Simulation of Electrochemical Corrosion Potential at the Steam Generator Tubes under the PWR Water Chemistry

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1. Introduction

Electrochemical Corrosion Potential (ECP) is commonly recognized as one of the important parameters in determining the impact of corrosion degradation and activity transport in the reactor coolant circuits of Pressurized Water Reactors (PWRs) [1-3]. Hydrogen is used to scavenge dissolved oxygen and suppress radiolysis in the primary reactor coolant of PWRs. The hydrogen dissolved in the reactor coolant affects the ECP as well as the crack growth rate in nickel-base alloys and stainless steels in the reactor coolant systems. Predictions of ECP values in the primary loop of PWRs depend on the values of a number of parameters that describe, or arise from, various physicochemical processes that occur in the system. The main parameters needed for the calculation of the ECP are the exchange current density, $i_0(H_2)$, and the Tafel constants for the electrochemical reactions that occur on the metal surface. These main parameters were obtained by one of the authors from experimental work with Alloy 600 under the same water chemistry as typical PWRs.

2. Mixed Potential Model

The Mixed Potential Model (MPM) [2,4] is based on the physical condition under which charge conservation must be obeyed at a metal surface when a corrosion process is in progress. The charge conservation constraint is

$$\sum_{j=1}^{N} i_{R/O,j}(E) + i_{corr}(E) = 0, \qquad (1)$$

where $i_{R/O,j}$ is the partial current density due to the jth redox couple in the system and i_{corr} is the corrosion current density of the material. For Alloy 600, the anodic corrosion current density, i_{corr}, was modeled as follows with the PDM as an empirical function of the solution temperature and overpotential [4];

$$i_{corr} = 1.18 \times 10^{-2} e^{-\frac{5411.3}{T}} + 2.23 \times 10^{-8} e^{\eta/0.12}, \quad (2)$$

where T is the solution temperature in Kelvin and η is the overpotential in volt.

The experimentally measured correlation of the exchange current density (partial redox current density at the equilibrium potential) for the hydrogen electrode reaction, $i_0(H_2)$ with temperature, $[H_2]$, and $[H^+]$, on the surface of Alloy 600 is expressed as [5, 6]:

$$i_{0,H^+/H_2} = 1.79 \times 10^{-10} e^{\frac{30562}{RT}} [H_2]^{0.64} [H^+]^{-1.39}, \quad (3)$$

where R is the gas constant, T is the solution temperature in Kelvin, and $[H_2]$ and $[H^+]$ denote the concentrations of hydrogen gas and hydrogen ions, respectively, in mol/kg [5].

3. Simulation Results and Discussion

The P-ECP code was used to calculate the ECP values of the steam generator tubes as a function of the reactor operating time and conditions. The P-ECP code is capable of calculating the pH and ECP values when the boron and lithium concentrations, as described above, are given as time-varying input parameters.
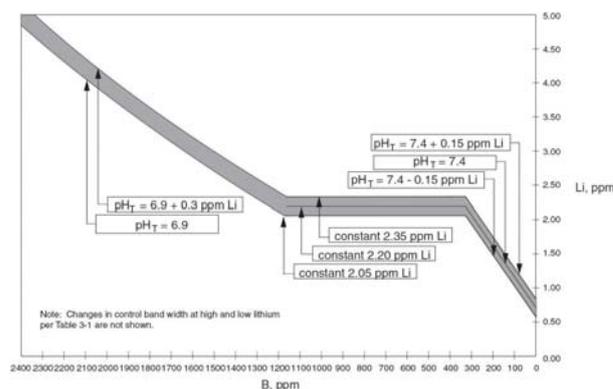

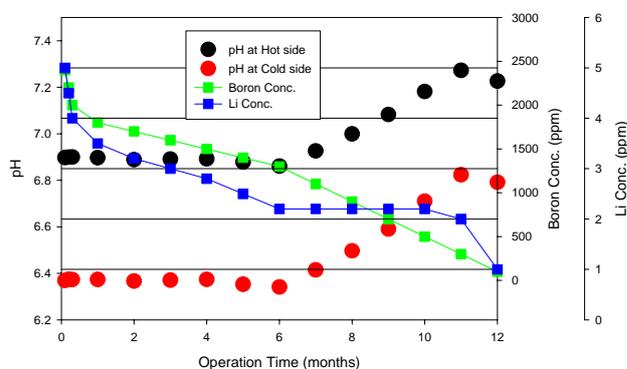**Figure 1: Schematic of an example of modified chemistry (at 300°C) [7]**

