Calculation of pH, Conductivity, and Corrosion Potential of Stainless Steels in High Temperature Water Chemistry Conditions

Dayu Fajrul Falaakh and Chi Bum Bahn[†]

ABSTRACT

A computer code that can calculate pH and conductivity in high-temperature water chemistry was developed. In the code, chemical species used in simulated reactor water conditions were considered. With given ionic concentrations, pH and conductivity of water could be computed at a given temperature. The corrosion potential of austenitic stainless steels (SSs) was also estimated based on the mixed-potential theory. With the given pH and dissolved gas (hydrogen, oxygen, and hydrogen peroxide), the corrosion potential could be estimated at a given temperature. The validation results showed that the code yielded reasonably accurate predictions compared to the experimental data. Therefore, predicted pH, conductivity, and corrosion potential can be used as input features for predicting stress corrosion cracking growth rates of SSs in nuclear power plant conditions.

Key Words : Nuclear plant chemistry, pH, Conductivity, Corrosion potential

기호설명

a_i = activity of species i

b_j = Tafel constant of reaction j

C = concentration of dissolved oxidizer

D = diffusivity of dissolved oxidizer

d = channel diameter

E = corrosion potential

E_0 = standard potential

E_j^e = equilibrium potential of reaction j

F = Faraday constant

i_{corr} = corrosion current density of metal substrate

i_j = current density due to the redox reaction of j-th oxidizer

i_l = limiting current density

i^0 = exchange current density

K_i = equilibrium constant of reaction i

M_i = molar concentration of ion i

Mr = molar mass

m_i = molal concentration of ion i

n = number of electron associated with a reaction

Q_i = equilibrium constant of reaction i

R = universal gas constant

T = temperature

V = flow velocity

z_i = charge of ion i

γ_i = activity coefficient of ion i

κ = conductivity

λ_i = equivalent conductivity of ion i

μ = ionic strength of solution

ν = kinematic viscosity

ρ = water density

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1. Introduction

Austenitic stainless steels (SSs) have been used as major structural materials in nuclear power plants because of their excellent mechanical properties and corrosion resistance in high temperature water conditions. However, some degradation of austenitic SSs in nuclear power

plants has been reported[1], including stress corrosion cracking (SCC) which is highly localized degradation and difficult to detect. Once SCC is detected, the plant operator should evaluate if the detected crack is allowed or needs to be repaired. For the evaluation, SCC growth rates of SSs need to be accurately predicted depending on the operating conditions. To measure SCC growth rates of SSs, lots of laboratory testing have been conducted under Boiling Water Reactor (BWR) or Pressurized Water Reactor (PWR) water conditions[1]. Although empirical equations for SCC growth rates are available, if data are compiled and analyzed according to advanced methods, such as machine learning, it may be possible to more accurately predict the SCC growth rate of austenitic SSs in nuclear power plant conditions.

Since pH and conductivity are influential factors on SCC growth rate, it is necessary to know the pH and conductivity of SCC testing conditions as input features for machine learning. However, some laboratory testing results did not report pH and conductivity at test temperature, instead concentrations of added chemicals and/or gas (hydrogen, oxygen, or hydrogen peroxide). Some commercial softwares are available for the high-temperature pH calculation, but they are basically not open to public use. In addition to the pH and conductivity, corrosion potential of austenitic SSs in such test conditions is also an important factor, which is determined by water chemistry conditions like pH and hydrogen concentration and hydrodynamic conditions like flow velocity. Earlier work[2] developed a computer code that can calculate the corrosion potential of SSs. Theoretical information on the code is available, but the code itself is not publically available.

In this study, a computer code that can calculate pH and conductivity with given ionic concentrations was developed. The corrosion potential of austenitic SSs was also estimated. By doing so, water chemistry conditions like pH, conductivity, and corrosion potential can be used as input features for predicting SCC growth rates of SSs in nuclear power plant conditions.

2. Calculation Methods

2.1 pH & Conductivity in BWR

Required information and data for the calculation of pH and conductivity include chemical reactions[2,3], equilibrium constants[4], activity coefficients[4], and equivalent conductivities[5-7]. The pH and conductivity can be computed as:

$$pH = -\log a_{H^+} \tag{1}$$

$$\kappa = \sum_i |z_i| M_i \lambda_i \tag{2}$$

where a_i is the activity of ion i, M_i is the molar concentration of ion i, z_i is the charge of ion i, λ_i is the equivalent conductivity of ion i, and κ is the solution conductivity containing ionic species.
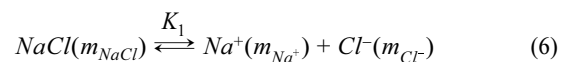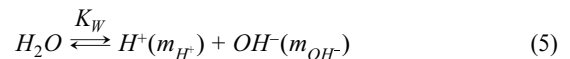
When the water is pure, the pH is computed as follows:
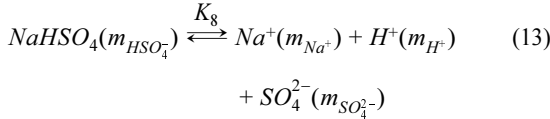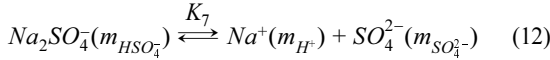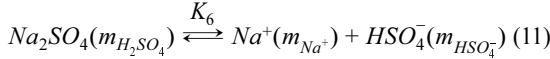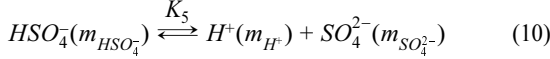
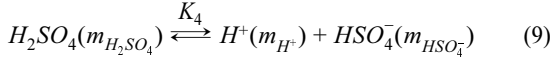$$pH(T) = -\log(\sqrt{K_W(T)}) = pK_W/2 \tag{3}$$

where $K_w(T)$ is the water dissociation constant and T is temperature. The pK_W as a function of temperature T(K) can be estimated using Eq. (4)[2]:

$$pK_w(T) = -4.098 - 3245/T + 2.23 \times 10^{-5}/T^2$$
$$- 3.998 \times 10^{-7}/T^2 + (13.95 - 1262.3/T$$
$$+ 8.56 \times 10^{-5}/T^2)\log\rho \tag{4}$$

where ρ is the water density.

In SCC testing in simulating BWR water conditions, $NaOH$, HCl, and H_2SO_4 are usually added to adjust the conductivity of test solution. These impurities in actual plants can enter the coolant through the regeneration system of the spent resin in the condensate polishing system[2]. Additionally, these impurities may become concentrated in crevices, such as at crack tips. The chemical reactions for these species are as follows[2,3]:

$$H_2O \overset{K_W}{\rightleftharpoons} H^+(m_{H^+}) + OH^-(m_{OH^-}) \tag{5}$$

$$NaCl(m_{NaCl}) \overset{K_1}{\rightleftharpoons} Na^+(m_{Na^+}) + Cl^-(m_{Cl^-}) \tag{6}$$

$$HCl(m_{HCl}) \overset{K_2}{\rightleftharpoons} H^+(m_{H^+}) + Cl^-(m_{Cl^-}) \tag{7}$$

$$NaOH(m_{NaOH}) \overset{K_3}{\rightleftharpoons} Na^+(m_{Na^+}) + OH^-(m_{OH^-}) \tag{8}$$

$$H_2SO_4(m_{H_2SO_4}) \overset{K_4}{\rightleftharpoons} H^+(m_{H^+}) + HSO_4^-(m_{HSO_4^-}) \tag{9}$$

$$HSO_4^-(m_{HSO_4^-}) \overset{K_5}{\rightleftharpoons} H^+(m_{H^+}) + SO_4^{2-}(m_{SO_4^{2-}}) \tag{10}$$

$$Na_2SO_4(m_{H_2SO_4}) \overset{K_6}{\rightleftharpoons} Na^+(m_{Na^+}) + HSO_4^-(m_{HSO_4^-}) \tag{11}$$

$$Na_2SO_4^-(m_{HSO_4^-}) \overset{K_7}{\rightleftharpoons} Na^+(m_{H^+}) + SO_4^{2-}(m_{SO_4^{2-}}) \tag{12}$$

$$NaHSO_4(m_{HSO_4^-}) \overset{K_8}{\rightleftharpoons} Na^+(m_{Na^+}) + H^+(m_{H^+}) \tag{13}$$
$$+ SO_4^{2-}(m_{SO_4^{2-}})$$
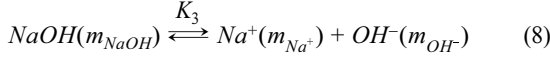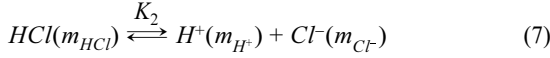
where K_i is the equilibrium constant of each reaction and m_j is the molality of species j. The equilibrium constant for each chemical reaction can be expressed as:

$$K_W = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} = \frac{m_{H^+}m_{OH^-}\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}} \tag{14}$$

$$K_1 = \frac{a_{Na^+}a_{Cl^-}}{a_{NaCl}} = \frac{m_{Na^+}m_{Cl^-}\gamma_{Na^+}\gamma_{Cl^-}}{m_{NaCl}\gamma_{NaCl}} \tag{15}$$

$$K_2 = \frac{a_{H^+}a_{Cl^-}}{a_{HCl}} = \frac{m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-}}{m_{HCl}\gamma_{HCl}} \tag{16}$$

$$K_3 = \frac{a_{Na^+}a_{OH^-}}{a_{NaOH}} = \frac{m_{Na^+}m_{OH^-}\gamma_{Na^+}\gamma_{OH^-}}{m_{NaOH}\gamma_{NaOH}} \tag{17}$$

