A STUDY FOR MODELING ELECTROCHEMISTRY IN LIGHT WATER REACTORS

A Thesis in
Nuclear Engineering
by
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ABSTRACT

Existing computer codes, developed by Macdonald et al. for modeling water chemistry and estimating the accumulated damage from the stress corrosion cracking in the operating environments of boiling water reactors (BWRs), were superseded by a new code, FOCUS which was improved in this study. This new code predicts water chemistry, electrochemical corrosion potential, and accumulated damage throughout BWR coolant circuits simultaneously under normal water chemistry or hydrogen water chemistry.

Using the frame of FOCUS, a new simulation code for the Pressurized Water Reactor (PWR) was developed in this study. In order to simulate the PWR, different radiological and chemical models for the calculation of individual chemical species concentrations were developed and equipped in this new code for PWRs. This new code was named P-ECP. Also, the pH model capable of calculating pH values with variations of temperatures and concentrations of the boric acid and lithium hydroxide was developed.

The surface area of the steam generator tubes accounts for seventy-five percent of the pressure boundary in typical Westinghouse three-loop PWRs; therefore, including the steam generator tubes into the corrosion simulation is critical in the simulation of the corrosion characteristics of PWRs. High temperature and high pressure experimental work was carried out in this study in order to seek the electrokinetic parameters of Alloys 600 and 690. Oxide film properties formed on the surface of the Alloy 690 were investigated by the Mott-Schottky analysis and the Point Defect Model. The obtained electrokinetic parameters were incorporated in the P-ECP code. The simulation results using the new code were in well agreement with the experimental work performed by other groups.

The newly developed P-ECP code is capable of calculating pH values and conductivity considering the radiolitic effect under the presence of the boric acid and lithium hydroxide from room temperature to the operating temperature of PWRs. In addition, ECP values throughout the reactor coolant circuits of Type 304 stainless steel and Alloys 600 and 690 can be simulated with the various reactor coolant environments
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<tr>
<td>ACEFM</td>
<td>advanced coupled environment fracture model</td>
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<tr>
<td>AOA</td>
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<td>boiling water reactor</td>
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<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PWR</td>
<td>pressurized water reactor</td>
</tr>
<tr>
<td>PWSCC</td>
<td>primary water stress corrosion cracking</td>
</tr>
<tr>
<td>RCS</td>
<td>reactor coolant system</td>
</tr>
<tr>
<td>SCC</td>
<td>stress corrosion cracking</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>SS</td>
<td>stainless steel</td>
</tr>
<tr>
<td>STP</td>
<td>standard temperature and pressure</td>
</tr>
</tbody>
</table>
Thanks are due to my advisors, professor Digby Macdonald and Arthur Motta for their encouragement and advising for this dissertation. I would like to acknowledge professors Mirna Urquidi-Macdonald, Lawrence Hochreiter, and Kostadin Ivanov for their precious comments on this thesis work.

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Chapter 1

Introduction

1.1 Purpose of this Dissertation

Stress Corrosion Cracking (SCC) is a crack propagation process under the combined effect of tensile stress and corrosive environments. SCC is considered one of the root causes of material degradation in Light Water Reactors (LWRs). The nuclear reactors impose harsh conditions to the integrity of material. High heat flux, high radiation fluence and high temperatures in acidic environments are very corrosive to the cladding material of nuclear fuels and to the internal structures of the pressure boundary. A total of 1511 piping and piping component failures on various safety and balance-of-plant systems have been reported to the U.S. Nuclear Regulatory Committee from 1961 to 1995. Forty-four percent of the total failures were corrosion-related events, with 14 percent caused by SCC [1].

Inter-Granular Stress Corrosion Cracking (IGSCC) of sensitized Type 304 stainless steel under normal Boiling Water Reactor (BWR) operating conditions (T=288°C, pure water) is primarily an electrochemical process that occurs at potentials that are more positive than a critical value of \(E_{\text{IGSCC}}\) (-0.23 \(V_{\text{SHE}}\), where \(V_{\text{SHE}}\) is a potential from the standard hydrogen electrode) [2]. However, the Crack Growth Rate (CGR) at \(E > E_{\text{IGSCC}}\) is also a function of potential, conductivity, degree of sensitization of the steel, flow velocity, mechanical load, and crack length. The Electrochemical Corrosion Potential (ECP) depends on the operation parameters of the Reactor Coolant System (RCS) in Nuclear Power Plants (NPPs) and on the water chemistry.

It was proved that the threshold potential for the occurrence of IGSCC of Alloy 600 in the PWR environment was -835 \(mV_{\text{SHE}}\), independent of the partial pressure of hydrogen [3]. IGSCC was found to occur ECP values that are more negative values than the threshold potential. Other types of SCC were observed at around -500 \(mV_{\text{SHE}}\) or more
positive ECP values [4]. Therefore, it is highly recommended that the ECP values in the PWR environment should be maintained in the range of greater than -835 mV\textsubscript{SHE} at 350°C and less than -500 mV\textsubscript{SHE} in order to minimize the material degradation caused by SCC.

Water chemistry is considered one of the most important parameters to reduce corrosion in the primary coolant circuit of NPPs. Even though strong efforts are focused on reducing corrosion, degradations due to corrosion in the RCS structures have been reported by the utilities of NPPs. Longer core cycles and higher enrichments of nuclear fuel, which require higher concentrations of boric acid and lithium hydroxide in RCS loops to increase the capacity factor of the NPPs, are recent trends in NPP operation. From the work experience in a commercial nuclear power plant, the goal of achieving higher capacity factors sometimes conflicts with the reduction of corrosion in NPPs. Therefore, it is vital the optimum conditions for a high capacity factor and low corrosive environment are determined.

In order to find the optimum conditions of the water chemistry in the LWR, an existing simulation code for the BWR environment was significantly upgraded. Also, using the improved BWR simulation code, a new simulation code for the PWR environment was developed in this study.

1.2 Overview

Computer simulation is widely used in the safety analysis of NPPs, from the initial design of NPPs to modification of the final safety analysis report. However there are insufficient computer codes available to simulate the electrochemistry of LWRs. Over the past decade or so, various groups have developed radiolysis codes for predicting the concentrations of radiolysis products around the primary coolant circuits of BWRs [5-8], but only two of those groups have predicted the ECP and CGR [9, 10]. REMAIN and ALERT are capable of predicting accumulated damage over specified Corrosion Evolutionary Paths (CEPs) such as nodes of the calculation paths [11, 12]. In this research, an advanced computer code FOCUS was developed. FOCUS is a further
development in the series of codes DAMAGE-PREDICTOR, REMAIN, and ALERT which have been used extensively in the past for modeling the primary coolant circuits of boiling water reactors (BWRs) [13]. The previous BWR simulation code, ALERT, was capable of calculating the effect of the sodium sulphate as impurities in the BWR coolant. In this study, sodium sulphate was replaced with sodium hydroxide and hydrogen chloride in order to observe the effect of different impurities. Those two different impurities could be included from the regeneration system of the spent resin in the condensate polishing system. The modified simulation code was named FOCUS.

The water chemistry of the primary side of the Pressurized Water Reactors (PWR) is quite different from the BWRs. PWRs use boric acid and lithium hydroxide for chemical shim, and hydrogen gas is injected into the reactor coolant in order to suppress the corrosion oxidants produced by the radiolytic decomposition of the coolant. Therefore the water chemistry in the PWRs is comparatively more complex than that of BWRs. Individual species concentrations and pH values are required in order to simulate the electrochemistry and to calculate the ECP for the PWR. Furthermore, the radiolytic model should be equipped in order to incorporate the effect of the gamma and neutron radiation. A computer code has been developed in order to calculate the concentration of individual species, pH and ECP values for PWRs. The computer codes developed from this research can be used to find the optimum radiochemistry condition for the reactor in order to reduce the corrosion degradations in the RCS pressure boundary and also to identify the mass transport and activity transport phenomena for the prevention of Axial Offset Anomaly (AOA) for PWRs.

The Mixed Potential Model (MPM) [2, 11, 14-17] was employed to calculate the ECP on the surface of the Alloy 600 and 690 tubes. This MPM has been developed for calculating ECP data for BWR in-vessel components and recirculation pipes using hydraulic and compositional data.

The newly developed simulation code for PWRs in this study, named P-ECP, is capable of calculating the radiolysis of the coolant, individual chemical species concentrations, and pH values at the operation temperature. Using those calculated data, the P-ECP code produces the ECP values using the MPM throughout the RCS loop
including the reactor internals, pressure vessel, RCS pipings, steam generator tubes, and pressurizer. For the calculation of the ECP values on Alloys 600 and 690, electrokinetic parameters obtained from the experimental work using the Alloy 600 and 690, were used in this study.

The Hydrogen Evolution Reaction (HER) has a dominant role in the corrosion of metals that occurs in high temperature aqueous systems, including corrosion processes and fuel cells. The most important factors governing the kinetics of HER and Hydrogen Oxidation Reaction (HOR) are the temperature, hydrogen pressure, and pH of the solutions [18-22]. In order to obtain the electrochemical kinetic parameters on Alloys 600 and 690 which are currently used as tube materials of the steam generators in pressurized water reactors (PWRs), steady-state measurements of the polarization curves of HER and HOR were carried out at different values of pH, 5.6, 7.3, and 10.2, and hydrogen pressures of 0.05, 0.5, and 5 bars, while the solution temperature was varied 30 °C stepwise from 160-250 °C. The steady-state potentiostatic polarization measurement was employed because the measured data between potentiodynamic scanning of the potential and the steady-state potentiostatic measurements showed significant differences in equilibrium potentials and corrosion currents, as shown in Figures 3.1 and 3.2. In order to obtain more exact data, a steady-state potentiostatic current measurement was employed in this research. Steady-state potentiostatic polarization measurements were used in order to derive empirical correlations of the metal dissolution currents using Alloys 600 and 690. Electrochemical Impedance Spectroscopy (EIS) measurements were employed in order to derive the Point Defect Model (PDM) of the metal dissolution currents using Alloy 690. The measured metal dissolution currents of Alloys 600 and 690 using the steady-state potentiostatic polarization methods were compared with the data measured by the potentiodynamic scanning method. The anodic corrosion currents of the steady-state measurements are lower than that of the measured data by potentiodynamic potential scanning method. A big difference exists also in the equilibrium potential of the steady-state measurement, which is 0.2 V more negative than that of the potential scanning polarization.
The empirically derived correlations using the steady-state measurement data were introduced into the P-ECP computer code to calculate the ECP values in a reactor coolant circuit of a PWR. In addition, the Point Defect Model (PDM) was adopted to identify the film properties of Alloy 690. The metal dissolution current as a function of applied potential was derived using the PDM and optimization method. Montemor et al. performed an investigation to identify properties of oxide films formed on Alloys 600 and 690 and reached the conclusion that the film formed on Alloy 600 showed that the nickel oxide dominated the semi-conducting properties, whereas chromium oxide dominated in the film formed on Alloy 690 [23]. Mott-Schottky plots were constructed using the obtained data from the steady-state potentiostatic polarization method using Alloy 690. The positive slope in the Mott-Schottky plot not only means the film has n-type semi-conducting property but also that a chromium oxide passive film dominates the semi-conducting property in the film formed on Alloy 690 [23, 24].

The P-ECP code developed in this study would make it possible for utilities to find the optimal electrochemical conditions for RCS coolant in order to minimize the corrosion damage in RCS loops. Also this code can be used to predict the accumulated crack damage after the proper crack growth model developed.
References


Chapter 2

The Electrochemical Corrosion Potential Code Development for BWRs and Simulation of the Crack Growth Rate

2.1 Introduction

In BWRs, degasified/demineralized pure water is used as coolant in the RCS loops. Since the discovery of core shroud cracking at Brunswick Unit 1 in 1990, subsequent inspections of other BWR internals have found IGSCC in many other sensitized stainless steel components. IGSCC and irradiation assisted stress corrosion cracking (IASCC) are now recognized as being not only serious threats to the safe operation of BWRs, but also as significant obstacles to extend the plant lives of light water reactors in general. IGSCC of sensitized Type 304 stainless steel (SS) has been a prominent problem in the recirculation piping and jet pumps of BWRs for more than three decades and it still represents the primary reason for the loss of availability of these systems. With respect to IGSCC, the most important environmental parameter is the ECP, because numerous laboratory and plant studies have shown that sensitized Type 304 SS suffers IGSCC only when the ECP is above some critical value (\(E_{IGSCC}\)). The value of \(E_{IGSCC}\) is found to depend on the degree of sensitization, temperature, pH, and the composition of the electrolyte, even though the Nuclear Regulatory Commission has sanctioned a single value of \(-0.23V_{SHE}\) at 288°C [1]. In order to suppress the ECP below \(E_{IGSCC}\), hydrogen injection operation was suggested to the BWR utilities, and this operation has been widely accepted in the BWR operation. The hydrogen injected into the RCS circuit reduces the concentration of oxygen and hydrogen peroxide produced from the radiolysis in the reactor core. If \(O_2\) and \(H_2O_2\) are reduced, the oxidation reaction will decrease and the corrosion potential is also suppressed as a result.
The Coupled Environment Fracture Model (CEFM) has been used extensively and successfully to model CGRs of Type 304 stainless steel in BWR coolant environments [2-7]. The medium in these coolant environments was basically pure water of low conductivity. Vankeerberghen et al. extended the CEFM to dilute sulphuric acid solutions over the temperature range 50-300ºC [8]. The changes were the incorporation of the effects of sulphuric acid and its dissociated species (HSO₄⁻ and SO₄²⁻) on the properties of the environment and the inclusion of a thermally activated crack tip strain rate. These modifications allow comparisons to be made of calculated and published experimental data on the effect of temperature on CGR in Type 304 SS in dilute sulphuric acid aqueous media over the temperature range of 50-300ºC. Such a model for calculating CGR over an extended temperature range is required for use in codes, such as DAMAGE PREDICTOR, REMAIN, and ALERT, which are currently being used to predict the accumulation of damage due to SCC in BWR primary coolant environments.

In this study, two different chemical impurities such as sodium hydroxide and hydrogen chloride were incorporated into the CEFM, and a corresponding pH calculation model was developed in order to calculate the ECP at the metal surface and crack tip. The modified CEFM is named the Advanced Coupled Environment Fracture Model (ACEFM). The ACEFM differs from the old CEFM in two important respects. Firstly, it incorporated thermally activated creep at the crack tip and hence include a temperature dependent crack tip strain rate that allows for more accurate simulation of the effect of temperature on the crack growth rate. The model has also been modified to incorporate more accurate calculation of conductivity by employing NaOH and HCl as basic and acidic electrolytes, respectively.

The newly developed ACEFM, pH calculation model, conductivity calculation model of the solution, and the Mixed Potential Model (MPM) were revised from an existing code, thereby the updated computer code was named FOCUS. The simulation results of electrochemistry and the prediction of the accumulated damages in BWRs were included in this study.
2.2 Coupled Environment Fracture Model

The original CEFM for intergranular stress corrosion cracking of Type 304 stainless steel in BWR primary heat transport circuits containing relatively pure water has been extended to incorporate the effects of sulphuric acid additions to the coolant and to include thermal activation of the crack tip strain rate [8, 9]. These extensions allow comparisons to be made between theoretically estimated and experimentally determined crack growth rates (CGRs) over a considerable temperature range after calibration at a single temperature.

![Diagram of Coupled Environment Fracture Model](image)

**Figure 2.1: Coupling of crack-internal and –external environments** [8].

The physico-electrochemical basis of the CEFM is shown in Fig. 2.1 [8]. Based on the charge conservation constraint, the crack advance is assumed to occur via the slip dissolution-repassivation mechanism,

\[
i_{\text{crack}} A_{\text{crack mouth}} + \int_S i_c^N ds = 0
\]

(2.1)
where $i_{\text{crack}}$ is the net (positive) current density exiting the crack mouth, $A_{\text{crack mouth}}$ is the area of the crack mouth, $i_{c}^{N}$ is the net (cathodic) current density due to charge transfer reactions on the external surface, and $ds$ is an increment in the external surface area. The subscript $S$ on the integral indicates that the integration is to be performed over the entire external surface. The CEFM performs its calculations in two steps. In the first step, it calculates the electrochemical potential of the external surface and in the second step the CGR is estimated. The electrochemical potential relatively far from the crack is assumed to be unchanged by the presence of the crack and, hence, is equal to the free corrosion potential (the ECP). The CGR calculation relies on splitting the crack environment into the crack-internal environment and the crack-external environment. To solve for the CGR, an electrochemical potential is assumed at the crack mouth, the boundary between the crack internal and external environments. This electrochemical potential is then changed until the crack internal current and crack external current match. Hence, the crack internal and external currents are calculated given a particular electrochemical potential at the crack mouth and for the prevailing ECP. For the calculation of the internal crack current an electrochemical potential is assumed at the crack tip. This electrochemical potential is changed until electro-neutrality is satisfied at the crack tip. For the calculation of the external current, a non-iterative procedure is followed involving the solution of Laplace’s equation. When Congleton’s approach is used for calculating the crack tip strain rate, which is a function of the CGR, an additional iteration must be performed to obtain the CGR [10].

2.3 Revised CEFM

A revised CEFM model has been developed to incorporate the effects of sodium hydroxide (NaOH) and hydrochloric acid (HCl) based on the model developed by Vankeerberghen and Macdonald [8]. In this study, the species have been changed from sulfuric acid to sodium hydroxide and hydrochloric acid those species could be included
from regeneration system of the resin in the condensate polishing system. Concentrations of HCl and NaOH (ppb) were taken as input and the pH of the solution was calculated from seven simultaneous equations. The dissociation reactions occurring in the solution are the following:

\[ H_2O \leftrightarrow K \rightarrow H^+ (m_{H^+}) + OH^- (m_{OH^-}) \]  \hspace{1cm} (2.2)

\[ NaCl(m_{NaCl}) \leftrightarrow K \rightarrow Na^+ (m_{Na^+}) + Cl^- (m_{Cl^-}) \]  \hspace{1cm} (2.3)

\[ HCl(m_{HCl}) \leftrightarrow K \rightarrow H^+ (m_{H^+}) + Cl^- (m_{Cl^-}) \]  \hspace{1cm} (2.4)

\[ NaOH(m_{NaOH}) \leftrightarrow K \rightarrow Na^+ (m_{Na^+}) + OH^- (m_{OH^-}) \]  \hspace{1cm} (2.5)

where the \( K_i \) are the equilibrium constants for the corresponding reactions and \( m_{H^+}, \) etc. are the molal concentrations of individual species. The sodium chloride forms by the combination of the sodium ions and chloride ions from the two impurities considered.

### 2.3.1 Electroneutrality

The solution after dissociation should be electrically neutral, as all the ingredients are neutral to begin with. This implies that the sum of concentrations of all the charged species multiplied by their charge values should be zero. In our case, since the charge for each species is either 1 or -1, the sum of concentrations of positively charged particles should be equal to that of negatively charged particles. The equation becomes the following where the symbols are taken from the reactions given above.

\[ m_{H^+} + m_{Na^+} - m_{OH^-} - m_{Cl^-} = 0 \]  \hspace{1cm} (2.6)
2.3.2 Mass Balance

The sum of concentrations of each species in the final solution should be equal to its concentration in the initial ingredients. If \( m_{NaOH}^0 \) and \( m_{HCl}^0 \) are the concentrations of NaOH and HCl which were mixed, then the equations become

\[ m_{Na^+} + m_{NaCl} + m_{NaOH} = m_{NaOH}^0 \quad (2.7) \]

\[ m_{Cl^-} + m_{NaCl} + m_{HCl} = m_{HCl}^0 \quad (2.8) \]

The equilibrium constants for the dissociation reactions in the system mentioned above are defined as

\[ K_a(T) = \frac{a_{H^+}a_{OH^-}}{a_w} = \frac{m_{H^+}m_{OH^-}\gamma_{H^+}\gamma_{OH^-}}{a_w} \quad (2.9) \]

\[ K_1(T) = \frac{a_{Na^+}a_{Cl^-}}{a_{NaCl}} = \frac{m_{Na^+}m_{Cl^-}\gamma_{Na^+}\gamma_{Cl^-}}{m_{NaCl}\gamma_{NaCl}} \quad (2.11) \]

\[ K_2(T) = \frac{a_{H^+}a_{Cl^-}}{a_{HCl}} = \frac{m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-}}{m_{HCl}\gamma_{HCl}} \quad (2.12) \]

\[ K_3(T) = \frac{a_{Na^+}a_{OH^-}}{a_{NaOH}} = \frac{m_{Na^+}m_{OH^-}\gamma_{Na^+}\gamma_{OH^-}}{m_{NaOH}\gamma_{NaOH}} \quad (2.13) \]

where the \( m_i \), \( a_i \) and \( \gamma_i \) are respectively the molal concentration, activity and activity coefficient of species \( i \) in the system. The activity of water \( a_w \) can be assumed to be unity.
for dilute solutions. The activity coefficients are calculated using the extended form of Debye-Huckel theory, as given in Naumov et al. [11]

$$
\log(\gamma_i) = -\frac{Az_i^2 \sqrt{\mu}}{(1 + B a^0 \sqrt{\mu})}
$$

(2.14)

where $\mu = 0.5 \times (m_i^2 z_i^2)$ is the ionic strength of the solution and $z_i$ is the ion charge, $a^0$ is the distance of closest approach and A and B are constants which depend on temperature, density (pressure) and dielectric constant. Values for A and B are given by Naumov et al. as [11]:

$$
A = 0.4241 + 0.00321 T - 2.0 \times 10^{-5} T^2 + 5.95143 \times 10^{-8} T^3
$$

(2.15)

$$
B = 0.3237 + 0.00019 T - 2.12586 \times 10^{-7} T^2 + 1.4241 \times 10^{-9} T^3
$$

(2.16)

where $T$ is the temperature in degrees Celsius. The value of $a^0$ in Eq. 2.14 has been taken as $4.5 \times 10^{-8}$ cm [11]. In this study, the calculation showed that $\gamma_H^+ = \gamma_{OH^-} = \gamma_{Na^+} = \gamma_{Cl^-}$. Therefore, they can be denoted by a common symbol $\gamma$. Also, $\gamma_{NaCl} = \gamma_{HCl} = \gamma_{NaOH} = 1$. Hence, all of the activity coefficients can be denoted as

$$
\gamma_H^+ \gamma_{OH^-} = \gamma_{Na^+} \gamma_{Cl^-} = \gamma_H^+ \gamma_{Cl^-} = \gamma_{Na^+} \gamma_{OH^-} = \gamma^2 = G
$$

(2.17)

The various dissociation constants were obtained as a function of temperature in Kelvin by curve fitting on experimental data from Naumov et al. [11] and

$$
pK_w = 4673.8604/T_K - 7.0269 + 0.0180 \times T_K
$$

(2.18)

$$
pK_1 = 483.7740/T_K - 5.0881 + 0.0091 \times T_K
$$

(2.19)
where $pK_i$ are the logarithmic represents of dissociation constants of reaction $i$ and $T_K$ is the temperature in Kelvin. So, on adding sodium hydroxide and hydrochloric acid to water four ionic species will be present in the solution: the hydrogen ion, $H^+$, the hydroxyl ion $OH^-$, the sodium ion $Na^+$ and the chloride ion $Cl^-$. Also, there are some amount of un-dissociated hydrochloric acid and sodium hydroxide left in the solution. $Na^+$ and $Cl^-$ combine to form some $NaCl$ in the solution. So, there are seven species in the solution whose concentrations are unknown. We have seven equations to solve for these seven unknowns. By solving this set of seven non-linear equations, we can get the concentrations of all the species in the solution.

