle start-up.

In order to deal with these issues the following solutions have been developed:

- Final stage HRSG attemperators and associated controls to adjust steam temperatures to steam turbine requirements independent of gas turbine load;
- Stress monitoring systems for the thick-walled components in the steam turbine and the HRSG with different start-up modes for flexible use of component life;
- Optimized main steam piping warm-up systems;
- Condensate polishing systems;
- Flexible steam purity requirements.

In addition to these, an improvement in the steam turbine start-up mode has been installed and tested in an operating unit, whereby the steam turbine is rolled off with the very first "cold" steam produced in the HRSG.

With these enhancements to operational flexibility an existing 400 MW CCPP can achieve a start-up time of less than 30 minutes after an overnight shutdown, which is approximately half the time required by a traditional combined cycle unit.

Richard Harries
Andy Rudge

PPChem 2008, 10(5), 274–277

Report on the BIAPWS 2008 Symposium on Power Plant Chemistry: Progress in Environmental and Cycle Chemistry

This contribution provides summaries of the seven papers presented at the symposium and two workshops of the 10th Power Plant Chemistry Symposium, organised by the British and Irish Association for the Properties of Water and Steam (BIAPWS), held on 10 April, 2008 in Beeston, Nottingham.

Jaroslav Bystrianský
Petr Haušild
Lubomír Junek
Jan Siegl
Bohumír Strnadel
Libor Vlček

PPChem 2008, 10(5), 284–290

Thermal Fatigue of Stainless Steel EN 1.4541 in Conditions Simulating Nuclear Energy Circuits

EN 1.4541 (UNS S32100) grade stainless steel is the steel most frequently used in circuits of WWER type nuclear power stations. In the past a discrepancy was observed between corrosion aggressiveness and the occurrence of transgranular damage when this type of steel was exposed to high temperature water and/or during heat transfer. Transgranular cracking can be created as a consequence of both corrosion and non-corrosion processes. This article describes a study of the initiation stages of thermal fatigue cracks in steel EN 1.4541 subjected to repeated thermal shocks. Thermal fatigue cracks initiated spontaneously under the experimental conditions used. Cracks

were fractographically investigated and the mechanism of main crack formation was revealed. Stress-strain analysis proves that stresses around the notch root are sufficient to cause mechanical fatigue damage.

Ling Li
Maohong Fan
Robert Clinton Brown
Jacek Adam Koziel
J. (Hans) van Leeuwen

PPChem 2008, 10(5), 291–301

Reduction of SO_2 in Flue Gas and Applications of Fly Ash: A Review

Flue gas and fly ash are the two most important wastes from power plants. This review focuses on technologies for SO_2 removal from emissions and on properties and applications of fly ash. It predominantly focuses on the non-European situation; in Europe, flue gas desulfurization and ash utilization have been extensively practiced during several decades. Flue gas desulfurization (FGD) technologies are the most commonly used methods in the removal of SO_2 in flue gas. Factors influencing SO_2 removal efficiency and optimal operation conditions are considered. Physical and chemical properties of fly ash make it useable in various fields, such as cement production, concrete admixtures, soil amendment, as a low-cost adsorbent of certain types of contaminants in wastewater, and in the production of effective wastewater coagulants.

David M. Gray

PPChem 2008, 10(6), 320–326

The Role of Dissolved Oxygen and ORP Measurements in Power Plant Chemistry

ORP (oxidation reduction or redox potential) and DO (dissolved oxygen) measurements can provide valuable information in makeup water treatment, cycle chemistry control and stator coolant. Taking the time to understand the principles of operation of these sensors is a worthwhile effort to help specify appropriate equipment and to obtain successful results with it. This discussion describes the various applications for DO and ORP measurements in power plants. It then provides detail on the significance of these measurements and operation of the sensors.

Jane Kucera

PPChem 2008, 10(6), 331–336

Reverse Osmosis Performance: Data Collection and Interpretation

The importance of properly monitoring and interpreting operating data to the successful and cost-effective operation of a reverse osmosis (RO) system cannot be understated. These data can reveal the health of the RO membranes and hence the health of the system. Knowing the condition of the system allows the optimization of operations and minimization of operating costs. This paper addresses the effective monitoring and accurate interpretation of RO operating data.

William E. Bornak

PPChem 2008, 10(6), 340–345

New Econometric Models for Ion Exchange Systems

The basic operation of a cation/anion demineralizer is reviewed to identify different ways to end the service cycle and the economic impact of such choices. The regeneration process is then reviewed to develop an economic metric based on cost per standard volume of demineralized water. The impact of resin fouling on the metric is identified, with a focus on natural organic fouling. The effects on the metric of the use of a new procedure for deep cleaning organic fouling from anion resins are illustrated with real plant data. In addition, a new monthly metric is introduced to clearly identify the optimal time to clean or replace resin. A simplified resin sampling device is illustrated in an effort to obtain more frequent resin samples for analysis and tracking of fouling.

Adam Prust

PPChem 2008, 10(6), 346–354

Converting a Supercritical Unit from AVT(O) to OT

Millmerran Power Station has two once-through supercritical variable pressure boilers that operate with a unit cycle chemistry philosophy to meet the EPRI guidelines for oxygenated treatment (OT). Prior to operating an oxygenated feedwater treatment regime both units had operated an oxidising all volatile treatment (AVT(O)) regime since commissioning.

The change of the feedwater chemistry for Unit 1, and subsequently Unit 2, from an AVT(O) to an OT philosophy was made with the expectation that direct and indirect costs associated with unit operation would be reduced. For Millmerran it is still early days to make quantitative estimates of cost reduction, therefore cost is qualitatively

discussed. This report outlines the impact of the change in feedwater chemistry at Millmerran including impacts on cycle chemistry outcomes and plant operation. The plant improvements initiated for improved feedwater treatment and monitoring are also briefly discussed. Specifically the iron corrosion products measured at the condensate pump discharge and economiser inlet during and after Unit 1 and Unit 2 conversion from AVT(O) to OT are reported and demonstrate that both units are currently operating feedwater treatment to EPRI guidelines and are achieving most of the expected beneficial outcomes.

Andreas Drexler
Alix Schneider
Bernhard Stellwag

PPChem 2008, 10(6), 365–372

Dissolution Behavior of Nickel and Nickel Oxide Particles in Simulated PWR Reactor Coolant at Temperatures below 100 °C

The dissolution behavior of nickel and nickel oxides at 30 °C and 90 °C was investigated by both thermodynamic calculations and experiments in a batch laboratory set-up. The calculations and the experiments were carried out at reducing as well as oxidizing conditions; the presence of B/Li as standard in primary cycles of pressurized water reactors was taken into account. The objective of the investigations was the optimization of shutdown and start-up conditions with the aim of removing nickel and its activated product ^{58}Co from the primary coolant system. As a result of the investigations conducted, two options for the optimization of nuclear power plant operation are presented.

Jasbir S. Gill

PPChem 2008, 10(7), 384–388

Selecting a Water Treatment Program – A Holistic Approach

Water treatment for any system should not be viewed simply as the addition of scale and corrosion inhibitors, dispersants, or biocides. It requires a thorough knowledge of many simultaneous processes responsible for scale corrosion and biofouling. These processes depend to a great extent on each other. The use of impaired waters is increasing due to the shortage of good quality water and for such systems the best solution may require a combination of chemical and non-chemical approaches. The paper discusses a systematic approach to developing a water treatment program by evaluating mechanical, operational, and chemical parameters and their impact on each other.

Ian Richardson

PPChem 2008, 10(7), 393–397

Cycle Chemistry Development at Kogan Creek

Kogan Creek Power Station was built with the intention of running with oxygenated treatment (OT) feedwater chemistry in accordance with EPRI Guidelines (pH 8.0–8.5, dissolved oxygen ~100 $\mu g \cdot kg^{-1}$). The use of an air-cooled condenser (ACC) to dramatically reduce site cooling water consumption has resulted in conventional OT being unsuitable for this 750 MW, all-ferrous once-through unit, due to significant flow-accelerated corrosion (FAC) issues in the condensate system. While the incidence of FAC within the condensate system is a result of several factors, changes in condensate pH are the only feasible short to medium term variable available to address this issue. The high levels of corrosion in the condensate have also presented challenges for boiler integrity as a result of the iron deposits likely to be forming within the boiler. Kogan Creek is attempting to address these issues by bringing together several different cycle chemistry techniques.

Colin Gwynne

PPChem 2008, 10(7), 398–407

Looking for Condenser Air Ingress – A Summary of Detection Methods and the Use of Carbon Dioxide as a Tracer Gas

The operation of steam turbine condensers at vacuum conditions creates the risk of air ingress into the water/steam cycle. This can lead to poor condenser backpressure and turbine efficiency issues, or increases in condensate dissolved oxygen and cation conductivity – which are all undesirable.

This paper briefly reviews the impact of air ingress and some of the traditional methods used to identify sources of ingress. It then introduces a methodology developed at Eraring Power Station which utilises some of the unique features of that site's 660 MW

plant, plus it includes the use of carbon dioxide as an alternate tracer gas, which has proved effective at locating sources of air ingress including a large, but not so obvious leak.

Klaus Kuhnke
Ladislav Bursik

PPChem 2008, 10(7), 412–416

High Temperature Boiler Cleaning with EDTA

A novel EDTA/NH_3/N_2H_4 process has been developed for the chemical cleaning of steam generators and has been successfully applied for preoperational and operational cleaning of fossil-fired steam generators and for the cleaning of the secondary side of steam generators in pressurized water reactors. This publication focuses on the application of this cleaning process in combined cycle units with heat recovery steam generators. The solvent characteristics and the application procedure are discussed. Among other advantages, the process is fast, has relatively low heat and water requirements, and produces a relatively low volume of wastewater.

Robert Muehlenkamp
Robert J. Derus

PPChem 2008, 10(7), 423–425

Bottom Ash Treatment Program Saves Midwest Coal Burning Utility More than US$50,000 Annually

The plant bottom ash spray headers were tested during each outage and most were found to be completely plugged with a white deposit. To repair the spray headers, most were replaced along with the damaged refractory and supply piping. GE Water and Process Technologies conducted preliminary testing on the deposit and found that it was predominately calcium sulfate. Water samples were collected to determine baseline system chemistry and to help define the treatment program. Based on these results, GE Water and Process Technologies's ScaleTrol PDC9326, was recommended for prevention of calcium sulfate scale formation.

Matthew R. Freije

PPChem 2008, 10(8), 444–447

Reducing the Risk of Legionnaires' Disease Associated with Cooling Towers

To reduce the health and legal risks associated with Legionnaires' disease, facility managers should take steps to minimize *Legionella* bacteria in plumbing systems, open industrial equipment, water features, cooling towers, and other aerosolizing water systems. The risk of Legionnaires' disease associated with cooling towers can be reduced by controlling *Legionella* bacteria in cooling water and preventing transmission of the bacteria from towers to people. This paper presents nine reasonable ways to accomplish these goals.

Arvind D. Belapurkar
Salil Varma
Archana Shirole
Jyoti Sharma

PPChem 2008, 10(8), 461–467

Cordierite-Supported Platinum Catalyst for Hydrogen-Oxygen Recombination for Use in Nuclear Reactors under LOCA

Platinum catalysts supported on cordierite honeycomb and plates were prepared and evaluated for H_2-O_2 recombination reaction under static reaction conditions using various concentrations of H_2 in air. The time required for reaction of 50 % of H_2 ($t_{1/2}$) and the maximum temperature attained by the catalyst during exothermic H_2-O_2 recombination (T_{max}) were evaluated. The rate of reaction and T_{max} were found to increase with an increase in H_2 concentration. Pt supported on cordierite honeycomb maintained its activity for > 15 months. The catalysts were found to be quite active for H_2-O_2 recombination and resistant to various contaminants like CH_4, CO_2, CO, and water vapor. Catalytic activity and structural stability of the catalyst were maintained after exposure to 610 Gy of gamma radiation. The study indicates that cordierite-supported Pt catalyst is a promising catalyst for H_2 mitigation for use in nuclear reactors under loss-of-coolant accident conditions.

PPChem 2008, 10(8), 468–470

A Brief Introduction to the International Association for the Properties of Water and Steam

In response to the requests of PowerPlant Chemistry readers, this paper provides a brief overview of the International Association for Properties of Water and Steam (IAPWS). The objectives of the IAPWS in regard to the properties of water and steam, particularly thermophysical properties and other aspects of high-temperature steam,

water and aqueous mixtures, as well as the organization's activities, which include annual meetings, international conferences, working groups, and the development of formulations, releases, guidelines and certified research needs, are presented.

Shun'an Cao
Rui Li
Yihua Qian
Kai Sheng

PPChem 2008, 10(8), 481–486

Overview of Research on Corrosive Sulfur in Transformer Oil

This paper gives an overview of research on corrosive sulfur in transformer oil. The mechanism of transformer failure due to corrosive sulfur, the test methods for total sulfur and corrosive sulfur, the source of corrosive sulfur, the basic groups of sulfur and sulfur compounds in crude oil, and possible mitigation techniques for cuprous sulfide formation are introduced. Additionally, potentially promising research topics on corrosive sulfur are discussed.

Miroslav Šťastný
Miroslav Šejna

PPChem 2008, 10(9), 504–509

Condensation of Water-Steam with and without NaCl Impurity in a Nozzle

Nucleation of two types can occur in the water-steam flowing in a nozzle or in a turbine: homogeneous (spontaneous) and heterogeneous. The effects of chemistry on the flowing steam nucleation and condensation are not quite explained. An approach is used in the paper which is based on binary nucleation of the main impurity NaCl and water. Physical and mathematical models are mentioned and are applied on the steam flow with condensation in a convergent-divergent nozzle. A binary nucleation numerical model is applied for the calculation of the flow with condensation in the nozzle with a low expansion rate in the divergent nozzle part $\dot{\bar{P}} = 1\,000\ s^{-1}$. Calculation results of pressure distribution are compared with experiments. The agreement between calculations and experiments is very good. The homogeneous nucleation and condensation of pure water-steam in the same nozzle is also calculated. The results are discussed. The main features of the binary nucleation and condensation of water and NaCl and of the homogeneous nucleation of pure water are compared.

Peter A. Yarnell

PPChem 2008, 10(9), 518–523

Development of Ion Exchange Resins with Ultra-Low Residuals for Condensate Polishing Applications

Graver Technologies developed and commercialized an ultra-low chloride strongly basic anion resin for condensate polishing applications. Multiple lots of this new resin were installed in a nuclear plant in the United States. The ultra-low chloride resin allowed this plant to increase their amine concentration and consequently to reduce iron transport.

Work is underway to develop a corresponding ultra-low sulfate strongly acidic cation resin for condensate polishing applications. The development study involves post-treatment of a number of commercially available strongly acidic cation resins under comparable, strictly controlled conditions. Sulfate leachables and total oxidizable carbon (TOC) measurements during and after the post-treatment operations serve as metrics for this project.

Robert Svoboda
Klaus Härtel

PPChem 2008, 10(9), 524–529

Steam Turbine Chemistry in Light Water Reactor Plants

Steam turbines in boiling water reactor (BWR) and pressurized water reactor (PWR) power plants of various manufacturers have been affected by corrosion fatigue and stress corrosion cracking. Steam chemistry has not been a prime focus for related research because the water in nuclear steam generating systems is considered to be of high purity. Steam turbine chemistry however addresses more the problems encountered in fossil fired power plants on all volatile treatment, where corrosive environments can be formed in zones where wet steam is re-evaporated and dries out, or in the phase transition zone, where superheated steam starts to condense in the low-pressure (LP) turbine. In BWR plants the situation is aggravated by the fact that no alkalizing agents are used in the cycle, thus making any anionic impurity immediately acidic. This is illustrated by case studies of pitting corrosion of a 12 % Cr steel gland seal and of flow-oriented corrosion attack on LP turbine blades in the phase transition zone. In PWR plants, volatile alkalizing agents are used that provide some buffering of acidic impurities, but they also produce anionic decomposition products.

It is recommended that such corrosion risks be addressed in future cycle chemistry guidelines for nuclear power plants. The present international guidelines give insufficient information and guidance for providing a non-hostile chemical environment in the steam turbine.

Vilém Hanzal
Václav Petr

PPChem 2008, 10(9), 530–536

Measurement of Heterogeneous Condensation Seeds in the Steam Phase Transition Zone

This paper presents a new set-up with an expansion chamber for the experimental prediction of the size and concentration of heterogeneous impurities occurring in the steam transition zone. The onset of steam droplet nucleation on existing heterogeneous impurities is realized by controlled pressure decrease in the test section – the expansion rate $\dot{P} < 11\ s^{-1}$. As a result these nuclei increase to the measurable values. The method for the prediction of the size and concentration of droplets is based on measuring the light attenuation of monochromatic light at two of the light wavelengths. Then the initial size and concentration of the seeds are determined using the heterogeneous condensation model to obtain the best fit of the calculated and measured light transmittances. The tests were carried out both in the laboratory at the Czech Technical University in Prague and in the power station Poc∑erady (200 MW LP steam turbine).

Patrick Colman
Michael A. Sadler

PPChem 2008, 10(9), 538–543

Development and Application of Condensate Polishing in the Electricity Supply Board of Ireland

The use of condensate polishing by the Electricity Supply Board (ESB) of Ireland dates back to 1969. The designs and procedures used have evolved and improved over the years as experience has been gained. The ESB were, in 1980, the first utility to adopt an innovative high efficiency resin separation/regeneration procedure and also developed a simple yet effective procedure for operating in the economical ammonium form. Based on their experience they consider that the use of condensate polishing makes a significant contribution to reducing corrosion and so continue to apply it on new power stations.

A. S. Kopylov
Valery F. Ochkov

PPChem 2008, 10(9), 544–546

Moscow Water Chemistry Forum 2008

This paper is a brief report about the Water Chemistry Forum, an event that took place in Moscow, Russia, in April 2008. One hundred fourteen participants attended more than 40 scientific and technical presentations reflecting the major topics of interest in the Russian power industry.

R. Barry Dooley
Kevin J. Shields
Stephen J. Shulder

PPChem 2008, 10(10), 564–574

How Repeat Situations Lead to Chemistry-Related Damage in Conventional Fossil and Combined Cycle Plants

The scientific understanding of most forms of chemistry-related damage in conventional fossil steam-water cycles and combined cycles with heat recovery steam generators (HRSGs) is very advanced and has been so for many forms of damage for more than 30 years. In spite of this, chemistry-related damage and the cost of availability losses related to deficient chemistry practices are often enormous. Damage and component failure incidents persist, in both fossil units and combined cycle units. Further, much of the damage is reported to be caused by damage modes that are well known and documented. It is thus very clear that the approaches taken by organizations operating fossil units to prevent such damage are frequently unsuccessful. Similarly, fossil industry usage of the response methodology by which chemistry-related damage events are reacted to (identification of the mechanism, assessment of the root cause, and implementation of actions to stop the mechanism) is often ineffective. Recent analysis of past cycle chemistry assessments and damage/failure reviews in over 100 organizations worldwide has lead to a very interesting new concept to prevent damage/failure proactively. This involves identifying repeat cycle chemistry situations which are allowed to continue by the chemistry staff or are imposed on the plant/organization as a consequence of inadequate management support for cycle chemistry.

Piti Srisukvatananan
Derek H. Lister
Chien-Ee Ng
Robert Svoboda
Karol Daucik

PPChem 2008, 10(10), 575–585

Corrosion Product Sampling in Power Plants under Water- and Steam-Cycle Conditions

Sampling of process systems is important in power plants because operating decisions often rely on water chemistry information. To obtain representative samples, a properly designed sampling system must take into account many factors. Sponsored by the International Association for the Properties of Water and Steam (IAPWS), an international collaboration among the University of New Brunswick, Canada, Alstom, Switzerland and DONG Energy, Denmark produced a comprehensive review of sampling techniques in nuclear and fossil power plants. This paper, reporting continuing work, includes a study on isokinetic sampling issues. A computational fluid dynamics (CFD) program was used to assess the collection efficiency for magnetite particles of sampling nozzles under water- and steam-cycle conditions. The effects of types of sampling nozzle and the velocities within the nozzle opening were investigated. It has been shown that for sampling magnetite particles from steam, where the fluid viscosity is low, the collection efficiency significantly depends on sampling velocity. Any practical sampling nozzle acts as an obstacle that disturbs the flow field and tends to remove the isokinetic condition. Although deviations from ideal sampling are small, in steam it is advisable to sample at appropriate rates. In liquid, sampling velocity has almost no effect within the ranges of the parameters studied.

David Addison
Les Lloyd

PPChem 2008, 10(10), 589–595

The Unique Application of a Separate Bed Condensate Polishing System (TRIPOL®) in a 400 MW Combined Cycle Gas Turbine Power Plant – The Huntly Power Station Experience

The use of condensate polishing on modern combined cycle gas turbine (CCGT) power plants is often neglected due to incorrect cost benefit assumptions and short term project objectives. This has resulted in very few CCGT plants worldwide having condensate polishing plants so the short term and long term benefits of condensate polishing have not been fully realised. The application of separate bed condensate polishing on CCGT plants has, until now, been unheard of. This situation has now changed with the construction and commissioning of Huntly Power Station Unit 5, a 400 MW CCGT plant that utilises a cost effective, high performance, easy to operate, separate bed condensate polishing system (TRIPOL®) that delivers clear short term and long term benefits over the entire life of the CCGT plant.

Andrew Howell

PPChem 2008, 10(10), 596–598

Silica Release from a Condensate Filter Containing Glass Fiber Media

Air-cooled condensers (ACCs) are designed with a very large surface area of carbon steel due to the relatively poor heat transfer provided by air cooling and to the high cost of non-ferrous alloys. Transport of particulate iron from ACCs is commonly very high, especially during unit startups. A combined cycle plant subject to frequent shutdown/startup cycles was experiencing significant startup delays due to excessive iron in feedwater. In order to address the problem, a full-flow condensate filter was installed for startup operation. After installation, it was discovered that while iron was reduced to very low concentrations during startups as anticipated, high silica concentrations also accompanied filter use. The problem resulted from the presence of glass fiber filtering media that was significantly soluble in the high-purity, pH 10 water in the steam cycle.

PPChem 2008, 10(10), 600–605

Procedures for the Measurement of Carryover of Boiler Water into Steam

A guidance document on the determination of carryover from drum boilers was developed within the IAPWS Power Cycle Chemistry Working Group. It was submitted to the IAPWS Executive Committee for review and was approved at the 2008 IAPWS meeting. This paper represents the complete technical part of this document. It outlines the considerations for periodic monitoring of carryover essential for chemistry control and the separation of mechanical carryover for warranty purposes. Total carryover is determined by measuring the mass concentration of sodium in the boiler water and in steam. The mechanical carryover represents the fraction of water entrained from the boiler drum into the steam and is determined by correcting the total carryover for any contribution of vaporous carryover. This document gives procedures and covers practical

aspects such as the choice of the sodium compound, test conditions, analytical procedures, plant parameters, and operating conditions to be considered.

Chris Bates

PPChem 2008, 10(10), 613–617

The Effects of Fouled Anion Resin on Condensate Polishing Plant Performance at Dungeness B Power Station

The return to power, after an outage, at Dungeness B Power Station was delayed because of problems in achieving an in-specification feedwater acid conductivity. Dungeness B has a full flow cation/mixed bed condensate polishing plant (CPP). Investigations showed that the acid conductivity was produced by carbon dioxide and organic impurities both by-passing the CPP and slipping through it. Resin analysis showed that the anion resin had severely impaired sulfate removal kinetics. The paper covers the work done to try and identify the nature and source of the organics and their effect on the anion resin. One significant finding was that the carbonate removal kinetics were as impaired as those for sulfate removal; this had not been previously experienced in the CPP at any British Energy plant.

Shunsuke Uchida

PPChem 2008, 10(11), 630–649

Corrosion of Structural Materials and Electrochemistry in High Temperature Water of Nuclear Power Systems

The latest experiences with corrosion in the cooling systems of nuclear power plants are reviewed. High temperature cooling water causes corrosion of structural materials, which often leads to adverse effects in the plants, e.g., increased shutdown radiation, generation of defects in materials of major components and fuel claddings, and increased volume of radwaste sources. Corrosion behavior is greatly affected by water quality and differs according to the water quality values and the materials themselves. In order to establish reliable operation, each plant requires its own unique optimal water chemistry control based on careful consideration of its system, materials and operational history.

Electrochemistry is one of the key issues that determine corrosion-related problems, but it is not the only issue. Most corrosion-related phenomena, e.g., flow accelerated corrosion (FAC), intergranular stress corrosion cracking (IGSCC), primary water stress corrosion cracking (PWSCC) and thinning of fuel cladding materials, can be understood based on an electrochemical index, e.g., the electrochemical corrosion potential (ECP), conductivities and pH. The most important electrochemical index, the ECP, can be measured at elevated temperature and applied to *in situ* sensors of corrosion conditions to detect anomalous conditions of structural materials at their very early stages.

James A. Mathews

PPChem 2008, 10(11), 650–656

Organics in the Power Plant Cycle – An EPRI Perspective

Irrespective of past practices and prejudices, the use of organic treatment chemicals to address new and ongoing concerns in the operation of power plant cycles is increasing. Electric Power Research Institute (EPRI) guidelines currently do not advocate the use of organic additives, citing that these additives should not be needed and that breakdown products pose problems with analytical measurement of cation conductivity and operation of condensate polishers. Some of the concerns about organic treatment are hidden in the association of "organics" with naturally occurring organic compounds from contamination sources such as cooling water, lubrication systems, or make-up water treatment and cleaning agents. However, conditions in the 2-phase fluid regions of low pressure heat recovery steam generators (HRSGs), feedwater heaters, the turbine phase transition zone (PTZ), and air-cooled condensers remain problematic and warrant investigation of conditioning with some complex amine type organic treatments. Nuclear plants have employed advanced organic amines such as ethanolamine to address concerns of low pH in condensing steam. Increasing understanding of the formation, morphology and dynamics of boiler deposits may demonstrate the capability to modify the deposit nature and restrict the accumulation of contaminants; what role potential organic treatments may have in this is unclear at this time. The aim of EPRI in the assessment of organics in the fossil power plant cycle is to accomplish a greater understanding of the role, risks and benefits of organic treatment and to more fully engage the technical community in adoption of best practices for the optimum use of these treatments.

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PPChem 2008, 10(11), 659–667

A Fundamental Study of Flow-Accelerated Corrosion in Feedwater Systems

A loop operating under power reactor feedwater conditions is used to determine chemistry and flow effects in flow-accelerated corrosion (FAC) at 140 °C in neutral and ammoniated water. Electrochemical corrosion potential (ECP) and corrosion rate are measured on-line; mechanisms are indicated through surface analyses. In this paper the results of several experiments are presented. In neutral water, FAC was mass transfer controlled, correlated to surface fluid shear stress and stifled at oxygen concentrations of about 40 $\mu g \cdot kg^{-1}$. Chromium in the steel reduced FAC significantly. Corroded surfaces were covered with thin magnetite films and some developed typical "scalloped" textures related to oxide structures of underlying metal grains. In ammoniated water, $pH_{25\,°C}$ 9.15–9.35, FAC was halved, not clearly mass transfer controlled, and extremely sensitive to oxygen. It was stifled at 1–2 $\mu g \cdot kg^{-1}$, apparently by a "front" of protective haematite-based oxide moving downstream as magnetite was progressively oxidised. The subsequent resumption of FAC when oxygen levels were reduced occurred at the upstream ends of probes.

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PPChem 2008, 10(11), 668–675

Commissioning of the First U.S. Hollow Fiber Condensate Filtration System

Exelon Corporation's Oyster Creek Generating Station, a boiling water reactor (BWR), is the first nuclear plant in the U.S. to install and operate a condensate filtration system using HFF (hollow fiber filter) technology developed in Japan. Oyster Creek is a 640 MW (electric)/1 930 MW (thermal) General Electric BWR-2 (non-jet pump plant) with cascaded heater drains. The plant began commercial operation in 1969, and is one of the two oldest operating commercial BWRs in the U.S. Both noble metal chemical addition (NMCA) and hydrogen injection are used for intergranular stress corrosion cracking (IGSCC) mitigation, and depleted zinc oxide (DZO) is injected for drywell radiation field control. The HFF filters, which were installed in preparation for the operating license renewal, were commissioned in November 2007 and are designed to treat 3 639 $m^3 \cdot h^{-1}$ (16 020 gallons per minute) using a total filtration surface area of 9 457 m^2 (101 796 ft^2). The particle retention rating of the hollow fibers is 0.14 µm, which is considerably smaller than the rating of 1–4 µm for filters commonly used in U.S. condensate filtration applications.

System performance and monitoring results during the initial year of operation are reported, including the use of a special hollow fiber health monitoring sampling system. Feedwater and reactor water chemistry control and monitoring strategies and results are discussed, including the effects of the transition from the highest feedwater iron to among the lowest in the U.S. BWR fleet. The projected annual average feedwater iron concentration is < 0.010–0.034 $\mu g \cdot kg^{-1}$. Data on the impact of low iron operation on reactor coolant activated corrosion products and the ratio of ^{60}Co (soluble)/Zn(soluble), the key parameter used to suppress drywell radiation dose rates, are presented. The zinc control strategy and results are presented, including the effect of low feedwater iron on the reactor water to feedwater zinc concentration factor. The potential need and strategy for future iron injection is also addressed.

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PPChem 2008, 10(11), 676–684

Modifications in the Secondary Circuit Chemistry Control of Embalse NPP

Embalse Nuclear Power Plant is a 648 MW CANDU-600 type pressurized heavy water reactor (PHWR). The primary heat transport system (PHTS) has two separate heat transport circuits, each of which has two steam generators (SGs) of the recirculating type. The SGs have Alloy 800 tubes and the PHTS piping is made of carbon steel. The primary coolant is lithiated heavy water pH (25 °C) = 10.2–10.4, hydrogen content 3–10 $cm^3 \cdot kg^{-1}$ D_2O. The secondary circuit (SC) has mixed metallurgy, i.e., copper alloys in the condenser tubing, carbon steel piping and stainless steel alloys in some specific locations of the steam/water cycle. In recent years a program to better understand the impact of chemistry on flow-accelerated corrosion has been set up together with an enhancement of the surveillance of the piping wall thickness in newly introduced inspection locations. This has been based on international and local experience as well as on theoretical predictions.

In order to maintain an up-to-date state of chemical control with regard to the mitigation of the aforementioned phenomena in consideration of certain materials and locations in the circuit, modifications in the dosing concentration of the alkaline agent (morpholine) have been carried out over the years with simultaneous verification of the diagnostic parameters. Recently, a different organic base has been chosen (ethanolamine) based on its properties, lower volatility and higher dissociation constant at any temperature, with the main target of promoting higher pH at temperature in the steam generator liquid phase. This modification has also been reviewed by the designers. The reasons for the modification are presented together with the main water chemistry parameters before and after the modification and their impact on the corrosion product transport in the feedwater and at other points of the cycle.

Roy van Lier
Gerard Janssen
Jo Savelkoul

PPChem 2008, 10(12), 696–707

Three Years of Experience with Polyamines in the High Pressure Steam System of a Naphtha Cracker

The design and operation of the high pressure steam system of a naphtha cracker pose specific problems which in some cases cannot be satisfactorily resolved with conventional water/steam treatment programs. Following a decade of operational experience with polyamine products at lower pressures at the Geleen (petro)chemical site in the Netherlands, the ammonia/morpholine treatment of the 12.5 MPa steam system of one of SABIC Europe's naphtha crackers was converted to a polyamine program in November 2005. In this paper, the characteristics of the cracker's steam system are first described. Particular aspects of the conversion are then discussed. Finally, the experience gained and insights obtained into the polyamine treatment during the first three years are elaborated.

Albert Bursik

PPChem 2008, 10(12), 708–715

Carbon Is Not Equal to Carbon – An Update (Comments on TOC Discussions)

Organics has resounded throughout the world. This paper tries to clarify some of the most frequently discussed organic matter-related issues. In particular focus are the behavior of organics and organic plant cycle treatment chemicals in fossil plant cycles and the pros and cons linked with the application of the polyamine/amine treatment. The importance of cation conductivity monitoring in the plant cycle is emphasized, if necessary by means of degassed cation conductivity instruments. It is demonstrated that further independent investigations of the polyamine/amine treatment are required.

Kateřina Vonková
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PPChem 2008, 10(12), 719–723

Primary Water Chemistry and High Temperature Filtration System Experience at Temelín WWER-1000 NPP

This paper contains a summary of the water chemistry utilized at the Temelín Nuclear Power Plant from the start of its operation, with a focus on the high temperature filtration (HTF) units. It contains the results of the monitoring of the radiation situation in the main system components with the help of in-situ gamma spectrometry and the measurement of radioactivity of corrosion products in the coolant and on the surface.

A positive effect of HTF has been observed during the early cycles of equipped reactor units. This paper deals with the issue of the behaviour of HTF and its effect on the entire primary circuit. An analysis of an HTF system is performed in this paper. Operation experience from the Temelín Nuclear Power Plant and other WWER (water-water energetic reactor, a Russian nuclear power reactor of pressurized water reactor type) units is compared.

Ivan Smieško
Igor Skorvaga

PPChem 2008, 10(12), 726–731

Influence of Operational and Shutdown Chemistry on Dose Rate Build-up at WWER-440 Units

This paper presents results of a study performed on the operating data of two WWER-440 reactors (water-water energetic reactor, a Russian nuclear power reactor of pressurized water reactor type) in the nuclear power plant Jaslovské Bohunice in Slovakia. The influence of the primary coolant pH at temperature, pH (T), during selected periods of operation (including the shutdown process prior to refueling outages) on dose rate build-up was studied. Coordinated shutdown chemistry was applied during several recent shutdown processes, and results are presented and discussed. The role of other operations performed during shutdown and outage was also analyzed.

Very good operating results of two WWER-440 units which have been operating for 24 years are presented. In-situ gamma spectrometry measurement results show low and relatively stable radiation fields of primary circulating loops. Some correlation was found between "beginning of cycle" chemistry and dose rate build-up. Coordinated shutdown chemistry based on moderation of primary coolant pH (T) changes during the shutdown process was tested during several shutdowns. The aim of such a treatment was suppression of activated corrosion product mobilization and redeposition. Experience with this treatment indicates some promising results, but analysis is hampered by the interference of various factors and more operating experience is needed for trustworthy conclusions. There were no clear correlations identified between shutdown and outage primary loop manipulations and dose rate build-up.

Andrew Howell

PPChem 2008, 10(12), 732–737

Carbon Steel Corrosion in Water-Cooled Condensers

Iron released from carbon steel components in the condenser is often not viewed by power plant operators as a major concern, but in some cases the amount of iron oxide transported to the feedwater can be significant and may contribute to the various problems that result from heavy boiler deposits (frequent chemical cleanings, boiler tube failures by a variety of deposit-induced mechanisms). As with any corrosion mechanism, steps to properly address the issue require knowledge of the corrosion process, however the mechanism for the corrosion of steel in water-cooled condensers has not yet been described. This contribution provides photographic documentation of carbon steel corrosion in a condenser, and proposes a partial mechanism for this corrosion. Then a scheme is proposed to help initiate further discussion and investigation towards the resolution of this issue.

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PPChem 2008, 10(12), 738–744

Photocatalytic Performance of Nano-Sized β- and γ-Ga_2O_3 for the Degradation of Hydrazine in Aqueous Solution under Ambient Conditions

We report on photocatalytic degradation of hydrazine (N_2H_4) using nanophased wide band gap ,β- and γ-Ga_2O_3 under ambient conditions using UV radiation (λ_{max} = 254 nm) and compare this with a benchmark photocatalyst, P-25 TiO_2 (Degussa). The average particle size of the combustion-synthesized photocatalysts was estimated (X-ray diffraction studies) to be 30 and 3 nm respectively for β- and γ-Ga_2O_3. Hydrazine degradation was followed by a complexometric spectrophotometric procedure. Though complete degradation of hydrazine was achieved in less than 2 h using all the catalysts, the kinetics of degradation was found to be in the order β-Ga_2O_3 ≥ P-25 TiO_2 > γ-Ga_2O_3. It was found that neutral and alkaline pH conditions favour the higher kinetics for hydrazine degradation whereas the acidic pH does not. Degradation of hydrazine results in the formation of innocuous products such as nitrogen and water in addition to trace quantities of nitrate. The requirement of the catalyst for the above degradation is as low as 3 mg for 1 000 mL of 100 mg · kg^{-1} hydrazine.

PPChem 101

Fossil Cycle Chemistry

University 101 courses are typically designed to help incoming first-year undergraduate students to adjust to the university, develop a better understanding of the college environment, and acquire essential academic success skills. The major task of the PowerPlant Chemistry 101 course "Fossil Cycle Chemistry" is to help all non-chemists responsible for chemistry-related tasks, all power industry newcomers, and all engineers, whether chemists or non-chemists, to learn the fossil cycle chemistry basics. In 2008, PowerPlant Chemistry presented the first ten lessons :

PPChem 2008, 10(2), 123-128

Lesson 1:
What is Plan Cycle Chemistry and Why Is It Important for Steam and Power Generating Plants?

PPChem 2008, 10(3), 187–192

Lesson 2:
Makeup Water Treatment

PPChem 2008, 10(4), 251–256	Lesson 3: Cycle and Component Design, Materials, Operating Mode and Plant Cycle Chemistry
PPChem 2008, 10(5), 312–316	Lesson 4: Feedwater Treatment
PPChem 2008, 10(6), 376–380	Lesson 5: All-Volatile Treatment
PPChem 2008, 10(7), 436–440	Lesson 6: Oxygenated Treatment
PPChem 2008, 10(8), 496–500	Lesson 7: Feedwater Treatment with Organic Chemicals
PPChem 2008, 10(9), 557–560	Lesson 8: Boiler Water Treatment – Part 1
PPChem 2008, 10(11), 685–688	Lesson 9: Boiler Water Treatment – Part 2
PPChem 2008, 10(12), 749–752	Lesson 10: Boiler Water Treatment – Part 3

2009's Scientific and Technical Contributions – Part 1

Bernt Bengtsson, Pernilla Svanberg, Ulrika Bothin, Glenn Svärd, and Anna Velin

PPChem 2009, 11(1), 6–17

Experience with Water Treatment Applications at Ringhals

The nuclear industry is considered to be a conservative industrial sector when it comes to replacing old or introducing new water treatment/purification systems to ensure a high water quality. Proven technology such as resin ion exchange, evaporation and once-through filtration still dominates in most applications, giving rise to high costs in materials, workload and for waste disposal. In other industries such as electronics and pharmaceuticals, new and supplemental technologies have been successfully introduced over the past decades, without their being fully accepted in the nuclear power plants (NPPs). In fact, rather little improvement seems to have been made in the new generation of light water reactors in this area. These issues need to be addressed to ensure that new as well as modernized existing power plants will be more competitive from environmental and economical points of view.

At Ringhals NPP in Sweden, some new technologies have been evaluated during the last years on a pilot scale as a part of various R&D projects and have sometimes been installed as full-scale systems. Examples are gas transfer membrane (GTM) systems to replace the use of hydrazine in closed cooling systems and to reduce the discharge of airborne ^{41}Ar, electro-deionization (EDI) systems for the recycling of steam generator blowdown and polishing of radioactive liquid effluents, electrochemical ion exchange (EIX) in the separation of boron and lithium, nanofiltration (NF) in the purification of radioactive wastewater and electrochemical oxidation (EO) to reduce organics in liquid concentrates.

This paper presents an overview of the objectives and results of the Ringhals experience and gives some additional proposals for possible applications where modern technology could already be considered useful in light water reactors (LWRs) or needs to be further developed.

Robert Svoboda

PPChem 2009, 11(1), 20–27

The Effect of Carbon Dioxide and Organics in a Steam Turbine

Power plants are designed to run with pure water and steam. For simple cycles (no export steam) no other products are necessary. If organic additives are used in plants with process steam applications, the possible side effects have to be carefully addressed.

Organic oxygen scavengers, dispersants, and chelants as well as organic impurities generally produce volatile acidic degradation products but with no cation for counterbalance. Therefore, such products must be considered as potentially corrosive. Ammonia or hydrazine provide only limited protection against acidic pH in the early condensation zone of the turbine.

Organic amines produce volatile acidic degradation products, but the amine provides cations for counterbalance.

In power plants only conditioned with ammonia and/or hydrazine the level of organics should be kept very low. Especially with low-level ammonia treatment (pH $\leq$ 9.0), the cation conductivity of steam should be kept less than 0.2 $\mu S \cdot cm^{-1}$ (30 $\mu g \cdot kg^{-1}$ acetate).

High alkalizing feedwater treatments, for example ammonia with pH $\geq$ 9.6, or morpholine or hydrazine treatment, are more tolerant to acetate. The contribution of organic acids to cation conductivity should in such cases be kept less than 0.5 $\mu S \cdot cm^{-1}$ (80 $\mu g \cdot kg^{-1}$ acetate).

Carbon dioxide, up to a cation conductivity of 2 $\mu S \cdot cm^{-1}$ in steam, does not influence the pH of the early condensate significantly.

Investigations with three current commercial polyamines did not show a pronounced positive effect on steam turbine efficiency.

Any organic matter in the steam/water cycle brings the risk of detrimental side effects and should thus be avoided unless necessary, for example in certain process steam systems.

Anton Banweg

PPChem 2009, 11(1), 30–33

Industrial Steam Purity: Requirements, Proper Sampling and Practical Considerations

Steam purity is an important consideration in industrial steam generating systems. Deviation from the required steam purity of a system can cause deposition and/or corrosion situations that can result in efficiency losses, impact availability and in some cases create a safety concern. Unfortunately though, many times the purity of steam from a boiler may not be determined until a problem occurs.

Typically isokinetic steam sampling nozzles are not installed in most boiler systems, and when installation is attempted the proper installation requirements for these nozzles may not be able to be met within the actual steam piping installed in the boiler system.

This paper will discuss steam purity requirements, steam sampling system requirements and practical applications.

Michael A. Sadler, Denis Aspden, Frances M. Cutler, and James A. Mathews

PPChem 2009, 11(1), 36–44

A Possible Use of Volatile Amines on Air-Cooled Fossil-Fired Boiler/Turbine Units

Volatile amines have been used to condition boilers in the power industry for over 70 years. More recently they have been successfully used in minimising two-phase FAC (flow-accelerated corrosion) in nuclear power plants. For a variety of reasons, operators of high temperature and pressure fossil-fired boilers have been reluctant to adopt the use of amines. This is possibly because they have found that oxygenated treatment (OT) provides a simple but effective way of conditioning their steam/water circuits and do not see the need to use additional treatment chemicals. For its successful use, OT demands that steam conductivities be maintained at a low level. There is possibly also a concern that use of organic additives could cause these conductivities to rise above the levels advised for OT and the limits set by turbine manufacturers.

A growing number of new power stations are now being equipped with air-cooled condensers. One of the most commonly used designs employs a large area of finned carbon steel tubes that has been shown to be prone to corrosive attack. It is known, however, that this attack can be minimised by increasing ammonia levels in the bulk condensate to a pH of about 9.8–10. This paper considers the possibility of using a volatile amine with ammonia to ensure that the pH in the early condensate droplets formed in air-cooled condensers is high enough to suppress any corrosion.

Abstracts 2008

PPChem 2009, 11(1), 45–60

2008's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Robert Svoboda and Donald A. Palmer

PPChem 2009, 11(2), 70–76

Behaviour of Copper in Generator Stator Cooling Water Systems

Water-cooled generators with hollow copper strands frequently suffer from deposition of copper oxides that clog them and thus impair cooling water flow. Solubility is one of the factors governing the release and the re-deposition of copper oxides. Results presented in this paper indicate that under generator cooling water conditions the solubility of copper oxides is dependent on pH and also, to a lesser degree, on temperature. In pure or moderately alkalized (pH < 10 at 25 °C) water, the solubility of copper oxides increases with increasing temperature. The dependence is stronger for Cu_2O than for CuO. At acidic conditions in a generator, the solubility of CuO decreases slightly with temperature. The apparently contradictory information in the literature – whether the solubility decreases or increases with increasing temperature – is probably a result of differing test conditions, or a differing mix of copper oxides, or of experimental differences, or of a combination of these effects. In strongly alkaline conditions (pH > 10 at 25 °C), which are however not relevant for generator water chemistry, the solubility of both oxides will again slightly decrease with increasing temperature.

Christian Sailer, Julia Rawlinson, and Paul Killeen

PPChem 2009, 11(2), 82–87

***Legionella* Control in Power Station Cooling Towers Using Oxidising Biocides**

Power stations have used oxidising biocides such as chlorine or bromine for many years to control microbial growth in their cooling towers. In this paper Ecolab™ looks at the direct effect halogen concentration has on *Legionella* populations in order to determine the most effective halogenation rate required to ensure that the site key performance indicator (KPI) of < 100 colony-forming units (cfu) per mL can be maintained.

Wolfgang Hater, Niels Rudschützky, and David Olivet

PPChem 2009, 11(2), 90–96

The Chemistry and Properties of Organic Boiler Feedwater Additives Based on Film-Forming Amines and Their Use in Steam Generators

Film-forming amines have been successfully used for a number of decades to treat boiler feedwater, especially in industrial power plants. The results of recent studies of their properties and the results of operational trials should close the existing gaps in our knowledge of film-forming amines, so that this technology can be incorporated into the appropriate guidelines for the treatment of steam generators.

Irvin J. Cotton

PPChem 2009, 11(2), 100–111

Effective Monitoring and Control in Steam Generating Systems

The objective of the water treatment for any type of boiler system is to prevent metal failure due to corrosion, minimize deposition on heat transfer surfaces, and to maintain steam purity.

This paper reviews the newer ASME recommended guidelines for sampling, monitoring and control of water chemistry in steam generating systems. Sample points, sampling parameters, recommended sample frequency and analytical methods and interferences are discussed. The need for site-specific water chemistry is discussed, including the requirements for process steam quality, potential contamination issues and meeting manufacturer's requirements.

An overview of various refinery and petrochemical steam generating systems, including HRSG designs, and major common water-related problems is given. Methods to minimize corrosion in these systems and basic corrosion reactions throughout the cycle, along with chemistry guidelines and monitoring requirements, are discussed.

Milan Teppler, Jonathan Wood, and Patrick Buzzell

PPChem 2009, 11(2), 115–121

Flue Gas Condensate and Energy Recovery

Energy plants in Europe are increasingly turning to biosolids as an alternative to traditional non-renewable fossil fuels. Biosolids have a high water content, resulting in a flue gas with 30–50 % water. Radscan has developed a process to treat and recover 90 % of this flue gas condensate for reuse as boiler makeup water, while recovering considerable energy from the hot gas. The process uses a combination of scrubbers, heat exchangers, ultrafiltration, reverse osmosis, membrane degasification and electrodeionization. This report will describe a commercial system that has been in operation for over two years, and has paid for itself in energy savings.

Barry Dooley and Bob Anderson

PPChem 2009, 11(3), 132–151

Assessments of HRSGs – Trends in Cycle Chemistry and Thermal Transient Performance

The paper provides information from one-day assessments of HSRGs with concentrations on the cycle chemistry and thermal transients. The primary goal of the work was to assist operators in being proactive in identifying the key drivers for cycle chemistry and thermal transient induced failure and damage mechanisms. In the former, the assessments have addressed the key factors for flow-accelerated corrosion (FAC), under-deposit corrosion (UDC) and pitting. In the latter, the assessments have addressed thermal fatigue and creep fatigue. In each area, the assessments have provided a clear picture of exactly where the weaknesses in the approaches are occurring, and it is not surprising that the current ranking order for HRSG Tube Failure has remained rather static for the last 10 years. The paper outlines the approaches to optimize the cycle chemistry to avoid FAC and UDC, the operation of attemperating systems and the configuration of drain systems to avoid the thermal transient driven damage mechanisms. These key messages can easily be applied by operators to change the current situation of waiting for failure to occur.

Gerhard Gericke and J. Denis Aspden

PPChem 2009, 11(3), 158–163

The Influence of Natural Organic Matter on Power Plant Cycle Chemistry

The improvement of condensate and feedwater quality in power generating plant is an on-going process in the power industry in light of the ever increasing use of high pressure and temperature boiler and turbine systems. One area of research that has become very topical is the removal of natural organic matter from power station make-up water. Where potable water is produced, which is also of concern to Eskom, the presence of organics can also lead to taste and colour problems, they can act as precursors for the formation of disinfection by-products and they can stabilise dispersed and colloidal particles during the clarification process. Although water demineralisation processes can cope with the removal of inorganic salts from raw water, the removal of organic matter poses a far greater problem. Some organic compounds can be removed via the ion exchange process, however fouling of the anion exchange resin, and to a lesser extent of the cation exchange resin, occurs during this process which can have an impact on the overall performance of the water treatment plant. Those organics that are not removed will find their way into the steam/water circuit, where they are decomposed through thermohydraulic processes, and these decomposition by-products can influence the quality of the steam and condensate. The mechanistic impact of organic matter on the materials of construction of the steam/condensate cycle is a very controvertial issue and the aim of this paper is therefore not to contribute to this debate, but rather to demonstrate the impact of organics on treatment processes and the quality of the water in the steam cycle.

Gary Cook,
Stan K. Lister,
Andy Rudge,
Ian S. Woolsey,
Mike Craven, and
Mike Angell

PPChem 2009, 11(3), 166–172

Corrosion Testing of Dimethylamine as an Alternative to Ammonia for Once-through Boiler Water Treatment

British Energy has been investigating the potential use of dimethylamine as an alternative to ammonia for boiler water treatment in order to mitigate rising boiler pressure drops in the once-through boilers at some of its advanced gas-cooled reactor (AGR) nuclear power stations. A programme of corrosion testing has taken place at British Energy's Wythenshawe Boiler Rig test facility to investigate whether dimethylamine or its thermal decomposition products could lead to enhanced boiler corrosion, in particular of austenitic superheater sections that have the potential to operate wetted. Tests carried out to-date appear to show corrosion defects resulting from dimethylamine chemistry, although the precise mechanism of formation of these defects remains unclear. This paper will present the latest findings in the test programme and the conclusions being drawn about the possible implication of dimethylamine, or its decomposition products, in the defects being observed.

Frances M. Cutler,
Michael A. Sadler, and
James Mathews

PPChem 2009, 11(3), 176–184

Fouling of Polisher Resin with Organic Leachables, Extractables, and Chemical Additives and Recovering Kinetic Performance

For almost 50 years, the power industry has used condensate polishing to ensure high purity feedwater to once-through boilers and nuclear steam generators and, more recently, to drum-type units operated on oxygenated treatment (OT) or all volatile treatment (AVT). High purity polisher effluent is required for these types of units during both normal operation and during a condenser leak. The major challenge is to maintain polisher performance during a condenser leak when the most important determinant of polisher performance is ion exchange kinetics. If the surface of a resin bead is fouled, diffusion of an ion across the thin liquid film surrounding each resin bead may be adversely affected resulting in slower exchange kinetics and "leakage" of contaminant ions. Consequently, the introduction of chemical additives to units with condensate polishers causes concern because of the possibility of resin fouling [1].

This paper discusses potential sources of polisher resin fouling and provides suggestions and data on resin cleaning techniques that have been tested in the laboratory and successfully used at power plants. Results indicate that appropriate resin cleaning may make the use of some chemical additives compatible with condensate polisher operation [2].

Al Tavares and
Robert A. Applegate

PPChem 2009, 11(3), 186–192

Condensate Polishing for Nuclear and Supercritical Power Plants for the 21st Century

This paper provides a brief history and timeline of condensate polishing from the 1950s to the present. It then discusses the equipment, designs, process strategies, and operating techniques that are being employed and developed to address the increasingly stringent requirements of plants in the 21st century.

Rik-Wouter Bosch,
Marcel Wéber, and
Willy Vandermeulen

PPChem 2009, 11(4), 198–205

Development and Testing of an In-Core YSZ High-Temperature Reference Electrode

The corrosion potential is a useful parameter to monitor the water chemistry of a nuclear power plant (NPP). However the harsh conditions in the core of a nuclear reactor make it difficult to construct a reference electrode for this location. An attempt has been made to construct such a reference electrode based on the well-known yttrium stabilized zirconia (YSZ) membrane electrode. The YSZ electrode is constructed only from radiation-resistant materials (ceramics and metals) and can survive temperatures up to 350 °C. Special emphasis has been put on the ceramic-metal seal, which is a crucial part of the design.

The YSZ electrode has been tested under PWR conditions over the course of one year (in 5 test campaigns of 3 weeks). Slight variations in the water chemistry (changes in the concentration of dissolved hydrogen) prove that the YSZ reference electrodes worked well. The corrosion potentials measured had values between –750 and –800 mV (SHE). The reference electrodes were mechanically intact after one year of testing. The electrochemical response was however no longer reliable as the electrode resistance had decreased over time. Originally this was attributed to leaking of the ceramic-metal sealing causing a "short circuit" in the reference electrode. Recent tests however have shown that the YSZ (9 weight percent yttrium) used up till now for the electrodes is not fully resistant to high-temperature water. Depending on the material structure, the lifetime varies between a few weeks to one year.

Tsung-Kuang Yeh, Mei-Ya Wang, Charles F. Chu, and Ching Chang

PPChem 2009, 11(4), 209–217

Predicted Effect of Power Uprating on the Water Chemistry of Commercial Boiling Water Reactors

The approach of power uprating has been adopted by operators of light water reactors in the past few decades in order to increase the power generation efficiency of nuclear reactors. The power uprate strategy is apparently applicable to the three nuclear reactors in Taiwan as well. When choosing among the three types of power uprating, measurement uncertainty, stretch power uprating, and extended power uprating, a deliberate and thorough evaluation is required before a final decision and an optimal selection can be made. One practical way of increasing the reactor power is to deliberately adjust the fuel loading pattern and the control rod pattern and thus to avoid replacing the primary coolant pump with a new one of larger capacity. The power density of the reactor will increase with increasing power, but the mass flow rate in the primary coolant circuit (PCC) of a light water reactor will slightly increase (usually by less than 5 %) or even remain unchanged. Accordingly, an uprated power would induce higher neutron and gamma photon dose rates in the reactor coolant but have a minor or no effect on the mass flow rate of the primary coolant.

The radiolysis product concentrations and the electrochemical corrosion potential (ECP) values differ largely in the PCC of a boiling water reactor (BWR). It is very difficult to measure the water chemistry data directly at various locations of an actual reactor. Thus the impact of power uprating on the water chemistry of a BWR operating under hydrogen water chemistry (HWC) can only be theoretically evaluated through computer modeling. In this study, the DEMACE computer code was modified to investigate the impact of power uprating on the water chemistry under a fixed mass flow rate in the primary coolant circuit of a BWR/6 type plant. Simulations were carried out for hydrogen concentrations in feedwater ranging from 0.0 to 2.0 $mg \cdot kg^{-1}$ and for power levels ranging from 100 % to 120 %. The responses of water chemistry and ECP to HWC at some selected locations in this BWR under different uprated power levels were successfully evaluated. Our analyses indicated that a particular uprate percentage would tend to promote a more oxidizing coolant environment for the structural components and therefore lead to downgraded HWC effectiveness on ECP reduction and corrosion mitigation. An 8 % or 15 % uprate percentage led to a poorer HWC efficiency at most of the evaluated locations of this BWR. In contrast, the HWC efficiency could be slightly improved at 20 % power uprate for most of the evaluated locations of this BWR. In summary, the impact of power uprating on the water chemistry in the primary coolant circuit of a BWR is expected to vary from location to location and possibly from plant to plant due to different degrees of radiolysis and physical dimensions.

Albert Bursik

PPChem 2009, 11(4), 220–229

Conductivity vs. pH – Comments on pH Monitoring via Conductivity Measurement

Operators of fossil power plants often do without pH monitors, instead applying data obtained through conductivity measurements to calculate the pH or compare with diagrams. This contribution looks at the quality of pH data supplied via the use of auxiliary quantities (specific and/or cation conductivity). Two approaches for pH calculation from measured conductivity are investigated. Actual and calculated pH values are compared for certain conditions, including the presence of the contaminants NaCl and CO_2. The author finds that the determination of boiler water pH (calculation) based on specific and cation conductivity measurement is relatively accurate. The calculation of feedwater pH based on specific conductivity data, however, is negatively influenced by the presence of contaminants, particularly carbon dioxide. Due to the importance of a correct pH for the plant cycle chemistry, certain application restrictions are thus imperative.

Palogi Chandramohan, Madapuzi Parthasarathy Srinivasan, Sinu Chandran, Sankaralingam Velmurugan, Srinivasan Rangarajan, and Sevilimedu Veeravalli Narasimhan

PPChem 2009, 11(4), 234–240

Modification of Magnetite Film on Carbon Steel by Polyol Addition in Alkaline Condition

The formation of oxide film on carbon steel in aqueous alkaline media with polyol was studied at high temperature (240 °C). Polyols (viz., ethylene glycol, diethylene glycol, polyethylene glycol and glycerol) modified the morphology, crystallite size and porosity of the oxide film. Oxide film formed on the metal surface under these conditions was characterized by XRD, Raman spectroscopy, SEM and electrochemical techniques. The thickness of oxide film formed under these conditions was found to be 0.7 µm after 14 days of exposure time. The results of electrochemical impedance analysis indicated that the oxide formed on the carbon steel surface in the presence of glycerol and polyethylene glycol as organic additive had higher film resistance as compared to the oxide film formed in their absence. Potentiodynamic anodic polarization studies showed lower current density for oxide film formed in the presence of 1 % (volume fraction) polyethylene glycol-400 and 1 % (volume fraction) glycerol as compared to the oxide formed in the simple alkaline condition. Raman spectroscopic (mapping) analysis showed that the film formed in the presence of polyols was of uniform single phase nature and coverage of the oxide film was complete. SEM micrographs showed that the crystallite size in the oxide film formed in the presence of glycerol was smaller as compared to the crystallites formed in the simple alkaline condition. Magnetite formed in the presence of ethylene glycol showed a broad crystallite size distribution in the film.

Yan Huang, Shun'an Cao, Lu Wang, and Shanshan Ding

PPChem 2009, 11(4), 244–249

A Film-Forming Additive for Layup of a 600 MW Unit with a Drum Boiler

This paper discusses the mechanism of corrosion damage during the layup of boilers, and emphasizes the necessity of protection through proper layup procedures. A new film-forming inhibitor, WDBH, and its method of application, process controlling and film-forming effectiveness when applied during layup to protect a boiler in a unit with an air-cooled condenser are introduced. This additive has excellent film-forming qualities (good hydrophobic performance of the protective film, strong anti-corrosion characteristics), can be applied over a wide range of pH, requires only simple technology, and has great practical benefits.

Brad Buecker and Kal Farooq

PPChem 2009, 11(4), 250–253

Turbine Lubricating Oil Varnish Control

Varnish formation in turbine lube oil and fluid hydraulic systems is an increasingly common problem with power generating units of many types (gas, coal, and nuclear). Varnish forms a sticky coating on surfaces inside the fluid system, including bearings, coolers, and valves, and negatively affects operation of these devices. Most notably, varnish causes stiction-induced failure of servo-valves. This article examines varnish formation fundamentals, discusses the difficulties derived thereby, and introduces a very promising control method.

R. Barry Dooley, J. Denis Aspden, Andrew G. Howell, and Francois du Preez

PPChem 2009, 11(5), 264–274

Assessing and Controlling Corrosion in Air-Cooled Condensers

An increasing number of air-cooled condensers (ACC) are being installed and operated on conventional and combined cycle plants worldwide. Unless understood and corrected, the corrosion associated with the ACC ducts and tube entries can become a major problem for operators of plant. Up to just a few years ago very little was known about the corrosion/ flow-accelerated corrosion (FAC) process. This paper starts to rectify the situation with a description of the corrosion/FAC process, a corrosion index and a relationship between the operating pH and the level of iron at the condensate pump discharge.

James A. Mathews

PPChem 2009, 11(5), 275–283

Challenges in Cycle Chemistry

The changing face of power generation in response to the worldwide economic and environmental concerns presents an increasing challenge. The focus in the operation of the power plant is to maintain the integrity and operability of the asset and reduce or eliminate performance and availability losses. Past EPRI International Conferences on Cycle Chemistry and Boiler/HRSG (Heat Recovery Steam Generator) Tube Failures provided a prioritization of cycle chemistry concerns and issues to be addressed. EPRI is providing guidance and technology addressing these issues. A brief discussion of the major concerns and some of the leading issues is provided. These issues and others will be topics of presentations at the Ninth International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators, June 30 – July 2, 2009, Boston, Massachusetts.

David Guzonas, Peter Tremaine, and Jean-Paul Jay-Gerin

PPChem 2009, 11(5), 284–291

Chemistry Control Challenges in a Supercritical Water-Cooled Reactor

The long-term viability of a supercritical water-cooled reactor (SCWR) will depend on the ability of designers to predict and control water chemistry to minimize corrosion and the transport of corrosion products and radionuclides. Meeting this goal requires an enhanced understanding of water chemistry as the temperature and pressure are raised beyond the critical point.

A key aspect of SCWR water chemistry control will be mitigation of the effects of water radiolysis; preliminary studies suggest markedly different behavior than that predicted from simple extrapolations from conventional water-cooled reactor behavior. The commonly used strategy of adding excess hydrogen at concentrations sufficient to suppress the net radiolytic production of primary oxidizing species may not be effective in an SCWR. The behavior of low concentrations of impurities such as transition metal corrosion products, chemistry control agents, anions introduced via make-up water or from ion-exchange resins, and radionuclides (e.g., ^{60}Co) needs to be understood. The formation of neutral complexes increases with temperature, and can become important under near-critical and supercritical conditions; the most important region is from 300–450 °C, where the properties of water change dramatically, and solvent compressibility effects exert a huge influence on solvation. The potential for increased transport and deposition of corrosion products (active and inactive), leading to a) increased deposition on fuel cladding surfaces, and b) increased out-of-core radiation fields and worker dose, must be assessed.

There are also significant challenges associated with chemistry sampling and monitoring in an SCWR. The typical methods used in current reactor designs (grab samples, on-line monitors at the end of a cooled, depressurized sample line) will be inadequate, and in-situ measurements of key parameters will be required.

This paper describes current Canadian activities in SCWR chemistry and chemistry control. Because the direct measurement of chemistry parameters under such extreme conditions of temperature, pressure, and radiation fields is difficult, the approach involves a combination of theoretical calculations, chemical models, and experimental work.

