Measurement and Calculation of Electrochemical Potentials in Hydrogenated High Temperature Water, including an Evaluation of the Yttria-Stabilized Zirconia/Iron-Iron Oxide (Fe/Fe₃O₄) Probe as a Reference Electrode

Steven A. Attanasio, David S. Morton, Mark A. Ando

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Measurement and Calculation of Electrochemical Potentials in Hydrogenated High Temperature Water, including an Evaluation of the Yttria-Stabilized Zirconia/Iron-Iron Oxide (Fe/Fe3O4) Probe as a Reference Electrode

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ABSTRACT
The importance of knowing the electrochemical corrosion potential (ECP, also referred to as \( E_{corr} \)) of nickel-base alloys in hydrogenated water is related to the need to understand the effects of dissolved (i.e., aqueous) hydrogen concentration ([\( H_2 \)]) on primary water stress corrosion cracking (PWSCC). Also, the use of a reference electrode (RE) can improve test quality by heightening the ability to detect instances of out-of-specification or unexpected chemistry. Three methods are used to measure and calculate the ECP of nickel-based alloys in hydrogenated water containing \( ~1 \) to \( 150 \) scc/kg \( H_2 \) (0.1 to 13.6 ppm \( H_2 \)) at 260 to 360°C. The three methods are referred to as the specimen/component method, the platinum (Pt) method, and the yttria-stabilized zirconia/iron-iron oxide (YSZ/Fe-Fe3O4) RE method. The specimen/component method relies upon the assumption that the specimen or component behaves as a hydrogen electrode, and its \( E_{corr} \) is calculated using the Nernst equation. The present work shows that this method is valid for aqueous \( H_2 \) levels \( \geq 5 \) to \( 10 \) scc/kg \( H_2 \). The Pt method uses a voltage measurement between the specimen or component and a Pt electrode, with the Pt assumed to behave as a hydrogen electrode; this method is valid as long as the aqueous \( H_2 \) level is known. The YSZ/Fe-Fe3O4 method, which represents a relatively new approach for measuring \( E_{corr} \) in this environment, can be used even if the aqueous \( H_2 \) level is unknown. The electrochemical performance of the YSZ/Fe-Fe3O4 probe supports its viability as a RE for use in high temperature hydrogenated water. Recent design modifications incorporating a teflon sealant have improved the durability of this RE (however, some of the REs do still fail prematurely due to water in-leakage). The Pt method is judged to represent the best overall approach, though there are cases where the other methods are superior. For example, the specimen/component method provides the simplest approach for calculating the \( E_{corr} \) of plant components, and the YSZ/Fe-Fe3O4 RE method provides the best approach if the \( H_2 \) level is unknown, or in off-nominal chemistry conditions. The present paper describes the use of these methods to determine the ECP of a specimen or component versus the ECP of the nickel/nickel oxide (Ni/NiO) phase transition, which is important since prior work has shown that this parameter (\( ECP - ECP_{Ni/NiO} \)) can be used to assess aqueous \( H_2 \) effects on PWSCC.

BACKGROUND
The importance of being able to measure and/or calculate \( ECP \) is related to the need to understand and predict the effects of aqueous \( H_2 \) level on PWSCC. It has been clearly shown that aqueous \( H_2 \) influences PWSCC [1-5]. However, evidence has been presented [3, 4] that ECP is a more fundamental measure of environmental effects on PWSCC. According to Cassagne [6], "the role of hydrogen is to fix the potential and consequently to control the oxide composition". In fact, aqueous \( H_2 \) effects are more readily understood if the data are correlated using the parameter 'ECP vs. the Ni/NiO equilibrium' (i.e., \( ECP - ECP_{Ni/NiO} \) or, alternatively, \( ECP_{Ni/NiO} - ECP \) [3, 4]. As shown in Figure 1, the maxima in SCC growth rate for three nickel-based alloys resides near the ECP of the measured Ni/NiO transition when data from multiple temperatures are plotted using this parameter [4, 7, 8]. The Ni/NiO phase transition used to construct Figure 1 is based on contact electric
resistance (CER) and corrosion coupon measurements [7]. Previous work [9] has shown that Pt behaves as a hydrogen electrode in high temperature hydrogenated water, and that Ni-based alloys often exhibit similar behavior. This observation is useful since potentials can be calculated and referenced to the standard hydrogen electrode (SHE) scale by using the Nernst equation to calculate the $E_{corr}$ of the hydrogen exchange reaction at the temperature, pH and $H_2$ level of interest. Electrodes based on the YSZ system (e.g., Cu/CuO, Hg/HgO, Ag/Ag$_2$O, Fe/Fe$_3$O$_4$) have been used as pH electrodes in previous studies [10], and acceptable performance relative to Pt (acting as a hydrogen electrode) was demonstrated at temperatures from 175 to 275°C [11]. It was pointed out by Niedrach [12] that if the pH of a given system is essentially constant and readily calculable, a YSZ-based electrode can also serve as a RE. In fact, YSZ-based electrodes have been used successfully as REs in boiling water reactor (BWR) environments at 288°C [13]. However, a detailed evaluation has not been performed for PWSCC environments, in which testing is typically conducted at higher temperatures and at much higher aqueous $H_2$ concentrations compared to either normal water chemistry (NWC) or hydrogen water chemistry (HWC) BWR environments. (e.g., HWC tests are typically conducted at ~ 0.15 ppm $H_2$ [14], which corresponds to ~ 1.7 scc/kg $H_2$). The YSZ/Fe-$Fe_3O_4$ RE has several key benefits: (i) it does not introduce contamination (e.g., chlorides) into the environment, (ii) it can be operated without placing Teflon™ in the hot water (and thus can function at > 288°C), and (iii) its potential can be referenced to the SHE scale.