### 2.3.3 Solution of Non-linear Equations

The simultaneous equations in Eq. 2.6 through Eq. 2.13 have been solved by using Newton-Raphson method for non-linear systems of equations. A typical problem gives $N$ functional relations to be zeroed, involving variables, $x_i$, $i = 1, 2, 3, \ldots, N$:

$$F_i(x_1, x_2, \ldots, x_N) = 0 \quad i = 1, 2, \ldots, N \quad (2.22)$$

where $x$ denotes the entire vector of variables $x_i$ and $F$ denotes the entire vector of functions $F_i$. In the neighborhood of $x$, each of the functions $F_i$ can be expanded as a Taylor series

$$F_i(x + \delta x) = F_i(x) + \sum(\frac{\partial F_i}{\partial x_j}) \delta x_j + O(\delta x^2) \quad (2.23)$$

where the summation is taken from $j = 1$ to $N$. The matrix of partial derivatives appearing in the above equation is the Jacobian matrix $J$. 

\[
pK_2 = \frac{2684.0060}{T_K} - 16.4465 + 0.0226 \times T_K \quad (2.20)
\]

\[
pK_3 = \frac{1324.6809}{T_K} - 8.2525 + 0.0120 \times T_K \quad (2.21)
\]
\[ J_{ij} \equiv \left( \frac{\partial F_i}{\partial x_j} \right) \]  \hspace{1cm} (2.24)

In matrix notation, the above equation becomes

\[ F(x + \delta x) = F(x) + J \delta x + O(\delta x^2) \]  \hspace{1cm} (2.25)

By neglecting the term of order \( \delta x^2 \) and higher and by setting \( F(x + \delta x) = 0 \), we get a set of linear equations for the correction \( \delta x \) that moves each function closer to zero simultaneously.

\[ J \delta x = -F \]  \hspace{1cm} (2.26)

This set of linear equations can be solved using Gauss elimination method and the new value of variables is given as

\[ x_{\text{new}} = x_{\text{old}} + \delta x \]  \hspace{1cm} (2.27)

This process is iterated till the values converge.

The system of seven non-linear equations is reduced to four functions, which have to be zeroed. The matrix \( F \) derived is given as

\[
F = \begin{bmatrix}
m_{OH} - K_w / m_{H^+} G \\
m_{H^+} + m_{Na^+} - m_{OH^-} - m_{Cl^-} \\
m_{Na^+} + m_{Na^+} m_{Cl^-} G / K_1 + m_{Na^+} G / K_3 - m_{NaOH}^0 \\
m_{Cl^-} + m_{Na^+} m_{Cl^-} G / K_1 + m_{H^+} m_{Cl^-} G / K_2 - m_{HCl}^0
\end{bmatrix}
\]  \hspace{1cm} (2.28)

The finite difference method was used to solve the Jacobian matrix. The step value while calculating the Jacobian matrix using finite difference method has been taken as \( 10^{-8} \), which is approximately square root of the machine precision. \( \delta x \) gives the Newton
direction in which the functions decrease. A full Newton step is taken first and the new value of the functions at $x_{\text{new}}$ is compared to value of the function at $x_{\text{old}}$. If the new value is less than the old value, then full Newton step is taken, otherwise the step in the Newton direction is reduced until the value of the functions at the $x_{\text{new}}$ is less than the value at $x_{\text{old}}$. This process is repeated until convergence.

It was observed that at very low concentrations of NaOH and HCl (less than 0.01 ppb respectively), the Newton-Raphson iteration method occasionally fails to converge. However, changing the initial guess to a more appropriate value allowed convergence. So, the initial guess value for $H^+$ ion was varied from a very low value to a maximum of $m_0^{HCl}$.

### 2.3.4 Modeling Results

The revised CEFM described above incorporates the effects of sodium hydroxide and hydrochloric acid to calculate the CGR in the RCS of BWRs. The input data for the calculations of the revised CEFM were shown in Table 2.1. This is the same geometry and data as the calculation of the CEFM by Vankeeberghen et al [8], except the concentrations of NaOH and HCl.

<table>
<thead>
<tr>
<th>Table 2.1: Input parameters for the calculation with the revised CEFM [8].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress intensity factor (MPa√m) = 33</td>
</tr>
<tr>
<td>Oxygen concentration (ppb O$_2$) = 200</td>
</tr>
<tr>
<td>Hydrogen concentration (ppb H$_2$) $&lt;&lt;$ 1</td>
</tr>
<tr>
<td>H$_2$O$_2$ concentration (ppb H$_2$O$_2$) $&lt;&lt;$ 1</td>
</tr>
<tr>
<td>Concentration NaOH (ppb NaOH) = 100</td>
</tr>
<tr>
<td>Concentration HCl (ppb HCl) = 100</td>
</tr>
</tbody>
</table>
The result included in Fig.2.2 pointed out the temperature dependency of the CGR. However the maximum value of the CGR was reached at around 125 ºC, and the CGR decreased after 125 ºC, then increased again after 275 ºC.

![Graph showing the effect of temperature on predicted CGR in Type 304 SS in dilute NaOH and HCl solution at ambient temperature (25ºC), conductivity of 0.27 µS/cm, and dissolved oxygen concentration of 200 ppb.]

**Figure 2.2:** The effect of temperature on predicted CGR in Type 304 SS in dilute NaOH and HCl solution at ambient temperature (25ºC), conductivity of 0.27 µS/cm, and dissolved oxygen concentration of 200 ppb.
2.4 Development of a New Computer Code using the Revised CEFM

The existing code, ALERT, has now been superseded by a new code, FOCUS. This new code predicts water chemistry (radiolysis), electrochemical corrosion potential, crack velocity, and accumulated damage (crack depth) in BWR primary coolant circuits at many points simultaneously under normal water chemistry (NWC) and hydrogen water chemistry (HWC) operating protocols over specified operating histories. FOCUS includes the ACEFM as a subroutine for estimating crack growth rate over a wide temperature range and hence is particularly useful for modeling BWRs that are subject to frequent start-ups and shut downs. Additionally, a more robust and flexible water chemistry code was incorporated into FOCUS that allows for more accurate simulation of changes in coolant conductivity under upset conditions. The application of FOCUS for modeling the chemistry, electrochemistry, and the accumulation of the IGSCC damage in BWR primary coolant circuits is illustrated in this study.

2.4.1 The FOCUS Code

2.4.1.1 Code Structure

FOCUS is designed to predict water chemistry radiolysis, ECP, crack velocity, and accumulated damage deterministically (i.e., based on natural laws governing material and electrochemical behavior). The code contains four principal sub-modules; the water radiolysis code (RADIOCHEM), an Advanced Mixed Potential Model (AMPM), an Advanced Coupled Environment Fracture Model (ACEFM), and a Damage Function Analysis (DFA) module that integrates the damage over the specified corrosion evolutionary path (CEP).

The algorithms employed in this code are shown in Fig. 2.3. The main body of the algorithm is the water radiolysis model, which yields the concentrations of radiolysis products from the decomposition of water under neutron and gamma irradiation, coupled
with homogeneous and heterogeneous chemical reactions, liquid/steam transfer of volatile species (H₂ and O₂), and fluid convection. After the species concentrations have been determined at every point around the heat transport circuit under steady-state conditions, the ECP is calculated using the AMPM.

2.4.1.2 Radiolytic Yield

The rate at which any primary radiolytic species produced is given by

\[
R_i = \left( \frac{G_i^\gamma \Gamma^\gamma}{100N_V} + \frac{G_i^n \Gamma^n}{100N_V} + \frac{G_i^\alpha \Gamma^\alpha}{100N_V} \right) F \rho
\]

(2.29)

where \( R_i \) is the radiolytic yield of species \( i \) having units of mol/cm³·s, \( G_i^\gamma \), \( G_i^n \), and \( G_i^\alpha \) are the radiolytic yields for gamma photons, neutrons, and alpha particles, respectively, in number of particles per 100eV of energy absorbed, \( N_V \) is Avogadro's number, \( F \) equals

**Figure 2.3: The algorithm of the FOCUS code.**
6.25x10^{13} \text{ (the conversion factor from Rad/sec to eV/gram-sec), and } \rho \text{ is the water density in g/cm}^3. \Gamma^\gamma, \Gamma^n, \text{ and } \Gamma^\alpha \text{ are the gamma photon, neutron, and } \alpha\text{-particle energy dose rates to the water, respectively, in units of Rad/s. Table 2.2 shows compiled } G \text{ values for the 13 radiolysis products.}

Table 2.2: G values for primary radiolytic species [12].

<table>
<thead>
<tr>
<th>Species</th>
<th>$G^\gamma$(No./100eV)</th>
<th>$G^n$(No./100eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>e$^-$</td>
<td>4.15</td>
<td>0.93</td>
</tr>
<tr>
<td>H</td>
<td>1.08</td>
<td>0.50</td>
</tr>
<tr>
<td>OH</td>
<td>3.97</td>
<td>1.09</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>1.25</td>
<td>0.99</td>
</tr>
<tr>
<td>HO$_2$</td>
<td>0.00</td>
<td>0.04</td>
</tr>
<tr>
<td>HO$_2^-$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O$_2^-$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.62</td>
<td>0.88</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>H$^+$</td>
<td>4.15</td>
<td>0.93</td>
</tr>
<tr>
<td>O$_2g$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>H$_2g$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The dose rate due to $\alpha$-particle ($^4$He$_2$ nuclei) is negligible and can be ignored, because these particles are effectively stopped by the fuel cladding. Accordingly, it is necessary to consider only gamma photons and neutrons when modeling BWR primary coolant circuits. A wide spectrum of gamma photon and neutron energies exist in a reactor core and any highly accurate simulation of the radiochemistry of the coolant should recognize these distributions. Furthermore, the core in any reactor is not homogeneous with regard to dose rate and hence the horizontal geometric dispersion of the dose rate should be incorporated in any accurate model. These factors are ignored in
the present work, as they are in other models. Note that the distributions in the gamma photon and neutron dose rates in the vertical direction through the core are incorporated in the FOCUS code.

2.4.1.3 Advanced Mixed Potential Model (AMPM)

The MPM, which was originally developed by Macdonald [13], is based on the physical condition that charge conservation must be obeyed at a metal surface when a corrosion process is in progress. The charge conservation constraint is

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

(2.30)

where $i_{R/O,j}$ is the partial current density due to the $j^{th}$ redox couple in the system and $i_{corr}$ is the corrosion current density of the material.

For the Type 304 SS, the steel oxidation current density, $i_{corr}$, was modeled as an empirical function of voltage [14].

$$i_{corr} = \frac{e^{(E-E_0)/b_f} - e^{-(E-E_0)/b_f}}{384.62e^{4416/T} + X}$$

(2.31)

where

$$X = \frac{e^{(E-E_0)/b_f}}{2.61 \times 10^{-3} e^{-4416/T + 0.52(5E-E_0)^{1/3}}}$$

(2.32)
\[ E_o = 0.122 - 1.5286 \times 10^{-3} T \]  

(2.33)

where \( E \) is the ECP, \( E_0 \) is the standard potential, and \( b_f \) and \( b_r \) are the forward and reverse Tafel constants, respectively, for the metal oxidation reaction, with values of 0.06V being assumed for both Tafel constants. The temperature, \( T \), is in Kelvin.

The current density \( i_{R/O} \) for a redox couple

\[ R \leftrightarrow O + ne \]  

(2.34)

(where \( R \) is the reduced species and \( O \) is the oxidized species) can be expressed in terms of a generalized Butler-Volmer equation as

\[
\frac{i_{R/O}}{i_0} = \frac{e^{(E-E^0_{R/O})/b_f} - e^{-(E-E^0_{R/O})/b_r}}{1 + e^{(E-E^0_{R/O})/b_f} - e^{-(E-E^0_{R/O})/b_r}} \quad \text{(2.35)}
\]

where \( i_0 \) is the exchange current density, \( i_{l,f} \) and \( i_{l,r} \) are the mass-transfer limited currents for the forward and reverse directions of the redox reaction, respectively. \( E^e_{R/O} \) is the equilibrium potential for this reaction as computed from the Nernst equation:

\[
E^e_{R/O} = E^0_{R/O} - \frac{2.303RT}{nF} \log \left( \frac{a_R}{a_O} \right) \quad \text{(2.36)}
\]

where \( a_R \) and \( a_O \) are the thermodynamic activities of \( R \) and \( O \), respectively, and \( E^0_{R/O} \) is the standard potential, which is readily calculated from the change in standard Gibbs energy for the cell reaction (\( \Delta G^0_{R/O} \));

\[
E^0_{R/O} = -\frac{\Delta G^0_{R/O}}{nF} \quad \text{(2.37)}
\]
where \( n \) is the oxidation state and \( F \) is the Faraday constant.

Limiting currents are calculated using the equation:

\[
i_{l,R/O} = \pm 0.0165nFC_d^{b\,R/O} \Re^{-0.86} Sc^{0.33} / d
\]

where the sign depends on whether the reaction is in the forward (+) or reverse (-) direction, \( F \) is Faraday's number, \( D \) is the diffusivity of the redox species, \( C_d^{b\,R/O} \) is the bulk concentration of R or O, as appropriate, \( \Re \) is the Reynolds number \( (\Re=Vd/\eta) \), \( Sc \) is the Schmidt number \( (Sc=\eta/D) \), \( d \) is the channel diameter, \( V \) is the flow velocity, and \( \eta \) is the kinematic viscosity.

The redox reactions of interest in this study are assumed to be:

\[
2\H^+ + 2e^- = \H_2
\]

\[
\O_2 + 4\H^+ + 4e^- = 2\H_2\O
\]

And

\[
\H_2\O_2 + 2\H^+ + 2e^- = 2\H_2\O
\]

In this regard, it is important to note that the maximum contribution that any given radiolytic species can make to the ECP is roughly proportional to its partial current given in Eq. 2.38, and hence concentration. Thus, in BWR simulations, the concentrations of \( \H_2 \), \( \O_2 \), and \( \H_2\O_2 \) are calculated to be orders of magnitude greater than those of any other radiolytic species and therefore only these three need to be considered.

The crack growth rate model, namely ACEFM, generates crack growth rate as a function of time and hence crack length for specific input parameters, including stress intensity, temperature, ECP, conductivity, pH, and flow velocity. Previous modeling
work has shown [15], and experimental observations have confirmed, that the crack growth rate depends on crack length, independent of the stress intensity. Thus, Macdonald, et al. [2] have shown that it is necessary to differentiate between the mechanical crack length (MCL), which, together with the stress, establishes the stress intensity, and the electrochemical crack length (ECL), which partly controls the potential distribution between the crack tip and the external surface. Because current flows through the path of least resistance, the electrochemical crack length may be defined as being, in many instances, the shortest distance between the crack tip and the external surface, where it is consumed by oxygen reduction. For a CT specimen, the ECL (distance between the crack tip and the side surfaces of the specimen) is independent of the mechanical crack length and remains approximately constant as the crack propagates through the specimen, even though the MCL increases. On the other hand, for a thumbnail crack in a surface, the MCL and the ECL, both being distributed quantities, appear to be virtually identical. For a thumbnail crack in an infinite plate, the stress intensity is lowest at the edge of the crack and is highest in the center. Likewise, the ECL is smallest at the crack edge and is greatest in the center. As the ECL increases, the IR potential drop down the crack reduces the potential drop across the external surface that is available for reducing oxygen, which consumes the coupling current between the crack and the external surface. Accordingly, the mechanical driving force for crack propagation decreases as one moves from the crack center to the crack edge whereas the electrochemical driving force (potential drop across the external surface) increases. It is found that the crack growth rate is higher at the edge than in the center, resulting in the formation of elongated thumbnail geometry, thereby illustrating the dominance of electrochemical factors over stress (intensity) in controlling the rate of environmentally-induced crack growth. Thus, an important conclusion is that the crack growth rate should decrease with increasing electrochemical crack length. This expectation is well illustrated in the calculated crack length plotted in Fig. 2.8.
2.4.1.4 Damage Function Analysis (DFA)

The cracks are assumed to grow from an initial length of 0.1 cm and the crack length, \( x_N \), over the anticipated service time of a component, \( t \), is obtained by an accumulation of the crack advances over \( N \) periods of time \( \Delta t_1, \ldots, \Delta t_i, \ldots \Delta t_N \).

\[
x_i = x_{i-1} + \text{CGR}_i \cdot \Delta t_i, \quad i = 1, \ldots, N
\]  

(2.42)

\[
t = \sum_{i=1}^{N} \Delta t_i
\]  

(2.43)

The crack growth rate, \( \text{CGR}_i \), was presumed to be time-independent for each interval, \( \Delta t_i \). The initial crack length, \( x_0 \), corresponds to the depth of a pre-existing crack (as may have been detected during an inspection or assumed for a safety analysis scenario).

2.4.2 Simulation of Plant Operation

A simplified BWR coolant circuit diagram is shown in Fig. 2.4. The reactor operates at approximately 288°C, producing steam at a pressure of about 68bar. FOCUS calculates the concentrations of chemical species, the corrosion potential, and the growth rate of a crack of any specified length at closely spaced points within each of the coolant circuit sections numbered from 1 to 10 in Fig. 2.4 under NWC and HWC conditions. The code also integrates the crack growth rate along the corrosion evolutionary path (CEP) to yield the crack length at any specified point along that path.

2.4.2.1 Corrosion Evolutionary Path

To illustrate the application of FOCUS, in the present analysis, it is presumed that the reactor was operated for 12 months from initial heat up and had one scram midway
through that period of operation. The reactor was maintained at 95% of full reactor power or at full power, in order to consider normal reactor power fluctuations (Fig. 2.5). The Corrosion Evolutionary Path (CEP), summarized in this figure, includes 24-hour start-up and outages (at 6 months) over which the reactor parameters (power level, flow velocity, temperature) were assumed to vary linearly with time. The electrolyte concentration (5ppb NaOH and HCl respectively) was maintained constant during the start-up and outage with the conductivity varying according to the model presented above and shown in Fig.2.8. During NWC operation, no hydrogen is added to the coolant while, under HWC operation, hydrogen is injected into the feedwater to maintain the concentration at 0.5ppm. Cracks with initial lengths of 0.1cm were assumed to exist in all sections of the primary coolant circuit. Furthermore, for the present calculations, the cracks are assumed to be loaded to stress intensity factors of 15 MPa$\sqrt{m}$ (in the core) or 27.5 MPa$\sqrt{m}$ (out of core). Finally, the concentrations of NaOH and HCl during normal operation were set at 5ppb. The four main predicted parameters, ECP, conductivity, CGR, and the crack depth, are displayed in Fig. 2.6 through 2.9.

Figure 2.4: Typical equipment and coolant flow in the BWR primary system.

Legend
1. Core Channel (CC)
2. Core Bypass (CB)
3. Upper Plenum (UP)
4. Mixing Plenum (MP)
5. Upper Downcomer (UD)
6. Lower Downcomer (LD)
7. Recirculation line (RE)
8. Jet Pump (JP)
9. Bottom of the Lower Plenum (BLP)
10. Top of the Lower Plenum (TLP)
Figure 2.5: Reactor power variation and feedwater hydrogen concentration over a single cycle (12 months).