Figure 2: The calculated pH variations of the coolant within the hot leg and cold leg tubes of a PWR steam generator during one year of power operation under a modified water chemistry protocol

The modified chemistry regime shown in Figure 1 is currently being used by the Korea Hydro and Nuclear Power Co.. The concentrations of boron and lithium in this regime are coordinated to maintain constant pH values during the beginning of the core cycle. The modified water chemistry under a PWR environment is simulated in this study in order to identify the hydrogen effects on ECP values. Figure 2 shows the calculated pH values on cold and hot side tubes of a steam generator. Note that the boron and lithium concentrations were given by the input file.
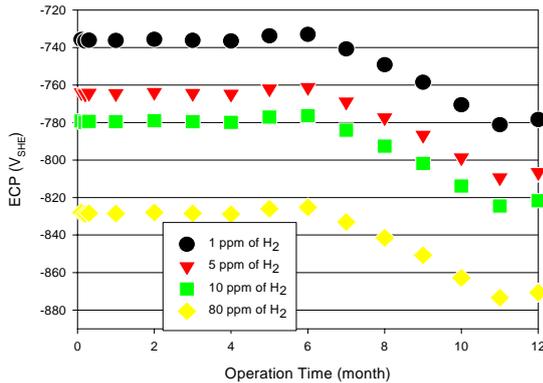
Figure 3: Calculated ECP within the cold leg tube of a PWR steam generator during one year of power operation under a modified water chemistry protocol.
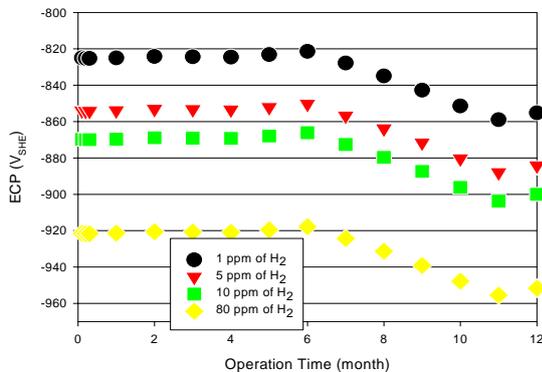
Figure 4: Calculated ECP within the hot leg tube of a PWR steam generator during one year of power operation under a modified water chemistry protocol.

The simulation results summarized in Figures 3 and 4 confirm that the ECP shifts to more negative values with increasing hydrogen concentrations in the reactor coolant. When the hydrogen concentration in the primary coolant is set to 1 ppm, the calculated ECP values were changed from -0.735 V_{SHE} to -0.778 V_{SHE} in the cold leg and from -0.824 V_{SHE} to -0.855 V_{SHE} in the hot leg over one year of operation in a typical PWR. However, at 80 ppm of hydrogen, those values were shifted in the more negative direction from -0.828 V_{SHE} to -0.870 V_{SHE} in the cold leg and from -0.921 V_{SHE} to -

0.951 V_{SHE} in the hot leg. Note also that the pH strongly influenced the ECP values.

4. Conclusion

Figures 3 and 4 show that when hydrogen is injected into the reactor coolant, the ECP values shift in a more negative direction to values as low as -0.95 V_{SHE}. The hydrogen concentration in the reactor coolant system of PWRs mist be decreased to avoid the ECP value of steam generator tubes lying below the critical potential of -0.82 V_{SHE} for hydrogen-induced cracking of Alloy 600 in a PWR coolant. The present model predicts that this outcome would require very low hydrogen concentrations, most likely due to the lack of redox reactions that involve oxidizing radiolysis species in the model. (Note that at hydrogen levels below about 5 ppm, there is no complete suppression of radiolysis, hence the residual O_2 and H_2O_2 produced by radiolysis tend to raise the ECP). A previous work suggests that the optimal hydrogen concentration is about 5 cc(STP)/kg (~ 0.5 ppm). The differences in the ECP values between the cold and hot legs of the steam generator tubes are caused by the pH differences produced by the different temperatures in those regions.

References

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