2018's Scientific and Technical Contributions

Emmanuel K. Quagraine

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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.

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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.