John M. Riviello and Archava Siriraks

PPChem 2009, 11(5), 292–296

Novel Electrodeionization Devices: Applications in Inorganic Analysis

Electrodeionization (EDI) is a well established technique for the production of ultrapure water (UPW). In this paper the authors discuss novel electrodeionization devices which have been developed primarily for use in chemical analysis. These EDI devices can be incorporated directly into the analytical instruments for on-line production of UPW, or can be used off-line for automated sample dilution or sample preparation. Applications of these EDI devices in trace analysis of inorganic anions will be shown.

Lihui Liu and Derek H. Lister

PPChem 2009, 11(5), 298–309

The Modification of Oxides on Nuclear Reactor Materials by Titanium Addition under Primary Coolant Conditions

Previous titanium injection studies showed that the transport and incorporation of soluble titanium species can modify the normal magnetite (Fe_3O_4) film on carbon steel and make it more protective. Subsequent experiments in a titanium autoclave system with well-conditioned surfaces have exposed samples of A106B carbon steel, 304L stainless steel, Alloy-600 and Alloy-690 for 1 100 hours to simulated CANDU coolant at 310 °C when freshly-machined titanium turnings were present and when they were absent. Detailed surface analyses indicated duplex oxide layers on all surfaces and substantial transport of soluble Ti in both cases, since $FeTiO_3$ was formed generally in the outer layers. Ulvöspinel was also found on the carbon steel and stainless steel surfaces. Differences between the exposures with fresh titanium metal and those without were minor; the former promoted larger but fewer outer-layer crystals of Ti-bearing oxides but suppressed the formation of $NiFe_2O_4$ crystals on Alloy-600. The turnings themselves developed TiO_2 (anatase) and $FeTiO_3$ crystals.

Ivan D. Dobrevski, Neli N. Zaharieva, Katia F. Minkova, and Nikolay B. Gerchev

PPChem 2009, 11(5), 312–319

Behavior of Antimony Isotopes in the Primary Coolant of WWER-1000-Type Nuclear Reactors in NPP Kozloduy during Operation and Shutdown

This paper focuses on the behavior of the antimony isotopes ^{122}Sb and ^{124}Sb in the coolant of the WWER reactors in the nuclear power plant Kozloduy (Bulgaria) during operation and shutdown. It is concluded that the chemical properties of their actual precursor, the isotope ^{121}Sb, determine the behavior of ^{122}Sb and ^{124}Sb during operation, load fluctuations, and shutdown as well as during the reactor coolant purification process. It is supposed that differences between the reactor bulk and the core fuel cladding surface chemistry as well as the presence of sub-cooled nucleate boiling at the fuel cladding may create conditions under which a local oxidizing environment may come into existence.

K. Anthony Selby

PPChem 2009, 11(6), 324–329

An Overview of Condenser Cooling Water Leak Detection

High pressure electric utility cycles require high quality feedwater. The steam surface condenser is a potential major source of contamination. Once the condenser has been confirmed as the source of the contamination, there are several chemical and physical techniques available to pinpoint the source of the contamination so that it can be eliminated. This paper reviews those techniques and discusses their applicability in various situations.

Geoff Bignold

PPChem 2009, 11(6), 334–337

Report on the BIAPWS 2009 Symposium on Power Plant Chemistry

The British and Irish Association for the Properties of Water and Steam held a Workshop on Chemical Aspects of Flexible Operation of Plant and a Symposium on Environmental and Operational Issues on 21–22 April 2009 at Beeston, Nottingham. Summaries of the eight papers presented at the symposium are provided.

Norbert Eimer and Martin Werner

PPChem 2009, 11(6), 338–343

Optimizing a Tail-End DeNOx System by Installing a Static Mixer

Units 3 and 4 of the Grosskraftwerk Mannheim AG (GKM) power plant in Germany are supercritical units with hard-coal-fired slag-tap steam generators with double flue gas reheat and were originally built in 1966 and 1970. The joint DeNOx system based on the SCR (selective catalytic reduction) procedure was commissioned in November 1988. For structural reasons as well as in order to prevent catalyst poisoning caused by complete ash recirculation, the DeNOx reactor was installed in a tail-end configuration, i.e., downstream of the flue-gas desulfurization plant (FGD). In order to obtain an optimal operating temperature for the catalytic conversion process, the flue gas is reheated by means of natural gas multiport burners.

Especially in plants where SCR systems are installed in a tail-end configuration, it is important that the ammonia is mixed with the flue-gas mass flow as homogeneously as possible before it enters the catalyst and that any existing temperature streaming is eliminated. After Unit 6 was modified for hard-coal firing, this precondition was no longer fulfilled. Owing to the given approval requirements, usually only one boiler is in service at a time – Unit 3 or Unit 4. For the DeNOx system, this results in partial-load operation with the flue gas velocities being accordingly low.

The following report describes the integration of a static mixer in the DeNOx system of Units 3 and 4. This measure was taken to level out both the temperature distribution downstream of the natural gas multiport burners and the NO_x concentration profile below the last catalyst layer – especially during partial-load operation – to such an extent that it was possible to substantially lower the flue-gas temperature upstream of the DeNOx reactor and reduce the natural gas consumption.

R. Barry Dooley, Kevin J. Shields, and Steve J. Shulder

PPChem 2009, 11(6), 352–361

Flow-Accelerated Corrosion (FAC) in Conventional Fossil Units: Cycle Chemistry Influences and Management Approach

The authors have reviewed flow-accelerated corrosion (FAC) programs used at various types of conventional fossil plants. The results and findings of the assessments are presented and discussed. A number of emergent areas of FAC damage have been added to the previous suite of recognized susceptible locations with a concentration on damage due to two-phase FAC. Several deficiencies related to feedwater chemistry and FAC management approaches were noted to be common among the plants. These characteristics may influence the FAC susceptibility and awareness at other plants.

Timothy S. Wood and Michael Lore

PPChem 2009, 11(6), 362–366

Moss Animals: A Growing Nuisance in Industrial Cooling Systems

Bryozoans are a common and natural part of biological communities in lakes and rivers. Sometimes called moss animals, they can also thrive in industrial pipelines, channels, and filters, where they become a serious nuisance. Total elimination of these pests is seldom an option. Management usually involves mechanical or chemical treatments, although other creative solutions are often possible. Effective control strategies require knowledge of the species involved and a grasp of life cycle timing for the geographic region.

M. López García and M. Lehtinen

PPChem 2009, 11(6), 373–380

EDI Modules Perform Well at Bioenergy Combine in Scandinavia

A case study is presented of the installation and operation of a water treatment system at a Swedish bioenergy combine power plant. Pretreatment (softening), reverse osmosis and electrodeionization (EDI) modules have been integrated into a single design. The environmental, operational and economical advantages of the use of EDI over that of mixed bed deionizers are discussed. After 15 months of operation, the water treatment system with EDI has been shown to optimize performance, maintain continuous product quality and to produce a sufficient amount of high purity product water while using low energy consumption.

Karol Daucik

PPChem 2009, 11(7), 388–393

The Design of Sampling Devices for the Water/Steam Cycle

Today, the importance of representative sampling from the water/steam cycle is widely recognized. However, there is still disagreement on the question of how to get a representative sample, particularly when the sample contains two phases. Sampling of corrosion products in particulate form often involves the risk of systematic error. Parameters affecting the representative sampling of particulates in steam are discussed in this paper. The application of these considerations to the appropriate design of sampling devices is the main objective of the study. Necessary compromises and some remaining questions are pointed out in the conclusion.

Thomas J. Feeley III, Lynn A. Brickett, B. Andrew O'Palko, and Andrew P. Jones

PPChem 2009, 11(7), 402–411

DOE/NETL's Mercury Control Technology R&D Program – Taking Technology from Concept to Commercial Reality

The U.S. Department of Energy, National Energy Technology Laboratory (DOE/NETL) has worked with industry, research organizations, and academia to develop advanced mercury control technology for coal-based power systems. Over the past seven years, this research has focused on the full-scale and slip-stream field testing of activated carbon injection (ACI) and flue gas desulfurization enhancements at nearly 50 U.S. coal-fired power plants. The goal of the field testing was to demonstrate high levels (50 % to 90 %) of mercury capture over an extended period of operation, while also reducing the cost of mercury removal. The field testing program has successfully met this goal. Due in large part to this success, coal-fired power plant operators have initiated commercial deployment of mercury control technology. As of April 2008, nearly 90 full-scale ACI systems have been ordered by U.S. coal-fired power generators, accounting for over 44 GW of coal-fired electric generating capacity. This paper will provide an update on DOE/NETL's mercury control technology research and development program, including an assessment of the cost of capture.

J. Denis Aspden, Frances M. Cutler, James A. Mathews, Michael A. Sadler, and David Swainsbury

PPChem 2009, 11(7), 412–430

The Use of Separate Bed Condensate Polishing on Fossil Power Stations

The use of condensate polishing on fossil power stations is recommended by EPRI. The majority of stations that have followed this advice have adopted polishing systems based on the use of deep beds of ion exchange resin. Mixed bed polishers have been shown over the last 50 years to be very effective and capable, in the proper hands, of yielding polished water containing less than 0.1 $\mu g \cdot kg^{-1}$ of the common ionic impurities. This is admirable and mixed beds are always used when condensate of the highest possible quality is required. Fossil power stations do not require such a high quality as they have been shown to operate satisfactorily with impurity levels of about 1 $\mu g \cdot kg^{-1}$ with EPRI "First Action Limits" being set at 3 $\mu g \cdot kg^{-1}$. Mixed bed polishers are widely and successfully used on fossil stations but some, particularly those with low manning levels, find that they are very demanding. Interest is now being shown in alternative, less demanding techniques that promise to yield a polished condensate of suitable quality for fossil power stations although not capable of meeting the requirements of nuclear power stations.

Deionization of water by the use of separate beds of cation and anion exchange resins predates the use of mixed beds. The very early condensate polishing plants, however, adopted mixed beds and their use has continued to the present time. It is of interest that as early as the 1960s separate bed polishers were employed in a few European countries. The designs used were based on conventional deep-bed service vessels and in-situ regeneration was favored, often together with counter-current regeneration. It is reported that perfectly acceptable polished water qualities are obtained and that improved designs of in-situ regenerated separate bed polishers have recently been installed on ultra-supercritical units in Denmark.

In the early 1980s an innovative separate bed system was devised in the UK in which layers of cation–anion–cation resin were contained in one service vessel, thus saving cost and space. This proprietary design of layered separate beds found favor in Australia, where its additional advantage of simplifying operation in the economical ammonium form was clearly shown. This paper reviews these developments and the various trials of separate bed polishing systems that have taken place. It considers the regeneration procedures for resins from such plants and particularly the problem of ensuring resins are thoroughly cleansed of any traces of the regenerants used. Also considered are the results and experience derived from separate bed polishers currently in use on power plants, differences in anion resin fouling in mixed bed condensate polishers versus separate bed and cation/mixed bed polishers, and the possibility of further improvements to the technique.

K. Anthony Selby

PPChem 2009, 11(7), 434–438

The 29th Annual University of Illinois Electric Utility Chemistry Workshop – Extending the Life and Reliability of Power Plant Equipment through Improved Chemical Control

In June this year, the 29th Annual University of Illinois Electric Utility Chemistry Workshop took place in Champaign, IL, U.S.A. The content of the workshop and abstracts of the papers presented at this event are compiled in this paper.

Joseph E. Schroeder

PPChem 2009, 11(7), 439–445

A HRSG Supplier's Water Chemistry Program Recommendations

Various international standards as well as EPRI recommend starting with good feedwater. Nooter Eriksen has adopted the EPRI philosophy for their heat recovery steam generator (HRSG) water chemistry program recommendations. The EPRI guidelines provide a simple means for treating and monitoring HRSG water chemistry. All-volatile treatment and phosphate treatment programs are discussed. Some differences from the EPRI guidelines are suggested depending upon the HRSG configuration.

2009's Scientific and Technical Contributions – Part 2

Robert L. Bryant

PPChem 2009, 11(8), 452–461

On-Line, Continuous Measurement of Makeup and Cycle Water "Particulates" at Low Parts per Trillion Levels

The effects of "particulate" material in makeup and cycle waters are frequently seen throughout the steam generation process. Problems such as reduced equipment performance in reverse osmosis or demineralizer systems due to colloidal material in feedwater or deposition of corrosion products on water-touched surfaces resulting in tube failures are often difficult to analyze and mitigate due, in part, to the lack of "real time" particulate monitoring and data collection. This paper presents basic technologies used for continuous detection of particulates at very low (parts per trillion) levels, and how this information can be used to improve boiler reliability. Case histories are presented where on-line particulate measurement defined the source of a problem, quantified the severity of the problem and provided a solution to the problem. It also discusses the possibility of using the measurement in conjunction with other chemistry parameters to optimize corrosion control additives in the steam/water cycle.

Wolfgang Hater

PPChem 2009, 11(8), 468–474

Organic Plant Cycle Treatment Chemicals – A PowerPlant Chemistry Interview

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David Addison and Les Lloyd

PPChem 2009, 11(8), 475–488

Condensate Polishing and Combined Cycle Gas Turbines – Technical and Financial Justification and Appropriate Technology Selection

Whilst the technical justification for the inclusion of a condensate polisher in a combined cycle gas turbine (CCGT) new generation project is simple and straightforward with the benefits of condensate polishing clearly understood, very few projects worldwide are specified and constructed with a condensate polisher. This situation often arises because the robust financial justification and cost benefit analysis required for the inclusion of a condensate polisher in a project often cannot be completed with the required level of detail to withstand the intense financial scrutiny of new CCGT projects.

Available condensate polishing technologies are reviewed with budget estimates provided for each key technology type. Technical and financial justification methodologies for the inclusion of condensate polishers in CCGT projects are outlined and discussed. The cost of condensate polishing in a new CCGT project is shown to be approximately 1 % of the cost of a standardised, new CCGT unit.

Larry Paul and Gregg Clark

PPChem 2009, 11(8), 489–495

A Higher Chromium Weld Overlay Alloy for Waterwalls and Superheaters

The use of corrosion resistant weld overlay materials has proven to be a very effective method to extend the life of boiler tubes in coal-fired boilers. In order to properly select the best material as a weld overlay, the demands placed upon the material need to be understood. The required material properties for a weld overlay can change with boiler design (such as once-through versus drum boilers), tube function (evaporator versus superheater tubes), and for various regions within the boiler (such as elevation or proximity to over-fire air ports). Material properties that need to be considered include the

physical, mechanical, and corrosion properties, as well as the cost and ease of fabrication. The score card in some of these areas has been less than desired for certain weld overlay materials. Nonetheless, there are usually multiple material choices that will work in most cases. When multiple choices are available, asset owners will generally select the material with the most experience. Since its introduction in 2003, Alloy 33 has continued to gain positive experience as a weld overlay in coal-fired boilers and is therefore gaining acceptance within the industry.

In the furnace region where combustion occurs, the waterwall tubes are exposed to high heat inputs along with corrosive combustion gases and deposits. These conditions can cause rapid corrosion by a mixed sulfidation/oxidation mechanism. The corrosion rates increase further if low NOx combustion practices are used, since this causes a reducing atmosphere that forms more corrosive sulfur species such as H_2S gases and FeS deposits. The corrosion rates increase with tube metal temperatures, which are controlled by the local tube pressure as well as the operating practices (i.e. heat flux rates). In the highest pressure units that operate above the water triple point (supercritical plants) cracking can sometimes also be an issue. This cracking is caused by a corrosion fatigue mechanism and is generally referred to as "circumferential cracking" in the industry. After 5 years of operation in multiple boilers, the high chromium Alloy 33 continues to perform very well with excellent resistance to both corrosion and cracking.

In the convection pass of boilers, high temperature corrosion can severely limit the life of tubing, particularly if a coal ash corrosion (molten salt) mechanism is operating. Some recent investigations have identified carburization and sulfidation as serious problems for convection pass tubes. Corrosion problems in the convection pass area seem to be aggravated by low NOx firing; the completion of combustion further up in the boiler fundamentally changes the corrosive environment that superheater and reheater tubes face. Fortunately, the resistance to all of these forms of corrosion has a common thread: increasing the chromium content of a material increases resistance to carburization, sulfidation, and coal ash corrosion. Because of its high chromium level Alloy 33 has been gaining increasing interest for use on high temperature convection pass tubing. Alloy 33 has been seen to resist corrosion in oil-fired boilers, black liquor recovery boilers, and of course in coal-fired boilers; the previously mentioned corrosion mechanisms operate in these other boiler types as well. Alloy 33 has now been in commercial service for over 3 years and continues to gain positive experience in the field.

Kenneth J. Galt

PPChem 2009, 11(8), 497–507

Cycle Chemistry for Eskom's New 4 800 MW Supercritical Stations

Eskom has begun building two giant new power stations: one, Medupi, in the Limpopo Province, and the other, Kusile, in the Mpumalanga Province of South Africa. Design and specification of a third station, as yet unnamed but designated Coal III, also to be located in Limpopo Province in the vicinity of Medupi and the existing Matimba Power Station, are already at an advanced stage. Each of these new stations consists of 6 x 800 MW (approx.) supercritical boilers with air-cooled condensers; the first units are scheduled to come on-stream in 2011, 2012 and (tentatively) 2014, respectively. The paper discusses the evolution of the cycle chemistry to be applied at these stations as well as its control and monitoring.

Luis Carvalho

PPChem 2009, 11(9), 516–518

Organic Plant Cycle Treatment Chemicals – A PowerPlant Chemistry Interview

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Peter G. Demakos

PPChem 2009, 11(9), 527–532

Improving Thermal Performance and Reducing Water Consumption in Simple and Combined Cycle Plants

Water (resource) issues will continue to have an increased impact on plant design and operation. Closed-loop, evaporative coolers can help deliver required cooling water temperatures and maintain plant performance while utilizing water streams currently considered to be unusable with conventional towers and heat exchangers. This paper introduces these versatile systems, explaining how they can provide solutions to water use, water quality, and outlet temperature, as well as contribute to a reduction in plant emissions (carbon footprint).

Robert D. Bartholomew

PPChem 2009, 11(9), 533–539

Sodium Balancing for Drum-Type Boilers on All Volatile Treatment

Base loaded drum-type boilers on all volatile treatment with good makeup purity and a tight condenser normally maintain boiler water cation conductivities below 0.5 $\mu S \cdot cm^{-1}$. Trace contamination can cause this cation conductivity to rise to 1 $\mu S \cdot cm^{-1}$ or higher. Conservative facilities use 1 $\mu S \cdot cm^{-1}$ as the maximum cation conductivity limit for all operating pressures. We prefer this approach. However, some facilities (particularly units which cycle) have sufficient baseline contamination that it is difficult to maintain cation conductivities below 1 $\mu S \cdot cm^{-1}$ in the boiler water. The higher levels of cation conductivity usually provide an indication of the mineral acid anions present in the boiler water. The amounts of these anions often exceed the equivalent amount of sodium present in the boiler water.

While the boiler water sample pH may be satisfactory (alkaline) when measured at room temperature, the high volatility and low dissociation constant of ammonia at operating temperatures can be insufficient to neutralize trace levels of mineral acids in the solution concentrating at tube surfaces during operation. If the concentration mechanism is sufficient, underdeposit acid corrosion and hydrogen damage can result. To avoid this corrosion, small amounts of sodium hydroxide can be easily estimated (one basically needs the boiler water sodium analyzer to read 54 $\mu g \cdot kg^{-1}$ (54 ppb) per $\mu S \cdot cm^{-1}$ of boiler water cation conductivity) and fed to ensure that the mineral acid anions at tube surfaces are neutralized. The amounts of caustic needed are noticeably lower than those used for boilers on caustic treatment. While not implemented, the basic concept was first developed and recommended to one of our clients in 2004. This paper provides background on the "sodium balancing" treatment approach and limitations and recommendations regarding its application.

Philip J. D'Angelo

PPChem 2009, 11(9), 551–557

Evaluation of Condensate Filtration Technologies in Fossil Plants

Long-term protection of electric power generating station boilers depends upon the quality of their feedwater chemistry with respect to the transport and deposition of corrosion products to the boilers from various corrosion sources in the plant's condensate and feedwater cycle. It is in the utility's best interests to expand their programs to include ways to reduce the transport of corrosion products, especially those that occur during plant start-ups. Condensate filtration is a strategy employed by some utilities with demonstrable results in minimizing corrosion product transport and achieving a return on their investment.

This paper provides a comparative review of available condensate filtration technologies as well as performance data from fossil plants with the new large diameter high flow filtration systems. Additionally, the paper identifies critical parameters to consider before installation as well as the necessity for agreement between utilities and suppliers on common filtration terminology definitions, to insure an "apple-to-apple" basis when comparing a system or technology from more than one supplier.

Geoffrey Bignold

PPChem 2009, 11(9), 558–563

Transport of Iron in Steam/Water Cycles – Sources and Sinks

Iron is transported around steam/water circuits as dissolved ions and particulate oxides. It is necessary, in operational plant, to minimise the source terms and to do whatever practicable to limit the formation of deposits.

The sources of soluble iron species are influenced by local changes in chemical conditions, particularly pH and redox potential. The mechanisms by which mobile particulate oxides are generated are discussed. These are also influenced by changing pH and redox conditions.

The accumulation of deposits is governed by flow effects, concentration processes in boiling zones and changes in solubility with temperature, as well as by electrochemical and local chemical factors.

Realistic targets for the limitation of the transport of iron in steam/water circuits are considered. Although it is concluded that some iron transport in steam/water circuits is inevitable, it remains practicable to set realistic targets, and to demonstrate that they can be achieved.

Miroslav Šťastný and Miroslav Šejna

PPChem 2009, 11(9), 566–572

Condensation of Steam with NaCl Impurity Flowing in a Nozzle and in a Turbine Cascade

The approach used in the paper for condensation of flowing steam is based on binary nucleation of the chemical impurity NaCl and water. Physical and mathematical models are briefly described and applied on the steam flow with condensation in a convergent-divergent nozzle and in a turbine cascade.

The binary nucleation numerical model is tested by the calculation of the flow with condensation in the nozzle with a low expansion rate in the divergent nozzle part of about $\dot{\bar{P}} = 1\,000\ s^{-1}$. Calculation results of pressure distribution are compared with experiments.

The binary nucleation numerical model is used for the calculation of the steam flow with condensation through the 2D-nozzle blade cascade of the first wet stage of the low pressure part of a condensing steam turbine. The calculated flow in the cascade is subsonic.

Piti Srisukvatananan, Derek H. Lister, Robert Svoboda, and Karol Daucik

PPChem 2009, 11(10), 576–581

A CFD Study of Corrosion Product Collection Efficiency of Sampling Nozzles under Power Plant Conditions

Representative sampling of water and steam cycles in power plants is crucial since its impact on operating decisions can be significant. Although industry guidelines for sampling are available, it is recognized that errors may still occur, so efforts to improve sample system design continue in attempts to achieve optimum techniques. This paper investigates the concepts of isokinetic sampling applied to sampling nozzles operating under power plant conditions using CFD (computational fluid dynamics) software. Two different designs of sampling nozzle are assessed for their effectiveness in capturing particles at the nozzle tip – deposition and release along the sample line are neglected. It is shown that the lower the sampling velocity, the higher the apparent concentration, and the effect of sampling velocity is more pronounced in the condition where the Stokes number is greater. The nozzle acts as an obstacle that disturbs the flow field and does not allow true isokinetic conditions to be established. The suggested design nozzle, "the inclined nozzle", is less sensitive to sampling velocity than the commercial nozzle.

Ian Richardson

PPChem 2009, 11(10), 592–597

Air-Cooled Condensers – Chemistry Implications at Kogan Creek Power Station

Corrosion within air-cooled condensers (ACC) is a well-documented phenomenon, however the problems caused by this corrosion and the solutions to these problems can vary from plant to plant. Kogan Creek Power Plant is a supercritical 750 MW coal-fired power plant in Australia that has previously reported severe ACC corrosion and proposed several management strategies. In this follow-up report the implementation and results of these strategies, including increasing the feedwater pH, increasing condensate polisher operating temperature and replacing condensate filters, are discussed. An update on the current situation at Kogan Creek Power Station and future options to further reduce corrosion are also discussed.

PPChem 2009, 11(10), 606–615

Instrumentation for Monitoring and Control of Cycle Chemistry for the Steam-Water Circuits of Fossil-Fired and Combined-Cycle Power Plants

A guidance document on the instrumentation for monitoring and control of cycle chemistry for the steam-water circuits of fossil-fired and combined-cycle power plants was developed within the IAPWS Power Cycle Chemistry Working Group. This technical guidance document has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Doorwerth, The Netherlands, 6–11 September, 2009, for issue by its Secretariat. The members of the IAPWS are: Britain and Ireland, Canada, the Czech Republic, Denmark, France, Germany, Greece, Japan, Russia, and the United States of America, and the associate members Argentina and Brazil, Italy, and Switzerland.

In order to achieve suitable chemical conditions in steam-water circuits it is essential to establish reliable monitoring of key parameters on every plant. This enables the demonstration of operation within cycle chemistry targets, and alerts the operators to the need to take corrective action when the target conditions are compromised. This technical guidance document considers conventional fossil and combined-cycle/HRSG plants and identifies the key instrumentation and monitoring techniques required for each plant type and cycle chemistry treatment. It is emphasized that this is an IAPWS guidance document and that, depending on local requirements, the use of simpler instrumentation may be adequate, whereas more complex techniques and instrumentation may be necessary when specific issues arise.

Pierre Bezzoli and Karsten Cramer

PPChem 2009, 11(10), 617–619

Organic Plant Cycle Treatment Chemicals – A PowerPlant Chemistry Interview

Kenneth J. Galt, Manas M. Masenya, Frikkie Fourie, and Sheila Eksteen

PPChem 2009, 11(10), 620–632

Eskom's New Generation Coal-Fired Power Stations: Reliability Starts at the Water Plant

As Eskom embarks on a new build programme to secure adequate power supplies for South Africa through to 2025 and beyond, its chemists and chemical engineers responsible for the provision of water treatment plant face a new set of challenges – deteriorating raw water qualities in a water-stressed country – whilst at the same time needing to ensure the highest quality demineralised water for power plant use and to adhere to Eskom's zero liquid effluent discharge policy. Selection of the right water treatment processes is critical to success and the reliability of the entire power plant. This paper describes the process selection for the first of these new plants, Medupi Power Station.

András Balogh and Zoltán Szabó

PPChem 2009, 11(11), 642–656

The Heller System: The Economical Substitute for Wet Cooling

As a result of growing environmental awareness – at least in the form of verbal statements – there is a consensus about the importance of applying water conservation type cooling systems. In practice, however, their application is still far behind that of the water-thirsty cooling methods. This paper introduces one of the proven dry cooling: the advanced Heller system (an indirect dry cooling) and its dry/wet derivatives. Besides giving a basic technical and environmental review, results of some economic case studies are also presented. These show how a natural draft Heller system can extend the economic viability of water conservation type cooling systems as compared to wet cooling.

Peter A. Yarnell

PPChem 2009, 11(11), 662–670

Update on the Development of Ultra-Low Residual Resin for Condensate Polishing Applications

This paper reports on the application of a strongly basic anion resin with ultra-low residual chloride content. The first resin charge installed five years ago at a pressurized water reactor nuclear power station remains in service, having produced more than 26 billion liters of condensate without any regeneration and with a current chloride leakage of significantly less than 10 $ng \cdot L^{-1}$. The development and testing of an ultra-low sulfate strongly acidic cation resin, particularly for use in condensate polishers in boiling water reactor units, is also discussed. Data from plant trials is presented.

Devesh Mittal, Venkat Jagannathan, and Narender Singh Bisht

PPChem 2009, 11(11), 671–679

Use of Unique Fractional Electrodeionization in Power Plant Applications

This paper reports on the application of fractional electrodeionization (FEDI) in the production of deionized water. The advantages of this two-stage dual-voltage technology over conventional electrodeionization (EDI) are discussed, including better quality of treated water, higher feed hardness tolerance, ability to handle feedwater quality fluctuations, optimized power consumption, and quick on-site regeneration of media. Operating data and experience from two power plants are presented.

Mark Robson

PPChem 2009, 11(11), 680–688

Chemical Aspects of Flexible Operation

This paper summarises the two sessions and discussion points of the workshop on the "Chemical Aspects of Flexible Operation" held at the recent British and Irish Association for the Properties of Water and Steam (BIAPWS) symposium. Plant design, sampling and instrumentation, and operational issues are addressed, as well as chemical control aspects, operational experience, and operator training.

James Robinson, Robin Kluck, Anthony Rossi, and Luis Carvalho

PPChem 2009, 11(11), 690–699

Organic Chemical Treatment of High Purity Boiler Feedwater – Advantages and Limitations

This paper addresses the application of organic chemicals to treat high purity boiler feedwater. The advantages and limitations of organic chemicals are presented to help plant operators assess the potential value of using organic chemicals in their systems. Their proper use can provide increased corrosion protection not available through the use of inorganic chemicals alone. The authors have found no evidence that these organic treatments or their decomposition products have caused corrosion problems as long as pH is adequately maintained. Many operators avoid using organic chemical treatments because their use causes them to exceed the turbine manufacturer's steam cation conductivity limits, although meeting such limits does not assure that potentially acidic species such as chloride and sulfate are within an acceptable range. Thus it is argued that improved criteria for steam purity and plant friendly methods of monitoring those criteria are needed.

Shunsuke Uchida, Masanori Naitoh, Hidetoshi Okada, Yasushi Uehara, Seiichi Koshizuka, Robert Svoboda, and Derek H. Lister

PPChem 2009, 11(12), 704–717

Effects of Water Chemistry on Flow Accelerated Corrosion and Liquid Droplet Impingement Accelerated Corrosion

Overlapping effects of flow dynamics and corrosion are important issues in determining the reliability and lifetime of major structures and components in light water reactor plants. Flow accelerated corrosion (FAC) and liquid droplet impingement (LDI) accelerated corrosion (LDI (corrosion)) are typical phenomena resulting from both interactions. In order to evaluate local wall thinning due to FAC and LDI (corrosion), a 6-step evaluation procedure for each has been proposed.

(1) Obtain the flow pattern along the flow path with a 1D computational flow dynamics (CFD) code.

(2) Calculate corrosive conditions, e.g., oxygen concentration along the flow path, with a oxygen-hydrazine reaction code for the FAC evaluation. Calculate the flow pattern of liquid droplets in high velocity steam and determine the possibility of their collision with the pipe inner surface for the LDI (corrosion) evaluation.

(3) Calculate the mass transfer coefficients at the structure surface with a 3D CFD code for the FAC evaluation. Calculate the frequency of oxide film rupture due to droplet collision for the LDI (corrosion) evaluation.

(4) Evaluate high risk zones for FAC and LDI (corrosion) occurrence by coupling major parameters.

(5) Calculate wall thinning rates with the coupled model of static electrochemical analysis and dynamic double oxide layer analysis at the identified high FAC and LDI (corrosion) risk zones.

(6) Make a final evaluation of residual life and the effectiveness of countermeasures.

It was demonstrated that the calculated FAC rates had good agreement with the measured rates. Further investigation of the accuracy of the LDI (corrosion) evaluation procedures is currently in progress.

Sang-Hea Shim

PPChem 2009, 11(12), 728–733

Cost-Effective New Liquid Halogen Biocide with Better Performance and Reduced Corrosivity

Halogen biocides, though widely used and largely effective, are corrosive and are unsatisfactory in controlling surface-attached microbes, such as slime. A newly patented product, composed of stabilized chlorine and unreacted bromide, controls surface-attached microbes, is much less corrosive and is much more cost-effective than other halogen biocides.

Ivan Dobrevski and Neli Zaharieva

PPChem 2009, 11(12), 734–739

Bulgarian Experience with the Implementation of ^{235}U Enriched Fuel in WWER-1000 Units

This paper reports on the results of the implementation of TVSA fuel assemblies with up to 4.3 % ^{235}U enrichment and an integrated burnable absorber (Gd) (U-Gd_2O_3 fuel with 5 % Gd_2O_3) in WWER-1000 reactors at Kozloduy Nuclear Power Plant in Bulgaria. Data from the first cycle with 100 % TVSA assemblies show that plant staff was able to maintain the coolant water chemistry within the range demanded by the plant's primary circuit water chemistry requirements. Data indicate that the corrosion processes in the primary circuit remained on the same low level as during previous cycles.

Russell Gerads and Jacob Meyer

PPChem 2009, 11(12), 743–747

Comparison of Different Technologies for the Quantitation of Total Mercury in Complex Waste Streams

Multiple methods promulgated by the EPA for compliance monitoring of mercury in wastewater were investigated and compared to cold vapor inductively coupled plasma mass spectrometry.

This study was performed to identify the limitations and benefits associated with each analytical method and to identify how varying waste streams can induce method failures.

Christian Kunze and Hartmut Spliethoff

PPChem 2009, 11(12), 748–758

Simulation of a Base Case for Future IGCC Concepts with CO_2 Capture

The simulation of complex IGCC (integrated gasification combined cycle) plants is a useful tool for the evaluation of new technologies and the identification of further potential. As part of the HotVeGas project this paper deals with the modelling of an IGCC plant with CO_2 capture using technology believed to be available beyond 2020. The concept developed will be the base case for comparison of emerging technologies and improved process integration. As simulation tools Aspen Plus is used for the gasification island and gas processing while Ebsilon Professional is applied for modelling the combined cycle.

The base design is a dry feed gasifier with full water quench, air side non-integrated air separation unit, 2-stage CO conversion, acid gas removal and combined cycle. The main processes are simulated in detail considering phenomena such as: heat and pressure losses, electrolytic dissociation, non-equilibrium, pH and gas solubility. The models are all verified by manufacturer information. The model developed is found to be capable of simulating complex gasification applications.

Furthermore, the optimum quench water temperature should be in the area of 165 °C. In the case of lignite the fluidized bed drying plant condensate as an alternative quench water source reduces efficiency by 0.3 % The compression of the Claus tail gas along with the CO_2 is efficient but reduces the purity of the stream. Therefore recycling of tail gas is recommended. The concept is adapted for generic hard coal as well as lignite and estimates an efficiency of approximately 37.0 % and 39.9 %, respectively.

Finally, an outlook on strategies for developing more efficient and reliable IGCC concepts is given. Major potentials for IGCC improvement are expected for integrated hot gas cleanup, for implementation of membranes and fuel cells as well as for integration of synthesis of chemicals.

PPChem 101

Fossil Cycle Chemistry

PPChem 2009, 11(1), 61–64

Lesson 11:
Layup of Fossil Plant Cycles

PPChem 2009, 11(2), 122–128

Lesson 12:
Minimum-Level Instrumentation for Plant Cycle Chemistry Monitoring

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PPChem 101

Boiler and HRSG Tube Failures

PPChem 2009, 11(8), 509–512

Boiler and HRSG Tube Failures, Lesson 1:
Introduction and Background

PPChem 2009, 11(10), 586–591

Boiler and HRSG Tube Failures, Lesson 2:
Corrosion Fatigue

PPChem 2009, 11(12), 760–763

Boiler and HRSG Tube Failures, Lesson 3:
Underdeposit Corrosion – A General Introduction

2010's Scientific and Technical Contributions

Robin W. Kluck and James O. Robinson

PPChem 2010, 12(1), 4–16

Optimizing Chemical Treatment of Condensate Systems in Industrial Plants – Tools, Methods, and Strategies

Effective chemical treatment of steam condensate is critical to industrial plant operation, yet in many plants condensate treatments continue to be widely misunderstood, misapplied and improperly monitored. This paper provides a review of the variables that influence condensate treatment performance and offers a suggested road map for designing or optimizing a condensate treatment and monitoring program.

Emmanuel K. Quagraine, Keith Dean Hill, and Fredrick Omorogbe

PPChem 2010, 12(1), 22–40

Evaluation of Organics Removal Options: A Case Study from a Zero Liquid Discharge Power Plant

Although the role of organics in power plant cycle chemistry still appears to be controversial, their adverse effects in the course of makeup water treatment are very familiar and include fouling of ion exchange resins. This paper describes the organic/bio-fouling experience in a boiler makeup water treatment train for a zero liquid discharge plant, which draws on treated sewage water and surface water for cooling and utilizes the cooling tower blowdown to make distillate water from an evaporator prior to final treatment with a mixed bed demineralizer. In a case study, which is the focus of this paper, the performance of the pilot plants of two recommended organic removal techniques (i.e. reverse osmosis and organic trap resin) were compared to the existing activated carbon bed for organic removal prior to the mixed beds. Parameters evaluated for these three techniques (before and after each unit) include bacteria plate counts, organic carbons, inorganic nutrients (e.g. NH_3-N, [NO_3^-+ NO_2^-]-N, P, Mn, and Fe), known parameters that could significantly impact on the performance of the mixed beds (i.e. SiO_2, Cl^-, SO_4^{2-}, Na^+), and various others like pH, conductivity, turbidity, HCO_3^- etc. The effects of oxidizing (i.e. bleach) and non-oxidizing (glutaraldehyde) biocides on the performance of the activated carbon filter were also evaluated.

Joseph Hook

PPChem 2010, 12(1), 42–47

Post-combustion CO_2 Capture: A Techno-Economical Comparison

Due to emissions being subject to increasing constraints following progressively stringent environmental legislation, a new technology is evolving to allow the continuation of energy production using coal-fired plant. This technology is carbon capture. Carbon capture is developing along three discrete routes: pre-combustion, post-combustion and oxyfuel processes. Post-combustion capture, a process of absorption and desorption of CO_2 from flue gas, is the topic of research in a many labs and test rigs across the world, each employing different techniques or absorption media. Two absorption media of interest in modern plant designs are monoethanolamine and chilled ammonia. The medium used defines the chemistry, the thermodynamics and the technical processes throughout the capture system and hence has a major influence on capital costs, operation costs and health and safety considerations. This paper considers the technical aspects of post-combustion capture using monoethanolamine and chilled ammonia and compares each case from an economic viewpoint.

Abstracts 2009

PPChem 2010, 12(1), 52–63

2009's Scientific and Technical Contributions – Part 1

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Mel J. Esmacher and Anthony Rossi

PPChem 2010, 12(2), 68–76

The Impact of Feedwater and Condensate Return Excursions on Boiler System Component Failures

During boiler operation, the transport of contaminants in boiler feedwater or condensate return via hardness excursions or transport of metal oxides due to corrosion can cause fouling and subsequent tube failure due to under-deposit corrosion or overheating. Case histories are reviewed and suitable corrective actions discussed.

Christophe Foret, Nicole Merlet, Guénolé Chaussec, Sergueï Martemianov, Bernard Tribollet, and Wolfgang Hater

PPChem 2010, 12(2), 80–86

Measurement of Biofilm Thickness: An Effective *Legionella* Risk Assessment Tool

The best way to prevent the risk of bacterial growth in water systems is to monitor and to control the microorganisms (biofilm) attached to pipe walls. Three years of laboratory research led two Centre National de Recherche Scientifique (French National Center for Scientific Research) teams (UMR 6008 and UPR 15) to develop a tool designed to determine the average biofilm thickness. The average biofilm thickness measurements carried out on pilot plants fed with natural water were sufficiently accurate and sensitive to monitor the formation and development of biofilm in a water system and to determine the efficiency of the applied treatments. The implementation of appropriate treatments (type and dose of the treatment product) leads to a significant reduction in or even complete removal of the porous layer on the material surface. A reduction of the attached biomass, measured by the sensor, is connected to a decrease in the density of the bacterial attached to the material (viable flora in the plate count agar environment).

Shelton Dias and Andreas Rudolph

PPChem 2010, 12(2), 98–109

Laboratory Evaluation of a Pd-Based Catalyst for Deoxygenation of Stator Cooling Water

The water-cooled stator windings in turbine generators suffer from various forms of corrosion induced by the presence of dissolved oxygen. In the current study, various laboratory experiments were conducted to identify a suitable catalyst for the deoxygenation of stator cooling water (SCW) systems and to qualify the material to be used in a field trial in order to confirm its deoxygenation performance. The work focused on evaluating the Lanxess (formerly Bayer) Lewatit K 7333 catalyst with respect to its physical, chemical, and oxidation stability through accelerated ageing tests as well as its performance under extreme dissolved oxygen and hydrogen concentrations. Potential effects of any water extractable leachables from the catalyst on the materials of construction of the SCW system were also studied. The catalyst was effective in removing dissolved oxygen in the presence of dissolved hydrogen and should be able to meet or exceed the dissolved oxygen specifications ($\leq 20\ \mu g \cdot kg^{-1}$) for SCW stations that operate under low-oxygen mode.

Vickie G. Olson

PPChem 2010, 12(2), 110–113

Evaluating On-Line High Purity Water Oxidizing-Reducing Potential Analysis for Boiler Feedwater Quality

Conditioned boiler feedwater was analyzed with a unique flowing-junction oxidizing-reducing potential (ORP) analyzer in comparison with dissolved oxygen and other parameters. Two different fossil plant boiler chemistries were utilized in the evaluation. Correlations were drawn between ORP, dissolved oxygen, and hydrazine levels to determine the usefulness of this ORP analysis for corrosion control.

Abstracts 2009

PPChem 2010, 12(2), 114–121

2009's Scientific and Technical Contributions – Part 2

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Niels Voges and Wolfgang Hater

PPChem 2010, 12(3), 132–138

Distribution Ratio and Average Surface Coverage of Film-Forming Amines

Film-forming amines have been successfully used as feedwater treatment additives for many years, particularly in industrial power plants. The results of systematic studies of their properties are intended to fill gaps in our knowledge of film-forming amines, so that this technology can be included in the appropriate guidelines for the treatment of steam generators.

Systematic experiments for determining the distribution ratio were therefore carried out in an operating pressure range from 20 to 100 bar using a steam generator pilot plant. Different film-forming amines were used at various initial concentrations. The distribution ratio was calculated by measuring the concentrations of the free film-forming amines in the condensate and in the steam generator (autoclave). The average surface coverage was also estimated by mass balance.

Based on the obtained results and on data from literature on the corrosive properties of chemicals, the film-forming amines were evaluated qualitatively with regard to their application in steam generators. It was found that oleyl propylenediamine has advantageous properties when compared with film-forming amines with different chemical structures.

Vadim Malkov and Dietmar Sievert

PPChem 2010, 12(3), 144–154

Oil-in-Water Fluorescence Sensor in Wastewater and Other Industrial Applications

In order to simplify and accelerate the analyses of oil and grease in industrial wastewaters, particularly those discharged from various parts of the oil-refining process, an ultraviolet fluorescent sensor sensitive to polycyclic aromatic hydrocarbons (PAH) was tested. The correlation between total oil-in-water concentration and the concentration of the model PAH compound was found to be attainable in samples containing stable contents of oils.

Zbyněk Kraus

PPChem 2010, 12(3), 162–169

Flue Gas Desulfurization in the Czech Republic – Lessons Learned

This paper presents experience with various flue gas desulfurization (FGD) systems at the power plants of the ČEZ Group, one of the ten largest energy companies in Europe. Lessons learned through the operation and maintenance of the first generation of FGD units, built and commissioned between 1994 and 1998, have been used to select appropriate design features for the reconstruction of old installations and the erection of new units, to enable compliance with even stricter legal regulations on emissions in the future.

Michael A. Sadler

PPChem 2010, 12(3), 170–178

A Discussion of the Use of Condensate Polishing on Ultra-supercritical Boilers

The ultra-supercritical (USC) boilers now entering service will probably employ condensate polishing to protect their steam/water circuits against corrosion and deposition. It is expected that designs of these advanced boilers will continue to evolve with operating temperatures up to 760 °C (1 400 °F) eventually being used. This paper reviews the types of deep-bed polishers that are currently available and suggests designs that could meet the requirements of future USC plants. If the target for common inorganic impurities is set at $< 1\ \mu g \cdot kg^{-1}$ (ppb), then any of the well-known systems will be suitable when used either in the conventional H-OH mode or in the economical ammonium form. These systems include naked mixed beds, cation-mixed beds, designs using separate beds in separate vessels and a proprietary layered separate bed process. There is a possibility that targets could eventually be set even lower, i.e., at $< 0.1\ \mu g \cdot kg^{-1}$ (ppb). Even this lower target can be met by some naked mixed bed and separate bed polishers and is certainly achievable by cation-mixed bed polishing plants.

Deep-bed polishers remove particulate matter with a reasonable but variable efficiency, so it may be considered necessary to use a prior filtration stage. A number of successful designs of filters are known and considerable plant experience has been gained in the nuclear power field.

Joseph R. Zimmerman

PPChem 2010, 12(3), 180–185

Real-Time Corrosion Product Transport Monitoring Using Online Particle Monitors

This paper introduces the particle monitor as an effective means for continuously sensing and tracking the corrosion product transport. Transient metal oxides, in their insoluble particulate form, can be detected with the particle monitor. When such corrosion product transport monitoring methods are utilized, real-time particulate measurement can be implemented as an additional core parameter for operating and controlling the power plant cycle.

R. Barry Dooley and Wendy Weiss

PPChem 2010, 12(4), 196–202

The Criticality of HRSG HP Evaporator Deposition: Moving towards an Initial Understanding of the Process

Deposition on the inside surfaces of heat recovery steam generator (HRSG) high pressure (HP) evaporator tubing is always a precursor to any of the under-deposit corrosion (UDC) HRSG tube failure (HTF) mechanisms, which continue to rank as the third most important around the world for combined cycle/HRSG units. However, prior to this current work very little was known about the process or morphology of deposition as a function of the HRSG cycle chemistry. Very few HP evaporator tubes had been removed (estimated at < 5 % of the total number of HRSGs) and about the same number of units had been chemically cleaned. About 45 HP evaporator tubes have now been analyzed in this study to characterize the effects of operating time and HRSG cycle chemistry. Some important relationships have become clear which are starting to provide guidance and confirmation of the optimum cycle chemistry that should be used not only to control the UDC mechanisms but which also have a major effect on flow-accelerated corrosion in the lower pressure parts of the cycle. There are also important implications for chemical cleaning of HRSG HP evaporators.

Ladislav Bursik and Albert Bursik

PPChem 2010, 12(4), 206–215

International Fossil Cycle Chemistry Guidelines – Part 1: The Electric Power Research Institute, U.S.A.

This paper, the first in a series of overviews of the most recognized international fossil cycle chemistry guidelines, introduces the Electric Power Research Institute (EPRI) and its current and planned fossil cycle chemistry guidelines. These guidelines cover, among other topics, all-volatile treatment, the phosphate continuum and caustic treatment, oxygenated treatment, the control of flow-accelerated corrosion, cycle chemistry in combined cycle/heat recovery steam generators, and the shutdown, layup, and startup of combined cycle units with heat recovery steam generators.

Marc D. Coleman, Rod A. Robinson, Matthew Williams, Robert Elliott, Martin Clack, and Andrew Curtis

PPChem 2010, 12(4), 218–222

Demonstrating Equivalence of an Alternative Method for SO_2 Emissions Monitoring Using NPL's Stack Simulator Facility

We report the results from a trial at the National Physical Laboratory Stack Simulator Facility of a new alternative method (TGN M21) drafted by the England and Wales Environment Agency for monitoring SO_2 emissions from flues and stacks. The alternative method has been written to address the desire of test houses to move from wet chemistry to instrumental techniques. The method is not instrument specific and can be used with any technique meeting the required performance characteristics, which are consistent with the England and Wales Environment Agency's Monitoring Certification Scheme and EN 15267. The equivalence of the alternative method to the standard reference method (SRM) with regard to the in-field tests was carried out in accordance with CEN TS 14793 using instrumental techniques (non-dispersive infrared, Fourier transform infrared, infrared gas-filter correlation, electrochemical cell and ultra-violet absorption). Using trial mixtures from 0–715 $mg \cdot m^{-3}$ SO_2 (STP) it was demonstrated that the alternative method conformed to the acceptance criteria for repeatability and correlation to the analogous SRM measurements.

Albert Bursik

PPChem 2010, 12(4), 224–230

Degassed Cation Conductivity – A Key Parameter for Steam Quality Surveillance?

With few changes, the cycle chemistry guidelines have advised using the same cycle chemistry parameters with the same or similar numerical values for the continuous plant cycle monitoring of fossil plant streams for several decades. One parameter, however, is conspicuously absent: degassed cation conductivity of steam. The brief appearance of this parameter in one of the guidelines and its subsequent non-inclusion in the revision do not seem appropriate considering the advantages of using this monitoring technique, in particular for cycling and peaking units. This contribution discusses what role degassed cation conductivity should play in the plant cycle chemistry monitoring, and argues for its inclusion in future cycle chemistry guidelines.

Khalid Farooq

PPChem 2010, 12(4), 232–239

Turbine Lubrication Fluid Varnish Mitigation

Varnish deposits on internal surfaces in turbine lube systems result in a number of adverse operational issues, especially the restriction and sticking of the moving parts of servo- or directional control valves, resulting in their malfunction. The lubrication fluid has limited solvency for the varnish-forming material, hence a typical turbine will have the majority of this material as deposits and a relatively small portion as suspension in the fluid phase, in quasi-equilibrium with the deposits. The lube system needs to be cleaned by removing the suspended varnish-forming material from the fluid phase, which allows the deposits to re-entrain into the fluid phase, until the majority of the transferable deposits are removed and the fluid carries no significant amount of the material to have any adverse effect. The methods used for the removal of varnish from turbine lube systems include chemical cleaning/flushing, electrostatic charge induced agglomeration/retention, and the adsorption of the varnish suspended in the oil on an adsorbent medium. The paper discusses an absorption-based removal method that utilizes a fibrous medium that has pronounced affinity for the removal and retention of the varnish-forming material from the fluid as well as the deposits from surfaces that are in quasi-equilibrium with the varnish precursors in the fluid. The filtration medium is a composite, made with cellulose bonded by specially formulated, temperature-cured resins. The absorptive medium exhibits high structural and chemical integrity and has been thoroughly tested on operating turbines, showing reduction in varnish levels from the critical range to below normal range in a relatively short time. The experience with the utilization of the absorptive medium in laboratory tests and in two operating turbines is presented.

Peter J. Clark

PPChem 2010, 12(4), 246–251

Effects of Steam Sample Degassing on CCGT Station Start-up Profile

Many power stations dose feedwater with oxygen scavengers such as carbohydrazide; these compounds remove the dissolved oxygen but release inorganic carbon dioxide into the water. The effect of carbon dioxide upon corrosion levels is a controversial subject and as such is not within the scope of the work discussed in this paper. The effect of carbon dioxide upon conductivity measurements is the major consideration.

Degassed cation conductivity (DGCC) is a widely used technique to remove dissolved gases from high purity water. A typical DGCC instrument consists of a reboiler which raises the temperature of the sample water above its saturation temperature, thus reducing the solubility of gases, such as carbon dioxide, effectively boiling the gas out of the water sample stream.

The present method used for measuring water or steam purity is cation (or acid) conductivity, often denominated as after-cation-exchange conductivity. This technique should indirectly assess levels of anions such as chloride, sulphate, formate and acetate for corrosion avoidance purposes. However, due to the presence of carbon dioxide dissolved in the sample, the monitoring results are not appropriate for this

purpose. The degassed cation conductivity technique can be applied to power station start-ups when the steam conditions have to be monitored closely. By removing the dissolved carbon dioxide from the sample stream, more accurate information about the actual purity of the water or steam is given. This paper will give the results and economic benefits when this monitoring technique is applied to a cold start on a combined cycle gas turbine (CCGT) power station.

Brozia Clark, Andrew Feicht, Andy Justason, and Derek H. Lister

PPChem 2010, 12(5), 256–263

The Effectiveness of Titanium Additions on Mitigating Flow-Accelerated Corrosion under PWR Feedwater Conditions

Titanium as an additive in CANDU® primary coolant has been shown to reduce the rate of flow-accelerated corrosion (FAC) of the carbon steel feeder pipes that direct the coolant from the core to the steam generators. The mechanism apparently depends upon the incorporation of titanium (Ti) into the magnetite oxide that normally forms on the steel in high-temperature water. Localized corrosion in steam generator crevices has also been mitigated by additions of Ti, apparently by a similar mechanism. It would seem possible, therefore, that Ti as an additive would mitigate FAC of carbon steel piping in pressurized-water reactor (PWR) feedwater systems. To explore this concept, an experimental program sponsored by the Electric Power Research Institute has utilized a high-temperature water loop to evaluate the effectiveness of adding Ti-based compounds to simulated PWR feedwater. On-line tubular probes measured corrosion directly at system conditions by monitoring the FAC-induced thinning of the tube walls with an electrical resistance technique. In the program, three compounds were tested in the loop, each at a concentration producing several $\mu g \cdot kg^{-1}$ equivalent of elemental Ti at the probes. Coolant chemistry conditions were: ammoniated water at $pH_{25\,°C}$ of 9.2, hydrazine at 40 $\mu g \cdot kg^{-1}$ (ppb) and temperature of 140 °C. For each additive, plots of the probe internal radius against time directly showed the progression of FAC, and comparison with periods before the addition demonstrated any mitigating effect of the Ti. Indications of the effects of coolant velocity on FAC during Ti addition were obtained by varying loop pumping rates. Destructive examination of probes after exposure revealed any change in surface appearance and constitution brought about by the additive. The paper describes the experiments and results and assesses the possibility of using Ti compounds for mitigating FAC in feedwater systems in operating PWRs.

Ladislav Bursik and Albert Bursik

PPChem 2010, 12(5), 266–275

International Fossil Cycle Chemistry Guidelines – Part 2: VGB PowerTech e.V., Germany

This paper, the second in a series of overviews of the most recognized international fossil cycle chemistry guidelines, introduces the VGB PowerTech and its current and planned fossil cycle chemistry-related guidelines and instruction sheets. In addition to plant cycle chemistry treatments, these documents cover, among other topics, the selection and the behavior of materials for condenser and heat exchanger tubing, makeup water and cooling water treatment, chemistry in district heating circuits, and internal cleaning and preservation of steam generators and other plant cycle components.

Shunsuke Uchida, Hideki Takiguchi, and Derek H. Lister

PPChem 2010, 12(5), 278–295

Instrumentation for Monitoring and Control of Water Chemistry for Light-Water-Cooled Nuclear Power Plants

Based on the IAPWS technical guidance on "Instrumentation for Monitoring and Control of Cycle Chemistry for Steam-Water Circuits of Fossil-Fired and Combined Cycle Power Plants," the latest situation regarding instrumentation for nuclear power plants is discussed.

As a result of the discussion, it is concluded that:

(1) Reliable and safe operation of plants is established by the application of suitable chemical conditions in plant cooling systems, which should be supported by the selection of suitable control targets for monitoring and by the application of reliable instruments.

(2) The minimum level of key instrumentation consists of on-line as well as off-line instruments for monitoring the key parameters:
- on-line: pH, conductivity, cation conductivity, O_2 and H_2 concentrations, electrochemical corrosion potential;
- off-line: radioactive nuclides (^{60}Co, ^{58}Co, ^{131}I, etc.), and the concentrations of metallic species (Fe, Cu, Co, etc.) and other species (B, Li, N_2H_4).

(3) The application of high-temperature water chemistry sensors for in-situ measurement of cooling water properties and diagnosis of anomalous conditions based on monitored data is an important consideration for the future.

(4) A technical guidance for nuclear plants, similar to the one issued for instrumentation and monitoring of chemistry in fossil-fired and combined-cycle plants, may be useful in the future, when common features could be combined in a unified guidance.

Stephen Bell and Frank Dunand

PPChem 2010, 12(5), 296–303

A Comparison of Amperometric and Optical Dissolved Oxygen Sensors in Power and Industrial Water Applications at Low Oxygen Levels (< 5 µg · kg^{-1})

In this paper, the performance of both optical and amperometric oxygen sensors in both fossil and nuclear power plant applications is compared and discussed. The results of independent tests conducted to evaluate the suitability of a new sub-µg · kg^{-1} optical sensor for use in power plants and industrial applications of different types are presented. The issues of stability and repeatability, the influence of dissolved hydrogen and performance under flow variation are addressed. In terms of repeatability, accuracy, response time and maintenance efforts the optical sensor is shown to be comparable or superior to amperometric sensors.

Rolf Nagel and Jürgen Brinkmann

PPChem 2010, 12(6), 316–324

Brackish and Seawater Desalination for Process and Demineralised Water Production for Large Power Plants in the North Sea Region

Large power plants for power generation from fossil fuels are constantly being optimised in order to improve their efficiency. One element of the overall considerations is once-through cooling with brackish or seawater on sites near the sea. In addition to the higher overall efficiency, such sites – thanks to their connection to ocean shipping – also offer infrastructural advantages regarding fuel supply and residual material disposal compared to inland sites. Because the cooling water intake and discharge structures have to be built anyway, they lend themselves to also producing the process and demineralised water from the brackish or seawater. In this case, the use of fresh or drinking water as resources can be minimised. In the following report, we present a pilot study using ultrafiltration and reverse osmosis on a North Sea site with raw water intake from a seaport basin.

Paul McCann and Mark Robson

PPChem 2010, 12(6), 328–332

Report on the BIAPWS 2010 Workshop and Symposium on Power Plant Chemistry

The British and Irish Association for the Properties of Water and Steam held its annual Workshop and Symposium on Power Plant Chemistry on 20–21 April 2010 at Chilwell, Nottingham. Summaries of the proceedings at the event are provided.

Geoff Bignold

PPChem 2010, 12(6), 336–343

Corrosion Control in HRSGs – The Influence of Flexible Operation Regimes

Many of the combined cycle plants in operation were designed and originally operated for base load operation. However, changes in fuel prices and in the overall margin of plant availability over demand have led to many units operating repeatedly at low load and with many shut-down/start-up cycles. It has become essential to understand and manage the additional complexities that derive from such operation.

On the waterside, the optimisation of the design for full load operation can lead to non-optimal thermal conditions at low load. Short term shut-downs can cause large scale accumulation of condensate in superheaters and reheaters. Longer term shut-downs require consideration of storage regimes that minimise corrosion. Cyclic operation can

cause additional transport of iron oxides within the circuit and can occasionally lead to corrosion fatigue failures. There are differences of behaviour between vertical duct and horizontal duct designs, which require different approaches to the storage options.

On the gas side, flexible operation frequently results in surface temperatures that are low enough to yield acidic dew formation. The resulting corrosion product on finned steel tube surfaces is porous and voluminous. It can impact upon heat transfer and lead to increased gas side pressure drop. Acid induced stress corrosion cracking has occasionally been observed. Approaches to the control of these problems remain to be improved to the point at which they can be regarded as solved.

Daniela Huenert, Wencke Schulz, and Axel Kranzmann

PPChem 2010, 12(6), 344–352

Simultaneous Oxidation and Carburization under Oxyfuel Conditions

The combustion of coal in CO_2-reduced oxyfuel power plants requires creep resistant and corrosion resistant materials which can withstand high temperatures up to 600 °C (873 K) and CO_2-rich atmospheres. Among the heat resistant materials, the 9–12 % chromium steels have been proven to resist high wall temperatures in conventional power plants and are suitable as membrane walls, superheaters and steam piping.

During oxyfuel combustion a flue gas is generated which consists mainly of H_2O (x_{H_2O}=0.3) and CO_2 (x_{CO_2}=0.7). The present paper is focused on the corrosion of 9–12 % chromium steels under oxyfuel conditions in a temperature range between 550 °C (823 K) and 625 °C (898 K).

Depending on the chromium content of the 9–12 % chromium steels, carburization of the base material, perlite formation and carbide formation were observed. Alloys with lower chromium content form a non-protective oxide scale with perlite at the scale–alloy interface. Steels with 12 % chromium have a small growing oxide scale with enlarged $M_{23}C_6$ particles at the scale–alloy interface. The carburization of the base material is found to be increased for the 9 % Cr steel. Higher pressure of the flue gas results in the formation of less resistant scales and causes accelerated carburization of the base materials. However, the carburization has an impact on the mechanical properties at the surface and leads to an embrittlement, which is deleterious during thermal cycling.

Oxidation kinetics, phase analysis of the scale (transmission electron microscope) and carburization depths (microprobe) of the base materials are presented.

Václav Koula, Martin Dráb, and Michal Havavka

PPChem 2010, 12(6), 358–367

Possibilities of the Acoustic Emission Method for the Detection of Flow-Accelerated Corrosion

The text presents possibilities for the detection of flow-accelerated corrosion (FAC) using the method of acoustic emission on power plant steam piping with steam pressures of 1.5–6.0 MPa and temperatures up to ca. 300 °C. A continuous acoustic emission (AE) signal sampling at the frequency of 2 MHz allows use of the current methods of signal analysis. AE signals were acquired both on steam piping in the unaffected state (without the FAC processes) and on locations where currently active FAC processes have already been confirmed (by measuring of the steam piping wall thickness). Data analysis revealed the spectral time variance (STV) parameter, which allows the detection of the FAC process during power plant operation. Based on this a special-purpose STV analyzer with very simple handling, allowing immediate evaluation of the acquired data, was designed and constructed. Its usage allows steam pipeline sections to be searched for active FAC processes during power plant operation. This helps refine the plans for time-consuming and expensive measurement of the wall thickness of the steam pipeline segments during operational shutdowns of the power plant blocks. It is possible to continue periodical measurements in places of already active FAC and in this way to monitor the FAC trend. Described procedures help reduce the costs for identification of the steam pipeline sections with active FAC and increase the safety of power plant operation.

Takahiro Nakane, Teruyuki Goto, Li-Bin Niu, and Hiroshi Takaku

PPChem 2010, 12(7), 376–383

Effect of Chloride and Sulfate Ions in Simulated AVT Waters on Electrochemical Corrosion Behavior and Oxide Film Characteristics of LP Steam Turbine Materials in Power Plants

Electrochemical corrosion behavior and film characteristics were investigated in simulated all-volatile treatment (AVT) waters containing both sulfate (SO_4^{2-}) and chloride (Cl^-) for 13Cr, 16Cr-4Ni, 3.5NiCrMoV and high-purity 9CrMoV steels of low-pressure (LP) steam turbines in power plants. Concerning the 13Cr, 16Cr-4Ni and high-purity 9CrMoV steels, the corrosion pit growth proceeded with an increasing content of SO_4^{2-} up to 50 mg · kg^{-1} in the test water with 100 mg · kg^{-1} Cl^-, although a SO_4^{2-} concentration above 50 mg · kg^{-1} in the test water suppressed the corrosion pit growth due to the combined effect of Cl^- and SO_4^{2-}. No corrosion pits occurred for 3.5NiCrMoV steel, which showed predominantly general corrosion in the test waters with Cl^- and SO_4^{2-}. It is concluded that both the heat-treatment-improved 16Cr-4Ni steel for blades and the newly developed high-purity 9CrMoV steel for rotors have a high resistance to pitting corrosion.