Table 2.3: Input parameters for the calculation with the FOCUS code.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress intensity factor (MPa√m) = 15</td>
<td>(in core), 27.5 (other regions)</td>
</tr>
<tr>
<td>Concentration HCl during the normal operation</td>
<td>= 5ppb</td>
</tr>
<tr>
<td>Concentration NaOH during the normal operation</td>
<td>= 5ppb</td>
</tr>
</tbody>
</table>

2.4.3 Simulation Results and Discussion

During full power operation, the ECP values in the coolant circuit under NWC operation were in the range of 271mV_{SHE} in the core channels to -36mV_{SHE} at the exit to the recirculation pipes. However, under HWC operation with 0.5 ppm of hydrogen in the feedwater, the ECP lay in the range from 270mV_{SHE} in the core channels to -623mV_{SHE} at the bottom of the lower plenum. The predicted ECP values in the core channels under both NWC and HWC were essentially identical, because hydrogen was removed from the liquid (water) phase in the core by boiling transfer to the steam phase. RADIOCHEM
predicted that the hydrogen concentrations in the core channels for both cases (NWC and HWC) were almost the same and were very low.

![Graph showing ECP values for NWC and HWC](image)

**Figure 2.6: ECP values of NWC (Top) and HWC (Bottom), 0.5 ppm of hydrogen**

The bulk conductivities for the reactor coolant involving NaOH and HCl species are shown in Fig. 2.6. The conductivity calculated using ACEFM was found to be a function of the NaOH and HCl concentrations and the bulk temperature with little contribution being apparent from the radiolysis products. Therefore, the difference in bulk conductivity for NWC and HWC operation was not significant. From a separate
calculation that was performed to investigate the effect of changes in temperature, the CGR was found to pass through a maximum at around 150-200ºC, as previously noted.

Figure 2.7: Bulk conductivity of NWC (Top) and HWC ((Bottom), 0.5 ppm of hydrogen) operation.

Figures 2.6 through 2.8 show that the electrochemical parameters and CGRs at the beginning of the operation near time zero and at the reactor trip near 6 months are pretty
higher than the normal operation. It is because the concentrations of impurities are higher than those of the normal operation and the reactor power is low to zero.

Figure 2.8: CGR values of NWC (Top) and HWC (Bottom), 0.5 ppm of hydrogen operation.

The predicted CGR in the coolant circuit components during NWC and HWC operation of the BWR is shown in Fig. 2.8. The data presented in Fig. 2.6 and 2.8 revealed a close correlation between the predicted ECP and CGR, no doubt reflecting the fact that the latter was a quasi exponential function of the former. Accordingly, it was
expected that the core internal components at high ECP values have high CGR values, and vice versa.

FOCUS predicts the accumulated damage (crack length) in components in the reactor primary coolant circuit under any given set of operating conditions. In this way, it is possible to compare the accumulated damage (crack depth) between NWC and HWC operating conditions over identical corrosion evolutionary paths (operating histories). In doing so, it is important to note that the damage is considered to develop from initial, 0.1cm deep cracks. This approach, of course, ignores the initiation process which, in this case, was the time for the crack to nucleate and grow to 0.1cm depth. Incorporation of the initiation process into FOCUS is underway, by introducing the deterministic Damage Function Analysis (DFA) for describing the dynamics of passivity breakdown and nucleus growth [16]. Because the crack growth rate in the fuel channels is virtually the same for both NWC and HWC (0.5ppm hydrogen in the feedwater), the accumulated damage is expected to be similar, as observed. On the other hand, the accumulated crack growth in the core bypass for the one year of NWC operation is 0.21cm, but is only 0.04cm for one year HWC operation. The accumulated damage (crack length) was distinctly lower as the result of HWC operation compared with NWC operation, at least for out-of-core components. Furthermore, because the ECP was much lower under HWC than under NWC in all components except those in the core and upper plenum, and assuming that passivity breakdown followed by micro pit growth is the precursor to IGSCC, DFA predicts that the initiation time will be considerably longer under HWC conditions than under NWC conditions [16]. Accordingly, it is likely that FOCUS significantly underestimates the benefits of HWC, but only in those regions where the ECP is greatly reduced.
Figure 2.9: Crack depth versus operating time for NWC (Top) and HWC ((Bottom), 0.5 ppm of hydrogen) operation of a BWR.

Focusing now on crack growth, the calculated damage at various points around the primary coolant circuit under both NWC and HWC conditions was summarized in bar-graph form in Fig. 2.10. These data again indicate that the CGR values in the BWR internals are closely related to the ECP values during both NWC and HWC operations. In particular they indicate only marginal benefit of HWC over NWC for cracks in the upper plenum (UP), the mixing plenum (MP), and the jet pumps (JP), where “marginal” was taken to be a diminution in CGR of no more than 50%. The calculations also demonstrate
that FOCUS can estimate accumulated damage at many locations within the coolant circuit simultaneously, while the plant traverses a complicated Corrosion Evolutionary Path (CEP). Clearly, the inclusion of a viable crack initiation model is an important future development.

![Graph comparing accumulated damage](image)

**Figure 2.10: Comparison of the accumulated damage of the Rx. internals after 12 month NWC and HWC operation.**

### 2.5 Verification

An important point that needs to be emphasized is that the maximum contribution that any given radiolytic species can make to the ECP is roughly proportional to its concentration. The accuracy of the mixed potential model and radio-chemistry model incorporated in the FOCUS code has been evaluated by comparing calculated ECP values for Type 304 SS against measured BWR plant data. Two sets of data have been employed, as shown in Table 2.4 and 2.5. ECP\textsubscript{calc} values in the same tables were calculated by the FOCUS code using the same operational conditions with the experimental conditions of the corresponding BWR power plants.
The first set of ECP data was measured by Indig et al. [1] in an autoclave attached to the recirculation piping of the Dresden-2 BWR. ECP values calculated using the same flow conditions and configuration with the experimental conditions are compared with the measured data in Table 2.4. The measured data and calculated data show a good agreement with each other in the ECP values. The FOCUS code used electrochemical kinetic parameters of Type 304 SS. It is expected that the measured ECP data and the actual (real) ECP values will be different because of the different radio-chemical plant conditions such as radiolitic products.

Table 2.4: Calculated vs. measured ECP data for Dresden-2 BWR [1].

<table>
<thead>
<tr>
<th>Test No.</th>
<th>([H_2]) (mg/kg)</th>
<th>([O_2]) (mg/kg)</th>
<th>ECP_{meas.}/V_{SHE}</th>
<th>ECP_{calc.}/V_{SHE}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>0.270</td>
<td>-0.040</td>
<td>-0.051</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>0.040</td>
<td>-0.185</td>
<td>-0.112</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
<td>0.020</td>
<td>-0.235</td>
<td>-0.146</td>
</tr>
<tr>
<td>4</td>
<td>0.135</td>
<td>0.005 to 0.020</td>
<td>-0.255</td>
<td>-0.224</td>
</tr>
<tr>
<td>5</td>
<td>0.135</td>
<td>0.005 to 0.023</td>
<td>-0.240</td>
<td>-0.218</td>
</tr>
<tr>
<td>6</td>
<td>0.135</td>
<td>0.003 to 0.030</td>
<td>-0.250</td>
<td>-0.206</td>
</tr>
<tr>
<td>7</td>
<td>0.135</td>
<td>0.007 to 0.019</td>
<td>-0.255</td>
<td>-0.227</td>
</tr>
</tbody>
</table>

Flow velocity = 5 cm/s. Hydrodynamic diameter = 10 cm. \(T = 288\) °C.

The second case, we employed measurement data shown in Table 2.5 that were obtained during a Hydrogen Water Chemistry (HWC) mini-test at the Leibstadt BWR in Switzerland. The ECP_{calc} values were also calculated by the FOCUS code using the input data which were the same as the experimental conditions. Excellent agreement was obtained in both measured and calculated ECP values agreeing within the combined uncertainty levels.
Table 2.5: Calculated vs. measured ECP data for the Leibstadt BWR [17].

<table>
<thead>
<tr>
<th>Feed water [H₂] (mg/kg)</th>
<th>Recirc. [H₂] (mg/kg)</th>
<th>Recirc. [O₂] (mg/kg)</th>
<th>ECP_{meas}/V_{SHE}</th>
<th>ECP_{calc}/V_{SHE}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.005</td>
<td>0.200</td>
<td>0.125</td>
<td>-0.031</td>
</tr>
<tr>
<td>0.5</td>
<td>0.070</td>
<td>0.004</td>
<td>-0.15</td>
<td>-0.321</td>
</tr>
<tr>
<td>0.8</td>
<td>0.200</td>
<td>0.002</td>
<td>-0.320</td>
<td>-0.322</td>
</tr>
<tr>
<td>1.2</td>
<td>0.400</td>
<td>0.002</td>
<td>-0.338</td>
<td>-0.323</td>
</tr>
<tr>
<td>1.5</td>
<td>0.450</td>
<td>0.002</td>
<td>-0.340</td>
<td>-0.324</td>
</tr>
<tr>
<td>2.0</td>
<td>0.700</td>
<td>0.002</td>
<td>-0.380</td>
<td>-0.324</td>
</tr>
</tbody>
</table>

Flow velocity = 50 cm/s. Hydrodynamic diameter = 2.54 cm. T = 279 °C.

2.6 Conclusion

From the simulation results for Normal Water Chemistry (NWC) operation, the highest ECP values occurred in the fuel channels and lay around 270 mV_{SHE}. This value was very high when compared to the critical potential for IGSCC in sensitized Type 304 SS, E_{IGSCC}, of about -230 mV_{SHE} at the BWR operating temperature of 288°C. While the ECP is lower than the core channel value in the balance of the primary coolant circuit, it was predicted to exceed (be more positive than) E_{IGSCC} for all sections under NWC conditions. On the other hand, except for the core channels, in which hydrogen was removed by boiling, the ECP values during the HWC operation were considerably lower than that during the NWC operation (by as much as 800mV). Under HWC operation, it is concluded that the injected hydrogen suppresses the radiolytic production of the oxygen and hydrogen peroxide and provides an additional oxidation reaction (the oxidation of molecular hydrogen) at very negative potentials, thereby shifting the ECP in the negative direction. The value that prevails is a delicate balance between the concentrations of hydrogen and hydrogen peroxide. The decomposition of hydrogen peroxide and its reaction with hydrogen, particularly in the downcomer, (where a sufficiently high γ dose
rate existed to facilitate the recombination process), was concluded to be the most important factor in controlling the ECP in BWR primary coolant circuits.

The calculated damage throughout the CEP around the primary coolant circuit under both NWC and HWC operation conditions included in Fig. 2.9 and 2.10 demonstrated that the effect of hydrogen injection was significant in the CB and TLP because of the viability of the injected hydrogen.
References


Chapter 3

The Steady-State Measurement of the Hydrogen Electrode Reactions
on Alloys 600 and 690

3.1 Introduction

The hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) play a dominant role in the corrosion of metals in acidic solutions. The HER and HOR are studied in the fuel cell area because the fuel cell uses HOR on noble metals such as platinum in order to generate the electricity. The HER makes the metal dissolution reaction possible in the presence of hydrogen in the acidic solutions.

It is widely accepted that the most important factors governing the kinetics of HER and HOR are the temperature, hydrogen pressure, and pH of the solutions [1-5]. In order to obtain the electrochemical kinetic parameters on Alloys 600 and 690 which are currently used as tube materials of the steam generators in pressurized water reactors (PWRs), steady-state measurements of the polarization curves of HER and HOR were carried out at different values of pH, 5.6, 7.3, and 10.2, and hydrogen pressures of 0.05, 0.5, and 5 bars, and the solution temperature was varied 30 °C stepwise from 160-250 °C. Because the exchange current density of HER and HOR is a function of pH values, dissolved hydrogen concentrations, and temperature of the solution, the experimental work of HER and HOR was carried out by changing these parameters. The measured data between potentiodynamic scanning of the potential and potentiostatic measurements at a steady-state show significant difference in equilibrium potentials around 0.55 V and corrosion currents as shown in Fig. 3.1 and 3.2. In order to obtain more exact data, steady-state potentiostatic current measurements were conducted in this research.

For this work, two different specimens of Alloys 600 and 690 were loaded simultaneously to measure the steady-state polarization curves at the same environmental
condition. The two specimens are electrically isolated from each other using Teflon holder which is designed to accommodate two specimens and a single reference electrode. All the measurements were done using a multi-channel Gamry machine with two different channels for the same time and conditions. Thereby, a good comparison of the corrosion characteristics between Alloy 600 and 690 steam generator tubes could be obtained in this study.

Alloy 600 and 690 tubes, provided by Doosan Heavy Industry (DHI) in Korea, are the same tube materials and same shapes of the real steam generator tube materials in PWRs designed by Combustion Engineering. Their chemical compositions are listed in Table 3.1.

Figure 3.1: Hydrogen electrode reaction polarization curves as measured using potentiodynamic and steady-state techniques using Alloy 600 at 5 bar of H₂ pressure, 220°C, and pH 7.3 (measured at room temperature).
Figure 3.2: Hydrogen electrode reaction polarization curves as measured using potentiodynamic and steady-state techniques using Alloy 690 at 5 bar of H₂ pressure, 220ºC, and pH 7.3 (measured at room temperature).

Table 3.1: Chemical compositions of Alloy 600 and 690 (wt%) [5].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>P</th>
<th>Ti</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>74.45</td>
<td>16.16</td>
<td>8.64</td>
<td>0.36</td>
<td>0.35</td>
<td>0.03</td>
<td>0.009</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>690</td>
<td>61.39</td>
<td>28.57</td>
<td>9.35</td>
<td>-</td>
<td>0.3</td>
<td>0.024</td>
<td>-</td>
<td>0.26</td>
<td>0.1</td>
</tr>
</tbody>
</table>

In order to create the same environment as is present in the RCS in PWRs, boric acid and lithium hydroxide were used as the buffer solution corresponding to the chemical environment and the water chemistry in commercial PWRs. Boron has a role of the neutron absorber and lithium controls the pH of the reactor coolant. The boron concentration in this work ranges from 2000 ppm to 0 ppm and lithium has a single value of 2 ppm. This solution changes the pH value from 5.6 to 10.2 at ambient temperature. As a matter of course, the typical commercial PWRs operate in a slightly basic environment.
at pH 7.6. However, in this research, the pH values are varied in wide ranges to observe the pH effect on HER and HOR. The estimation of pH values in elevated temperatures was done using the pH code developed by the author. This pH code was verified using a pH meter (Accumet AR 15) with the same buffer solutions at room temperature. The measured and calculated pH values are listed in Table 3.2.

**Table 3.2: Measured and calculated pH values of solutions at room temperature.**

<table>
<thead>
<tr>
<th>Chemical concentrations</th>
<th>Measured pH</th>
<th>Calculated pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ppm of B(OH)₃, 2ppm of LiOH</td>
<td>10.2</td>
<td>10.3</td>
</tr>
<tr>
<td>200 ppm of B(OH)₃, 2ppm of LiOH</td>
<td>7.2</td>
<td>7.3</td>
</tr>
<tr>
<td>2000 ppm of B(OH)₃, 2ppm of LiOH</td>
<td>5.6</td>
<td>5.6</td>
</tr>
</tbody>
</table>

The predictions of the 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. Because most of these parameters cannot be calculated theoretically, they must be derived experimentally. The main parameters needed for the calculation of the ECP values are the exchange current densities, \( i_0(H_2) \), and Tafel constants for the electrochemical reactions that occur on the metal surface outside of a crack. The reduction reaction which occurs at the presence of hydrogen, is defined as HER. The HER in an acid solution is expressed as,

\[
2H^+ + 2e^- \rightarrow H_2 \quad (3.1)
\]

and in an alkaline solution

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3.2)
\]

The oxidation reaction is called HOR and is expressed as
\[
\text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \tag{3.3}
\]

When the reaction proceeds in the forward direction in Eq. 3.1, the electrode consumes electrons, and this reaction is referred to HER. In the reverse reaction in Eq. 3.3, hydrogen gas is oxidized and electrons are produced. This reaction is referred to HOR.

The relationships between the exchange current density, \(i_0(\text{H}_2)\), the standard exchange current density, \(i_0^o(\text{H}_2)\), the solution pH, and the dissolved gas concentration are given by [6]

\[
i_0(\text{H}_2) = i_0^o(\text{H}_2)e^{-\frac{E_{ac}}{RT}[\text{H}_2]^\alpha[H^+]^\beta} \tag{3.4}
\]

Once the electrokinetic parameters are derived as a function of the reactant concentrations, temperatures, and pH values, the reaction orders, \(\alpha\) and \(\beta\), the activation energy, \(E_{ac}\), and the standard values of the exchange current densities, \(i_0^o(\text{H}_2)\), can be obtained using the optimization between the measured data and the proposed equation in Eq. 3.4.

### 3.2 Experimental Work

The parameters needed to calculate the ECP values on steam generator tubes whose materials are Alloys 600 and 690 are the exchange current densities \([i_0(\text{H}_2)\] and Tafel constants for the electrochemical reactions that occur on the surface of Alloys 600 and 690. Alloy 600 and 690 tubes provided by DHI were used for this work. Two specimens of Alloy 600 and 690 tubes were loaded at a same time. The steady-state electrochemical parameters were measured using a multi-channel Gamry instrument simultaneously.
3.2.1 High Temperature High Pressure Studies

The hydrogen evolution and oxidation reactions are sluggish at low temperatures, because of their comparatively high activation energy [1]. Therefore, the experimental work was done at high temperatures from 160-250°C: the range of active hydrogen recombination temperatures. The high temperature was limited to 250°C because the maximum operating temperature of Teflon, used for a specimen holder in this work, is 260°C.

The amount of hydrogen dissolved in the solution, \( m_{H_2}^T \) (mol/kg of water), is determined by the temperature-dependent Henry’s law,

\[
m_{H_2}^T = K_H^T f_H^T = K_{H_2}^{T_0} f_{H_2}^{T_0}
\]

(3.5)

where \( K_H^T \) is Henry’s law constant in mol/kg-atm, \( f_{H_2}^{T_0} \) is the fugacity of hydrogen gas in the standard state, and \( f_H^T \) is the temperature dependent fugacity of hydrogen gas both in atm. Henry’s law constant for hydrogen gas in water is given as [7]

\[
\log(K_{H_2}^T) = \frac{1321}{T} - 10.703 + 0.010468 \times T
\]

(3.6)

Hence the fugacity of hydrogen gas at any temperature in the solution is given as

\[
f_H^T = \frac{K_{H_2}^{T_0}}{K_H^T} f_{H_2}^{T_0} \approx \frac{K_{H_2}^{T_0}}{K_H^T} P_{H_2}
\]

(3.7)

where \( P_{H_2} \) is the dissolved hydrogen gas pressure. The calculated dissolved hydrogen concentrations at the different temperatures and pressures are provided as a variable to the equation of the exchange current density in Eq. 3.4. Finally the equilibrium potential can be calculated using the Nernst equation for HER and HOR in Eq. 3.1 and 3.3 as
\[ E^\circ = E^0 - \frac{2.303RT}{2F} \log f_{H_2}^T - \frac{2.303RT}{F} \cdot pH \] (3.8)

where \( E^0 \) is the standard equilibrium potential, \( R \) is the gas constant, \( F \) is the Faraday’s constant, and \( T \) is the temperature in Kelvin. The related parameters and calculated equilibrium potentials at different temperatures and pressures are listed in Table 3.3. In this table, the pH values were calculated using the P-ECP code developed in this thesis work.
Table 3.3: Equilibrium potential of the hydrogen electrode reaction and related parameters at the experimental temperatures and pressures.

<table>
<thead>
<tr>
<th>Temp (ºC)</th>
<th>160</th>
<th>190</th>
<th>220</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^3 K_{H_2}^T$</td>
<td>0.76</td>
<td>0.99</td>
<td>1.37</td>
<td>1.98</td>
</tr>
<tr>
<td>$f_{H_2}^T$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05bar</td>
<td>0.977</td>
<td>0.748</td>
<td>0.541</td>
<td>0.374</td>
</tr>
<tr>
<td>0.5 bar</td>
<td>1.396</td>
<td>1.068</td>
<td>0.773</td>
<td>0.534</td>
</tr>
<tr>
<td>5 bar</td>
<td>5.585</td>
<td>4.272</td>
<td>3.092</td>
<td>2.137</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 ppm of B(OH)$_3$</td>
<td>7.99</td>
<td>7.75</td>
<td>7.61</td>
<td>7.59</td>
</tr>
<tr>
<td>2 ppm of LiOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 ppm of B</td>
<td>7.06</td>
<td>7.04</td>
<td>7.06</td>
<td>7.15</td>
</tr>
<tr>
<td>2 ppm of Li</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000 ppm of B</td>
<td>5.92</td>
<td>5.96</td>
<td>6.05</td>
<td>6.02</td>
</tr>
<tr>
<td>2 ppm of Li</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^e_{(V_{SHE})}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0ppm, B</td>
<td>0.05 bar</td>
<td>-0.686</td>
<td>-0.661</td>
<td>-0.642</td>
</tr>
<tr>
<td>2ppm Li</td>
<td>0.5 bar</td>
<td>-0.692</td>
<td>-0.667</td>
<td>-0.649</td>
</tr>
<tr>
<td></td>
<td>5 bar</td>
<td>-0.718</td>
<td>-0.693</td>
<td>-0.675</td>
</tr>
<tr>
<td>200ppm, B</td>
<td>0.05 bar</td>
<td>-0.606</td>
<td>-0.599</td>
<td>-0.595</td>
</tr>
<tr>
<td>2ppm Li</td>
<td>0.5 bar</td>
<td>-0.613</td>
<td>-0.606</td>
<td>-0.601</td>
</tr>
<tr>
<td></td>
<td>5 bar</td>
<td>-0.639</td>
<td>-0.632</td>
<td>-0.628</td>
</tr>
<tr>
<td>2000ppm, B</td>
<td>0.05 bar</td>
<td>-0.508</td>
<td>-0.507</td>
<td>-0.508</td>
</tr>
<tr>
<td>2ppm Li</td>
<td>0.5 bar</td>
<td>-0.515</td>
<td>-0.513</td>
<td>-0.515</td>
</tr>
<tr>
<td></td>
<td>5 bar</td>
<td>-0.541</td>
<td>-0.539</td>
<td>-0.541</td>
</tr>
</tbody>
</table>
3.2.2 Experimental Apparatus

A test loop shown in the schematic diagram in Fig. 3.3 was employed for measuring HER and HOR kinetic parameters at high temperature and high pressure aqueous environments. The system consists of a solution storage reservoir, a high pressure positive displacement pump, a regeneration heat exchanger, a heat exchanger cooled by fresh water and an autoclave vessel with an electrical heater and a magnetic stirrer. The experimental autoclave is a 600 ml Type 316 stainless steel PARR benchtop reactor, fitted with a PARR magnetic drive.

