ABSTRACTS

Corrosion of Structural Materials and Electrochemistry in High Temperature Water of Nuclear Power Systems
Shunsuke Uchida

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.

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Organics in the Power Plant Cycle – An EPRI Perspective
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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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Commissioning of the First U.S. Hollow Fiber Condensate Filtration System
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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 m³ · h⁻¹ (16 020 gallons per minute) using a total filtration surface area of 9 457 m² (101 796 ft²). 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 μg · kg⁻¹. Data on the impact of low iron operation on reactor coolant activated corrosion products and the ratio of ⁶⁰Co(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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Modifications in the Secondary Circuit Chemistry Control of Embalse NPP
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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 cm³·kg⁻¹ D₂O. 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.

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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 µg · 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, pH₂⁰°C 9.15–9.35, FAC was halved, not clearly mass transfer controlled, and extremely sensitive to oxygen. It was stifled at 1–2 µg · 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.
In the February 2008 issue, we introduced our project PPChem 101 "Fossil Cycle Chemistry" with the first lesson (What Is Plant Cycle Chemistry and Why Is It Important for Steam and Power Generating Plants?). In March the second lesson (Makeup Water Treatment) followed, in April the third lesson (Cycle and Component Design, Materials, Operating Mode, and Plant Cycle Chemistry), in May the fourth lesson (Feedwater Treatment) followed, in June the fifth lesson (All-volatile Treatment), in July the sixth Lesson (Oxygenated Treatment), in August the seventh Lesson (Feedwater Treatment with Organic Chemicals), and in September the eight lesson (Boiler Water Treatment – Part 1). The focus of this lesson is on the boiler water treatment in which solid chemicals such as phosphates and caustic (sodium hydroxide) are applied.

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