Holger Topp, Dieter Steinbrecht, Wolfgang Hater, and André de Bache

PPChem 2010, 12(7), 388–395

The Influence of Film-Forming Amines on Heat Transfer during Saturated Pool Boiling

The heat transfer coefficients during pool boiling of water at steel heating surfaces are subject to irreversible temporal changes. The influence of the responsible physicochemical processes on the steel surface was investigated by thermo-technical measurements in a special apparatus using conditioned water. For this purpose an oxide layer, whose surface structure, composition and thickness vary with the respective kind of treatment, was generated on steel tube samples under specified conditions.

Due to their surface activity, film-forming amine-based organic corrosion inhibitors feature a theoretical improvement potential regarding the heat transfer in nucleate boiling at steel heating surfaces. The intensifying impact of these filming agents on bubble evaporation during pool boiling compared to a classic water treatment was quantified in long-term tests. The impact of the corresponding conditioning program was examined and characterised by means of analytical methods. Significantly higher heat transfer coefficients were determined for film-forming amine treated tubes as compared to classic conditioning.

Ladislav Bursik

PPChem 2010, 12(7), 396–399

The Cetamine® Symposium "Film-Forming Amines in Plant Cycles"

This contribution gives an overview of the Cetamine® Symposium "Film-Forming Amines in Plant Cycles" held in Essen, Germany, on May 19, 2010. Brief summaries of all the presentations at the symposium are given.

Manuel Sigrist

PPChem 2010, 12(7), 402–413

Seven Sins of Steam Sampling

Over the past 20 years the main components of power plants such as gas turbines, steam turbines, boilers, and plant control systems have been continuously improved. Strangely, during the same period an auxiliary system with interfaces to several of these main components has hardly seen any changes: the steam/water sampling and analysis system (SWAS).

For engineering, procurement, and construction contractors and boiler manufacturers, it is still common practice to specify designs which are out of date. Neither the changed requirements of modern power plants nor the possibilities offered by state-of-the-art online instrumentation are taken into account.

With a broad palette of sampling system examples from around the world, the most common SWAS design "sins" are illustrated. Alternatives presented illustrate that a water/steam sampling system does not have to be a purgatory for the plant chemist and that reliable measurements, ease of maintenance and low cost of ownership can be achieved.

Tony Juratowitch

PPChem 2010, 12(7), 414–425

The Applicability of Using Underwater Acoustic Sensors in Polisher Separation Regeneration Vessels for Determining Polisher Resin Total Levels and Resin Interface Levels

The applicability of using underwater acoustic sensors in polisher separation regeneration vessels for measuring polisher resin total levels and resin interface levels was determined on Eraring Energy's polishing regeneration plant. Ascertaining the total resin volumes and resin interface levels at certain stages of the resin regeneration process in the polisher separation vessels is extremely important. Total volumes need to be checked at early stages of the regeneration process to ensure the hydraulically transported resin has not remained in the pipework or service vessels. Interface levels of the resins are important to prevent cross-contamination of either the cation or anion resin by regenerant chemicals.

Verification of resin levels within the polisher vessels involves manual intervention and current procedures require operating staff to ascend portable steps to platform heights of 3.3 m above floor level. Eraring Energy recognised the potential for accidents to occur when staff were accessing the platforms and sought to eliminate this manual check procedure.

Investigations led Eraring Energy to trial sophisticated level detection equipment which had the capability of underwater material profiling. Eraring Energy's primary objective centred on eliminating the manual check procedure by installing detection equipment which could purposely detect and trend the total resin volumes and the resin interface levels. Accurate and reliable detection of resin levels would also permit Eraring Energy to automate the resin checking requirement and thus provide quicker turnaround times on polisher regenerations as no 'stop and hold' steps would then be required in the regeneration process control system program.

This paper details the process in investigating, sourcing and trialling a proprietary acoustic underwater sensor to determine the polisher resin total volume and interface levels in Eraring Energy's condensate polishing regeneration vessels.

The outcome of the trial has provided encouraging results in regard to the instrument's capability in determining total resin volumes and this may allow Eraring Energy in the future to eliminate the safety issues from staff accessing platforms at heights. However, the instrument's failure to detect resin interface levels requires on-going fine-tuning and modifications, and Eraring Energy are implementing strategies to overcome this problem.

Massimo Bienati and Paolo Cavezzale

PPChem 2010, 12(7), 426–433

Fabric Filter Design and Operation Experience in Coal-Fired Power Plants

This paper is focused on providing a brief overview of the experiences of the Termokimik Corporation (TKC) in particulate removal by means of fabric filtration in coal-fired power plants. From the first commercial installation at the end of nineties to the most advanced filters worldwide performing in Torrevaldaliga Nord, the main design criteria and technical results are summarized. TKC experience in fabric filtration is now exceeding 40 years and covers a wide range of applications from glass factories, foundries and steel plants, blast furnaces to waste incinerators. Experience with coal-fired power plants is relatively new because only recently did several utilities start using fabric filters instead of electrostatic precipitators. In particular, ENEL, one of the most important power companies in Europe, began making extensive use of fabric filters on coal-fired boilers during the end of the nineties. Since then, TKC has accumulated more than 4 600 MW of references on coal-fired boilers.

The International Association for the Properties of Water and Steam

PPChem 2010, 12(8), 440–456

Volatile Treatments for the Steam-Water Circuits of Fossil and Combined Cycle/HRSG Power Plants

A guidance document on volatile treatments for the steam-water circuits of fossil and combined cycle/HRSG power plants was developed within the IAPWS Power Cycle Chemistry Working Group. This technical guidance document has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Niagara Falls, Canada, 18–23 July 2010, for issue by its Secretariat. The members of IAPWS are: Britain and Ireland, Canada, the Czech Republic, Denmark, France, Germany, Greece, Japan, Russia, and the United States of America, and Associate Members Argentina and Brazil, Italy, and Switzerland.

In order to control corrosion throughout the steam/water circuits of fossil and combined cycle/HRSG plants, it is essential for the operator of the plant to choose and optimize a chemical treatment scheme that is customized to that plant. Normal target values for the appropriate level of instrumentation around the cycle must be chosen.

This technical guidance document considers fossil and combined cycle/HRSG plants and identifies the normal target values for each plant type when operating with a volatile treatment. It is emphasized that this is an IAPWS guidance document and that, depending on local requirements, the normal or target values will need to be customized for each plant depending on the actual conditions of operation, the equipment and materials installed, and the condenser cooling media.

Mark Wyburn

PPChem 2010, 12(8), 460–474

Cycle Chemistry Improvement Program at Eraring Power Station

This paper discusses the cycle chemistry improvement program being undertaken at Eraring Power Station in the state of New South Wales, Australia. This program commenced in 2007 following an external benchmarking audit that found the cycle chemistry performance was low compared with other worldwide organisations. The aim of the program is to achieve the best practice in cycle chemistry within the limitations of the plant. Details are given on why this improvement program was necessary, what problems were discovered by plant investigations, how change is being achieved, and what is planned for the future.

K. Anthony Selby

PPChem 2010, 12(8), 478–483

The 30th Annual University of Illinois Electric Utility Chemistry Workshop – Extending the Life and Reliability of Power Plant Equipment through Improved Chemical Control

In June this year, the 30th Annual University of Illinois Electric Utility Chemistry Workshop took place in Champaign, IL, U.S.A. The content of the workshop and abstracts of the papers presented at this event are compiled in this paper.

André Zander and Helmut Nopper

PPChem 2010, 12(8), 484–489

Evaluation of Wall Thinning Affects Caused by Superposition of Flow-Induced Degradation Effects with the COMSY Code

The surveillance of wall thinning effects caused by flow-induced degradation in piping and vessels is one of the key issues for the safe operation of thermal power plants, as wall thinning may cause spontaneously occurring component failures. For the safe identification of system areas which are sensitive to wall thinning, a comprehensive plant-wide strategy needs to be applied, considering the effects and superposition of different degradation modes.

Flow-induced corrosion (FIC), e.g., flow-accelerated corrosion (FAC), liquid droplet impingement corrosion (LDI) and cavitation corrosion is a degradation process resulting in wall thinning of piping, vessels, heat exchanger and further equipment made of carbon and low-alloy steel. The FIC degradation mechanism occurs only locally under specific condition of flow, water chemistry, temperature and materials applied.

In some cases combined effects can occur. These are for single-phase flow conditions FAC and cavitation corrosion or for two-phase flow conditions, the combined occurrence of FAC and LDI.

Within the scope of this paper two examples will be given for the identification and detailed evaluation of a sub-system affected by the superposition of FAC with cavitation erosion and LDI.

David M. Gray

PPChem 2010, 12(8), 492–498

Practical Quality Assurance of On-Line Analytical Measurements

Much has been presented about analytical instrumentation, its use in making on-line measurements, and plant control based on the results. This article presents a summary of practical recommendations for achieving good results and verifying them for parameters of conductivity, pH, ORP and dissolved oxygen. The old saying GIGO (garbage in: garbage out) certainly applies to analytical measurements. Means to assure quality of the input to improve the reliability and accuracy of the output are provided.

Christopher Hegger

PPChem 2010, 12(9), 504–507

Colloidal Silica and Its Effect on Water Treatment Plants and Boiler Chemistry

A sudden increase in source water colloidal silica can ultimately lead to significant impacts on boiler chemistry compliance and costly unit load reductions if not adjusted for in primary water treatment systems. In this paper an actual event is described in which significant quantities of colloidal silica in the source water passed through into the condensate system of a coal-fired plant undetected. The steps taken to correct the situation are discussed, as well as the lessons learned and measures taken to prevent such an occurrence in the future.

R. Barry Dooley, Kevin J. Shields, and Stephen J. Shulder

PPChem 2010, 12(9), 508–520

Lessons Learned from Fossil FAC Assessments

In their work the authors have noted great diversity in the Flow-Accelerated Corrosion (FAC) Programs used at conventional fossil power plants. The results and findings of FAC Program assessments conducted at 22 conventional plants are summarized and discussed. By comparing the FAC Program characteristics and relevant unit features with damage and failure experiences, a number of common factors requiring attention from fossil utility organizations have been identified. The assessment experiences have also provided a picture of trends in specific FAC activities and general awareness within the conventional fossil fleet. One of the most important aspects of these studies is that while a few new locations of FAC have been found, there is some consolidation of the most frequently found locations.

Peter S. Jackson, David S. Moelling, and Mark J. Taylor

PPChem 2010, 12(9), 526–531

Ten-Year Retrospective Look at HRSG FAC Assessment and Incidence

A decade of experience with flow-accelerated corrosion in heat recovery steam generator pressure parts is summarized in this paper. Flow-accelerated corrosion problems in the earlier combined cycle plants are compared to those in later plants. Further development of predictive models for flow-accelerated corrosion in heat recovery steam generators as well as improving technology for nondestructive evaluation of poor accessible finned tube areas and bare tube segments at headers of horizontal gas path heat recovery steam generators is required.

Flow-accelerated corrosion is shifting from a rapid wear phenomenon affecting large areas of heat recovery steam generator components to a slower wear process with the risk of locally higher rates. In many cases the higher wear rates are not detectable by wear measurements in other more accessible locations in relation to gross flow models. More detailed fluid modeling tools are required to identify local high-risk locations as well as the impact of operational changes on flow-accelerated corrosion wear.

Chip Westaby

PPChem 2010, 12(9), 534–539

Hydrocarbon in Water Monitors Using Fluorescence

Quick and reliable monitoring for hydrocarbons in wastewater, cooling and heating water is valuable to industrial facilities. Water monitors using fluorescence are capable of detecting hydrocarbon concentrations in water as low as 5 $\mu g \cdot L^{-1}$, and can thus give operators an early warning of oil leaks and spills, allowing costly repairs, cleanup and fines to be avoided. This paper introduces the fluorescence monitors and presents data from recent studies to illustrate the detection levels of the technology.

George J. Licina

PPChem 2010, 12(9), 540–548

Principles of Corrosion Monitoring

Power plants continue to experience failures in various components as a result of numerous corrosion mechanisms. Changes in chemistry regimes alone are often not sufficient because there is no real measure taken of their effectiveness. Corrosion monitoring provides a simple and economical method for evaluating the effectiveness of water chemistry and operational controls on the corrosion of plant materials. It provides important insight into the condition of plant materials, including the timing of degradation, the influence of plant operating history, and the effectiveness of treatments. This paper reviews the principles of corrosion monitoring tools, and how and where to best apply them.

Shunsuke Uchida, Masanori Naitoh, Hidetoshi Okada, Taku Ohira, Seiichi Koshizuka, and Derek H. Lister

PPChem 2010, 12(9), 550–559

Evaluation of FAC Simulation Code Based on Verification and Validation

In order to apply a computer simulation code of flow-accelerated corrosion to evaluate the effects of water chemistry improvement on the wall thinning of pressurized water reactor (PWR) secondary piping, the accuracy and applicability of the code were confirmed based on verification and validation processes. The verification process of the code and the validation process based on data from laboratory experiments have been reported previously. In the present paper, the validation process of the code based on wall thinning rates measured at a PWR plant is discussed. Corrosive conditions were calculated with a O_2-N_2H_4 reaction analysis code. Precise flow turbulence at major parts of the system was analyzed with 3D CFD codes to obtain mass transfer coefficients at structure surfaces. Then, wall thinning rates were calculated with the coupled model of electrochemical analysis and oxide layer growth analysis by applying the corrosive conditions and the mass transfer coefficients. From comparison of the calculated wall thinning rates with hundreds of measured results at the secondary piping of the actual PWR plant, it was confirmed that the calculated wall thinning rates agreed with the measured ones within a factor of 2 and the accuracy of the evaluation model for residual pipe wall thickness was within an error of less than 20 %. Finally, the FAC simulation code was applied to the evaluation of the effects of oxygen injection into the feedwater line.

Andy Rudge, Ian S. Woolsey, and Andrew Moore

PPChem 2010, 12(10), 564–576

Wythenshawe Boiler Rig – Thirty Years of Support to the UK Nuclear Power Industry

The Wythenshawe Boiler Rig in Manchester, UK, recently celebrated thirty years of operation in support of the UK nuclear power industry. The Boiler Rig, owned by EDF Energy and operated on EDF Energy's behalf by Serco plc, is a full scale once-through boiler test facility for the investigation of chemistry and corrosion related topics. This paper presents an overview of the design and operation of the Boiler Rig together with some of the technical highlights from its thirty years of operation, many of which have relevance to power plant operations beyond those plants for which the work was performed.

R. Barry Dooley and Robert W. Anderson

PPChem 2010, 12(10), 579–588

Flow-Accelerated Corrosion (FAC) in HRSGs

The paper provides information on flow-accelerated corrosion (FAC) programs for heat recovery steam generators (HRSGs) gathered from one-day assessments of 19 HRSGs worldwide. The primary goal of these assessments was to assist operators in being proactive in identifying the key drivers for flow-accelerated corrosion, but they have also provided a clear picture of exactly where the weaknesses in addressing FAC are occurring. The paper outlines the approaches to optimizing the cycle chemistry to avoid FAC. These key messages can easily be applied by operators to change the current situation of waiting for FAC failures and damage to occur.

Derek H. Lister and Shunsuke Uchida

PPChem 2010, 12(10), 590–597

Reflections on FAC Mechanisms

Flow-accelerated corrosion of carbon steel in steam-raising systems is obviously dominated by fluid-dynamic parameters such as turbulence and by water chemistry that promotes dissolution of the normally protective magnetite film; the mechanism is often formulated simply as the product of the mass transfer coefficient and the undersaturation in dissolved iron. Additives to the coolant, such as dissolved oxygen or ammonia, and elements in the steel, such as chromium, are then considered to inhibit flow-accelerated corrosion (FAC) by making the magnetite less soluble.

This approach can be useful for predicting locations susceptible to FAC and for supporting proposals for palliative treatments, for example. It is rarely an accurate predictor of FAC rate, however, which may be attributable to its being applied in situations where surface reactions play a part. These issues are discussed in the light of recent research results and it is suggested that mechanisms introducing elements of mixed control may often be more appropriate.

PPChem 2010, 12(10), 598–599

Flow-Accelerated Corrosion (FAC) in Fossil and Combined Cycle/HRSG Plants: First International Conference, June 29 – July 1, 2010

This conference marked the first international gathering of scientists and engineers at a meeting focused on the subject of FAC in fossil and combined cycle steam and power systems. Five organizations were involved with the conference:

- CEATI (Centre for Energy Advancement through Technological Innovation) International (Canada)
- Combined Cycle Journal
- Electric Power Research Institute (EPRI)
- PowerPlant Chemistry Journal
- Structural Integrity Associates, Inc. (SI)

Barry Dooley (Conference Chairman), Kevin Shields (Conference Co-Chairman) and Steve Shulder of SI organized the conference, assembled the technical program and arranged the exhibition.

The organizers worked with an International Advisory Group of 20 FAC specialists from around the world. In all there were 177 registered attendees from 21 countries. The technical program consisted of 40 papers presented by researchers, plant operators and representatives of service organizations.

By design the meeting was linked with FAC2010, organized by Electricité de France (EDF), a conference focusing on FAC in nuclear power stations, held in May 2010 in Lyon, France. Common attendees of the two conferences helped to connect the knowledge from the fossil and nuclear areas.

Ian Richardson,
Bruce Kerr,
Ian Rawlings,
Denis Doucet, and
Gary Joy

PPChem 2010, 12(10), 602–609

CS Energy's Flow-Accelerated Corrosion Experience (Part 1 of 2)

Flow-accelerated corrosion (FAC) is a common problem encountered by operators of thermal power plants around the world. This two-part paper describes the experiences of the Australian electricity generation company CS Energy in identifying and addressing the problems associated with FAC. This paper discusses the different approaches and strategies used to deal with both single- and two-phase FAC in drum boilers with copper alloyed feedwater heaters, drum boilers with all-ferrous metallurgy, once-through supercritical units, heat recovery steam generators (HRSGs) and air-cooled condensers (ACCs).

Natasha Cudmore

PPChem 2010, 12(10), 612–623

Determination of Copper in Salt Cooling Water by Anodic Stripping Voltammetry to Optimise Condenser Performance

Successful management of the ferrous chloride dosing system and the Taprogge ball condenser tube cleaning system at Eraring Power Station (EPS), NSW, Australia, relies on measurements of copper in the salt cooling water prior to and after each condenser pass. However, obtaining an accurate copper measurement in the challenging matrix of salt water used has proven difficult. EPS conducted trials of two methods for the measurement of copper in natural waters, differential pulse anodic stripping voltammetry (DPASV) and graphite furnace (electrothermal) atomic absorption spectroscopy (GFAAS). This paper discusses the results of copper measurements from the various trials undertaken on the condenser systems. Based on the trials of this instrument, DPASV was chosen as the preferred method of analysis for the purposes of optimising condenser performance and efficiency, minimising ferrous chloride chemical dosing and tube corrosion, and maximising heat transfer.

Stefan Ritter,
Vasil Karastoyanov,
Sousan Abolhassani-Dadras,
Ines Günther-Leopold,
and Niko Kivel

PPChem 2010, 12(11), 628–635

Investigation of Noble Metal Deposition Behaviour in Boiling Water Reactors – The NORA Project

NobleChem™ is a technology developed by General Electric (nowadays GE-Hitachi) to reduce stress corrosion cracking (SCC) in reactor internals and recirculation pipes of boiling water reactors (BWRs) while preventing the negative side effects of classic hydrogen water chemistry. Noble metals (Pt, Rh) acting as electrocatalysts for the recombination of O_2 and H_2O_2 with H_2 to H_2O and thus reducing the corrosion potential more efficiently are injected into the feedwater during reactor shutdown (classic method) or on-line during power operation. They are claimed to deposit as very fine metallic particles on all water-wetted surfaces, including the most critical regions inside existing cracks, and to stay electrocatalytic over long periods of time. The effectiveness of this technology in plants still remains to be demonstrated. Based on highly credible laboratory experiments down to the sub-$\mu g \cdot kg^{-1}$ Pt concentration range, SCC mitigation may be expected, provided that a stoichiometric excess of H_2 and a sufficient surface coverage with very fine Pt particles exist simultaneously at the critical locations [1]. Very little is known about the deposition and (re-)distribution behaviour of the Pt in the reactor.

For the validation of this technique the research project NORA (noble metal deposition behaviour in BWRs) has been started at the Paul Scherrer Institute (PSI) with two main objectives: (i) to gain phenomenological insights and a better basic understanding of the Pt distribution and deposition behaviour in BWRs; (ii) to develop and qualify a non-destructive technique to characterise the size and distribution of the Pt particles and the local concentration of Pt on reactor components. This paper presents the objectives of the project, the planned work and a brief description of the status of the project.

Amiel Herszage and Daniel Zinemanas

PPChem 2010, 12(11), 638–644

Flow-Accelerated Corrosion: Numerical Simulations of the Flow Field and Mass Transport in Fittings

In the current study numerical analyses of the flow field and mass transport in various fittings were performed using computational fluid dynamics (CFD) methods. Their main aim was defined as the evaluation of the concentration profiles and local mass transport flux characteristics and the investigation of the transport factors affecting the flow-accelerated corrosion (FAC) wear mechanism. The cases studied here include the flow in nozzles and two T type bifurcations. In all cases, a good match between the predictions for the turbulent mass transfer distribution and observations was found. These findings suggest that the mass transfer flux at the wall and transfer coefficient, and thus the FAC rate and location, are in fact primordially determined by the local turbulent concentration and velocity fluctuations near the wall, as given by the turbulent mass transport term $\overline{c'u'_j}$ and not by the mean axial flow or other hydrodynamic variables to which they are generally linked. Interestingly, the results show that this turbulent mass transfer mechanism explains why FAC can take place even in locations where the local axial flow is relatively low. The approach implemented here seems to satisfactorily predict the mass transfer coefficients and locations prone to single-phase FAC and seems to be straightforwardly applicable to other fittings and geometries.

Andrew G. Howell

PPChem 2010, 12(11), 646–651

Carbon Steel Corrosion in the Low-Pressure Turbine Exhaust Environment

Corrosion of carbon steel on the steam side of condensers has long been observed by power plant operators, but the mechanism has not been well understood. Characteristics of the corrosion are areas of bare metal resulting from intergranular attack intermixed with black or red iron oxide, condensing high-purity steam with high local velocities, the lowest temperature in the steam cycle, and relative constancy over time in the macroscopic corrosion pattern. Effective mitigation would reduce iron transport into the steam cycle from the condenser, and might also reduce the likelihood of through-wall leaks in the cooling tubes of air-cooled condensers.

Wataru Sugino, Taku Ohira, and Kimitoshi Yoneda

PPChem 2010, 12(11), 652–662

Effect of Water Chemistry Improvement on Flow-Accelerated Corrosion in PWR Secondary Systems

Flow-accelerated corrosion (FAC) of carbon steel (CS) piping has been one of the main issues in light-water nuclear reactors (LWRs). Wall thinning of CS piping due to FAC increases the potential risk of pipe rupture as well as the costs for inspection and replacement of damaged pipes. In particular, corrosion products generated by FAC of CS piping can lead to steam generator (SG) tube corrosion and degradation of thermal performance when they enter and accumulate on secondary side of pressurized water reactors (PWRs). To maintain SG integrity by suppressing the corrosion of CS, high pH all-volatile treatment (AVT) chemistry (High-AVT) (feedwater pH 9.8±0.2) was adopted in Tsuruga-2 (1 160 MW PWR, in commercial operation since 1987) in July 2005 to replace the conventional Low-AVT chemistry (feedwater pH 9.3). After adopting High-AVT, the accumulation rate of iron in the SG decreased to one-quarter of that observed under conventional Low-AVT. As a result, the previously declining SG thermal efficiency was improved. However, it has become clear that High-AVT chemistry is ineffective against FAC in the regions where the flow turbulence is much greater.

By contrast, wall thinning of CS feedwater pipes due to FAC has been successfully controlled by oxygen treatment (OT) for long time in boiling water reactors (BWRs). This is due to the fact that the magnetite film formed on CS surfaces under AVT chemistry has a higher solubility and porosity in comparison with hematite film, which is formed under OT.

In this paper, the behavior of FAC under various pH and dissolved oxygen concentrations is discussed based on actual wall thinning rates of BWR and PWR plants and on experimental results in a FAC test-loop. It has been established that FAC is suppressed even under extremely low dissolved oxygen concentrations such as 2 $\mu g \cdot kg^{-1}$ under AVT conditions in PWRs. Based on this result, we propose oxygenated water chemistry

for PWR secondary systems, as it can mitigate FAC of CS piping without any adverse effects on the SG integrity. Furthermore, the applicability and effectiveness of this concept developed for FAC suppression in PWR secondary systems is discussed based on results of an in-plant test at Tsuruga-2.

Amy Sieben and Lester Stanley

PPChem 2010, 12(11), 663–675

HRSG Designs and Their Effect on FAC Risk

Flow-assisted (or -accelerated) corrosion (FAC) is one of the most common failure mechanisms in heat recovery steam generators (HRSGs). FAC risk is affected by boiler water chemistry and design factors. This paper focuses on the effects of design factors, including velocity, impingement, temperature profile, materials of construction, and steam quality. Case studies of several HRSGs with serious FAC damage are provided, including photographs and the design background. These examples emphasize the need for HRSG FAC risk design review, analysis, and monitoring.

Ronald L. Pietrowski

PPChem 2010, 12(11), 678–683

Identification and Control of Factors Influencing Flow-Accelerated Corrosion in HRSG Units Using Computational Fluid Dynamics Modeling, Full-Scale Air Flow Testing, and Risk Analysis

In 2009, Consolidated Edison's East River heat recovery steam generator units 10 and 20 both experienced economizer tube failures which forced each unit offline. Extensive inspections indicated that the primary failure mechanism was flow-accelerated corrosion (FAC). The inspections revealed evidence of active FAC in all 7 of the economizer modules, with the most advanced stages of degradation being noted in center modules. Analysis determined that various factors were influencing and enabling this corrosion mechanism. Computational fluid dynamics and full-scale air flow testing showed very turbulent feedwater flow prevalent in areas of the modules corresponding with the pattern of FAC damage observed through inspection. It also identified preferential flow paths, with higher flow velocities, in certain tubes directly under the inlet nozzles. A FAC risk analysis identified more general susceptibility to FAC in the areas experiencing damage due to feedwater pH, operating temperatures, local shear fluid forces, and the chemical composition of the original materials of construction. These, in combination, were the primary root causes of the failures. Corrective actions were identified, analyzed, and implemented, resulting in equipment replacements and repairs.

David G. Daniels

PPChem 2010, 12(12), 688–693

Innovative Lay-up and Startup Methods

A number of EPRI Cycle Chemistry target members have developed innovative procedures and processes for the protection of the steam cycle when the unit is off-line and for starting up the units with properly treated water. In developing lay-up practices, the turbine is often neglected. This paper discusses a number of lay-up methods for the entire steam cycle including the turbine. This paper also discusses methods for the proper deaeration and treatment of the boiler fill water prior to startup and how utilities have used these methods to minimize corrosion.

Andreas Drexler, Volker Schneider, and Jörg Fandrich

PPChem 2010, 12(12), 700–707

Chemistry Related On-Line Monitoring of PWRs

The requirements for availability and operating economy of nuclear power plants have steadily become more stringent in recent years. In addition to implementing technological advances at new and operating power plants (e.g., in the form of advanced designs, processes and materials), plant operators are also increasingly applying supplementary measures to enhance undisturbed operation with high availability and reliability of nuclear power plants.

To help perform effective and reliable monitoring of the water chemistry of nuclear power plants, a number of guidelines for the chemist and the plant operator have been developed to define the necessary parameters with respect to the selected chemistry treatment. This paper deals with the definition of this parameter set, especially with respect to the most recent VGB Guidelines, and gives an overview of the optimal chemistry monitoring strategy.

David Addison

PPChem 2010, 12(12), 708–713

The Experiences of the New Zealand Fossil Power Industry with the Challenges of Flow-Accelerated Corrosion in HRSGs – Issues and Solutions

The fossil power industry in New Zealand is comprised of a combination of 1970s and 1980s vintage gas- and coal-fired conventional units, three large F Class single-shaft combined cycle stations from different manufacturers commissioned from 1998 to 2007, all with horizontal, triple-pressure heat recovery steam generators (HRSGs), and a number of small aero-derivative gas turbine/HRSG co-generation plants.

Flow-accelerated corrosion (FAC) issues, in varying degrees, have occurred at all sites with a number of different monitoring and resolution strategies employed to ensure plant reliability and safe operation. These strategies have included operating and cycle chemistry changes, improved monitoring, increased non-destructive testing (NDT), and improved specification of later units.

This paper provides a summary of the New Zealand fossil power industry experiences with FAC in combined cycle gas turbine plants and future activities planned in relation to FAC.

Stephen J. Shulder, Michael R. Riffe, and Richard J. Walp

PPChem 2010, 12(12), 714–721

Microbiological Treatment for Removal of Heavy Metals and Nutrients in FGD Wastewater

In efforts to comply with the Clean Air Act many coal-fired fossil plants are installing wet flue gas desulfurization (WFGD) systems, also known as scrubbers, to remove sulfur dioxide (SO_2). Limestone slurry is injected into an absorber to promote the formation of calcium sulfate ($CaSO_4$) or gypsum. Chloride (chlorine in the fuel) becomes dissolved and increases in the absorber loop, which can lead to a more corrosive environment. Inert matter in the limestone also enters the absorber and must be reduced to meet the gypsum quality specification. To control the buildup of chloride and fines in the flue gas desulfurization (FGD) system a continuous blowdown or purge stream is utilized. Environmental regulations on the discharge of treated FGD wastewater are becoming increasingly more stringent to control impacts on the receiving body of water (stream, lake, river, or ocean). These new limitations often focus on heavy metals such as selenium and nutrients including nitrogen and phosphorus compounds. The FGD chloride purge stream is typically treated by chemical addition and clarification to remove excess calcium and heavy metals with pH adjustment prior to discharge. However this process is not efficient at selenium or nutrient removal. Information on a new approach using biological reactor systems or sequencing batch reactors (SBRs) to achieve reductions in selenium and nitrogen compounds (ammonia, nitrite, and nitrate) is discussed. A brief discussion on the physical/chemical pretreatment is also provided.

Hugh Fallon and George J. Licina

PPChem 2010, 12(12), 722–735

Optimization of Biofilm Control Using an On-Line Monitor: Case Studies from around the World

The presence of biofilm in water systems can contribute to severe plant problems, such as microbiologically influenced corrosion (MIC) and under-deposit corrosion, reduction in heat transfer efficiency, increased chemical costs, and health and safety risks. While it is standard practice to apply treatment chemicals to a water system to control biofilm formation and growth, it is often unclear how these chemicals are performing or will perform in the future – the limited information available to the operator (usually from bacterial plate counts from the bulk water) reflects a system that has since moved several hours or even days into the future, and does not actually tell the operator anything about the sessile bacteria populations on system surfaces.

However, on-line and real time monitoring of the water system condition is available that can provide early warning of unsatisfactory biocide performance as well as allow optimization of the chemical dosing regime. Process problems relating to biofilm

formation, such as MIC, heat transfer losses and chemical efficacy, can be known and countered before they develop. This performance-based approach to biocide dosing is not only more environmentally sustainable, but costs less and puts less stress on plant materials.

The electrochemical biofilm activity monitoring system is described, and experiences with the use of this on-line, real time technology for biofilm control in a variety of water systems and plant types are presented.

PPChem 101	Boiler and HRSG Tube Failures
PPChem 2010, 12(2), 122–127	Boiler and HRSG Tube Failures, Lesson 4: Hydrogen Damage
PPChem 2010, 12(3), 188–192	Boiler and HRSG Tube Failures, Lesson 5: Caustic Gouging
PPChem 2010, 12(6), 368–372	Boiler and HRSG Tube Failures, Lesson 6: Acid Phosphate Corrosion
PPChem 2010, 12(12), 738–743	Boiler and HRSG Tube Failures, Lesson 7: Flow-Accelerated Corrosion

2011's Scientific and Technical Contributions – Part 1

Markus Bernasconi

PPChem 2011, 13(2), 69–73

Low-Level Oxygen Measurement in Power Plants: What Really Matters

Although new technologies have been introduced to the market, amperometric oxygen measurement remains the most accurate technology for detecting trace oxygen levels. This contribution shows how an amperometric oxygen sensor works, addresses how much maintenance is really necessary, and describes the verification and calibration of these instruments.

Eric V. Maughan

PPChem 2011, 13(2), 75–82

State of the Art Automated On-Line Analysis with Chemical Expert System for Eskom Medupi Power Station

Eskom has embarked on a new-build programme to enhance its already aging fleet of power stations, thereby ensuring secure and adequate power supply into the current century. However technology and operating philosophy have changed considerably since the last power plant was constructed in South Africa. This presentation describes the challenges which faced the engineering team and how these were overcome during the design phase. With the requirement of minimum staffing, full automation of on-line analysis becomes essential. The paper describes how this will be achieved using state of the art technology and artificial intelligence.

Stéphane Trévin, Matthieu Persoz, Séverine Friol, and Hamid Hanifi

PPChem 2011, 13(2), 84–92

Flow-Accelerated Corrosion Mitigation at EDF with BRT-CICERO™ – First Application on Fossil Plant Le Havre Units 2 and 4

Électricité de France (EDF) used a software called BRT-CICERO™ for the surveillance of the secondary piping systems of its PWRs which enables the operator to calculate the flow-accelerated corrosion (FAC) wear. This is a major tool for the operators for organizing maintenance and planning inspections, and is recognized by the French authorities for FAC surveillance on the secondary pipework of the EDF nuclear power plants. It takes advantage of the experience feedback of the French fleet and of R&D improvements and is frequently updated. International events that have occurred recently have made it necessary to improve the basic surveillance of FAC on fossil plants. BRT-CICERO™ was tested on the reference fossil plant Le Havre (two 600 MW units) to determine whether this software is also applicable to fossil units.

Robin Kluck, Juan Torres, Adolfo Antompietri, and José Rivera

PPChem 2011, 13(2), 94–103

Experiences Using Neutralizing Amines to Control pH and Minimize FAC in a Combined-Cycle Power Plant

Flow-accelerated corrosion (FAC) can result in catastrophic equipment failures, reduced plant reliability, increased costs, reduced revenues and safety concerns. Many combined-cycle power plants utilize ammonia for feedwater pH control and to mitigate FAC, but there are often limitations and disadvantages to its use. This paper discusses experiences and lessons learned in implementing a feedwater pH control program using neutralizing amines to minimize FAC at EcoEléctrica in Peñuelas, Puerto Rico.

Keith Fruzzetti

PPChem 2011, 13(2), 105–115

Operating Experience Driven Advancements in Plant Chemistry Practices and Standards

Improved water chemistry control is essential to:

- Minimize materials degradation (e.g., stress corrosion cracking (SCC) of steam generator (SG) tubes, primary water stress corrosion cracking (PWSCC), corrosion of fuel);
- Minimize corrosion product transport (e.g., transport into the steam generators (SGs), where it can foul tube surfaces and create crevice environments for the concentration of corrosive impurities, transport and deposition on the fuel);
- Minimize dose rates.

Water chemistry control must be optimized to provide overall improvement considering the sometimes variant constraints of the goals listed above. New approaches to mitigate materials degradation, reduce corrosion product transport, and minimize plant dose rates are continually sought. The industry needs to address system integrity issues through the application of promising, innovative chemistry initiatives, focusing on long-term integrity and viability while maintaining fuel integrity and minimizing dose rates.

This paper summarizes some of the major initiatives with respect to pressurized water reactor (PWR) primary and secondary system chemistry to effectively address these goals as they pertain to SGs.

Robert Svoboda and Matthias Svoboda

PPChem 2011, 13(3), 128–135

Chemistry-Related Monitoring of Generator Cooling Water Systems

The generator is a key component of an electric power plant, and if the generator is not functioning, the rest of the power plant cannot fulfill its proper purpose. Therefore, adequate generator water chemistry and its monitoring are essential to avoiding component damage and loss of availability. Automatic monitoring parameters are conductivity and in some cases also oxygen. Measuring pH is not recommended. A novel technique provides the electrochemical potential, which research indicates may be more meaningful than oxygen and pH. Laboratory analyses of the quantity of copper in the spent mixed-bed resin are also a useful indicator of long-term abnormal situations.

Robert L. Bryant

PPChem 2011, 13(3), 139–145

Optimizing Coagulation and Filtration Using Streaming Current Measurement

The old axiom "garbage in, garbage out" has its place in the world of steam/power generation. The concern is that less-than-optimal operation of clarifiers and filters in the power plant can cause problems downstream. Inadequate removal of turbidity and natural organic matter (NOM) will not only present potential problems for reverse osmosis and demineralizer systems, but can ultimately cause significant problems in the steam cycle as well. In many cases these water quality issues can be traced to pretreatment equipment mechanical problems, improper chemical dosages, or some combination of both. This paper reviews how streaming current measurement is used to optimize clarification/filtration processes.

Bernt Bengtsson, Anna Velin, Rolf Ingemarsson, and Gustav Settervik

PPChem 2011, 13(3), 147–156

Electrochemical Ion Exchanger in the Water Circuit to Measure Cation Conductivity

At Ringhals Nuclear Power Plant (NPP), more than four years of successful operation with a full-scale electrodeionization (EDI) unit for the recycling of steam generator blowdown gave the inspiration to modify and scale down this EDI process. As part of this project, the possibility of replacing the cation exchanger columns used for cation conductivity analysis with some small and integrated electrochemical ion exchange cells was explored. Monitoring the cation conductivity requires the use of a small cation resin column upstream of the conductivity probe and is one of the most important analyses at power plants. However, when operating with high alkaline treatment in the steam circuit, there is the disadvantage of rapid exhaustion of the resins, necessitating frequent replacement or regeneration. This causes interruptions in the monitoring and gives rise to a high workload for the maintenance staff.

This paper reports on the optimization and testing of two different two-compartment electrochemical cells for possible replacement of the cation resin columns for analyzing cation conductivity in the secondary steam circuit at Ringhals NPP. Field tests during start-up conditions and more than four months of steady operation together with real and simulated tests for impurity influences indicate that an electrical ion exchange (ELIX) process could be successfully used to replace the resin columns in Ringhals while operating with high-pH all-volatile treatment (AVT) using hydrazine and ammonia.

Installation of an ELIX system downstream of a particle filter and upstream of a small cation resin column will introduce additional safety and further reduce the maintenance and possible interruptions. Performance of the ELIX process together with other chemical additives (morpholine, ethanolamine, 3-methoxypropylamine, dimethylamine) and dispersants may be further evaluated to qualify the ELIX process as well as steam generator blowdown electrodeionization for wider use in nuclear applications.

Nestor van Eeden, Nomalanga Tasana, and Herman J. Morland

PPChem 2011, 13(3), 159–166

Analysis of Boron at Koeberg Power Station

Soluble reactivity poisons, also called chemical shim, produce spatially uniform neutron absorption when dissolved in reactor coolant water. The ^{10}B isotope, having a high neutron absorption coefficient, is used in commercial pressurised water reactors (PWR) to limit and control reactivity. This is achieved at Koeberg Nuclear Power Station (KNPS) and the majority of commercial PWRs worldwide by the addition of natural boric acid to the reactor coolant. The boric acid dissolved in the coolant decreases the thermal utilisation factor, causing a decrease in reactivity. By varying the concentration of boric acid (and hence also the ^{10}B concentration) in the coolant, a process referred to as boration and dilution, the reactivity of the core can be easily managed. An increase in boron concentration (boration) creates negative reactivity and if the boron concentration is reduced (dilution), positive reactivity is added. The changing of boron concentration in a PWR is used primarily to compensate for fuel burn-up or poison build-up. The variation in boron concentration allows control rod use to be minimised, which results in a flatter flux profile over the core than can be produced by control rod manipulation.

Accurate laboratory and on-line chemical analysis of boron concentration is important because of its operational implications associated with reactivity control and also for nuclear safety. In a normal fuel cycle, as the nuclear fuel is being consumed, the reactor coolant boric acid (^{10}B) concentration must be reduced by dilution with purified water to maintain the reactor at constant power. Besides in the reactor coolant water, boric acid concentration is also important in the chemical and volume control system and reactor make-up system for operation. For nuclear safety, boric acid concentrations are technical specification parameters, maintained and monitored in the spent fuel system and safety injection systems. Boron concentration determination is also required for boron recovery and liquid waste treatment.

This paper discusses the typical chemical analysis methods for boron determination used in the power industry. The alkalimetric titration method is described in terms of applicability, accuracy, precision, quality control and limitations. Uncertainty of measurement is determined for the autotitration method used at KNPS. Some operating experiences at KNPS involving boron determination are presented, one involving a safety injection tank that went out of specification on boron concentration and another where an erroneous quality control check caused an apparent boron dilution concern.

Boron has two naturally occurring isotopes, ^{10}B (19.9 %) and ^{11}B (80.1 %). ^{10}B is consumed through neutron absorption, which alters the natural relative abundances of the two isotopes in the reactor coolant water. Since it is specifically the ^{10}B isotope that is responsible for the ability to control reactivity, it is important to determine not only total boron concentration but also to have specific knowledge of the boron isotopic ratio, ^{10}B:^{11}B. The implementation of isotopic boron analysis (by inductively coupled plasma – mass spectrometry) at KNPS is explained and the advantage of the programme is illustrated.

Bernhard Stellwag, Alexander Ländner, Steffen Weiss, and Frank Hüttner

PPChem 2011, 13(3), 167–173

Water Chemistry Control Practices and Data of the European BWR Fleet

Nineteen boiling water reactor (BWR) plants are in operation in Europe, nine built by ASEA Atom, six by Siemens KWU and four by General Electric. This paper gives an overview of the water chemistry operation practices and parameters of the European BWR plants. General design characteristics of the plants are described. Chemistry control strategies and underlying water chemistry guidelines are summarized. Chemistry data are presented and discussed with regard to plant design characteristics.

The paper is based on a contract of the European BWR Forum with AREVA on a chemistry sourcebook for member plants. The survey of chemistry data was conducted for the years 2002 to 2008.

Albert Bursik

PPChem 2011, 13(3), 178–183

Relating Five Decades of Fossil Cycle Chemistry with FAC Control

The appearance of the first reports of a puzzling form of erosion corrosion, today well known as flow-accelerated corrosion (FAC), coincided with the introduction and increasing use of deionized and demineralized water in fossil power generation. This contribution briefly reviews the history of the battle to understand and avoid single-phase FAC, concentrating on improvement of the cycle chemistry, the most applicable approach to mitigating FAC and the concurrent corrosion product transport in already existing units. Although open issues remain, great progress has been made over the past six decades, and low $\mu g \cdot L^{-1}$ feedwater corrosion product levels are achieved today that the plant chemists of the past wouldn't even have dreamed of.

Derek H. Lister, Andrew D. Feicht, Kazutoshi Fujiwara, Mahsa Khatibi, Lihui Liu, Taku Ohira, and Shunsuke Uchida

PPChem 2011, 13(4), 188–196

The Mitigation of Flow-Accelerated Corrosion in the Feedwater Systems of Nuclear Reactors – The Influence of Dissolved Oxygen under Different Operating Conditions

In order to improve our understanding of the flow-accelerated corrosion (FAC) of carbon steel piping in feedwater systems, a collaborative research program between Japan and Canada has investigated the combined effects of system operating parameters. A major objective was to optimize techniques for minimizing degradation; accordingly, we report here the influence of dissolved oxygen on FAC rate under a range of conditions as examined in the laboratory with a high-temperature water loop.

Most of the experiments were done at 140 °C in neutral water, in ammoniated water at $pH_{25\,°C}$ 9.2 and in ammoniated water at $pH_{25\,°C}$ 9.2 with 100 $\mu g \cdot kg^{-1}$ hydrazine. Several flow rates were imposed and two grades of carbon steel were employed for test probes: one containing 0.019 % chromium and the other containing 0.001 % chromium. Probes were designed to monitor continuously both FAC (by an electrical resistance technique) and electrochemical corrosion potential, ECP (relative to a Ag/AgCl reference electrode). During a typical experiment, probes of different diameters were installed in series. Downstream of the "resistance probes" to measure FAC, removable probes for detailed surface examination by techniques such as laser-Raman microscopy, scanning-electron microscopy and energy-dispersive x-ray analysis were also installed.

In neutral water, FAC rates reached ~6 mm per year and were apparently controlled by mass transfer, which led to a numerical correlation with fluid shear stress at the tube wall. The steel with the lower chromium content had a greater FAC rate by a factor of about 2.4. An oxygen concentration of almost 40 $\mu g \cdot kg^{-1}$ was required to stifle FAC.

In ammoniated water, FAC rates were relatively low and correlations depending on mass transfer were dubious. Hydrazine reduced the FAC rate, possibly because it affected the pH locally at the metal surface. It also increased the stifling oxygen concentration at $pH_{25\,°C}$ 9.2 to ~3 $\mu g \cdot kg^{-1}$. At $pH_{25\,°C}$ 10, FAC could not be detected, even with oxygen concentrations as low as 0.3 $\mu g \cdot kg^{-1}$.

Graham P. Quirk, Ian S. Woolsey, and Andy Rudge

PPChem 2011, 13(4), 198–208

Use of Oxygen Dosing to Prevent Flow-Accelerated Corrosion in Advanced Gas-Cooled Reactors

Flow-accelerated corrosion (FAC) was recognized as a major threat to the carbon steel feed and economizer tubing of the once-through boilers of the UK's advanced gas-cooled reactors (AGRs) following the observation of FAC damage of the boiler inlet orifice assemblies at two plants in 1977 and subsequent review of the likelihood of further damage elsewhere within the boilers of all AGRs. In most cases, replacement of susceptible tubing was not feasible due to the inaccessibility of the boiler components within the reactor concrete pressure vessel. Preventing further FAC damage within the boilers therefore had to rely largely on changes to the boiler feedwater chemistry. Following extensive research programs carried out in the late 1970s and early 1980s two main feedwater chemistry regimes were adopted to suppress FAC in different AGRs.

The four units found to be at greatest risk of FAC damage adopted an oxygen dosed all-volatile treatment (AVT) regime during commissioning, while four other units retained the original deoxygenated ammonia dosed AVT regime, but with an increased feedwater pH. The deoxygenated ammonia dosed chemistry regime was also adopted in four AGR units subsequently built, which used 1%Cr0.5%Mo feed and economizer tubing in their once-through boilers.

The oxygen dosed AVT chemistry regime adopted in four units having helical once-through boilers has proved highly effective in preventing FAC, with no evidence of damage after around 150 000 h of operation. However, FAC damage was eventually found in some of the other units operating with a deoxygenated feedwater chemistry regime, in spite of having adopted an elevated feedwater pH. These units have now successfully converted to an oxygen dosed AVT feedwater chemistry regime to prevent further FAC damage, with the result that all 14 AGR reactors now operate with variants of the original oxygen dosed feedwater chemistry regime developed during the 1980s.

The paper outlines the development of the oxygen dosed feedwater chemistry regimes now used by all AGRs, and describes their successful deployment under operational conditions.

Jim Stevens and Seifollah Nasrazadani

PPChem 2011, 13(4), 212–220

New Advanced Amine for Secondary Systems in Pressurized Water Reactor Plants

Comanche Peak Nuclear Power Plant (CPNPP) augmented morpholine chemistry in the secondary system with dimethylamine (DMA) chemistry after discovering the benefits from Italian fossil plant experience. As a result of the operational success with DMA, CPNPP began searching for other amines with similar properties that may provide greater benefit. The amine discovered to have the most favorable potential benefits was 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which is a strong base with a pKa of 13.4.

Corrosion and compatibility testing was performed in reference to existing amines and followed the pattern of the qualification testing performed for the implementation of DMA. This work describes the candidate testing that led to the selection of DBU and the qualification testing for operation at CPNPP. Testing was performed on carbon steel for balance of plant considerations and on Alloy 600 steam generator tubing material. Also described is an unexpected finding from the testing. One test regime indicated a corrosion protection benefit of DBU beyond a simple pH effect, which may be the result of surface modification or surface reaction with the carbon steel oxide.

Kateřina Vonková, Vladimír Švarc, Jan Kysela, Miroslav Maláč, and Igor Petrecký

PPChem 2011, 13(4), 224–231

Operation Experience with Elevated Ammonia

The 10 VVER units in the Czech and Slovak Republics are all in very good water chemistry and radiation condition, yet questions have arisen regarding the optimization of cycle chemistry and improved operation in these units. To address these issues, a comprehensive experimental program for different water chemistries of the primary circuit was carried out at the Řež Nuclear Research Institute, Czech Republic, with the goal of judging the influence of various water chemistries on radiation build-up. Four types of water chemistries were compared: standard VVER water chemistry (in common use), direct hydrogen dosing without ammonia, standard VVER water chemistry with elevated ammonia levels, and zinc dosing to standard VVER water chemistry. The test results showed that the types of water chemistry other than the common one have benefits for the operation of the nuclear power plant (NPP) primary circuit. Operation experience with elevated ammonia at NPP Dukovany Units 3 and 4 is presented which validates the experimental results, demonstrating improved corrosion product volume activity.

Joachim Weiss

PPChem 2011, 13(5), 244–254

Ion Chromatography for the Power Generating Industry – From In-Line Preconcentration Techniques to Reagent-Free IC in Capillary Format

The power generating industry was one of the earliest adopters of ion chromatographic techniques for monitoring ionic impurities in cooling water, steam generators, and condensates, replacing unspecific conductivity measurements. In the past, preconcentration techniques using small concentrator columns were the only way to determine ions at trace levels. With the introduction of high-capacity ion exchangers in recent years, large-volume direct injections allow detection limits down to mid $ng \cdot L^{-1}$ levels. Today, reagent-free ion chromatography with electrolytic sample preparation (RFIC-ESP) is the ultimate concept for fully automated in-line sample preconcentration and in-line calibration down to the single-digit $ng \cdot L^{-1}$ level. Based on the technology of miniaturized electro-deionization, this novel concept uses only one analytical pump for eluent delivery and sample transfer. Large-volume injections and sample preconcentration can also be performed in the capillary format, which offers a 100 times higher mass sensitivity as compared to analytical ion chromatography on a 4 mm column, thus facilitating ultra-trace analysis.

Michael Bolz, Birgit Felgenhauer, Rolf Schorle, Andreas Speck, Siegfried Schumacher, and Herrmann Wacker

PPChem 2011, 13(5), 257–261

Comparison of Iron Measurements: ICP-MS, AAS and UV-Vis Photometry

A comparison of measurements of the reactor water of the boiling water reactor Philippsburg 1 and of the feedwater of the pressurized water reactor Philippsburg 2 has shown that the classical photometric iron measurement can be replaced by inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) measurements. As the detection limits of ICP-MS and AAS are significantly lower than those of photometric measurements, more information can be obtained. Under the oxidizing conditions of the boiling water reactor, the reactor water iron is mainly undissolved, while in the reducing feedwater of the pressurized water reactor part of the iron is dissolved and part is undissolved (particulates).

The examination will be continued to find out even more about how much is dissolved and how much is undissolved.

George J. Verib

PPChem 2011, 13(5), 262–269

An Alternative Chemistry for Both Operational and Layup Protection of High-Pressure Steam-Water Cycles Using an Organic Filming Amine

Current economic conditions have caused many fossil-fired units to cycle load where previous operation had been a constant-load operation. At best, this operation has become a low-load, or minimum-load, operation during off electric demand periods and full-load operation during peak-load periods. At the most demanding times, the operation of these units has been a daily startup–shutdown situation. Current cycle chemistry guidelines have not minimized corrosion and have not provided protection of unit equipment during economic reserve off periods. Current unit protection strategies are limited

since the units must be operationally ready if called upon to generate. The FirstEnergy Corp. has been using an alternative proprietary, organic filming amine to protect units during operation and short-term non-operational periods. This proprietary chemistry has shown the ability to successfully and significantly reduce corrosion throughout the steam-water cycle during transient load situations and during non-operational periods.

Mike Caravaggio

PPChem 2011, 13(5), 270–280

Practical Application of Phosphate Treatment

Phosphate treatment has been applied to subcritical fossil power boilers for well over half a century, as well as being used frequently in heat recovery steam generators. The use of this treatment has evolved over the decades, with the operating sodium to phosphate ratio being the defining factor for the evolution of the treatment. The evolving prescribed sodium to phosphate ratios have been based on the scientific research results and operating experience available at the time, and in the latest EPRI Guidelines issued in 2004 are set at a minimum sodium to phosphate ratio of 3:1, with provision to add up to 1 mg · L^{-1} of additional free caustic. The ratio limitation has always been set in an effort to minimize the potential for corrosion caused by the potential misapplication of the treatment. Typically, the operating ranges for phosphate treatments are depicted on an x-y plot with the x-axis the phosphate concentration and the y-axis the corrected pH value based on the maximum sodium to phosphate ratio allowed for by the treatment. These operating range plots define the theoretical operating range of a phosphate treatment. This paper briefly discusses the origin of the current phosphate control limits in the EPRI Guidelines, discusses phosphate chemistry, outlines the limitations involved when applying a phosphate treatment and provides additional practical guidance for overcoming these limitations and minimizing the potential for corrosion induced by the

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Wolfgang Spiegel, Thomas Herzog, Gabriele Magel, Wolfgang Müller, and Werner Schmidl

PPChem 2011, 13(5), 281–293

Corrosion in Boilers with Difficult Fuels

Waste-to-energy (WTE) plants may be considered power plants with "difficult fuels". The waste, biomass and processed waste, i.e. biogenic fuels, used by these plants present great challenges to process engineering due to the corrosion damage on heat transfer surfaces hit by the flue gas. The corrosion processes, which are generally influenced by the fuel properties, the firing system and the heat transfer in the boiler, have a direct impact on investment and maintenance costs, availability, and achievable energy efficiency in WTE plants. This contribution reviews the causes and mechanisms of this corrosion, giving a survey of the current research aimed at maximising energy efficiency and availability in WTE plants.

Paul McCann and Mark Robson

PPChem 2011, 13(5), 294–299

Proceedings of the BIAPWS 2011 Workshop and Symposium on Power Plant Chemistry

The British and Irish Association for the Properties of Water and Steam held its annual Workshop and Symposium on Power Plant Chemistry on 6–7 April 2011 in Chilwell, Nottingham. Summaries of the event proceedings are provided.

PPChem 101	Boiler and HRSG Tube Failures
R. Barry Dooley and Albert Bursik PPChem 2011, 13(2), 118–123	Lesson 8: **Stress Corrosion Cracking in Superheater and Reheater Austenitic Tubing**
R. Barry Dooley and Albert Bursik PPChem 2011, 13(4), 236–240	Lesson 9: **Oxide Growth and Exfoliation of Materials in Steam Tubing**

2011's Scientific and Technical Contributions – Part 2

Sevilmedu V. Narasimhan

PPChem 2011, 13(6), 308–312

Water Chemistry Programme in India

The paper briefly reviews the history of the water chemistry programme within the Indian nuclear energy programme. Chemistry challenges early in the operation of some of India's reactors led to the establishment of water and steam chemistry research in the country, a major part of which was the founding of a dedicated laboratory at the Bhabha Atomic Research Centre (BARC) to embark upon large R&D initiatives to understand and improve the existing water chemistry practices in nuclear power plants. Many of the past and current R&D programmes in water chemistry are described.

P. Sriyutha Murthy, P. Veeramani, M. I. Mohamed Ershath, and V. P. Venugopalan

PPChem 2011, 13(6), 314–319

Biofouling Evaluation in the Seawater Cooling Circuit of an Operating Coastal Power Plant

Chlorination is the most commonly used method of biofouling control in the cooling water systems of coastal power stations. Here we report results of fouling studies in the cooling water system of an operating power station. Biofouling samples were collected from the cooling water conduits, heat exchanger water boxes, pipelines, heated discharge conduits and outfall section during the annual maintenance shutdown of the plant in three consecutive years. Simultaneous monitoring of biofouling on test coupons in coastal waters enabled direct comparison of the fouling situation on test panels with that in the cooling system. The data showed a significant reduction in biofouling inside the cooling circuit as compared to in the coastal waters. However, a significant amount of fouling was still evident at several places, indicating inadequacy of the biocide treatment regime. The paper analyses the data in light of the operation history of the plant and makes suggestions for improvement.

Palogi Chandramohan, Madapusi P. Srinivasan, Sinu Chandran, Srinivasan Rangarajan, Sankaralingam Velmurugan, and Sevilmedu V. Narasimhan

PPChem 2011, 13(6), 320–329

Modification of Magnetite Coating Formation in the Presence of Alkaline Acrylic Acid

In Indian pressurized heavy water reactors (PHWRs), the hot conditioning of the primary heat transport (PHT) system is carried out to form a protective magnetite coating on the inner surfaces of the PHT system at the start-up of the reactor and also after decontamination of the PHT system to minimize the release of loose crud particulates and corrosion of the PHT system. An attempt has been made to modify the chemistry conditions of the formation of the protective magnetite coating on carbon steel (CS) coupons in a static autoclave at 240 °C to observe its impact on the nature of the protectivity. Static autoclave experiments were carried out to understand the formation of the protective magnetite coating on carbon steel specimens in the presence of acrylic acid (AA) and polyacrylic acid in alkaline conditions. These coupons were characterized by X-ray diffraction, Raman spectroscopy and scanning electron microscopy. The nature of the film formation was monitored by electrochemical studies using impedance spectroscopy and anodic polarization. Studies show that the addition of acrylic acid resulted in a reduction in crystallite size and a change in morphology. Thread-like bundles with a thread diameter of 100 nm and a bundle diameter of 1 μm for 50 mg · L^{-1} of acrylic acid were observed. Raman and X-ray diffraction studies show the single-phase nature of the magnetite oxide film. Raman spectroscopic data also revealed an increase in the adsorbed organic with an increase in the concentration of the acrylic acid. Raman mapping analysis shows uniform coverage of the magnetite film. Potentiodynamic anodic polarization (PDAP) studies indicate better film protectivity for a magnetite coating formed in 50 mg · L^{-1} acrylic acid. The corrosion rate is observed to be less for CS coupons in the presence of 50 and 100 mg · L^{-1} AA. The tendency for the film formed to dissolve is less for coatings developed in both 50 and 100 mg · L^{-1} AA in comparison to coatings developed in LiOH alone. The impedance studies indicated the pore resistance

of the film increased two fold and seven fold for 50 and 100 mg · L^{-1} acrylic acid cases in comparison to the simple LiOH case, whereas the charge transfer resistance at the double layer decreased for AA cases. The capacitance of the double layer also supports the charge transfer resistance observation.

Hariharan Subramanian, Valil S. Sathyaseelan, Srinivasan Rangarajan, Sankaralingam Velmurugan, and Sevilmedu V. Narasimhan

PPChem 2011, 13(6), 330–336

The Effect of Carbon Steel Microstructure on High-Temperature Aqueous Corrosion

Carbon steels of the type 106 Gr-B/A-333 Gr. 6 are being used in the primary and secondary heat transport systems of pressurized heavy water reactors. The carbon steel microstructure can change significantly on heat treatment either during the manufacture of the piping or during fabrication/welding of the piping at site. The resultant microstructure can vary anywhere from pearlite to martensite or bainite, depending on the carbon content. This can also influence the corrosion rates of these materials in the reactor. In this paper two carbon steel materials of different microstructures (pearlite-ferrite/bainite) were exposed to simulated pressurized heavy water reactor primary water chemistry conditions in a recirculating test facility. Corrosion release rates for the specimen with the bainite microstructure remained higher for the entire duration of exposure. The specimens were withdrawn at regular intervals and characterized by electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis to assess the differences in the film properties. The oxide film formed on the material with the bainite microstructure showed higher n-type defect density, lower film resistance and lower charge transfer resistance. These characteristics explain the sustained higher corrosion observed on the material with the bainite microstructure. The distinct difference between the specimens is more evident on films formed in a shorter time span. This observation is of importance for piping prone to flow-accelerated corrosion, where the corrosion product film is extremely thin and is continuously being replenished. A carbon steel material with a bainite microstructure in these regions can increase the rate of wall thickness reduction.

Veena Subramanian, Palogi Chandramohan, Sinu Chandran, Madapusi P. Srinivasan, Srinivasan Rangarajan, Sankaralingam Velmurugan, and Sevilmedu V. Narasimhan

PPChem 2011, 13(6), 337–345

Evaluation of a Process for the Decontamination of Radioactive Hotspots Due to Activated Stellite Particles

Some of the Indian pressurized heavy water reactors (PHWRs) which use Stellite balls in the ball and screw mechanism of the adjustor rod drive mechanism in the moderator circuit have encountered high radiation fields in the moderator system due to ^{60}Co. Release of particulate Stellite is responsible for the hotspots in addition to the general uniform contamination of internal surfaces with ^{60}Co. Extensive laboratory studies have shown that it is possible to dissolve these Stellite particles by adopting a three-step redox process with permanganic acid as the oxidizing agent. These investigations with inactive Stellite in powder form helped to optimize the process conditions. Permanganic acid was found to have the highest dissolution efficiency as compared to alkaline and nitric acid permanganate. The susceptibility of Stellite to corrode or dissolve was found to depend on the concentration of the permanganate, pH and temperature of the process and microstructure of the Stellite alloy. This process was evaluated for its effectiveness on components from nuclear power plants. Component decontamination was carried out on adjustor rod drive assemblies which had ^{60}Co activity due to Stellite particles with the radiation field ranging from 3 R · h^{-1} to 20 R · h^{-1}. They were subjected to decontamination with permanganic acid as the oxidizing agent, followed by citric acid and a solution containing ethylenediaminetetraacetic acid, ascorbic acid and citric acid in a 4:3:3 ratio by weight as the reducing formulation. In the first trial, one adjustor rod drive mechanism was subjected to decontamination. After two cycles of treatment, an average decontamination factor (DF) of 6.8, with a maximum DF of 11.7, was achieved. The same process but with one cycle was repeated on eight more adjustor rod drive mechanisms. ^{60}Co activity in the range of 13–93 mCi was removed from these adjustor rods. Loose contamination of the order of 30 000–40 000 decays per min and cm^2 observed before decontamination was reduced to 1 000 decays per min and cm^2 after the decontamination. On drive assemblies, an average decontamination factor of 3.7 with a maximum value of 5 was achieved.