The autoclave vessel has three outlets: a counter electrode, a reference electrode, and a working electrode. Two working electrodes of Alloy 600 and 690 share the outlet for the working electrode. The specimen holder, which is capable of containing two specimens at a same time, was placed into the specimen housing. An electrical magnetic impeller was located on the top of the specimen holder. Two electrically insulated wires made from nickel base alloys were connected to the working electrodes (Alloy 600 and 690 specimens). The counter electrode, made of a Type 316 stainless steel bar, was inserted from the bottom of the autoclave. A spiraled platinum wire is used for the reference electrode which was connected to the bottom of the autoclave vessel. A previous study on an identical channel showed that linear flow velocities of several meters per second were achieved at the same experimental temperatures [6].

Steady-state potentiostatic polarization measurements were performed using a multi-channel Gamry instrument (PC14 of Gamry instrument). Two lead wires from the working electrodes were connected to the two different signal process channels of the Gamry machine respectively. Those two channels share the counter electrode and reference electrode. All potentiostatic polarization measurements were performed after the corrosion current reached the steady state plateau. Starting from the 0.5V overpotential to the cathodic branch, the measurement proceeded 0.1V stepwise towards the anodic direction.
The steady state currents were measured at six points for the cathodic branch and seven points for the anodic branch to plot a steady state polarization curve. This steady state polarization curve was measured at three different pH values of 5.6, 7.3, and 10.2 at room temperature, three different hydrogen pressures of 0.05, 0.5, and 5 bars, and four different temperatures of 160, 190, 220, and 250 ºC. Thirty-six polarization curves for the steady state HER and HOR were plotted for the Alloy 600 and 690 specimens respectively. When the solution was changed in order to move to the different pH values, the specimen was also replaced with a new one.

3.2.3 Specimen preparation

In order to obtain the corrosion kinetic parameters of HER and HOR close to the real environment of the primary coolant in NPPs, real steam generator tubes of Alloys 600 and 690 provided by DHI were used in this experimental work. The specimens were
machined to a length of 0.5 inch and polished with fine sand paper. The Ni-Cr wire was soldered to the specimen wall using a silver solder. Both Alloy 600 and 690 specimens were accommodated in the specimen holder made of Teflon. The attached Ni-Cr wires are insulated using NTFE (Polytetrafluoroethylene) tubes and connected to the working electrode sensors.

3.2.4 Solution

In order to make the experimental condition similar to the primary side of a PWR, three different boron concentrations of 2000, 200, and 0 ppm were prepared with 2 ppm of lithium hydroxide. The boron concentration of 2000 ppm corresponds to the boron concentration of the beginning of the core life in NPPs and 200 ppm corresponds to the end of core life. For the purpose of identifying the pH effect of the HER and HOR, 0 ppm of boron with 2 ppm of lithium hydroxide was also used.

The hydrogen pressure was changed from 0.05, 0.5, and 5 bars in order to observe the effect of the hydrogen concentration. In a PWR nuclear power plant, typically 5 ppm of hydrogen concentration corresponding 25 ~ 50 cc/kg of H₂O at STP is used in order to suppress the oxidant concentrations such as oxygen and hydrogen peroxide produced radiolytically from the active nuclear core [8]. The boric acid and lithium hydroxide were solved into de-ionized water (milli-Q system, 18.2 MΩ/cm). The prepared solution was deoxygenated by hydrogen purging after argon purging for one hour. The hydrogen content of the solution was controlled by injecting ultra-high purity hydrogen gas through the solution in the reservoir, and then maintained at least 24 hours at a standstill.
3.3 Analysis of Hydrogen Evolution Reaction and Hydrogen Oxidation Reaction

3.3.1 Calculation of Electrochemical Kinetic Parameters

For the hydrogen electrode reaction, we can relate the exchange current density, \( i_0 \), with the dissolved hydrogen concentration, \([H_2]\), solution pH, \([H^+]\), and the system temperature, \( T \), as Eq. 3.1. In Eq. 3.1, the standard exchange current density, \( i_0^0 \), is expressed as a function of temperature and activation energy,

\[
i_0^0 = i_0^0 e^{E_{ac}/RT}
\]  

(3.9)

where \( i_0^0 \) is the standard reaction constant, \( E_{ac} \) is the activation energy of the hydrogen electrode reaction in kJ/mol, \( R \) the gas constant, and \( T \) is the solution temperature in Kelvin. For the electrode reaction, the current density, \( i \), is given by the generalized Butler-Volmer equation given in Eq. 2.35. In this case, the cathodic limiting current density is comparatively larger than the anodic limiting current density. Therefore, Eq. 2.35 can be rewritten as:

\[
i = \frac{e^{\eta/b_a} - e^{-\eta/b_c}}{1 + \frac{e^{\eta/b_a}}{i_{l,a}}} \frac{1}{i_l}
\]  

(3.10)

where \( \eta \) is an overpotential expressed as the difference between the applied potential, \( E \), and the equilibrium potential, \( E^{eq} \). \( b_a \) and \( b_c \) are the anodic and cathodic Tafel constants and \( i_{l,a} \) is the anodic limiting current density.
3.3.2 The Effects of the Variation of Operation Parameters

In order to observe the effects of variations of hydrogen concentrations, pH values, and system temperatures, the potentials and currents of HER at steady-state conditions were measured using Gamry instrument. Each of the three parameters, pH, hydrogen concentration, and temperature, was individually changed to investigate the effect on the corrosion potential and current while two variables were fixed. When any variable was varied, the system was held until steady state was reached. After the current reached a long range plateau, the potential and current were measured, then moved to next point. As a result, taking any one point on the potential/current plot took 30 to 60 minutes, and one plot of potential/current took about 5 hours.

3.3.2.1 Temperature Effect

As the temperature was increased, the current increased for the same potential. This temperature effect is shown in Fig 3.4 and 3.5 at different pH values and hydrogen pressures. Also the anodic limiting currents were increased as temperature increased. The effect of higher anodic currents is shown in the generalized Buttler-Volmer equation in Eq. 3.11 that the corrosion current in the passive region is increased as the anodic current increased. In Fig. 3.4 and 3.5 it can be seen that there are marked effects on the corrosion current as the solution temperature increases. The temperature effect in connection with the equilibrium potential of HER and HOR on the Alloy 600 and 690 tubes has shown that the equilibrium potential shifts in the negative direction as temperature increases. This agrees with the Nernst equation of the HER equilibrium potential in Eq. 3.8.

It was observed that the redox current on Alloy 690 is slightly lower than that of Alloy 600 as shown in Fig. 3.4 and 3.5.
Figure 3.4: Potential vs. Current density relation of an Alloy 600 tube at $P_{\text{H}_2} = 5$ bar and pH = 7.3 (measured at room temperature).

Figure 3.5: Potential vs. Current density relation of an Alloy 690 tube at $P_{\text{H}_2} = 5$ bar and pH = 7.3 (measured at room temperature).
3.3.2.2. Hydrogen Pressure Effect

As the hydrogen pressure increases, the hydrogen evolution reaction becomes active, which increases the redox current of the HER. In the low pH region, the hydrogen pressure effect on equilibrium potential is pronounced. But in the high pH region, the pH effect dominates the equilibrium potential, and therefore the hydrogen pressure effect is restricted to a small range. The hydrogen pressure effects are seen in Fig 3.6 to 3.7 at different temperatures and pH values.

Figure 3.6: Potential vs. Current density as a function of hydrogen pressure on Alloy 600 tube at 250ºC and pH = 7.3 (measured at room temperature).
Figure 3.7: Potential vs. Current density as a function of hydrogen pressure on Alloy 690 tube at 250°C and pH = 7.3 (measured at room temperature).

3.3.2.3 pH Effect

All electrode couples whose reactions include hydrogen ions have potentials which are dependent upon the pH of the solution in which they exist. This potential dependence on the pH of the solution could be seen in the Nernst equation (Eq. 3.8). The pH effect on equilibrium potential is more pronounced than the other two parameters because of the linear proportionality of the pH term in the Nernst equation. Fig. 3.8 and 3.9 include the pH effect on the equilibrium potential.
Figure 3.8: Potential vs. Current density as a function of pH on Alloy 600 and 690 tubes at 190°C and 5bar of $P_{H_2}$.

Figure 3.9: Potential vs. Current density as a function of pH on Alloy 600 and 690 tubes at 250°C and 5bar of $P_{H_2}$.
3.4 Optimization

The data in a Tafel region of the whole dataset were chosen to obtain the electrokinetic parameters of HER and HOR on Alloys 600 and 690 such as forward and reverse transfer coefficients and equilibrium corrosion density of each experimental condition. DataFit™ software (Version 8.0, Oakdale Engineering) was employed in this work for optimization in order to carry out nonlinear regression analysis. The solver of DataFit software utilizes the Levenberg-Marquardt method to perform nonlinear regression. This algorithm seeks the values of the parameters that minimize the sum of the squared differences between the values of the observed and predicted values of the dependent variable. Through this regression step, DataFit tries to find the closest parameters in a given equation and finds the parameters which cause the equation to most closely fit to the experimental data, using Eq. 3.11. Both the equation and initial parameter values must be provided.

The anodic and cathodic Tafel coefficients can be converted into the forward and reverse transfer coefficients using the following relations,

\[ b_a = \frac{RT}{\alpha_a F} \]  
\[ b_c = \frac{RT}{\alpha_c F} \]  

where \( \alpha_a \) and \( \alpha_c \) are the anodic and cathodic transfer coefficients respectively.

Optimization was carried out in two stages. In the first stage, three variables from the generalized Butler-Volmer Equation, forward Tafel constant, \( b_a \), backward Tafel constant, \( b_c \), and exchange current density, \( i_0 \), were obtained by regression calculation using the applied overpotentials, \( \eta \), measured currents, \( i \), and anodic limiting current densities, \( i_{l,a} \).
The obtained Tafel coefficients and equilibrium current densities were used again to work nonlinear regression analysis to obtain the values of $\alpha$, $\beta$, and also $i_0^0$, in Eq. 3.4, which are power of the concentration of hydrogen effect, the power of the pH effect and remaining terms which contain the standard exchange current density and its temperature effect shown in Eq. 3.10.

By taking the natural logarithm in both sides of Eq. 3.10, the linear relation between the standard current density and reciprocal of the temperature can be obtained as:

$$\ln(i_0^0) = -\frac{E_{ac}}{R} \frac{1}{T} + \ln(i_0')$$

(3.13)

The activation energies, $E_{ac}$, of both hydrogen reactions on the surfaces of the Alloy 600 and 690 tubes were obtained from linear regression between $\ln(i_0^0)$ and $1/T$ as shown in Eq. 3.13 and Fig 3.10. The obtained activation energies are 30.5 KJ on the surface of Alloy 600 and 35.6 KJ on Alloy 690.

The parameters shown in Table 3.4 were obtained by taking the mean values of the calculated parameter in respective conditions. The obtained values of the activation energy are in agreement with the results of other work [2].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$i_0^0$ ($H_2$) (A/cm$^2$)</th>
<th>$E_{ac}$ (kJ/mol)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$E_{ac}$ from other work (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>1.79E-10</td>
<td>30.5</td>
<td>0.64</td>
<td>-1.39</td>
<td>29 [2]</td>
</tr>
<tr>
<td>690</td>
<td>1.18E-10</td>
<td>35.6</td>
<td>0.54</td>
<td>-1.45</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.10: Relation between standard exchange current density and temperature at 0.05bar of $P_{H_2}$ (pH values were measured at room temperature).

All these optimization procedures were performed twice for Alloys 600 and 690, respectively. The obtained correlation of equilibrium exchange current density of hydrogen electrode reaction, $i_0(H_2)$ on the surface of the Alloys 600 and 690 are follows:

For Alloy 600

$$i_0(H_2) = 1.79 \times 10^{-10} e^{\frac{30562}{RT}} [H_2]^{0.64}[H^+]^{-1.39}$$  \hspace{1cm} (3.15)
and for Alloy-690

\[
i_0(H_2) = 1.18 \times 10^{-10} e^{-\frac{35619}{RT}} [H_2]^{0.54} [H^+]^{1.45}
\]  

(3.16)

where \([H_2]\) and \([H^+]\) denote the concentrations of hydrogen gas in mol/kg and hydrogen ions in mol/kg respectively.

**Figure 3.11:** Standard reaction constants for Alloys 600 (A) and 690 (B).
3.5 Verification

The derived equilibrium exchange current density of hydrogen electrode reaction, \(i_0(H_2)\) on the surface of Alloys 600 and 690 were compared with the exchange current density obtained from the optimization of the experimental data. Fig. 3.12 and 3.13 show this comparison for Alloys 600 and 690 respectively. The remaining data of different hydrogen concentrations and pH values are shown in Table 3.5. The derived equations in Eq. 3.14 and 3.15 are in agreement with the obtained data.

![Graph](image)

**Figure 3.12:** Comparison of the exchange current density of optimized data and calculated data using derived correlations of Alloy 600 (\(P_{H_2} = 5\) bar and \(pH = 10.2\)).

![Graph](image)

**Figure 3.13:** Comparison of the exchange current density of optimized data and calculated data using derived correlations of Alloy 690 (\(P_{H_2} = 5\) bar and \(pH = 10.2\)).
Table 3.5: Exchange current density of optimized data and calculated data using derived correlations.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>H₂ Pr.</th>
<th>pH</th>
<th>Optimized data using measured curr.</th>
<th>Calculated data using correlation</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>iₒ (A600)</td>
<td>iₗ (A690)</td>
<td>iₒ (A600)</td>
</tr>
<tr>
<td>160</td>
<td>0.05</td>
<td>5.92</td>
<td>1.46E-06</td>
<td>7.40E-07</td>
<td>6.59E-08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.06</td>
<td>7.60E-07</td>
<td>5.13E-07</td>
<td>2.53E-06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.99</td>
<td>7.80E-07</td>
<td>6.60E-06</td>
<td>4.97E-05</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>5.92</td>
<td>4.30E-07</td>
<td>2.10E-07</td>
<td>8.29E-08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.06</td>
<td>9.80E-07</td>
<td>3.40E-07</td>
<td>3.18E-06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.99</td>
<td>8.10E-05</td>
<td>1.20E-04</td>
<td>6.25E-05</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.92</td>
<td>3.23E-06</td>
<td>1.25E-06</td>
<td>2.01E-07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.06</td>
<td>1.12E-06</td>
<td>8.34E-06</td>
<td>7.73E-06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.99</td>
<td>1.00E-04</td>
<td>1.25E-04</td>
<td>1.52E-04</td>
</tr>
<tr>
<td>190</td>
<td>0.05</td>
<td>5.96</td>
<td>1.36E-06</td>
<td>9.27E-07</td>
<td>1.30E-07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.04</td>
<td>7.80E-07</td>
<td>4.84E-07</td>
<td>4.12E-06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.75</td>
<td>2.21E-06</td>
<td>8.80E-06</td>
<td>4.00E-05</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
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<td>1.26E-04</td>
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</table>
3.6 Conclusion

The measured equilibrium potentials in Fig. 3.4 through 3.9 show good agreement with the Nernst equation in Eq. 3.8. As shown in Figure 3.1 and 3.2, the potentiodynamic scanning method of the potential did not show the passivity in the anodic oxidation reaction, while the steady-state potentiostatic method showed good behaviors of the passive region. It is important to mention that the equilibrium potential measured using the potential scanning method changes from time to time, but the steady-state potentiostatic method provided good consistency.

The correlations of equilibrium exchange current density of hydrogen electrode reaction, \( i_0(H_2) \) on the surface of Alloys 600 and 690 were derived from the experimental work using the boric acid and lithium hydroxide which provide a similar environment compared to the operation conditions of the commercial PWR. The derived empirical correlation was compared with the exchange current density obtained from the optimization of the experimental data to verify the deviations of the derived correlations with the optimized data. The derived correlations show reasonable accuracy with the optimized data. When the pH is high, the deviation is lower than when pH is low. The maximum deviation is two orders of magnitude, occurring at 5 bar of hydrogen, 5.6 pH, and 250 °C which is at the condition of the highest temperature, highest hydrogen pressure, and highest pH value in this experimental work.
References


Chapter 4

The Measurement of Anodic Metal Dissolution Current and Electrochemical Impedance Spectroscopy on Alloys 600 and 690

4.1 Introduction

Electrochemical Corrosion Potential (ECP) is the mixed potential connected with the charge conservation of redox reactions occurring on a metal surface and the metal dissolution reactions in a solution. The Mixed Potential Model (MPM) [1-6] was employed to calculate the electrochemical potential on the surface of the Alloy 600 and 690 tubes. This MPM has been developed for calculating ECP data for BWR in-vessel components and recirculation pipes using hydraulic and compositional data [1]. The water chemistry of the primary side of the PWR has an advantage compared to the water chemistry in BWR with regard to the oxygen concentration [7]. The reactor coolant circuits in PWRs are separated from the steam condenser which is easily polluted by impurities such as chloride from the sea water and oxygen from the air; therefore, the oxygen concentration in PWR coolant circuits is negligibly small at just a few ppb (parts per billion). Furthermore, 25 to 50 cc/kg of hydrogen is injected into the RCS loops through the Chemical Volume Control System (CVCS). This injected hydrogen also suppresses the oxygen and hydrogen peroxide concentrations produced from the radiolytic decomposition of the coolant in the nuclear reactors; therefore, it was not necessary to consider the effect of oxygen and hydrogen peroxide as oxidants in the MPM for this study.

In chapter 3, the potential of the hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) were derived as a function of pH, hydrogen concentration, and the temperature of the solutions. The hydrogen evolution reaction plays the role of the cathodic reaction in the metal corrosion. Hence, anodic corrosion parameters are needed
in order to balance the charge transfer reactions. In this study, steady-state potentiostatic polarization measurements were employed in order to measure the metal dissolution currents which were used as input data for the derivation of empirical correlations of the metal dissolution currents of Alloys 600 and 690. The measured metal dissolution currents of Alloys 600 and 690 using the steady-state potentiostatic polarization methods were compared with the data measured by the potentiodynamic scanning method in Fig. 4.1 and 4.2. The anodic corrosion currents of the steady-state measurement are lower than that of the measured data by the potentiodynamic potential scanning method. A big difference existed also in the equilibrium potential of the steady-state measurement, which is 0.2 V more negative than that of the potential scanning polarization.

Alloy 690, which has comparatively high chromium content, forms a duplex structure in its oxide layers having a chromium rich inner layer and a nickel/chromium rich outer layer [8, 9]. Machet et al. have found that the Cr$_2$O$_3$ inner layer becomes thicker at the expense of the outer layer [10]. In the case of Alloy 600 the presence of mixed iron-nickel oxide in the outer layer controls the semi-conducting properties of the film at pH 8 [8]. Baek et al. [11] showed that the film formed on Alloy 600 at 0.2 V vs. Ni behaved as a p-type semiconductor, which agreed well with Montemor’s suggestion [8]. The contribution of the alloy components formed on Alloy 600 is unclear, whereas the chromium oxide dominates the barrier layer formed on Alloy 690.

In addition to the steady-state potentiostatic polarization measurements of the metal dissolution currents of Alloy 690, Electrochemical Impedance Spectroscopy (EIS) measurements using Alloy 690 were performed in order to derive the corrosion current using the Point Defect Model (PMD) developed by Macdonald [12, 13]. The measured metal dissolution currents of Alloys 600 and 690 using the steady-state potentiostatic polarization methods were compared with the data measured by the potentiodynamic scanning method in Fig. 4.1 and 4.2. The anodic corrosion currents of the steady-state measurement were lower than the data measured by the potentiodynamic potential scanning method. A big difference existed also in the equilibrium potential of the steady-state measurement, which is 0.2 V more negative than that of the potential scanning polarization.
The empirically derived correlations using the steady-state measurement data were included into the P-ECP computer code to calculate the ECP values in a reactor coolant circuit of a PWR. In addition, the corrosion current correlation obtained from PDM was also implanted into the P-ECP code. The calculation results of the ECP values throughout the RCS loop of a PWR were included in Chapter 5.

