

Abstracts

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 [15]. The modifications include the inclusion of additional species and reactions taken from other models that have been developed by others (e.g., Christensen [17]) 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 [1]. 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 hypothetical 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 [10–15] to simulate a BWR. We modified the present model to simulate a hypothetical 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.

Tribute to Professor Ulrich Grigull

In this issue an obituary appears for Professor Ulrich Grigull, a scientist and university teacher known and acknowledged worldwide. Why is PowerPlant Chemistry dedicating an honorable reference to a specialist who was active in a non power plant chemistry-related field? Grigull was a very active supporter of cycle chemistry within the International Association for Properties of Water and Steam and helped to establish the power plant chemistry group within that association. The result? The IAPWS is the only international scientific organization dealing with power cycle chemistry.

Barry R. Dooley, Steve R. Paterson, and 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 occurs 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.

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.

CORROSION NACExpo 2004

The PowerPlant Chemistry staff is constantly looking for conferences related to power plant chemistry or at which at least part of the conference (some sessions or papers) is plant chemistry related and possibly interesting or important to our readers. In this issue, we focus on next year's *CORROSION NACExpo 2004*. During this international conference, many papers will cover power plant chemistry topics. Convince yourselves.

Several of the technical symposia at CORROSION/2004 will be of interest to power industry chemists and engineers. The relevant meetings are listed. Naturally, not all the papers that will be presented deal with power plant chemistry-related topics. Nevertheless, many of them would justify taking part in *CORROSION NACExpo 2004*.

Robert F. Rathbone and 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) DeNO_x 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.

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