Pavel Hübner PPChem 2011, 13(7), 426–435	**Organics Removal in Water Treatment Plants** Organics present in the feedwater may have adverse effects on boilers and turbines. This contribution looks at the sources of organics in the feedwater and how the organics levels can be reduced to safe values. The various water treatment technologies are differently effective in removing the various organics fractions, thus depending on the raw water used, different combinations of technologies may be necessary to achieve desired conductivity and total organic carbon levels.
Robert Svoboda PPChem 2011, 13(7), 438–440	**Meeting of the IAPWS Working Group 'Power Cycle Chemistry' in Pilsen (Czech Republic), September 4–8, 2011 – Update**
PPChem 2011, 13(8), 448–449	**Highlights – International Association for the Properties of Water and Steam 2011 Meeting**
Manuel Sigrist PPChem 2011, 13(8), 450–456	**How to Improve Sample Line Blowdow** Whoever is familiar with online water-steam analysis systems knows that keeping sample lines clean is essential for proper operation of online analysers. Clogged sample lines, lack of sample flow, and particle storms in samples will negatively affect the online analysers. The indirect consequences can be disturbances in the dosing of chemicals, undetected critical conditions, extended start-up times and/or higher manpower requirements. This paper deals with different aspects of keeping sample lines free of particles, from the prevention of dirt to design considerations for sample line blowdown systems.
Miroslav Šťastný and Miroslav Šejna PPChem 2011, 13(8), 460–467	**Effects of Expansion Rate on Binary Condensation of NaCl and Steam Flowing in a Turbine** The approach used in the paper for the condensation of flowing steam is based on binary nucleation of the representative chemical impurity NaCl and water. Physical and mathematical models are briefly described and applied to the steam flow with condensation in a turbine cascade. The binary nucleation numerical model is used for the calculation of the steam flow with condensation in the 2D-nozzle blade cascade of the first wet stage of the low-pressure (LP) part of a condensing steam turbine. The calculated flow in the cascade is transonic and/or subsonic.
PPChem 2011, 13(8), 472–481	**Head for Orlando, FL!** This year the 72nd Annual International Water Conference® (IWC) will take place in Orlando, FL on November 13–17. This contribution presents introductions to the 21 sessions at this conference, including abstracts of some of the papers to be presented that may be of particular interest to power plant chemists and engineers working on power plant chemistry-related issues.
Shawn Gowatski and Gary Miner PPChem 2011, 13(8), 484–491	**The Use of the Low Frequency Electromagnetic Technique to Detect and Quantify the Amount of Magnetite Deposits in Stainless Steel Superheater Tubes Due to Exfoliation** Many supercritical boilers are designed with austenitic stainless steel tubes in the superheat and reheat sections. The growth of magnetite on a tube's inner diameter wall occurs when the operating temperatures are above 540 °C. After the boiler is taken off line, the scale exfoliates and accumulates in the lower tube bends; this can block steam flow and may result in the tube overheating and ultimately rupturing. The low frequency electromagnetic technique, a non-destructive examination (NDE) procedure to detect and roughly quantify the amount of magnetite in a stainless steel tube, is described in this contribution. This detection method can pinpoint the location of the magnetite within the tube and can size the amount of blockage within 5 %, allowing a marked reduction in the manpower and time required for maintenance.

Robert Svoboda, Brett A. Reinboth, and Matthias Svoboda

PPChem 2011, 13(8), 496–502

Monitoring Generator Cooling Water System Chemistry by the Electrochemical Potential

The electrochemical potential (ECP) is a factor that governs corrosion processes. Research work has indicated that the ECP may be a good parameter for monitoring oxide deposition in stator cooling water systems. This publication reports on field experience with such a device.

The effects of a sudden air ingress, of chemical cleaning, and of alkalization could be clearly seen by ECP monitoring. This qualifies ECP measurement as a valid diagnostic tool.

During normal operation, however, the ECP was above the normal operation specification level, near the immediate action level, indicating the presence of an abnormal situation with stator water chemistry. In fact, during this period, the stator suffered hollow conductor plugging by oxides.

Even though ECP monitoring seems more like a scientific tool, it is nevertheless strongly recommended to consider this technique for routine monitoring.

PPChem 2011, 13(9), 508–527

Technical Guidance Document: Phosphate and NaOH Treatments for the Steam-Water Circuits of Drum Boilers of Fossil and Combined Cycle/HRSG Power Plants

This technical guidance document was authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Plzeň, Czech Republic, 4–9 September, 2011, for issue by its secretariat. The members of IAPWS are Britain and Ireland, Canada, the Czech Republic, Germany, Greece, Japan, Russia, Scandinavia (Denmark, Finland, Norway and Sweden), and the United States of America, and the associate members are Argentina and Brazil, Australia, France, Italy, New Zealand and Switzerland. The document represents the accumulated experience of the IAPWS Power Cycle Chemistry (PCC) Working Group with representation from 15 countries.

This technical guidance document considers fossil and combined cycle/heat recovery steam generator (HRSG) plants and identifies the normal target values for each plant type when operating with a phosphate or NaOH (caustic) treatment. It is emphasized that this is an IAPWS technical guidance document and that, depending on local requirements, the normal or target values will need to be customized for each plant depending on the actual conditions of operation, the equipment and materials installed, and the condenser cooling media.

Further information about this technical guidance document and other documents issued by IAPWS can be obtained from the executive secretary of IAPWS or from http://www.iapws.org.

Masamichi Miyajima, Masaki Yoshida, Senichi Tsubakizaki, and Hiroshi Takaku

PPChem 2011, 13(9), 532–541

Results and Future Prospects Concerning Water Treatments for HRSGs at CEPCO

Twenty-five years have already passed since a combined cycle power plant with heat recovery steam generation (HRSG) was introduced at the Chubu Electric Power Co., Inc (CEPCO) for the first time in 1988. CEPCO has been investigating the research on feedwater and boiler water treatments, such as caustic treatment (CT), all-volatile treatment (oxidizing) (AVT(O)), oxygenated treatment (OT) and so on for application in combined cycles with heat recovery steam generators (HRSGs) since 1994. Thereby, AVT(O) has been selected for actual use, taking the initiative with the first application among the utilities in Japan. At present, we have been proceeding with the application of AVT(O) to four systems (24 units, in total 6 500 MW capacity). In this paper, the details of our research and the achievements of the feedwater and boiler water treatments for HRSG plants are described based on operational experience and research results for the various components. A new proposal is also described for a water treatment method in which a relatively low level of oxygen (5 to 20 $\mu g \cdot L^{-1}$) is injected into the feedwater in units with a very tight condenser (seawater cooling).

Shunsuke Uchida, Masanori Naitoh, Hidetoshi Okada, and Hiroaki Suzuki

PPChem 2011, 13(9), 544–556

The Fukushima Dai-ichi NPP Accident Crisis and Its Influence on Energy Policy in Japan

Fossil fuel power plants (FPPs) and nuclear power plants (NPPs) along the northern Pacific coast of Japan experienced a mega earthquake and resulting tsunamis on March 11, 2011, which resulted in serious damage. More than half of the FPPs have returned to supplying electricity, while all NPPs are still shut down.

In particular, Fukushima Dai-ichi Nuclear Power Plant (NPP) of the Tokyo Electric Power Co. experienced a nuclear accident crisis unprecedented in both scale and timeframe. This paper gives a brief overview of the events and their propagation based on the International Atomic Energy Agency (IAEA) report and the authors' studies on accident analysis, and offers considerations on root causes of the propagation, e.g., problems in hardware, software and accident management, by comparing the responses of Fukushima Dai-ichi NPP with those of other reactors at the Fukushima Dai-ni, Tokai, Onagawa and Higashidori NPPs, where cold shutdowns were successfully maintained even though they had also been affected by the earthquake and tsunamis. Future technical subjects for safe NPP operation and the influence of the events on Japanese energy policy are presented.

PPChem 2011, 13(9), 560–563

International Scientific/Technical Conference "Use of Water in Thermal Energetics"

This conference was dedicated to the 90th anniversary of the All-Russian Scientific Research Institute of Thermal Engineering (VTI) . This institute was founded in July 1921 for "structured scientific research, development of approaches to solving practical questions of thermal systems and the resulting technical and economical tasks, as well as for education of highly qualified specialists." Nowadays the institute is divided into ten scientific-technical departments dealing with all areas of thermal energetics (e.g., department for steam generators and furnaces, department for turbines and heating systems, department for water-chemical processes, etc.). The institute operates an experimental heating power plant.

In the following, brief abstracts of most of the technical conference presentations are given. Some papers are missing in this report; unfortunately, we did not have all the original papers at our disposal.

Shunsuke Uchida, Masanori Naitoh, Hidetoshi Okada, Hiroaki Suzuki, Souji Koikari, Seiichi Koshizuka, and Derek H. Lister

PPChem 2011, 13(10), 572–581

The Effects of Ferrous Ion Transport in Bulk Water on FAC Rate

Flow-accelerated corrosion (FAC) is determined by six parameters, i.e., the flow dynamics parameter (mass transfer coefficient), the chromium content in materials, temperature, pH, oxygen concentration, and ferrous ion concentration ($[Fe^{2+}]$) in the bulk water. Six calculation steps were prepared for predicting FAC occurrence and evaluating wall thinning. The necessary conditions for FAC occurrence are designated as overlapping conditions, where each FAC parameter is found in its own risk region. The effects of the first five parameters on FAC have been discussed previously; in the paper, the effects of $[Fe^{2+}]$ on wall thinning are discussed. Ferrous ion can contribute to the formation of an oxide film on the material surface, which mitigates serious wall thinning. The synergetic effects of $[Fe^{2+}]$ and the mass transfer coefficient on the wall thinning rate were evaluated by combining ferrous ion transport through surface boundary layers (major FAC process) and its transport along the pipe surface (accelerated process for oxide film formation). The synergetic effects can be considered as major causes of variation in FAC rates, where both a high thinning rate with a thin oxide film and a low thinning rate with a thick oxide film can be observed under almost the same flow conditions; this has been reported for piping at Mihama-3.

Morgane Riviere, Daniel Missault, Kenneth Wong, Valérie Bossoutrot, Patrick Mauvais, Martine Carré, and Tracey Jacksier

PPChem 2011, 13(10), 584–589

Analytical Validation of Near-Zero Emissions from Coal-Fired Plants and How to Enable Compliance with Regulations

Coal accounts for a significant percentage of the worldwide electricity generation. However, coal is one of the most impure fuels. The impurities include Al, Fe, S and Hg. These impurities, which are generated during combustion, can be adsorbed onto particles which result from the combustion process and can be emitted into the atmosphere. Oxycombustion along with purification is a leading technology to create a near-zero emissions plant by eliminating almost all of the mercury, SOx, NOx, and particulate pollutants from plant emissions. This technology provides a > 90 % CO_2 stream which is suitable for safe and permanent storage (carbon capture and sequestration). The decreased generation of impurities in the CO_2 stream will prevent release of these impurities into the environment. The capability of this solution is based on analytical validation of the impurities in the process stream(s). The complexity of NOx and SOx measurements in CO_2-rich streams, which will enable compliance to both existing and emerging regulations, is discussed in this contribution.

Volker Schmid and Robert DeRosier

PPChem 2011, 13(10), 590–597

Experiences with Mercury Emissions Monitoring Using Sorbent Traps in the U.S.

Despite a 2008 court ruling that eliminated the U.S. Environmental Protection Agency's (EPA) federal Clean Air Mercury Rule (CAMR), many U.S. coal-fired power plants have been monitoring smokestack mercury (Hg) emissions for the last three years to meet individual state requirements. Anticipated federal standards for electric utilities and recently enacted regulations such as those for cement manufacturing facilities will continue to require U.S. industries to address Hg emissions monitoring. Hg can be monitored via continuous emissions monitoring systems (Hg CEMS) or a less complex sorbent-based monitoring approach. Both approaches have been used for compliance reporting purposes in the U.S. Although originally intended as either a back-up to or a way of independently validating Hg CEMS, sorbent-based monitoring systems have become more accepted as primary monitoring systems. As Hg concentrations are reduced by more stringent regulations, the sorbent trap approach, with its inherent ability to measure very low concentrations, becomes the preferred compliance monitoring approach.

Katrin Stiller, Tobias Wittig, and Michael Urschey

PPChem 2011, 13(10), 602–611

The Analysis of Film-Forming Amines – Methods, Possibilities, Limits and Recommendations

Treatment concepts of the water-steam cycle based on film-forming amines are attracting increased attention due to their advantageous properties. This type of treatment requires a reliable and, under field conditions, simple analytical method for the determination of the free (not surface bound) proportion of the amine. This is not a trivial task because of the intrinsic physicochemical properties of film-forming amines. An overview of common determination methods on the market is given. BKG Water Solutions has studied the Bengal rose method described in the literature and performed detailed optimization and validation work. Recommendations are given regarding the sampling and rinsing procedures and the necessary quality of the dye.

The detection sensitivity of film-forming amines depends on their chemical structure and exceeds the detection sensitivity of typical components of the sample matrix by several orders of magnitude. Interferences caused by the sample matrix exist in the form of increased measurement values but are acceptable under practical conditions. The method has a detection limit of about 0.1 $mg \cdot L^{-1}$ free film-forming amine; an optical pathlength of 5 cm is advantageous. The method has also been validated using two independent methods based on different measurement principles and is currently being developed into an online determination tool by BKG Water Solutions.

Richard J. Jones

PPChem 2011, 13(10), 614–620

Generator Cooling Water Systems: Modelling Flammable Mixture Formation in Hydrogen Detraining Tanks

In modern power stations, generator cooling is achieved by circulating hydrogen gas around the frame and by passing high purity demineralised water through the winding conductors. Hydrogen can leak into the cooling water due to a pressure differential across the two systems and is removed in the detraining tank. As oxygen over a wide concentration range can also be dissolved in the water, there is the possibility for flammable mixture formation within the tank. A conservative model has been employed to assess this risk and results suggest that flammable mixture formation is not unfeasible at higher oxygen concentrations.

Haruka Kido,
Taro Ichihara, and
Senichi Tsubakizaki

PPChem 2011, 13(10), 623–627

Alternatives to Hydrazine in Water Treatment at Thermal Power Plants

Hydrazine is generally used as an oxygen scavenger for corrosion control in thermal power plants. Although hydrazine is very effective in this application, it is a genotoxic carcinogen. The use of alternative chemicals such as nontoxic oxygen scavengers and new oxygen scavenger-free water treatment technologies is recommended or required in many countries. Even in Japan, such new approaches to water treatment would contribute to environmental protection, increased confidence, and a reduction in power plant operating costs.

2012's Scientific and Technical Contributions

Shunsuke Uchida, Masanori Naitoh, Hidetoshi Okada, and Hiroaki Suzuki

PPChem 2012, 14(1), 4–17

Water Chemistry Guidance in Nuclear Power Plants in Japan

Water chemistry plays important roles in safe and reliable plant operation which are very critical for future power rate increases as well as aging plant management. Water chemistry control is required to satisfy the need for improved integrity of target materials, and at the same time it must be optimal for all materials and systems in a plant. Optimal water chemistry can be maintained by expert engineers who are knowledgeable about plant water chemistry, who have sufficient experience with plant operation, and whose knowledge is based on fundamental technologies. One of the latest subjects in the field of water chemistry is achieving suitable technical transfers, in which the achievements and experience with plant water chemistry accumulated by experts are successfully transferred to the next generation of engineers. For this purpose, documents on experience with water chemistry are being compiled as the guidance for water chemistry control and water chemistry standards, e.g., standards for chemical analysis procedures and guidance for water chemistry control procedures. This paper introduces the latest activities in Japan in establishing water chemistry guidance involving water chemistry standards, guidance documents and their supporting documents.

Mohammed Mahmoodur Rahman, Abdul-Ghani I. Dalvi, Ashfaq K. Rabbani, Saad A. Al-Sulami, Faisal Z. Mandili, Hani M. Al-Khaledi, and Bandar Al-Jowdi

PPChem 2012, 14(1), 20–32

Application of Fuel Additives to Reduce Corrosion and Stack Emissions in Saline Water Conversion Corporation's Boilers

This paper deals with the burning of heavy residual fuel oil containing ~ 3.5 % sulfur and low vanadium (~ 40 ppm) under conditions prevalent in heating boilers to assess the use of fuel chemical additives on the formation of noxious and corrosive products of combustion.

Saline Water Conversion Corporation's (SWCC's) boilers that are attached to the dual-purpose desalination/power plants in the Western Province of Saudi Arabia using heavy residual fuel oil are reported to have chronic corrosion problems causing unscheduled shutdown and frequent replacement of equipment resulting in high maintenance costs and loss of production besides creating environmental problems. The effectiveness of fuel chemical additives in controlling boiler internal corrosion and reducing the emission of hazardous gases was tested. Three magnesium-based compounds (A, B & E), one organic-based compound (C), and another hydrocarbon-based non-metallic (D) additive were selected based on the literature provided by the companies. Evaluation was carried out by online monitoring of flue gas parameters such as SO_2, SO_3, CO_2 and NO_x, acid dew point, rates of acid build-up and quantitative determination of boiler soots. The effects of the additives on the boiler performance were also monitored by evaluating boiler load, efficiency, flue gas outlet temperature, opacity, fuel and steam flows. The boiler's internals were inspected before and after the testing of each additive.

The results of the three MgO-based slurries tested were quite comparable. The organically based Mg-compound and the non-metallic additive showed lower efficiency in the cold end of the boiler. Though there was a slight decrease in the performance of the additives as the dose rates decreased, the optimum dose rates determined were 150–160 $mg \cdot kg^{-1}$ for chemical A, 200–250 $mg \cdot kg^{-1}$ for chemical B, 180–190 $mg \cdot kg^{-1}$ for chemical C, 500 $mg \cdot kg^{-1}$ for chemical D and 250 $mg \cdot kg^{-1}$ for chemical E to be effective. Based on the studies, chemical A was found to be the most effective and economical among the five chemicals tested.

Holger Topp, Wolfgang Hater, Andre de Bache, and Christian zum Kolk

PPChem 2012, 14(1), 38–48

Film-Forming Amines in Shell Boilers

Studies were conducted with the aim of providing answers to important questions concerning the use of film-forming amines in steam generators. Tests were carried out in test steam generators under controlled conditions to study the three following application areas: the influence of film-forming amines on boiling behavior and heat transfer, the influence of film-forming amines on oxidic protective layer formation, and the influence of film-forming amines on critical operating conditions. In the experiments water treatment with trisodium phosphate (which is normally used with shell boilers) was compared with treatment with film-forming amines. In all three areas the treatment with film-forming amines achieved comparable or better results than the treatment with trisodium phosphate.

Kal Farooq

PPChem 2012, 14(1), 54–58

Upgrade of Condensate Filtration Systems with High Efficiency Disposable Filters

Many power plants with designs of condensate polishers that date to the 1960s and early 70s were originally provided with a pre-filtration stage. In many cases these pre-filters are no longer used because of the effort required to keep them working [1]. Thus, the use of the pre-filters ahead of these early polishing plants at fossil units has largely ceased. Advances in filtration technology in recent years have made the deployment of filtration in condensate systems very effective in terms of both performance and cost. The use of disposable filter cartridges to control the transport of solids, especially during the startup phase when the suspended solids content is at its highest, has proven to be a very effective upgrade with a quick payback for the power plants. These filtration systems using cartridges engineered for optimum solids holding capacity, high flow rate, low pressure loss and compact size are highly efficient and cost effective. The paper discusses several case studies on the use of the disposable filter cartridges, made using a proprietary pleat design that gives the filter cartridge an exceptionally high flow capacity and contamination holding capacity while providing 99.98 % particulate removal efficiency at the rated µm size. Experience with filtration system installations at several fossil power plants are discussed including the upgrade of a 1 000 MW power plant in northern Italy that was using back-washable metal filter cartridges with cellulose-based filter-aid and two US power plants that utilize the filtration system during the critical startup phase.

Abstracts 2011

PPChem 2012, 14(1), 60–67

2011's Scientific and Technical Contributions – Part 1

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Adelina Henderson and David Brazil

PPChem 2012, 14(2), 76–82

Failure Analysis of HP Feedwater Line Elbow

In early 2011 water was found leaking from the lagging of the high-pressure (HP) feedwater line during operation start-up at a combined cycle gas turbine (CCGT) plant in Ireland. After investigation, the leak was found to be from a small pinhole at the outside of a 90° bend (elbow) immediately downstream of a flow restriction orifice on the equalisation pipe.

A microscopic examination of the cut-out elbow showed evidence of heavy erosion taking place. This was confirmed by the presence of heavy twinning, which is indicative of mechanical deformation. It is possible that the impact from the water removed the protective oxide leaving the base material exposed to attack.

The operating temperature of the feedwater line is below the usual temperature range expected for flow-accelerated corrosion (FAC) [1]. Additionally the characteristic

features expected for FAC were not evident in the samples examined microscopically. FAC damage occurs only under specific conditions of flow, water chemistry, geometry, and material type [1]. The type of attack seen on the sample received appears to initially start with erosion of the protective oxide and then is followed by a corrosive attack, which leads to cracking and further weakening of the material. While the term "flow-accelerated corrosion" is preferred as it reflects the chemical nature of the attack, "erosion corrosion" would be more appropriate in this instance, as it appears to be primarily a mechanical means of damage accumulation, which then results in a corrosive attack.

Claudio Mosti and Vincenzo Cenci

PPChem 2012, 14(2), 84–88

Chemistry in Zero Liquid Discharge Systems

During the last few years Enel has installed zero liquid discharge (ZLD) systems to treat and recover flue gas desulfurization (FGD) wastewater from five coal-fired power plants. Each of these systems relies on the operation of a softening-evaporation-crystallization (SEC) plant, committed to evaporating wastewater to a pure reusable distillate. The power plants burn a wide variety of coal with corresponding large fluctuations in the FGD wastewater blowdown quantity and quality. So chemistry control of the upstream evaporation becomes a relevant issue to allow the systems to operate properly. Recent efforts have been aimed at also including wastewater coming from other treatment plants into the ZLD systems. One of the critical issues that emerged after the initial operational experience is related to gypsum and calcite saturation in circulating water. In the major installed systems water desaturation has been achieved through operational arrangements and additional capital expenses, so now the ZLD systems are working properly, allowing full wastewater recovery with no liquid discharge from the power plant. The same results are to be achieved for all the remaining systems in the very near future. This paper discusses design considerations and operational issues related to ZLD systems that were faced after a few years of operational experience.

David M. Gray

PPChem 2012, 14(2), 92–97

Advanced On-Line Sodium Measurement

Water treatment performance and determination of purity have depended on sodium measurement for nearly four decades, over which period the ion-selective electrode method has continuously been refined. Described here are further improvements to sodium measurement technology including a combination electrode system that measures pH as well as sodium to assure proper reagent delivery. The presented analyzer provides enhanced ability to reliably monitor water quality while minimizing operator time requirements.

Emmanuel K. Quagraine and Jonathan P. Ruffini

PPChem 2012, 14(2), 98–111

Chloride Contamination of the Water/Steam Cycle in Power Plants
Part I: Evidence from a Case Which Could Not Be Explained in Terms of Currently Familiar Sources

This is the first of a three-part publication series on the findings from investigations performed at the Shand Power Station of SaskPower to determine a hitherto unfamiliar source(s) of chloride contamination to the water/steam circuit. For this plant, which is usually on automatic grid control (AGC), unit ramping is common and there is some reason to associate this with the initiation of the chloride ingress. The present paper presents a systematic approach to examining the various familiar sources currently known to plant operators, chemists and the like as potential culprits and provides the bases for eliminating these as responsible agents in this case. Based on routine plant operating data and purposeful intermittent grab sample analyses as well as numerical analysis of chloride cycling in the boiler, these well-known potential causative factors, which include condenser tube water leaks, make-up chloride, halo-organics from the water treatment plant, and contaminated ammonia feed sources, could not be found to individually or cumulatively account for the magnitude of chloride contamination observed in this plant. The extent of the chloride cycling required too frequent blowdowns from the boiler, and a cost analysis of the implications from such frequent blowdowns is also presented as one of the incentives that drove the search for the root

cause of such a level of contamination. There were some indications that surplus condensate from the hotwell to the boiler make-up storage tanks was a significant chloride origin, but this could not account for the level of contamination, and the source seems to be distinctly different from the traditionally known condenser tube water leaks. Furthermore, there were some indications that ammonia injection was associated with the chloride crises, although there was ample evidence to eliminate this as the source. These associations formed the basis for further investigations, the findings of which will be reported as Part II and Part III of this series.

Tero Luukkonen, Reijo Hukkanen, Jaakko Pellinen, Jaakko Rämö, and Ulla Lassi

PPChem 2012, 14(2), 112–119

Reduction of Organic Carbon in Demineralized Make-up Water with Activated Carbon Filtration

Organic compounds in the water-steam cycle are an emerging issue at recovery boiler plants. Decomposition products of organic compounds, mainly organic acids with low molecular weight and carbon dioxide, are often related to corrosion. Removal of organics from recovery boiler make-up water with activated carbon (AC) was investigated both in pilot and full scale experiments. AC was used in a novel way to remove organic compounds from demineralized water. AC is conventionally used before demineralization, but when implemented later in the process the lifetime of AC can be extended. Total organic carbon (TOC), conductivity, silica concentration and composition of organic compounds were monitored during the experiments. Results show that AC filtration is a suitable technology for TOC removal from demineralized water. A TOC reduction of 38–70 % was achieved. Mixed-bed ion exchange after the AC filters proved to be necessary to remove conductivity, which was increased in the AC bed.

Abstracts 2011

PPChem 2012, 14(2), 123–131

2011's Scientific and Technical Contributions – Part 2

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Lewis E. Crone

PPChem 2012, 14(3), 140–147

Further Experience with Amine Form Operation of Deep Bed, Full Flow Condensate Polishers at Millstone Power Station

This paper reports on a process for converting and operating deep bed condensate polishing resins in the amine form that has been designed, tested, and implemented at Dominion's Millstone Power Station. The plant employs amine form polishers as part of a strategy to reduce balance of plant corrosion and iron transport, while continuously providing protection of the primary pressure boundary inside the steam generators from chemical assault in the event of a condenser tube leak. Over the last year, Millstone Unit 2 (MP2) has been able to elevate secondary cycle pH to a level congruent with non-polishing plants, and the corresponding decrease in iron transport has allowed Millstone 2 to enter the industry top decile for final feedwater iron concentration. The paper describes the method by which MP2 was able to increase pH using a combination of hydrazine injection and full flow amine form polishers, and the effect on steam generator and balance of plant control parameters.

Gregory Bachman, Douglas Kellogg, and Marty Wilkes

PPChem 2012, 14(3), 148–154

Amine Chemistry – Update on Impact on Resin

Impurity removal in the steam cycle and the associated prevention of corrosion and/or fouling of system components are the goals of ion exchange resins. However, in many instances (such as a switch to amine chemistry or a change in product specifications), resins do not remove, and, in fact, contribute impurities to the steam cycle. This paper reviews recent data compiled to determine the direct and indirect effects of amines on ion exchange resins used in the power industry. Water chemistries have improved in recent years, in large part due to changes in chemistry and resins, but it is necessary to continue to develop products, processes and techniques to reduce impurities and improve overall water chemistry in power plant systems.

Pavel M. Gotovtsev and Viktor N. Voronov

PPChem 2012, 14(3), 158–162

Cycle Chemistry Monitoring Systems

One of the tasks of water chemistry control and monitoring at fossil power plants is prevention of water chemistry failure. This aim may be achieved by prediction of impurity concentrations in different parts of the cycle and calculation of the water chemistry parameters that cannot be measured directly by standard analyzers. One of the ways to accomplish these tasks is based on mathematical modeling of the water chemistry state with application of artificial neural networks (ANNs). This article gives a brief introduction to this topic and shows examples and problems of mathematical modeling of water chemistry and ANN applications.

Michael Bolz and Andreas Speck

PPChem 2012, 14(3), 164–173

Impact of Load-Follow Operation on the Chemistry of the Primary and Secondary Circuits of a Pressurized Water Reactor

In Germany, renewable energy forms have priority in being fed to the grid. More and more load operation of the nuclear power plants still in operation is necessary to stabilize the grid. This report summarizes the deviations in the chemical parameters experienced one particular weekend, when one nuclear power plant had to reduce power from full load (1 465 MW) to 1 020 MW and 860 MW, and generally assesses the expected impact of load-follow operation on chemistry and radiology. It concludes that if possible changes in the behaviour of the corrosion products and the corrosion process are monitored with an effective surveillance programme so that deviations can be addressed in time to take appropriate countermeasures, nuclear energy and renewable energies can complement each other.

Emmanuel K. Quagraine and Jonathan P. Ruffini

PPChem 2012, 14(3), 174–185

Chloride Contamination of the Water/Steam Cycle in Power Plants
Part II: Evidence for Two Previously Unknown Routes from Condenser Cooling Sources

This is the second paper in a series of publications on findings from investigations performed at the Shand Power Station of SaskPower to identify the root cause(s) of chloride contamination of the water/steam cycle experienced in the plant, which appeared quite elusive initially. In the first paper, we showed a case where the chloride ingress could not be explained by the current literature reported routes of chloride ingress. In this current paper, photographic evidence and sample test analyses – both qualitative and quantitative by methods such as N, N-diethyl-p-phenylenediamine (DPD) reagent spectrometric determination for residual chlorine, scanning electron microscopy–energy dispersive spectroscopy, inductively coupled plasma mass spectrometry, and combustion ion chromatography (AQF-IC) determination of anions – are presented to support a hypothesis that chloride ingress was emanating from the re-circulating condenser cooling water, but by a pathway(or pathways) completely different from the traditionally known condenser tube water leaks. Evidence is provided that residual chlorine compounds and/or chlorides were ingressing in both gaseous forms and aqueous forms into the condenser hotwell through weak seals of tube-to-tubesheet joints. The latter route, via a water-borne pathway, was shown to be distinctly different from that of the well-known condenser tube leaks by means of condensate contamination; it appears to follow a mechanism based on solubility differences to selectively contribute more chloride than sulphate from cooling water sources into the hotwell water. It was however determined to be only a minor contributor. The former route, however, was implicated as the dominant route. By this pathway, chlorinated species of relatively high vapour pressures (some of which are strong oxidizing agents) would ingress into the condensate portion of the condenser via tube-to-tubesheet joints. Dezincification of the brass tubesheet was found to be likely to occur by this means, causing deposition of ZnO at the point of contact on the condensate side of the condenser as observed.

Masamichi Miyajima, Yoshiaki Itou, Hiroaki Yamamoto, Senichi Tsubakizaki, Noboru Kawai, and Hiroshi Takaku

PPChem 2012, 14(3), 192–199

Evaluation of the Applicability of AVT(O) Feedwater Treatment to Cycles with HRSGs

In Japan, all-volatile treatment will be continued to be used even if hydrazine injection must be stopped, because the condenser performance is usually excellent. For the first time in Japan, we have conducted demonstration tests of the applicability of the oxidizing all-volatile treatment, AVT(O), without hydrazine due to concerns about the carcinogenicity of this chemical. No difference has been observed in water quality parameters such as the dissolved oxygen and the total iron concentrations between reducing all-volatile treatment, AVT(R), and AVT(O), and also no difference in the corrosion damage to the system equipment has been observed between the two water treatments. Furthermore, for heat recovery steam generators stored with water containing hydrazine during lay-up/outage, laboratory and power plant tests with hydrazine-free water have clearly shown that corrosion prevention is possible if the ammonia concentration is 50 $mg \cdot L^{-1}$ for less than one month and also 100 $mg \cdot L^{-1}$ for longer than one month. Based on these results, the application of AVT(O) has begun in several systems (14 units/3 400 MW) at Chubu Electric Power Co.

Markus Theobald and Frank Udo Leidich

PPChem 2012, 14(4), 205–213

Cold End Corrosion in Steam Turbines – Diagnosis and Remedies

During outages, general corrosion or even localized pitting corrosion can take place if no preservation measures are applied. Due to deregulated markets and the increasing availability of electricity produced by renewable energy sources like wind farms or solar power, conventional steam power plants are nowadays operated with frequent start-ups and shutdowns. Hence, turbines are commonly not designed for the period between shutdown and start-up, and specific preservation measures are needed to avoid corrosion on the turbine. With CECD (Cold End Corrosion Diagnostics), Alstom provides a diagnostic method which enables a cause-and-effect analysis of corrosive attacks and can also be used for determining whether there is a high probability of corrosion in the exhaust-steam area of condensing turbines.

Especially during short-term outages, when quite often no specific preservation measures are applied, CECD offers a benefit for the customer by selective modification of the shutdown procedure in order to avoid high relative humidity inside the low-pressure casing.

The paper gives a brief description of the method, focusing on examples of applications of this method that have already been carried out successfully.

Emmanuel K. Quagraine and Jonathan P. Ruffini

PPChem 2012, 14(4), 214–231

Chloride Contamination of the Water/Steam Cycle in Power Plants Part III: Computational Analysis and Plant Operational Evidence in Support of Cooling Water Source Gaseous Ingress Hypothesis

This is the third and final paper in the series of publications on investigations performed at the Shand Power Sation of SaskPower to determine a hitherto unfamiliar source(s) of chloride contamination to the water/steam circuit. The first paper showed that current popularly known causative factors were not individually or cumulatively responsible as root causes of the chloride ingress. The second paper provided evidence that the chloride ingress emanates from the cooling water, but through two different (gaseous and water-borne) pathways, each of which is distinctly different from the common condenser water leaks. The gaseous ingress pathway was identified as the likely main source of the contamination. In this final paper, computational analysis and plant operational data are used in support of this idea. The working hypothesis is that chlorinated compounds with significant vapour pressures (e.g. free chlorine species HOCl and Cl_2, chloramines NH_2Cl, $NHCl_2$ and NCl_3, trihalomethanes (THMs), haloacetic acids, HCl, etc.) ingress in gaseous forms into the condenser hotwell through weak seals of tube-to-tubesheet joints. Henry's constants and other equilibrium expressions have been used

to estimate gaseous ingress from these species (expressed as chloride) at different pH values of the re-circulation water. Under typical operation conditions in this plant, an estimated cumulative chloride concentration of up to 4.5 $\mu g \cdot L^{-1}$ (ppb) in the boiler feedwater is possible. Although the actual ingress experienced from these sources varies, it is estimated to be between 2 to 10 % of that from the expected cumulative sources. Under normal operating conditions, the three expected most dominant contributors of chloride are $CHCl_3$, followed by NH_2Cl and $CBrCl_2$. Two other chlorinated species of modest but significant chloride contribution are HOCl and $NHCl_2$, and their contributions are expected to be relatively higher under low cooling water pH excursion conditions.

Victor Marcu, Yosef Shechtman, Sara Moskovich, Eli Gal, and Michael Mengel

PPChem 2012, 14(4), 234–240

A Study of Possible Sources of Water for the FGD Project at the Orot Rabin Power Station

One of the problems of the wet flue gas desulfurization (FGD) technology is the large increase in water demand per unit power. While the present fresh water demand of the 6 units on the site under discussion is less than $1 \cdot 10^6$ m^3 per year, the addition of the future FGD plants means another $1.5 \cdot 10^6$ m^3 per year, for units 5 and 6 only. Since the water supply in Israel is scarce, several options were examined. The focus of the present paper is on "boronic water." Boronic water is a reject from the neighboring desalination plant. This stream results because of the regulatory demand of less than 0.5 $mg \cdot L^{-1}$ B in the final product. It is a basic salt water (pH = 10–11, NaCl = 400–500 $mg \cdot L^{-1}$, B = 30–90 $mg \cdot L^{-1}$). Its use would give rise to up to 3 000 $mg \cdot L^{-1}$ B in the absorber, which might cause various problems including limestone blinding. To check if its use in FGD is an option, experiments were performed, including 3 sets of trials that we called: equilibrium, kinetic and "process-like." In all the experiments, a suspension of limestone in water was titrated with sulfuric acid. The pH evolution was recorded, and the solution and solids analyzed for calcium, boron, chloride and sulfate. The results seem to indicate that the boronic water represents a realistic option for the FGD process in terms of quality, quantity, and economic and ecologic value.

Albert Bursik

PPChem 2012, 14(4), 252–257

Chemistry-Related Instrumentation in Combined Cycles – Helping Operators to Help Themselves

This contribution shows how employees at utilities and in industrial steam and power generation can pursue finding answers to their questions about topics such as the necessary extent of instrumentation and plant cycle treatment by turning to readily available (and free) sources such as the Technical Guidance Documents of the International Association for the Properties of Water and Steam. By studying the most current information about plant cycle chemistry and its monitoring, employees may be able to easily answer and solve many seemingly complicated questions and problems themselves, without having to ask other individuals or organizations for advice.

James A. Mathews

PPChem 2012, 14(5), 268–274

EPRI Assessment of Amines in Power Plant Chemistry Applications

All-volatile treatment (AVT) has become the industry standard for condensate, feedwater and steam chemistry in electric generating power plant cycles. Ammonia is the most commonly used alkalizing chemical for pH control in these cycles but exhibits poor dissociation and high volatility, which often result in less than adequate pH control in the first-formed condensate and liquid fraction of two-phase water/steam environments. Neutralizing amines offer characteristics to overcome the apparent deficiencies of ammonia and are finding increased usage in nuclear power and industrial boiler applications. EPRI investigations of the application of selected neutralizing amines have demonstrated that the decomposition rate of the amines often results in ammonia remaining as the principal alkalizing agent as well as an appreciable inventory of organic acids (namely formate and acetate) and carbon dioxide and only a minor or moderate residual of the original amine. While there still remains no quantifiable evidence that the breakdown products directly contribute to power plant damage, research has implicated organic acids involvement in stress corrosion cracking, and equipment suppliers are

reluctant to accept exceeding limits of cation conductivity from the accumulation of these by-products. Results of assessments of amines for use in power plant chemistry applications are presented with a query for more definitive scientific information on the potential corrosion risks and damage mechanisms associated with the high levels of the decomposition by-products.

Brian Windsor and David Hayhurst

PPChem 2012, 14(5), 282–287

A Practical Guide to Investigating Operating Problems on In-situ Regenerated Polishing Mixed Beds

This paper looks back at the historical problems that are still being frequently encountered on polishing mixed beds, these being typically apparent as very long rinse times to quality after regeneration, or consistently poor treated water quality (high conductivity). Over 95 % of mixed bed problems are caused by one or more problems in the following four areas of regeneration: poor resin separation, inadequate slow displacement rinsing, poor drain control prior to remixing, and air blowers. This article is designed to help plant chemists and operators in troubleshooting mixed bed problems by identifying the issues involved, as well as to give all readers a better understanding of polishing mixed bed operation.

Takashi Suzuki, Tetsuo Yamamoto, Masanobu Maekawa, Jun Hishida, Satoshi Kuwano, and Kazumitsu Takanishi

PPChem 2012, 14(5), 288–297

The Application of High AVT(O) in Gas Turbine Combined Cycle Plants

There is growing demand for reduced use of hydrazine at power plants due to the adverse health effects of this agent. Moreover, many combined cycle plants are affected by flow-accelerated corrosion (FAC), especially in feedwater systems, low-pressure boiler evaporators and other subassemblies.

Under such circumstances, modified oxidizing all-volatile treatment AVT(O) – high AVT(O) – was applied in the feedwater treatment system of combined cycle plants. The objective was to discontinue hydrazine injection into the feedwater, and to suppress FAC more effectively compared to AVT(O) by increasing the pH of the feedwater. Throughout four years of operation, the water condition was measured under all plant conditions such as normal operation, startup/shutdown operation, and unit outage for maintenance. In addition, the corrosion rate was followed closely by measuring the piping thickness at FAC-affected points. These test data clearly showed that this water treatment could keep ideal water conditions and is effective for suppressing FAC.

Albert Bursik

PPChem 2012, 14(5), 312–321

The Long Road from Potatoes and Wood Shavings to Combined Amine Mixtures

Although the use of organics in plant cycles has been a highly debated topic, there has been relatively little basic research conducted on the influence of organics and their decomposition products on the plant components; importantly, however, there is no scientifically based evidence to date that organics have caused serious availability problems. After a brief overview of some of the many questions and open issues related to the application of organic plant cycle treatment chemicals, this paper turns to its main theme, the history of the use of these additives and the modern forms which are being used in steadily increasing numbers.

George J. Verib

PPChem 2012, 14(6), 332–339

Operational and Layup Cycle Protection of High-Pressure Fossil-Fired Utility Boilers Using an Organic Filming Amine

Economic conditions have caused many fossil-fired units to either drastically cycle load or shut down during low demand periods, where previously the units had been under a constant-load operation. The most current cycle chemistry guidelines employed are excellent in protecting the steam-water cycle during constant-load operation, but they have not minimized corrosion and provided protection of unit equipment during economic reserve off periods. Alternate methods of off-line protection and transient-load operation have been explored to minimize corrosion during these periods. The

FirstEnergy Corp. has been using an alternate proprietary, organic filming amine to protect units during operation and short-term non-operational periods. Explored are the initial issues of high steam cation conductivity, use of the filming amine to protect the cycle during idle production periods, and the chemical amounts needed. The proprietary chemistry has shown the ability to successfully and significantly reduce corrosion throughout the steam-water cycle during transient-load situations and during non-operational periods while maintaining the chemistry guidelines of the industry and OEMs.

Kenneth J. Galt and Sumayyah Sulliman

PPChem 2012, 14(6), 346–361

Use of Filming Amine Treatment for Cycle Chemistry Operation on an 8.4 MPa Drum Boiler Unit after 20 Years of Storage

In the late 1980s Eskom was faced with a large overcapacity situation (≈ 30 %) and several stations were either shut down/mothballed or changed to two-shifting operation. By 2004, instead of overcapacity, there was an impending power shortage. Eskom began to build new stations and return mothballed plants to service. After 20 years of storage, Komati Unit 7 was the first mixed-metallurgy unit to be returned. Instead of implementing AVT(R) chemistry a decision was made to operate the unit under filming amine treatment (FAT). Although targeting compliance with existing Eskom cycle chemistry specifications (and the major international guidelines), the real criterion of success was minimisation of corrosion product (CP) transport, with Unit 7 being measured by comparison with CP transport on Unit 9, an all-ferrous unit operating AVT(O). The iron transport figures obtained showed comparable results on the two units, while copper transport was below detection levels. For Komati the ultimate goal is implementation of FAT on all 9 units; this paper relates the Komati FAT experience to date.

David Addison and Judy Weir

PPChem 2012, 14(6), 362–369

The Role of the Chemist/Chemical Engineer for the Trouble-Free Operation of Thermal Plants with Heat Recovery Steam Generators

The importance of a chemist/chemical engineer for the reliable and efficient operation of combined cycle gas turbine (CCGT) plants is discussed along with the key differences between routine and strategic chemistry and how these potentially impact on CCGT plant operation. Potential risks and issues with the full outsourcing of cycle chemistry services for a CCGT plant to chemical service providers are outlined. Also discussed are the interactions between a chemist/chemical engineer and plant management, operations, engineering and maintenance personnel. Proposed chemist/chemical engineer staffing levels for a number of hypothetical CCGT plants are also discussed.

Chris Armstrong, Andrew E. A. Bull, Malcolm S. Mitchell, Graham P. Quirk, Andy Rudge, and Ian S. Woolsey

PPChem 2012, 14(6), 372–379

Dimethylamine as a Replacement for Ammonia Dosing in the Secondary Circuit of an Advanced Gas-Cooled Reactor (AGR) Power Station

Increasing flow resistance observed over recent years within the helical once-through boilers in the four advanced gas-cooled reactors at Hartlepool and Heysham 1 Power Stations have reduced boiler performance, resulting in reductions in feedwater flow, steam temperatures, and power output and in the need to carry out periodic chemical cleaning. The root cause is believed to be the development of magnetite deposits with high flow impedance in the 9Cr1Mo evaporator section of the boiler tubing. To prevent continued increases in boiler flow resistance, dimethylamine is being trialled, in one of the four affected units, as a replacement to the conventional ammonia dosing. Dimethylamine increases the pH at temperature around the secondary circuit and, based on full scale boiler rig simulations, is expected to reduce iron transport and prevent flow resistance increases within the evaporator section of the boiler.

The dimethylamine plant trial commenced in January 2011 and is ongoing. The feedwater concentration of dimethylamine has been increased progressively towards a final target value of 900 $\mu g \cdot kg^{-1}$ and its effect on iron transport and boiler pressure loss is being closely monitored. The high steam temperature (> 500 °C) of the secondary circuit leads to some decomposition of dimethylamine, which is being carefully monitored at

various locations around the circuit. The decomposition products identified with dimethylamine dosing include ammonia, methylamine, formic acid, carbon dioxide and, as yet, unidentified neutral organic species.

The effect of dimethylamine dosing on iron transport and boiler pressure drops and its decomposition behaviour around the secondary circuit during the plant trial will be presented in this paper.

James A. Mathews

PPChem 2012, 14(7), 396–409

Optimizing the Continuum of Cycle Chemistry

In 2011 EPRI issued the fourth (4th) major revision to the cycle chemistry guidelines for fossil plants, re-combining the previously segregated "treatment" guidelines into a comprehensive document. As with each of the series of previous revisions, the 2011 updated guidelines focus on the optimization of chemistry practices for maintaining the availability, reliability, and economic performance of fossil power plants. A key element in the development and revision of the guidelines is extensive research conducted over the past fifty (50) plus years. Providing an understanding of the elements of the power plant cycle and the interrelationships of the best chemistry practices are a basic tenet of the introductory chapters of the guidelines. The target values for each treatment practice and location in the cycle are discussed with specific emphasis on optimization and customization to achieve excellent corrosion protection and elimination of deposition and component damage and failure. The rationale for proper chemistry is presented; for example properly maintaining oxidizing potentials, impact of temperature on pH control, assuring alkaline (sodium) neutralization for controlling boiler corrosion, and other considerations.

Masamichi Miyajima, Masaki Yoshida, Kazuo Marugame, and Hiroshi Takaku

PPChem 2012, 14(7), 410–417

Effect of Some Parameters on Single-Phase Flow-Accelerated Corrosion Evaluated by Jet-in-Slit Testing Method for Materials of Combined Cycle Power Plants with HRSGs

Flow-accelerated corrosion (FAC) of the equipment and pipes in combined cycle power plants with heat recovery steam generators (HRSGs) was evaluated by using a testing apparatus developed by the authors (the jet-in-slit testing method). It was confirmed that this testing method was useful for the investigation of FAC behavior in a relatively short testing time. It was demonstrated that an increasing dissolved oxygen concentration (DO) induced a decreasing mass loss for both ordinary and reverse water flows. An increased pH up to 9.8 has almost the same effect on the mass as increased DO up to 100 $\mu g \cdot kg^{-1}$. In contrast, the low-alloy steel STBA 24 showed an extremely small mass loss of 20–32 % of the carbon steel. Pre-treatment of the specimens with a carboxyl-based agent was most effective for the suppression of FAC as compared with AVT(O) and also low-alloy steel containing chromium.

Nestor van Eeden, Mandisibuntu Stwayi, and Gerhard Gericke

PPChem 2012, 14(7), 424–431

An Organic Profile of a Pressurised Water Reactor Secondary Plant

Make-up water addition to the steam/water cycle at Koeberg Nuclear Power Station usually results in a corresponding increase of the chloride concentration in the steam generator blowdown system. During plant transients, when higher than normal make-up is required to the secondary plant, the concentration of chloride occasionally exceeds the limiting value for the station chemistry performance indicator. Irrespective of this, the demineralised water make-up supply tanks, which are routinely analysed for chloride, are within all recognised acceptable standards for secondary water make-up and therefore these tanks do not initially appear to be the source of chloride contamination.

Water treatment at the plant relies essentially on ion exchange, which has been proven to be very effective in removing inorganic ionic species such as chloride. Organic compounds are less effectively removed by ion exchange and may pass through the treatment system, and these organics can reside undetected in the make-up water tanks.

Historically, the elevated chloride concentration following high system make-up has been attributed to chlorinated organic compounds known as trihalomethanes being present in the make-up water tanks, but no rigorous study had been undertaken.

As it has been assumed that the majority of chloride in the secondary system originates from the make-up water organic impurities, it was considered important to confirm this by compiling an organic profile of the secondary plant. The use of organic additives was also taken into account in the profile.

This work has confirmed the contribution from trihalomethanes and has also found that other organochlorides contribute even more significantly to the overall chloride inventory of the secondary plant.

Peter Janssen and Jo Savelkoul

PPChem 2012, 14(7), 440–448

In Search of an Alternative High-Pressure Boiler Water Treatment Program

In the early eighties, traditional inorganic chemistry treated high-pressure (HP) industry boilers, in the Netherlands and elsewhere, suffered from boiler tube failures (BTFs). Benchmarking and root cause analyses showed BTFs to be indisputably connected to a combination of high heat transfer rates and magnetite deposits. From 1980 to 1995, research was carried out on boiler water problems and on treatment of chemicals both in HP autoclaves at the DSM Water Laboratory and in real DSM plant boiler systems. Moreover, thorough desk studies were carried out.

Polyamine treatment came out as the most promising option to mitigate BTFs. It has been in use in Dutch industrial high-pressure boilers since 1996. This paper presents results from our research and from boiler and turbine experience and inspections totaling 15 years of polyamine treatment.

Viacheslav A. Ryzhenkov, Tamara I. Petrova, and Artem V. Ryzhenkov

PPChem 2012, 14(7), 449–454

The Influence of Molecular Layers of Amines on the Hydraulic Resistance of Piping Systems and Power Plant Equipment

The current state of pipeline systems and power equipment has a high accident rate due to intense corrosion, the accumulation of deposits on heat and in-line transfer surfaces, and high hydraulic resistance. Analysis and synthesis of published results shows that the solution to improving the efficiency of pipeline systems and power equipment can be approached from two directions: (i) the impact on the properties of transported media and (ii) changes in the properties of functional surfaces of pipelines and equipment. Improving the "quality" of the technological agents involves very substantial capital and operating costs, so the most promising way is to modify the surface properties.

Studies conducted at the National Research University MPEI showed that these problems are solved more effectively by means of molecular layers of adsorbed amines on the functional surfaces of pipes and equipment. When present in a certain way with the optimal number of molecular amine layers, these significantly alter the surface properties of conventional structural materials, which leads to very substantial improvement in the hydrodynamic characteristics: reduction of the hydraulic resistance of pipelines and equipment (up to 40 %), almost complete stoppage of corrosion processes (up to 7 times), and a multiple (up to 10-fold) reduction in the rate of deposit accumulation. The method of adsorption of molecular amine layers and the equipment for its implementation developed on the basis of this research will not only reduce flow resistance, but will also significantly improve the operating efficiency of pipeline systems and power equipment generally.

Heinz Wagner

PPChem 2012, 14(7), 455–469

Influence of Temperature on Electrical Conductivity of Diluted Aqueous Solutions

As conductivity is temperature dependent, all values reported in the major cycle chemistry guidelines are specified for a standard temperature of 25 °C. For this reason, most current conductivity monitors have an integrated temperature sensor and offer algorithms to convert measured values to the standard temperature. This article looks at the physical- chemical basics of electrical conductivity measurement and discusses the temperature dependence of specific and acid conductivity for different dissolved chemical substances. It is concluded that the conversion of a conductivity value to 25 °C can be approximated by a single equation that is applicable to samples composed of any electrolytes.

Judy Weir and David Addison

PPChem 2012, 14(8), 480–487

Minding Your R and Q's – Improving Water Treatment Plant Performance

Water treatment plants need to reliably produce water with the correct quality and required quantity for boiler and heat recovery steam generator feedwater, gas turbine water injection, or co-generation plant feedwater. Without the quality guarantees, the process that utilises the water will suffer from corrosion and/or deposition issues, and if the quantity is not produced reliably, then the process which uses the final water product cannot operate correctly. This paper discusses the practical tools to ensure "Reliability", "Quality" and "Quantity" – the "R & Q's" of a water treatment plant, in the form of a performance management plan and two water treatment plant case studies.

Elise Ring

PPChem 2012, 14(8), 489–507

Start-up, Shut-down and Lay-up Improvements at Eraring Power Station

In 2010 Eraring Power Station (Eraring) embarked on a program to improve their start-up, shut-down and lay-up procedures. Investigations showed that large amounts of copper and iron were being transported during start-up, reaching the boiler and turbine. Eraring is unable to meet EPRI key requirements for lay-up, and optimisation within the limitations of the plant has been the key focus. The improvement program implemented operational change with no capital expenditure occurring to date. The improvements have reduced standby corrosion and metals transportation and have allowed chemical parameters to be inside normal chemical operating limits within hours of the unit starting.

Along with the cycle chemistry advantages, the program has reduced Eraring's coming out of service times, allowing quicker access to the unit for maintenance, reduced the resource load on operating staff during coming out of service and return to service activities, and improved the overall understanding of personnel site-wide on the importance of appropriate unit lay-up. Eraring has improved the start-up, shut-down and lay-up strategies of its units in an effort to reduce metals transportation.

Masamichi Miyajima, Senichi Tsubakizaki, Toshiaki Ishihara, and Hiroshi Takaku

PPChem 2012, 14(8), 508–515

The Effect of the Injection of Trace-Content Oxygen on Flow-Accelerated Corrosion in Feedwater Treated with High AVT(O) for Combined Cycle Power Plants

To mitigate the reduction in pipe thickness caused by flow-accelerated corrosion and the formation of scale in the feedwater systems of combined cycle power plants with heat recovery steam generators, a design review was conducted for the modification of equipment and operational guidance before applying oxidizing all-volatile treatment (AVT). Based on the results obtained, the modified water quality standard was introduced as AVT(O)H for the boiler feedwater treatment. By changing the oxygen supplying method from the cylinder method to the use of instrument air, the equipment and running costs of the latter method could be reduced to approximately 1/4 of those of the former one.

Valil Sreedharan Sathyaseelan, Hariharan Subramanian, Yadavalli Venkata Harinath, Tulasi Venkata Krishna Mohan, and Sankaralingam Velmurugan

PPChem 2012, 14(8), 522–525

Dissolved Oxygen Removal by Catalyst-Loaded Ion Exchange Resin – Studies in a Simulation Loop

Dissolved oxygen control is important to reduce corrosion of various structural materials in the primary coolant system of pressurized heavy water reactors. Under normal operating conditions, in the presence of a radiation field, the added hydrogen scavenges any dissolved oxygen. Similar control is desirable under reactor shutdown conditions as well. This scavenging of oxygen is not available under shutdown conditions due to the lack of a radiation field. Conventional methods such as sodium sulphite, hydrazine addition, etc. can alter the water chemistry and are not very effective. In this work, a catalyst-loaded ion exchange resin, aiding the recombination reaction, was evaluated in a recirculating loop for its suitability to remove dissolved oxygen in nuclear reactor water coolant systems. The process was successfully demonstrated and the dissolved oxygen level could be brought down to 0.01 $mg \cdot L^{-1}$. The extent of palladium leaching from the resin was also investigated.

Randy C. Turner

PPChem 2012, 14(8), 526–533

Cation Conductivity Monitoring in Cycling Plants – A New Approach

Due to substantial fuel costs, environmental issues, and economic impact, there has been increased pressure in recent years to reduce start-up times for all units, particularly combined cycle units. Any shortening of the time between start-up and reaching full load is of paramount importance. Cation conductivity is still the decisive measurement for the start-up of the steam turbine and the focus is now on how fast the cation conductivity results are available and how reliable they are. The time necessary to obtain correct and representative analysis values is greatly influenced by the design of the sampling and monitoring system. Employing various measures for the optimization of continuous monitoring equipment and employing optimally designed analyzers can reduce the response time of the instrumentation by more than half, thus providing significant economic rewards. The costs of the improvements are negligible compared to the benefits of reducing the time operating in bypass mode.

Matthew K. Heermann

PPChem 2012, 14(9), 548–556

Chemistry Data Collection for Statistical Analysis – Characterizing Plant Waters for Scope Documents

Specification of water treatment projects requires sufficient data to characterize the feedwater to water treatment systems. Ideally, the data provided by plant owners and operators should cover the seasonal variations associated with the water supply. However, projects are often initiated based on limited sampling and analysis. In some cases, data from merely a few days or weeks, or even from a single sample, are all that is provided. This is particularly the case with respect to trace metal analysis, which is not normally included in a plant's routine chemistry sampling regimen.

Insufficient data can result in problems that compound one another. Inadequate sampling and analysis leads to inadequate characterization of water streams. Inadequate characterization leads to inadequate or inappropriate selection of treatment equipment.

Routine sampling, collection, and retention of plant water data are important for properly scoping treatment equipment and also operating the equipment after installation. Unintended consequences include over- or under-design of the system.

Surface and ground waters are both subject to seasonal variations in water quality, such as in total suspended solids (TSS) and total organic carbon (TOC), as well as other constituents. Single-sample analyses, and, similarly, small sets of sample analyses taken over a short period, do not detect seasonal variability in feedwaters. Routine monthly or quarterly water sampling and data analysis does detect seasonal variation. These variations need to be analyzed and recorded in order to properly determine the scope of a water treatment system.

Large datasets also enable operators to determine whether a particular datum is an outlier. Outliers are not only caused by actual stream conditions, but by poor analysis technique, transcription errors, and other factors. Without other data points to compare with the potential outlier, a mathematical determination to remove the outlier cannot be made and a treatment system may be improperly sized, especially if the outlier is low.

This paper discusses the basics of statistical analysis and the benefits of routine sampling and analysis, such as the determination of statistical outliers. It compares a single analysis with the mean and with the 99 % statistical maxima of an extended dataset, and compares results from season to season of an extended dataset.

Marco Lendi and Peter Wuhrmann

PPChem 2012, 14(9), 560–567

Impact of Film-Forming Amines on the Reliability of Online Analytical Instruments

There are very few reports describing the effects of the dosing of film-forming amines (FFAs) on the online monitoring equipment. This paper describes controlled, laboratory-like tests performed to ascertain the impact of three different brands of film-forming amines on system parameters. Specific conductivity, pH drift, cation resin retention, pH stability, sodium step response, sodium calibration, oxygen sensor response and ORP probe response were considered. While with some measurements no negative influence could be observed, with other equipment there was a loss of sensitivity and speed of response time due to coating effects. There were also differences in some results depending on the FFA used.

Haruka Kido, Taro Ichihara, and Senichi Tsubakizaki

PPChem 2012, 14(9), 568–574

Success of CWT Application and Introduction of Countermeasures for Powdered Scale Deposit

Oxygenated feedwater treatment (OT) using oxygenation methods for boiler feedwater was first introduced at a thermal power utility plant in Japan in 1990 based on the success of combined water treatment (CWT) applications in Europe. It is now operational at 53 Japanese electric utility thermal power plants, 20 years after its introduction. Recently, some CWT plants have experienced increased iron concentrations in the drain system of the low-pressure feedwater heaters. In addition, a powdered scale deposit has been generated and has attached to the inside of the furnace wall tubes, contributing to an increase in the wall tube temperature. As a countermeasure, a high-temperature filter was used to remove the iron suspended in the drain system; the results validated the effectiveness of the filter.

James Robinson, Luis Carvalho, and Gregory Robinson

PPChem 2012, 14(9), 579–591

The Pros and Cons of Using Organic Amines to Treat High-Purity Boiler Feedwater

Organic amines have been used for decades and continue to be used to protect steam plant equipment and maintain reliable, efficient plant operations. Their proper use can provide increased corrosion protection not available through the use of inorganic chemicals alone. Research has found that these organic treatments or their decomposition products have low corrosion risk as long as pH is adequately maintained. In the power industry, many avoid using organic chemical treatments because their use causes them to exceed the turbine manufacturer's steam cation conductivity limits. Yet, meeting those limits does not assure that potentially acidic species, such as chloride and sulfate, are within an acceptable range. Thus improved criteria for steam purity and plant-friendly methods of monitoring those criteria are needed.

Christopher J. Strahler, Stephen E. Winter, and Donald J. Broton

PPChem 2012, 14(9), 592–597

Validation of a TGA Method for Routine Monitoring of Wet Limestone Forced Oxidation Scrubbers with Emphasis on $CaSO_3 \cdot 0.5H_2O$ Detection

A validated thermogravimetric analysis method has been developed for daily monitoring of $CaSO_3 \cdot 0.5H_2O$ in flue gas desulfurization (FGD) solids and gypsum byproduct. The method demonstrated acceptable performance to reliably and accurately measure $CaSO_3 \cdot 0.5H_2O$ down below 1 %. Reliable detection of sulfite is important for modern wet limestone forced oxidation scrubbers because its presence beyond a few percent as $CaSO_3 \cdot 0.5H_2O$ can indicate oxidation chemistry issues. The method should provide plant FGD laboratories with a proven instrumental alternative to wet chemistry while offering the convenience of determining many FGD parameters (free moisture, $CaSO_4 \cdot 2H_2O$, $CaSO_3 \cdot 0.5H_2O$, and $CaCO_3$) with one method.

Fernando-Mario Roumiguière, Jörg Fandrich, Ute Ramminger, Stephan Hoffmann-Wankerl, and Andreas Drexler

PPChem 2012, 14(10), 608–620

Secondary Side Water Chemistry pH Control Strategy Improvements

When selecting a pH control strategy, plant design and operation characteristics have to be carefully considered. The strategy should be tailored to the plant-specific needs and requirements. Owing to the complexity of the interrelated variables, the best way is to perform a modeling with a suitable computer code. This work investigated the possibility of complementing the classic high pH all-volatile treatment (H-AVT) by addition of an organic amine at low concentrations complementarily to ammonia dosing to locally increase the pH in the water phase of the wet steam areas to counteract flow-assisted corrosion (FAC). Alternative conditioning scenarios were considered and calculated for comparative analysis using a computer code. The results obtained argue for the convenience of using ammonia as the main alkalizing agent whenever possible, avoiding multiple amine concepts and their associated drawbacks.

Michael Sheedy and George Di Falco

PPChem 2012, 14(10), 624–630

High Purity Boiler Water Production Using Municipal Wastewater at a Combined Cycle Gas-Fired Generating Station

The recovery of wastewater for industrial uses presents many challenges for the design and operation of water treatment equipment. Since the term wastewater can be applied to a wide range of water sources from municipal sewage to storm runoff to industrial discharge water, the water characteristics may have great variability. As such, the equipment to treat wastewater must be robust and forgiving. When these wastewaters are used to produce ultra high purity boiler feedwater, the challenges become magnified.