Figure 4.1: Metal dissolution current of a potentiodynamic scanning measurement and a steady-state potentiostatic measurement using Alloy 600 at 250°C, and pH 7.3 (measured at room temperature).
Figure 4.2: Metal dissolution current of a potentiodynamic scanning measurement and a steady-state potentiostatic measurement using Alloy 690 at 250°C, and pH 7.3 (measured at room temperature).

Film properties formed on the Alloy 600 and 690

Montemor et al. performed an investigation to identify the film properties formed on Alloys 600 and 690, shown in Fig. 4.3, and reached the conclusion that the film formed on Alloy 600 showed that the nickel oxide dominated the semi-conducting properties, whereas chromium oxide dominated in the film formed on Alloy 690 [8]. The Mott-Schottky plots shown in Fig. 4.4 were plotted using the steady-state potentiostatic polarization method using Alloy 690 in this study. The positive slope in the Mott-Schottky plot not only means the film has n-type semi-conducting property but also that a chromium oxide passive film dominates the semi-conducting property in the film formed on Alloy 690, which is in good agreement with other works [8, 13].
Figure 4.3: Auger depth profiles of the oxide film formed on Alloys 600 and 690 in the aqueous environment at pH 10 (Exposure time: 1000 hours) [8].
Figure 4.4: Mott-Schottky plot of the oxide film formed on Alloy 690 in the aqueous environment of 200 ppm of B(OH)$_3$ and 2ppm of LiOH (measured after 24 hours film growth at 0.25V from $E_{OC}$).

4.2 Experimental Work

In order to apply the MPM, anodic corrosion currents need to be measured in order to setup the charge conservation constraint. From the experimental work of HER and HOR, the electrochemical kinetic parameters of cathodic branches were obtained. Hence it is time to move to the experimental work for the anodic branch in the MPM. It is widely accepted that the metal dissolution currents are functions of the temperature and pH values of the solution [14-16]. However, the metal dissolution current is not simply coupled with the temperature and pH values of the solution. Alternatively, the PDM is well developed to correlate the metal dissolution current with the solution environments. The basis of the PDM is that the barrier layer is a highly defective, semiconductor oxide in which the vacancies act as electronic dopants. Under anodic polarization conditions, there exists a net flow of oxygen vacancies from the metal-barrier layer interface to the
barrier layer-solution interface and a net flow of cation vacancies in the reverse direction [12].

In this study, the steady-state metal dissolution currents were measured, and also the EIS experimental work was carried out in order to seek the electrokinetic parameters to apply the PDM and to derive the empirical correlations of the anodic dissolution current for Alloys 600 and 690. In order for derivation of both the empirical correlations and the PDM, the optimization method was used to obtain the related parameters such as Tafel constants, rate constants, and the film thickness.

4.2.1 The Measurement of Metal Dissolution Current at High Temperature and High Pressure

Anodic metal dissolution currents at a steady-state on the surfaces of Alloys 600 and 690 were measured to derive empirical correlations, and the electrochemical impedance was measured in order to derive a metal corrosion current correlation using the PDM. Prior to the beginning of the measurement, both specimens of Alloys 600 and 690 had a polarization potential of 0.25 V applied from the open circuit potential for the 24 hour film growth. Electrochemical impedance spectroscopy, as a method for obtaining information from a linear system requires that the system be stable to ensure the data are valid. Because a steady-state interface should generate the same response regardless of whether the measurements are made in the forward or reverse frequency sweep directions, the impedance plots should be in good agreement when the frequency is scanned (stepped) from high to low values and then immediately stepped in the reverse direction. Two different solutions which were 1000 ppm and 200 ppm of boron concentrations with 2 ppm of lithium concentration, respectively, were prepared to observe the metal dissolution effects on the Alloy 600 and 690 tubes.
4.2.2 Experimental Apparatus, Solutions, and Specimens

The experimental apparatus for this work is the same as used in chapter 3 for the measurement of the hydrogen evolution reaction and hydrogen oxidation reaction. Two solutions having 1000 ppm and 200 ppm of boron concentrations with 2 ppm of lithium concentration, corresponding to 6.1 and 7.3 pH respectively, were prepared for the steady-state potentiostatic polarization measurements and EIS measurement. The boric acid and lithium hydroxide solutions were purged by high purity argon for one hour in order to remove all the oxidants from the solution. Specimens prepared for this work were the same as prepared for the HER and HOR measurements. Both the measurement for the steady-state potentiostatic polarization measurements and EIS measurement were carried out using the Gamry instrument.

4.2.3 Reference Electrode

As a result of having no hydrogen in the solution, the platinum reference electrode was replaced with a tungsten/tungsten oxidized electrode which is a wire of 1 mm diameter. The tungsten electrode was oxidized using a propane gas torch in air for five minutes until it became red. This electrode was insulated by the PTFE tube leaving 0.3 inches exposed to the solution at the end of the electrode.

The electrochemical reaction on a tungsten/tungsten oxide electrode in the de-aerated boric acid solution is given as [17, 18]

\[ W_{4}O_{12} + 24H^{+} + 24e^{-} = 4W + 12H_{2}O \]  

(4.1)

The potential of tungsten/tungsten oxide electrode given by the Nernst equation can be expressed as
\[ E = E_{W_4O_{12}/W}^0 - \frac{2.303RT}{F} \log a_{H_2O} \] (4.2)

The standard potentials of Eq. 4.2 on the tungsten/tungsten oxide electrode, \( E_{W_4O_{12}/W}^0 \), at the experimental temperatures were calculated using HSC™ Chemistry software and included in Table 4.1. The activity of water, \( a_{H_2O} \), can be assumed to be unity for dilute solutions.

**Table 4.1: Standard potential of a W/W_4O_{12} electrode reaction calculated by HSC™ software.**

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Potential (V SHE)</th>
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<tr>
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</tr>
<tr>
<td>200</td>
<td>-0.031</td>
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<tr>
<td>250</td>
<td>-0.009</td>
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</table>

### 4.2.4 Measurements of the Anodic Dissolution Current and the Electrochemical Impedance Spectroscopy

Anodic dissolution currents were measured when the corrosion current reached steady state. This experimental work was carried at different solution temperatures: 150ºC, 200ºC, and 250ºC. At each temperature the overpotentials were also varied from 0.1-0.4 V and measured from the reference electrode. All of these measurements were carried out in steady state conditions. The obtained potential and current data at steady state conditions were used to derive empirical correlations of the anodic dissolution currents as the similar type of the Butler-Volmer equation (Eq. 3.10).

For the EIS measurements, electrochemical impedances were measured using Alloy 690 at the steady state conditions of each temperature and overpotential. The obtained impedance data were decomposed into their real and imaginary components.
The PDM [13] was employed to derive the anodic corrosion currents of the passive film on the Alloy 690 tube. The obtained data using the steady-state potentiostatic polarization method are listed in Tables 4.2 and 4.3, in which the forward current was measured while increasing the potential from $0.1-0.4V_{OC}$ ($V_{oc}$ is the open circuit potential); whereas, the backward current was measured while decreasing the current for the purpose of identifying the steady-state. As shown in the tables, the currents had reached steady-state.

### Table 4.2: Overpotentials and corrosion currents of Alloy 600 measured in a steady state at pH 6.1 (1000 ppm of Boron and 2 ppm of Lithium, pH was measured at room temperature).

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Over Pot. (V)</th>
<th>Current(I) Forward (μA)</th>
<th>Current(I) Backward (μA)</th>
<th>Current Density (A/cm²)</th>
<th>log(i)</th>
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Table 4.3: Overpotentials and corrosion currents of Alloy 690 measured in a steady state at pH 6.1 (1000 ppm of Boron and 2 ppm of Lithium, pH was measured at room temperature).

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<th>Temp. (°C)</th>
<th>Over Pot. (V)</th>
<th>Current(I) Forward (μA)</th>
<th>Current(I) Backward (μA)</th>
<th>Current Density (A/cm²)</th>
<th>log(𝑖)</th>
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<td>-5.42</td>
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<td>6</td>
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<td>7.47E-06</td>
<td>-5.12</td>
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</table>

4.3 Experimental Results and Data Analysis

The potentiodynamic curves of Alloy 600 and 690 were measured at three different temperatures in pH 7.3 and are shown in Fig. 4.1 and 4.2. Corresponding anodic metal dissolution currents as a function of overpotentials measured at steady-state are shown in the same figure. The EIS measurement data for Alloy 690 can be found in Nyquest plots in Fig. 4.8 and in Bode plots Fig 4.9 through 4.11. Also, related data are
included in Appendix 4. These EIS data sets of Alloy 690 were used in the PDM model in order to derive the formula of the anodic corrosion current.

4.3.1 Derivation of an Empirical Correlation of the Anodic Corrosion Current

The anodic current density, $i$, was considered because it follows a similar type of the generalized Butler-Volmer equation (Eq. 3.10) as follows,

$$i = \frac{e^{\frac{\eta}{b_a}} - e^{-\frac{\eta}{b_c}}}{1 + \frac{e^{\frac{\eta}{b_a}}}{i_p \cdot e^{\alpha \eta}}} \quad (4.3)$$

where $i_p$ is the passive exchange current density, $\eta$ is the overpotential, $b_a$ and $b_c$ are anodic and cathodic Tafel constants, and $\alpha$ and $n$ are the adjusting constants. The measured data in Table 4.2 and 4.3 for Alloys 600 and 690 were set as input data for the optimization in order to calculate the passive exchange current densities. The calculated passive exchange current densities are shown in Table 4.4.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$i_p$ for A-600 (μA/cm²)</th>
<th>$i_p$ for A-690 (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>200</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>250</td>
<td>0.36</td>
<td>0.43</td>
</tr>
</tbody>
</table>
With passive exchange current densities and reciprocal of the temperature in Kelvin shown in Fig. 4.5 and 4.6, the activation energy can be obtained using the Arrhenius equation in Eq. 4.4 and 4.5. The derived empirical correlations of passive exchange current densities as a function of the temperatures are as follows. For Alloy 600,

\[ i_p = 1.18 \times 10^{-2} e^{\frac{5411.3}{T}} \]  

(4.4)

and for Alloy 690,

\[ i_p = 3.13 \times 10^{-4} e^{\frac{3572.7}{T}} \]  

(4.5)

where \( T \) is in Kelvin. At low temperature, the passive exchange current density of Alloy 600 is lower than that of Alloy 690, but at high temperature, the difference is not conspicuous.

Finally the anodic corrosion current density on Alloys 600 and 690 can be obtained as

For Alloy 600

\[ i_{corr} = \frac{e^{\eta/0.035} - e^{-\eta/0.095}}{1 + \frac{e^{\eta/0.035}}{1.18 \times 10^{-2} e^{\frac{5411.3}{T}} + e^{\frac{5411.3}{T}} \cdot e^{7.18 \eta^{0.44}}}} \]  

(4.6)

and for Alloy 690

\[ i_{corr} = \frac{e^{\eta/0.055} - e^{-\eta/0.095}}{1 + \frac{e^{\eta/0.055}}{3.13 \times 10^{-4} e^{\frac{3572.7}{T}} + e^{\frac{3572.7}{T}} \cdot e^{6.41 \eta^{0.45}}}} \]  

(4.7)
Figure 4.5: Passive exchange current densities and reciprocal of the temperatures using Alloy 600 at pH 7.3.

Figure 4.6: Passive exchange current densities and reciprocal of the temperatures using Alloy 690 at pH 7.3.
4.4 Point Defect Model

The PDM is an atomic diffusion model that describes the formation, growth and breakdown of the passive film on the metal surface. This model presumes that the passive layer formed on the metal surface is highly defective and that the defect layer has semiconductor properties in which the vacancies act as the electronic dopants. The vacancies are generated and annihilated at the interfaces. Under anodic polarization conditions, there exists a net flow of oxygen vacancies from the metal (M)/barrier layer (BL) interface to the BL/solution interface and a net flow of cation vacancies in the reverse direction [19].

\[
\begin{align*}
(1) \quad & Cr \xrightarrow{k_1} Cr_i^{x^+} + V_{Cr} + \chi e' \\
(2) \quad & Cr \xrightarrow{k_2} Cr_{cr} + \frac{\chi}{2} V_O + \chi e' \\
(3) \quad & Cr_i^{x^+} \xrightarrow{k_{31}} Cr^{r^+} + (\Gamma - \chi) e' \\
(4) \quad & V_O + H_2O \xrightarrow{k_{41}} O_O + 2H^+ \\
(5) \quad & CrO_{\frac{\chi}{2}} + \chi H^+ \xrightarrow{k_{51}} Cr^{r^+} + \frac{\chi}{2} H_2O + (\Gamma - \chi) e'
\end{align*}
\]

Figure 4.7: Schematic process on barrier layer (Cr$_2$O$_3$) on passive film of Alloy 690. Cr is chromium atom; $Cr_i^{x^+}$ interstitial chromium cation; $V_{Cr}$ the chromium vacancy in the film; $Cr_{cr}$ the chromium cation in a normal cation position; $Cr^{r^+}$ the chromium cation in the solution phase; $V_O$ the oxygen vacancy; $O_O$ is the oxygen ion in an anion site; $\chi$ and $\Gamma$ cation oxidation states in the barrier layer and solution [13].
The film formed on Alloy 690 reveals the duplex character of chromium oxide for the BL and iron-nickel oxide for the outer layer [8]. Because the outer layer is highly porous [20], we ignored this outer layer effect in this study. For simplification of the derivation of the PDM an n-type monolayer is postulated in this study for the passive film formed on Alloy 690. Figure 4.7 shows the simplified PDM of the general PDM which includes the generation and annihilation of cation vacancies [12].

Reaction (1) and (3) in Fig. 4.7 describe the injection of the metal interstitial, \(Cr_i^{x^+}\), into the barrier layer and ejection into the solution. Reaction (2) results in the growth of the BL into the bulk alloy via the generation of oxygen vacancies. Reaction (4) denotes the annihilation of oxygen vacancies at the film/solution interface. Reaction (5) represents the destruction of the BL by dissolution. Reaction (1), (3), and (4) are lattice conservation processes, which means that those reactions do not contribute the movement of the interface, while reaction (2) and (5) are lattice non-conservative processes [12].

Therefore the change on the barrier layer thickness can be written in terms of the rates of the two lattice non-conservative reactions as [13]

\[
\frac{dL}{dt} = -\frac{2\Omega}{\chi}J_0 - \Omega k_{eH}^{\omega}.
\] (4.8)

where \(\Omega\) is the volume of the barrier layer per mole of cation, \(J_0\) is the oxygen vacancy flux at the alloy/film interface corresponding to the BL growth, and the last term describes the dissolution of the BL via the reaction (5) in Fig. 4.7. The total current density at the interfaces between alloy/film and film/solution interfaces is the difference of the electron productions and consumptions at the interfaces, which is expressed as,

\[
j = F\left[\chi j_i^{tie} - 2j_0^{tie} - (\Gamma - \chi)j_i^{tie} + (\Gamma - \chi)k_{eH}^{\omega}\right]
\] (4.9)

where \(F = 96,487 \text{ C/mol}\) is Faraday’s constant, and \(\Gamma = 3\) is the oxidation state of chromium in solution in the passive range.
It is widely accepted that the chromium interstitial has negligible effects on the metal-oxide film of high oxidation states [21]; therefore, the chromium interstitial effect on the current flux through the BL was not considered in this research, for simplification. Being combined with the rate constants, the current density is expressed as

\[
j = \mathcal{F} \left[ \chi e^{nV} e^{\Delta L} + (\Gamma - \chi) k_e e^{nV} e^{nV} \right]
\]  

(4.10)

The current density, \( j \), is derived from the fluxes of the point defects in the film which is governed by the Nernst-Planck relation and may be written as

\[
J_o = -D_o \frac{\partial c_o}{\partial x} - \chi K D_o c_o
\]  

(4.11)

for oxygen vacancies, where \( D \) is the diffusion coefficient, \( c \) denotes concentrations, \( K = \varepsilon F / RT \), and \( R \) is the gas constant, \( \varepsilon \) is the electric field strength which is considered to be a constant, and \( T \) is the absolute temperature. The continuity equation, \( \partial c / \partial t = -\nabla J \), can be applied to Eq. 4.11, then becomes

\[
\frac{\partial c_o}{\partial t} = D_o \frac{\partial^2 c_o}{\partial x^2} + \chi K D_o \frac{\partial c_o}{\partial x}
\]  

(4.12)

The Faradaic admittance is defined as a reciprocal of the impedance

\[
Y_j = \frac{\partial j}{\partial V} = \left( \frac{\partial j}{\partial V} \right)_L + \left( \frac{\partial j}{\partial L} \right)_V \frac{\Delta L}{\Delta V} + j \omega C
\]  

(4.13)

where \( C \) is the capacitance of the barrier layer.
\[
\frac{\Delta L}{\Delta V} = \frac{\Omega(k_2^0 a^e 2 e^{-b_2 L} - k_5^0 a^v c^n_2)}{\Omega k_2^0 b^e e^{-b_2 L} + j \omega}
\] (4.14)

Taking partial derivative of Eq. 4.10, we obtain the expression of \( \left( \frac{\partial j}{\partial V} \right)_L \) and \( \left( \frac{\partial j}{\partial L} \right)_V \) as

\[
\left( \frac{\partial j}{\partial V} \right)_L = F[a_2 \chi k_2^0 e^{-b_2 L} - a_5(\Gamma - \chi) k_5^0 e^{-b_2 L}]
\] (4.15)

and

\[
\left( \frac{\partial j}{\partial L} \right)_V = -F \chi b_2 k_2^0 e^{-b_2 L}
\] (4.16)

Substitute these two derivations and Eq.4.14 into Eq. 4.13, the Faradaic admittance is expressed as

\[
Y_j = Fa_2 \chi k_2^0 e^{-b_2 L} - F \chi b_2 k_2^0 e^{-b_2 L} \frac{\Omega(a_2 k_2^0 e^{-b_2 L} - a_5 k_5^0 e^{-b_2 L})}{\Omega b_2 k_2^0 e^{-b_2 L} + j \omega} + j \alpha C
\] (4.17)

The decomposition of this formula into the real and the imaginary part gives:

\[
Y_j[\text{Re}] = Fa_2 \chi k_2^0 e^{-b_2 L} - \frac{F \chi(a_2 k_2^0 e^{-b_2 L} - a_5 k_5^0 e^{-b_2 L})}{1 + \omega^2 \tau^2}
\] (4.18)

\[
Y_j[\text{Im}] = \omega C \left[ 1 + \frac{\pi F \chi(a_2 k_2^0 e^{-b_2 L} - a_5 k_5^0 e^{-b_2 L})}{1 + \omega^2 \tau^2} \right]
\] (4.19)

where
When the applied potential is in the passive region, the Faradaic admittance can be simplified to be

\[
\tau = \frac{1}{\Omega b_2 k_2^0 e^{c_1 V} e^{-b_1 L}} \tag{4.20}
\]

\[
Y_j[\text{Re}] = F a_2 \chi k_2^0 e^{a_2 V} e^{-b_2 L} - \frac{F \chi k_2^0 a_2 e^{a_2 V} e^{-b_2 L}}{1 + \omega^2 \tau^2} \tag{4.21}
\]

\[
Y_j[\text{Im}] = \frac{\omega \tau F \chi k_2^0 a_2 e^{a_2 V} e^{-b_2 L} + \omega C (1 + \omega^2 \tau^2)}{1 + \omega^2 \tau^2} \tag{4.22}
\]

In those expressions, \(a_2 = \alpha_2 (1-\alpha) \gamma\), \(b_2 = \alpha_2 \chi \gamma\), \(\gamma = F/RT\), \(V\) is the applied voltage, \(L\) is the BL thickness, \(C\) is the barrier layer capacitance, and \(k_2^0\) is the standard rate constant for Reaction (2) in Fig 4.7.

### 4.4.1 EIS experimental results

All the EIS measurements were carried out twice starting from high frequency (5000 Hz), to decreasing low frequency (0.02 Hz) and increasing from low frequency (0.02 Hz) back to the high frequency (5000 Hz) to confirm the consistency of the measurement in a steady-state condition. Figure 4.8 shows one of the Nyquist plots measured from the EIS experimental work. The x-axis is the real and Y-axis is imaginary components of the measured impedance. Both measurements during decreasing and increasing the frequency are in good consistency. Which means the measurement condition is in steady-state. All of the measured data are included in Appendix 4 in the form of the Nyquist plots and the Bode plots.
4.4.2 Optimization

From the theory of potential charge transfer, the rate constants for defect generation at the metal/barrier interface are given as [15]

\[
k_2 = k_2^0 e^{-a_2 V} e^{b_2 L}
\]  

(4.23)

where \(k_2^0\) is the standard reaction rate for the formation of the oxygen vacancies in the barrier layer, \(a_2\) and \(b_2\) are the transfer coefficients having units of \(V^{-1}\) and \(cm^{-1}\) respectively, \(V\) is applied potential, and \(L\) is the barrier layer thickness. These can be expressed by the Arrhenius formula as

\[
k_2^0 = k_2^{00} e^{\frac{E_{a0}}{RT}}
\]  

(4.24)
where \( k_2^{0} \) and \( E_{ac} \) are the standard reaction constant and activation energy respectively. From the optimization between \( k_2^{0} \) and temperature, the standard reaction constant, \( k_2^{0} \), is given as 6.36\( \times \)10\(^{-11}\) mole/sec-cm\(^{2}\) and the activation energy, \( E_{ac} \), is 9.7 KJ/mole. Therefore the reaction coefficient, \( k_2 \), is given as

\[
k_2 = 6.36 \times 10^{-11} e^{-\frac{1162.6}{T}}
\]

(4.25)

Substituting Eq. 4.25 into Eq. 4.23, then

\[
k_2 = 6.36 \times 10^{-11} e^{-\frac{1162.6}{T}} e^{x\alpha_2 (1-a)\gamma} e^{-x\alpha_2 \gamma L}
\]

where \( a \) is the polarizability of the interface. Therefore the current flux at the interface between the alloy and the barrier layer, \( J_0(L) \), is given as

\[
J_0(L) = -\frac{\kappa}{2} \times 6.36 \times 10^{-11} e^{-\frac{1162.6}{T}} e^{x\alpha_2 (1-a)\gamma} e^{-x\alpha_2 \gamma L}
\]

(4.27)

Finally the anodic corrosion current, \( i_{corr} \), is given as

\[
i_{corr} = -6.363 \times 10^{-11} F\chi e^{-\frac{1162.6}{T}} e^{x\alpha_2 (1-a)\gamma} e^{-x\alpha_2 \gamma L}
\]

(4.28)

where the constants obtained from the optimization are listed in Table 4.5.

