

2020's Scientific and Technical Contributions

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 $0.5 \, \rm mg \cdot kg^{-1}$ 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 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 1013mbar atmospheric pressure, the equilibrium for oxygen in water is 8.4mg·kg⁻¹. With 410ppm CO₂ in air, its mass fraction in water is 694µg·kg⁻¹ CO₂, where 595µg·kg⁻¹ are present as dissolved gas and 99µg·kg⁻¹ are ionized to HCO_3^- . The result is a slightly acidic water with pH=5.65 and 0.89µS·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 (2.6mEq·mL⁻¹ of resin as against 2.0mEq·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 D₂O and H₂O, 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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