This paper describes a water treatment system, fed with municipal wastewaters, for the production of high purity boiler feed makeup water at a combined cycle gas-fired power plant, and the experiences of the plant operator after five years of continuous operation. This fully automatic water treatment system consists of micro-media filtration, reverse osmosis and a short bed ion exchange demineralizer/polisher, and requires minimal operator attention and maintenance.

Peter Nicoll, Neil Thompson, and Victoria Gray

PPChem 2012, 14(10), 632–640

Forward Osmosis Applied to Evaporative Cooling Make-up Water

Modern Water is in the process of developing a number of forward osmosis based technologies, ranging from desalination to power generation. This paper outlines the progress made to date on the development and commercial deployment of a forward osmosis based process for the production of evaporative cooling tower make-up water from impaired water sources, including seawater.

Evaporative cooling requires significant amounts of good quality water to replace the water lost by evaporation, drift and blowdown. This water can be provided by conventional desalination processes or by the use of tertiary treated sewage effluent. The conventional processes are well documented and understood in terms of operation and

power consumption. A new process has been successfully developed and demonstrated that provides make-up water directly, using a core platform 'forward osmosis' technology.

This new technology shows significant promise in allowing various raw water sources, such as seawater, to be used directly in the forward osmosis step, thus releasing the use of scarce and valuable high grade water for other more important uses. The paper presents theoretical and operational results for the process, where it is shown that the process can produce make-up water at a fraction of the operational expenditure when compared to conventional processes, in particular regarding power consumption, which in some cases may be as low as 15 % compared to competing processes. Chemical additives to the cooling water (osmotic agent) are retained within the process, thus reducing their overall consumption. Furthermore the chemistry of the cooling water does not support the growth of *Legionella pneumophila*. Corrosion results are also reported.

George Licina

PPChem 2012, 14(10), 641–649

Modern Materials – Are They Better or Worse?

Many plants have ordered replacement materials for piping, heat exchanger tubing, etc. but found that the replacement material, intended to be a like for like replacement, has provided much poorer performance than the material from original construction. In the absence of additional background, plant personnel are at a loss for why more modern materials and components fabricated from more modern materials often provide service inferior to that of original equipment.

Replacement components that commonly exhibit service that is poorer than that of the original equipment are heat exchangers, including heat exchangers tubed with copper alloys or stainless steels, stainless steel piping, stainless steel castings (e.g., valve bodies, pumps), and many other components where the same part number as the original has been ordered, but where the replacement part provides dramatically inferior service.

Ellen Kemp,
Bruce Kerr,
Robert Drane, and
Toyin Ayodeji

PPChem 2012, 14(10), 653–663

Water Management Recovery at CS Energy's Callide Power Station in Response to the 2011 Rain Event in Queensland, Australia

Prior to the 2011 floods in Queensland, CS Energy commenced a comprehensive Waste Management Improvement Program at the remote Callide Power Station located near Biloela, in Central Queensland. A Hatch employee was seconded into CS Energy to coordinate the strategy for developing and implementing actions for ash, water, and salt management in the short, medium, and long term. The unprecedented flooding drastically altered the timeline for some of these plans. In March 2011, the project schedule was changed to address the immediate need for water disposal and the addition of the Ash Dam Remediation Project. This paper reviews the relevant experiences and discusses the success of the project execution.

Reports on Selected International Events

Ruedi Germann

PPChem 2012, 14(4), 244–249

Report on the SWAN/PowerPlant Chemistry Power Cycle Instrumentation Seminar in Bangkok, Thailand

This contribution is a report on the first Power Cycle Instrumentation Seminar, held in Bangkok, Thailand, on March 27–28, 2012. The presentations of the four seminar sessions, Chemical Regimes and the Respective Chemistry-Related Surveillance Requirements, Analytical Methods and Instruments, Cooling Water Sampling and Monitoring, and a Hands-On Session, are summarized.

Paul McCann and Mark Robson

PPChem 2012, 14(5), 298–305

Proceedings of the BIAPWS 2012 Symposium on Power Plant Chemistry

The British and Irish Association for the Properties of Water and Steam held its annual Symposium on Power Plant Chemistry on 28–29 March 2012 in Chilwell, Nottingham. Summaries of the event proceedings are provided.

Ladislav Bursik

PPChem 2012, 14(6), 386–391

The Third International Conference "Interaction of Organics and Organic Cycle Treatment Chemicals with Water, Steam, and Materials"

The Third International Conference "Interaction of Organics and Organic Cycle Treatment Chemicals with Water, Steam, and Materials" was held on May 21–23, 2012, in Heidelberg, Germany. Abstracts of the papers presented at the conference are provided.

K. Anthony Selby

PPChem 2012, 14(7), 433–439

Workshop – Extending the Life and Reliability of Power Plant Equipment through Improved Chemical Control

In June this year, the 32nd Annual University of Illinois Electric Utility Chemistry Workshop took place in Champaign, IL, U.S.A. The content of the workshop and abstracts of the papers presented at this event are compiled in this paper.

Michael Rziha

PPChem 2012, 14(10), 672–674

Meeting of the IAPWS Working Group 'Power Cycle Chemistry' in Boulder, CO, U.S.A., September 30 – October 5, 2012

The International Association for the Properties of Water and Steam (IAPWS) working group "Power Cycle Chemistry" (PCC) recently held its annual meeting in Boulder, Colorado, U.S.A. PCC brings together scientists and engineers, power plant operators, equipment manufacturers and other relevant interested parties to collaborate and share results of scientific and engineering research, address gaps in technical information relating to power cycle chemistry, and to seek resolution of these gaps through international cooperative projects and the release of appropriate documents. The activities of PCC and the IAPWS are presented in more detail and a summary is given of this year's meeting.

2013's Scientific and Technical Contributions

J. Tucker Palmer, Philippe Dekleva, Matthew Heim, and Kenneth Ogan

PPCHEM 2013, 15(1), 4–10

On-Line Monitoring of Chloride and Sulfate in the Steam Cycle with a New Analytical Technique

EPRI guidelines recommend keeping chloride and sulfate concentrations in the steam cycle at less than 3 $\mu g \cdot L^{-1}$ in order to keep corrosion problems at bay. However, EPRI also notes the challenge of making routine, on-line measurements of these ions at these low concentrations. This presentation describes the development of a new approach to on-line monitoring of trace levels of chloride and sulfate, based on microchip capillary electrophoresis (MCE). In this prototype system, replenishment of the sample and electrolyte in the analytical microchip has been automated to provide fully unattended operation. This new analytical system provides very high sensitivity (at the single $\mu g \cdot L^{-1}$ level) for the simultaneous determination of chloride and sulfate, comparable to that of ion chromatography. It also provides rapid single assays (< 8 min), or fast, repetitive assays (4 in 16 min), which produce an estimate of the measurement variability as well. A consequence of the high sensitivity of this system was the discovery of a variety of unexpected contamination sources. Suitable operating procedures have been developed to prevent external contamination in order to ensure accurate results from this system. In addition to reporting on the accuracy and reproducibility of the instrument in laboratory testing, we also report on the results from several extended tests of the instrument at power plants.

Dan Sampson

PPCHEM 2013, 15(1), 14–24

No Easy Answers: ZLD Improvement Options for a 720 MW Power Generation Facility

The zero liquid discharge (ZLD) system of a relatively new 720 MW power generation facility receives cooling tower blowdown as the primary feedwater. Although the ZLD system allowed unrestricted power plant operation for the first three years following commissioning, in subsequent years ZLD system bottlenecks have restricted plant operation and required a significant amount of off-site wastewater disposal.

This paper examines the plant's ZLD system in detail, focusing on the following questions:

1. Why is the ZLD system a problem now when it wasn't a problem in the past?
2. What process improvements have been attempted in the past and with what results?
3. What options exist for eliminating or mitigating the ZLD process bottlenecks and at what cost?

The discussion answers these questions with the goal of providing a clear understanding of the current situation and the options to improve the system in the future.

Marvin Drake, Gary Willer, Ramraj Venkatadri, Spence Wise, and Narasimha Charan

PPCHEM 2013, 15(1), 25–31

Treatment of Cooling Tower Blowdown Water with Membranes in a Zero Liquid Discharge (ZLD) Power Plant

The Indiantown Cogeneration Plant has recently modified their zero liquid discharge scheme to incorporate membranes to treat the blowdown from their cooling tower. This was originally sent to two brine concentrators. The plant required the flexibility to use any combination of makeup water. It was also desirable to replace the brine concentrators due to corrosion and to achieve savings in power. The integrated membrane system (microfiltration and reverse osmosis) was commissioned in 2011. It allowed the brine concentrators to be replaced and generates high-quality permeate for boiler feed while maintaining zero liquid discharge.

Albert Bursik

PPCHEM 2013, 15(1), 35–39

Important Recently Issued Fossil Plant Cycle Chemistry Guidelines

In response to requests by readers, the PowerPlant Chemistry editor introduces three new fossil plant cycle chemistry guidelines (one issued by the Electric Power Research Institute (EPRI) and two issued by the VGB PowerTech (VGB)). Background information about these two influential organizations and their activities is also presented.

Emmanuel K. Quagraine

PPCHEM 2013, 15(1), 41–61

Chloride Contamination of the Water/Steam Cycle in Power Plants

Part IV: Association with Tubesheet Dealloying as Evident during a Condenser Re-tubing

This paper is a continuation of a series of publications on investigations performed at the Shand Power Station (SaskPower) to determine a hitherto unfamiliar source(s) of chloride contamination to the water/steam circuit. The first showed that current popularly known causative factors were not individually or cumulatively responsible root causes of the chloride ingress. The second provided evidence from overhaul inspections and sample test results that the chloride ingress emanates from a cooling water source, but through two different (gaseous and water-borne) pathways, each of which is distinctly different from the common condenser tube water leaks. The gaseous ingress pathway was identified as the likely main source of the contamination. In the third paper, computational analysis and plant operational data were used in support of this idea. The working hypothesis was that chlorinated compounds with significant vapor pressures (e.g. free chlorine species HOCl and Cl_2, chloramines NH_2Cl, $NHCl_2$ and NCl_3, trihalomethanes (THMs), haloacetic acids, HCl, etc.) ingress in gaseous forms into the condenser hotwell through weak seals of tube-to-tubesheet joints. Apart from some THMs (i.e. $CHCl_3$ and $CBrCl_2$), which are likely to be lost significantly through air ejection and deaeration processes, NH_2Cl, HOCl and $NHCl_2$ were noted to be potential significant contributors of chlorides to the water/steam cycle from the re-circulating cooling water. Dezincification was implicated as the corrosion mechanism occurring from the attack of these oxidizing chlorinated compounds on weak naval brass tube-to-tubesheet joints, thus creating a pathway for the vapor of these relatively volatile inorganic solutions to enter the shell side of the condenser. This fourth paper first provides a brief literature background and follows up with pictorial evidence of the dezincification process and results of more detailed laboratory analyses of samples collected during the condenser tube removal and re-tubing periods in support of the above hypotheses.

Abstracts 2012

PPCHEM 2013, 15(1), 63–79

2012's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Karol Daucik

PPCHEM 2013, 15(2), 92–99

Quantification of Chemistry Related Asset Damage

At the yearly meeting of the Working Group Power Cycle Chemistry of the International Association for the Properties of Water and Steam (IAPWS) in 2007, a task group entitled "Quantification of chemistry related asset damage" was established. The goal of the task group was to try to define a system for the manageable evaluation of the connection between chemistry and economy in the power industry. It is very difficult to quantify the value of chemical control as the link between chemistry and economic consequences is usually indirect, and benefits or damage may be the result of a combination of factors over time. This contribution presents the results reached by the task group.

Jeanette Shoemaker, Christopher Huth, and Kumar Sinha

PPCHEM 2013, 15(2), 146–153

Conserving Gallons and Kilowatts: Challenges of Today's Solar Power Plants – An EPC* Perspective

With the increasing restrictions on CO_2 emissions, the utilization of solar power is emerging as an effective way to increase the renewable portfolio for utility power. For example in California, the utilities' current renewable portfolios must increase from 20 % to 33 % by 2020. This drive has made renewable power considerably more desirable. However, fresh water availability and optimal solar irradiation are generally two mutually exclusive local characteristics that make locating and designing these plants challenging. Not only is fresh water scarce at the desert locations where these solar plants are generally located, but options for disposal of wastewater can be very limited as well. These factors have pushed the design of these plants to develop a fine balance between conserving and reusing water to the greatest extent practical and reducing parasitic electrical loads.

This paper addresses the challenges associated with developing solar power plant designs that optimize house electrical load while minimizing water footprint. Through the implementation of operational water management techniques and optimized water treatment processes, water usage can be reduced to manageable levels. Utilizing systems that recover and recycle wastewater, the system can be further optimized to reduce the overall water footprint. Case studies are presented for multiple sites detailing the individual optimization required based on the water quality provided. Lessons learned during plant siting and permitting are provided to shed light on the current issues associated with wastewater disposal in these areas and utilization of evaporation ponds. In addition, various design philosophies are discussed to guide the reader through the difficulties of determining the right mix of initial capital cost, optimized water usage, minimized operating cost and minimized parasitic electrical load.

* EPC = Engineering, Procurement and Construction

Qiuyang Cao, Zhouhai Qian, and Liwei Zhu

PPCHEM 2013, 15(2), 155–159

Troubleshooting and Treatment of Declining Boiler Feedwater Quality

The conductivity of aqueous solutions is one of the most commonly used analytic readings in the field of water chemistry. In thermal power plants, to avoid the interference of ammonia, cation conductivity is used to show the purity of feedwater, boiler water, and steam instead of specific conductivity.

The cation conductivity of the feedwater of Unit 2 at Changxing Power Plant increased substantially and the sodium content in the feedwater fluctuated frequently. This paper describes the process of troubleshooting and treating the deteriorating feedwater quality of Unit 2 at Changxing Power Plant.

R. B. Dooley and K. J. Shields

PPChem 2013, 15(3), 168–180

Fossil and Combined Cycle / HRSG Plant Layup with "Continuum of Protection" Philosophy

Significant damage of steam-water cycle components may develop during operation as a consequence of unprotected shutdown of utility fossil units. A "Continuum of Protection" approach is presented which may be applied to evaluate and develop effective procedures for protection of steam- and water-touched surfaces.

Chaiwat Lertsurasakda, Piti Srisukvatananan, Lihui Liu, Derek Lister, and James Mathews

PPCHEM 2013, 15(3), 181–189

The Effects of Amines on Flow-Accelerated Corrosion in Steam-Water Systems

A laboratory study has elucidated the effects of additives on FAC under two-phase steam-water conditions at 200 °C. On-line monitoring with electrical-resistance probes in a high-temperature water loop indicated the rate of attack of carbon steel under several conditions of steam voidage and flow rate with and without the amines ammonia and ethanolamine. Ethanolamine was introduced without any of its breakdown products such as acetic acid that normally accompany it in industrial plant. Selective sampling of

the flow regime during ammonia addition indicated the rapid distribution of ammonia between steam and water and allowed estimates to be made of the extent of the liquid film at the flow channel wall – an important parameter for modelling FAC. The results of the study and their interpretation are presented, and the implications for operating steam-water cycles discussed.

David R. Addison and Lester S. Stanley

PPCHEM 2013, 15(3), 191–203

Chemistry and Mechanical Field Assessment Actions for Effective Flow-Accelerated Corrosion Minimisation in Heat Recovery Steam Generators

The existence or otherwise of flow-accelerated corrosion (FAC) in a heat recovery steam generator is often determined via a field assessment during a plant outage. For a FAC field assessment to be successful pre-reviews of the cycle chemistry and mechanical aspects of the FAC risk factors for a heat recovery steam generator (HRSG) need to be undertaken. This allows for the production of a detailed prioritised list of inspection locations for the HRSG for visual and borescope inspections and for ultrasonic thickness measurements. It also includes an assessment of the effectiveness or otherwise of the cycle chemistry program in relation to FAC minimisation. The use of a prioritised list of inspection locations increases the probability of the early detection of FAC (or the confirmation that FAC is not occurring) so that remedial actions such as cycle chemistry optimisation and engineering modifications to the HRSG can be undertaken to minimise the risk of future FAC failures occurring. The effective management of FAC is a continuous process requiring ongoing cycle chemistry reviews and mechanical FAC field assessments.

Nathan A. Parker and Andrew G. Howell

PPCHEM 2013, 15(3), 212–215

Reduction of Condenser Carbon Steel Corrosion with Neutralizing Amines

Distinct changes in the appearance of the surface oxides on carbon steel condenser steamside walls and supports were directly correlated with a move away from an amine blend used for condensate pH control. The change resulted in the formation of large patches of bare metal; subsequent use of a mixture containing methoxypropylamine resulted in rapid regrowth of the oxide layer. The facility plans to continue to feed amines with the hope of better protection of the plant systems, as demonstrated by less iron corrosion and transport.

Karsten Thomsen

PPCHEM 2013, 15(3), 216–230

Handling a Serious Seawater Contamination of the Water-Steam Circuit of a Once-through Boiler at Amagerværket

In February 2012 a major contamination of the water-steam circuit occurred during a start-up of the once-through unit AMV3 at Amagerværket in Copenhagen. The contamination was due to a broken tube in the condenser and was not caught in the condensate train because of only partial condensate polishing. The condenser was equipped with titanium tubes, so a leakage was unexpected, and it was not discovered until the salt had reached the evaporator. Although the condensate and feedwater trains and the boiler were flushed intensively afterwards and during the following start-up, it became apparent that all salt had not been removed from the system when passing from recirculation to once-through operation. For several days the acid conductivity of feedwater and steam stayed far above the recommended values (operation in action level 2) and the contamination thus spread to the superheaters and the turbine.

The paper describes the countermeasures taken to handle the situation when the extent of the contamination of the complete water-steam circuit was realized. As a first step preparations were made for rapid dry air conservation at the next stop, and possibilities to clean the system were considered. Due to a trip of the unit in March, these actions had to be implemented with short notice. It was decided to perform a wash of the superheaters and turbines with wet steam to dissolve and remove the deposited salts. The basic idea was that wet steam could be achieved by increasing the amount of spray water injected during operation with limited steam production. Since there was no standard procedure available for this, experience had to be gained during the process. It turned out that the wet steam conditions could only be achieved in the reheaters and in

the intermediate-pressure turbines for short periods during transient conditions. Fortunately, this was sufficient to dissolve and remove the salts, and the overall impression was that the salts were successfully washed away.

Following the incident the instrumentation was reviewed to explain why the initial contamination was discovered so late. It turned out that the measured parameters were essentially correct; however, the response times were far too long to handle a contamination of a system with only partial condensate polishing. The subsequent improvements in monitoring are briefly mentioned.

Sang-Kwon Lee, Wenjun Kuang, James A. Mathews, and Digby D. Macdonald

PPCHEM 2013, 15(4), 240–250

Monitoring Crevice Corrosion via the Coupling Current
Part I: Detecting Crevice Activation, Inversion, and Inhibition

A simple crevice corrosion monitor was developed to monitor crevice corrosion in 1018 mild steel, Type 304 SS, and Type 410 SS in NaCl solutions with and without the addition of a chemical corrosion inhibitor. The monitor, which measures the electron coupling current, accurately followed the evolution of crevice activity in a manner that can be understood in terms of the cathodic process that occurs on the external surface and the partial anodic process that develops within the crevice, due to the accumulation of H^+ and Cl^-. The crevice initiation time is typically very short, but appears to depend upon the chloride concentration and possibly on the inhibitor concentration. The coupling current increases with time after initiation, passes through a maximum and then decreases, eventually changing sign to mark crevice inversion. The inversion is attributed to the gradual build-up of H^+ in the crevice to the extent that proton reduction within the crevice becomes the principal cathodic reaction in the system, while the anodic reaction moves to the external surfaces. In addition, amines are effective corrosion inhibitors of crevice corrosion of mild steel and stainless steels in NaCl solutions, provided that they are present in sufficiently high concentrations.

Shunsuke Uchida, Masanori Naitoh, Hidetoshi Okada, Hiroaki Suzuki, Seiichi Koshizuka, and Derek H. Lister

PPCHEM 2013, 15(4), 252–263

Determination of High-Risk Zones for Local Wall Thinning due to Flow-Accelerated Corrosion

A 6-step evaluation procedure based on the 3D computational fluid dynamics (CFD) code has been developed to evaluate local wall thinning due to flow-accelerated corrosion (FAC). As a result of verification and validation (V&V) evaluation of the 3D FAC code, it was confirmed that a wall thinning rate could be predicted with an accuracy of a factor of 2. One of the disadvantages of the 3D FAC code was that it required a lot of computational time and memory. In order to minimize computational time, a speedy and easy-to-handle FAC code based on 1D CFD analysis was developed. As a result of a V&V evaluation based on a comparison of calculated and measured wall thinning, it was confirmed that regional maximum wall thinning rates could be predicted with an accuracy within a factor of 2.

Then it was applied for FAC risk evaluation for entire plant systems to point out the locations where future problems might occur and to prepare for continuous pipe inspections and early implementation of suitable countermeasures. For this purpose, not only the probability of serious wall thinning occurrence in the future but also a hazard scale of pipe rupture due to the serious wall thinning was analyzed. FAC risk was defined as the mathematical product of the possibility of serious wall thinning occurrence and its hazard scale.

James Malloy, Mark Taylor, Andreas Fabricius, Marc Graham, and David Moelling

PPCHEM 2013, 15(4), 264–274

Evaluating Contributions of Flow-Accelerated Corrosion and Liquid Droplet Impingement to Pipe Thinning in HRSG Evaporator Tubes

Recent research indicates that liquid droplet impingement (LDI) is a potentially significant contributing factor, alongside flow-accelerated corrosion (FAC), in the incidence of boiler tube and pipe wall thinning. The difficulty remains in predicting the relative contribution of each phenomenon in a given set of operating conditions. Results from several field investigations into tube thinning and failures in the two-phase regions of

low-pressure evaporator circuits of heat recovery steam generators (HRSGs) are presented. The primary mechanism for the observed wear is attributed based on the observed wear morphology, rate of wall thinning, water chemistry and location in the HRSG circuit. The attributed wear mechanism is compared with predictions obtained using well-known semi-empirical formulations for material loss due to FAC and LDI. Process conditions used in the formulations are generated using a boiler simulation program. Using the results, basic rules are proposed for evaluating the relative potential of LDI and FAC to contribute to flow-induced wall thinning in HRSG components.

Wolfgang Hater and André de Bache

PPCHEM 2013, 15(4), 289–301

Considerations on Conductivity and pH in Water/Steam Cycles Using Organic Cycle Chemistry

Conductivity and pH are important parameters for monitoring and controlling water/steam cycles. For all-volatile treatment (AVT) with ammonia, pH is frequently calculated from conductivity measured on-line. The impact on the calculated pH is discussed for systems treated with volatile organic amines instead of ammonia. By means of an equation describing the dependence of the pH on thermodynamic data, the difference in pH between ammonia and various amines is analyzed. The necessary data for film-forming amines have been determined with a specific measuring unit minimizing the adsorption. From the obtained data the conductivity and pH of solutions of amine mixtures with and without film-forming amines are calculated and compared to data from steam generators. The acid conductivity measured in water/steam systems treated with film-forming amines is analyzed in dependence on operation data from the plant as well as analytical data from liquid chromatography – organic carbon detection and ion chromatography. The data are discussed with regard to water/steam quality specifications for organic cycle chemistry based on filming amines, and recommendations for monitoring are given.

PPCHEM 2013, 15(4), 303–315

Instrumentation for Monitoring and Control of Cycle Chemistry for the Steam-Water Circuits of Fossil-Fired and Combined Cycle Power Plants

A guidance document on the instrumentation for monitoring and control of cycle chemistry for the steam-water circuits of fossil-fired and combined cycle power plants was developed within the IAPWS Power Cycle Chemistry Working Group. This technical guidance document was first issued in 2009. In response to comments received, the 2012 revision includes a small number of minor updates and clarifications. These do not constitute significant changes to the scope of the document or to the guidance contained in it. This technical guidance document was authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Boulder, Colorado, USA, 30 September to 5 October, 2012, for issue by its Secretariat. The members of the IAPWS are: Britain and Ireland, Canada, the Czech Republic, Germany, Japan, Russia, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States of America. Associate Members are Argentina and Brazil, Australia, France, Greece, Italy, New Zealand, and Switzerland. The document represents the accumulated experience of the IAPWS Power Cycle Chemistry (PCC) Working Group with representation from 15 countries.

In order to achieve suitable chemical conditions in steam-water circuits it is essential to establish reliable monitoring of key parameters on every plant. This enables the demonstration of operation within cycle chemistry targets, and alerts the operators to the need to take corrective action when the target conditions are compromised.

This technical guidance document considers conventional fossil and combined cycle/HRSG plants and identifies the key instrumentation and monitoring techniques required for each plant type and cycle chemistry treatment. It is emphasized that this is an IAPWS guidance document and that, depending on local requirements, the use of simpler instrumentation may be adequate, whereas more complex techniques and instrumentation may be necessary when specific issues arise.

PPCHEM 2013, 15(5), 328–349

Steam Purity for Turbine Operation

This Technical Guidance Document has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in London, UK, 1–6 September 2013, for issue by its Secretariat. The members of IAPWS are Britain and Ireland, Canada, the Czech Republic, Germany, Japan, Russia, Scandinavia (Denmark, Finland, Norway and Sweden), and the United States of America, and the associate members are Argentina and Brazil, Australia, France, Greece, Italy, New Zealand and Switzerland. The document represents the accumulated experience of the IAPWS Power Cycle Chemistry (PCC) Working Group with representation from 17 countries.

This Technical Guidance Document considers steam turbines from power plants using fossil, combined cycle, nuclear, alternative and geothermal energy, including turbines in industrial applications. It is emphasized that this is an IAPWS technical guidance Document and that, depending on local requirements, the normal or target values will need to be customized for each case, depending on the actual conditions of operation, the type of generation and use of the steam, and the power cycle chemistry.

Further information about this Technical Guidance Document and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS or from http://www.iapws.org.

Robert Svoboda, R. Barry Dooley, and Jüri Tavast

PPCHEM 2013, 15(5), 350–354

The New IAPWS Steam Purity Guidance Document – And How to Use It

The IAPWS Steam Purity Guidance Document covers all variations of steam turbines and accounts for the different chemistries. Because it gives background applicable to all steam turbines, it is basically of a general nature and cannot provide a one-fits-all guideline. Individual customization is required to produce guidelines for the specific range of application. Examples are given for customization to a cycling plant with elevated cation conductivity at each of the many cold starts, to a plant operating with elevated levels of silica in steam, and to a turbine that has chronic deposits of salt from seawater inleakage.

Wenjun Kuang, Sang-Kwon Lee, James A. Mathews, and Digby D. Macdonald

PPCHEM 2013, 15(5), 356–365

Monitoring Crevice Corrosion via the Coupling Current
Part II: The Effect of Anodamine

The electron coupling current and the mixed open circuit potential were measured to monitor crevice corrosion on Type 410 stainless steel (SS) in sodium chloride solution. The effect of the proprietary filming amine inhibitor Anodamine on the crevice corrosion behavior of Type 410 SS was also studied. Anodamine could inhibit the partial anodic process on Type 410 SS in sodium chloride solution or suppress the reduction of oxygen, or both. However, once passivity breakdown occurred, the proprietary filming amine had little inhibitory effect. Anodamine could mitigate ongoing crevice corrosion by suppressing the cathodic reaction on the external surface. However when the solution was stirred, the inhibitory effect was compromised. The initiation of crevice corrosion could not be prevented in the presence of Anodamine, due to the limited inhibitory effect of the amine inhibitor in acid solution. Acidification plays an important role in the initiation of crevice corrosion in Type 410 SS in NaCl solution.

Emmanuel K. Quagraine, Shawn Hood, Trever McNabb, Taneal Weiss, and Brenna Janzen

PPCHEM 2013, 15(5), 366–389

BAC & GAC in Tandem for Removing Organics in Boiler Make-up Water: Performance Evaluation from a ZLD Facility

The results of a case study evaluating organic removal options for a zero liquid discharge power plant have been presented previously [1,2]. At this site, a granular activated carbon (GAC) filter was best suited and it was later shown that the mechanism of organic removal was mainly via adsorption at the early stages of operation, but was dominated by biodegradation of organics as the GAC bed(s) aged [3]. It was hence proposed that by operating an aged and biologically active carbon (BAC) bed (i.e. BAC filter) in series with a freshly replaced GAC filter bed, an advantage can be gained for

organic removal via biological degradation with the upstream bed and adsorption by the downstream bed. And with such a process, it is possible to reduce excessive microbial growth on the downstream bed, to extend the life of the downstream bed to enable organic removal principally by adsorption, and to minimize carryover of organic and biofouling potential to downstream demineralizing beds. The current paper evaluates the performance of a BAC filter (aged ~4 years) in series with a freshly replaced downstream bed (i.e. a BAC-GAC process) for organic removal from distillate from a brine concentrator with a tendency towards biofouling in a boiler make-up treatment train. Changes in the concentration of various physico-chemical and biological parameters (including total organic carbon (TOC), pH, conductivity, turbidity, dissolved oxygen (DO), total inorganic carbon (TIC), silica, and heterotrophic plate counts) across each of the two beds were monitored. An overall average of 81 % TOC removal was observed across the two beds in series: 43.7 % by the BAC bed and an additional 37.2 % by the GAC bed (i.e. 66.2 % removal from upstream bed effluent). Correlation studies during the 8th and 9th weeks of operation showed a consistent increase in TIC, and a decrease in DO and pH concentrations across each of the filters, and each correlated significantly with ΔTOC (or % TOC removed). ~25–29 % and ~3–7 % of TOC removed by the BAC and GAC beds, respectively, was related to changes in all three parameters. These portions of removed TOC were therefore attributed to organic bio-mineralization into CO_2. Changes in concentrations of silica and other inorganic species concentrations across the beds were more complex: consistent increases for most parameters across the GAC bed occurred in the early stages of operation, but more erratic changes (i.e. removal and/or releases) occurred on the BAC bed and on the GAC bed later in operation when bioactivity was a factor. Magnesium and calcium, however, were exceptional: these ions were generally removed by the BAC filter throughout the study period and by the GAC bed from the 18th day of operation. Isolated cases of silica removal seem to relate to influent TOC: particularly with the downstream bed, when bioactivity was a factor, low influent TOC concentration seemed to favour silica removal, but more work is required to confirm this.

Digby D. Macdonald

PPCHEM 2013, 15(6), 400–443

Understanding the Corrosion of Metals in Really Hot Water

The chemistry and electrochemistry of water and aqueous solutions at high subcritical and at supercritical temperatures is reviewed with particular emphasis on the corrosion of metals. It is shown that sensible electrochemical measurements can be made at supercritical temperatures, even though, at pressures lower than 500 bar, the environment resembles a compressed gas with a low dielectric constant of about 2 and hence water under these conditions can be classified as a "non-ionizing" solvent. The standardization of the pH scale and the development of reference electrodes, hydrogen sensors, oxygen sensors, redox sensors, and pH electrodes that have been used at temperatures as high as 528 °C is described. Two corrosion mechanisms are defined: "chemical oxidation (CO)," which does not involve partial anodic and cathodic reactions and hence does not generate electrochemical noise (EN), and "electrochemical oxidation (EO)," which occurs via partial anodic and cathodic reactions, which generate EN. In the case of carbon steel, the CO mechanism dominates at densities below about $0.06\ g \cdot cm^{-3}$, while the EO mechanism dominates at higher densities. The corrosion rate under EO conditions (high density) was found to be conveniently monitored using the standard deviation or the root mean square (RMS) of the band-pass filtered EN measured between two identical metal specimens using a zero resistance ammeter. The corrosion of 1013 carbon steel and of Type 304 SS in water or dilute acids and bases was found to be due to acid attack by H^+ and to pass through a maximum at low supercritical or high subcritical temperatures, respectively, which is attributed to the competitive effects of temperature upon activation and upon the density and degree of dissociation of the acid producing electrolyte (HCl and NaOH, but including H_2O). The corrosion rate of Type 304 SS at both subcritical and at supercritical temperatures was found to increase with pressure from which volumes of activation were calculated. At subcritical temperatures, the effect of pressure on the reaction rate is dominated by the activation

process involving bond making and breaking, whereas at supercritical temperatures the reaction rate is dominated by the compressibility of the environment and hence by the impact of pressure upon the density, reactant (H^+) concentration, and degree of dissociation of the electrolyte.

Grigory V. Tomarov and Andrey A. Shipkov

PPCHEM 2013, 15(6), 444–455

Basic Principles of Solving Erosion-Corrosion Problems in Russian Nuclear Power Plants

The phenomenon of erosion-corrosion of the metal of power equipment is considered a two-sided physicochemical interaction of a single- or two-phase flow with metal. Some results of experimental investigations into the regularities and the inhibition of erosion-corrosion in a two-phase flow are given. Results obtained from using the domestically developed computation code RAMEK for power units are presented and prospects for implementing it in designing new power units of nuclear power stations are determined. A calculation diagram and an engineering procedure for determining the pH of the liquid phase in the wet-steam plants of power units in dependence on the concentration of corrective additions, the steam wetness ratio, and temperature are suggested. It is shown that substances produced by the mechanism of general erosion-corrosion are the main source of the ionic-colloid form of iron, which is the main component of deposits in a steam generator. Ways of controlling the formation of deposits in a nuclear power plant's steam generator are proposed together with methods for estimating their efficiency.

Haruka Kido, Taro Ichihara, Senichi Tsubakizaki, Yasuhiro Takei, Yasunori Sakamoto, Takashi Naganum, Taichi Nishi, and Yoshitaka Uchida

PPCHEM 2013, 15(6), 462–469

Successful Experience with High-AVT Operation at the Tuxpan Power Station

Generally in the water treatment of Japanese combined cycle plants, ammonia and hydrazine are used in the feedwater system and phosphates are used in the boiler system. However, in Mexico, the Tuxpan Unit 2 and Unit 5 power plants have adopted high all-volatile treatment (high-AVT), a high-pH water treatment in which ammonia is used to set the pH of feedwater higher than the conventional level and which requires no phosphates in the boiler system. Unit 2 of the Tuxpan power plant started commercial operation in 2001. Since then, more than 10 years have passed with no problems having been found during equipment inspections. In response to such good operational results, we will introduce high-AVT as an option for the water treatment of combined cycle plants.

Reports on Selected International Events

PPCHEM 2013, 15(3), 232–235

Report on the SWAN/PPCHEM Power Cycle Instrumentation Seminar in Dubai, United Arab Emirates

After their successful introduction last year, Waesseri GmbH, publisher of PPCHEM, decided to continue organising the Power Cycle Instrumentation Seminars. For reports on two of the past seminars in 2012, see [1]. In the current year two seminars have already taken place, the first (March 12–13, 2013) in Kuala Lumpur, Malaysia, and the second (April 22–23, 2013) in Dubai, United Arab Emirates. Both events were held under the sponsorship of PPCHEM and SWAN Analytical Instruments.

This report focuses on the seminar held in Dubai as it was the first time the seminar series stopped over in the Middle East. Like the seminars held last year, the seminar consisted of a well-proven mixture of both presentations given by technical

experts and a hands-on session in which the participants worked with real instruments. The presentations were topically divided into two groups, the first having a more general focus on the context of power cycle instrumentation requirements, and the second concentrating on analytical methods and instruments.

PPCHEM 2013, 15(4), 318–323

33rd Annual Electric Utility Chemistry Workshop, Champaign, IL, U.S.A., June 11–13, 2013

The 33rd Annual Electric Utility Chemistry Workshop took place June 11–13 of this year in Champaign, Illinois, U.S.A. This contribution gives a brief introduction to the workshop as well as abstracts of the presentations given there.

PPCHEM 2013, 15(5), 390–392

16th International Conference on the Properties of Water and Steam and International Association for the Properties of Water and Steam 2013 Meeting

Continuing a series of conferences that started in 1929 in London, 230 scientists and engineers from 28 different countries met from 1–5 September 2013 at the University of Greenwich in London, United Kingdom, for the 16th International Conference on the Properties of Water and Steam (ICPWS). The conference is sponsored every four or five years by the International Association for the Properties of Water and Steam (IAPWS) and, in 2013, it was organised and hosted by the British and Irish Association for the Properties of Water and Steam (BIAPWS) and the Institution of Mechanical Engineers (IMechE). The highlights of the IAPWS working group sessions and general conference proceedings are summarised in this release.

From the PPCHEM Mail Room

Albert Bursik

PPCHEM 2013, 15(1), 62

Honor to Whom Honor is Due

Albert Bursik

PPCHEM 2013, 15(2), 162

Waesseri Is Not a Consulting Company

Albert Bursik

PPCHEM 2013, 15(3), 206–210

Problems with the Conductivity Nomenclature – A New Babylonian Language Confusion?

Albert Bursik

PPCHEM 2013, 15(4), 302

To Be, or Not to Be – Normal Target Values or Normal Operation Ranges

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Albert Bursik

PPCHEM 2013, 15(5), 393–395

To Be, or Not to Be – Normal Target Values or Normal Operation Ranges: Continuation 1

2014's Scientific and Technical Contributions

Marco Lendi, Heinz Wagner, and Peter Wuhrmann

PPCHEM 2014, 16(1), 4–11

pH Calculation by Differential Conductivity Measurement in Mixtures of Alkalization Agents

Proper measurement of pH is a key factor in corrosion risk surveillance in water-steam cycles. Since it still seems difficult to measure the sample pH directly with glass electrodes, pH calculation, using the difference between sample conductivity before and after a strong acid ion exchanger, is a frequently used alternative. The precision and reliability of this measuring method is well known and proven in water-steam cycles containing one alkalization agent only.

For applications using mixtures of alkalization agents, the pH calculation model has never been verified. We investigated calculation models to predict the precision and limitations of pH calculation by differential conductivity measurement in morpholine-ammonia and ethanolamine-ammonia mixtures.

Fiona Spellissy, William Hickey, Fionn Griffin, and Elizabeth Stack

PPCHEM 2014, 16(1), 13–20

Analysing the Influence of Anions on After-Cation Conductivity of HRSG Steam Samples during Startup Using Ion Chromatography

The current running regime for a combined cycle gas turbine (CCGT) power plants has seen a rapid rise in the number of unit starts per annum. Each startup requires the steam samples to achieve a pre-determined chemical purity level before release to the steam turbine. At ESB Aghada Generating Station, chemical clearance of the steam is based on conductivity after cation exchange (CACE). In an attempt to alter startup steam clearance requirements and to decrease the time taken for chemical clearance, an assessment was made of the types and quantities of anions present in the steam samples prior to steam release. This paper describes a detailed analysis of the quantities of chlorides and sulphates in the startup steam samples and their contribution to the observed steam CACEs. This investigation into the parameters contributing to startup conductivities has lead to an increased understanding as to the cause of conductivity fluctuations. This has in turn lead to decreased startup times by reducing the time taken to achieve chemical clearance by allowing modifications to steam release requirements.

Kevin Boudreaux, Steve Biggar, and Ellie Palomo

PPCHEM 2014, 16(1), 25–37

Troubleshooting and Antifoam Application Minimizes ZLD Plant Operating Costs and Downtime

To process waste streams via thermal evaporation, zero liquid discharge (ZLD) plants typically employ brine concentrators (BCs) and crystallizers. Excessive foaming is a very common problem among these systems, with the root causes ranging from mechanical, to operational, to chemical. This paper discusses how a ZLD plant experiencing an unexplained foaming event answered the following questions: "What has changed?", "What is creating the foam?" and "How is the problem going to be addressed long term?" It also discusses how the foaming was managed during the troubleshooting period without a loss of plant availability.

Wenjun Kuang, Sang-Kwon Lee, James A. Mathews, and Digby D. Macdonald

PPCHEM 2014, 16(1), 38–47

Monitoring Crevice Corrosion via the Coupling Current – Part III: Mechanistic Studies

The coupling current and the mixed open circuit potential were measured to follow the development of crevice corrosion in Type 410 SS in sodium chloride solution, and the corrosion morphologies of the crevice walls were studied to elucidate the crevice corrosion process. During the initiation stage, the coupling current increased smoothly up to a steady-state value, while the mixed open circuit potential decreased smoothly. Such an activation process is induced by general passivity breakdown on the crevice wall due

to the formation of acidified solution in the crevice. During the steady-state stage, transient current spikes were observed, corresponding to pitting events on the crevice wall. The pitting occurs through the formation and detachment or dissolution of salt scales. The crevice tip area is only lightly attacked, because increased potential drop results in reduced over-potential for anodic reaction, and attack much deeper into the crevice is mitigated.

Albert Bursik

PPCHEM 2014, 16(1), 48–53

From the PPCHEM Mail Room

To Be, or Not to Be – Normal Target Values or Normal Operation Ranges: Conclusion

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Abstracts 2013

PPCHEM 2014, 16(1), 54–64

2013's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Pascal V. Grundler and Stefan Ritter

PPCHEM 2014, 16(2), 76–93

Noble Metal Chemical Addition for Mitigation of Stress Corrosion Cracking: Theoretical Insights and Applications

Stress corrosion cracking (SCC) has caused significant economic losses and has challenged component integrity in boiling water reactors (BWRs) over the last three decades. A low electrochemical corrosion potential (ECP), which is beneficial for SCC mitigation, can be achieved by neutralising the oxidising species O_2 and H_2O_2. Combined introduction of noble metals and H_2 into the reactor feedwater can accomplish this. Soluble noble metal compounds, injected into the reactor feedwater, rapidly undergo thermolysis to yield metallic nanoparticles which deposit on all water wetted surfaces. These particles exhibit a high catalytic activity for the reaction of O_2 and H_2O_2 with H_2.

This review presents the noble metal chemical addition (NMCA) technology itself but also briefly describes its impact on reactor environment and provides further information on noble metal nanoparticles, with a focus on their structure, formation and catalytic properties. Finally, possible developments of NMCA and alternative SCC mitigation methods are discussed. The paper aims at providing a comprehensive and interdisciplinary but non-exhaustive overview of the subject.

Thomas Bauer, Matthias Svoboda, Sindy Dockheer, and Robert Svoboda

PPCHEM 2014, 16(2), 94–104

Chemical Cleaning of Water-Cooled Generators: Effect on System Materials

As an option to return efficiency to and avoid damage in water-cooled generators, plugged hollow conductors are cleaned using various methods. Chemical cleaning employs either acids or chelating agents. For this to be efficient, the cleaning solution should contain an oxidizer. However, these solutions attack the system materials more than those without an oxidizer. A study was conducted in which stator cooling water system materials were exposed to commonly used chemical cleaning agents and their corrosion resistance was analyzed. Of the investigated solutions, ammonium persulfate and a mixed acid solution with sulfuric acid, phosphoric acid and hydrogen peroxide were by far the most aggressive, followed by acids without an oxidizer. The least aggressive chemicals with regard to the generator materials are based on chelant cleaning, provided it is carried out in a carefully controlled and coordinated manner.

David Addison

PPCHEM 2014, 16(2), 106–112

Cycle Chemistry Challenges with Enhanced Geothermal Systems (EGS) Surface Power Plants

Enhanced geothermal systems (EGS) is a new technology that involves the hydraulic enhancement of the permeability of deep (3–5 kilometres) hot rock underground sys-

tems to allow the extraction of thermal energy to the surface. High-pressure cold water is injected under pressure via an injection well into the fractured hot rock, whereby the water increases in temperature as it travels through the rock. This water returns to the surface via a production well where the thermal energy of the water is then extracted with a non-contact heat exchanger into another working fluid, in this case demineralised water, which is heated and converted into saturated steam. This secondary loop is then used to power a conventional steam turbine. The condensed steam is returned to the heat exchanger loop and the cooled EGS water is then returned to the injection well as both systems operate as essentially closed loops.

The paper provides a brief background to EGS systems and then focuses on the potential cycle chemistry issues associated with an EGS surface power plant, with the Geodynamics Limited, Habanero 1 MW EGS proof of concept plant at Innamincka in the Cooper Basin in South Australia described in detail.

Jan Stodola

PPCHEM 2014, 16(2), 118–125

Operating Experience with Sodium Phosphates in Drum Boilers

The paper describes experiences of Ontario Power Generation Inc. (OPG, formerly Ontario Hydro) with four types of treatments in fossil-fuel-fired drum boilers in units varying in size from 100 to 500 MW. A major part of the paper addresses a period of approximately ten years from the early 1970s to the early 1980s when boiler operators faced problems associated with the phosphate hide-out phenomenon, such as unstable alkalinity control and increased corrosion. The paper also refers to a major OPG-driven research and development program which was designed to optimize phosphate-based boiler water chemistry control and minimize associated corrosion. This effort culminated in the publication of the Equilibrium Phosphate Treatment (EPT) Guidelines, which have been used by the OPG boiler operators virtually unchanged ever since. The paper discusses the key developments of the last sixty years, from the early 1950s till the present, while also including the main features of the EPT and the general experience with it.

Frank de Vos,
Paul van Daele,
Jeff Gabster,
Danny Sherban,
Rony Mehr,
Dror Yitzhak,
Ines Bettermann,
Stefan Weuster,
Wolfgang Ansorge,
Herman Teunis,
Zandrie Borneman, and
Ludwin Daal

PPCHEM 2014, 16(2), 126–142

Pilot Test to Capture Water from the Flue Gas of a Coal-Fired Power Station

One of the major challenges of this century is the provision of water for a growing population and the industry. The shortage in water resources in arid areas requires the availability of more efficient and cheaper water production processes. A large source of water is found in the form of evaporated water emitted from different industrial processes. This water vapour can be selectively removed by gas-gas separation membranes. Within the European CapWa project, thirteen partners set out to upscale this technology and pilot test the membranes in a coal-fired power plant. The pilot test was conducted for a period of 3 months at the Rutenberg plant. It can be concluded that a large scale pilot plant produces similar fluxes to lab findings and that the water quality easily fulfils drinking water standards (except for pH). The measured energy consumption values support previously conducted modelling work.

Dan Sampson

PPCHEM 2014, 16(3), 152–160

Municipal Recycled Water Use in Industry: A Roadmap

Industrial users are increasingly encouraged, sometimes required, to replace fresh water with municipal recycled water. Recycled water use usually focuses on cooling systems, but purveyors encourage other uses (demineralized water production, for example). Many users have transitioned to recycled water without careful preplanning and suffered as a consequence. Recycled water can successfully replace other sources, but risks must be clearly understood and mitigated where possible. This paper discusses challenges associated with recycled water use and describes key components of a recycled water project.

Ladislav Bursik

PPCHEM 2014, 16(3), 162–166

Use of the Film-Forming Feedwater Treatment Is on the Rise

This paper is a short report on the Cetamine® Meeting held in Graz, Austria, in April 2014. Brief abstracts of all the papers presented are provided as well as a comprehensive reference list of publications (without any claim to completeness) covering the theoretical bases of film-forming amine application, analytics, and the results of film-forming amine use.

PPCHEM 2014, 16(3), 167–189

Corrosion Product Sampling and Analysis for Fossil and Combined Cycle Plants

The Technical Guidance Document Corrosion Product Sampling and Analysis for Fossil and Combined Cycle Plants has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in London, UK, 1–6 September 2013, for issue by its Secretariat. The members of IAPWS are Britain and Ireland, Canada, the Czech Republic, Germany, Japan, Russia, Scandinavia (Denmark, Finland, Norway and Sweden), and the United States of America, and the Associate Members are Argentina and Brazil, Australia, France, Greece, Italy, New Zealand and Switzerland. The document represents the accumulated experience of the IAPWS Power Cycle Chemistry (PCC) Working Group with representation from 21 countries.

This Technical Guidance Document considers the sampling and monitoring of total iron and copper corrosion products in fossil and combined cycle/HRSG plants.

Further information about this Technical Guidance Document and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS or from http://www.iapws.org.

Kimitoshi Yoneda, Jérôme Ferrari, Carine Mansour, Sophie Delaunay, Mathieu Guingo, and Céline Caruyer

PPCHEM 2014, 16(3), 194–206

Approach to a Numerical Simulation Method for Tube Fouling Phenomena

An approach to numerical simulation methods to predict tube fouling phenomena has been investigated. Simulations were performed to evaluate two major phenomena among several aspects of tube fouling in a water single-phase flow situation: deposition and precipitation. Simulations for the phenomena inside an autoclave with heat transfer tubes were run using a computational fluid dynamic program. Lagrangian simulation for particle deposition on the wall surface was conducted, followed by additional precipitation evaluation on the tube surface with Eulerian simulation. Chemical conditionings with amines in pressurized water reactor (PWR) secondary circuits were investigated: ammonia, morpholine and ethanolamine. For the deposition simulations, morpholine is the only chemical conditioning that induces notable deposition on the wall surface since it is the only one to create attractive interaction between particles and the wall surface in the DLVO model. Precipitation on the tube surface was evaluated based on the over-saturated amount of soluble magnetite concentration related to the local temperature profile.

Paul McCann and Mark Robson

PPCHEM 2014, 16(4), 216–224

Highlights of the BIAPWS 2014 Power Plant Chemistry Symposium

The British and Irish Association for the Properties of Water and Steam (BIAPWS) held its annual Symposium on Power Plant Chemistry on 2–3 April 2014 in Nottingham. Summaries of the event proceedings are provided. The Symposium consisted of introductory sessions on the fundamentals of plant preservation and closed circuit cooling water chemistry, followed by presentations on 'Power Plant Chemistry and Corrosion' and 'Environmental and Water Treatment Issues', which included a case study of poor steam quality as a result of boiler water carryover at a new plant, the application of film forming amines and the environmental consenting of a new build nuclear power plant in the UK.

Ladislav Bursik

PPCHEM 2014, 16(4), 226–231

The European HRSG Forum – Another Type of Event

At the first meeting of the European HRSG Forum, held May 12–13, 2014, in Heidelberg, Germany, a number of interesting presentations were given on various aspects of HRSGs and their operation. Ample time was provided to discuss these talks, as well as any topics of interest relating to the operation and maintenance of HRSGs. Abstracts of the presentations are given in this contribution.

Fiona Spellissy, Fionn Griffin, and Elizabeth Stack

PPCHEM 2014, 16(4), 232–239

Analyzing the Influence of Increased Ammonia Dosing to CCGT Condensate Systems

Iron corrosion in single-phase sections of feedwater/condensate systems is controlled by maintaining adequately high oxygen levels due to the low temperatures present in this part of the water/steam cycle. To minimize iron transport in this part of the circuit, oxygen levels should be maintained between 10 $\mu g \cdot L^{-1}$ and 20 $\mu g \cdot L^{-10}$. Iron corrosion in two-phase sections of feedwater/condensate systems is controlled by maintaining an alkaline pH of at least 9.8 [1]. At ESB Aghada the feedwater/condensate pH is controlled by dosing ammonia to the condensate system based on conductivity to ensure protection for the entire condensate/feedwater system. Ammonia dosing to the condensate is feasible because there is no condensate polisher in place. A consequence of dosing higher amounts of ammonia to the condensate is higher conductivity after cation exchange (CACE) across condensate/feedwater and steam sample points in the water/steam cycle. This paper describes a detailed analysis of the resultant fluctuations observed in CACE for all sample streams. It also describes the impact of increased ammonia dosing to the condensate on the iron content of the HP, IP and LP drums.

Albert Bursik

PPCHEM 2014, 16(4), 244–249

Pieces of Ancient Wisdom Make Sense Even for Modern Combined Cycles with HRSGs: A Quite Unusual View

Although all the information necessary to avoid or at least reduce the number of HRSG tube failures is available, the power industry has not been able to use this knowledge to its advantage. Considering the example of flow-accelerated corrosion, the most common HRSG tube failure mechanism, the author shows that all the information necessary to greatly reduce the occurrence of flow-accelerated corrosion incidents has been easily accessible for over thirty years. This leads to the question: Why haven't the responsible persons in the industry been using it?

Michael F. Caravaggio and Stephen J. Shulder

PPCHEM 2014, 16(4), 254–259

EPRI Comprehensive Cycle Chemistry Guidelines for Combined-Cycle/Heat Recovery Steam Generators

The purity of water and steam is central to ensuring combined-cycle/heat recovery steam generator (HRSG) plant component availability and reliability. The Electric Power Research Institute (EPRI) has issued the third edition of its *Comprehensive Cycle Chemistry Guidelines for Combined Cycle/Heat Recovery Steam Generators (HRSGs)* [1]. These guidelines provide information on the application of all-volatile treatment (AVT), oxygenated treatment (OT), phosphate treatment (PT), caustic treatment (CT), and amine treatment. These guidelines can help operators reduce corrosion and deposition and achieve significant operation and maintenance cost reductions and greater unit availability. This paper gives a brief overview of these new guidelines and highlights significant changes from and enhancements of the previous versions.

Carl M. Atkinson and Richard J. Jones

PPCHEM 2014, 16(5), 276–283

Trial Results for the Control of Stator Cooling Water Dissolved Oxygen Concentrations Using Palladium-Doped Resin

Control of dissolved oxygen concentrations in stator water cooling systems is essential if oxide plugging of the copper conductor bars, through which the cooling water flows,

is to be minimised. There is great benefit to operating at low oxygen concentrations through effective leak management and minimisation of air ingress. To aid low oxygen control, palladium-doped ion exchange resins can be used to catalyse the reaction between oxygen and hydrogen. For trialling purposes, Pd-resin was installed at two EDF Energy Nuclear Generation sites in 2008 and 2009; results to date suggest there are potential benefits to its use.

Wolfgang Hater, Andre de Bache, and Thomas Petrick

PPCHEM 2014, 16(5), 284–292

Dry Lay-up of Steam Generators with Film Forming Amines: Studies and Field Experiences

The operational regime of steam generators may demand short- or long-term shutdown, during which protective measures have to be taken to avoid damage of equipment due to corrosion. Lay-up procedures are available depending on the duration of the shut-down and operation conditions. Dry lay-up is recommended for long-term shutdown periods (several months) by guidelines. Although generally providing good results, the procedures demand significant effort and a plant design which is not always available or acceptable for the operator.

Film forming amines provide an excellent potential for lay-up of steam generators due to their specific mode of action. The film forming molecules adsorb onto the surface and thereby create a barrier on the surface against corrosive media. Practical experiences in steam generators with frequent short-term shutdowns have encouraged the extension of the application to dry lay-up of several months with a sharply simplified procedure, i.e. without nitrogen blanketing or keeping the steam generator warm.

The adsorption and desorption behavior of film forming amines on three different metals have been studied in the laboratory. It could be shown that adsorption takes place on all three metals tested. Surface coverage depends on the metal and temperature as well as on the structure of the molecule. Furthermore, corrosion protection was determined by electrochemical impedance spectroscopy. Excellent corrosion inhibition can also be achieved with comparably thin films. This underlines the importance of the proper choice of film forming molecule.

Test specimens from carbon steel were exposed to oxygenated deionized water. Whereas the untreated coupon already showed corrosion after one day of exposure, the coupons treated before with a filming amine showed no corrosion even after two weeks, reflecting the high stability of the film.

The positive findings of the lab studies were fully confirmed in the field: In a combined heat and power plant the film forming amine technology was applied to protect the steam generator during the summer shutdown. One month prior to the shutdown the treatment of the water/steam system was switched from ammonia to Cetamine treatment based upon a combination of alkalizing and film forming amines. The dosage station of the ammonia treatment was used and dosage was proportional to the make-up water into the feedwater line. Thereafter, the system was emptied.

Plant inspection proved a complete plant protection. No stand-by corrosion or deposits were observed after six months. 12 hours after restarting, the plant water parameters were already fully in compliance with the operational specifications. The year before no Cetamine treatment had been carried out and iron levels between 50 and 90 $\mu g \cdot kg^{-1}$ had been measured in the start-up condensate. The lay-up with film forming amines resulted in a gain of time at the restart of the plant. Dry lay-up with Cetamine now is regularly applied during the summer shutdown period.

Zhigang Li, Wanqi Huang, Songyan Cao, and Hongbo Zhang

PPCHEM 2014, 16(5), 294–304

Boiler Feedwater Oxygenated Treatment in Power Plants in China

This paper presents the development of the oxygenated treatment (OT) technique application in power plants in China. The oxide morphologies of boiler tubes (economizer and water wall) under three different feedwater treatment techniques – all-volatile treatment under reducing conditions (AVT(R)), all-volatile treatment under oxidizing conditions (AVT(O)) and oxygenated treatment (OT) – were analyzed, and it was found that the reddish brown Fe_2O_3 coating layer formed by oxygen in feedwater only extended as far as the economizer inlet section. This paper also has a detailed discussion about the CrO_4^{2-} release phenomenon and demonstrates that the CrO_4^{2-} detected in the steam cycle comes from sampling tubing and apparently does not originate from the boiler tube material.

PPCHEM 2014, 16(5), 318–323

Meeting of the IAPWS Power Cycle Chemistry Working Group in Moscow, Russia, 23–27 June 2014

This paper reports on the proceedings of the Power Cycle Chemistry (PCC) working group during the 2014 annual meeting of the International Association for the Properties of Water and Steam (IAPWS) in Moscow, Russia. The paper highlights current PCC working group activities, including the proposals for new IAPWS Technical Guidance Documents and activities in areas considered to be in need of basic research or improved knowledge transfer. A summary of the presentations that were made during the PCC meetings is also provided.

PPCHEM 2014, 16(5), 328–331

Report on the PPCHEM/SWAN Power Cycle Instrumentation Seminar in Seoul, South Korea

In the third year since its introduction, the PPCHEM/SWAN Power Cycle Instrumentation Seminar Series continues its mission to expand the knowledge of cycle chemistry and the understanding of analytical instruments. This year the seminar series stopped over in Wadowice, Poland (May 12–13, 2014), Manila, Philippines (September 21–23, 2014), and Seoul, South Korea (September 24–26, 2014).

The events were held under the patronage of Waesseri GmbH, publisher of PPCHEM, and SWAN Analytical Instruments provided financial support.

This report focuses on the seminar held in Seoul – the two other seminars addressed the same topics, however the speakers and their presentations differed from place to place. All of the seminars consisted of the well-proven mixture of presentations given by technical experts and a hands-on session in which the participants worked with real instruments. The presentations were topically divided into two groups, the first having a more general focus on the context of power cycle instrumentation, and the second concentrating on analytical methods and instruments.

Wanqi Huang, Yuzhong Chen, Songyan Cao, Huai-tian Lu, and Weipeng Sun

PPCHEM 2014, 16(6), 336–343

Analysis and Assessment of the Effects of Long-Term Oxygenated Treatment on 1 000 MW Ultra-supercritical Units

In this paper the effects of oxygenated treatment (OT) on the boiler feedwater of Unit 2 (a 1 000 MW ultra-supercritical unit) at Huaneng Haimen Power Plant are summarized and analyzed.

Since OT has been used for the unit, the iron concentration at the economizer inlet and in the high-pressure heater has decreased to less than 1 $\mu g \cdot L^{-1}$, a decrease of more than 80 % of that under all-volatile treatment under oxidizing conditions (AVT(O)); this effectively inhibits flow-accelerated corrosion in the feedwater and high-pressure heater drainage systems, reduces the iron transport and lowers the scaling rate in the economizer and on the water wall. The long-term operating experience shows that OT can not

only slow down the boiler pressure dropping rate and avoid blocking of the drainage water control valve for the high-pressure heater, but can also increase the periodic water output of the mixed bed in the condensate polishing system from 80 000 tons to 400 000 tons, indicating a very considerable energy savings and reduction in consumption, which significantly improves the safety, reliability and economy of the unit.

Matthias Svoboda and Thomas Bauer

PPCHEM 2014, 16(6), 344–351

Changing Stator Cooling Water Chemistry

Large generators employ direct water cooling to remove heat losses in the stator winding. This is done by including hollow conductors in the stator bars. To prevent plugging of the hollow conductors, several regimes for stator cooling water chemistry have been established. Occasionally it can be beneficial to change from one regime to the other. However, changing regimes can introduce instability in the copper oxide layers, ultimately causing plugging of the cooling water channels.

Changing a chemical regime requires thorough planning and can involve major hardware upgrades as well as procedural changes. It is important to have contingency plans ready if conditions deviate from the expected during and after the changes to facilitate troubleshooting.

Rewinds require special attention if the current cooling water system is reused. They also present an opportunity to directly investigate problems within the stator bars and water boxes.

As recommended by different original equipment manufacturers (OEMs) it might be useful to chemically clean the entire stator cooling water system to provide a clean system for the change. After the change, the system needs increased attention for a few years until it is certain that conditions are sufficiently stable.

Robert Svoboda

PPCHEM 2014, 16(6), 352–360

Review of Alkaline Treatment for Generator Stator Cooling Water Systems

Alkaline treatment is a proven tool for reducing the occurrence of flow restrictions in copper hollow conductors caused by oxide deposits. Its action is based on the reduced solubility of Cu^{++} in alkaline water. Hydrodynamic parameters like water flow velocity, turbulences, temperature etc. also play a role. Therefore alkaline treatment is beneficial but is not the only decisive parameter for avoiding flow restrictions.

However, there are indications that alkaline treatment produces thicker oxide layers than with neutral water. These oxide layers are nevertheless very thin and are of no concern as long as they do not migrate, e.g. by variations in the oxygen concentration or by fluctuations of pH. It is therefore very important to always keep alkaline treatment under good control. This also includes during shutdown periods.

Alkalization with an injection pump is the simplest and most reliable method. Parallel dual beds are also used for alkalization, but they need careful expert supervision and follow some often overlooked rules, especially in regard to proper priming of the alkalization and a very restricted use of the neutral mixed bed.

Christophe Forêt, Gabriela Stoianovici, Philippe Blériot, Wolfgang Hater, and Jürgen Matheis

PPCHEM 2014, 16(6), 361–375

Film Forming Amines for Closed Cooling/Heating Water Systems

The corrosion inhibition of closed loop cooling water systems is quite a challenging task, mainly due to very long holding times. As a consequence, any contamination entering the system will remain and accumulate over time in the water. Besides excellent corrosion inhibition, the inhibitor should not be harmful to humans or the environment.

This paper presents a new corrosion inhibitor based on film forming amines (FFAs). Corrosion protection is realized by the adsorption of the film forming amines on metal

surfaces. The corrosion inhibition properties of FFAs have been studied by means of electrochemical methods and in pilot plants simulating two different scenarios of practical application.

As shown in the lab and pilot plant studies, FFA-based corrosion inhibitors provide a very high level of corrosion protection for carbon steel, yellow metals, and aluminium, meeting at least the performance of standard corrosion inhibitors based on molybdate or nitrite.