$$K_4 = \frac{a_{H^+}a_{HSO_4^-}}{a_{H_2SO_4}} = \frac{m_{H^+}m_{HSO_4^-}\gamma_{H^+}\gamma_{HSO_4^-}}{m_{H_2SO_4}\gamma_{H_2SO_4}} \tag{18}$$

$$K_5 = \frac{a_{H^+}a_{SO_4^{2-}}}{a_{HSO_4^-}} = \frac{m_{H^+}m_{SO_4^{2-}}\gamma_{H^+}\gamma_{SO_4^{2-}}}{m_{HSO_4^-}\gamma_{HSO_4^-}} \tag{19}$$

$$K_6 = \frac{a_{Na^+}a_{NaSO_4^-}}{a_{Na_2SO_4}} = \frac{m_{Na^+}m_{NaSO_4^-}\gamma_{Na^+}\gamma_{NaSO_4^-}}{m_{Na_2SO_4}\gamma_{Na_2SO_4}} \tag{20}$$

$$K_7 = \frac{a_{Na^+}a_{SO_4^{2-}}}{a_{NaSO_4^-}} = \frac{m_{Na^+}m_{SO_4^{2-}}\gamma_{Na^+}\gamma_{SO_4^{2-}}}{m_{NaSO_4^-}\gamma_{NaSO_4^-}} \tag{21}$$

$$K_8 = \frac{a_{Na^+}a_{H^+}a_{SO_4^{2-}}}{a_{NaHSO_4}} = \frac{m_{Na^+}m_{H^+}m_{SO_4^{2-}}\gamma_{Na^+}\gamma_{H^+}\gamma_{SO_4^{2-}}}{m_{NaHSO_4}\gamma_{NaHSO_4}} \tag{22}$$

where γ_j is the activity coefficient of species j. The activity coefficient γ_j can be estimated from Debye-Hückel theory, which can be given as[2]:

$$\log(\gamma_j) = \frac{-Az_j^2\sqrt{\mu}}{(1 + Ba^0\sqrt{\mu})} \tag{23}$$

where $\mu = \sum 0.5 m_j z_j^2$ is the ionic strength of the solution, z_j is the ionic charge, a^0 is the distance of the closest approach, and A and B are constants. The value of a^0 has been assumed as 4.5×10^{-8} cm[2]. Values of A and B can be computed as:

$$A = 0.4241 + 0.00321T_C - 2.0 \times 10^{-5}T_C^2 \\ + 5.95143 \times 10^{-8}T_C^3 \tag{24}$$

$$B = 0.3237 + 0.00019T_C - 2.12586 \times 10^{-7}T_C^2 \\ B = +1.4241 \times 10^{-9}T_C^3 \tag{25}$$

where T_C is temperature in *CLSUPo*. It can be computed that $\gamma_{H^+} = \gamma_{OH^-} = \gamma_{Na^+} = \gamma_{Cl^-}$ and $\gamma_{NaCl} = \gamma_{HCl} = \gamma_{NaOH} = 1$. It is also assumed that H_2SO_4 and Na_2SO_4 are completely dissociated, i.e., K_4 and K_6 are not needed to be considered. The water dissociation constant can be computed using Eq. (4). The remaining dissociation constants can be computed as functions of temperatures, written as[2,4]:

$$pK_1 = 483.7740/T_K - 5.0881 + 0.0091T_K \tag{26}$$

$$pK_2 = 2684.0060/T_K - 16.4465 + 0.0226T_K \tag{27}$$

$$pK_3 = 1324.6809/T_K - 8.2525 + 0.0120T_K \tag{28}$$

$$pK_5 = 318.5/T_K - 4.146 + 0.01687T_K \tag{29}$$

$$pK_7 = 10.61 - 0.08T_K + 1.85 \times 10^{-4}T_K^2 \\ - 1.5 \times 10^{-7}T_K^3 \tag{30}$$

$$pK_8 = 6.07 - 0.04T_K + 8.58 \times 10^{-5}T_K^2 \\ + 6.6 \times 10^{-8}T_K^3 \tag{31}$$

As for the electroneutrality, the total charge of the solution should be zero after the dissociation, since all the substances are initially neutral. Therefore, the sum of concentrations of all charged ions multiplied by their

charge (+ or −) should be equal to zero. In the case of BWR conditions, the electroneutrality equation can be expressed as:

$$m_{H^+} + m_{Na^+} - m_{OH^-} - m_{Cl^-} - m_{HSO_4^-} \qquad (32)$$
$$- m_{NaSO_4^-} - 2m_{SO_4^{2-}} = 0$$