In Eq. 4.28, the thickness of the boundary layer at steady-state, \( L_{ss} \), is proposed as \[13\]

\[
L_{ss} = \frac{1}{\varepsilon} \left[ 1 - \alpha - \frac{\alpha \alpha_2}{\alpha_2} \left( \frac{\Gamma}{\chi} - 1 \right) \right] V + \frac{1}{\varepsilon} \left[ \frac{2.303 n}{\alpha_2 \chi \gamma} - \beta - \frac{\alpha \beta (\Gamma - \chi)}{\alpha_2 \chi} \right] pH + \frac{1}{\alpha_2 \chi K} \ln \left( \frac{k_2^0}{k_5^0} \right)
\]
where $\Gamma$ is the oxidation state of Cr in solution (3 or 6) and $\chi$ is the oxidation state of chromium in the BL.

### Table 4.5: Optimized parameters using obtained impedance data from Alloy 690 at pH 7.3 (measured at room temperature).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>250°C</th>
<th>200°C</th>
<th>150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$: capacitance of barrier layer (F/cm$^2$)</td>
<td>7.57E-05</td>
<td>6.53E-05</td>
<td>4.69E-05</td>
</tr>
<tr>
<td>$L$: barrier layer thickness (cm)</td>
<td>3.58E-06</td>
<td>2.13E-06</td>
<td>1.12E-06</td>
</tr>
<tr>
<td>$a$: Polarizability of interface</td>
<td>6.59E-01</td>
<td>7.09 E-01</td>
<td>7.59 E-01</td>
</tr>
<tr>
<td>$a_2$: transfer coefficient ($V^{-1}$)</td>
<td>1.41 E-01</td>
<td>1.93 E-01</td>
<td>2.57 E-01</td>
</tr>
<tr>
<td>$\varepsilon$: electric field strength (V/cm)</td>
<td>1.77 E+04</td>
<td>3.35 E+04</td>
<td>5.64 E+04</td>
</tr>
<tr>
<td>$k^0_2$: standard reaction rate (mol/s-cm$^2$)</td>
<td>6.77E-11</td>
<td>5.72E-11</td>
<td>3.91E-11</td>
</tr>
</tbody>
</table>

### 4.5 Comparison of Models with Data

The measured data of the corrosion current by the potentiostatic steady-state measurement and the potentiodynamic potential scanning method show remarkable deviations (Fig. 4.1 and 4.2) in the metal dissolution current density and equilibrium potentials. The derived empirical correlations in Eq. 4.6 and 4.7 using the experimentally measured data are plotted and compared with the measured data in Fig 4.12 and 4.13 for Alloys 600 and 690 respectively. The difference between measured currents and calculated currents using the derived correlations is within 10 percent error at 250°C, whereas, the difference is close to a half decade at low temperature.
The calculated results of the impedance using the derived Faradaic admittance from the PDM in Eq. 4.21 and 4.22 were compared with the measured impedance data by the Bode plots in Fig. 4.9 through 4.11. The derived metal dissolution current density, $i_{\text{corr}}$, using the PDM for Alloy 690 in Eq. 4.28 was also plotted and compared with the experimentally measured corrosion current density and the calculated data using the empirical correlation in Eq. 4.7. Both the empirically derived correlations of Alloy 690 and the correlation using the PDM show less than 10 percent deviation when the applied voltage is 0.35 $V_{OC}$ at 250°C with the experimentally measured data.

Figure 4.9: Bode plots of the measured impedance and the calculated impedance by the derived PDM of Alloy 690 at 150°C and pH 7.3 (measured at room temperature).
Figure 4.10: Bode plots of the measured impedance and the calculated impedance by the derived PDM of Alloy 690 at 200°C and pH 7.3 (measured at room temperature).

Figure 4.11: Bode plots of the measured impedance and the calculated impedance by the derived PDM of Alloy 690 at 250°C and pH 7.3 (measured at room temperature).
Figure 4.12: Comparison of the corrosion current density of the measured data and the calculated data using the empirically derived correlation of Alloy 600 at 250ºC and 7.3 pH.

Figure 4.13: Comparison of the corrosion current densities of the measured data and calculated data by the empirically derived correlation and the PDM of Alloy 690 at 250ºC and 7.3 pH.
References


Chapter 5

The Development of the Simulation Code for the Electrochemical Corrosion Potential in the Reactor Coolant Circuits of PWRs

5.1 Introduction

Commercial nuclear power reactors are designed for several decades of power operation. Unexpectedly, structural material degradations have been found in the reactor coolant circuits in NPPs. Some of these degradations could cause the design base accident or develop into a severe accident in the nuclear core. The biggest challenge for structural material degradation in the RCS is considered to be Stress Corrosion Cracking (SCC). SCC is the propagation of a crack under the influence of the combined effects of mechanical stress and electrochemical corrosion environments. The mechanical stress is settled in a basic design and it is not a controllable parameter; therefore, the only parameter which the utilities of NPPs can control in order to mitigate the SCC is the electrochemical corrosion environments. Several factors can influence electrochemical corrosion environments, including chemical concentrations of boric acid and lithium hydroxide, pH, dissolved oxidants concentration, and hydrogen concentration in the RCS. Currently there is insufficient information identifying which combination of parameters is optimal to minimize the corrosion effect on the SCC.

The ECP in the RCS loop is also the most important parameter of the accumulation of activated corrosion products into the oxide films [1, 2]. The deposition of corrosion products can cause the Axial Offset Anomaly (AOA) in PWRs [2]. In addition, the accumulation of the activated corrosion products causes the radiation exposure to the workers in NPPs during the refueling outage and increases the man-rem exposures. Also the accumulated corrosion products contribute to increasing the amount of radioactive waste materials. Several computer codes of radiolysis, chemical, and
electrochemical simulation for predicting concentrations of radiolysis products around the primary coolant circuits have been developed to describe the corrosion phenomena in the RCS loops for BWRs [3-6] and PWRs [1]. Also, the ECP values depend on the corrosion properties and the chemistry of the solutions. Unfortunately, there are not many experimental results for the structural materials in the primary coolant loops in PWRs. Therefore, the corrosion properties of Alloys 600 and 690, which are the materials of the steam generator tubes, were carried out in this group in order to calculate the accurate ECP values on the steam generator tubes. It should be noted that the surface of the steam generator tubes occupies more than 75 percent of the pressure boundary in the RCS of PWRs [7].

In order to develop a new simulation code for the environment of the PWRs, a pH calculation model was required with the chemical reaction model and radiolytic yield model of individual chemical species. It was necessary that redox reactions should be incorporated into the computer code with those information of individual species concentrations, pH values, and radiolytic model. This information was included in the new computer code for the PWR environment, named ‘P-ECP’. P-ECP is capable of predicting ECP values over specified corrosion evolutionary paths (CEPs) throughout the whole RCS loops including reactor vessel, steam generator U-tubes, and hot-legs and cold-legs. This P-ECP code equipped radiolysis model, chemical reaction model in order to calculate the individual species concentrations using 45 different chemical reactions, pH calculation model, and the Mixed Potential Model (MPM). The cathodic current densities obtained from HER and HOR in Chapeter 3 and the anodic corrosion current densities in Chapter 4 were also incorporated into the P-ECP code.
The obtained pH value was provided as an input parameter in order to calculate the ECP values. The ECP depends on the material properties and electrochemical corrosion characteristics, therefore electrochemical properties, such as the HER and anodic metal dissolution current density are necessary in order to calculate the ECP of the individual structural material in the RCS loops. Using the obtained parameters, empirical correlations of hydrogen electrode reactions and anodic corrosion current densities of Alloys 600 and 690 were proposed. Finally the ECP values throughout the RCS loop were calculated using the P-ECP code and compared with the experimentally measured data obtained by other group.

5.2 Water Chemistry in PWRs

In general, the primary coolant in PWRs contains boron at concentration ranging from 2400 ppm (typical value of PWR at the beginning of core life, BOC) to 100 ppm (typical value of PWR at the end of core life, EOC). The pH is controlled by the concentration of lithium hydroxide injected through the CVCS. Controlling the pH of the coolant is recommended in order to minimize corrosion product transport and corrosion degradation in the RCS [8]. In an aqueous solution boron dissociates to polyborates and...
the least hydrolyzed form of boron in aqueous solution is boric acid, B(OH)₃ [9]. The pH can be obtained from the calculation of the boric acid and lithium hydroxide dissociation reactions. The reactions involved are [10]

\[
B(OH)_3 + OH^- = B(OH)_4^- \tag{5.1}
\]

\[
2B(OH)_3 + OH^- = B_2(OH)_7^- \tag{5.2}
\]

\[
3B(OH)_3 + OH^- = B_3(OH)_{10}^- \tag{5.3}
\]

\[
4B(OH)_3 + 2OH^- = B_4(OH)_{14}^{2-} \tag{5.4}
\]

\[
5B(OH)_3 + 3OH^- = B_5(OH)_{18}^{3-} \tag{5.5}
\]

\[
Li^+ + OH^- = LiOH \tag{5.6}
\]

\[
Li^+ + B(OH)_4^- = LiB(OH)_4 \tag{5.7}
\]

\[
H_2O = H^+ + OH^- \tag{5.8}
\]

Two polyborate species, \( B_3(OH)_{14}^{2-} \) and \( B_5(OH)_{18}^{3-} \), do not need to be considered, because of their rarity in the coolant [11], so the two polyborate species in Eq. 5.4 and 5.5 were ignored for the purpose of simplification of the calculation. Note that the pH value obtained from the calculation is the value caused by the effects of boric acid and lithium hydroxide. As a matter of course, it is necessary to add the effects of the radiation yields from neutron, gamma, and alpha irradiations. But it was difficult to find the changing rate of the boron in an aqueous solution caused by radiolytic decomposition of boron. Whereas, the concentration of boron is controlled by boration or dilution of the reactor coolant through the CVCS in typical commercial PWRs, thereby the pH value should be maintained at a target value by chemical engineers in commercial NPPs. Therefore it is not necessary to consider the radiolytic effect on changing the concentration of boron in the RCS.
5.3 Development of the ECP Calculation Code for PWRs

Mass transport, activity transport, and axial offset anomaly are currently pervasive issues of concern in PWR operations. It is considered that these three phenomena arise from the same chemical/electrochemical/thermal hydraulic processes that occur in the reactor primary coolant circuits in PWRs. In order to properly analyze these phenomena, exact pH and ECP values throughout the RCS loops are required. It is necessary to consider that pH and ECP values are functions of the operation time, because of the boron and lithium concentration variations as consuming the excess reactivity of nuclear cores. But, existing code developed in this group is capable of calculating the pH and ECP values at specific times instead of at full operation time [1]. On top of that, the calculation time for one static point is over 60 minutes. Therefore, it was necessary to develop a new code to calculate the pH and ECP values with respect to functions of a reactor operation time, boron concentration, lithium concentration, and also a fast-run time code.

5.3.1 pH Calculation Considering Boron and Lithium Variations in the PWR Operation Environments

The reactions involved in the calculation of the pH values in the PWR coolant which contains boron and lithium are:

\[ B(OH)_3 + OH^- = B(OH)_4^- \]  \hspace{1cm} (Q_1) \hspace{1cm} (5.9)
\[ 2B(OH)_3 + OH^- = B_2(OH)_7^- \]  \hspace{1cm} (Q_2) \hspace{1cm} (5.10)
\[ 3B(OH)_3 + OH^- = B_3(OH)_{10}^- \]  \hspace{1cm} (Q_3) \hspace{1cm} (5.11)
\[ Li^+ + OH^- = LiOH \]  \hspace{1cm} (Q_4) \hspace{1cm} (5.12)
\[ Li^+ + B(OH)_4^- = LiB(OH)_4 \]  \hspace{1cm} (Q_5) \hspace{1cm} (5.13)
\[ H_2O = H^+ + OH^- \]  \hspace{1cm} (W_K) \hspace{1cm} (5.14)
where $Q_i$ is the reaction quotient of the individual reaction $i$ and $W_K$ is the water dissociation constant. This seven species pH calculation model was based on Urquidi-Macdonald’s nine species pH calculation model [12].

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_H$</td>
<td>$H^+$</td>
</tr>
<tr>
<td>$C_{OH}$</td>
<td>$OH^-$</td>
</tr>
<tr>
<td>1</td>
<td>B(OH)$_3$</td>
</tr>
<tr>
<td>2</td>
<td>B(OH)$_4^-$</td>
</tr>
<tr>
<td>3</td>
<td>B$_2$(OH)$_7^-$</td>
</tr>
<tr>
<td>4</td>
<td>B$<em>3$(OH)$</em>{10}^-$</td>
</tr>
<tr>
<td>5</td>
<td>Li$^+$</td>
</tr>
<tr>
<td>6</td>
<td>LiOH</td>
</tr>
<tr>
<td>7</td>
<td>LiB(OH)$_4$</td>
</tr>
</tbody>
</table>

From Eq 5.14, the concentration of $OH^-$ ion is given as

$$C_{OH^-} = \frac{W_K}{C_{H^+} \gamma_{H^+} \gamma_{OH^-}}. \quad (5.15)$$

where $\gamma_{H^+}$ and $\gamma_{OH^-}$ are the activity coefficients of $H^+$ and $OH^-$ ions respectively.

From Eq 5.9, the concentration of B(OH)$_4^-$ ion is given as

$$C_2 = \frac{Q_1 C_{OH^-} \gamma_1 \gamma_{OH^-}}{\gamma_2}. \quad (5.16)$$
where $\gamma_i$ are the the activity coefficients of species $i$.

From Eq 5.10, the concentration of $\text{B}_2(\text{OH})_7^-$ ion is given as

$$C_3 = \frac{Q_2 C_i^2 C_{\text{OH}}^- \gamma_i^2 \gamma_{\text{OH}}^-}{\gamma_3} \quad (5.17)$$

From Eq 5.11, the concentration of $\text{B}_3(\text{OH})_{10}^-$ ion is given as

$$C_4 = \frac{Q_3 C_i^3 C_{\text{OH}}^- \gamma_i^3 \gamma_{\text{OH}}^-}{\gamma_4} \quad (5.18)$$

From Eq 5.12, the concentration of $\text{Li}^+$ ion is given as

$$C_5 = \frac{T_{\text{Li}}}{1 + \frac{Q_4 C_{\text{OH}}^- \gamma_5 \gamma_{\text{OH}}^-}{\gamma_6} + \frac{Q_5 \gamma_5 \gamma_2}{\gamma_7} \cdot \frac{Q_1 \gamma_1 \gamma_{\text{OH}}^-}{\gamma_2} C_1 C_{\text{OH}}^-} \quad (5.19)$$

where $T_{\text{Li}}$ is the total lithium concentration injected in order to control the pH through CVCS. And the concentration of $\text{LiOH}$ is given as

$$C_6 = \frac{Q_6 C_{\text{OH}}^- \gamma_5 \gamma_{\text{OH}}^-}{\gamma_6} \quad (5.20)$$

From Eq 5.13, the concentration of $\text{LiB(OH)}_4$ ion is given as

$$C_7 = \frac{Q_7 C_2^2 C_5 \gamma_2 \gamma_5}{\gamma_7} \quad (5.21)$$
In order to solve the simultaneous equations (Eq 5.15 through 5.21), two additional equations are needed: electroneutrality and mass balance have to be satisfied in the solution.

From electroneutrality, following relationship can be set up,

\[
F_{10} = C_{H^+} + C_5 - C_{OH^-} - C_2 - C_3 - C_4 \quad (5.22)
\]

And from mass balance,

\[
F_{20} = T_B - C_1 - C_2 - 2C_3 - 3C_4 - C_7 \quad (5.23)
\]

where \( T_B \) is the total boron concentration injected through CVCS.

Now, the number of variables and the number of simultaneous equations are balanced. The detailed solution of the seven nonlinear equations which are used to obtain the individual species concentrations and pH value is included in Appendix 3.

### 5.3.2 Radiolytic and Chemical Reactions Yielding Oxidants in the Reactor Coolant Circuits of PWRs

The most important source of chemical redox species in a commercial power reactor is the radiolitic dissociation of coolant in the nuclear core. Water dissociates a variety of species and ions because of radiation exposure, and at the same time other species and chemicals are produced because of the chemical reactions between them [1]. Therefore, it is not a simple problem to predict the concentrations of exact chemical species. In this research, a deterministic method is used to predict the chemical species produced from the radiation exposures using 45 reactions for PWR (refer to Appendix 2).

The rate at which any primary radiolytic species are produced is given by

\[
R_i^y = \left( \frac{G_i^y \Gamma^y}{100N_y} + \frac{G_i^n \Gamma^n}{100N_y} + \frac{G_i^\alpha \Gamma^\alpha}{100N_y} \right) \rho_\Gamma
\]

(5.24)
where \( R_i \) has units of mol/cm\(^3\).s, \( G_i \), \( G^n \), and \( G^\alpha \) are the radiolytic yields for neutrons, gamma photons, and alpha particles, respectively, in number of particles per 100 eV of energy absorbed, \( N_v \) is Avogadro's number, \( \tilde{F} \) equals \( 6.25 \times 10^{13} \) (the conversion factor from Rad/sec to eV/gram-sec), and \( \rho \) is the water density in g/cm\(^3\). \( \Gamma \), \( \Gamma^n \), and \( \Gamma^\alpha \) are the gamma photon, neutron, and \( \alpha \)-particle energy dose rates, respectively, in units of Rad/s. Compiled \( G \) values for 11 species are shown in Table 5.2. The \( G \)-values for the radiolytic yields for various species considered in the radiolysis model were taken from Christensen [13] for BWRs and taken from Uchida for PWRs [14].

**Table 5-2: \( G \) values for primary radiolytic species** [13, 14].

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>Christensen (BWR)</th>
<th>Uchida (PWR)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( G^\gamma )</td>
<td>( G^n )</td>
</tr>
<tr>
<td>1</td>
<td>e(^-)</td>
<td>2.66</td>
<td>0.61</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>0.55</td>
<td>0.34</td>
</tr>
<tr>
<td>3</td>
<td>H(^+)</td>
<td>2.76</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>OH</td>
<td>2.67</td>
<td>2.02</td>
</tr>
<tr>
<td>5</td>
<td>OH(^-)</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>6</td>
<td>H(_2)O(_2)</td>
<td>0.72</td>
<td>0.65</td>
</tr>
<tr>
<td>7</td>
<td>HO(_2)</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td>8</td>
<td>HO(_2)(^-)</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9</td>
<td>O(_2)</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>O(_2)(^-)</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>11</td>
<td>H(_2)</td>
<td>0.45</td>
<td>1.26</td>
</tr>
</tbody>
</table>
5.3.3 Mixed Potential Model for PWR

The resulting radiolysis produces radicals, ions, and molecular species that are highly reactive at the elevated temperatures corresponding to normal operating conditions. The highly oxidizing species such as O\textsubscript{2} and H\textsubscript{2}O\textsubscript{2}, are very corrosive to the primary circuit. The ability of these species to affect the corrosion properties of the coolant circuit components is reflected in the ECP by means of participating in the cathodic reactions.

The MPM can be used to obtain ECP on the structural materials in PWR environments. This MPM is based on the charge conservation constraint in the system. The charge transferred from the electrochemical reactions across the metal-solution interface should be consumed by the charge consumption reactions. The former reactions correspond to the anodic metal dissolution reaction and the latter belong to the redox reactions. Charge conservation demands that

\[ i_{R/O,H_2}(E) + i_{corr}(E) = 0 \]  \hspace{1cm} (5.25)

where \( i_{R/O,H_2} \) is the current density due to the redox reaction of HER in the steam generator and \( i_{corr} \) is the corrosion current density of the substrate. The current density for the redox reaction of HER may be expressed in terms of a generalized Butler-Volmer equation in Eq. 3.10. It should be noted that the redox current depends on the potential drop across the metal-solution interface.

It should be noted that the redox reactions of interest in this study are the HER and HOR in Eq. 3.1 through 3.3. Because of high concentration of hydrogen gas injected from the chemical volume control system, the oxidant concentrations such as oxygen and hydrogen peroxide are suppressed to a negligible amount in the RCS. The exchange current density data for these reactions were obtained from the HER and HOR
experimental work using the Alloy 600 and 690 tubes under various pH values, temperatures, and hydrogen concentrations in the previous chapter. The derived empirical correlations of the redox current densities were provided in Eq. 3.14 for the Alloy 600 tubes and Eq. 3.15 for the Alloy 690 tubes.