Two field studies on the changeover of the treatment program from molybdate to film forming amines show a significant improvement in corrosion inhibition as reflected in a significant reduction in the heavy metal content in the cooling water. As a consequence, partial or complete flushing of the systems could be sharply reduced, thus leading to important water savings.

Hayden Henderson

PPCHEM 2014, 16(6), 382–391

Increased Corrosion Product Transport Caused by Cycling Operation

This paper analyses the effect of cycling operation on corrosion product transport. It also reviews the use of laser nephelometery as a surrogate technique for iron monitoring. The paper discusses some of the possible reasons for the increased corrosion product transport seen during cycling operation and suggests future experiments to determine whether or not the source of corrosion product is active corrosion or benign and where precisely on the plant corrosion product is coming from.

Robert Svoboda

PPCHEM 2014, 16(6), 392–395

The EPRI Steam Turbine Generator Workshop: Discussions on Alkaline Treatment

A session on experiences with alkaline treatment for stator water cooling systems was part of the 14th EPRI Steam Turbine Generator Workshop (August 11–14, 2014, Chicago, IL, U.S.A.). The session included seven presentations and a panel discussion. The presentations are summarized in this contribution.

2015's Scientific and Technical Contributions

Marco Lendi

PPCHEM 2015, 17(1), 8–13

Continuous Photometric Determination of Film-Forming Amines

A procedure has been developed for the continuous photometric determination of film-forming amines (FFAs) or fatty amines. The method should allow the continuous control of residual FFAs in steam condensate systems where film-forming amines are dosed as a corrosion inhibitor.

The concentration of FFAs is determined by a direct flow injection procedure of eosin and a buffer to measure the colored amine-eosin complex without further treatment of the sample. A detection limit of 0.02 $mg \cdot kg^{-1}$ as octadecylamine has been achieved with the method. The selectivity of the method for selected single carbon chain organic amines (C_4–C_{18}) and diamines was tested. Short chain organic amines as well as high amounts of ammonia do not interfere.

Keith Pearson and Larry Hill

PPCHEM 2015, 17(1), 22–25

Stator Cooling Water Chemistry: Trying a New Approach Utilizing Sodium Form Cation Resin

This paper describes the changes in chemistry control of the stator cooling water system at several lignite-fired power plants in Texas. The changes involve the use of demineralizing resins to alkalize the stator cooling water in order to control corrosion in the system. Information is given about the successful conversion from neutral pH to alkalized control.

Ian Richardson, Simon Addison, and Rebecca Lawson

PPCHEM 2015, 17(1), 30–40

Chemistry Challenges in Geothermal Power Generation

Geothermal power plants operate with heated fluid extracted from underground reservoirs; the chemistry of these geothermal fluids can present significant challenges for the reliable and efficient operation of power plants. The issues experienced in each plant can vary, as the fluid chemistry changes from reservoir to reservoir and the plant designs are customised based on early reservoir data to make best use of the available resource. This paper discusses several of the challenges faced by Mighty River Power (MRP) in generating reliable and efficient power from geothermal fluids, including issues of scaling and deposition management, corrosion management, steam turbine challenges and cooling water management. This paper discusses the measures that MRP is taking to address and manage these issues.

Abstracts 2014

PPCHEM 2015, 17(1), 52–60

2014's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Kevin Boudreaux

PPCHEM 2015, 17(2), 82–91

Cooling Water Chemistry Programs for High Silica Waters

To reduce their impact on the nation's freshwater resources, industrial plants are searching for and utilizing alternative water sources for their cooling water needs. Many have turned to well water or gray water sources, which often contain high concentrations of silica, especially when compared to commonly used surface waters. For instance, surface waters such as lakes and rivers may contain 10–15 $mg \cdot kg^{-1}$ of silica, but it is not uncommon for well waters or gray waters to contain 30–50 $mg \cdot kg^{-1}$. Once cycled up in the cooling tower, silica concentrations can easily exceed silica saturation limits and lead to precipitation. Depending on which silica species are present, precipitated silica forms a tenacious scale or deposit that inhibits heat transfer across heat exchangers or cooling tower fill.

Experience has shown that a clear understanding of silica chemistry, specifically its various species and behavior in different cooling water environments, as well as silica monitoring methods to identify precipitation potential are not widespread throughout the water treatment community. This paper discusses general silica chemistry, various methods for minimizing silica scaling, monitoring and testing for silica, and most importantly, why plants should care.

Kenneth Kuruc and Luke Johnson

PPCHEM 2015, 17(2), 94–97

Further Advances in Monitoring Low-Level Iron in the Steam Cycle

In an earlier paper [1], it was discussed how a laser nephelometer could be used to detect the transfer of corrosion products in a heat recovery steam generator (HRSG) power plant at $\mu g \cdot L^{-1}$ levels with particles in the sub-micron size range. Also, a modified trace-level iron test was documented using colorimetric methods on a lab spectrophotometer to measure total iron levels to 1 $\mu g \cdot L^{-1}$.

In this paper, further advances are outlined which improve the accuracy and repeatability of the lab method, while providing further insight into the level of protection being provided to steam cycle components against flow-accelerated corrosion (FAC) and other corrosion mechanisms. The focus is on understanding the chemistry of the measurement so as to provide more specific data to plant personnel regarding the level and species of iron being observed.

Mandi Richardson, Paul Chu, and Charles Dene

PPCHEM 2015, 17(2), 106–115

Evaluation of the Origin of Dissolved Organic Carbon and the Treatability of Mercury in FGD Wastewater

This paper presents and discusses the results of an EPRI-funded study to investigate the impact of dissolved organic carbon (DOC) present in flue gas desulfurization (FGD) systems on the treatability of mercury in FGD wastewater. The role of DOC was explored through investigations of the speciation of the organic matter present as well as bench-scale experiments designed to further the understanding of the treatability of dissolved mercury in the presence of DOC. A geographically wide-ranging selection of 26 limestone samples was analyzed for total organic carbon (TOC) content as well as for speciation of the organic carbon, based on operational definitions of organic species types. FGD purge water was collected from five different FGD systems that experience different levels of success with mercury treatability. Multiple analytical tests were conducted to speciate the yellow-colored DOC in the FGD purge water samples. The impacts of DOC on the success of mercury removal treatments in wastewater were examined for three treatment chemistries, each having a different sensitivity to DOC interferences. Current investigations involve the isolation of organic matter according to operationally defined methodology and spiking synthetic FGD wastewater liquors with this matter to quantify impacts on mercury treatability.

Li Tian, Xin Dai, Xiaoxiang Shen, and Xuehua Mao

PPCHEM 2015, 17(2), 120–126

Discussion on the Measurement of Organics in Power Plant Water-Steam Cycles

Due to the practical problems which have arisen in many power plants, the influence of organic matter content in the water-steam cycle, which effects the acid conductivity in steam, the safety of heating equipment, and the effluent quality in the ion exchange process, has been further studied in this paper. Based on the actual situation, the organic characterization parameter TOCi (total organic carbon ion) is proposed, and some recommendations on how to monitor the organic matter content of the water-steam cycle in power plants are made.

Albert Bursik

PPCHEM 2015, 17(3), 150–157

Plant Cycle Chemistry Customizing – A Conditio Sine Qua Non Also for HRSG Power Plants

There is no single optimum cycle chemistry for all plant cycles. Thus customization of plant cycle chemistry that takes into account all the particulars of the individual cycle is absolutely indispensable. Although there are various guidelines available to use as the foundation of such a customized plant cycle chemistry program, some are more helpful

or accessible to plant operators than others. This contribution takes a look at some of these guidelines and shows how they can be used to create a specific cycle chemistry program for a given plant cycle configuration.

Barry Dooley, Michael Rziha, and Paul McCann

PPCHEM 2015, 17(3), 160–166

IAPWS Technical Guidance on Power Cycle Chemistry Monitoring and Control for Frequently Cycling and Fast-Starting of HRSGs

Because of the market situations in numerous countries worldwide, many combined cycle units require rapid startup and/or are cycled frequently (such as daily or twice daily start / stop). Under these conditions, there is minimal time for operators to prepare steam-water cycle on-line chemical sampling and monitoring equipment and to carry out chemistry checks. However, operators at most plants will still have to monitor steam purity to demonstrate that it is suitable for admission to the steam turbine with minimal delays to startup times. It is also critical that on-line chemical monitoring instrumentation is set up so that serious cycle contamination during startups can be detected and alerted to operators. To provide initial guidance towards addressing these issues, Technical Guidance Documents produced by the IAPWS Power Cycle Chemistry Working Group have now been updated to reflect the international consensus of experience in these areas. The key points are summarised in this update.

Kevin Boudreaux

PPCHEM 2015, 17(3), 168–176

Using Biodetergents to Recover Megawatts Cheaply and with Minimal Environmental Impact

Losing megawatt production due to cooling water system fouling is an all too familiar issue throughout the power industry. It is also an issue that, with a few exceptions, can be eliminated with an investment that is pennies on the dollar when compared with the profits recovered. Biodetergents, as a supplement to the current water treatment program, have proven to be very effective in maintaining clean cooling water systems. This paper discusses fouling mechanisms, biodetergent mechanisms and implementation, and most importantly, how biodetergents improve plant performance while reducing the overall environmental impact of the chemistry program.

Iain Duncanson, Robert Svoboda, Adam Gurecky, Robert Ragsdale, and Chancey Pence

PPCHEM 2015, 17(3), 181–191

Loss of Alkalization in an Alkaline Treated Stator Cooling Water System

Alkaline treatment of stator cooling water (SCW) systems with copper hollow conductors performs best when pH and dissolved oxygen are kept constant. In the event of loss of alkalization, pH will return to neutral and this will destabilize existing copper oxide layers. Operating experience, however, indicates that infrequent and short-term loss of alkalization does not result in a detrimental buildup of copper oxides in the stator hollow conductors. Thus there is the question as to how long and how often a loss of alkalization can be tolerated.

Although operating experience suggests that loss of alkalization can be tolerated for short periods, it is not recommended to allow this routinely and, to the extent practical, SCW pH should be kept constant. Although there is no hard data to support this, an international expert consensus has been found that loss of alkalization of up to one week, and not more than two occurrences per year, can be tolerated. Upon loss, alkalization should be restored to normal as soon as possible. If the loss of alkalization is longer, it is recommended to monitor the water pressure drop across the coils and, if available, also the stator bar temperatures.

Luke Johnson

PPCHEM 2015, 17(4), 218–222

Monitoring Iron Transport in the Steam Cycle via Grab Sample and Online Methods

Quantitative online monitoring of iron corrosion product transport is an ongoing technical challenge. Total iron measurements require digestion of the particulate and colloidal iron oxides which constitute the majority of these products. Particle monitoring is fast and simple, but is not quantitative.

The present study combines a modified total iron analysis with a laser nephelometer to create a quantitative online monitoring system. This system is applicable in the steady-

state flow regime, where flow corrosion products are consistent. The calibration is specific to the particular corrosion product characteristics present at the individual nephelometer installation site.

Alwin Verstraeten

PPCHEM 2015, 17(4), 228–235

A Practical Approach to an Optimum Cycle Chemistry in an HRSG System

Sloecentrale is a combined cycle plant which went into commercial operation at the end of 2009. In order to assure proper operation during the lifetime of the plant, an assessment was made of the flow-accelerated corrosion (FAC) risk and chemistry.

The result of this assessment has been a step-by-step optimization of the chemistry in the plant. The iron monitoring has been optimized by implementing inductively coupled plasma atomic emission spectroscopy (ICP-AES) technology for low-level iron analysis. This results in solid a data set, which can be used for the evaluation of the chemistry and optimizations.

The pH was chosen as the primary parameter to change because this is the easiest to do and the cost is minor. The pH has been increased step by step from 9.2 to 9.5 in the low-pressure (LP) feedwater and to 9.4 in the intermediate-pressure (IP) feedwater.

Taking the Technical Guidance Document of the International Association for the Properties of Water and Steam (IAPWS) [1] into account, the iron levels are targeted below 2 $\mu g \cdot L^{-1}$ for the feedwater and below 5 $\mu g \cdot L^{-1}$ for the drums. The result of the increased pH is that the iron levels are improving and getting closer to the targets. There is still room for improvement; further steps will be taken in the near future.

PPCHEM 2015, 17(4), 237–239

International Association for the Properties of Water and Steam

Continuing a series of conferences that began in 1929 in London, 88 scientists and engineers from 21 different countries, along with 14 accompanying persons, attended the annual meeting of the International Association for the Properties of Water and Steam (IAPWS). The Scandinavian National Committee of IAPWS (SIAPWS) hosted the meeting between 28th June and the 3rd July 2015 at the Scandic Ariadne hotel in Stockholm, Sweden. The highlights of the IAPWS working group sessions and other proceedings of the executive committee are summarised in this release.

Ladislav Bursik

PPCHEM 2015, 17(4), 251

The Second Meeting of the European HRSG Forum

The second meeting of the European HRSG Forum took place in Munich, Germany, on May 11–13, 2015. Following the successful first meeting in 2014, it brought together 87 participants from 17 countries from around the world (Bahrain, Belgium, Brazil, Czech Republic, Finland, France, Germany, Ireland, Israel, Italy, the Netherlands, Poland, Portugal, Switzerland, Spain, U.S.A., and the United Kingdom). The structure of the meeting with 26 presentations on various aspects of HRSGs and their operation remained the same as in the first meeting. The presentations were surrounded by extensive discussions on topics concerning operation, maintenance, and operating problems raised by the participants before and during the meeting.

David Addison and Barry Dooley

PPCHEM 2015, 17(5), 266–281

The Critical Importance of Accurate Steam Sampling and Analysis

The failure to accurately sample and analyse saturated, superheated and reheated steam from boilers or heat recovery steam generators (HRSGs) can lead to significant deposition and corrosion related failures of the steam path in boilers, HRSGs, steam turbines and any process equipment that comes into contact with the steam. Minimum acceptable equipment standards for sampling and online analysis of steam from boilers and HRSGs are discussed along with the need for routine carryover testing. Multiple real world case studies of steam sampling, analysis and purity issues are presented with key lessons identified.

Bernhard Hoock, Wolfgang Hater, and André de Bache

PPCHEM 2015, 17(5), 283–293

Thirteen Years of Experience with the Treatment of the Water-Steam Cycle of the MVV Enamic Power Plant with Film-Forming Amines

Conditioning of the water-steam cycle in the MVV Enamic gas-fired power plant in Ludwigshafen has been carried out with a conditioning agent based on film-forming amines (FFAs) for the last thirteen years. The power plant supplies an industrial park in the south of Ludwigshafen with electricity, steam and water. Although facing the typical challenges of an industrial power plant with a complex steam network, the water and steam parameters usually correspond to the internal specifications. The acid conductivity of the vapor that is used to drive the double-extraction/condensing turbine is above the recommendation of the VGB standard. Two different on-line analyzers have been successfully tested for monitoring the concentration of the film-forming amine. Inspections of the heat recovery steam generator and the results of the last turbine overhaul showed that the plant is in excellent condition. Conditioning of the water-steam cycle with film-forming amines is evaluated as being very satisfactory.

Barry Dooley and Kevin Shields

PPCHEM 2015, 17(5), 296–305

Using Corrosion Product Transport as a Metric for Feedwater Treatment Efficacy in Fossil Plants

Feedwater treatment of fossil plant steam-water cycles is practiced to protect metal surfaces from corrosion, thereby limiting the transport of iron and copper to the steam generator. Effective treatment reduces deposition of these metals on high heat transfer surfaces and, in so doing, helps to avoid corrosion damage and extends the time interval between chemical cleanings. However, the reality at a significant number of plants is that corrosion products are not monitored or the program used for monitoring is subject to one or more deficiencies. Attributes of successful monitoring programs are identified and discussed. Goals for corrosion product transport are identified and a strategy for feedwater treatment optimization is outlined.

Josué Duran Rosas

PPCHEM 2015, 17(5), 312–314

The Buffer Effect of Water in Cooling Towers

The alkalinity of water contributes to the buffer capacity against acids, and this ability is strengthened when the cycles of concentration are increased in cooling towers. A high buffer capacity means a higher resistance to the adjustment of the pH-value of the water. In this study the behavior of the buffer effect with the dosage of sulfuric acid is investigated and the results of an implemented improvement are presented.

Shunsuke Uchida, Satoshi Hanawa, and Derek H. Lister

PPCHEM 2015, 17(6), 328–339

Advanced Water Chemistry Control Based on Parameters Determined with Plant Simulation Models

In nuclear power plants, radiation makes the relationship between structural materials and water chemistry much more complex than that in fossil-fueled power plants. It is difficult to maintain safer and more reliable plant operation by controlling water chemistry based on only a restricted number of measured data. It is often necessary to control water chemistry with suitable assistance from computer models, which can extrapolate measured water chemistry parameters to those at the required locations and predict future trends in the interactions between structural materials and water chemistry. In the paper, water chemistry control based on parameters determined with plant simulation models and major computational models to be applied for water chemistry control are discussed.

Albert Bursik and Wolfgang Hater

PPCHEM 2015, 17(6), 342–353

All-Volatile Treatment with Film Forming Amines – A First Suggestion for an Application Guidance

The positive properties of filming amines with respect to corrosion protection in water-steam cycles have been known for many decades. The application of film forming amines in industrial and utility steam-water cycles is constantly increasing. However, there are still no internationally accepted recommendations or guidelines covering the

application of film forming and neutralizing amine blends. In this paper, the positive long-term field experience with film forming amines is summarized and an attempt is made to develop a first draft of a guidance for the use of alkalizing and film forming amines with all-volatile treatment. It is hoped that the proposed guidance will serve as a first blueprint for further discussions.

Roy van Lier, Fabrice Cuoq, Rick Peters, and Jo Savelkoul

PPCHEM 2015, 17(6), 356–363

Ten Years of Experience with Polyamines in the High-Pressure Steam System of a Naphtha Cracker

A decade ago, the ammonia/morpholine treatment of the 12.5 MPa steam system of one of SABIC Europe's naphtha crackers was successfully converted to a polyamine program. Although application of film forming chemistry does not come without challenges, experience in Geleen, Netherlands, generally has been positive.

The changeover to polyamines was instigated by fouling and corrosion problems in the steam system that could not be solved using classic alkalization programs. The transition was inspired by Einstein's quote "We can't solve problems by using the same kind of thinking we used when we created them."

This paper provides an update on the cracker's polyamine application, including the results of the most recent turbine inspections. Ten years of experience is interpreted and discussed in relation to the state-of-the-art of conventional water/steam cycle treatment programs and in respect to recent film forming amine related publications.

Karsten Thomsen

PPCHEM 2015, 17(6), 366–378

Quality Assurance and Quality Control in Relation to the IAPWS TGD on Corrosion Product Sampling

The International Association for the Properties of Water and Steam technical guidance document (TGD) on corrosion product sampling from 2013 focuses not only on the proper design, operation, and maintenance of the sampling system, but also on the analytical techniques that are appropriate for this purpose, and on suitable methods of quality assurance. This report briefly reviews the means mentioned in the TGD to ensure the quality of the complete measurement chain from sampling to result. The validation of an applicable analytical technique will be exemplified together with the estimation of the uncertainty associated with the sampling process. Inter-laboratory comparison may also be a rewarding tool to investigate the proficiency of the participating laboratories. Experience with two setups at different levels of sophistication will be discussed.

Soliman Cheraghi

PPCHEM 2015, 17(6), 382–393

Effects of Raw Water Composition Changes on Chemistry Control

The power plant under study had frequent problems with deposition and corrosion in the cooling water and water-steam cycle as a result of a change in the composition of the raw water and a lack of modern treatment facilities. The power plant is located in Ahwaz, Iran, in a dry tropical climate zone. Due to a long period of dry weather, the water flow in the river Karun (source of the make-up water) was significantly reduced. With that reduced flow, the amount of total dissolved solids and the total hardness increased.

As a result, major water chemistry excursions began to take place in the cooling water and water-steam cycle. These included condenser tube plugging and leaks, severe deposition in the boiler, superheater and reheater tubes, and erosion and failure of steam turbine blades. After a detailed examination of the make-up water treatment system and the chemistry program in the water-steam cycle, recommendations were made for improvement. After major changes to the water treatment plant and chemistry program, the major corrosion and deposition problems that were present in all six generating units decreased significantly.

2016's Scientific and Technical Contributions

Shunsuke Uchida, Satoshi Hanawa, Jan Kysela, and Derek H. Lister

PPCHEM 2016, 18(1), 6–17

Corrosion of Structural Materials and Electrochemistry in High-Temperature Water – Relationships among Water Chemistry, Corrosion, Oxide Film and Electrochemical Corrosion Potential

In order to establish reliable nuclear power plant operation, each plant requires its own unique optimal water chemistry control based on careful consideration of its system, materials and operational history. Electrochemistry is one of the key issues that determine corrosion-related problems, e.g., flow-accelerated corrosion (FAC), intergranular stress corrosion cracking and primary water stress corrosion cracking. Most phenomena of corrosion can be understood based on an electrochemical index, e.g., electrochemical corrosion potential (ECP), conductivities and pH. Based on the relationships among ECP, metal surface conditions, exposure time and other environmental conditions, a model to evaluate the ECP and corrosion rate of steel was developed by coupling an electrochemical model and an oxide layer growth model.

Major conclusions obtained on the coupled model are as follows.

1. The effects of water chemistry improvement and mass transfer coefficients due to local flow velocity on the FAC wall thinning rate and ECP could be successfully evaluated with the proposed model.
2. The effects of H2O2 and O2 concentrations on ECP were evaluated with the model. Then, exposure time dependent ECPs were also successfully explained as the effects of oxide film growth on the specimens.
3. Decreases in ECP due to neutron exposure were explained well by radiation-induced diffusion in the oxide layers.

Fiona Spellissy, Thomas Walsh, P. J. Tymon, Shauna Concannon, and Adrian Dennehy

PPCHEM 2016, 18(1), 20–27

An Overview of Iron Analysis in Feedwater, Condensate and Boiler Systems

This paper considers two aspects of iron analysis within a water-steam cycle, the analysis of grab samples for total iron analysis and the use of particle counters to calculate total iron concentrations. Accurate total iron analysis techniques are a vital part of maintaining water-steam cycle chemistry to monitor for and control flow-accelerated corrosion (FAC). An iron analysis study was carried out to establish optimum analysis techniques, involving the analysis of water-steam cycle grab samples from three ESB stations. A comparison was then made between two acid digestion methods to determine which yields the most accurate/reproducible results. The use of three different acids for digestion was investigated and the analytical results for two detection techniques (inductively coupled plasma – optical emission spectrometry (ICP-OES) and ultra-violet spectrometry (UV)) were compared. A study of iron concentrations with online data from a particle counter installed on sample lines within the water-steam cycle was completed to determine if a linear relationship exists between both parameters.

Guan-ping Cai and Ying Li

PPCHEM 2016, 18(1), 32–37

Analysis of the Requirements for the Water Quality of Reverse Osmosis/Post-Mixed Bed Water Treatment

The traditional concept of reverse osmosis (RO) as a desalination device for high salinity water only is becoming less common in the design of boiler make-up water treatment systems. Due to higher make-up water quality requirements and environmental restrictions on the effluent, more and more importance is given to the requirements that the water treatment should minimize the unit feedwater impurities, such as organic content, colloidal silicon or total organic carbon content, as well as save on the amount of acids and alkalis used and reduce the need for wastewater discharge. Therefore, the RO permeate must go through ion exchange devices in order to further remove residues of water-soluble impurities. This paper proposes an index for the water quality at the inlet of the reverse osmosis/post-mixed bed, based on the characteristics of the reverse osmosis (RO) permeate, and on the basis of experience with existing RO/mixed bed operation.

Abstracts 2015

PPCHEM 2016, 18(1), 46–51

2015's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Daniel Zinemanas

PPCHEM 2016, 18(2), 64–73

Online Monitoring and Control of Boiler Phosphate Treatment Using Cation vs Specific Conductivity Diagrams

Phosphate treatment (PT) is a standard boiler chemical conditioning method that has been widely implemented, in its different versions, in conventional fossil as well as in heat recovery steam generator (HRSG) units. Control of this treatment is, however, more complex than with other treatments and is generally pursued through pH vs phosphate concentration diagrams and the sodium to phosphate ratio. Yet these useful tools are, in many cases, difficult to implement since not all the required data, e.g., boiler phosphate, sodium and ammonia concentrations, are monitored online. In order to overcome these limitations, whenever they exist, it is the purpose of this article to propose the cation conductivity (conductivity after cation exchange (CACE)) vs specific conductivity (SC) diagram as a complementary or alternative practical and reliable method to simplify and improve the chemical monitoring and control processes. The major advantages of this method lie in the fact that all the data required are normally measured continuously online, thus allowing the use of these data together with tailored theoretical diagrams for each specific boiler condition for surveillance of the boiler water chemistry. Sodium to phosphate ratios as well as phosphate concentration and contamination can also be directly, easily and accurately estimated, and corrections of the treatment, if needed, can be closely tracked. The methodology to build these theoretical diagrams for each specific boiler, how to interpret them and how to use them successfully in juxtaposition with online data from actual operating units to monitor and control the water treatment are described in detail.

Kevin Boudreaux

PPCHEM 2016, 18(2), 78–86

Eliminating Hydroid Fouling Reduces Derates and Down Powers in a Nuclear Power Plant

Biofouling is perhaps the most common reason for condenser performance degradation throughout the power industry. In this case study, hydroid growth was causing flow restrictions and condenser macrofouling in a nuclear power plant using estuary water for once-through condenser cooling, leading to condenser performance degradation and an increase in MW penalty. Together with Nalco and the University of Maryland Center for Environmental Science Chesapeake Biological Laboratory, a bio-control strategy was developed and tested. After full-scale implementation of the biocide program, not only did the plant recover lost megawatts, but plant availability, reliability, and safety were also drastically improved.

Shawn S. Simmons

PPCHEM 2016, 18(2), 92–98

Use of Isothiazolin and DBNPA to Control Biofouling of RO Membranes Used for Side-Stream Circulating Water Treatment

Mountainview Generating Station in Redlands, California, uses a reverse osmosis system to deconcentrate the total dissolved solids of the circulating water in the cooling towers. Since the generating station started operation in 2006, the reverse osmosis membranes to the system have rapidly fouled, repeatedly. The primary foulants have been calcium hardness, iron, and bacteria slime. Fouling from calcium hardness and iron was reduced by modifying the water treatment processes upstream of the reverse osmosis (RO) trains. Fouling from iron was reduced by decreasing ferrous chloride feed to the clarifier, which is also upstream. Adding 2,2-dibromo-3-nitrilopropionamide (DBNPA) biocide to the RO membrane cleaning solution and extending the soak period for the alkaline cleaner has improved the effectiveness of membrane cleanings. Addition of isothiazolin biocide to the RO feedwater during operation and shutdown has improved permeate flux rates and extended the life of cartridge pre-filter elements from 1–2 weeks to 2–3 months.

Arockiam Lawrence, Chellappa Chandrabose, Seeni Thiagarajan, and Ramakrishna Iyer Easwaran

PPCHEM 2016, 18(2), 104–112

Chemical Cleaning – An Important Tool To Minimize Deposition-Related Boiler Tube Failures In Power Plants

Advancements in thermal power plants with higher ratings, specifically increased operating pressure and temperature, higher heat fluxes in boilers and cycles with higher thermal efficiencies have resulted in increased emphasis on equipment cleanliness. Over the last twenty years, substantial improvements have been made in the understanding and control of fossil plant cycle chemistry. In spite of these advances, waterside deposits in boiler tubes remain an issue of concern to many power plants.

Deposits and/or scale within boiler tubes reduce heat transfer, creating an insulating barrier resulting in higher tube metal temperatures, which leads to accelerated material degradation by creep fatigue. In addition, the deposits also act as a location for the concentration of low level impurities present in the bulk boiler water up to significant corrosive levels at the deposit/tube interface. Depending on the nature of the concentrated impurities, different forms of damage occur – strong alkaline conditions lead to caustic damage and acidic conditions lead to hydrogen damage.

Proper chemical cleaning decisions based on the nature of the failure, the type of boiler, the type of materials to be cleaned and the characteristics of the deposits have to be made to remove the deposits and thus minimize deposit-related boiler tube failures (BTF).

Juxing Bai, Stefan Ritter, and Hans-Peter Seifert

PPCHEM 2016, 18(3), 130–150

Literature Survey on the Effect of Hydrogen on Stress Corrosion Cracking Behaviour in Ni-Base Alloys under Light Water Reactor Conditions

The assurance of safe and economic long-term operation of nuclear power plants in the context of materials ageing is a key topic for both the nuclear power industry and nuclear safety authorities. Pressure boundary components in the primary coolant circuit of light water reactors (LWRs) are made of low-alloy steels, stainless steels and Ni-base alloys and are very critical components with regard to safety and lifetime. Stress corrosion cracking (SCC) of structural materials in pressurized (PWRs) and boiling water reactors (BWRs) is one of the biggest challenges. Ni-base alloys have been shown to be prone to SCC. Accurate knowledge of the system conditions which may lead to SCC initiation and growth is thus evidently indispensable to ensuring safe and economic long-term operation in this context.

In the initial stage of a research project on the effect of dissolved hydrogen on SCC initiation in Alloy 182 under BWR conditions, a literature survey has been performed on the topic of SCC initiation and growth in Ni-base alloys under LWR conditions with a focus on dissolved hydrogen effects, oxide films and mechanisms. The current paper summarizes the most important findings.

Chris Morris and Ed Mroczek

PPCHEM 2016, 18(3), 152–163

Geothermal Turbine Scaling

Scaling, or mineral deposition, in geothermal turbines is an industry-wide problem. It is caused by the superheating of mineralised wet steam as it passes through the turbine nozzles. The superheat conditions result from the normal turbine operating process and cannot be eliminated without significant detrimental effects to performance. The steam supply has a small fraction of water carryover from separator breakdown. This is normally removed by pipeline scrubbing or demisters, but these are not totally effective. Low drainpot efficiency exacerbates the problem. A sample of wet steam collected by isokinetic probes is rarely representative of the total impurities. The authors propose a more effective practical standard to assess geothermal steam cleanliness.

Tapio Werder

PPCHEM 2016, 18(3), 166–171

Report on the PowerPlant Chemistry Forum in Johannesburg, South Africa

This contribution is a report on the first PowerPlant Chemistry Forum, held in Johannesburg, South Africa, on March 24–26, 2016. The forum consisted of four sessions covering different aspects of water/steam cycle chemistry: life-cycle chemistry optimization, start-up chemistry and early operation experience, combined cycle power plant and utility plant chemistry, as well as plant failures and subsequent chemistry adjustments were the topics covered during the two days. Each session consisted of two to three presentations given by an expert in the field, followed by open floor discussions. A short summary of each presentation is given in this report.

James C. Bellows

PPCHEM 2016, 18(4), 184–189

Chemical Processes in Steam Turbines

The chemical processes occurring in steam turbines are controlled both by thermodynamics and kinetics. The equilibrium solubility of sodium chloride in steam in a fossil turbine is reviewed. The deposition rates for fossil turbines are also reviewed. The deposition rates are applied to a real turbine showing the concentration of impurity remaining in the steam and the quantity of salt deposited at each stage. The implications for the operation of turbines and the need for steam purity at low loads are discussed.

Andrew G. Howell

PPCHEM 2016, 18(4), 192–197

Sulfite and Sulfate in the Steam Cycle

Sulfite and sulfate are introcuced into the water-steam cycle of boilers either by intentional addition to remove oxygen or as a result of system contamination. These compounds can cause problems for steam cycle components. Failures can occur in high-pressure waterwalls and steam tubing under certain conditions, and sulfate contamination in steam can lead to disastrous turbine pitting and corrosion cracking. The chemical interactions that take place with sulfite and sulfate in the steam cycle must be understood and problem issues resolved in a timely and technically suitable manner. Appropriate monitoring and management of their concentrations is important to optimizing equipment reliability.

Brad Buecker

PPCHEM 2016, 18(4), 202–207

The Importance of Steam Generation Chemistry Control and Monitoring as Illustrated by Case Histories

During the heyday of coal-fired power plant operation, many lessons were learned regarding proper water/steam chemistry control. These lessons were and continue to be greatly aided by research from such organizations as the Electric Power Research Institute (EPRI), the International Association of the Properties of Water and Steam (IAPWS), and others. Now, combined-cycle power plants dominate new plant construction. Unfortunately, many of the previously learned lessons from coal plants are not carried over to the heat recovery steam generators (HRSG) of combined-cycle units, even though these steam generators operate at high temperatures and pressures. A contributing factor to the lack of knowledge transfer is that combined-cycle units are often minimally staffed, with few or no chemistry-trained personnel. This paper utilizes case histories to outline issues that can arise due to improper chemistry control and monitoring, and examines such issues as waterwall tube failures due to corrosion and hydrogen damage, single-phase and two-phase flow-accelerated corrosion (FAC), steam system damage due to transport of impurities from the boiler, and turbine blade fouling and corrosion, also due to transport of impurities.

Ladislav Bursik

PPCHEM 2016, 18(4), 210–211

The Third Meeting of the European HRSG Forum (EHF 2016)

The third EHF (European Heat Recovery Steam Generator Forum) meeting took place in Prague, Czech Republic, on May 9–11, 2016. The successful format of the first two meetings was implemented again – excellent presentations combined with extended open floor discussions.

Tapio Werder

PPCHEM 2016, 18(4), 213–217

Report on the Third Power Cycle Instrumentation Seminar in Beijing, China

The third Power Cycle Instrumentation Seminar was held in Beijing, China, on June 18–19, 2016. The seminar consisted of two sessions: The presentations on the first day were dedicated to the choice of appropriate chemical treatments for water/steam cycles. Experts from China and abroad presented case studies on the conversion of the chemical regime in coal-fired units as well as on the choice of a chemical regime for newly built heat recovery steam generators.

The second session focused on the management of cycle chemistry. Enough time was given for plenary discussions in which the participants and speakers could discuss the presentations from the first day and use the possibility to exchange ideas with their colleagues from all around the world. The second session was completed with presentations on advances in on-line monitoring and the latest developments regarding the PowerPlant Chemistry Journal.

A short summary of the two days is given in this report.

Brad Buecker

PPCHEM 2016, 18(5), 232–237

A Thermodynamic Review of Equipment That Power Plant Chemists Are Supposed to Protect

Experience has shown the importance of proper water treatment and monitoring in protecting critical plant components as well as the necessity of comprehending the thermodynamics of steam generator heat transfer in order to better understand these chemistry requirements. This article provides an overview of several important heat transfer concepts, and discusses associated chemistry control and monitoring issues. It briefly reviews why combined-cycle power generation and co-generation, with their high efficiencies, are so highly favored these days.

Jan Stodola and Mike Caravaggio

PPCHEM 2016, 18(5), 242–250

Rationale for the Sodium Phosphate Based Boiler Corrosion Protection Guidelines

The paper explores the root cause of unstable alkalinity and corrosion still experienced by some boiler operators. The focus is on modeling boiler water chemistry in the steam generation zone, where solids are known to concentrate by factors up to 1 000 and perhaps higher. Of particular concern is the impact of potential contaminants, such as chloride and sulfate salts, and treatment chemicals, such as caustic (NaOH) and sodium phosphate salts. For this purpose, the Electric Power Research Institute (EPRI) MULTEQ computer code has been used to first simulate bulk boiler water conditions at operating temperatures, and then the impact of contamination with alkali forming waters, such as from the Great Lakes, and of seawater contamination on boiler water within porous deposits. A separate chapter addresses the high-temperature chemistry of concentrated sodium phosphates in contact with protective magnetite and conditions leading to phosphate-induced corrosion.

In the Discussion, the paper outlines a corrosion protection strategy based exclusively on pH control and no phosphate concentration control limits in the standard boiler water sample.

Albert Bursik

PPCHEM 2016, 18(5), 256–259

A 2016 Outlook for Cycle Chemistry for HRSGs

Although not an oracle, in this contribution an experienced former power plant chemist presents his prognosis for the future of cycle chemistry in combined cycles with heat recovery steam generators (HRSGs). It is suggested that the use of organic plant cycle treatment chemicals (film forming and alkalizing amines) has exceptionally positive prospects for improving or avoiding typical chemistry-related HRSG problems, and that their use in combined cycles with HRSGs will become increasingly widespread. Whether and how quickly this prediction may be fulfilled, however, will depend on how soon utility chemists are willing to embrace these new treatment options.

Julia Gath,
Heini Maurer, and
Heinz Wagner

PPCHEM 2016, 18(5), 266–275

Conventional Resin Cation Exchangers versus EDI for CACE Measurements – An Ion Chromatography Study

As a result of the simple measuring principle, the sensitivity and its high reliability, the online measurement of conductivity after water has passed through a column of strongly acidic cation exchange resin has become one of the most commonly used analytical method in power plants with steam generators.

However, the limited amount of cation exchange resin in the exchanger column is spent after some time and the alkalizing agent breaks through, resulting in false high conductivity measurements. Therefore, the cation exchange resin has to be replaced on a regular basis, which leads to an interruption of the measurement. In power plants with a high pH in the feedwater, such as in the secondary circuit of pressurized water reactors or in frequently cycling power plants, the resin has to be changed frequently. At high pH, the problems with the discontinuous measurement of the conductivity after a cation exchange resin, such as the high maintenance effort and resin consumption, become obvious. Here, cation exchange with an electro-deionization (EDI) device might offer a continuous alternative.

This paper provides a comparison to the classic design using a passive cation exchange resin, showing that constantly lower CACE values can be achieved with the EDI device. The effects of the ion exchange resin and the EDI have been analyzed using ion chromatography, providing a detailed chemical picture of the relevant processes influencing the measurement results.

Shunsuke Uchida,
Hidetoshi Okada,
Masanori Naitoh,
Yasuyoshi Seki,
Fumio Kojima,
Seiichi Koshizuka, and
Derek H. Lister

PPCHEM 2016, 18(6), 288–300

Improving Plant Reliability Based on Inspection and Maintenance of Local Wall Thinning due to Flow-Accelerated Corrosion

Early detection and prediction of flow-accelerated corrosion (FAC) along major piping systems and application of suitable countermeasures such as water chemistry improvements are essential for preventing pipe rupture in aged nuclear power plants (NPPs). There are generally two approaches to evaluating future wall thinning in FAC-affected zones: one is based on inspection and the other on prediction or estimation. The fusion of the estimation and inspection procedures can lead to effective and reliable preparation against FAC occurrence and propagation. At the same time, the fusion is effective in mitigating the system risks for level 4 of the "defense in depth" concept.

In order to minimize computational time, a speedy and easy-to-handle FAC code based on one-dimensional (1D) computational fluid dynamics (CFD) analysis has been developed. As a result of a verification and validation (V&V) evaluation based on a comparison of calculated and measured wall thinning, it was confirmed that regional maximum wall thinning rates could be predicted with an accuracy within a factor of 2. Then the code could be applied for FAC risk evaluation for all plant systems to point out the locations where future problems might occur and to prepare for continuous pipe inspections and early implementation of suitable countermeasures. For this purpose, not only the probability of serious wall thinning occurrence in the future but also the probabilistic risks caused by pipe rupture due to the serious wall thinning were analyzed based on probabilistic risk evaluation.

The latest version of the 1D FAC code and its application to the prediction of wall thinning rates under miscellaneous operational conditions are introduced. It is demonstrated how great a contribution can be expected to mitigating plant risks from the total inspection of piping, sampling inspection, and only wall thinning prediction.

Andrew G. Howell and Jeff Aguilar

PPCHEM 2016, 18(6), 304–310

Deposition and Internal Oxide Growth in a Supercritical Boiler

To avoid overheating boiler tube failures, the growth rate and structure of internal deposits and tube metal oxidation on the waterside of supercritical boiler tubing are important to know for evaluating the risk of under-deposit contaminant concentration and for assessing the need for chemical cleaning.

Deposition of iron oxides transported from the feedwater is largely a result of flow-accelerated corrosion (FAC) in the pre-boiler equipment. Single-phase FAC in steam cycle feedwater can be managed well with elevated pH, or with the addition of oxygen. Maximum reduction of iron transport may still be achieved with oxygen addition, however. Two-phase FAC should also benefit from elevated pH, although not from the addition of oxygen. For units with condensate polishing, economics dictate that when operating with elevated pH the cation resin be operated in ammonium form. Polisher performance is not optimal at elevated pH.

Detailed laboratory examination of boiler tubes can provide important information regarding the condition of waterside deposits and their potential to promote damage to boiler tubing, and can assist in the scheduling of their removal by chemical cleaning.

IAPWS

PPCHEM 2016, 18(6), 312–327

Technical Guidance Document: TGD7-16
HRSG High Pressure Evaporator Sampling for Internal Deposit Identification and Determining the Need to Chemical Clean

This Technical Guidance Document has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Dresden, Germany, 11–16 September 2016. The members of IAPWS are: Britain and Ireland, Canada, Czech Republic, Germany, Japan, New Zealand, Russia, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States of America. Associate Members are Argentina and Brazil, Australia, Egypt, France, Greece, and Switzerland. The President at the time of adoption of this document was Professor Hans-Joachim Kretzschmar.

IAPWS

PPCHEM 2016, 18(6), 328–353

Technical Guidance Document: TGD8-16
Application of Film Forming Amines in Fossil, Combined Cycle, and Biomass Power Plants

This Technical Guidance Document has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Dresden, Germany, 11–16 September 2016. The members of IAPWS are: Britain and Ireland, Canada, Czech Republic, Germany, Japan, New Zealand, Russia, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States of America. Associate Members are Argentina and Brazil, Australia, Egypt, France, Greece, and Switzerland. The President at the time of adoption of this document was Professor Hans-Joachim Kretzschmar of Germany.

Michael Rziha and Tapio Werder

PPCHEM 2016, 18(6), 358–363

Report on the Power Cycle Chemistry Working Group Meeting in Dresden, Germany

This short report summarizes the work of the Power Cycle Chemistry (PCC) working group (WG) during the 2016 Annual Meeting of the International Association for the Properties of Water and Steam (IAPWS) in Dresden, Germany. Nearly 30 members of the PCC WG attended the meetings, joint workshops, and task group sessions during the week. Highlights of the week as well as an overview of all the activities within the working group are given in this report.

2017's Scientific and Technical Contributions

Eric Kangas and Anton Banweg

PPCHEM 2017, 19(1), 4–9

Monitoring Industrial Steam Purity: Why Wait?

Industrial steam generating systems provide steam for a wide range of uses. It is the intended use of steam that defines the required purity of steam utilized in a process. Contaminants that impact steam purity may come from mechanical or vaporous carry-over or be introduced through contaminated attemperation spray water. Inadequate steam purity can create conditions that result in efficiency losses, equipment failures, decreased product quality and potential safety concerns. Unfortunately, some industrial steam users wait to evaluate steam purity until after their operations have been impacted by one or more of these concerns. Continuous or periodic monitoring of steam purity provides visibility of potential issues before they become significant operational concerns.

This paper discusses steam purity requirements, methods for accurate monitoring and important considerations in industrial applications. The case study reviews how mechanical, operational and chemical changes to a sugar mill boiler system contributed to failures that could have been prevented with proper attention to steam purity dynamics.

Ian Richardson, David Addison, Simon Addison, Toby Gresham, and Rebecca Lawson

PPCHEM 2017, 19(1), 12–23

Online Steam Purity Analysis for Geothermal Power Generation

Steam purity can have a major impact on steam turbine performance and reliability. Online steam purity monitoring is considered standard practice in thermal and nuclear power plants with steam turbines to enable the rapid identification of out of specification steam purity that could lead to turbine damage. Steam purity is not routinely monitored in real time in geothermal power plants for a variety of reasons, including the difficulty of conditioning samples for analysis with online instrumentation. This is a result of high levels of non-condensable gases that interfere with analysis techniques, as well as concerns as to whether a steam sample is representative of the bulk steam flow due to the two-phase nature of many geothermal steam supplies. Operators may also have concerns about what actions they have available to them to improve steam purity should it be found to be insufficient.

This paper describes the considerations to be taken into account when developing online steam purity monitoring systems for geothermal power plants. A case study demonstrating some of the benefits of geothermal steam purity monitoring is also discussed.

Daniel Zinemanas and Amiel Herszage

PPCHEM 2017, 19(1), 30–38

FAC: How Does Flow Accelerate Corrosion?

Flow plays a very important role in flow-accelerated corrosion (FAC), however, this role and its coupling to the mass transport, which is in fact one of the major factors directly responsible for the corrosion rate, are not fully understood and most significantly are also difficult to evaluate theoretically.

In this communication thus, the general particularities of the effects of the flow on single-phase FAC are reviewed, the governing equations required to evaluate the flow and concentration fields are described, and some results from numerical analysis of the flow and mass transport in different cases and geometries are presented and discussed. These results show that under various conditions the effects of the turbulent flow have more marked effects on the mass transport when the flow is not parallel but has a perpendicular component towards the surface as found in most FAC cases.

In contrast to the theory of developed flow in straight pipes, where mass transport increases due to a thinning of the boundary layer thickness at increased velocities, mass

transport in others geometries, in which the flow is neither fully developed nor parallel to the surface, is dominated by the local coupling between the flow and concentration fluctuations through the principal convective mass flux term, $\overline{v'c'}$. Thus, this enhanced local mass transport, which is in fact responsible for the mass removal from the surface, does not have to be related to vague concepts such as "turbulence", as it generally is, but can be evaluated from the flow and concentration fields calculated from a numerical solution of the momentum and mass conservation balances. A very good agreement is obtained between the numerical calculations and experimental data regarding the FAC locations. In addition, the development of the surface roughness that is also characteristic of the FAC phenomenon is found to be directly related to the flow and mass transport perturbations at the wall and their nonlinear coupling.

Merve Avci Çetin

PPCHEM 2017, 19(1), 40–45

Optimizing a Water Chemistry Program by Switching to Oxygenated Treatment

In supercritical power plants, it is still a challenge to switch from all-volatile treatment under reducing conditions (AVT(R)) to oxygenated treatment (OT) for many organizations. It is known that oxygen may initiate and accelerate corrosion mechanisms. This results in a reluctance to apply it in many utilities. In this article we compare the differences between the two conditioning regimes and present the results of a successful conversion from AVT(R) to OT.

Abstracts 2016

PPCHEM 2017, 19(1), 50–56

2016's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Tamara Petrova

PPCHEM 2017, 19(2), 68–74

Use of ODA at Russian Power Plants

The first use of octadecylamine (ODA) in Russia was at the beginning of the 1960s; extensive investigation of ODA properties started in the 1970s. The following topics were studied: thermolysis of ODA in water environments, sorption of ODA on metal surfaces, the effect of ODA on the corrosion rate, the washing power of ODA, the volatility of ODA, and the effects of ODA on the composition of deposits. This contribution summarizes the results of the research conducted in Russia over the last decades.

Kevin J. Shields

PPCHEM 2017, 19(2), 77–85

Repeat Cycle Chemistry Situations: Precursors to Future Damage in Industrial Utility Plants

Chemistry-related damage events in fossil utility steam generators and steam turbines can be linked to operation with certain repeat cycle chemistry situations. When multiple repeat cycle chemistry situations are present, the risk of future damage is significant. Repeat cycle chemistry situations should be regarded as root causes of damage mechanisms. Application of the repeat cycle chemistry situations philosophy to an industrial cogeneration facility is presented as a case study.

James Malloy, Jan Rusås, and Mark Taylor

PPCHEM 2017, 19(2), 92–102

Understanding Variations in Flow-Accelerated Corrosion Wear Rates in HRSG Evaporator Tubes

Very large differences in the rates of tube wall thinning due to flow-accelerated corrosion (FAC), or in some cases fluid erosion, are observed in the low-pressure (LP) evaporator tubes of certain HRSG designs. The tubes located near the duct wall and occasionally near the gaps between module bundles have more rapid thinning. Tubes in a given row nominally should have very similar process conditions, both on the gas-side and on the waterside. Different wall thinning rates mean that process conditions differ across the tube row.

Computational fluid dynamics (CFD) simulations have been used to investigate the gas-side process conditions in tube assemblies and to determine the impact of tube location in the row on heat transfer. The impact of differing tube heat fluxes on waterside process conditions was analyzed by thermohydraulic simulations using a computer model of the tube assemblies. A correlation between increased thinning rates as a function of tube position and LP evaporator process conditions was identified.

Damien Pain, Agnieszka Kuczynska, and Fraser Hardie

PPCHEM 2017, 19(2), 104–113

Internal NDT Inspection of HRSG Finned Tubes

Boiler tubes, which are a predominant feature of heat recovery steam generator (HRSG) pressure parts, can be susceptible to various degradation mechanisms. The range of defects, including flow-accelerated corrosion (FAC), pitting corrosion and fatigue cracking, can cause unpredicted in-service failures. HRSGs have by design a reduced footprint and this compact design imposes severe access restrictions for inspection. There are no established, off-the-shelf, internal inspection solutions for finned tubes. Doosan Babcock conducted a 3-year (2014–2016) project aimed at developing a tube inspection product for use in plant life assessment to help establish the life expectancy and maintenance requirements of customers' assets. The challenge was to develop a qualitative and quantitative non-destructive testing (NDT) technique which can be remotely deployed on HRSG headers through standard inspection stubs during an outage.

In this paper, an eddy current near field array (NFA) is used to generate an image, called a C-scan, absolute traces and Lissajous patterns to characterise the internal integrity of HRSG finned tubes. The method is demonstrated on finned tube samples with experimental work conducted in a laboratory controlled environment. It is shown that indications can be successfully detected and sized using a clearly defined post-processing strategy.

Bill Smith, Paul McCann, Kazuyoshi Uchida, Shintarou Mori, Julia Jasper, and Wolfgang Hater

PPCHEM 2017, 19(3), 129–140

Determination of Oleyl Propylenediamine, a Commonly Used Film Forming Amine, on the Surfaces of Water-Steam Cycles

Organic cycle chemistry based on oleyl propylenediamine (OLDA), a commonly used film forming amine (FFA), provides an excellent treatment option for water-steam cycles, especially for plants operating in cycling mode where preservation is required during shutdowns but unit availability must be maintained. Uniper has successfully trialled this treatment in the triple-pressure combined cycle gas turbine (CCGT) power plant at Connah's Quay, United Kingdom.

During a trial phase over almost three years at Connah's Quay, a comprehensive monitoring and control program was carried out. This paper reports the results of studies to determine the presence of OLDA on the surfaces of the water-steam cycles in two units. These included inspections of the heat recovery steam generator (HRSG) drums and low-pressure steam turbines during plant outages and, additionally, the sampling and off-site analysis of boiler tubes taken from the high-pressure evaporator and reheater circuits. A study on superheater tubes from a pilot boiler at the Kurita Global Technology Center in Japan complemented the field results.

Three different methods of analysis were applied: the non-specific hydrophobicity or droplet test using a spray of demineralised water, Kurita's own newly developed surface wipe test specific for OLDA, and x-ray photoelectron spectroscopy to check for amine nitrogen on material surfaces. The first two tests were carried out on-site, the third one off-site.

OLDA could be detected on the surfaces of all investigated components of the water-steam cycles from both units at Connah's Quay. This included components operated not only under wet conditions, but also under dry conditions. The film forming amine

was also detected on the superheater tubes from the pilot boiler treated with FFA-based cycle chemistry. The film forming amine could not be measured on surfaces which had not been exposed to a cycle chemistry with FFAs.

The OLDA film was present on all surfaces of the water-steam cycle in components that were examined in the Connah's Quay units. A key operational control was to ensure that a small residual FFA concentration was analytically detected in the condensate before unit shutdown. This finding supports the practical approach for the control of FFA-based cycle chemistry, where the analytical proof of FFA in the condensate indicates complete film formation in the water-steam cycle. The Kurita wipe test is an easy tool to apply which enables operators to verify complete film formation by the specific measurement of OLDA on water-steam cycle surfaces during plant inspections.

The results strongly indicated that OLDA is present on surfaces throughout the complete water-steam cycle in both water circuits and in dry steam stages. Therefore, the technology has the capability to protect all components in water-steam cycles if the FFA is applied correctly.

Shawn S. Simmons

PPCHEM 2017, 19(3), 142–148

Cleanup of the Closed Cooling Water System at AES Alamitos Units 5 and 6

Early in 2016 it was discovered that the closed cooling water system at AES Alamitos Units 5 and 6 was severely fouled with bacteria slime. The buildup of slime occurred over time due to the chemical addition of nitrite-based corrosion inhibitor, inadequate monitoring, and an absence of biocide treatment. The fouling resulted in unit load restrictions due to cooling water temperatures becoming too hot. This paper describes the system cleanup and its restoration to normal conditions.

Karsten Thomsen

PPCHEM 2017, 19(3), 154–163

Corrosion Product Sampling and Analysis – The Distribution behind the Results

In relation to the ongoing revision of the International Association for the Properties of Water and Steam (IAPWS) Technical Guidance Document (TGD) on Corrosion Product Sampling and Analysis a field trial has been conducted. These first parallel measurements have given consistent results indicating that the content of corrosion products in a series of samples is distributed according to the log-normal distribution function. This matches observations over the last few years for samples acquired over both short and longer periods. Working under the basic assumption that corrosion product results are log-normally distributed alleviates the problem often encountered in practice of obtaining 10–20 % high, outlying results in a series of samples. Two statistical figures characterise the distribution of results: the median and the 95th percentile. Both are easy to understand, interpret and communicate; thus, they are well suited as convenient routine quality parameters.

This paper summarises the results of the field trial and gives examples of log-normally distributed corrosion product data covering periods of a couple of years.

Judy Weir and David Addison

PPCHEM 2017, 19(3), 164–173

Ion Exchange Challenges in a Dairy Product Processing Factory Cogeneration Plant

This paper outlines the challenges of an ion exchange plant used to produce high-quality make-up water for heat recovery steam generators producing steam for use in both dairy food processing and electricity production via a steam turbine at a large dairy factory in New Zealand.

It discusses the processes that site management and operators went through to improve the plant's reliability and water quality. These included the identification of key problem areas, changes to the ion exchange plant operation and maintenance, investigation into measurement of the dairy factory condensate return quality, the implementation of a performance management program for the plant, and training of the key personnel.

Tapio Werder

PPCHEM 2017, 19(3), 174–178

Report on the International Conference on Film Forming Amines and Products in Lucerne, Switzerland

The first International Conference on Film Forming Amines and Products was held in Lucerne, Switzerland, on April 3–6, 2017. The conference was organized by the International Association for the Properties of Water and Steam (IAPWS) with the support of the Swiss Committee for the Properties of Water and Steam (SCPWS).

The main purpose of this conference was to advance the knowledge about film forming amines and products, including the latest science. Scientific papers and case studies provided excellent insights into the most recent developments in this field of cycle chemistry, and numerous examples of the application of film forming amines and products in fossil, combined cycle, nuclear, and other plants were given during the three-day conference.

A short summary of the conference events is given in this report.

Marisa Abadeço and Una Nowling

PPCHEM 2017, 19(4), 187–192

The Influence of Ash Composition on Fouling and Slagging Propensity in a Coal-Fired Power Plant Boiler

Coal is a very complex fuel due to its chemical and physical properties. The effects of coal combustion behavior, such as fly ash loss on ignition or slagging and fouling, will affect power plant performance, such as boiler efficiency and possible load deviations. The most common causes for slagging and fouling are a low excess of oxygen, high primary airflows, burner damage, poor coal pulverizer conditions, and coal chemistry. This paper addresses the last point, analyzing the influence of the sodium and iron content in coal on fouling and slagging phenomena in pulverized coal boilers. The formation of eutectic mixtures from the different oxides causes a drop in the fusion temperatures in the boiler convective zone.

James C. Bellows

PPCHEM 2017, 19(4), 197–201

Chemistry Aspects of Industrial Turbines

Industrial turbines appear in a wide variety of applications and under a wide variety of operating conditions. They may be operating at variable speed, particularly in marine turbines.

They may be used as backpressure turbines, where their primary purpose is to reduce high-pressure steam to pressures used in a process, but producing electric power as a byproduct. In this use, the steam may be removed from the turbine in the superheated state and there is no moisture transition. The implications of backpressure are explored.

Another use is for district heating. In this application, turbines have been configured so that a single condenser is shared among multiple turbines. If the steam is not needed, one turbine may be idle over an operating condenser.

Most industrial turbines are not reheat turbines, and the implications of this fact, such as the possibility of on-line washing to remove water soluble deposits, are also explored. The common idea that salts may be more concentrated in steam to non-reheat turbines than in steam to utility turbines is erroneous. Salt concentrations should be the same as for utility turbines. Silica requirements might be a bit higher than for utility turbines.

Maarten C. M. Bruijs, Lars P. Venhuis, and Ludwin Daal

PPCHEM 2017, 19(4), 203–209

Global Experiences in Optimizing Biofouling Control through Pulse-Chlorination®

Cooling water systems provide optimal conditions for the settlement and growth of fouling species, e.g. mussels, oysters and barnacles. Excessive biofouling results in major operational upsets and even unplanned shutdowns. Controlling micro- and macrofouling organisms in once-through cooling water systems is key to safe, reliable

operation. For this, chlorination is globally still considered one of the best technology options. Sodium hypochlorite is applied either as bulk-product or is produced on site by means of an electro-chlorination plant. The common industry practice is continuous dosing, often combined with shock dosing.

However, despite this approach many installations still experience significant operational and economic consequences. The likelihood and frequency of operational issues is site specific and in addition may result from increasingly strict permit limits, the need to operate with dwindling (human) resources and settlement of new types of fouling species. Pulse-Chlorination® (PC) is an optimized intermittent dosing procedure, implemented through a science-based assessment procedure on site. It has proven to be highly effective regardless of the geographic location and species of concern. In addition, PC is not only applicable to sodium hypochlorite, but to any biocide that is able to trigger and alter the behavior of the fouling species. In general, the dosing technology reduces the required volumes of hypochlorite up to 50 % compared to continuous dosing, leading to a significant reduction in operational costs and environmental impact, while the mitigating efficacy is high. Motivated by increasingly strict environmental regulations, a focus on operational cost reductions and increased plant availability, installation owners are looking for environmental and cost-saving alternatives.

PC has globally received recognition as a proven technology and is implemented at many industrial sites throughout Europe, the Middle-East, Asia and Australia. The efficacy of the optimized dosing schedule is controlled by in-plant monitoring of biofouling trends and the continuity of the applied dosing regime by strategic monitoring of residual oxidant levels.

Emmanuel K. Quagraine

PPCHEM 2017, 19(4), 213–222

Insights and Lessons Learnt from a Scaling Event in a Cooling Tower Part I: Statement of the Problem and Introduction to the Methodology of the Investigation

This is the first half of a two-part article on a scaling incident that occurred at the Shand Power Station, SaskPower. The event exemplifies scaling as a costly operational problem associated with the reuse of secondary treated municipal effluent when logistical challenges compel operations outside designed limits. The plant, which was commissioned in 1992 and operates on a zero liquid discharge program, has since 1994 been using treated sewage effluent as a significant but variable portion of its cooling tower make-up water. As far as scaling is concerned, apart from the early adjustment periods, the operation had been largely successful, especially in the previous twelve years. Over the summer of 2014, however, due to restricted outlets to manage the blending of the treated sewage effluent with fresh surface water, the plant by its contractual obligation had to take untypically disproportionate amounts of the treated effluent whilst also faced with a series of cooling water treatment equipment breakdowns. This forced cooling tower operations to the water chemistry fringes, where the scaling potential was high; ultimately, fouling of the condenser occurred, resulting in significant electricity generation unit derates. The paper describes the event, the operating conditions, and an assessment of the chemical treatment effectiveness, as well as the mitigation efforts made, including an on-line acid clean to restore the generation unit back to normal load. Several lessons to be learnt from the event are outlined.

Ladi Bursik

PPCHEM 2017, 19(4), 223

The Fourth Meeting of the European HRSG Forum (EHF 2017)

The fourth EHF (European Heat Recovery Steam Generator Forum) meeting took place in Amsterdam, the Netherlands, on May 16–18, 2017. The successful format from the first three meetings was followed again – presentations mixed with extended open floor discussions.

Dennis Bitter and Ytzhak Rozenberg

PPCHEM 2017, 19(5), 235–239

Non-Chemical Disinfection & Dechlorination to Protect RO and Demineralizer Treated Boiler Make-up Water

Chlorine and biocides have traditionally been used to mitigate biofouling and manage microbial induced corrosion, and are commonly injected into the feed lines of the water treatment process at power plants to reduce the microbial load. However, when the water treatment process consists of reverse osmosis (RO) trains, it is important to make sure the membranes are protected from oxidation by chlorine. Therefore, dechlorination is undertaken to remove free chlorine compounds from the feedwater in order for the RO trains and other chlorine-sensitive equipment to operate properly.

In this paper, a technology is evaluated which uses broad-spectrum ultraviolet (UV) lamps for the reduction of chlorine and disinfection. Through photodecomposition by UV light, the system decomposes the free chlorine oxidant. Additionally, the technology provides disinfection to reduce the membrane biofouling potential.

The core of the discussed UV system is its water disinfection chamber made of high-quality quartz surrounded by an air block instead of traditional stainless steel. This configuration uses fiber optic principles to trap the UV light photons and recycle their light energy. The photons repeatedly bounce through the quartz surface back into the chamber, effectively lengthening their paths and their opportunities to inactivate microbes.

The efficacy of the technology, coupled with its specific operating principles and ease of use, allows for a unique non-chemical approach to dechlorinating and disinfecting boiler make-up water.

Shivakamy Krishnan, Chitra Sengadir, and Biplob Paul

PPCHEM 2017, 19(5), 245–252

Removal of ^{125}Sb from Radioactive Liquid Waste

This paper describes the synthesis, characterisation and application of a composite exchanger – hydrous zirconium oxide (HZO) coated on polyurethane foam – for the removal of ^{125}Sb from radioactive waste. In batch studies, removal of 80–100 % of Sb(V) was observed in the pH range of 1–13. The presence of competing anionic species up to 1 000 mg · L^{-1} and dissolved solids up to 3 000 mg · L^{-1} had an insignificant impact on antimony removal. The exchange capacity of HZO was found to range between 0.7–0.9 mEq · g^{-1}. The role of surface hydroxyl groups in the removal of antimony could be established by x-ray diffraction and Fourier-transform infrared spectroscopy studies. In column studies, complete removal of antimony was observed up to 1 200 bed volumes of 1 mg · L^{-1} Sb(V) solution prepared in tap water. In trials with ^{125}Sb-bearing waste samples, an average decontamination factor of 4 was obtained despite very high dissolved solids concentrations of 30 g · L^{-1}.