As for the mass balance, the sum of all species concentrations after dissociation should be equal to their initial concentrations in the original substances. If m_{Na}^0, m_{Cl}^0 and $m_{SO_4}^0$ were initial concentration of Na^+, Cl^- and SO_4^{-2}, the following mass balance equations can be obtained:

$$m_{Na}^0 = m_{Na^+} + m_{NaCl} + m_{NaOH} + m_{NaSO_4^-} + m_{NaHSO_4} \quad (33)$$

$$m_{Cl}^0 = m_{Cl^-} + m_{HCl} + m_{NaCl} \qquad (34)$$

$$m_{SO_4}^0 = m_{HSO_4^-} + m_{NaSO_4^-} + m_{SO_4^{2-}} + m_{NaHSO_4} \qquad (35)$$

There are 7 ionic species with unknown concentrations; including H^+, Na^+, OH^-, Cl^-, HSO_4^-, $NaSO_4^-$, and SO_4^{2-}. In addition, $NaOH$ and HCl are not dissociated completely. $NaHSO_4$ can also be formed in the solution from a reaction between Na^+, H^+, and SO_4^{2-}. Na^+ may also react with Cl^- to form $NaCl$. Therefore, there are in total 11 species with unknown concentration. We have also obtained 11 equations needed to compute those concentration. The concentration of each species can be computed by solving the obtained simultaneous non-linear equations using the Newton-Raphson method.

To compute the conductivity κ, the equivalent conductivity of each ion λ_i is needed. The value of λ_i of each ion can be computed as Eq. (36):

$$\lambda_i = a + bT_K + cT_K^2 + dT_K^3 \qquad (36)$$
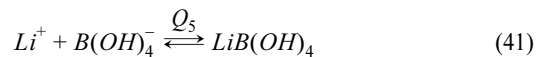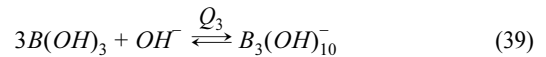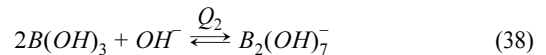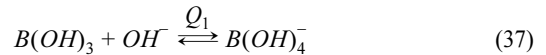
Coefficients in Eq. (36) are listed in Table 1.

2.2 pH & Conductivity in PWR

The primary coolant of PWR typically contains boron at a concentration ranging from 2,400 ppm at the beginning of a fuel cycle to around 100 ppm at the end. In addition, Lithium hydroxide is injected to control the pH, in order to mitigate corrosion in the reactor coolant system (RCS).

Table 1 Coefficients used in Eq. (36) for equivalent conductivity estimation[5-7]

Ionic species	a	b
H^+	−2894.15699	+1.85702 × 10^1
OH^-	−928.6152	+3.3097
HSO_4^-	+223.6316	−2.7003
$NaSO_4^-$	+218.4087	−2.6372
SO_2^-	+468.5866	−5.53736
Na^+	+85.69767	−1.8218
Cl^-	−150.74094	−0.49215
Li^+	−205.63642	+0.518438
$B(OH)_4^-$	+644.6921	−5.6529464
$B_2(OH)_7^-$	+296.91823	−3.362067
$B_3(OH)_{10}^-$	−46.616317	−0.175917

Ionic species	c	d
H^+	−3.10769 × 10^{-2}	+1.7819 × 10^{-5}
OH^-	+3.7512 × 10^{-3}	−7.3268 × 10^{-6}
HSO_4^-	+9.0029453 × 10^{-3}	−6.337456 × 10^{-6}
$NaSO_4^-$	+8.7926 × 10^{-3}	−6.1894 × 10^{-6}
SO_2^-	+1.8042 × 10^{-2}	−1.286 × 10^{-5}
Na^+	+7.2609 × 10^{-3}	−5.13945 × 10^{-6}
Cl^-	+5.545104 × 10^{-3}	−4.39614528 × 10^{-6}
Li^+	+6.9396 × 10^{-4}	+1.287777 × 10^{-6}
$B(OH)_4^-$	+1.498271 × 10^{-2}	−9.6719382 × 10^{-6}
$B_2(OH)_7^-$	+1.08055 × 10^{-2}	−8.49017 × 10^{-6}
$B_3(OH)_{10}^-$	+1.53107 × 10^{-3}	−5.24867 × 10^{-7}

