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2023's Scientific and Technical Contributions

PPCHEM® Journal, January/February 2023, 25(1), 4–13

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® Journal, January/February 2023, 25(1), 16–34

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® Journal, January/February 2023, 25(1), 38–50

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® Journal, January/February 2023, 25(1), 52–59

2022'S SCIENTIFIC AND TECHNICAL CONTRIBUTIONS

PPCHEM® Journal, March/April 2023, 25(2), 72–78

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® Journal, March/April 2023, 25(2), 82–97

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® Journal, March/April 2023, 25(2), 100–105

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® Journal, March/April 2023, 25(2), 108–109

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.

PPCHEM® Journal, May/June 2023, 25(3), 124–147

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® Journal, May/June 2023, 25(3), 148–154

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.

PPCHEM® Journal, May/June 2023, 25(3), 158–174

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.

PPCHEM® Journal, July/August 2023, 25(4), 190–198

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® Journal, July/August 2023, 25(4), 202–210

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·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.

PPCHEM® Journal, July/August 2023, 25(4), 220–226

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).

PPCHEM® Journal, September/October 2023, 25(5), 240–244

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 µg·L^{-1} oxygen consistently from a makeup water with 1–10 mg·L^{-1} oxygen at a 189–1514 L·min^{-1} flow rate. The catalyst doping, reaction mechanism, and some operational details are discussed.

PPCHEM® Journal, September/October 2023, 25(5), 250–251

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.

PPCHEM® Journal, September/October 2023, 25(5), 256–275

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.

PPCHEM® Journal, November/December 2023, 25(6), 296–299

SODIUM ANALYZERS AND FILM-FORMING SUBSTANCES: WORKING TOGETHER?

Eric M. Etter and Harold Stansfield

The increasing application of film-forming substances (FFS) in power generation and process steam applications as a corrosion mitigation strategy has raised concerns regarding their impact on plant systems, particularly valves, piping, and instrumentation. This study focuses on the adverse effects reported by users of film-forming amine (FFA) products, including loss of instrumentation sensitivity, premature electrode failure, sensor fouling, and overall accuracy and reliability issues.

Experiments aimed at replicating field conditions have revealed rapid sensor fouling occurring well before standard maintenance cycles for electrode cleaning and replacement. The observed accelerated fouling necessitates frequent mechanical cleaning, posing risks of electrode damage, increased downtime, and additional labor for maintenance. Because the fouling does not result in

calibration failures, this creates a situation where the analyzer appears to be functioning normally, but is no longer capable of responding to adverse events such as a condenser leak. These highly dampened responses will follow trends over time but are incapable of rapidly reflecting transient spikes or changes in values.

PPCHEM® Journal, November/December 2023, 25(6), 310–318

COOLING TOWER OPERATING AND WATER TREATMENT FUNDAMENTALS – PART 2

Brad Buecker

Cooling water systems are an integral component of many power plants and industrial facilities of all types. Performance degradation from microbiological fouling, scale formation, and corrosion can seriously impact plant operation and revenue. Severe cases may force unit process or plant shutdowns. The remainder of this series examines the most problematic fouling, scaling, and corrosion mechanisms, and it outlines modern control methods for all of them. This installment focuses on microbiological fouling, with much of the discussion extracted from Reference 1.

PPCHEM® Journal, November/December 2023, 25(6), 322–325

WHY DO SAMPLE COOLERS FAIL?

Aditya Sanjay Kanetkar

In steam and water analysis systems (SWAS), the sample cooler is one of the most important components. The main function of the sample cooler is to reduce the temperature of high-temperature samples from elevated temperatures to the temperature required for analyser sensors. In the case of steam sampling, the steam samples are not just cooled, but are condensed to water (phase change).

PPCHEM® Journal, November/December 2023, 25(6), 330–337

ADDITIVES FROM NATURAL RESOURCES – THE WAY TO THE FUTURE?!

Wolfgang Hater

Additives from natural resources have been known since the end of the 19th century and have had a renaissance in recent years due to the demand to replace mineral-oil-based chemistry with materials from nature. They are considered to be green and sustainable. In spite of their positive image and a huge number of research papers, hardly any new compounds from natural materials have successfully found their way onto the market.

The assumption that natural equals harmless, green, or sustainable is quite common but does not always hold. While the criteria for green and sustainable are not well defined, the European Community has developed a standardized risk-based approach for the evaluation of whether a chemical can be safely applied.

This paper describes the major advantages and drawbacks related to natural material or biobased material. On the one hand, the production process is generally more simple and raw materials are cheap, especially if waste/recycled materials or residues are processed. On the other hand, a serious obstacle is the high variability of their chemical composition as well as the presence of components with no function.

Selected examples of studies and the application of additives from natural resources for water treatment are briefly discussed which show the potential but also the roadblocks for market success. It can be expected that they will play an increasing role in the future. Legislation will also be a strong influencing factor.

PPCHEM® Journal, November/December 2023, 25(6), 338–339

REVIEW VGBE CHEMISTRY CONFERENCE 2023 OCTOBER 24 TO 26, 2023 IN INGOLSTADT

Around 170 participants attended the 59th vgbe Chemistry Conference from October 24 to 26, 2023. The wide-ranging lecture programme was once again rounded off by an accompanying trade exhibition with 20 exhibitors who presented their products and services relating to power plant chemistry.

The vgbe conference team would like to thank all speakers, exhibitors and sponsors as well as the interested participants for their support and looks forward to the next vgbe Chemistry Conference, which will take place in Potsdam from October 22 to 24, 2024.

PPCHEM® Journal, November/December 2023, 25(6), 340–341

ABHUG 2023 HIGHLIGHTS

The annual meeting of ABHUG held on the 14th–16th November 2023 in Brisbane, Australia was chaired by Barry Dooley of Structural Integrity Associates, UK and Bob Anderson, Competitive Power Resources, USA. This ABHUG conference included conventional fossil plant technology and issues closely related to those in HRSGs. ABHUG2023 attracted 100 participants from Australia, New Caledonia, New Zealand, Singapore, Switzerland, UK and USA. About 55 % of the participants were Users.

The next meeting of ABHUG will be in Brisbane around early December 2024.