Emmanuel K. Quagraine

PPCHEM 2017, 19(5), 261–277

Insights and Lessons Learnt from a Scaling Event in a Cooling Tower Part II: Results and Discussion on the Efficacies of Scale Predictive Indices, Scale Inhibitor(s), and On-Line Cleaning Method(s)

This is the second half of a two-part article on a scaling incident that occurred at the Shand Power Station, SaskPower. The paper describes a simple scale predictive index based on the ratios of conductivity to calcium and magnesium concentrations for the early detection of supersaturation and a high tendency towards scale deposition on heat exchanger surfaces within recirculating cooling waters treated with scale inhibitors. With this predictive index, the effectiveness of the scale inhibitor is evaluated based on the dosage concentrations vis-à-vis the water chemistry during the scaling incident. Using empirical data, the dependability and limitations of currently reported Ca^{2+} and SO_4^{2-} ionic product guidelines in preventing calcium sulfate scale deposition are also assessed. A distinction is made between the operational adverse impacts of $CaCO_3$ and $CaSO_4$ scale deposition and their remedies. Details of on-line acid cleans to restore the generation unit back to normal load are also described. The paper concludes with remarks listing various lessons learnt from the scaling episode.

PPCHEM 2017, 19(5), 278–279

International Association for the Properties of Water and Steam 2017 Annual Meeting, Kyoto, Japan

Continuing a series of conferences that began in 1929 in London, 102 scientists, engineers and accompanying persons from 13 countries attended the annual meeting of the International Association for the Properties of Water and Steam (IAPWS). The Japanese National Committee of IAPWS hosted the meeting between the 27th August and the 1st September 2017 at the Kyoto Research Park in Kyoto, Japan. The highlights of the IAPWS working group sessions and other proceedings of the executive committee are summarized in this release.

Adrian Dennehy

PPCHEM 2017, 19(6), 291–300

Use of Control Charts in Monitoring Water-Steam Cycle Chemistry

Control of chemical parameters within a power plant's water-steam cycle is necessary in order to identify deviations from normal operation. Historically, values for normal operation were set by the original equipment manufacturer (OEM), which closely followed international guidelines. The VGB PowerTech (VGB) Standard "Feed Water, Boiler Water and Steam Quality for Power Plants / Industrial Plants" recommends that values for normal operation (N-range) should be set for each plant specifically and that statistical process control (SPC) charts for variables (commonly known as control charts) can be used to monitor system performance.

This study used online and grab sampling data from an operating power plant and applied statistical tools using a statistical software package called Minitab to implement the VGB Standard's recommendations (N-range and control charts) for the chemical control of three key chemistry parameters.

It found that for two key parameters, high-pressure (HP) main steam conductivity after cation exchange (CACE) and feedwater CACE, the existing values for normal operation set by the OEM were easily met by the plant studied to such an extent that it is possible for chemical contamination to enter the system in small amounts and not trigger any warnings or alarm. In this respect, optimisation of the normal limit values is possible following the VGB approach. The process capability analysis suggested that in order to achieve a process capability index, C_p, greater than 1, 125 % of the VGB N-range should be used.

For the other key parameter, the existing value for normal operation as set by the OEM was fit for purpose ($C_p > 1$) and no optimisation of the value as per VGB should be undertaken as this would result in a $C_p < 1$.

Haruka Kido,
Sho Shinotsuka,
Akihiro Hamasaki,
Satoshi Umeda, and
Jun Hishida

PPCHEM 2017, 19(6), 305–311

Optimization of Chemistry in Himeji No. 2 Leads to Significant Reduction of Total Iron

The revised Japanese Industrial Standard "Water Conditioning for Boiler Feed Water and Boiler Water" (JIS B 8223) was issued in 2015. The upper limit value of feedwater pH in the absence of copper-based materials was increased as a countermeasure against flow-accelerated corrosion (FAC). In addition, hydrazine is being used less often as an oxygen scavenger since it is considered to be a carcinogen and because of concerns regarding an increase in FAC.

To avoid single-phase FAC problems and the possible impact of hydrazine on health, Himeji No. 2 Power Station in Japan adopted a treatment with a high pH in the feedwater under low oxidizing conditions, which means the concentration of dissolved oxygen is under 5 $\mu g \cdot L^{-1}$ without dosing an oxygen scavenger such as hydrazine. This treatment is being successfully applied at Himeji No. 2 combined cycle power plant based on the revised JIS B 8223 issued in 2015.

Michael Rziha and Tapio Werder

PPCHEM 2017, 19(6), 313–317

Report on the Power Cycle Chemistry Working Group Meeting in Kyoto, Japan

This report summarizes the work of the Power Cycle Chemistry (PCC) working group (WG) during the 2017 Annual Meeting of the International Association for the Properties of Water and Steam (IAPWS) in Kyoto, Japan. Nearly 30 members of the PCC WG and additional guests attended the meetings, joint workshops, and task group sessions of the PCC WG during the week. Highlights of the week as well as an overview of all the activities within the working group are given in this report.

Tapio Werder

PPCHEM 2017, 19(6), 323–331

Report on the PowerPlant Chemistry Forum in Bangkok, Thailand

This contribution is a report on the fourth PowerPlant Chemistry Forum, held in Bangkok, Thailand, on October 11–12, 2017. The forum consisted of six sessions covering different aspects of water/steam cycle chemistry: life-cycle chemistry optimization, film forming amines, condensate polishing, zero liquid discharge, case studies, and monitoring and analytics were the topics covered during the two days. Each session consisted of two to three presentations given by an expert in the field, followed by open floor discussions at the end of each day. A short summary of each presentation is given in this report.

Barry Dooley

PPCHEM 2017, 19(6), 333–334

AHUG 2017 Highlights and Press Release

Another hugely successful tenth annual meeting of AHUG was held on the 14th–16th November 2017 in Sydney, Australia chaired by Barry Dooley of Structural Integrity. AHUG 2017 attracted about 60 participants from Australia, New Zealand, Finland, Japan, UK, and USA.

AHUG is supported by the International Association for the Properties of Water and Steam (IAPWS), and is held in association with the US HRSG Forum (HF). There were four exhibitors: Duff and Macintosh Pty. Ltd., HMA, Swan Analytical Instruments, and Vahterus Oy.

The meeting provided a highly interactive forum for the presentation of new information and technology related to HRSGs, case studies of plant issues and solutions, and for open discussion among plant users, equipment suppliers, and industry consultants. AHUG again provided a unique opportunity for plant users to discuss questions relating to all aspects of HRSG operation with the industry's international experts.

2018's Scientific and Technical Contributions

Emmanuel K. Quagraine

PPCHEM 2018, 20(1), 4–22

Chloride Contamination of the Water/Steam Cycle in Power Plants: Part V. Evidence for Chlorinated Compound Vapor Ingress Even after Condenser Re-tubing and Tubesheet Coating

This paper builds on earlier hypotheses that at the power plant under discussion chlorinated compounds with significant vapor pressures can ingress in gaseous form into the condenser shell through weak seals and/or porous de-alloyed brass tubesheet at tube-to-tubesheet joints and are converted into chloride in the water/steam circuit. Aqueous seepage from the cooling water (CW) is also implicated, but is minor. Dezincification is the main corrosion mechanism.

The issue was addressed by tubesheet hole repairs with titanium epoxy and plastic epoxy application on all tubesheet faces. Yet failures linked with chlorine species attacks became obvious soon after such repairs, showing variations in the boiler chloride to sodium ratio. More sustained chloride cycling in the boiler to levels before the condenser repairs was observed only after an episode which led to spikes in the condensate extraction pump (CEP) dissolved oxygen (DO), CEP sodium, CEP conductivity after cation exchange (CACE), and steam sodium, and to increasing of the differential oxidation reduction potential at the CEP and deaerator outlets. Merely ~ 4.3 % of the chloride ingress from the CW system was estimated to be due to water leakage; the remainder was attributed to vapor ingress of chlorinated compounds. Inspection of the condenser waterboxes and the shell confirmed deterioration of epoxy cladding and tube-to-tubesheet joints.

The current paper provides further evidence from the period in which breaches may have occurred to the epoxy coating to support the concept that it is gaseous chlorine compounds and not necessarily water from the recirculating CW which is responsible for the chloride contamination of the water/steam cycle.

Mohammed Mahmoodur Rahman,
Saad Abdullah Al-Sulami, and
Fahad A. Almauili

PPCHEM 2018, 20(1), 34–49

Carbohydrazide vs Hydrazine: A Comparative Study

Hydrazine has been extensively used by the Saline Water Conversion Corporation (SWCC) in high-pressure boilers as an effective oxygen scavenger for the last several decades. However, due to its toxicity there have been serious thoughts of replacing it with a safer and more effective alternative.

Carbohydrazide, which is marketed under different trade names, was believed to be a good alternative to hydrazine that provides all of the additional benefits desired of an alternative oxygen scavenger of being safe to handle but without the deleterious impact on the cycle chemistry.

Trial tests with carbohydrazide on one of Al-Jubail Power Plant's boilers provided evidence that it is a good alternative to hydrazine. After two weeks of optimization, it was found that maintaining residual hydrazine in the range of 30–40 $\mu g \cdot kg^{-1}$ in feedwater (economizer inlet) was an appropriate method of controlling the dose rate of carbohydrazide and hence provided the optimum conditions for passivating the boiler. Accordingly, a dosing rate of 0.7 $mg \cdot kg^{-1}$ of carbohydrazide was found satisfactory for running the boiler smoothly.

This paper is a summary of the initial trials performed 12 years ago and serves as an introduction to a second article which will be published later this year in this journal. During the past 12 years, SWCC has been using carbohydrazide in all of its 8 plants. SWCC has done some studies with different brands and with 6–12 % carbo-hydrazide used in the steam cycle as well as during lay-up – this experience will be presented in the next paper.

Abstracts 2017

PPCHEM 2018, 20(1), 54–62

2017's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Ute Ramminger, Ulrich Nickel, and Jörg Fandrich

PPCHEM 2018, 20(2), 72–79

Investigation of the Efficiency of Film Forming Amines for System Component Corrosion Protection by the Inhibition of the Electrocatalytic Reaction of *N,N*-diethyl-*p*-phenylenediamine with Chloropentaaminecobalt(III) Complex

The application of film forming amines (FFAs) as an effective protection against general and selective corrosion phenomena has been proven as a successful water chemistry improvement method for water-steam cycles of pressurized water reactors (PWRs). Since 2011 Framatome GmbH (formerly AREVA GmbH) has performed ten FFA applications worldwide as a regular complement to the applied secondary side water chemistry treatment with the main goal of establishing a hydrophobic and protective film on all inner surfaces of the water-steam cycle which are exposed to corrosion attack.

So far well-known practices have been applied to evaluate the effectiveness of the film formation on metal and metal oxide layers, for example hydrophobicity testing and contact angle measurements. Electrochemical methods have been investigated with respect to their applicability to provide additional information on the homogeneity of FFA films on metal and metal oxide surfaces and thus their ability as corrosion inhibitors.

This paper describes a method to determine qualitatively the completeness and homogeneity of the film formation on FFA pretreated corrosion specimens by the inhibition of the electrocatalytic reaction of a *N,N*-dialkylated *p*-phenylenediamine with chloropentaaminecobalt(III).

Zhi-gang Li, Yu-bo Zhang, and Bing-yin Yao

PPCHEM 2018, 20(2), 82–89

Case Studies and Findings on High-Temperature Oxidation in Supercritical/Ultra-Supercritical Boilers

After investigating and analyzing several cases where large areas of the oxide layer exfoliated from the steam-touched surfaces of tubes in the high-temperature areas in supercritical and ultra-supercritical boilers in 2013, this paper sorts out factors affecting the growth of oxide layers in high-temperature areas of the boiler and exfoliation of these oxide layers from the steam-touched tube surfaces.

The results indicate that, firstly, stainless steel (TP347H) tubes with coarse grain size show a faster rate of oxide growth at high temperatures; secondly, early oxide layer exfoliation tends to appear in boilers with steam temperatures lower than the design value; thirdly, alarm values for the tube wall temperature from boiler manufacturers cannot effectively prevent oxide growth; and finally, there is no direct relationship between oxygenated treatment of the boiler feedwater and the exfoliation of large areas of the oxide layer.

Emmanuel K. Quagraine

PPCHEM 2018, 20(2), 94–112

Chloride Contamination of the Water/Steam Cycle in Power Plants: Part VI. Confirmation of Chlorinated Vapor Ingress Hypothesis by Regression Model Prediction of Boiler Chloride to Sodium Ratios

This paper builds on earlier hypotheses that chlorinated compounds with significant vapor pressures can ingress in gaseous/vapor forms into the condenser shell through weak seals and/or porous de-alloyed brass tubesheet at tube-to-tubesheet joints. The issue was addressed by tubesheet hole repairs with titanium epoxy and plastic epoxy application on all tubesheet faces.

The paper consists of two parts: 1) a cursory review of the literature on oxidative degradation of polymers and how it can initiate leak paths for gas, vapor, and liquid permeation; and 2) derivations and validations of predictive models to account for variations in boiler chloride to sodium ratios (BCSRs) at various stages of operation after the epoxy resin repairs and condenser re-tubing. The models (developed using multiple regression analysis) explained the variations well and confirmed the hypotheses of chlorinated compound vapor ingress alongside water seepage into the condenser shell from the cooling water (CW).

Earlier (the first 1½ years) in operation, vapor diffusion flux of chloramines, being favored by temperature increase, was implicated as the dominant process of chlorine contaminant transfer from the CW into the water/steam cycle, resulting in higher BCSRs. However, this mode of transport was sporadic in these early stages. At later stages of operation, after an episode that seemed to have caused damage to the titanium epoxy and tube-to-tubesheet joints, the chloride cycling became more persistent. The derived model at this stage however showed (by p-statistics) a weak influence of temperature. It also suggested: a) a blend of both diffusive and convective flows of chloramines as transfer processes promoting higher BCSRs, and b) convective flux of liquid (aqueous CW) contributing relatively higher sodium (than chloride), thereby lowering BCSRs. Through all stages, CW free chlorine was found as the main influencing factor on the convective flux of aqueous CW into the water/steam cycle.

Barry Dooley

PPCHEM 2018, 20(2), 116–117

Film Forming Substances (FFS) Conference, FFS2018 Highlights and Press Release

The second FFS International Conference was held on the 20th – 22nd March 2018 in Prague, Czech Republic chaired by Barry Dooley of Structural Integrity. FFS2018 attracted about 70 participants from 30 countries.

FFS is supported by the International Association for the Properties of Water and Steam (IAPWS).

The meeting provided a highly interactive forum for the presentation of new information and technology related to FFS, case studies of plant applications, and for open discussion among plant users, equipment and chemical suppliers, university researchers and industry consultants. The conference provided a unique opportunity for plant users to discuss questions relating to all aspects of FFS with the industry's international experts. A panel session was held which focused on a number of the key questions and uncertainties about FFS some of which are highlighted below.

Wolfgang Hater, Bill Smith, Paul McCann, and André de Bache

PPCHEM 2018, 20(3), 136–144

Experience with the Application of a Film Forming Amine in the Connah's Quay Triple Stage Combined Cycle Gas Turbine Power Plant Operating in Cycling Mode

Due to the changing conditions of the energy market, many power plants have various periods of non-operation, ranging from a few days to months. Unprotected unit shutdown represents a serious corrosion risk and thus a risk for the integrity of key plant parts, such as the boiler or steam turbine. However, the established conservation methods of the water-steam cycle are not always applicable under the constraints of the modern power market, with unpredictable shutdown periods, while at the same time the plants have to remain available and may be required to run at short notice. Film forming amines (FFAs) offer excellent potential for the required flexible conservation process. The Uniper combined cycle gas turbine power plant located at Connah's Quay, UK, has assessed the applicability of FFAs for boiler and steam turbine protection.

Besides a product based on a combination of FFAs with alkalising amines, a newly developed product containing solely the FFA was applied. Some key benefits could be demonstrated. The protection of the boiler and steam turbine could be achieved for a period of at least one month. The technology was able to protect all components of the water-steam cycle, including the areas of predominantly dry steam. Compared to dehumidification or nitrogen capping, minimal manpower was required for conservation. By the application of the newly developed product, the drawback of increased cationic conductivity levels was overcome, which remained close to the normal operation values. Due to the encouraging results, FFAs are now applied in all 4 units of the Connah's Quay power plant.

Robert Svoboda

PPChem 2018, 20(3), 154–162

Interpretation of Stator Cooling Water Chemistry Data

Key parameters for chemistry monitoring of stator cooling water are conductivity, electrochemical potential (ECP), pH, and the concentrations of oxygen, copper, and of possible chemical additives (like NaOH for alkaline treatment). While conductivity, oxygen, and ECP merit continuous supervision, periodic analysis (e.g. once a month) may be sufficient for the other parameters.

The relation between the copper concentration and conductivity permits an assessment of the susceptibility of the system with regard to deposition and corrosion, as well as of possible impurity ingress. For alkaline treatment, measurement of conductivity and the sodium concentration indicates whether the alkalization is running properly. Oxygen concentration is a valuable indicator, but is ambiguous with low-oxygen regimes. Here, oxygen ingress may be detected by an elevated oxygen concentration in the water. However it is also possible that the oxygen is being consumed so rapidly that it does not show up in the water analysis.

Akash Trivedi

PPChem 2018, 20(3), 164–167

Use of Microfluidic Capillary Electrophoresis to Measure Chloride and Sulfate at $\mu g \cdot kg^{-1}$ Levels

This paper describes a new approach to on-line monitoring of trace levels of chloride and sulfate based on microfluidic capillary electrophoresis (MCE). In this new analytical system, replenishment of the sample and reagent in the MCE cartridge has been automated to provide fully unattended operation. This system provides very high sensitivity (at the single $\mu g \cdot kg^{-1}$ level) for simultaneous determination of chloride and sulfate, comparable to that of ion chromatography. The instrument has been successfully deployed in a power plant application.

Barry Dooley

PPChem 2018, 20(3), 168–169

European HRSG Forum (EHF2018) – Highlights and Press Release

Another hugely successful fifth annual meeting of EHF was held on the 15th–17th May 2018 in Bilbao, Spain chaired by Barry Dooley of Structural Integrity. EHF2018 attracted 72 participants from 16 countries including: Belgium, China, Czech Republic, France, Germany, Greece, Hungary, Iran, Ireland, Israel, Spain, Scotland, Switzerland, The Netherlands, UK and USA.

EHF is supported by the International Association for the Properties of Water and Steam (IAPWS), and is held in association with the Australasian HRSG Forum (AHUG) and the US HRSG Forum (HF). There were four exhibitors: Anodamine, Atlantium, Mettler-Toledo / Manvia and PPChem / Waesseri. The host organization was Bahia de Bizkaia Electricidad, S.L. (BBE) with Mr. Jose-Maria Bronte, Director General, in attendance.

This year the EHF included 28 presentations, a Panel Discussion on Attemperation and a Workshop on HRSG Materials Aspects. The meeting provided a highly interactive forum for the presentation of new information and technology related to HRSGs, case studies of plant issues and solutions, and for open discussion among the plant users,

equipment suppliers, and industry consultants. EHF again provided a unique opportunity for plant users representing 18 generators to discuss questions relating to all aspects of HRSG operation with the industry's international experts.

Conference

PPCHEM 2018, 20(4), 188

EPRI 12th International Conference on Cycle Chemistry in Fossil and Combined Cycle HRSG Plants (ICCC12): Details Advances in R&D

Another immensely successful International Conference on Cycle Chemistry in Fossil and Combined Cycle HRSG Plants was conducted June 26–28, 2018, in Arlington, Virginia, by the Electric Power Research Institute (EPRI). Pre- and post-conference workshops were conducted on cycle chemistry program treatment and optimization and on neutralizing amines and film-forming products (FFP).

Conference

PPCHEM 2018, 20(4), 190–192

17th International Conference on the Properties of Water and Steam (ICPWS) and International Association for the Properties of Water and Steam (IAPWS) 2018 Executive Committee and Working Group Meetings

Between September 2nd–7th, 2018, 140 scientists and engineers representing 27 countries convened in Prague, Czech Republic for the 17th International Conference on the Properties of Water and Steam (ICPWS) and the annual meetings of the IAPWS Executive Committee and Working Groups. The ICPWS conferences began in 1929 in London, UK and are typically held every fourth or fifth year in conjunction with the annual IAPWS meetings. The purpose of the conference is to connect scientists with the engineers who use their information, providing the researchers with guidance on useful problems and the engineers with the latest research results.

Barry Dooley and Derek Lister

PPCHEM 2018, 20(4), 194–244

Flow-Accelerated Corrosion in Steam Generating Plants

Flow-accelerated corrosion (FAC) has been researched for over 50 years at many locations around the world, and scientifically all the major influences are well recognized. However, the application of this science and understanding to fossil, combined-cycle/HRSG and nuclear plants has not been entirely satisfactory. Major failures are still occurring and the locations involved are basically the same as they were in the 1980s and 1990s. This paper reviews the latest theory of the major mechanistic aspects and also provides details on the major locations of FAC in plants, the key identifying surface features of single- and two-phase FAC, the cycle chemistries used in the plants and the key monitoring tools to identify the presence of FAC. The management aspects as well as the inspection, predictive and chemistry approaches to arrest FAC are described, and the different approaches that are needed within fossil, HRSG and nuclear plants are delineated.

Mike Caravaggio and Brad Burns

PPCHEM 2018, 20(5), 264–275

Smart Cycle Chemistry Alarms: Intelligent, Actionable Alarms

Fossil and combined cycle power plant operations continue to evolve and introduce new challenges to the management of the cycle chemistry program. Two of the main drivers have been cost reduction and increased flexible operation. This has led to a reduction in cycle chemistry expertise at plants, while there has been a simultaneous increase in the complexity of managing the chemistry program. The development of smart cycle chemistry alarms is a methodology to respond to these challenges and improve corrosion and deposition control at power plants. The concept is simple: use independent signals to diagnose and confirm excursions and chemistry events as they occur in the power plant so that non-expert personnel can respond appropriately. This paper discusses the philosophy for developing smart alarms. It builds on cycle chemistry validation work presented at previous Electric Power Research Institute (EPRI) International Cycle Chemistry conferences and will include some application examples of the EPRI approach to smart cycle chemistry alarms.

Iain Duncanson, Dan Sicking, Keith Fruzzetti, Michael Garner, Charles Clinton, and Chancey Pence

PPCHEM 2018, 20(5), 278–288

Dispersant Injection Strategy Optimization at South Texas Project

The use of dispersants in pressurized water reactors has been extensively qualified by the Electric Power Research Institute (EPRI) as a viable and effective technology for significantly reducing the fouling rate of steam generators and has contributed to improvements in steam generator thermal performance. Several specific strategies for the application of dispersants are qualified for use at utilities including continuous online injection, steam generator wet layup and long-path recirculation (start-up).

The South Texas Project has been at the forefront of the industry dispersant implementation program and is the first nuclear utility to implement dispersant injection with the use of full flow, deep bed condensate polishing. The South Texas Project dispersant injection program was implemented as a continuous, online strategy for optimizing steam generator thermal performance and managing steam generator deposit inventories. Operating experience has shown that an online batch-type dispersant injection strategy may provide similar benefits to those realized from an online continuous injection strategy whilst providing cost saving benefits and minimizing exposure of condensate polisher resin to dispersant. This paper summarizes South Texas Project dispersant experiences and provides rationale for transitioning to a batch-type injection strategy.

Robert Svoboda and Wolf-Dietrich Blecken

PPCHEM 2018, 20(5), 290–294

Corrosion and Deposits in Water-Cooled Generator Stator Windings: Overview of Water Cooling of Generators

The most common and severe problem related to corrosion and deposits that has arisen with generator water cooling throughout its more than 50 years of history is plugging of copper hollow conductors. This article gives an introduction to a series of four additional articles to appear in this journal on these issues, in particular problems with copper hollow conductors. The main goal of this series is to give a detailed update on the mechanism, prevention, diagnosis, and removal of flow restrictions in water-cooled generator windings.

Robert Svoboda

PPCHEM 2018, 20(5), 297–309

Corrosion and Deposits in Water-Cooled Generator Stator Windings: Part 1: Behaviour of Copper

The most common and severe problem that has arisen with generator water cooling throughout its more than 50 years of history is plugging of copper hollow conductors. A 4-step model of the occurrence of this plugging was developed to indicate the influencing parameters. The steps are oxidation of the copper surface, release of the oxidized copper, migration of the released copper, and re-deposition of the migrating copper. It is observed that these steps are influenced by water chemistry as well as by system and component design. From the operating side, adherence to a suitable water chemistry regime as well as proper lay-up practice help to avoid or mitigate flow restrictions.

Robert Svoboda and Russell Chetwynd

PPCHEM 2018, 20(6), 326–336

Corrosion and Deposits in Water-Cooled Generator Stator Windings: Part 2: Detection of Flow Restrictions

Useful methods for detecting flow restrictions in stator bar cooling channels include review of operating parameters and history vs. original design, of generator cooling water chemistry, of strainer and filter clogging history and of results from diagnostic chemical cleaning, as well as monitoring of stator water flow vs. pressure drop, individual stator bar water flow measurements, monitoring of on-line stator temperatures, visual inspections, and DC high-potential (Hipot) testing. A combination of these methods can be selected under consideration of plant specific hardware features and cost-to-benefit relation.

A proactive approach to detecting flow restrictions is recommended in order to permit advanced planning of any needed corrective actions, thus reducing the risk of

unplanned maintenance downtime, or even component failure. Managing flow restrictions at an early stage reduces the risk of severe plugging of conductors that may well prove difficult to remove later on.

Daniel M. Wells, Paul L. Frattini, Keith Fruzzetti, Susan Garcia, Joel McElrath, and Michelle Mura

PPCHEM 2018, 20(6), 338–345

The Future of Nuclear Power Plant Chemistry Control

Chemistry control in nuclear power plants continues to evolve in the types of additive chemistry and purification technologies applied, as well as in how important parameters are monitored and controlled. New chemistry technologies are being evaluated, qualified, and demonstrated throughout the industry that have the potential to fundamentally alter and significantly improve chemistry control in these plants. Many of these technologies could improve operations and maintenance, as well as economic viability.

For example, filming products (including filming amines) could significantly reduce pressurized water reactor (PWR) secondary flow-accelerated corrosion (FAC) and corrosion product transport, improving steam generator (SG) performance and reducing the need for SG chemical cleanings. The application of potassium hydroxide (KOH) to the reactor coolant system (RCS) for pH control in "Western-designed" PWRs may ultimately result in significant cost savings for the industry, both relative to the cost of the bulk chemical it replaces (compared to costly enriched lithium-7, ^{7}Li), and in the reduced risk of lithium-assisted corrosion issues of irradiated stainless steels and zirconium-based fuel cladding alloys. In boiling water reactors (BWRs) materials mitigation technologies such as online noble chemistry continue to expand throughout the industry, with utilities seeking more options – including continuous application, which would reduce the overall cost of the application. Demonstration of these technologies over the next few years will further the ability of other plants to complete their own cost-benefit analysis and start utilizing them.

Regarding chemistry monitoring in nuclear power plants, most continue to rely on manually intensive methods for both sampling and analysis. Several utilities have applied online monitoring methods for some parameters but may still struggle with maintenance of older instruments. Many utilities may have purchased older generations of technologies only to find the maintenance costs and performance did not live up to expectations. Outside of nuclear power plant applications, technologies such as online ion chromatography and inductively coupled plasma (ICP) analyses have continued to evolve and improve, and are applied widely. Moving to completely automated and higher frequency analysis of chemistry parameters may allow for reducing the total number of monitored parameters while also moving toward fully automated plant chemistry, which may eventually include automated control. This paper highlights the current development status of these new technologies and provides a vision for the overall future impacts of full utilization in nuclear power plants.

Raymond M. Post, Rajendra P. Kalakodimi, and Brad Buecker

PPCHEM 2018, 20(6), 346–352

An Evolution in Cooling Water Treatment

For over four decades, the most common water treatment program for power plant and large industrial cooling tower systems has relied on a combination of inorganic and organic phosphate (phosphonate) chemistry. The formulations were designed to minimize scale formation and provide corrosion protection, primarily through precipitation chemistry and operation at an alkaline pH. Two important factors are driving an evolution away from phosphate-based chemistry towards polymer treatment methods. One is the increasingly problematic issue of phosphorus discharge and its effects on the formation of toxic algae blooms in receiving bodies of water. The second is the growing evidence that well-formulated polymer programs are more effective than phosphate/phosphonate technology for scale prevention and corrosion protection. This article examines important aspects of this evolving chemistry, and how it can improve cooling system reliability at many plants.

Tapio Werder

PPCHEM 2018, 20(6), 354–364

Report on the PowerPlant Chemistry Forum in Delhi, India

This contribution is a report on the seventh PowerPlant Chemistry Forum (PPCF), held in Delhi, India, on November 22–23, 2018. The PPCF Delhi was organized by Waesseri GmbH, publisher of the PowerPlant Chemistry Journal, together with the International Association for the Properties of Water and Steam (IAPWS). Both SWAN Analytische Instrumente AG, Switzerland, and Forbes Marshall Pvt. Ltd., India, provided financial and organizational support by their sponsorship.

The agenda consisted of six sessions covering different aspects of water/steam cycle chemistry: cycle chemistry for fossil supercritical and subcritical units, chemistry in generator cooling water systems, cycle chemistry in nuclear plants, sampling and instrumentation as well as new technologies were the topics covered during the two days. Each session consisted of two to three presentations given by an expert in the field, followed by open floor discussions. A short summary of each presentation is given in this report.

For the first time in this series of events, a workshop on the activities of the IAPWS was included in the agenda. During this workshop the formation of a preliminary national committee of India was discussed and an initial group of interested experts formed as a result.

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PowerPlant Chemistry, January/February 2019, 21(1), 8–20

CORROSION AND DEPOSITS IN WATER-COOLED GENERATOR STATOR WINDINGS: PART 3: REMOVAL OF FLOW RESTRICTIONS

Thomas Bauer, Matthias Svoboda, and Robert Svoboda

Flow restrictions in generator stator bar hollow conductors can be removed either mechanically or chemically. Both methods have their advantages and disadvantages and in certain cases only a combination of both leads to success.

Mechanical cleaning can open up completely plugged hollow conductors at the inlet or outlet of the bars, while chemical cleaning thoroughly removes all copper oxides, also within the bars. However, as with all chemical cleaning methods, there must be access for the chemicals to the copper oxide deposits so the chemicals can dissolve and remove the plugging.

To prevent metallic deposits, it is important that the chemical cleaning be performed under oxidizing conditions. Additionally, it might also be useful to apply a post-cleaning surface treatment under certain conditions.

It is recommended to take any kind of plugging seriously and to start reacting when first signs of plugging occur. Once severe conditions have developed, this might lead to power downrates, a decrease in insulation lifetime, forced outages or in the worst case even irreversible damage to the generator.

PowerPlant Chemistry, January/February 2019, 21(1), 26–39

ELECTROCHEMICAL CORROSION POTENTIAL MONITORING IN BWRS

Yoichi Wada, Kazushige Ishida, Masahiko Tachibana, Nobuyuki Ota, and Makoto Nagase

The status of Hitachi-GE Nuclear Energy's electrochemical corrosion potential (ECP) sensor development and ECP measurement in boiling water reactors (BWRs) is reviewed. Hitachi-GE Nuclear Energy (Hitachi-GE) has been dedicated to developing and providing ECP sensors and applied ECP monitoring to various BWRs since the ECP has been an index of stress corrosion cracking (SCC). Hitachi-GE considers simultaneous use of at least 2 types of ECP sensor and employment of a guard drive circuit for the ECP measuring system to be essential. Results of ECP measurement in hydrogen water chemistry (HWC) showed that the ECPs were above 0.1 V(SHE) before HWC and decreased with an increase in the hydrogen concentration in the feedwater. Compared to the bottom region, the ECP in the primary loop recirculation system decreased at lower hydrogen dosage. Hitachi-GE recommends long-term and in-situ ECP monitoring because the ECP is affected by core management and the direct measurement of the ECP is more meaningful for SCC evaluation.

PowerPlant Chemistry, January/February 2019, 21(1), 40–41

POWERPLANT CHEMISTRY® INTERVIEW

Tapio Werder

On January 1st, 2019, the publishing house Waesseri GmbH was transformed into the new company PPCHEM AG. To introduce this chan ge to our readers, Tapio Werder, Editor in Chief of the PowerPlant Chemistry® journal, talks to Michael Rziha, Chief Key Expert for Plant Chemistry at PPCHEM AG.

PowerPlant Chemistry, January/February 2019, 21(1), 42–49

2018'S SCIENTIFIC AND TECHNICAL CONTRIBUTIONS

PowerPlant Chemistry, March/April 2019, 21(2), 62–72

CORROSION AND DEPOSITS IN WATER-COOLED GENERATOR STATOR WINDINGS: PART 4: OPERATING EXPERIENCE WITH FLOW RESTRICTIONS IN STATOR COOLING WATER SYSTEMS

Matthias Svoboda and Thomas Bauer

A common problem with water-cooled generator stator windings is plugging of the hollow conductors that act as cooling channels. The causes are sometimes difficult to identify, but some common factors can be found. Insufficient layup during outages is a common one. The importance of good monitoring and maintenance practices is highlighted throughout the discussed examples.

The stator is the main concern, because of its vulnerability to oxide deposits in the hollow conductors and the fact that if it fails, the whole power plant has to be shut down. Strainers and filters can also plug up and act as early warning devices for stator plugging. If replacing them is not an option, chemical cleaning can help, but it usually only removes the symptoms.

Proactive treatment of these problems should be a priority, as damages can go into the millions. Even when cleaning is still possible, persistent deposits can often only be removed by more invasive treatments.

PowerPlant Chemistry, March/April 2019, 21(2), 78–83

A REVIEW OF IMPORTANT WET-LIMESTONE SCRUBBING DETAILS

Brad Buecker

Coal combustion releases a number of harmful compounds that need to be removed from the flue gas before discharge to the atmosphere. One of these compounds is sulfur dioxide (SO_2). The most common process to remove SO_2 is wet-limestone flue gas desulfurization (WFGD). This article examines the fundamentals of this process and discusses modern developments to maximize scrubbing efficiency in these systems.

PowerPlant Chemistry, March/April 2019, 21(2), 90–127

IAPWS TGD9-18: AIR IN-LEAKAGE IN STEAM–WATER CYCLES

The International Association for the Properties of Water and Steam

This Technical Guidance Document considers the phenomenon of air in-leakage (AIL) in fossil, combined cycle / HRSG, and biomass plants. It covers the importance of AIL to the performance and cycle chemistry control of generating plants. The sources of AIL are delineated as well as the background science. The monitoring equipment/techniques are provided in Section 4. Controlling guidance for AIL in the most common generating plants worldwide is covered in Section 6, as well the customization aspects for other plants with varying equipment in Section 7. The document represents the accumulated experience of the IAPWS Power Cycle Chemistry (PCC) Working Group with representation from 24 countries.

PowerPlant Chemistry, March/April 2019, 21(2), 130–131

FILM FORMING SUBSTANCES (FFS) CONFERENCE, FFS2019 – HIGHLIGHTS AND PRESS RELEASE

The third FFS International Conference was held on the 19th – 21st March 2019 in Heidelberg, Germany chaired by Barry Dooley of Structural Integrity. FFS2019 was a unique conference on a narrow topic in cycle chemistry control of power plants but attracted over 70 participants from 22 countries.

PowerPlant Chemistry, May/June 2019, 21(3), 142

OUTSTANDING MEETINGS OF TWO NATIONAL IAPWS COMMITTEES – PRESS RELEASE

The International Association for the Properties of Water and Steam (IAPWS) is the world's leading body for power station chemistry. With AGL's Principal Chemist Hayden Henderson being the Chairperson of the Australian branch (AUSAPWS), AGL hosted the first ever Australian AUSAPWS workshop for power station chemists in April 2019 in Melbourne.

PowerPlant Chemistry, May/June 2019, 21(3), 146–154

ADSORPTION OF OLEYL PROPYLENEDIAMINE ON METAL SURFACES

Duygu Disci-Zayed, Julia Jasper, and Wolfgang Hater

Operation of water/steam cycles is threatened by corrosion unless proper conditioning measures are taken. As an alternative to traditional cycle chemistry, film forming amines (FFAs) are becoming increasingly important.

It is essential to understand the adsorption behavior of FFAs. This paper presents the results of an extensive study on the adsorption characteristics of FFAs on metal surfaces: stainless steel, carbon steel, copper, and aluminum alloys. Moreover, to reflect the plant conditions in a more realistic way, experiments with an iron oxide ('magnetite') layer were performed.

Adsorption trials were carried out with different film former concentrations and at different temperatures in a custom-made polytetrafluoroethylene vessel. The focus of this research was mainly on the use of oleyl propylenediamine (OLDA), one important FFA, which is included in the Technical Guidance Document issued by the International Association for the Properties of Water and Steam [1]. Nevertheless, other FFAs (homologues of OLDA) were also tested for comparison.

The adsorption isotherms were described with the Henry adsorption model due to the limited number of experiments and for the sake of simplicity. Adsorption of FFA accelerates with temperature and follows first order kinetics. Moreover, surface coverage by FFA was determined by mass balance, which is influenced by the nature of the metal and the FFA used.

For selected metals the surface coverage data of FFAs were compared to polarization resistance data obtained from electrochemical impedance spectroscopy. These data showed that the same degree of corrosion protection is achieved with lower amounts of OLDA compared to oleylamine (OLA).

The time dependence of surface coverage by OLDA showed the same tendency as the polarization resistance data on steel and aluminum.

PowerPlant Chemistry, May/June 2019, 21(3), 158–188

TRENDS IN HRSG RELIABILITY – A 10-YEAR REVIEW

Barry Dooley and Bob Anderson

By 2008 the authors had conducted assessment surveys at a small number of combined cycle/heat recovery steam generator (HRSG) plants in the areas of cycle chemistry, flow-accelerated corrosion (FAC), and thermal transients. The results clearly showed some important trends on why the major failure/damage events occurred on these plants. In the interim period the authors have extended the number of plants worldwide to 90 to allow a ten-year review of combined cycle/HRSG reliability. There has been a remarkable increase in knowledge and understanding of the main drivers of damage/failure, and in combination with the tools developed for the assessments, this paper now includes clear direction on how to address the reliability issues retroactively and how to avoid them proactively. The major cycle chemistry influenced issues are: HRSG Tube Failures due to FAC, under-deposit corrosion, deposits in high pressure (HP) evaporators, and failure in the phase-transition zone of the steam turbine. The main thermal transient aspects of thermal and corrosion fatigue relate to inappropriate/inadequate operation and maintenance of attemperators, poor drain control of superheaters and reheaters, HP drum ramp rates, and forced cooling. Another emerging issue is severe erosion of bypass pressure control valves. The paper discusses each and provides directions by which plants can avoid the issues in the future.

PowerPlant Chemistry, May/June 2019, 21(3), 192–193

EUROPEAN HRSG FORUM (EHF2019) HIGHLIGHTS AND PRESS RELEASE

A hugely successful sixth annual meeting of EHF was held on the 14th – 16th May 2019 in Athens, Greece chaired by Barry Dooley of Structural Integrity. EHF2019 attracted 76 participants from 17 countries. EHF is supported by the International Association for the Properties of Water and Steam (IAPWS) and is held in association with the Australasian Boiler and HRSG Users Group (ABHUG) and the US HRSG Forum (HF).

PPCHEM® Journal, July/August 2019, 21(4), 218–229

AN INTERLABORATORY TEST OF ANALYSIS METHODS FOR CORROSION PRODUCTS

Karsten Thomsen and Maja Skou Jensen

This report describes the outcome of an interlaboratory comparison of analysis methods for iron among a group of laboratories in the power and heat industry. The samples sent out to the laboratories were real samples of feedwater and district heating water that had an inherent inhomogeneity due to the particulate nature of the corrosion products. The analysis methods compared were the standard methods based on spectrophotometry and inductively coupled plasma spectroscopy as well as analysis of filtered material on a 0.45 µm membrane filter. The filtered material from a 1 L sample was digested and dissolved to a 50 mL final sample volume, which gave a concentration factor of 20, enhancing the sensitivity of the method relative to the others. The purpose of the interlaboratory comparison was twofold: to qualify the filter method to be recommended for corrosion product analysis by the International Association for the Properties of Water and Steam in a Technical Guidance Document, and to give the laboratories an opportunity to test their methods on realistic samples against a group of other professional laboratories. For accredited laboratories, proficiency testing like this is a well-known and prescribed means of quality control and often supplements the internal quality control nicely.

Although measures had been taken to minimize the heterogeneity of the samples, the district heating samples turned out to be not even close to homogeneous. By assuming a log-normal distribution and independent results of the double determinations from each laboratory, the inhomogeneity of the samples could be handled, and the performance of the laboratories compared. The comparison shows that the reproducibility of the filter method matches the reference methods, and that both feedwater and district heating water samples fit nicely to the log-normal distribution. The results indicate that the filter method is reproducible when transferred from one laboratory to another.

PPCHEM® Journal, July/August 2019, 21(4), 232–241

THIRTY YEARS OF EXPERIENCE WITH FILM-FORMING AMINES AT A NORWEGIAN FERTILIZER PRODUCTION SITE

Roy van Lier, André de Smet, Lene-Marie Olsen, Matej Halasa, and Trond Arve Fjærem

In Glomfjord, Norway, above the Arctic Circle, Yara produces some 400 000 t (100 % equivalent) per year of nitric acid in two older units. All of the acid is used in downstream plants on site to produce a range of fertilizer grades.

The Glomfjord site has been of great importance both to the pioneering of ammonia and nitric acid synthesis technology and to the history of Norsk Hydro, which eventually divested its fertilizer activities as Yara International. It is also a location with some of the longest operational experience with film-forming amines for industrial steam system treatment, certainly in relation to nitric acid production.

The present paper first provides background information on the Glomfjord site. Steam generation in nitric acid plants in general is then succinctly explained. Yara's operational experience is subsequently elaborated in the context of the specificities of the Glomfjord application, and of filming amine and water chemistry in the Nordic countries. This includes analysis of a possibly unique case of fouling and damage that illustrates the importance of adequate boiler feedwater quality, regardless of the chemical treatment program in place.

PPCHEM® Journal, July/August 2019, 21(4), 242–249

CRITICAL CHEMICAL ISSUES DURING PRE-COMMISSIONING

Andrés Rodríguez Pérez

Most cases of severe corrosion and consequent failure in the commercial operation of water-steam cycle and boiler systems are initiated during the first stages of a project, frequently because of a lack of preservation, an absence of regular inspections, inadequate water quality for pressure tests and a lack of understanding of corrosion processes by many of the parties involved.

Selecting an appropriate pre-commissioning program control will mitigate the risk of corrosion during the progression of the project, and subsequently, minimize potential failures upon commissioning.

Putting together an effective pre-commissioning strategy requires a great deal of coordination among different departments, the integration of practical lessons learned and great common effort throughout the project. Even engineers involved in the first stages need to retain responsibility for keeping a long-term vision for the success of the final results.

PPCHEM® Journal, September/October 2019, 21(5), 270–285

COMPARISON OF TWO CORROSION PRODUCT SAMPLING METHODS AT ERARING POWER STATION

Mark Wyburn

Cycle chemical conditions have been modified several times over the last 20 plus years at Eraring Power Station (EPS) in Australia. The mixed metallurgy of the condensate system had proved difficult to manage with respect to minimising flow-accelerated corrosion (FAC) and copper transportation.

A project to convert all units from all-volatile treatment under reducing conditions (AVT(R)) to all-volatile treatment under oxidising conditions (AVT(O)) has been underway since 2016. Units 1, 2 and 4 have now had their 35-year-old brass-tubed low-pressure (LP) heaters replaced with stainless-steel-tubed heat exchangers, and Unit 3 will be converted in late 2019.

After each AVT(O) conversion, intensive corrosion product sampling and analysis has been undertaken over several months to measure the success of the project in reducing iron transportation. This has involved simultaneously using integrated sampling and an on-line voltammetric analyser, which was previously trialled in 2015. This analysis has revealed some interesting trends during the chemistry change.

This paper compares the results from integrated sampling and the voltammetric analyser and discusses the relative merits of each process under the constraints of major power plant operations in a competitive market.

PPCHEM® Journal, September/October 2019, 21(5), 290–292

INTERNATIONAL ASSOCIATION FOR THE PROPERTIES OF WATER AND STEAM (IAPWS)2019 EXECUTIVE COMMITTEE AND WORKING GROUP MEETINGS

PRESS RELEASE

Between September 29th – October 4th, 2019, 92 scientists, engineers and guests representing 16 countries descended on the Banff Centre for Arts and Creativity in Banff, Alberta, Canada for the annual meeting of the IAPWS Executive Committee and Working Groups. This continues a series that began in 1929 in London, UK with the purpose to connect researchers and scientists with the engineers who use their work providing the researchers with guidance on topical problems within industry and

providing the engineers with the latest research results. Areas of application include power cycle chemistry, high temperature aqueous technologies applicable to steam cycles and steam injection, the use of high temperature water and supercritical steam in chemical and metallurgical processes, supercritical synthesis of new materials and destruction of toxic wastes, hydrothermal geochemistry, hydrometallurgy, oceanography and global climate modelling, power cycles with CO_2 capture and storage systems and combined heat and power systems.

PPCHEM® Journal, September/October 2019, 21(5), 292–297

KNOWLEDGE TRANSFER AND SUCCESSION PLANNING FOR POWER PLANT CHEMISTRY

Bertil C. Valenkamph, Paul E. Schrock, Brian S. Snyder, and K. Anthony Selby

Electric utilities are faced with a shortage of skilled personnel in the coming years due to normal retirements, early retirements, and plant closings. This is true in chemistry departments as well as other departments.

There are many aspects to succession planning to successfully fill the upcoming vacancies. For chemistry departments one important tool is to develop comprehensive written plans for chemical control of the systems impacted by chemistry. These plans can be termed control plans or strategic plans. The chemistry plans should be developed for several individual plant systems, including boiler cycle chemistry, open cooling water, closed cooling water, makeup treatment systems, glycol systems, and wastewater treatment systems, among others.

Another very important tool is the comprehensive chemistry data acquisition system – a collection of supervisory control and data acquisition (SCADA) nodes at each generating station, accompanied by a combined web-based management system overview. These systems are vital in monitoring all the process chemistry systems explained in the aforementioned control/strategic plans.

This paper describes the development and content of control/strategic plans for chemistry control in these various systems as well as several other succession planning items.

PPCHEM® Journal, September/October 2019, 21(5), 302–359

IAPWS TGD11-19: APPLICATION OF FILM FORMING SUBSTANCES IN INDUSTRIAL STEAM GENERATORS

The International Association for the Properties of Water and Steam

This Technical Guidance Document addresses the use of film forming substances in the water/steam cycles of industrial steam generating plants.

In order to control corrosion throughout the water/steam circuits of industrial steam generating plants, it is essential for the operator of the plant to choose and optimize a chemical treatment scheme that is customized to that plant. IAPWS has provided guidance on the use of volatile treatments as well as for phosphate and caustic treatments; this document addresses the use and application for the range of chemicals referred to as film forming substances (FFS). As well as providing background information on FFS, the document includes guidance in Section 8 for determining if a FFS should be applied, the tests required before application, the locations for the addition, the optimum dosage level, and tests to determine the benefits of applying FFS. It is emphasized that this is an IAPWS guidance document and that, depending on local plant requirements, the application of FFS will need to be customized (Section 9) for each industrial plant depending on the actual conditions of operation, the equipment and materials installed, the condenser cooling media, and applicable regulations.

PPCHEM® Journal, November/December 2019, 21(6), 374–395

PRACTICAL OBSERVATIONS AND INTERPRETATION OF OXIDE GROWTH AND EXFOLIATION IN STEAM

Barry Dooley and Ian Wright

Over the last 40 years oxide growth and exfoliation (OGE) in superheater and reheater tubing have been responsible for a number of power plant problems which seriously have affected reliability. In the same time period, the authors have collected a data base of scale morphologies that has been used to describe in detail the progression of oxide scale development to the point where failure can occur. The concomitant evolution of knowledge of the factors that determine the mode of scale growth and failure in steam has provided the foundation for defining the specific stages in that progression, understanding differences among ferritic and austenitic alloys, and for categorizing the influence of plant operating characteristics. In particular, while tube/steam temperature and the maximum temperature drop at plant shutdown are major variables, the specific cycle chemistry used for the plant feedwater has very little influence. Key stages in the progression of scale growth to the point of failure are identified as OGE indices that are specific for ferritic and austenitic steels. These indices are intended to be used proactively to determine the current condition of a superheater or reheater on the path to exfoliation and possible plant damage. Also, by analyzing samples of exfoliant or oxide deposits responsible for damage, the origin of the oxide, and thus a possible superheater or reheater problem, can be identified retroactively

PPCHEM® Journal, November/December 2019, 21(6), 396–397

ABHUG 2019 HIGHLIGHTS AND PRESS RELEASE

Bertil C. Valenkamph, Paul E. Schrock, Brian S. Snyder, and K. Anthony Selby

The first annual meeting of ABHUG held on the 30th October to 1st November 2019 in Brisbane, Australia was chaired by Barry Dooley of Structural Integrity Associates. This first ABHUG conference followed 11 annual meetings of AHUG (Australasian HRSG Users Group) and included conventional fossil plant technology and issues closely related to those in HRSGs. ABHUG 2019 attracted 75 participants from Australia, Japan, New Zealand, Thailand, UK, and USA. About 50% of the participants were Users, which is the highest of the other HRSG forums worldwide.

PPCHEM® Journal, November/December 2019, 21(6), 400–439

IAPWS TGD10-19: CHEMISTRY MANAGEMENT IN GENERATOR WATER COOLING DURING OPERATION AND SHUTDOWN

The International Association for the Properties of Water and Steam

This Technical Guidance Document applies to all generators with water-cooled windings. From the operating side, adherence to a suitable water chemistry regimen as well as proper layup practices help to avoid or mitigate flow restrictions. Other influencing factors are design and materials. It is emphasized that this is an IAPWS Technical Guidance Document and that, depending on local requirements, the normal or target values will need to be customized for each case, depending on the actual conditions of operation and maintenance.

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PPCHEM® Journal, January/February 2020, 22(1), 10–17

DEPENDENCE OF THE CORROSIVE ENVIRONMENT IN BWRS ON OPERATING CONDITIONS

Yoichi Wada, Kazushige Ishida, Nobuyuki Ota, and Makoto Nagase

The effects of core management in a boiling water reactor (BWR) on radiolytic oxygen and hydrogen peroxide concentrations in the reactor water have been studied based on a radiolysis model. An increase in core flow promoted radiolysis of water in the core region since the amount of water present in the core region became larger and mass transfer from water to steam slowed down. Also, a decrease in core peripheral power at the end of the cycle reduced the effectiveness of hydrogen water chemistry (HWC) applied to reduce radiolytic oxygen and hydrogen peroxide and the subsequent electrochemical corrosion potential for mitigation of stress corrosion cracking since the downcomer dose rate became weaker with operation. These caused an increase in the sum of the oxygen and hydrogen peroxide concentrations at the same hydrogen injection rates and the effectiveness of HWC decreased. The effectiveness of noble metal chemical addition was not affected by changes in operating conditions at a $0.5\,mg \cdot kg^{-1}$ hydrogen injection rate.

PPCHEM® Journal, January/February 2020, 22(1), 20–29

WATER CHEMISTRY MANAGEMENT FOR THE PRIMARY CIRCUIT OF THE FIRST EPR UNIT DURING HOT FUNCTIONAL TESTING

Zhu Wang, Zhi-Wei Ge, and Zi-Tao Liu

The paper describes in detail the water chemistry control during the hot functional testing (HFT) of the first European pressurized reactor (EPR) unit worldwide, and focuses on the water chemistry control during passivation treatment of the component surfaces in the primary circuit with hydrogen injection, higher $pH_{300°C}$ and impurity control. Two identical surveillance coupons made of Inconel 690 TT steam generator (SG) tube samples were placed in the reactor pressure vessel (RPV) to evaluate the final passivation results. Water chemistry data and metallographic analysis results show that an excellent protective film was formed on the surface of the tubes, which reduces the corrosion rate of materials and the release of corrosion products, thereby also reducing radiation source terms during commercial operation of the unit. In addition, a brief comparison of the passivation film and passivation process between two types of the 3rd generation pressurized water reactors (PWRs), especially the hydrogen injection and zinc injection technologies, was made. The benefit of the passivation process during HFT for the dose rate is preliminary, and the dose rate reduction effectiveness also depends on the applied water chemistry control methods during future power operation of the unit.

PPCHEM® Journal, March/April 2020, 22(2), 64–70

CORROSION ISSUES CAUSED BY CHANGES IN PIPE CROSS-SECTIONS

Andrés Rodríguez Pérez

Among the most detrimental corrosion phenomena observed in the power industry are those related to a sudden expansion of a fluid beyond the saturation point. The effects of such types of corrosion may be particularly aggressive due to a combination of physical factors and a variety of chemical mechanisms that could potentially be involved. Based on data collected from over one hundred inspections carried out in the power industry and refineries, this publication is aimed at building a stronger understanding of the issues to allow plant operators to predict areas of vulnerability, mitigate the risk of potential failures, and specify a correct chemical treatment program to operate their plant at its maximum level of performance and reliability.

PPCHEM® Journal, March/April 2020, 22(2), 72–88

FINAL VERDICT ON VAPOR INGRESS OF CHLORINATED COMPOUNDS VIA WEAK TUBE/TUBESHEET JOINTS

Emmanuel K. Quagraine, Trever McNabb, Suzanne McNabb, Sheldon McNabb, Taneal Weiss, Gillian Bailey, Ashley Ponak, Brenna Janzen, and Janet Meyers

This paper concludes a series of publications on investigations at Shand Power Station (SaskPower) to understand selective chloride cycling in this plant. With naval brass tubesheet, dezincification was implicated as the corrosion mechanism at naval brass tube-to-tubesheet joints, which created vapor pathways for recirculating cooling water (RCW) chlorine compounds into the water/steam circuit, eventually forming chlorides. Replacing the tubesheet with Duplex 2507 SS, the expectation was that the chloride cycling would end. Yet it persisted. The paper provides evidence that even with new metallurgies, vapor ingress via weak tube-to-tubesheet joints has mainly been responsible for the persisting chloride cycling. Organochlorine compounds leaching from the tubesheet/shell interface gasket have also been shown to potentially contribute to the chloride cycling, to a major extent earlier on, but becoming less significant over time. Plugging of the leaking tubes at tube-to-tubesheet joints reduced the average daily increases in boiler chloride from $28.4\,\mu g \cdot L^{-1}$ to $2.7\,\mu g \cdot L^{-1}$, supporting the notion that the RCW was the principal source of the chloride contamination.

PPCHEM® Journal, May/June 2020, 22(3), 104–109

TREATING MAKE-UP WATER AND CONDENSATE BY REVERSE OSMOSIS IN AN LP VINYL RECORDS PRESSING PLANT

Pavel Hübner

At the Czech company GZ Media a.s., which produces vinyl records, the vinyl presses are heated by steam and after pressing, the steam is rinsed from the press by cooling water. The condensate therefore contains a high proportion of cooling water.

In the original system, the losses of steam and cooling water were replaced by filtrated and softened raw water. The polluted condensate was also treated by filtration and softening. The water used as make-up, which was originally considered drinking water, has been replaced for economic reasons by surface water with high salinity and alkalinity. Due to high operational costs and other considerations the original design was replaced with a new one in 2019.

The new system treats the mixture of raw water and cooled condensate by on-line coagulation followed by reverse osmosis. The hot condensate is cooled by heat exchange, which transfers the heat to the permeate as feedwater.

The new system exhibits very low boiler blow-down, minimal consumption of chemicals and low operator attendance.

PPCHEM® Journal, May/June 2020, 22(3), 112–116

CALCULATIONS TO MANAGE PHOSPHATE AND CAUSTIC TREATMENT

Randy C. Turner

Phosphate and/or caustic (NaOH) treatment boiler water treatment is often employed to reduce the risk of corrosion.

This paper describes empirical calculations for proper control of phosphate and caustic treatment which could be incorporated into an Excel spreadsheet which includes several calculations, of which the most important are:

1. Boiler water ammonia corrected pH
2. Sodium to phosphate molar ratio
3. Free sodium hydroxide concentration
4. Amount of phosphate and/or caustic to dose for a specific concentration at the current operating pressure

This can also be used to calculate how much caustic must be added to an AVT treated boiler to achieve a desired pH-value.

PPCHEM® Journal, May/June 2020, 22(3), 118–129

THE IMPACT OF LOW-LOAD OPERATION ON POWER PLANT CHEMISTRY

Frank Udo Leidich

Nowadays conventional power plants are more challenged in regard to load flexibility and especially frequent (very) low-load operation. While the so-called "dark doldrums" must be managed without de-stabilizing the grid, a bright sunny and windy day requires almost no conventional power generation. This kind of operation not only stresses the plant components mechanically and thermally, leading to accelerated aging of the plant, but the physico-chemical operation also becomes more challenging. This paper highlights the most important aspects of the impact of low-load operation on the chemical operation of a power plant. It is shown that it pays to operate the unit with water and steam that is as clean as possible.

PPCHEM® Journal, July/August 2020, 22(4), 142–150

SAMPLING POINTS AND PARAMETERS FOR LOW-PRESSURE INDUSTRIAL STEAM GENERATORS

Brad Buecker and Ken Kuruc

Although thousands of low-pressure steam generators exist at industrial plants around the globe, the chemistry of such units has not received the same attention as that of high-pressure units. The conditions in these steam generators are typically not as harsh as in utility units, yet water/steam chemistry control is still very important for the plants' steam/condensate systems. This article discusses many of the most important sampling points and parameters for industrial steam generators, and it illustrates the benefits of proper chemistry control to maintaining equipment reliability and availability.

PPCHEM® Journal, July/August 2020, 22(4), 152–157

MODELLING OF MECHANICAL OXYGEN REMOVAL IN A POWER PLANT DEAERATOR

Daniel Zinemanas

Oxygen removal is an integral part of the water/steam cycle chemical treatment in power plants and is generally performed in the deaerator. Understanding of this process, particularly during transient conditions, is important to analyze the plant data, and for this goal modelling of this process can be helpful. It is thus the main motivation of this paper to develop a simple workable theoretical model of the mechanical oxygen removal process in a power plant deaerator. Results of the model are compared to power plant operational data and show a very good match between the calculated and the measured data. Thus, the model can be useful in understanding the deaerator's behavior and performance as well as for design or training.

PPCHEM® Journal, July/August 2020, 22(4), 160–169

A PRACTICAL VIEW ON THE DISSOLUTION OF AIR IN DEMINERALIZED WATER

Robert Svoboda

The equilibrium of the components of air with water can be calculated by means of Henry's law and the ionization equilibria. This article gives guidance for such calculations and covers conditions up to 100 °C. At 25 °C and 1013 mbar atmospheric pressure, the equilibrium for oxygen in water is 8.4 $mg \cdot kg^{-1}$. With 410 ppm CO_2 in air, its mass fraction in water is 694 $\mu g \cdot kg^{-1}$ CO_2, where 595 $\mu g \cdot kg^{-1}$ are present as dissolved gas and 99 $\mu g \cdot kg^{-1}$ are ionized to HCO_3^-. The result is a slightly acidic water with pH = 5.65 and 0.89 $\mu S \cdot cm^{-1}$ conductivity. In generator cooling water systems with neutral water treatment, this will cause an increase in copper release. With alkaline water treatment, the contact with untreated air can lead to the deterioration of alkaline conditions.

PPCHEM® Journal, September/October 2020, 22(5), 182–194

FILM FORMING CORROSION INHIBITOR WITH IMPROVED HANDLING, FEEDING, AND CORROSION CONTROL PROPERTIES FOR STEAM GENERATORS

Mahesh Budhathoki, Donald Meskers Jr., Claudia Pierce, and Gregory Robinson

Film forming amine (FFA) products containing octadecylamine (ODA) or oleyl propylenediamine (OLDA) are known to provide excellent corrosion protection to the alloys used in the steam-water cycle of power plants. However, product formulations based on these filming amines exhibit poor water solubility, which often hinders successful application due to formulation stability, feeding, and handling. In this work, the water solubility of an OLDA-based FFA product is significantly improved with the addition of a co-surfactant and its efficacy as a corrosion inhibitor in steam generators is evaluated. Research boiler experiments indicate that the vapor-liquid distribution ratio of OLDA decreases by enhancing its water solubility. Also, the conductivity after cation exchange (CACE) measured in steam suggests that under normal boiler operation conditions, unlike neutralizing amines or co-solvents, the added co-surfactant does not contribute to the CACE in steam. Furthermore, electrochemical and corrosion testing indicates that the water-soluble FFA product can effectively inhibit corrosion, which is attributed to its ability to form a hydrophobic film on metal surfaces, as suggested by the contact angle measurements.

PPCHEM® Journal, September/October 2020, 22(5), 196–203

TESTING THE SUITABILITY OF THE AMI CACE MONITOR FOR THE WATER-STEAM CYCLE AT LIPPENDORF POWER PLANT

Karla Georgi-Kruggel

In the period from January 06, 2020, to June 30, 2020, an analyzer for the automatic and continuous determination of conductivity before and after a cation exchanger with electro-deionization was tested at the Lippendorf Power Plant of Lausitz Energie Kraftwerke AG, Germany.

This report describes the setup and outcome of the trial. In summary, the proof of suitability of the analyzer for the monitoring of the water-steam cycle and the control of the conditioning agent quantities was positively demonstrated for all tested measuring points

PPCHEM® Journal, September/October 2020, 22(5), 204–213

COMPARATIVE STUDY ON THE ION EXCHANGE REMOVAL OF GADOLINIUM NITRATE UNDER THE CONDITIONS OF THE MODERATOR SYSTEM OF A NUCLEAR REACTOR USING STYRENE- AND ACRYLIC-ACID-BASED MACROPOROUS WEAK BASE ANION

A. L. Rufus, Padma S. Kumar, C. S. Sanjana, and S. Velmurugan

The fission reaction in a nuclear reactor is regulated by adding "neutron poison" to the system. Gadolinium has a high neutron absorption cross section and hence is used for this purpose in the form of aqueous solution of gadolinium nitrate. After its intended use, the neutron poison is removed from the system using mixed-bed (MB) ion exchange resin columns. A comparative study between the styrene- and acrylic-acid-based macroporous weak base anion (MWBA) resins in the MB column was carried out. Based on the parameters evaluated, which include (i) extent of utilization of the ion exchange capacity, (ii) precipitation of gadolinium in the ion exchange column, (iii) pressure drop across the column and (iv) radiation stability, the use of acrylic-acid-based resin in the MB ion exchange column was found to be good. The ion exchange capacity for acrylic-acid-based MWBA resin was higher (2.6 mEq·mL^{-1} of resin as against 2.0 mEq·mL^{-1} for styrene-based MWBA resin), 65% utilization capacity as against 50% for styrene-based MWBA resin, less precipitation of gadolinium (0.001% as against 0.004%), a favorable pressure drop and better retention of ion exchange capacity on irradiation.