The chemical reactions in the PWR environments include[2]:

$$B(OH)_3 + OH^- \overset{Q_1}{\rightleftharpoons} B(OH)_4^- \qquad (37)$$

$$2B(OH)_3 + OH^- \overset{Q_2}{\rightleftharpoons} B_2(OH)_7^- \qquad (38)$$

$$3B(OH)_3 + OH^- \overset{Q_3}{\rightleftharpoons} B_3(OH)_{10}^- \qquad (39)$$

$$Li + OH^- \overset{Q_4}{\rightleftharpoons} LiOH \qquad (40)$$

$$Li^+ + B(OH)_4^- \overset{Q_5}{\rightleftharpoons} LiB(OH)_4 \qquad (41)$$

$$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^- \qquad (42)$$

The equilibrium constants for these reactions are obtained as:

$$pQ_1 = -1573/T_K - 28.6059 - 0.012078T_K$$
$$+13.2258\log T_K \tag{43}$$

$$pQ_2 = -2756.1/T_K + 18.966 - 5.835\log T_K \tag{44}$$

$$pQ_3 = -3339.5/T_K + 8.8084 - 1.497\log T_K \tag{45}$$

$$Q_4 = 1.99 \tag{46}$$

$$Q_5 = 2.12 \tag{47}$$

The equilibrium constants can also be obtained based on the concentrations of species in the reactions:

$$Q_1 = \frac{m_{B(OH)_4^-}\gamma_{B(OH)_4^-}}{m_{B(OH)_3}\gamma_{B(OH)_3}m_{OH^-}\gamma_{OH^-}} \tag{48}$$

$$Q_2 = \frac{m_{B_2(OH)_7^-}\gamma_{B_2(OH)_7^-}}{(m_{B(OH)_3}\gamma_{B(OH)_3})^2 m_{OH^-}\gamma_{OH^-}} \tag{49}$$

$$Q_3 = \frac{m_{B_3(OH)_{10}^-}\gamma_{B_3(OH)_{10}^-}}{(m_{B(OH)_3}\gamma_{B(OH)_3})^3 m_{OH^-}\gamma_{OH^-}} \tag{50}$$

$$Q_4 = \frac{m_{LiOH}\gamma_{LiOH}}{m_{Li^+}\gamma_{Li^+}m_{OH^-}\gamma_{OH^-}} \tag{51}$$

$$Q_5 = \frac{m_{LiB(OH)_4}\gamma_{LiB(OH)_4}}{m_{Li^+}\gamma_{Li^+}m_{B(OH)_4^-}\gamma_{B(OH)_4^-}} \tag{52}$$

For electroneutrality, the following equation can be written:

$$m_{H^+} + m_{Li^+} - m_{OH^-} - m_{B(OH)_4^-} - m_{B_2(OH)_7^-} \tag{53}$$
$$- m_{B_3(OH)_{10}^-} = 0$$

For the mass balance, the following equations can be obtained:

$$m_{LiOH}^0 = m_{Li}^0 = m_{Li^+} + m_{LiOH} + m_{LiB(OH)_4} \tag{54}$$

$$m_{B(OH)_3}^0 = m_B^0 = m_{B(OH)_3} + m_{B(OH)_4^-} + 2m_{B_2(OH)_7^-} \tag{55}$$
$$+ 3m_{B_3(OH)_{10}^-} + m_{LiB(OH)_4}$$

There are six ionic species (e.g., H^+, Li^+, OH^-, $B(OH)_4^-$, $B_2(OH)_7^-$ and $B_3(OH)_{10}^-$) and three neutral species (e.g., $B(OH)_3$, $LiOH$ and $LiB(OH)_4$) with unknown concentrations. We also have made nine equations to compute these concentrations. The equivalent conductivities needed to compute the conductivity can be obtained using Eq. (36).

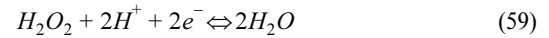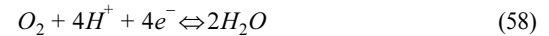Coefficients for each ionic species are listed in Table 1.

2.3 Corrosion Potential Estimation

The corrosion potential of metal substrate like stainless steels can be estimated using the mixed potential theory (after pH and conductivity computation)[8,9]. The mixed potential theory assumes that the net anodic current density must be equivalent to the net cathodic current density. This can be mathematically expressed as:

$$\sum_{j=1}^{n} i_j + i_{corr} = 0 \tag{56}$$

where i_j is the particular current density due to the redox reaction of j-th oxidizer and i_{corr} is the corrosion current density of the metal substrate[8,9].

The oxidizers considered here include dissolved hydrogen, oxygen, and hydrogen peroxide. The half-cell reactions involved are as follows:

$$2H^+ + 2e^- \Leftrightarrow H_2 \tag{57}$$

$$O_2 + 4H^+ + 4e^- \Leftrightarrow 2H_2O \tag{58}$$

$$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O \tag{59}$$

For each reaction, the partial current density is written as:

$$i_j = \frac{\exp\{(E - E_f^e)/b_f\} - \exp\{-(E - E_r^e)/b_r\}}{\dfrac{1}{i_0} + \dfrac{1}{i_{l,f}}\exp\{(E - E_f^e)/b_f\} - \dfrac{1}{i_{l,r}}\{(E - E_r^e)/b_r\}} \tag{60}$$