The redox currents obtained from the redox reactions should be balanced by the corrosion current, $i_{\text{corr}}$ (E). The corrosion currents were obtained from the anodic metal dissolution experimental work using the Alloy 600 and 690 tubes, in the previous chapter. The derived anodic corrosion currents were provided in Eq. 4.6 for the Alloy 600 tubes and Eq. 4.7 for the Alloy 690 tubes. All the above experimental data were obtained from the steady-state potentiostatic polarization measurements. In addition that, the PDM model was employed in order to derive the anodic metal dissolution current density using the Alloy 690 tubes.

In order to use the generalized Butler-Volmer equation (Eq. 3.10), the open circuit potentials, $E_{\text{oc}}$, of the Alloy 600 and 690 tubes are required to calculate the overpotentials, $\eta$. Using the obtained data from the anodic metal dissolution current experimental work, the open circuit potentials for the alloys were derived as a function of the temperature and pH as:

for the Alloy 600 tubes;

$$E_o = 1.8 - 7.43 \times 10^{-3}T - 9.13/pH + 0.038T/pH$$  \hspace{1cm} (5.26)

for the Alloy 690 tubes;

$$E_o = 0.91 - 5.2 \times 10^{-3}T - 4.9/pH + 0.027T/pH$$  \hspace{1cm} (5.26)

where T is in Kelvin.

These empirically derived correlations were substituted into the charge conservation constraint (Eq. 5.25), and then iterated in order to calculate the ECP.
5.3.4 Corrosion Evolutionary Path

A simplified PWR coolant circuit diagram is shown in Fig. 5.2. The P-ECP code can simulate 10 RCS structures and equipment such as the reactor core, hot leg, steam generator, cold leg, downcomer, etc. Typical PWRs operate at pressure of 15.5 MPa and the highest and lowest temperatures are approximately $326^\circ C \left(T_{\text{hot}}\right)$ and $292^\circ C \left(T_{\text{cold}}\right)$ respectively. Various structural materials are used in the RCS loops. The steam generator tubing in PWRs was originally made from Alloy 600 and this material is being replaced by Alloy 690 in order to reduce the sensitization problems in the steam generator tubes. The steam generator tubing accounts for 75 percent of the total pressure boundary in typical PWRs. The contact portion of the structural equipment in the RCS is shown in Table 5.3.

**Table 5.3:** Materials and contact portion with the reactor coolant of component equipments in a typical WH PWR [15].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Compositions</th>
<th>Purposes</th>
<th>Contact Portion with Coolant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>71%Fe, 19% Cr, 10% Ni</td>
<td>Cladding of RPV</td>
<td>3%</td>
</tr>
<tr>
<td>Alloy 600</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 690</td>
<td>75% Ni, 15% Cr, 8% Fe</td>
<td>SG tubing</td>
<td>75%</td>
</tr>
<tr>
<td>Zircaloy</td>
<td>98.3% Zr, 1.5% Sn, 0.12% Fe, 0.1% Cr</td>
<td>Fuel Cladding</td>
<td>20%</td>
</tr>
<tr>
<td>Stellite</td>
<td>45% Co, 30% Cr, 20% W, 5% Fe</td>
<td>Valve sheet, CRDM</td>
<td>Very small</td>
</tr>
<tr>
<td>Cr-Mo Steel</td>
<td>0.21% C, 0.21% Cr, 0.47% Mo, etc.</td>
<td>RPV, PZR, SG</td>
<td>0% (SS cladding)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RCS Piping</td>
<td>2%</td>
</tr>
</tbody>
</table>

Currently, the uranium enrichment level is being increased to extend the cycle operation period, as a result, the capacity factor also increases. The cycle operation period which was 12 months a decade ago, now been extended to 18 months. With the increase in the uranium enrichment level, a high borate concentration is needed to control
reactivity. In addition to the extension of the fuel burnup, most of the utilities are trying to increase the electrical power of the NPP, through power uprates. This requires higher coolant temperature and higher thermal outputs. The corrosive impact of these factors is significant in most situations, and may be critical in other cases.

![Figure 5.2: RCS flow in the PWR primary system.](image)

<table>
<thead>
<tr>
<th>1. Core Channel</th>
<th>(CC)</th>
<th>2. Upper Plenum</th>
<th>(UP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3. Hot Leg</td>
<td>(HL)</td>
<td>4. S/G Tube Hot Leg Side</td>
<td>(SGHL)</td>
</tr>
<tr>
<td>5. S/G Tube Cold Leg Side</td>
<td>(SGCL)</td>
<td>6. Cold Leg</td>
<td>(CL)</td>
</tr>
<tr>
<td>7. Downcomer</td>
<td>(DC)</td>
<td>8. Lower Plenum</td>
<td>(LP)</td>
</tr>
</tbody>
</table>
5.4 Sensitivity Study

The P-ECP code newly developed in this study can compute some electrochemical parameters for PWRs such as pH, ECP and the concentrations of reduction and oxidation species. This code takes into account the effectiveness of the water-chemistry of PWRs. The water chemistry contains water radiolysis, chemical reactions, and convection of the injected chemicals such as hydrogen injection, boron and lithium (to maintain the proper pH). The combination of these source terms, along with mass transport and conservation is evaluated at each time and distance in the primary reactor loop to calculate the spatial-temporal concentration variation of 11 chemical species and ECP values.

In order to illustrate the performance of the P-ECP code, simulations on a typical PWR power plant (shown schematically in Fig. 5.2) have been carried out. Normally, PWR water chemistry is accomplished by a chemical volume control system, where hydrogen is injected to maintain around 25-50 cc/kg (which corresponds to 5 ppm). For the purpose of code evaluation in this study, the calculations of the ECP values throughout the reactor coolant circuit were carried out under variation of the pH values, hydrogen pressures, and also different temperatures. It should be noted that the P-ECP code equipped the ECP calculation model in the full range of pH values, 0 to 5 bar of hydrogen pressures, and the extrapolated high temperature range.

5.4.1 Operation Scenario

The typical Westinghouse (WH) reactor operates at a normal power of 2700 MWth and normal pressure of 15.5 MPa. As mentioned before, the cycle of the nuclear core has designed up to 18 month or more. However, in this study the one cycle operation period is presumed to be 12 months. The reactor power is also assumed normal condition for 12 months. The boron concentration varies from 2400 ppm at the BOC to 200 ppm at the EOC. However the lithium concentration is fixed with a single value of 2 ppm in order to observe the pH variation effect as a function of the boron concentration. The
hydrogen concentration is always fixed in commercial reactors. In this study, four cases of different hydrogen concentrations, 0, 2, 5, and 10 ppm, were considered in order to identify the hydrogen effect on the ECP in the RCS. It should be noted that Type 304 stainless steel was assumed to be the structural material of the RCS, and Alloys 600 and 690 were assumed as the steam generator tube materials.

Fig. 5.3 to 5.7 show the concentration of boron dropped sharply at the beginning of the operation because of xenon build-up. Then the decreasing rate of the concentration of boron became sluggish, because the Burnable Poison Rod Assembly (BPRA) contributed to absorb the excess reactivity. The BPRA is consumed while absorbing excess neutrons. After depleting the BPRA, the decreasing rate of the concentration of boron inclined more than when the BPRA was active. This boron consumption profile was provided as an input file to the P-ECP code in order to simulate the reaction operation closer to the real operation conditions.

5.4.2 Comparison of ECP Values on Steam Generator U-tubes

ECP values obtained from the calculation using three different correlations of Alloy 600, Alloy 690, and PDM of Alloy 690 at the steam generator tubes (Eq. 4.6, 4.7, and 4.28 respectively), were compared in Fig.5.3 for the hot side and Eq. 5.4. for the cold side of the U-tubes. Those figures show that the pH values at the bottom and top of the reactor core were increased as the concentration of boron decreased. In addition, also the pH values of the bottom and top of the reactor core were different because of the different temperatures. The difference of ECP values between Alloys 600 and 690 was within 10 mV. In addition to the ECP values obtained from the empirical correlation using Alloy 690, the ECP value calculated using the correlation derived from the PDM was also compared in the same figures. One of the reasons of the difference of the ECP values between Alloys 600 and 690 is the difference of the activation energies of HERs, which are 30.5 and 35.6 kJ/mol for both Alloy 600 and 690 respectively.
Figure 5.3: Comparison of ECP values calculated using the correlations of Alloy 600, 690, and the PDM for A690 at 5ppm of H$_2$ and 2ppm of Li at the cold side of U-tubes (where the PDM correlation used the information of Alloy 690).

Figure 5.4: Comparison of ECP values calculated using the correlations of Alloys 600, 690, and the PDM for A690 at 5ppm of H$_2$ and 2ppm of Li at the hot side of U-tubes (where PDM correlation used the information of Alloy 690).
5.4.3 Simulation of a RCS loop

The RCS loop consists of different materials, as shown in Table 5.3. In order to protect the structural carbon steel, the RCS loops of typical WH PWRs are clad in stainless steel; therefore, in most cases the reactor coolant contacts with the stainless steel except the steam generator tubes. The P-ECP code uses the electrokinetic parameters of Type 304 stainless steel obtained previously by this group, for the simulation of RCS loops which are consisted of the Type 304 stainless steel. The detailed review of the electrochemical characteristic of Type 304 stainless steel is out of the scope of this study.

The pressure vessel, reactor internals, and RCS pipings were considered to consist of Type 304 stainless steel, and the steam generator tube material was considered to consist of Alloys 600 and 690. ECP values calculated using the empirical correlation of Alloy 600 throughout the RCS loop were included in Fig. 5.5. Fig. 5.6 shows the calculated data using the empirical correlation of Alloy 690 in Eq. 4.7, and Fig. 5.7 shows the calculated data using the PDM in Eq. 4.28.

![Figure 5.5: Comparison of ECP values throughout the RCS loop at 5ppm of H₂ and 2ppm of Li (ECPs at U-tube were calculated using Alloy 600).](image)
Figure 5.6: Comparison of ECP values throughout the RCS loop at 5ppm of H₂ and 2ppm of Li (ECPs at U-tube were calculated using Alloy 690).

Figure 5.7: Comparison of ECP values throughout the RCS loop at 5ppm of H₂ and 2ppm of Li (ECPs at U-tube were calculated using PDM of Alloy 690).
5.4.4 Effect of Neutron Flux Tilting

Ideally the axial neutron flux shape should be the cosine profile and symmetrical from the center line of the reactor core. In a reality, the shape is tilted either downward or upward because of the neutron leakage and feedback effect in the nuclear reactor core. In order to observe the tilting effect of the neutron flux shape, the operation time was divided by three time regions. In the first time region, the flux tilted downward for four months. In the second time region, the flux had the cosine profile for four months. Finally, the neutron flux tilted upward for the last four months. Figure 5.8 shows the postulated change of the neutron flux tilting in a reactor core. The calculated results are shown in Fig. 5.9.

![Figure 5.8: Postulated neutron flux shape change for 12 month operation (Time 1: 1-4 months, Time 2: 5-8 months, Time 3: 9-12 months).](image-url)
Figure 5.9: ECP values calculated using the correlations of Alloy 600 under the flux shape variations (RCS conditions: 5ppm of H₂ and 2ppm of Li at the bottom and top of the core).

5.5 Verification

Park et al. measured the ECP on Alloy 600 and Type 308 stainless steel in boric acid solutions at temperatures between 150 and 316°C [16]. The comparison between these measured ECP values on Type 308 SS and calculated ECP on Type 304 SS are shown in Fig. 5.10. The calculation conditions were set to the same conditions as the experimental work performed by Park et al. The deviations between the measured and calculated ECP values using the P-ECP are within the 10 percent error bars. The experimentally measured ECP values using Alloy 600 were shown in Fig. 5.11. The calculated ECP values using the P-ECP code were within or close to the 10 percent error bars of the measured data by Park et al.
Figure 5.10: Comparison of the measured and calculated ECP (measured on Type 308 SS in water containing 1000ppm of boron, 2 ppm of lithium, and 2ppm of dissolved hydrogen ECP) [16].

Figure 5.11: Comparison of the measured and calculated ECP (measured on Alloy 600 in water containing 1000ppm of boron, 2 ppm of lithium, and 2ppm of dissolved hydrogen ECP) [16].
5.6 Conclusion

From the sensitivity study, it was shown that the ECP became more negative as the hydrogen concentration increased. When the hydrogen concentration was set to zero, the calculated ECP values were -0.663 V\textsubscript{SHE} at the cold leg, -0.716 V\textsubscript{SHE} at the hot leg, and -839 at the U-tube. In the presence of 5 ppm of hydrogen, those values were shifted to more negative direction as -0.709, -0.795, and -0.877 V\textsubscript{SHE}, respectively. It was observed that pH values strongly influenced the ECP values. As pH values changed from 5.99 to 6.91, the ECP changed from -0.664 to -0.709 V\textsubscript{SHE} at the bottom of the core.

Predictions of the ECP values were carried throughout the whole RCS loops using the anodic corrosion current density of Type 304 stainless steel and steam generator tube materials of Alloys 600 and 690. In addition, the ECP values calculated by the P-ECP code were compared with the measured ECP data using Type 308 SS and Alloy 600 in the aqueous solution containing 1000 ppm of boron, 2 ppm of lithium, and 2 ppm of dissolved hydrogen. The deviations between the measured by Park et al. and the calculated ECP values using the P-ECP were within the 10 percent error bars. Also, the calculated ECP values on Alloys 600 and 690 using the P-ECP code were within or close to the measured data using Alloy 600.
References


technologies and diagnostics for Water Chemistry and corrosion control in water-cooled reactors), 2004.


Chapter 6
Conclusions and Suggestions for Future Work

6.1 Conclusions

In this dissertation, electrochemistry simulation codes were developed for BWRs and PWRs. Also experimental work was performed for HER/HOR and anodic metal dissolution currents on Alloys 600 and 690. The simulation code for PWRs, named P-ECP, was newly developed from this dissertation work. The P-ECP code is capable of simulating whole reactor coolant loops in PWRs with the same operation conditions. In order to develop the P-ECP code, experimental work using Alloys 600 and 690 was carried out in order to obtain exact electrochemical corrosion parameters. Also electrochemical impedance spectroscopy measurement was performed using Alloy 690, so that the empirical anodic metal dissolution current could be compared to the correlation derived from the PDM using EIS data. The conclusions from this study are:

1) From the simulation results for BWRs, the highest ECP values occur in the fuel channels and are around 270 mV$_{\text{SHE}}$ under the NWC operation. This value is very high when compared to the critical potential for IGSCC in sensitized Type 304 SS at the BWR operating temperature of 288$^\circ$C. Calculations using the FOCUS code predict the hydrogen injection operation suppresses the ECP to below $E_{\text{IGSCC}}$ at about -230 mV$_{\text{SHE}}$. Under HWC operation, it is concluded that the injected hydrogen suppresses the radiolytic production of the oxygen and hydrogen peroxide. The decomposition of hydrogen peroxide and its reaction with hydrogen, particularly in the downcomer, (where a sufficiently high gamma dose rate exists to facilitate the recombination process), is concluded to be the most important factor in controlling the ECP in BWR primary coolant circuits.
2) From the HER and HOR experimental work, the measured equilibrium potentials under the steady-state condition were in good agreement with the Nernst equation. The potential scanning method did not show passivity in the anodic oxidation reaction, while the steady-state potentiostatic method shows good behavior of the passive region. The measured data under the steady-state condition showed consistency in regards to the equilibrium potential. The derived empirical correlation was compared with the exchange current density obtained from the optimization of the experimental data. This comparison proved to be within 10 percent deviation when the temperature was 250ºC. When the pH is high, the deviation is lower than that of low pH. The maximum deviation is two order of magnitude different, occurring at 5 bar of hydrogen, 5.6 pH, and 250 ºC which is at the condition of the highest temperature, highest hydrogen pressure, and highest pH value in this experimental work.

3) From anodic metal dissolution reactions of Alloys 600 and 690, the measured data of the corrosion current by the steady-state potentiostatic method and the potentiodynamic scanning method show remarkable deviations in the metal dissolution current density and equilibrium potentials. The derived empirical correlations using the experimentally measured data were plotted and compared with the measured data and the difference between measured currents and calculated currents using the derived correlations is within 10 percent error at 250ºC, whereas, the difference is close to a half decade at low temperature.

4) The derived metal dissolution current density, using the PDM for Alloy 690 compared with the experimentally measured corrosion current density and the calculated data using the empirical correlation. Both the empirically derived correlations of Alloy 690 and the correlation using the PDM show less than 10 percent deviation when the applied voltage is 0.35 $V_{OC}$ at 250ºC with the experimentally measured data.

5) From the sensitivity study using the P-ECP code, it is predicted that the ECP was increased to more negative as presence of hydrogen. When the hydrogen
concentration was set to zero, the calculated ECP values were -0.663 V\textsubscript{SHE} at the cold leg, -0.716 V\textsubscript{SHE} at the hot leg, and -839 V\textsubscript{SHE} at the hot side of the U-tube. But at the presence of 5 ppm of hydrogen, those values were shifted to the more negative direction as -0.709, -0.795, and -0.877 V\textsubscript{SHE} respectively. It was observed that pH values strongly influenced the ECP values. As pH value changed from 5.99 to 6.91, the ECP at the bottom of the core changed from -0.664 to -0.709 V\textsubscript{SHE}.

The calculated ECP value of Alloy 600 is always 10 mV more negative than that of Alloy 690. One of the reasons of the difference of the ECP values between Alloys 600 and 690 is the difference of the activation energies of HERs, which are 30.5 and 35.6 kJ/mol for both Alloy 600 and 690 respectively. When the activation energy is low, the corrosion current becomes high, and this high current density shifts the ECP more negative.

6.2 Suggestions for Future Work

ECP is considered the basic parameter in order to analyze the corrosion related material degradations such as pitting corrosion, SCC, and hydrogen embrittlement. Also, it was shown that the ECP is a key parameter in activity transport in RCS loops. Therefore it is essential to predicting the exact ECP for further analytical approach to corrosion related material failures. The P-ECP code developed in this study could be used in the following areas:

1) Activity transport in RCS loops

Corrosion products, known as CRUD (Chalk River Unidentified Deposit), are deposited on heat transfer surfaces (fuel sheaths and steam generator tubes), resulting in degradation of the thermal output of the NPPs. The elements of the CRUD that are deposited in the core become activated by neutron irradiation (e.g., $^{59}$Co(n, $\gamma$)$^{60}$Co) and subsequently released to the coolant. Transportation to out-of-core surfaces and are subsequent incorporation into corrosion product films contribute greatly to the
man-REM exposure during the refueling outage in commercial power plants. It is well known the pH and ECP are key parameters in activity transport [1, 2]. The calculated pH and ECP values obtained from this research can be used as input parameters to calculate the activity transport phenomena as a function of operation time.

2) *Hydrogen embrittlement in the PWR environments*

Irradiation-assisted SCC is found above a radiation fluence of $3 \times 10^{25} \text{n/m}^2$, $E > 1\text{MeV}$) at low ECP (around $-0.5 \text{V}_{\text{SHE}}$) [3], and hydrogen embrittlement has been suggested as one of the main reasons of the SCC in PWRs [3]. It is also well known that the dissolved hydrogen in the reactor coolant of PWRs affects the Primary Water SCC (PWSCC) of nickel base alloys such as Alloy 600. When the proper hydrogen embrittlement model is developed, that model could be included into the P-ECP code to calculate the crack growth rate.