PPCHEM® Journal, November/December 2020, 22(6), 230–250

CORROSION PRODUCT MONITORING – KEY PARAMETERS TO ACHIEVE HIGH ACCURACY AND RELIABLE ANALYSIS

Niken Wijaya

Efforts have been made at AGL's Liddell Power Station, Australia, to determine the best corrosion product monitoring practices in order to establish baseline data that are reliable and accurate. This effort is an outcome of the decision made to apply a film forming product (FFP) at Liddell Power Station, with the goal of minimising corrosion product transport from the boiler feed system to the boiler on all four units until its scheduled closure in 2022. Despite guidelines and studies done on this subject, there are still many knowledge gaps that need to be addressed. This paper aims to evaluate the accuracy of onsite ferrozine and porphyrin analyses for iron and copper analysis and how they compare to external analyses by inductively coupled plasma mass spectroscopy with an octopole reaction cell. This paper also investigates the influence of several key parameters on corrosion product monitoring

including the use of an integrated corrosion product sampler, the use of smaller pore filter paper, the forms of corrosion products in the system, and the use of cation paper, which are critical in establishing the best practices for corrosion product monitoring. Liddell's baseline data on corrosion product were used to evaluate the efficiency of the current cycle chemistry program and to verify the need for FFP dosing for corrosion protection.

PPCHEM® Journal, November/December 2020, 22(6), 252–259

THE CHALLENGES OF INDUSTRIAL BOILER WATER TREATMENT

Brad Buecker and Tim Hughes

High-pressure steam generators for power production require high-purity makeup and feedwater and controlled boiler water chemistry to minimize corrosion and scale formation in the boilers, superheater/reheater circuits, and turbines. Numerous articles in the PPCHEM® journal over the last two decades have outlined these chemistries and their evolution.

However, while many heavy industries have high-pressure steam generators for co-generation needs, these plants and many other smaller facilities also have low-pressure boilers that produce process steam. The lower heat fluxes and pressures in these steam generators somewhat alleviate the stringent treatment requirements necessary for high-pressure units but offer more complexity in the choice of optimum treatment methods.

This article provides an overview of modern methods for protecting lower-pressure steam generators from factors that typically do not plague their high-pressure counterparts.

PPCHEM® Journal, November/December 2020, 22(6), 262–273

HEAT TRANSFER ADD-ON TO THE UNB-CNER CANDU-6 PHT SYSTEM MATERIAL TRANSPORT MODEL

Olga Y. Palazhchenko, William G. Cook, Alex L. Martin, and Dean C. Taylor

Reduced heat transfer in steam generators has safety consequences such as the risk of fuel dryout due to increasing reactor inlet header temperature (RIHT). To maintain the RIHT within the safe operating envelope, it is necessary to model factors that contribute to its rise, including chemical processes such as corrosion product transport and deposition and mechanical effects such as component degradation.

In the recent add-on to the UNB-CNER PHT Corrosion Product and Activity Transport Code, a combination of heat transfer mechanisms, updated thermodynamic equations for the properties D_2O and H_2O, station data, and the existing model capability of predicting primary-side material transport are used to create and optimize a one-dimensional simulation of a typical CANDU-6 boiler. Data from Point Lepreau Nuclear Generating Station is used to benchmark various model parameters, allowing for predictive simulations, where RIHT trends can be forecasted into the future using desired outage and boiler cleaning schedules.

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PPCHEM® Journal, January/February 2021, 23(1), 4–16

TECHNOECONOMIC BENEFITS OF FILM-FORMING AMINE PRODUCTS APPLIED TO STEAM SURFACE CONDENSERS

Sean H. Hoenig, Mahesh Budhathoki, Gregory Robinson, Claudia Pierce, Donald Meskers, Michael C. Ellis, and Richard W. Bonner III

In a conventional Rankine cycle, the majority of power plants employ surface condensers that use pumped cooling water to reject heat from the cycle. In such cases, heat rejection occurs in a shell and tube heat exchanger by filmwise condensation of low-pressure steam on stainless steel, titanium, brass, or copper-nickel tubing. To improve the thermal performance of steam surface condensers, a replenishable film-forming substance (FFS) can be applied to the condenser tubing to promote efficient dropwise condensation. Conventionally, film-forming amine product (FFAP) coatings protect boiler surfaces from oxidative corrosion, which substantially reduces the operation and maintenance costs. To quantify the technical and economic benefits of FFAP coatings applied to condenser tubing due to the promotion of dropwise condensation, a thermal resistance network model was established. Using a representative steam surface condenser, the improvements in thermal performance (overall heat transfer coefficient) and process parameters (net plant efficiency, cooling water flowrate, and turbine backpressure) were determined due to the enhancement in the condensation heat transfer coefficient. Experimentally measured condensation heat transfer coefficients for common condenser materials were compared with the modeling results and were found to be within attainable bounds. Finally, the trend in total heat exchanger cost reduction is generalized to understand the trade-off between reduced surface area for heat rejection and increase in coating application costs for a replenishable coating system.

PPCHEM® Journal, January/February 2021, 23(1), 20–30

THE ROLE OF HUMAN PERFORMANCE SCIENCE IN CYCLE CHEMISTRY IMPROVEMENT – IS THIS THE MISSING LINK?

Brad Burns and Doug Hubbard

On most units assessed by the Electric Power Research Institute (EPRI) across the world, cycle chemistry is well controlled and good results are obtained a majority of the time. Fossil and combined cycle power plants on a global scale continue to boast higher cycle chemistry benchmarking scores, installation of new instrumentation and alarming, and management support for cycle chemistry. The exception, however, continues to be major cycle chemistry excursion events that happen infrequently, yet with great consequences.

Often, when an unmitigated major cycle chemistry upset event occurs, root cause investigations pin the event on inadequate skills or knowledge (of individuals). It is therefore believed that additional training and/or disciplinary corrective action solves the root cause of the event and will prevent poor operator response to out-of-spec chemistry from recurring.

But does this approach produce desired results? This article examines that question and offers an approach with the potential to lead your organization toward a more critical review of systems and processes where countermeasures and defenses are checked and tested to determine efficacy.

Incorporating the science of human and organizational performance into a cycle chemistry program may well be the "missing link" to obtaining true cycle water chemistry improvement by preventing chemistry-influenced damage that occurs when plant personnel don't properly respond to acute and chronic cycle chemistry upsets.

PPCHEM® Journal, January/February 2021, 23(1), 34–37

ISSUES RELATED TO THE MEASUREMENT OF THE PH-VALUE IN PURE AND ULTRAPURE WATER

Michael Rziha

In all my years working in the area of power plant chemistry, I have been repeatedly confronted with either specifications or operators requesting the measurement of the pH-value either in pure water or even in ultrapure water. This often results in useless, time consuming discussions when those "measurements" are made, where some "experts" simply compare those results versus "specifications" and request that this pH-value must be 7±0.5, or something similar. When asked why this is specified for an ultrapure water (e.g. outlet mixed bed filter) with a conductivity of <0.1 $\mu S \cdot cm^{-1}$, the most classic answer is we don't know, but it is specified, hence it must be fulfilled. Consequently, those specifications and the hopeless and wrong trial to measure it will lead in many projects to costly delays and consumption of precious working hours of many people involved.

Every chemist with a sound chemical education and understanding will of course immediately understand that this measurement is not only useless (I would even say nonsense), but also unnecessary.

In this brief article, the background and scientific, chemical facts will be explained for why this measurement is dispensable.

PPCHEM® Journal, March/April 2021, 23(2), 56–72

NGATI TUWHARETOA GEOTHERMAL ASSETS LTD REBOILER PLANT WATER/STEAM CHEMISTRY IMPROVEMENTS TO RESOLVE ONGOING CORROSION ISSUES AND PREVENT FUTURE TUBE FAILURES

David Addison, Nik Vandervegte, and Nellie J. Olsen

Since its commissioning in 2010, the Ngati Tuwharetoa Geothermal Assets Ltd Kawerau reboiler plant has suffered from major corrosion and plant failure issues. Corrosion-related failures which occurred due to water/steam chemistry issues and interactions with plant materials have led to premature complete replacement of the tube bundles.

In 2018 a major root cause analysis was undertaken into the failures that included a detailed chemical and metallurgical investigation and successfully identified the failure mechanisms. A number of simple chemical treatment changes, including hydrogen sulfide neutralisation, pH correction and the application of corrosion inhibiting film forming substances, were carried out to successfully mitigate ongoing corrosion of the plant and to significantly extend asset life.

PPCHEM® Journal, March/April 2021, 23(2), 74–81

A NOVEL COMBINATION OF CMIT/MIT WITH A NEW NON-BIOCIDE DISPERSANT IN COOLING TOWER BIOFILM CONTROL

Henk A. Jenner

Microbial biofilm communities are a significant problem in recirculating cooling water systems resulting in reduced heat transfer efficiency, and the risk of microbial influenced corrosion (MIC) and Legionella infection of operators. Most biocides are generally only effective in the control of microorganisms when in the water phase. A new dispersant was tested that is able to remove biofilms from their substrate, releasing the biofilm community into the water phase. This study investigated how the effectiveness of (chloro)methylisothiazolinone/methylisothiazolinone (CMIT/MIT) (non-oxidizing biocide) in a heavily fouled scale cooling tower model with condenser tubes could be improved by the new dispersant. Dosing tests with CMIT/MIT separately and combined with the new dispersant were performed with different CMIT/MIT concentrations. Microbial activity in both water samples and biofilm samples was measured by the analysis of adenosine triphosphate (ATP). Additionally, the biofilm mass in the transparent condenser tubes was visually inspected by photos. The new dispersant was shown to be effective in loosening the biofilm and the biocidal efficacy of CMIT/MIT was greatly increased due to this combination.

PPCHEM® Journal, March/April 2021, 23(2), 86–91

ONLINE ANALYSIS OF FILM FORMING AMINES

Harold Stansfield

Waltron has developed an online colorimeter for online analysis of film forming amines (FFA). The design basis and development process are discussed. Data from beta testing and two working case studies are presented. The analyzer can monitor FFA-based products in a working range of 0–1000 $\mu g \cdot L^{-1}$, with an accuracy of ± 2 % of full scale or ± 5 $\mu g \cdot L^{-1}$, with a lower detection limit of <5 $\mu g \cdot L^{-1}$ as FFA.

PPCHEM® Journal, March/April 2021, 23(2), 92–93

IAPWS FOURTH INTERNATIONAL CONFERENCE ON FILM FORMING SUBSTANCES (FFS2021) HIGHLIGHTS AND PRESS RELEASE

Barry Dooley

The IAPWS Fourth International Conference on Film Forming Substances (FFS2021) was held on the 23rd and 25th March 2021 as a virtual event chaired by Barry Dooley of Structural Integrity Associates. FFS2021 was a unique conference on a narrow topic in cycle chemistry control of power plants and steam generating facilities. In 2021 the conference attracted a record number of 130 participants from 28 countries which included 41 plant operators/users and 27 people from the Film Forming Substances chemical suppliers.

The FFS conferences are developed and supported by the International Association for the Properties of Water and Steam (IAPWS), and the FFS2021 was organized by PPCHEM AG, publisher of the PPCHEM® Journal. Three sponsors supported FFS2021: Trace Analysis, Fineamin Swiss Water-Treatment Chemicals and Swan Analytical Instruments.

PPCHEM® Journal, May/June 2021, 23(3), 108–119

AVOIDANCE OF COMMON MISTAKES DURING FAILURE ANALYSES AND MISINTERPRETATION OF LAB RESULTS – PART 1: SAMPLING

Frank Udo Leidich

For a proper failure analysis or root cause analysis (RCA) a great deal of data and evidence-based information is needed. Within this context, various types of samples from different locations need to be taken for chemical and/or metallurgical examination. Therefore, proper and correct sampling, without alteration of the composition or contamination of the samples, is of utmost importance. Unfortunately, this is often not practiced correctly and so the risk of incorrect conclusions is high. This article is intended to help personnel obtain these samples in a proper manner and avoid common and repeated mistakes.

PPCHEM® Journal, May/June 2021, 23(3), 122–131

UPDATE ON PREDICTING RIHT USING THE UNB-CNER CANDU-6 PHT SYSTEM MODEL

Olga Y. Palazhchenko, William G. Cook, Alex L. Martin, and Jennifer Lennox

Reduced heat transfer in CANDU steam generators has safety consequences such as lower margins to fuel dryout due to higher reactor inlet header temperature (RIHT). To identify methods to maintain the RIHT within operational margins, it is necessary to model the effect of thermal degradation mechanisms on boiler heat transfer.

A comprehensive steam generator heat transfer and fouling add-on has been developed at the University of New Brunswick, Canada, and previously benchmarked using historic data from Point Lepreau Nuclear Generation Station. The one-dimensional, steady-state heat transfer code mechanistically predicts the effect of primary-side fouling, and semi-empirically models the effects of divider plate leakage and secondary-side fouling. This paper presents the most recent predictive modelling, where simulations of post-refurbishment operation (2012–2042) were conducted based on the benchmarked mechanisms. The predictive simulations inform the timeline for mitigating strategies such as a primary-side clean during the plant's operating lifetime.

PPCHEM® Journal, May/June 2021, 23(3), 132–133

IAPWS SEVENTH MEETING OF THE EUROPEAN HRSG FORUM (EHF2021) HIGHLIGHTS AND PRESS RELEASE

Barry Dooley and Bob Anderson

The seventh annual IAPWS European HRSG Forum was held on the 18th and 20th May 2021 as a virtual event. It was chaired by Barry Dooley of Structural Integrity and Bob Anderson of Competitive Power Resources. EHF2021 attracted 90 participants from 17 countries and included 55 users.

EHF is supported by the International Association for the Properties of Water and Steam (IAPWS) and is held in association with the Australasian Boiler and HRSG Users Group (ABHUG) and the US HRSG Forum (HF). The 2021 EHF had two sponsors: Trace Analysis and Swan Analytical Instruments. The conference was organized by PPCHEM AG.

PPCHEM® Journal, May/June 2021, 23(3), 134–142

ATP TESTING – A REAL TIME MONITORING OF MICROBIOLOGICAL GROWTH IN THE COOLING WATER SYSTEMS OF POWER PLANTS

Kiran Diwakar, Rajendra K. Saini, Upain Kumar Arora, Janakiraman Pattabhiraman, and Gopi Kanta Nayak

In power plants, the warm environment of recirculating cooling systems is ideal for the growth of microorganisms. As microorganism communities grow in cooling systems, they can attach to tubes,

pipe walls, and cooling tower fills, and form biofilms. Uncontrollable biological growth causes fouling, loss of heat exchange capacity, equipment failure, and energy wastage.

Due to the large volume of a cooling system with a flow rate of 60000–75000 $m^3 \cdot h^{-1}$ (500 MW plus unit) and the diverse types of bacteria, spores, and algae, no one chemical can kill everything. There must be proper selection of a biocide, adequate contact time, and real time monitoring techniques to allow control of biological problems.

The best solution for any system is the fast and early detection of biological contamination, and the setting up of proactive actions and subsequent corrective treatments. For the measurement of microbiological counts, we can use culture tests like the heterotrophic plate count (HPC) method. However, these culture tests only measure culturable organisms while adenosine triphosphate (ATP) testing measures all microorganisms within a sample. There are two types of ATP – intracellular ATP contained within living biological cells and extracellular ATP located outside of biological cells, which has been released from dead or stressed organisms.

In one thermal power plant cooling water system of NTPC Ltd., India, this technique was demonstrated with successful results.

PPCHEM® Journal, July/August 2021, 23(4), 152–157

MONITORING INDUSTRIAL PLANT DISCHARGE METALS AND TOC

Brad Buecker and Ken Kuruc

Industrial facilities such as refineries, petrochemical plants, steel mills, metal finishing facilities, pulp and paper mills, pharmaceutical plants, etc. require substantial wastewater treatment, as some processes at these facilities can release many complex carbon compounds or other toxic constituents, including metals, to waste streams.

While various techniques are available for measuring trace level metals in process water, to date they have been rather unavailable to many industrial locations because of capital cost requirements or the need for specially trained technicians. Two well-known techniques are inductively-coupled plasma and atomic absorption spectroscopy, which need specially trained operators and require complex sample preparation and expensive instrumentation.

This article discusses another existing technology, colorimetry, which has been modified for on-line monitoring. The method is suitable for many facilities and can be operated by a wide range of plant personnel. In many cases, the readings can be enhanced with TOC analyses to provide additional protection for industrial water/steam systems.

PPCHEM® Journal, July/August 2021, 23(4), 162–175

FILM FORMING AMINES – AN APPRAISAL

Wolfgang Hater

The technology of film forming amines or more generally film forming substances in water treatment has been well known for decades. The acceptance of their application in water-steam cycles was significantly increased by two IAPWS Technical Guidance Documents issued in 2016 and 2019. These documents provide a brief synopsis of the scientific know-how, and, more importantly, give practical guidance to people interested in this technology. This paper reviews and summarizes the scientific progress since then and identifies further research needs. Film forming substances have an important potential for the reduction of plant emissions, which, in addition to the demand for molecules with improved environmental properties, is looked upon as a driving force for future development.

PPCHEM® Journal, July/August 2021, 23(4), 180–185

CONFERENCES AND SEMINARS ORGANIZED BY PPCHEM AG – AN OVERVIEW

Tapio Werder and Michael Rziha

Since 2012, PPCHEM AG and its precursor organization, Waesseri GmbH, have organized more than 30 conferences and seminars around the world with the mission of expanding the knowledge of cycle chemistry and the understanding of analytical instruments. Over the past 9 years, different formats of events have been developed to fit the different needs and interests within the power plant chemistry community.

The first kind of event series developed was called Power Cycle Instrumentation Seminars (PCIS), with the mission of expanding the knowledge of cycle chemistry and the understanding of sampling techniques and analytical instruments. Based on the feedback from the PCIS participants a new series of events – PowerPlant Chemistry Forums (PPCF) – was introduced in 2016. Compared to the PCIS the PPCF does not concentrate exclusively on sampling and instrumentation, but instead includes a wide variety of nearly all aspects of power plant chemistry, such as life-cycle chemistry optimization, start-up chemistry and early operation experience, and plant failures and subsequent chemistry adjustments. The forum is basically a typical conference, where numerous international speakers from many different organizations present, hence it is a platform for all participants to exchange information and knowledge and for networking.

Beside the PCIS and the PPCF, educational seminars have also been developed and offered. These seminars are typically focused on a "hot topic" from power plant chemistry and usually they are conducted by PPCHEM's chief key expert power plant chemistry Michael Rziha.

This contribution outlines the developments in the past years and gives more details on the different formats of events which are currently organized by PPCHEM AG.

PPCHEM® Journal, July/August 2021, 23(4), 186–187

PRESS RELEASE: EPRI 13TH INTERNATIONAL CONFERENCE ON CYCLE CHEMISTRY IN FOSSIL AND COMBINED CYCLE HRSG PLANTS (ICCC13): DETAILS ADVANCES IN R&D

EPRI's 13th International Conference on Cycle Chemistry in Fossil and Combined Cycle HRSG Plants was conducted virtually June 22–24, 2021.

The conference was attended by 146 different professionals representing 10 countries, including Australia, Canada, Malaysia, Philippines, Taiwan, South Africa, Switzerland, United Kingdom, United Arab Emirates, and the United States.

The EPRI Boiler and Turbine Steam and Cycle Chemistry R&D program (Program 226) conducts collaborative research led by Program Manager Brad Burns. The collaborative program is a global leader in comprehensive research in power plant steam and water cycle treatment to minimize corrosion and deposition.

The conference is hosted by EPRI every three years. This latest event featured 21 presentations by international experts, equipment manufacturers, chemical suppliers, and power plant chemistry users. Discussions on a wide range of cycle chemistry-related topics added participation value to plant users, equipment and chemical suppliers, and researchers.

PPCHEM® Journal, September/October 2021, 23(5), 198–205

CONSIDERATIONS FOR COMPLEX INDUSTRIAL COOLING WATER MONITORING AND TREATMENT

Brad Buecker and Rajendra P. Kalakodimi

Heat exchangers are, of course, a critical component of power and heavy industrial plants. Many of these are water cooled, with the source being a cooling tower (commonly known as an open cooling system) or sometimes once-through cooling. Often, "closed" systems are also present, which are cooled by primary heat exchangers, but whose chemistry is significantly different from that of open systems. Successful chemical tre atment of the wide variety of cooling systems in plants requires analysis of many factors, including the potential for corrosion, scaling, and microbiological fouling, system metallurgy, operating temperatures, and others, all of which are examined in this article. Also discussed are several significant improvements to chemical treatment programs in recent years, improvements that maintain proper heat transfer and reliability of cooling systems.

PPCHEM® Journal, September/October 2021, 23(5), 206–210

WEIGHTED SALT HOURS – A NEW APPROACH IN CYCLING PLANTS

Frank Udo Leidich

Thus far, the chemist in a power plant has quite often been regarded as a necessary evil or as inevitable costs. To leverage the activity of the power plant chemist and make his/her work observable and tangible in an economic sense to the management, it is proposed to introduce a new parameter, weighted salt hours, that can be used to link the key chemistry parameters with key economic performance indicators. To do this, data mining and application of statistical methods, like gauging of repeatability and reproducibility, multi-factor analysis, and others analyses, are needed. Of course, such efforts can only be successful if a very high number of power plants participate and contribute to this.

PPCHEM® Journal, September/October 2021, 23(5), 212–220

FLEXIBLE OPERATIONS IN THE ENERGY TRANSFORMATION: HIGH-LEVEL IMPACTS ON CYCLE CHEMISTRY

Mike Caravaggio

Electricity generation is changing, and these changes impact all aspects of the plant. The following paper sets out some of the key changes and the high-level impacts on cycle chemistry in thermal plants. It is incumbent upon power plant chemists and chemical engineers to understand the details of how flexible operation affects their specific units, so that they can develop optimal, unit-specific solutions.

PPCHEM® Journal, September/October 2021, 23(5), 222–228

ASSESSING CORROSION IN AIR-COOLED CONDENSERS AT ESKOM MEDUPI POWER STATION

Sabelo Khanyile, Stephanie Marais, Setsweke Phala, Zanele Dladla, and Nestor van Eeden

Steam side surfaces of air-cooled condensers (ACC) are prone to corrosion. If the corrosion mechanism is not understood and mitigated, it can lead to ACC tube failure(s), and subsequent vacuum and/or condensate chemistry deterioration. Most importantly, the total iron levels entering the condensate and feedwater systems will be much greater than international guidance. This paper reports on the ACC corrosion assessment performed on Unit 5 of Medupi power station. The ACC condensate chemistry is reviewed and the "Dooley Howell ACC Corrosion Index" is reported. The latter was derived from the physical inspections of the internal surfaces of the ACC. The inspections were conducted when the unit was on all-volatile treatment, under oxidising conditions (AVT(O) regime), as well as after transitioning to an oxygenated treatment (OT) regime. The benefits of transitioning from AVT(O) to OT are also reported.

PPCHEM® Journal, November/December 2021, 23(6), 242–252

HUMAN PERFORMANCE & CYCLE CHEMISTRY – THE MISSING LINK? PART 2

Brad Burns and Doug Hubbard

On most units assessed by the Electric Power Research Institute (EPRI) across the world, cycle chemistry is well controlled and good results are obtained 99.9 % of the time. Fossil and combined cycle power plants on a global scale continue to boast higher cycle chemistry benchmarking scores, installation of new instrumentation and alarming, and management support for cycle chemistry. The exception, however, continues to be major cycle chemistry excursion events that happen infrequently, yet with great consequences.

Often, when an unmitigated major cycle chemistry upset event occurs, root cause investigations pin the event on inadequate skills or knowledge (of individuals). It is therefore believed that additional training and/or disciplinary corrective action solves the root cause of the event and will prevent poor operator response to out-of-spec chemistry from recurring.

But does this approach produce the desired results? This article continues part 1, which was published in the January/February 2021 edition of this publication. Human performance improvement was described as the potential "missing link" to achieve true cycle chemistry improvement. This article builds upon the previous one by providing practical examples and suggestions for implementing improved defenses in a plant.

PPCHEM® Journal, November/December 2021, 23(6), 254–263

THE ECONOMIC BENEFITS AND GOALS OF POWER PLANT CHEMISTRY

Frank Udo Leidich and Michael Rziha

Thus far, the chemist in a power plant has quite often been regarded as a necessary evil or as inevitable costs. The purpose of this paper is to explain the economic benefits of a chemist, the need to have a specialist on the operation team, the purpose and goals of the job, and the expectations of the chemist from the power plant management's point of view.

Of course, the economic impact, the possible risks, and (monetary) damage that might arise if the job is not done as it should be are discussed here as well.

This paper concentrates on the goals and purpose of the chemist's activities regarding the water/steam cycle and the components therein. Future papers will also deal with the chemist's footprint on the cooling system, including the cooling water make-up system, the flue gas path, and the treatment of other systems and machines.

PPCHEM® Journal, November/December 2021, 23(6), 264–270

ACCURACY, TRUENESS AND PRECISION OF MEASUREMENT METHODS AND RESULTS

Michael Rziha

The present paper is an updated revision of a paper presented 22 years ago at the joint European NUSIS-ICMG-VGB Chemistry Online Process Instrumentation Seminar in Brügge, Belgium (April 20–22, 1999).

The original paper was prepared by Dr. J. Fahlke, Grosskraftwerk Mannheim, Mannheim Central Power Station, Mannheim; W. Fichte, Consultant, Ismaning; E. V. Maughan, Tablar Messtechnik, Duisburg; H. D. Pflug, Consultant, Bergen-Enkheim; and H.-G. Seipp, ABB, Mannheim – all located in Germany.

I would like to express my sincerest thanks to Dr. J. Fahlke for providing me with the original paper and permitting me to use it as the basis for this updated version.

This paper is an attempt to facilitate understanding of the rather abstract and in part complicated definitions of the ISO 5725 by combining them with some illustrations. This approach, although it may require getting used to, will help to promote a better understanding between manufacturers, suppliers, purchasers and operators of continuously operating measuring instruments in plant cycle chemistry.

PPCHEM® Journal, November/December 2021, 23(6), 272–274

PPCHEM® INTERVIEW WITH WOLFGANG ROST

Tapio Werder

Wolfgang Rost joined the PPCHEM team in October 2021 as Senior Key Expert for Power Plant Technology. Tapio Werder, Editor in Chief of the PPCHEM® journal, has interviewed Wolfgang to introduce him to our readers.

24/2022 January to December 2022

PPCHEM

The Journal of All Power & Plant Chemistry Areas

2022's Scientific and Technical Contributions

PPCHEM® Journal, January/February 2022, 24(1), 4–8

DEVIATION IN TURBIDITY READINGS AT A LOW RANGE

Irene Rüegg

Various factors contribute to deviations encountered in low turbidity readings by different analyzers. Turbidity measurement is instrument-dependent; different instruments calibrated with formazine according to the standard methods only show identical readings on a sample if the instruments incorporate the deviation factors. This article examines the interferences that affect a "zero" measurement and demonstrates how the concept of the Swan AMI Turbiwell turbidity analyzer reduces these inaccuracies.

PPCHEM® Journal, January/February 2022, 24(1), 10–23

CLEANING OF NEWLY ERECTED STEAM BOILER PLANTS AND ASSOCIATED PIPEWORK

Wolfgang Rost

Experience gained over the years has shown that the strict adherence to prudent industry practice regarding the clean assembly of steam generator and water/steam cycle systems is the key to quickly establishing normal and trouble-free steam turbine operation of newly built power plants. It is therefore most valuable to understand what kinds of contamination can occur in what production step, what adverse consequences they imply, and how to generally avoid them by setting up very simple guidelines to start with. In addition, it is very helpful to know what sort of remedies exist as effective corrective measures if things go wrong in the first place. The knowledge of what state-of-the-art cleaning procedures exist and how they are conducted properly is also a very important key to success. If all the aforementioned points are adhered to, a reduction in execution time and money expenditure will be the result at the end of the day.

PPCHEM® Journal, January/February 2022, 24(1), 28–29

REVIEW – VGBE CHEMISTRY CONFERENCE 2021

Andreas Wecker and Sabine Kuhlmann

The 57th vgbe Chemistry Conference took place again as an attendance event. As usual, this chemistry conference was also accompanied by a trade exhibition with 21 national and international exhibitors. The approximately 160 participants were offered an interesting lecture programme.

PPCHEM® Journal, January/February 2022, 24(1), 30–31

HINTS FROM THE EXPERTS

HOW IAPWS-IF97 CAN BE USED TO OPTIMIZE THE SO-CALLED "CLEANING FORCE RATIO" DURING THE STEAM CLEANING OF POWER PLANTS

Throughout the entire process of the fabrication and construction of newly erected power plants, contaminants are introduced into the systems of the steam generator and the water/steam cycle due to the nature of the work. Some of these contaminants may not be removed successfully during chemical cleaning. Thus, due to the cleanliness requirements regarding the absence of particles, steam systems of power plants must undergo steamblow operation prior to commencing the first steam admission to the turbine.

Therefore, all steam pipes routed to the steam turbine must be steam-blown by using enough "force" to remove solid contaminants effectively. The so-called "Cleaning Force Ratio" (CFR) is used to determine whether this required "force" is achieved during steam cleaning.

PPCHEM® Journal, January/February 2022, 24(1), 32–40

2021'S SCIENTIFIC AND TECHNICAL CONTRIBUTIONS

PPCHEM® Journal, March/April 2022, 24(2), 52–63

CONDUCTIVITY LIMITS FOR DIRECT WATER-COOLED GENERATORS

Robert Svoboda and Wolf-Dietrich Blecken

For normal operation, a conductivity limit of ≤0.2µS·cm^{-1} is an indirect indicator of correct pH and restricts undue corrosion. With protective additives, e.g., NaOH for alkaline treatment, a higher limit corresponding to the objective of the treatment is appropriate.

With too high conductivity the water inside the insulating hoses of high-voltage stator windings will warm up and if it boils there is a risk of electric flashover inside the insulating hose with damaging consequences. Therefore, a short-term action limit in the order of 10µS·cm^{-1} has been set by the industry in the past.

With correct water flow, conductivity inside the insulating hoses at these values does not warm up the water significantly and there are no restrictions regarding the duration of such an event.

However, when cooling water flow is lost, the water inside the insulating hoses will warm up exponentially with time. The time until boiling has a strong (square) dependence on the rated generator voltage, as well as on the insulating hose length, and has a linear dependence on water resistivity. The spatial position of insulating hoses (hoses are mounted vertically, horizontally, or bent) is also of importance. In addition, the stationary cooling water inside the stator bars, as well as the entire stator winding, is subjected to critical temperatures, especially at high load conditions. Therefore, appropriate action must be taken prior to reaching the water boiling level. To avoid a costly stator winding breakdown, the cooling water flow must be restored at once. Otherwise, the generator has to be shut down completely as soon as possible.

PPCHEM® Journal, March/April 2022, 24(2), 70–75

AVOIDANCE OF COMMON MISTAKES DURING FAILURE ANALYSES AND MISINTERPRETATION OF LAB RESULTS – PART 2: LAB ANALYSES/SAMPLE HANDLING, PREPARATION, AND ANALYTICAL PROCEDURES

Frank Udo Leidich

For a proper failure analysis or root cause analysis (RCA), a great deal of data and evidence-based information is needed. Within this context, various types of samples from different locations need to be taken for chemical and/or metallurgical examination. In addition to proper and correct sampling without alteration of the composition or contamination of the samples, which is described in the first article of this short series [1], it is of utmost importance to use the right analytical methods and execute sample preparation carefully. This includes being aware of the basic principles of the methods applied and of course knowing their limits. This article discusses the analytical part of an RCA and is the second part in a short series of ongoing articles.

PPCHEM® Journal, March/April 2022, 24(2), 76–81

HINTS FROM THE EXPERTS

CONSIDERATIONS FOR THE CONTROL OF THE DOSING OF TRISODIUM PHOSPHATE (Na_3PO_4) IN BOILER WATER

In the recent past, various organizations have been trying to establish a more or less full automatization of the dosing control for the phosphate boiler water treatment (typically called PT), similar to the well-established and well-functioning automatic dosing control of ammonia. Although this may sound easy, as nowadays very reliable instruments and sampling systems are available, it is relatively difficult to implement, especially for PT, as the entire phosphate chemistry is very complex compared to that of ammonia. Therefore a safe and reliable automatic control of PT involves a lot of traps and risks which must be considered. The most common and challenging issues in this respect are described here. Although this list may not be complete, it could be used to reconsider the idea of fully automated control of phosphate dosing.

PPCHEM® Journal, May/June 2022, 24(3), 96–103

SAMPLING AND MONITORING – THE DAILY ROUTINE, WHICH IS ANYTHING BUT TRIVIAL OR SIMPLE

Michael Rziha

This article highlights some crucial and essential topics related to sampling and monitoring and how to obtain correct and representative samples and useful results.

Some classic mistakes, still experienced today in numerous plants, are highlighted as well.

Hints are given on how to avoid such mistakes and how to minimize the bias of samples. This article focuses on the most important basic rules for correct and representative sampling, but also draws attention to the most common mistakes being made.

PPCHEM® Journal, May/June 2022, 24(3), 108

TRIBUTE TO KEN GALT

It is our sad duty to inform you that Ken Galt passed away on May 1, 2022. He had been a member of the International Advisory Board (IAB) of the PPCHEM journal since the summer of 2020. Ken Galt was an outstanding scientist in the field of power plant chemistry, contributing a wealth of valuable research findings, notably studies on many topics.

PPCHEM® Journal, May/June 2022, 24(3), 118–119

HINTS FROM THE EXPERTS

MAKING CONTROL LOOPS SMARTER

For some applications in power plants, it is not a good option to wait until control loops reach the setpoint based solely on the reaction to the control deviation over time, as this may cause activation of warning signals or, in the worst case, may even trigger protection commands due to a delay in reaching the required setpoint. Some control loops are additionally susceptible to undesired oscillations. Hence, these affected control loops should be made smarter, so they behave more stably and react faster. How this can be easily achieved is explained here with various examples.

PPCHEM® Journal, May/June 2022, 24(3), 120–121

FOUNDATION OF THE GERMAN-SWISS ASSOCIATION FOR THE PROPERTIES OF WATER AND STEAM (GSAPWS) ON APRIL 1, 2022, IN POTSDAM, GERMANY

On 1 April 2022, 13 delegates met in Potsdam, Germany, for the founding meeting of the German Swiss Association for the Properties of Water and Steam. This meeting was also the first in-person meeting of the German and the Swiss National Committees since the start of the Covid-19 pandemic.

PPCHEM® Journal, May/June 2022, 24(3), 122–123

PRESS RELEASE: LAST REGULAR MEETING OF THE VGB WORKING GROUP LWR-CHEMISTRY AT THE NPP EMSLAND

Dr. Timo Stoll & Jörg Fandrich

On May 3–4, 2022, the last regular meeting of the VGB Working Group Light Water Reactor (LWR)-Chemistry took place at the nuclear power plant (NPP) Emsland, Germany. In addition to the technical experts of most of the German nuclear power plants, experts from all the Swiss nuclear power plants, the Netherlands, Spain and Belgium as well as from Framatome GmbH as consulting plant manufacturer participated.

PPCHEM® Journal, July/August 2022, 24(4), 136–159

DECHLORINATION CONTROL AND OPTIMIZATION IN INDUSTRIAL WATER APPLICATION

Vadim Malkov and Gregory Fleck

The use of reverse osmosis (RO) membranes for water treatment has almost doubled in the last five years [1]. The use is widespread across many industries, from municipal water and wastewater treatment to ultrapure water production in various industrial applications. For efficient RO membrane operation, it is important to accurately monitor and control the residual chlorine concentration in the feedwater, which allows for minimizing of RO membrane maintenance and extension of membrane life. Multiple studies demonstrate that prolonged exposure of RO membranes to free chlorine exceeding 38µg·L^{-1} (ppb) (based on 1000mg·L^{-1}-hours over three years [2]) is detrimental to the membrane structure and integrity, while the absence of the disinfectant and/or excess of dechlorinating agents promotes biofouling and causes loss of recovery. To maintain this delicate balance, membrane operators must accurately monitor oxidant concentration and addition of bisulfite, especially in the RO feedwater.

PPCHEM® Journal, July/August 2022, 24(4), 164–169

CAUSES AND EFFECTS OF INSUFFICIENT STEAM PURITY AND THE NECESSARY MEASURES

Michael Rziha

As is well known, contamination in the steam very quickly leads to impairment of the steam turbine, ranging from loss of efficiency to a massive reduction in service life, or even to rapid destruction.

The causes and sources for the entry of contamination are very diverse, especially in industrial plants. Plant-specific knowledge of the possible entry points and the types of possible contamination is of crucial importance for the determination of a suitable monitoring strategy for the most trouble-free and damage-free operation of the steam turbine.

In addition, if such contamination occurs, suitable measures must be taken very quickly in order to avoid long-term, undesirable and, above all, cost-intensive damage to the steam turbine.

The most common sources and causes, their detection, and recommendations or necessary avoidance strategies from the perspective of power plant chemistry are presented.

PPCHEM® Journal, July/August 2022, 24(4), 170–173

HINTS FROM THE EXPERTS

SAVING MONEY WITH CLEVER BLOWDOWN MANAGEMENT

Clean chemical conditions within the water-steam cycle and the steam generator systems are of utmost importance for trouble-free operation and to maintain the required steam purity for steam turbine operation. If the control of the chemical regime is not managed correctly, the introduced contaminants will lead to the build-up of layers on the blading of the turbine, reducing steam turbine efficiency and leading to corrosion processes which can cause considerable damage in the water-steam cycle and steam generator systems. In the worst case the steam generator or the turbine will be reduced to scrap metal. To control these contaminants and to avoid an excessive concentration within the evaporator, the blowdown of evaporator water is used to keep the concentration of the contaminants within allowable limits. However, this method of concentration limitation has the negative side-effect of a loss of valuable enthalpy. It also increases the consumption of demineralized water and chemicals.

PPCHEM® Journal, July/August 2022, 24(4), 174–182

APPLICATION OF CHLORAMINE AS A BIOCIDE FOR COOLING TOWER WATER CONSUMPTION REDUCTION

Anderson José Beber

This paper shows the results of the application of a mild oxidizer on a large cooling tower at a power plant in southern Brazil. This cooling tower utilizes grey water (tertiary treated domestic sewage) as make-up. With the application of this technology, there was an improvement in both microbiological control and corrosion rates. Additionally, the plant was able to increase the concentration cycles from an average of 4.5 up to 6.5, resulting in an annual savings of over 400 000 USD.

PPCHEM® Journal, September–December 2022, 24(5, 6), 196–206

ALKALISATION AND PH STABILITY IN WATER-STEAM CYCLES

Wolfgang Hater

The pH adjustment in the water-steam cycle is an important and widely applied measure to maintain plant integrity. The impact of the most common alkalising agents on pH and conductivity is discussed as well as the behaviour of mixtures. A methodology to calculate pH and conductivity from base constant and equivalent conductivity including possible intrusion of acid substances is presented.

With increasing basicity of the alkalising agent, the molar quantities needed to obtain the desired pH value decreases, reaching the minimum value for sodium hydroxide. At the same time, the impact of an ingress of an alkaline or acidic substance increases. Of the alkalising agents discussed in this paper, ammonia shows the highest and sodium hydroxide the lowest stability against pH excursions

Mixtures of alkalising agents change their properties with regard to pH stability linearly as a function of the composition. Their pH stability reflects the properties of the individual components: a mixture of sodium hydroxide and ammonia has a lower resilience against acid ingress compared to mixtures of trisodium orthophosphate and ammonia.

A high pH stability of the alkalising agent is an important measure to reduce the possible impact of acidic substances entering the system by leakage or decomposition of organic matter. Therefore, this has to be carefully considered when choosing the chemical for alkalisation.

PPCHEM® Journal, September–December, 24(5, 6), 208–213

SOME BRIEF COMMENTS ON MICROBIOLOGICALLY INFLUENCED CORROSION (MIC) IN POWER PLANTS

Reza Javaherdashti

This article deals with the most practical aspects of microbially influenced corrosion (MIC) in power plants. The issues discussed here are mainly where to expect MIC in power plants, the inaccurate nature of the term "biofilm" and the possibility of whether bacterial adaptation to biocides can occur. These issues are particularly important from an operation and maintenance point of view because they play an undeniably significant role in reducing the useful service life by increasing the risk of MIC and the cost of its treatment in power plants.

PPCHEM® Journal, September–December, 24(5, 6), 214–223

OXIDATIVE TREATMENT OF WASTE CONTAINING EDTA FOR ITS SAFE DISPOSAL – CHOICE OF OXIDANT AND MODE OF ADDITION FOR FIELD APPLICATIONS

Rajini P. Antony and A. L. Rufus

High amounts of ethylenediamine tetra acetic acid (EDTA) containing liquid waste along with metal ions (predominantly iron) at pH ~ 8 are generated during the process of chemical cleaning of steam generators in pressurized heavy water reactors and pressurized water reactors. Hence, proper waste disposal involving complete or partial decomposition of EDTA is indispensable. Three different oxidants, viz., air, H_2O_2, and ozone, were explored for the decomposition of a test solution. Their efficacy was found to be in the order: H_2O_2 > ozone > air. The lower rate of decomposition in the case of ozone and air is due to their solubility limitations. Investigations on the mode of addition of H_2O_2 revealed that a bulk/one-time large addition of H_2O_2 and continuous addition of small quantities at a controlled flow rate yield identical results. On weighing the practical risks/hazards involved in bulk addition during field applications, continuous addition is suggested as a better option.

PPCHEM® Journal, September–December, 24(5, 6), 224–229

INDUSTRIAL PLANTS AND STEAM PURITY FOR TURBINE OPERATION – A TOO FREQUENT AND ALMOST CLASSIC DILEMMA

Michael Rziha

Worldwide there are countless industrial installations using steam as a "byproduct" to drive a steam turbine. The steam is generated by many different sources, such as quench boilers and trans-line-exchangers, which are often found in refineries and petrochemical plants. Waste heat boilers in refineries and petrochemical plants can be water tube boilers and shell boilers. Fired flame tube boilers with low or medium pressure (5–50bar) are also used in many installations.

Industrial steam generators often have special requirements regarding load gradients (extremely fast load requirements and/or load reduction). Process steam extraction and process steam condensate return are very common in these plants, and carry the additional risk of the ingress of various contaminants from the different processes, finally leading to a heavy impairment of the steam purity.

Guidelines which are applicable for the feed- and boiler water for the different boiler types and operating pressures are misleadingly taken as "lead documents" although they do not provide the special individual consideration needed for steam purity. It must be emphasized that all such guidelines and standards are only valid for safe boiler operation, and do not address the needs of steam turbines.

In consequence, low-pressure boilers are often operated with softened water. From the perspective of boiler suppliers and boiler operators this might certainly be correct, as the generated steam is used for heating only, where the requirements on steam purity may be more relaxed.

However, and without exception, as soon as the steam is to be used to drive any kind of steam turbine, the relevant standards and guidelines for steam need to be followed. As a matter of principle this will always have an impact on the make-up water, feedwater, and boiler water purity. For example, boilers with a low operating pressure are allowed to be operated with softened or partially demineralized water. This is true and correct for the boiler/steam generator, but it is definitely wrong for any steam turbine tied into this process.

Steam turbine users should be aware of the risks associated with contaminants of the steam, which may initiate, promote, or enhance stress corrosion cracking, corrosion fatigue, general corrosion, erosion, and deposit build-up. Contaminants that are contained in steam generally lead to deposits and corrosion in steam turbines and thus potentially negatively affect their functioning and operational safety, as well as their lifetime. It must also be emphasized that corrosion and/or deposit build-up and consequently damage and/or impairment of performance or availability depend not on the size of the turbine, but only on the impurity level and composition of the steam.

Especially when softened water is used, the concentration of sodium in the water is significantly increased by the softening process! The thermal decomposition of sodium carbonates and sodium bicarbonates (products due to softening) always leads to the formation of caustic soda (NaOH), which strongly increases the risk of alkaline stress corrosion cracking of the turbine material! Consequently, when softened water is used as make-up water, a steam turbine operation is clearly excluded!

PPCHEM® Journal, September–December, 24(5, 6), 238–240

REPORT ON THE POWER CYCLE INSTRUMENTATION SEMINAR (PCIS) AUSTRIA 2022 IN LINZ, AUSTRIA

Tapio Werder

For the first time in the history of these events, the Power Cycle Instrumentation Seminar (PCIS) series stopped over in a German-speaking country. The PCIS Austria 2022 in Linz was held under the patronage of PPCHEM AG, and SWAN Analytical Instruments provided financial support.

Since 2012, PPCHEM AG and its precursor organization, Waesseri GmbH, have organized more than 30 conferences and seminars around the world with the mission of expanding the knowledge of cycle chemistry and the understanding of analytical instruments. Over the past 10 years, different formats of events have been developed to fit the different needs and interests within the power plant chemistry community.

This report summarizes the two days of the PCIS Austria 2022.

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January / February

ABSTRACTS

Remember the 3Ds of Alkalizing Amines: Dissociation, Distribution, and Decomposition
Brad Buecker and Steve Shulder

Carbon steel corrosion control of condensate lines, feedwater piping, and boiler internals is critically important in all steam generation applications. A key corrosion control aspect is establishing and maintaining a mildly alkaline pH throughout these networks. Organic-based alkalizing amines have a place in lower- and intermediate-pressure boilers, industrial plant condensate-return systems, and nuclear power plant secondary cycles. However, careful evaluation and research is needed when selecting a program. This article examines the "3Ds" of alkalizing amines, dissociation, distribution, and decomposition, and how these properties influence the selection of the compounds for controlling condensate and feedwater chemistry. Dissociation and distribution are equilibrium or reversible reactions while decomposition is irreversible. The article examines these properties for high-pressure utility units and offers some comparisons/contrasts for lower-pressure industrial systems, which often have extensive steam and condensate-return networks.

PPCHEM® 2023, 25(1), 4–13

A Low pH Excursion Exclusive to the IP Evaporator/Drum at a Combined Cycle Plant during a Start-up – Part I: Contamination Pathway
Emmanuel K. Quagraine, Philip Boutin, Jordan Rothwell, Cedric Huang, Nikki L. Wirtz, Jackie Sliva, Kellsey Hamel, Dwayne Selensky, Amy Tetlock, and Pratik Pansuriya

This is the first of a two-part article on the investigation of a low pH excursion which occurred exclusively in the intermediate-pressure (IP) evaporator/drum of a combined cycle plant at a start-up. The selective contamination occurred as glycol from closed-circuit cooling water (CCCW). The proposed contamination route is via a boiler feed pump (BFP), specifically O-ring seals separating the CCCW from the feedwater. The estimated leak rate is 8.0–22.9 $mL \cdot h^{-1}$, which is sufficient to cause the pH excursion. At start-up, the BFP would have charged the IP (and not the high-pressure (HP)) circuit line with water whilst in recirculation mode; this was later used to fill the IP drum. The HP drum was filled an hour later. Thus, accumulated glycol that leaked into the pump casing would have been pumped more exclusively into the IP circuit, resulting in the selective contamination. Through recirculation, glycol that potentially entered the low-pressure circuit, eventually feeding the HP circuit, would have been sufficiently diluted to prevent such an excursion in these two corresponding evaporators/drums.

PPCHEM® 2023, 25(1), 16–34

PPCHEM
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January / February

Some Basics of Power Plant Chemistry – Corrosion and Deposition
Frank Udo Leidich

Undesired corrosion and deposition reduce the lifetime of a power plant or its specific components. Even before a component in the water/steam cycle (WSC) is damaged or destroyed, economic damage has already been caused in terms of a reduction in efficiency, deterioration in availability, and increased maintenance and repair costs. In order to limit corrosion and deposition to acceptable levels, monitoring and control of the physico-chemical parameters of the working media is necessary. It is also necessary to purify (treat) the working medium (water/steam) and add chemicals suitable for reducing corrosion reactions and deposit formation on the components and parts of the WSC. This paper gives an overview of the different types of corrosion, where they occur in the WSC, and the potential hazards they pose. The most widespread deposits, their composition, impact, and origin are also discussed.

PPCHEM® 2023, 25(1), 38–50

2022's Scientific and Technical Contributions

PPCHEM® 2023, 25(1), 52–59

PPCHEM
The Journal of all Power & Plant Chemistry Areas
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March / April

ABSTRACTS

Connecting the Dots between Steam Generator Chemistry and Fundamental Thermodynamics
Brad Buecker

Experience has shown the importance of the necessity of comprehending the thermodynamics of steam generator heat transfer to better understand the chemistry requirements. Besides the corrosion aspects of water- and steam-side impurity ingress, efficiency losses can be expensive.

To minimize efficiency losses, condenser performance should be monitored diligently and it must be ensured that cooling water chemical treatment programs are operating properly and that air in-leakage has not become excessive. Reheating improves efficiency only by a few percent, but basic thermodynamic calculations show that steam reheating and introduction of the hot reheat to the intermediate-pressure turbine and crossover to the low-pressure (LP) turbine keeps the steam significantly drier in the LP turbine, with final moisture content usually below 10 % (and thereby minimizing water droplet erosion of the last stage blades).

In this article, we make the connection between major steam generator design details (and the thermodynamic principles behind them) and condensate/steam chemistry fundamentals.

PPCHEM® 2023, 25(2), 72–78

A Low pH Excursion Exclusively in the IP Evaporator/Drum at a Combined Cycle Plant during a Start-up – Part II: Lessons Learned
Emmanuel K. Quagraine, Philip Boutin, Jordan Rothwell, Cedric Huang, Nikki L. Wirtz, Jackie Sliva, Kellsey Hamel, Dwayne Selensky, Amy Tetlock, and Pratik Pansuriya

This is the second of a two-part article on a low pH excursion which occurred exclusively in the intermediate-pressure (IP) evaporator/drum of a combined cycle plant, with the other circuits (low-pressure (LP) and high-pressure (HP)) showing normal pH. This is an odd situation, and the first half of the article explains how this was possible. Part II however describes how this unexpected situation confounded interpretations of the plant's on-line instrumentation readings and the decision-making based on this data, which led to delays and inadequate response to the low pH excursion. A lot of confusion and uncertainties around pH readings were experienced and the causes have been identified. The plant also experienced a protracted period to clear the contaminant and attain desired steam purity for operation, the reasons for which are discussed. Lessons learnt and recommendations are also given to ensure early leak detection, prevention, or proper response to such pH excursions in the future.

PPCHEM® 2023, 25(2), 82–97

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On the Usefulness of Bypass Clean-up Systems
Volker Ender and Jens Weber

Instead of a simple water exchange, another possible method to correct the water quality in circulation systems is the method of bypass clean-up. To estimate the efficiency of a bypass clean-up, one must consider the inner efficiency as well as the outer efficiency. The inner efficiency is influenced exclusively by the method of cleaning being used, while the outer efficiency is ultimately decisive for an efficient application of bypass clean-up systems. The outer efficiency is determined by the relation between the different rate constants of the various processes which contribute to the decrease (or increase) in the concentration of the water constituents under consideration. Hence, one can find applications where a bypass clean-up can have high efficiencies, but there are also cases in which only low overall efficiencies may be achieved, despite high inner efficiencies. Using the framework presented here, it should be possible to estimate the effects on a theoretical basis.

PPCHEM® 2023, 25(2), 100–105

IAPWS Film Forming Substances (FFS) Conference, FFS2023
Highlights and Press Release

The sixth IAPWS FFS International Conference was held on the 21st–23rd March 2023 in Prato, Italy chaired by Barry Dooley of Structural Integrity Associates, UK and David Addison of Thermal Chemistry, New Zealand. The FFS conferences are unique on a narrow topic in cycle chemistry control of power plants and steam generating facilities. In 2023 the conference attracted 70 participants from 28 countries which included 20 plant operators / users and representatives from 11 FFS chemical suppliers.

The FFS conferences are developed and supported by the International Association for the Properties of Water and Steam (IAPWS), and FFS2023 was arranged in Prato by Mecca Concepts, Australia and Combined Cycle Journal, USA. The sponsors of FFS2023 were Kurita Europe GmbH, Nalco Water an Ecolab Company and Termanox Water Treatment Solutions.

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ABSTRACTS

Effect of Zinc Water Chemistry on the Corrosion and Stress Corrosion Cracking Behavior of Structural Materials in Light Water Reactors – A Review
Xianglong Guo, Kai Chen, Hans-Peter Seifert, and Stefan Ritter

Zinc (Zn) injection into light water reactor coolants has attracted increasing attention since the reporting of its positive effects on reducing the susceptibility to stress corrosion cracking (SCC) of steam generator tubes made of Alloy 600. Revealing the corrosion and SCC mechanisms of structural materials exposed to Zn water chemistry (ZWC) has gained importance in quantifying potential benefits for the safe long-term operation of nuclear reactors. This paper reviews the open literature on the current understanding of ZWC effects on the (uniform) corrosion and SCC behavior of structural materials used in western light water reactor plants. Some research with promising results has been conducted, but more detailed and systematic work is still needed to draw meaningful conclusions on the SCC mitigation capabilities of the ZWC.

PPCHEM® 2023, 25(3), 124–147

Impurities in Water Supplies (Natural and Reclaim) and Modern Control Methods for Industrial Plant Makeup – Part 1
Brad Buecker

Makeup water for power and industrial plants typically contains numerous impurities. Many come from natural processes, while others, often in slight but at times potentially troublesome amounts, come from human activities. The contaminants can cause fouling, scaling, and other problems in cooling, service, and high-purity makeup systems unless treatment methods are employed to reduce impurity concentrations. This series examines how impurities enter water supplies, and it provides an overview of modern treatment methods.

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Cooling Tower Disinfection Switch to Chlorine Dioxide Reduces Boiler Chloride Cycling: Why and How? – Part 1

Emmanuel K. Quagraine, Trever McNabb, Taneal Weiss, Gillian Bailey, Nikki Wirtz, Khrystyna Vasylkiv, and Daniel Schorr

This is the first half of a two-part article which discusses the abatement of selective boiler chloride cycling (SBCC), which has plagued the subject power plant, upon switching the recirculating cooling water (RCW) biocide from NaOCl to ClO_2. Evidence has been given to attribute this mainly to gaseous ingress of volatile chlorinated compounds (VCCs) through weak tube-to-tubesheet joints. Based on Henry's constants in aqueous solutions, ClO_2 partitions more into the gaseous phase compared to chlorine species associated with NaOCl, i.e., chloramines, Cl_2, HOCl, and OCl^-. The SBCC abatement hence seems paradoxical. Based on literature and operational data, this is explained. Properties of ClO_2 make keeping residual ClO_2 in RCW difficult, if not impractical. At the cooling tower, major losses occur physically and chemically and even when residual remains, its high solubility in water at such low concentrations causes deviation from Henry's law, i.e., a lower tendency to form $ClO_{2(g)}$. In addition, inside the condenser, where $ClO_{2(g)}$ may occur, it reacts quickly with oxidizable gases and (bio)organic compounds selectively yet versatilely, where it is not only consumed but avoids formation of VCCs, thereby preventing their ingress into the condensate side.

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ABSTRACTS

Cooling Tower Operating and Water Treatment Fundamentals – Part 1
Brad Buecker and Rich Aull

Process cooling is an important operational factor in many industrial plants and commercial office buildings around the world. Most of these plants use cooling towers for primary cooling. A large facility may have dozens of towers scattered throughout the premises. Often, plant personnel are focused on process engineering and chemistry, potentially neglecting cooling systems until a serious disruption occurs that threatens plant production or, worse, jeopardizes employee safety.

This article forms the basis of a short series of articles dealing with the chemistry of cooling systems. In this first part of the series, we examine the fundamentals of heat transfer in the cooling tower and the methods that have been developed to improve heat exchange in the tower. Subsequent parts discuss modern water treatment methods to ensure reliable performance.

PPCHEM® 2023, 25(4), 190–198

Cooling Tower Disinfection Switch to Chlorine Dioxide Reduces Boiler Chloride Cycling: Why and How? – Part 2
Emmanuel K. Quagraine, Trever McNabb, Taneal Weiss, Gillian Bailey, Nikki Wirtz, Khrystyna Vasylkiv, and Daniel Schorr

This is the second half of a two-part article discussing the abatement of selective boiler chloride cycling (SBCC) upon switching the recirculating cooling water (RCW) biocide from NaOCl to ClO_2. The use of ClO_2 treatment significantly reduces SBCC, with only sporadic spikes observed to a much lower extent. These spikes are found to be related to the plant's operation, coinciding with sudden load drops and increased air injector flows. It is suggested that these spikes may be caused by small $ClO_{2(g)}$ residuals condensing at the air injector condenser and entering the feedwater, eventually reducing to chloride ions (Cl^-) in the water/steam cycle. Unlike chlorination, ClO_2 treatment prevents the formation and persistence of volatile chlorine compounds (VCCs), including $ClO_{2(g)}$. The residual ClO_2 in the RCW that is responsible for the highest observed daily boiler chloride rise during ClO_2 treatment is estimated to be $4.05–9.74 \cdot 10–5\ mg \cdot L^{-1}$. However, this concentration range represents only 0.02–0.23 % of the highest to the least measured residual concentrations, confirming the previous assertions that maintenance of substantial residual ClO_2 in RCW, especially when using treated municipal wastewater as make-up, is unlikely. Overall, the operational data supports the switch from NaOCl to ClO_2 as an effective method for reducing SBCC in the water/steam cycle, with ClO_2 treatment showing superior performance and minimal VCC formation compared to NaOCl.

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Chemistry Requirements of the Steam Turbine

Frank Udo Leidich

Safe and trouble-free operation of a steam turbine requires monitoring and control of the operating medium "steam." In particular, it is necessary to prevent impurities in steam from causing corrosion attacks on turbine components, which, depending on the form of corrosion, can lead to sudden, unpredictable component failure. This PPCHEM 101 describes typical damage and failures that will eventually occur if the quality of the water and steam does not meet the requirements as stated in the operation manual of the steam turbine manufacturer and/or global standards and technical guidance documents as released by, for example, the International Association for the Properties of Water and Steam (IAPWS).

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ABSTRACTS

A Specialty Ion Exchange Resin for Deoxygenation Treatment of Boiler Makeup Water

Zhendong Liu, Amy Peddie, and Juan Carlos Pinilla

Oxygen level control can be very important in the cycle chemistry of power plants. Sometimes a higher oxygen level is desired for all-ferrous materials due to its creation of the more corrosion-resistant ferric oxide hydrate layer in the natural magnetite. This is practiced as either all-volatile treatment under oxidizing conditions (AVT(O)), or oxygenated treatment (OT). However, for some alloy materials (e.g., copper alloys and nickel alloys) used in the steam generation/recirculation systems, a reducing environment and very low oxygen levels are favored to avoid corrosion. This paper reports on a specialty ion exchange resin and its use in treating the makeup water for a pressurized water reactor (PWR) nuclear power plant. The resin is coated with a precious metal as catalyst for the oxygen-hydrogen reaction to generate water. It requires minimum maintenance (only annual backwashes), and has fast reaction kinetics, a small footprint, and a long operating life (> 20 years). The case study shows the resin can achieve $< 10\ \mu g \cdot L^{-1}$ oxygen consistently from a makeup water with $1–10\ mg \cdot L^{-1}$ oxygen at a $189–1\,514\ L \cdot min^{-1}$ flow rate. The catalyst doping, reaction mechanism, and some operational details are discussed.

PPCHEM® 2023, 25(5), 240–244

Press Release – IAPWS Annual Meeting 2023

Between September 3rd – 8th, 2023, 62 scientists, engineers and guests representing 20 countries converged in Turin, Italy at the Star Hotel Majestic for the annual meetings of the IAPWS Executive Committee and Working Groups. This continues a series of meetings that began in 1929 in London, UK with the purpose to connect scientists and researchers with the industry operators, engineers and managers who use their work. Collaboration and engagement across these varied groups provides guidance to the researchers on topical problems within industry and provides the engineers with the latest research results for direct application in their facilities.

The main meetings included discussions around power cycle chemistry, high temperature aqueous technologies applicable to steam cycles and hydrogen generation, oceanography and global climate modelling, geothermal steam, electrode boilers, power cycles with CO_2 capture and storage systems and combined heat and power systems.

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The Role of Organics in Relation to Corrosion in Steam-Water Systems

Yu Xue, Karlien Dejaeger, Ben Bischoff Tulleken, Duygu Disci, Peter Janssen, Andrea M. Brunner, David Moed, Wolfgang Hater, Emile R. Cornelissen, and Marjolein Vanoppen

A sampling campaign was conducted in a film-forming amine product (FFAP) treated high-pressure steam-water system of an ammonia producing plant to optimize the cycle chemistry. Cycle chemistry guidelines were assessed to be applicable with modifications fitting the local situation according to the pH and conductivity. Methanol, a main organic compound originating from the production process, entered the steam-water system with the process condensate and was tested possible to degrade. Furthermore, organic compounds from cation exchange resin were found in blowdown streams, suspected to originate from resin carryover. No operational and corrosion issues were observed.

Lab-scale first condensate experiments confirmed that a lower pH was present in the first condensate compared with the bulk steam, however, it was still partially buffered by ammonia. Via corrosion tests it was observed that oleyl propylenediamine (OLDA), in addition to ammonia, formed a smoother and more uniform magnetite layer. Moreover, magnetite layers formed under OLDA added to ammonia were more resistant against acidic conditions (pertinent to condensate return systems) than layers formed under the ammonia only chemistry and blank chemistry (without a chemical additive), with less reduction of the magnetite layer thickness.

These studies in combination with the plant experiences confirm that the steam-water system can be safely run with the selected FFAP treatment concept even with organics from the production process.

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