where E is the corrosion potential, E_f^e and E_r^e are the equilibrium potential of the forward and reversed reactions, respectively, and b_f and b_r are the Tafel constants for the forward and reversed reactions, and $i_{l,f}$ and $i_{l,r}$ are the diffusion limiting current densities for the forward and reversed reactions, respectively, and i_0 is the exchange current density. The equilibrium potentials of the considered oxidizers are:

$$E_{f/r,H_2}^e = E_{0,H_2} + \frac{RT}{2F}\ln(1000Mr_{H_2}k_{H_2}) \tag{61}$$
$$- \frac{RT}{2F}\ln(C_{H_2}^{ppm}) - 2.303\frac{RT}{F}pH$$

$$E^e_{f/r,O_2} = E_{0,O_2} - \frac{RT}{4F}\ln(1000Mr_{O_2}k_{O_2}) \quad (62)$$
$$+ \frac{RT}{4F}\ln(C^{ppm}_{O_2}) - 2.303\frac{RT}{F}pH$$

$$E^e_{f/r,H_2O_2} = E_{0,H_2O_2} - \frac{RT}{2F}\ln(1000Mr_{H_2O_2}k_{H_2O_2}) \quad (63)$$
$$+ \frac{RT}{2F}\ln(C^{ppm}_{H_2O_2}) - 2.303\frac{RT}{F}pH$$

where $E_{0,j}$ is the standard potential of oxidizer j, F is Faraday's constant, Mr_j is the molar mass of oxidizer j, k_j is the Henry's law constant for oxidizer j, and C^{ppm}_j is the concentration in ppm of oxidizer j. The limiting current density is computed as:

$$i_l = \pm 0.0165nFDCRe^{0.86}Sc^{0.33}/d \quad (64)$$

where the sign is positive for forward reaction or negative for reverse reaction, n is the number of electron involved in the reaction, D is the diffusivity, C is the concentration of dissolved oxidizer in the bulk solution, Re is the Reynolds number (i.e., $Re = Vd/\nu$), Sc is the Schmidt number (i.e., $Sc = \nu/D$), d is the channel diameter, V is flow velocity, and ν is the kinematic viscosity.

The corrosion current density of the metal substrate is computed using an empirical equation written as:

$$i_{corr} = \frac{\exp\{(E-E_0)/b_{f,SS}\} - \exp\{-(E-E_0)/b_{r,SS}\}}{\dfrac{1}{i^0_p} + \dfrac{\exp\{(E-E_0)/b_{f,SS}\}}{i^0_p\exp\{0.523(E-E_0)^5\}}} \quad (65)$$

where $b_{f,SS}$ and $b_{r,SS}$ are the Tafel constants for the forward and reversed reactions for the stainless steels, i^0_p is the exchange current density for the reaction of stainless steels in high-temperature water conditions, and $i_{corr} = 0$ if $E < E_0$. Table 2 shows values for the parameters used for the corrosion potential estimation of SSs. The Newton-Raphson method was used to solve the mixed-potential equations to obtain the corrosion potential.

3. Estimation Results

To validate the methods used in this work, the estimated values are compared with the measured values from laboratory tests.

3.1 pH & Conductivity

For BWR environments, very limited pH or conductivity

Table 2 Values for the parameters used for the corrosion potential estimation of SSs[9]

Parameter	Value
E_{0,H_2} (V_{SHE})	0
E_{0,O_2} (V_{SHE})	$1.52 - 0.001T_K + 6.02 \times 10^{-7}T_K^2$ $-3.27 \times 10^{-10}T_K^3$
E_{0,H_2O_2} (V_{SHE})	$1.98 - 0.0007T_K + 9.9 \times 10^{-8}T_K^2$ $-3.68 \times 10^{-10}T_K^3 - 1.37 \times 10^{-13}T_K^4$
pk_{H_2}	$-1321/T_K + 10.73 - 0.01T_K$
pk_{O_2}	$-1202/T_K + 9.622 - 0.01T_K$
ν (cm^2/s)	$\exp(-6.14 + 1103.16/T_K - 457155.3/T_K^2)$
D_{H_2} (cm^2/s)	$\exp(-5.7 + 296.74/T_K - 288379.2/T_K^2)$
D_{O_2} (cm^2/s)	$8.03\exp(-3490/RT_K)$
$D_{H_2O_2}$ (cm^2/s)	$8.03\exp(-3490/RT_K)$
i_{0,H_2} (cm^2/s)	$0.01 \times C_{H_2}^{0.5} \times \exp(-14244/RT_K)$
i_{0,O_2} (cm^2/s)	$0.01 \times C_{O_2}^{0.486} \times \exp(-14244/RT_K)$
i_{0,H_2O_2} (cm^2/s)	$0.01 \times C_{H_2O_2}^{0.486} \times \exp(-14244/RT_K)$
b_{f,H_2}, b_{r,H_2}	0.065
b_{f,O_2}, b_{r,O_2}	0.071
b_{f,H_2O_2}, b_{r,H_2O_2}	0.071
$b_{f,SS}$, $b_{r,SS}$	0.06
E_0 (V_{SHE})	$0.12 - 1.53T_K^{-3}$
i^0_p (cm^2/s)	$2.6 \times 10^{-3} \times \exp(-4416/T_K)$