3) *Development of a simulation computer code of the secondary side of the steam generator in PWRs*

The secondary side of the steam generator is in a highly corrosive environment in PWRs. Sludge produced from the steam condensers and feed water pipes tends to pile up on the top of the tube sheet in the steam generator. This sludge adheres on to the tube and tube sheet. It forms a small crevice between the sludge pile and tubes, and this crevice could be a source of crevice corrosion. The secondary side of PWRs is similar to BWRs; therefore, the FOCUS code can be converted to the simulation code for secondary side of PWRs, if the chemistry and material information is changed.
References


Appendix 1

Reaction set used in the radiolysis model of the FOCUS code for BWRs.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate constant (L/mol-sec)</th>
<th>Activation energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e^- + H_2O = H + OH^-$</td>
<td>1.6E+01</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>$e^- + H^+ = H$</td>
<td>2.4E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>$e^- + OH = OH^-$</td>
<td>2.4E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>$e^- + H_2O_2 = OH + OH^-$</td>
<td>1.3E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>$H + H = H_2$</td>
<td>1.0E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>$e^- + HO_2 = HO_2^-$</td>
<td>2.0E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>7</td>
<td>$e^- + O_2 = O_2^-$</td>
<td>1.9E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>8</td>
<td>$2e^- + 2H_2O = 2OH^- + H_2$</td>
<td>5.0E+09</td>
<td>3.0</td>
</tr>
<tr>
<td>9</td>
<td>$OH + OH = H_3O_2$</td>
<td>4.5E+09</td>
<td>3.0</td>
</tr>
<tr>
<td>10</td>
<td>$OH + HO_2 = H_2O + O_2$</td>
<td>1.2E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>11</td>
<td>$OH + O_2^- = OH^- + O_2$</td>
<td>1.2E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>12</td>
<td>$OH^- + H = e^- + H_2O$</td>
<td>2.0E+07</td>
<td>3.0</td>
</tr>
<tr>
<td>13</td>
<td>$e^- + H + H_2O = OH^- + H_2$</td>
<td>4.5E+08</td>
<td>3.0</td>
</tr>
<tr>
<td>14</td>
<td>$e^- + HO_2^- + H_2O = OH + 2OH^-$</td>
<td>6.3E+07</td>
<td>3.0</td>
</tr>
<tr>
<td>15</td>
<td>$H^+ + OH^- = H_2O$</td>
<td>1.44E+11</td>
<td>3.0</td>
</tr>
<tr>
<td>16</td>
<td>$H_2O = H^+ + OH^-$</td>
<td>2.6E-05</td>
<td>3.0</td>
</tr>
<tr>
<td>17</td>
<td>$H + OH = H_2O$</td>
<td>2.0E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>18</td>
<td>$OH + H_2 = H + H_2O$</td>
<td>3.4E+07</td>
<td>4.6</td>
</tr>
<tr>
<td>19</td>
<td>$OH + H_2O_2 = H_2O + HO_2$</td>
<td>2.7E+07</td>
<td>3.4</td>
</tr>
<tr>
<td>20</td>
<td>$H + H_2O_2 = OH + H_2O$</td>
<td>4.4E+07</td>
<td>4.5</td>
</tr>
<tr>
<td>21</td>
<td>$H + O_2 = HO_2$</td>
<td>1.9E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>22</td>
<td>$HO_2 = O_2^- + H^+$</td>
<td>8.0E+05</td>
<td>3.0</td>
</tr>
<tr>
<td>23</td>
<td>$O_2^- + H^+ = HO_2$</td>
<td>5.0E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>24</td>
<td>$2HO_2 = H_2O_2 + O_2$</td>
<td>2.7E+06</td>
<td>4.5</td>
</tr>
<tr>
<td>25</td>
<td>$2O_2^- + 2H_2O = H_2O_2 + O_2 + 2OH^-$</td>
<td>1.7E+07</td>
<td>4.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Reaction</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>$H + HO_2 = H_2O_2$</td>
<td>2.0E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>27</td>
<td>$H + O_2^- = HO_2^-$</td>
<td>2.0E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>28</td>
<td>$e^- + O_2^- + H_2O = HO_2^- + OH^-$</td>
<td>1.8E+08</td>
<td>4.5</td>
</tr>
<tr>
<td>29</td>
<td>$OH^- + H_2O_2 = HO_2^- + H_2O$</td>
<td>1.8E+08</td>
<td>4.5</td>
</tr>
<tr>
<td>30</td>
<td>$2H_2O_2 = 2H_2O + O_2$</td>
<td>1.9973E-06</td>
<td>14.8</td>
</tr>
<tr>
<td>31</td>
<td>$H + H_2O = H_2 + OH$</td>
<td>1.04E-04</td>
<td>3.0</td>
</tr>
<tr>
<td>32</td>
<td>$H_2O + HO_2^- = H_2O_2 + OH^-$</td>
<td>1.02E+04</td>
<td>3.0</td>
</tr>
<tr>
<td>33</td>
<td>$HO_2 + O_2^- = O_2 + HO_2^-$</td>
<td>1.5E+07</td>
<td>4.5</td>
</tr>
<tr>
<td>34</td>
<td>$H_2O_2 = 2OH$</td>
<td>7.7E-04</td>
<td>7.3</td>
</tr>
</tbody>
</table>
## Appendix 2

**Reaction set used in the radiolysis model of the P-ECP code for PWRs**

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Rate constant (L/mol-sec)</th>
<th>Activation energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e^- + H_2O = H + OH^-$</td>
<td>1.6E+01</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>$e^- + H^+ = H$</td>
<td>2.4E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>$e^- + OH = OH^-$</td>
<td>2.4E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>$e^- + H_2O_2 = OH + OH^-$</td>
<td>1.3E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>$H + H = H_2$</td>
<td>1.0E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>$e^- + H_2O_2 = HO_2$</td>
<td>2.0E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>7</td>
<td>$e^- + O_2 = O_2^-$</td>
<td>1.9E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>8</td>
<td>$2e^- + 2H_2O = 2OH^- + H_2$</td>
<td>5.0E+09</td>
<td>3.0</td>
</tr>
<tr>
<td>9</td>
<td>$OH + OH = H_2O_2$</td>
<td>4.5E+09</td>
<td>3.0</td>
</tr>
<tr>
<td>10</td>
<td>$OH + HO_2 = H_2O + O_2$</td>
<td>1.2E+10</td>
<td>3.0</td>
</tr>
<tr>
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<td>$OH + O_2^- = OH^- + O_2$</td>
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<td>3.0</td>
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<td>13</td>
<td>$e^- + H + H_2O = OH^- + H_2$</td>
<td>4.5E+08</td>
<td>3.0</td>
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<tr>
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<tr>
<td>25</td>
<td>$2O_2^- + 2H_2O = H_2O_2 + O_2 + 2OH^-$</td>
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<td>4.5</td>
</tr>
<tr>
<td>26</td>
<td>$H + HO_2 = H_2O_2$</td>
<td>2.0E+10</td>
<td>3.0</td>
</tr>
</tbody>
</table>

---

*J. Pitt, MS Thesis at Pennsylvania State Univ., 2005*
<table>
<thead>
<tr>
<th></th>
<th>Reaction</th>
<th>K (M$^{-1}$)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>$H + O_2^- = HO_2^-$</td>
<td>2.0E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>28</td>
<td>$e^- + O_2^- + H_2O = HO_2^+ + OH^-$</td>
<td>1.8E+08</td>
<td>4.5</td>
</tr>
<tr>
<td>29</td>
<td>$OH^- + H_2O_2 = HO_2^- + H_2O$</td>
<td>1.8E+08</td>
<td>4.5</td>
</tr>
<tr>
<td>30</td>
<td>$2H_2O_2 = 2H_2O + O_2$</td>
<td>1.9973E-06</td>
<td>14.8</td>
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<td>3.0</td>
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<tr>
<td>34</td>
<td>$H_2O_2 = 2OH$</td>
<td>7.7E-04</td>
<td>7.3</td>
</tr>
<tr>
<td>35</td>
<td>$OH + HO_2^- = O_2^- + H_2O$</td>
<td>7.88E+09</td>
<td>3.0</td>
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<tr>
<td>36</td>
<td>$OH + OH^- = O^- + H_2O$</td>
<td>1.28E+10</td>
<td>3.0</td>
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<tr>
<td>37</td>
<td>$e^- + HO_2^- = O^- + OH^-$</td>
<td>3.97E+09</td>
<td>3.0</td>
</tr>
<tr>
<td>38</td>
<td>$O_2^- + O_2^- + H^+ = HO_2^- + O_2$</td>
<td>6.42E+14</td>
<td>3.0</td>
</tr>
<tr>
<td>39</td>
<td>$H_2O_2 = H_2O + O$</td>
<td>2.72E-03</td>
<td>15</td>
</tr>
<tr>
<td>40</td>
<td>$e^- + O_2^- = O_2^{2^-}$</td>
<td>1.3E+10</td>
<td>3.0</td>
</tr>
<tr>
<td>41</td>
<td>$H_2O_2 + HO_2 = H_2O + O_2 + OH$</td>
<td>0.5E+00</td>
<td>3.0</td>
</tr>
<tr>
<td>42</td>
<td>$O_2^- + H_2O_2 = OH + OH^- + O_2$</td>
<td>0.13E+00</td>
<td>3.0</td>
</tr>
<tr>
<td>43</td>
<td>$H_2O_2 = H^+ + HO_2^-$</td>
<td>2.56E-08</td>
<td>3.0</td>
</tr>
<tr>
<td>44</td>
<td>$e^- + HO_2 + H_2O = H_2O_2 + OH^-$</td>
<td>1.39E+10</td>
<td>3.2</td>
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<tr>
<td>45</td>
<td>$e^- + O_2^- + H_2O = HO_2^- + OH^-$</td>
<td>1.39E+10</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Appendix 3

Calculation sheet of the pH value of PWR environment considering Boric acid and Lithium hydroxide

Calculation of coolant pH values under consideration of boron and lithium. The reactions considered are:

\[
\begin{align*}
B(OH)_3 + OH^- &= B(OH)_4^- \\
2B(OH)_3 + OH^- &= B_2(OH)_7^- \\
3B(OH)_3 + OH^- &= B_3(OH)_{10}^- \\
Li^+ + OH^- &= LiOH \\
Li^+ + B(OH)_4^- &= LiB(OH)_4 \\
H_2O &= H^+ + OH^- 
\end{align*}
\]


- Species symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Species</th>
</tr>
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<tbody>
<tr>
<td>C_H</td>
<td>H^+</td>
</tr>
<tr>
<td>COH</td>
<td>OH^-</td>
</tr>
<tr>
<td>1</td>
<td>B(OH)_3</td>
</tr>
<tr>
<td>2</td>
<td>B(OH)_4^-</td>
</tr>
<tr>
<td>3</td>
<td>B_2(OH)_7^-</td>
</tr>
<tr>
<td>4</td>
<td>B_3(OH)_{10}^-</td>
</tr>
<tr>
<td>5</td>
<td>Li^+</td>
</tr>
<tr>
<td>6</td>
<td>LiOH</td>
</tr>
<tr>
<td>7</td>
<td>LiB(OH)_4</td>
</tr>
</tbody>
</table>
From Eq (A.R.6), the concentration of OH\(^{-}\) ion is given as

\[ C_{\text{OH}^{-}} = \frac{W_K}{C_{\text{H}^{+}} \gamma_{\text{H}^{+}} \gamma_{\text{OH}^{-}}} \]

\[ D_{\text{OH}} = \frac{\partial C_{\text{OH}}}{\partial C_{\text{H}}^{+}} = -\frac{W_K}{\gamma_{\text{H}^{+}} \gamma_{\text{OH}^{-}} C_{\text{H}^{+}}} \]

\[ D_{H2} = \frac{\partial C_{\text{OH}^{-}}}{\partial C_{1}} = 0 \]

From Eq (A.R.1), the concentration of B(OH)\(_4\)\(^{-}\) ion is given as

\[ C_2 = \frac{Q_1 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{2}} \]

\[ D_{21} = \frac{\partial C_2}{\partial C_{\text{H}}} = \frac{Q_1 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{2}} \]

\[ D_{22} = \frac{\partial C_2}{\partial C_1} = \frac{Q_1 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{2}} \]

From Eq (A.R.2), the concentration of B\(_2\)(OH)\(_7\)\(^{-}\) ion is given as

\[ C_3 = \frac{Q_2 C_1^2 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{3}} \rightarrow D_{31} = \frac{\partial C_3}{\partial C_{\text{H}}} = \frac{Q_2 C_1^2 \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{3}} \]

\[ D_{32} = \frac{\partial C_3}{\partial C_1} = 2 \cdot \frac{Q_2 C_1^2 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{3}} \]

From Eq (A.R.3), the concentration of B\(_3\)(OH)\(_{10}\)\(^{-}\) ion is given as

\[ C_4 = \frac{Q_3 C_1^3 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{4}} \rightarrow D_{41} = \frac{\partial C_4}{\partial C_{\text{H}}} = \frac{Q_3 C_1^3 \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{4}} \]

\[ D_{42} = \frac{\partial C_4}{\partial C_1} = 3 \cdot \frac{Q_3 C_1^3 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{4}} \]

From Eq (A.R.4),

\[ Q_4 = \frac{C_6 \gamma_{6}}{C_5 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}} \rightarrow \frac{C_6}{C_5} = \frac{Q_4 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{6}} \rightarrow \frac{C_5 + C_6}{C_5} = 1 + \frac{Q_4 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{6}} \]

From Eq (A.R.5), the concentration of Li\(^{+}\) ion is given as

\[ Q_5 = \frac{C_7 \gamma_{7}}{C_5 C_2 \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}} \rightarrow \frac{C_7}{C_5} = \frac{Q_5 \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{7}} \rightarrow \frac{C_5 + C_6 + C_7}{C_5} = 1 + \frac{Q_5 C_{\text{OH}} \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{6}} + \frac{Q_5 \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{7}} \cdot \frac{Q_5 \gamma_{\gamma_{\text{OH}}} \gamma_{\gamma_{\text{OH}}}}{\gamma_{2}} = \frac{T_{\text{Li}}}{C_5} \]
From Eq (A.R.4), the concentration of LiOH ion is given as

$$Q_4 = \frac{C_6 \gamma_6}{C_5 \gamma_5 \gamma_6} \Rightarrow C_6 = \frac{Q_4 C_5 \gamma_5 \gamma_6}{\gamma_6}$$

$$D_{61} = \frac{\partial C_6}{\partial C_H} = \frac{Q_4 \gamma_5 \gamma_6 (C_5 \gamma_2 \gamma_5 + C_1 \gamma_2 \gamma_5)}{\gamma_6}$$

$$D_{62} = \frac{\partial C_6}{\partial C_1} = \frac{Q_4 \gamma_5 \gamma_6 C_1 \gamma_2 \gamma_5}{\gamma_6}$$

From Eq (A.R.5), the concentration of LiB(OH)$_4$ ion is given as

$$Q_5 = \frac{C_7 \gamma_7}{C_5 \gamma_5 \gamma_7} \Rightarrow C_7 = \frac{Q_5 C_2 \gamma_2 \gamma_5}{\gamma_7}$$

$$D_{71} = \frac{\partial C_7}{\partial C_H} = \frac{Q_5 \gamma_2 \gamma_5 \gamma_7 \partial (C_5 \gamma_2 \gamma_5)}{\gamma_7} = \frac{Q_5 \gamma_2 \gamma_5 (C_5 \gamma_2 \gamma_5 + C_1 \gamma_2 \gamma_5)}{\gamma_7}$$

$$D_{72} = \frac{\partial C_7}{\partial C_1} = \frac{Q_5 \gamma_2 \gamma_5 \gamma_7 \partial (C_5 \gamma_2 \gamma_5)}{\gamma_7} = \frac{Q_5 \gamma_2 \gamma_5 (C_5 \gamma_2 \gamma_5 + C_1 \gamma_2 \gamma_5)}{\gamma_7}$$

We need two more constitutive equations to solve the individual species concentrations. The electroneutrality and the mass balance are considered as the natural
laws all the chemical reactions should obey. From the electroneutrality, we can setup following relation.

\[ F_{10} = C_H + C_5 - C_{OH} - C_2 - C_3 - C_4 \]

Take derivation both sides by \( C_H \) and \( C_1 \):

\[
A_1 = \frac{\partial F_{10}}{\partial C_H} = \frac{\partial C_H}{\partial C_H} + \frac{\partial C_5}{\partial C_H} - \frac{\partial C_{OH}}{\partial C_H} - \frac{\partial C_2}{\partial C_H} - \frac{\partial C_3}{\partial C_H} - \frac{\partial C_4}{\partial C_H}
\]

\[
= 1.0 + D_{51} - D_{OH} - D_{21} - D_{31} - D_{41}
\]

\[
B_1 = \frac{\partial F_{10}}{\partial C_1} = \frac{\partial C_H}{\partial C_1} + \frac{\partial C_5}{\partial C_1} - \frac{\partial C_{OH}}{\partial C_1} - \frac{\partial C_2}{\partial C_1} - \frac{\partial C_3}{\partial C_1} - \frac{\partial C_4}{\partial C_1}
\]

\[
= D_{52} - D_{22} - D_{32} - D_{42}
\]

And from the mass balance, we obtain,

\[ F_{20} = T_B - C_1 - C_2 - 2C_3 - 3C_4 - C_7 \]

\[
A_2 = \frac{\partial F_{20}}{\partial C_H} = \frac{\partial T_B}{\partial C_H} - \frac{\partial C_1}{\partial C_H} - \frac{\partial C_2}{\partial C_H} - 2\frac{\partial C_3}{\partial C_H} - 3\frac{\partial C_4}{\partial C_H} - \frac{\partial C_7}{\partial C_H} = -D_{21} - 2D_{31} - 3D_{41} - D_{71}
\]

\[
B_2 = \frac{\partial F_{20}}{\partial C_1} = \frac{\partial T_B}{\partial C_1} - \frac{\partial C_1}{\partial C_1} - \frac{\partial C_2}{\partial C_1} - 2\frac{\partial C_3}{\partial C_1} - 3\frac{\partial C_4}{\partial C_1} - \frac{\partial C_7}{\partial C_1} = -1.0 - D_{22} - 2D_{32} - 3D_{42} - D_{72}
\]

Establish a Jacobian matrix:

\[
J_i(F_j) = \begin{bmatrix}
\frac{\partial F_{10}}{\partial C_H} & \frac{\partial F_{10}}{\partial C_1} \\
\frac{\partial F_{20}}{\partial C_H} & \frac{\partial F_{20}}{\partial C_1}
\end{bmatrix} = \begin{bmatrix}
A_1 & B_1 \\
A_2 & B_2
\end{bmatrix} \Rightarrow |X| = A_1B_2 - A_2B_1
\]

Therefore the adjoint matrix is given as:

\[
\text{Adj}(X) = \begin{bmatrix}
B_2 & -B_1 \\
- A_2 & A_1
\end{bmatrix}
\]

The inverse matrix is obtained as:
\[ X^{-1} = \frac{adj \ X}{|X|} \]

\[
\begin{bmatrix}
C_H \\
C_1
\end{bmatrix} = X^{-1} \begin{bmatrix} F_{10} \\ F_{20} \end{bmatrix}
\]

Therefore the solution is given as:

\[
C_H = C_{H0} - \frac{1}{|X|} \left[ B_2 F_{10} - B_1 F_{20} \right]
\]

\[
C_1 = C_{10} - \frac{1}{|X|} \left[ -A_2 F_{10} + A_1 F_{20} \right]
\]

where \( C_{H0} \) and \( C_{10} \) are the initial concentrations of \( H^+ \) and \( B(OH)_3 \) respectively.

From Eq. (A3.1),

\[
F_{10} = \frac{|X|(C_{H0} - C_H) + B_1 F_{20}}{B_2}
\]

Substitute this into Eq. (A3.2), then we can obtain \( C_1 \) as a function of \( C_H \) and \( F_{20} \). Finally we obtain the solution of hydrogen ion and boric acid concentrations as follows:

\[
C_H = C_{H0} + \frac{B_1 F_{20} - B_2 F_{10}}{B_2 A_1 - B_1 A_2}
\]

\[
C_1 = \frac{A_2 C_{H0} + B_2 C_{10} - A_2 C_H - F_{20}}{B_2}
\]
Appendix 4

Measurement Data of Steady-State Potentiostatic Anodic Corrosion Density and Electrochemical Impedance Spectroscopy of Alloys 600 and 690

Figure A4.1: Measured anodic current densities of Alloys 600 and 690 at 150 °C and pH 7.3 (measured at room temperature).
Figure A4.2: Measured anodic current densities of Alloys 600 and 690 at 200 ºC and pH 7.3 (measured at room temperature).
Figure A4.3: Measured anodic current densities of Alloys 600 and 690 at 250 °C and pH 7.3 (measured at room temperature).
Figure A4.4: Measured anodic current densities of Alloys 600 and 690 at 150 °C and pH 6.1 (measured at room temperature).
Figure A4.5: Measured anodic current densities of Alloys 600 and 690 at 200 °C and pH 6.1 (measured at room temperature).
Figure A4.6: Measured anodic current densities of Alloys 600 and 690 at 250 °C and pH 6.1 (measured at room temperature).
Figure A4.7: Nyquist plot of Alloy 690 at 0.12 V overpotential, 250 ºC and pH 7.3 (measured at room temperature).
Figure A4.8: Nyquist plot of Alloy 690 at 0.22 V overpotential, 250 °C and pH 7.3 (measured at room temperature).
Figure A4.9: Nyquist plot of Alloy 690 at 0.07 V overpotential, 200 °C and pH 7.3 (measured at room temperature).
Figure A4.10: Nyquist plot of Alloy 690 at 0.17 V overpotential, 200 °C and pH 7.3 (measured at room temperature).
Figure A4.11: Nyquist plot of Alloy 690 at 0.27 V overpotential, 200 °C and pH 7.3 (measured at room temperature).
Figure A4.12: Nyquist plot of Alloy 690 at 0.05 V overpotential, 150 °C and pH 7.3 (measured at room temperature).
Figure A4.13: Nyquist plot of Alloy 690 at 0.15 V overpotential, 150 °C and pH 7.3 (measured at room temperature).
Figure A4.14 Nyquist plot of Alloy 690 at 0.25 V overpotential, 150 °C and pH 7.3 (measured at room temperature).
VITA

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Han Sang Kim was born on September 2, 1962 (Korean lunar calendar) in Gwangju Metro City, Republic of Korea. He finished his undergraduate study in the department of mechanical engineering at Chonnam National University in 1988. He started his carrier at SK engineering company in 1987, and joined KEPCO (Korea Electric Power Corporation) in 1989. This company has been divided into several companies after deregulation in the electricity market in Korea. He has continued his work at KHNP (Korea Hydro and Nuclear Power Company) since 2001. Based on the support of his company, he obtained his MS degree of nuclear engineering at KAIST (Korea Advanced Institute of Science and Technology) in 2000. He joined Pennsylvania State University in 2003 and worked with Dr. Macdonald in the department of materials science and engineering. He is expecting to get his Ph.D degree in the department of nuclear engineering in December, 2007.