Table 3 Comparison of measured and estimated conductivities in simulated BWR water conditions

Reference	Conditions	Measured conductivity (μS/cm)	Estimated conductivity (μS/cm)
Ljungberg et al. [10]	25 ppb SO_4^{2-}, 25°C	0.4	0.23
	100 ppb SO_4^{2-}, 25°C	0.8 to 1	0.9
	Clean, 288°C	3.0	2.9
	25 ppb SO_4^{2-}, 288°C	3.3	3.08
	100 ppb SO_4^{2-}, 288°C	3.7	3.65
Round robin study [11]	25 ppb SO_4^{2-}, 25°C	Mostly 0.24 to 0.33	0.23
Andresen et al. [12]	29 ppb SO_4^{2-}, 25°C	0.27	0.27
	3.65 ppb Cl^-, 25°C	0.077	0.078
	18.25 ppb Cl^-, 25°C	0.224	0.232
Du et al. [13]	30 ppb Cl^-, 25°C	0.35 to 0.39	0.37

Table 4 Comparison of measured and estimated pH in simulated BWR and PWR water conditions

Reference	Conditions	Reported pH	Estimated pH
Bojinov et al. [14]	1,000 ppb SO_4^{2-}, 25°C	4.4	4.69
	3,000 ppb SO_4^{2-}, 25°C	4.1	4.21
	6,000 ppb SO_4^{2-}, 25°C	3.8	3.91
	8,000 ppb SO_4^{2-}, 25°C	3.7	3.79
	10,000 ppb SO_4^{2-}, 25 C	3.7	3.69
Kim et al. [2]	2 ppm of Li, 0 ppm of B, 25°C	10.2	10.46
	2 ppm of Li, 200 ppm of B, 25°C	7.2	7.42
	2 ppm of Li, 2,000 ppm of B, 25°C	5.6	5.82
Zhao et al. [15]	70 ppm of Li, 0 ppm of B, 360°C	10.56	10.48
	70 ppm of Li, 100 ppm of B, 360°C	10.4	10.36
	70 ppm of Li, 1,000 ppm of B, 360°C	9.83	9.75
	100 ppm of Li, 20 ppm of B, 360°C	10.76	10.59
	100 ppm of Li, 200 ppm of B, 360°C	10.71	10.4
Wang et al. [16]*	2.7 ppm of Li, 3,675 ppm of B, 300°C	6.42	6.41
	2.5 ppm of Li, 1,900 ppm of B, 300°C	6.75	6.77
	2 ppm of Li, 595 ppm of B, 300°C	7.15	7.15
	1.5 ppm of Li, 194 ppm of B, 300°C	7.37	7.37
	1 ppm of Li, 4 ppm of B, 300°C	7.52	7.51
Peng et al. [17]*	0 ppm of Li, 500 ppm of B, 300°C	5.4	5.4
	0 ppm of Li, 1,100 ppm of B, 300°C	5.25	5.25
	2.3 ppm of Li, 0 ppm of B, 300°C	7.88	7.88
	3.5 ppm of Li, 0 ppm of B, 300°C	8.05	8.06
	4.5 ppm of Li, 0 ppm of B, 300°C	8.15	8.17

* The pH was estimated using commercial software HSC4.

data at operating temperatures are reported in earlier literatures[10-13], as shown in Table 3.

It is noted that the measured conductivities and pH were obtained either in inlet or outlet water of the test systems. As shown in Table 3, Ljungberg et al.[10] and Round robin study[11] reported higher conductivities of test solution with 25 ppb of SO_4^{2-} than the estimation of this study. Other impurities, such as chromate, might be present in the test systems, which might affect the water conductivities especially at room temperature.

For the pH comparison, reported data[2,14-17] was used to validate the pH estimation in BWR and PWR environments, as shown in Table 4. The predicted pH values at room temperature and higher temperatures appear to show a good agreement with the reported results in earlier literature[2,14,15], although some polyborates, which are usually rare in the coolant, are not considered in this calculation. The prediction errors are mostly within ±0.2, which is judged to be acceptable. These slight errors might be due to the presence of other impurities in the experiments, measurement errors, etc. For the reported pH values in simulated PWR primary water conditions[16,17], which were estimated by a commercial software, are almost identical to the estimated pH in this work.
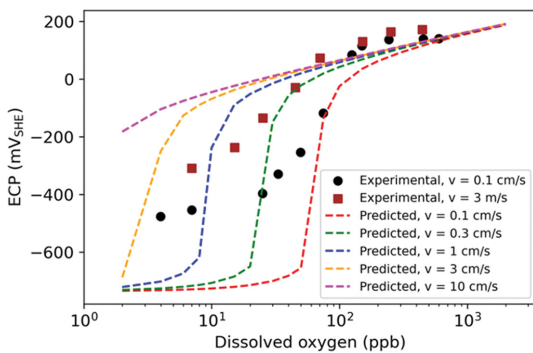
3.2 Corrosion Potential Estimation

Table 5 shows the comparison of measured and estimated corrosion potential of SSs in high-temperature water conditions. It is noted that some parameters listed in Table 2 could be dependent on other factors; anodic curve of SSs may be affected by the steel compositions and acid concentration in the water[18]. In addition, flow velocity or channel diameter was assumed (i.e., $V = 5$ cm/s and $D = 20$ cm) when values were not reported. Nevertheless, the predicted potentials are mostly within ±0.05 V from the measured values.

The corrosion potential of SSs in high-temperature water conditions is highly dependent on the exchange current density and limiting current density (e.g., concentration of dissolved oxidizer and hydrodynamic conditions). Fig. 1 shows the estimated corrosion potential of SSs as functions of dissolved oxygen concentration and flow velocity, which was compared with measurements for 304 SS by Kim et

Table 5 Comparison of measured and estimated corrosion potential of SSs

Conditions	Measured	Estimated
0.01 ppm H_2, 0.27 ppm O_2, 289°C [9]	−0.04	−0.046
0.08 ppm H_2, 0.04 ppm O_2, 289°C [9]	−0.185	−0.214
0.15 ppm H_2, 0.02 ppm O_2, 289°C [9]	−0.235	−0.284
0.135 ppm H_2, 0.013 ppm O_2, 289°C [9]	−0.255	−0.307
0.135 ppm H_2, 0.014 ppm O_2, 289°C [9]	−0.240	−0.301
0.135 ppm H_2, 0.0.016 ppm O_2, 289°C [9]	−0.265	−0.293
0.135 ppm H_2, 0.017 ppm O_2, 289°C [9]	−0.250	−0.289
0.01 ppm H_2, 0.2 ppm O_2, 288°C [10]	−0.01 to 0.05	−0.056
0.01 ppm H_2, 0.2 ppm O_2, 100 ppb of SO_4^{2-}, 288°C [10]	−0.06 to 0.03	−0.039
0.125 ppm H_2, 0.015 ppm O_2, 288°C [10]	−0.190 to −0.070	−0.291
0.125 ppm H_2, 0.015 ppm O_2, 100 ppb of SO_4^{2-}, 288°C [10]	−0.320 to −0.05	−0.278
0.125 ppm H_2, 0.005 ppm O_2, 288°C [10]	−0.400 to −0.320	−0.383
0.125 ppm H_2, 0.005 ppm O_2, 100 ppb of SO_4^{2-}, 288°C [10]	−0.540 to −0.230	−0.369

Fig. 1 Estimated corrosion potential of SSs as functions of dissolved oxygen and flow velocity.

al.[19]. Assuming that hydrodynamic diameter d = 30 cm and other dissolved gasses than oxygen are not present, several predicted curves corresponding to certain flow velocities are drawn in Fig. 1. The discrepancy between the prediction and measurement is likely because the exact

concentration of other oxidizers than dissolved oxygen (e.g., dissolved hydrogen) was not reported. In addition, the exact hydrodynamic conditions like Re or Sc were unknown, which affect the limiting current density. Macdonald[9] also reported the large scatter band of corrosion potential measurement data especially at lower dissolved oxygen conditions.

4. Summary & Conclusions

A computer code that can calculate pH and conductivity in high-temperature water chemistry was developed. In the code, three chemical species ($NaOH$, HCl, and H_2SO_4) were considered for BWR water chemistry conditions, whereas H_3BO_3 and $LiOH$ were considered for PWR conditions. With given concentrations of chemical species, pH and conductivity of solution could be computed at a given temperature. The corrosion potential of austenitic SSs was also estimated based on the mixed-potential theory. With the given pH and dissolved gas (hydrogen, oxygen, and hydrogen peroxide), the corrosion potential could be estimated at a given temperature. The developed code was validated by comparing the predicted values with experimental ones. The results showed that the code yielded reasonably accurate predictions. Therefore, predicted pH, conductivity, and corrosion potential can be used as input features for predicting SCC growth rates of SSs in nuclear power plant conditions. As further work, improvements in the proposed code is still possible. For pH and conductivity calculations, more data may be necessary to confirm the dissociation constants and equivalent conductivities of considered chemical species. For the ECP calculation, modifications in the exchange current densities of oxidizers and corrosion current density of the substrate are also possible, if more relevant data are available. Moreover, if new chemical species related to the secondary water chemistry conditions of PWR are added, the developed code can be used as a prediction tool for the primary and secondary water chemistry of PWR.

Acknowledgement

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