EXPERIMENTAL

Testing was conducted in deaerated water buffered to a high temperature pH of ~ 6.5 to 6.75. The desired $H_2$ concentrations were obtained by varying the feed tank $H_2$ overpressure according to Henry's law. The room temperature $H_2$ calculations were conducted using a Henry's law coefficient [15] of 0.85 psia/(scc/kg). Mixed gas of 4 or 14.7% hydrogen with the balance being argon was used to obtain aqueous $H_2$ levels less than 20 scc/kg $H_2$. ECP measurements were made using voltmeters with input impedance $\geq 10$ GΩ. Testing was performed in recirculating autoclaves which have been described previously [16]. Additional details regarding ECP measurement hardware (e.g., the YSZ/Fe-$Fe_3O_4$ RE) are discussed later in this paper.

The ECP data were supplemented in some cases by using a silver/palladium (Ag/Pd) tube to measure autoclave $H_2$ pressure at 260°C. This device has been used by others, mainly at high temperatures (e.g., 360°C), as discussed by Scott [3]. The measurements were performed using a 75% Pd-25% Ag tube having 0.127 mm wall thickness, 4.7 mm outside diameter and 63.5 mm length: the tube also has an internal spine to support high external pressure. The Ag/Pd tube is brazed to a stainless steel (SS) cap on one end and to a SS tube on the other end, with the SS tube connected to a vacuum pump and a pressure transducer. The measurement is conducted by pumping down the inside of the tube and then valving the pump out of the circuit so that the pressure transducer registers the buildup of hydrogen gas within the tube. The vacuum formed by the pump creates a driving force for hydrogen in the autoclave to diffuse through and build up inside the Ag/Pd tube. The pressure in the tube builds up to a steady-state pressure, which is equal to the hydrogen partial pressure in the autoclave.

RESULTS

Details are provided in this section for the three methods used to measure and/or calculate $E_{corr}$. Only methods for which $E_{corr}$ can be referenced to the SHE scale are discussed, since ECP measurements can only be quantitative in nature if the measurements are referenced to a standard scale.
Method (1): Specimen/Component Calculational Method: This method requires that the aqueous H\textsubscript{2} level, temperature, Henry’s law coefficient and the pH at the temperature of interest be known. The specimen is assumed to act essentially as a hydrogen electrode (Figure 2), and thermodynamic data for the hydrogen exchange reaction are used to calculate the potential of the specimen or component. Data are plotted in Figure 3 to assess the ability of nickel and several types of nickel-based alloys (Alloy X-750 in the HTH and AH heat treatments and Alloy 600) to act as hydrogen electrodes. In Figure 3, it is shown that for nickel and the nickel-based alloy specimens, the steady-state electrochemical corrosion potential of the specimen is very similar to that of platinum (i.e., within 0 to 6 mV, which is a minor difference) for aqueous H\textsubscript{2} levels \( \geq 5 \) to 10 scc/kg. Since platinum is known to act as a hydrogen electrode in this environment (based on prior work [9], and supported by data generated in the present study), Figure 3 implies that the \( E_{\text{corr}} \) of nickel or a nickel-based alloy can be readily calculated using available thermodynamic data for the hydrogen exchange reaction, provided that the aqueous hydrogen level is known and the concentration is \( \geq 5 \) to 10 scc/kg H\textsubscript{2}.

The reason why Ni-based alloys begin to deviate from hydrogen electrode behavior below \( \sim 5 \) to 10 scc/kg H\textsubscript{2} (Figure 3) while Pt continues to behave as a hydrogen electrode in this regime is related to the fact that a competing reaction (i.e., metal oxidation) is present on the Ni-based alloys but not on Pt (Figure 4 (a)). For Ni-based alloys, at relatively high aqueous H\textsubscript{2} levels the rate of H\textsubscript{2} oxidation is much greater than the rate of metal corrosion, and thus the hydrogen oxidation reaction dominates the anodic kinetics, resulting in an \( E_{\text{corr}} \) that is only negligibly different from that of a hydrogen electrode (Figure 4(b)). However, since the rate of the H\textsubscript{2} oxidation reaction is monotonically related to the aqueous H\textsubscript{2} level, a point is eventually reached as the aqueous hydrogen level is lowered at which metal corrosion begins to influence the total anodic current, and thus affect the ECP (Figure 4(c)).

Procedure: The calculations utilize the Nernst Equation for the reaction 2 H\textsuperscript{+} + 2 e\textsuperscript{-} \( \rightleftharpoons \) H\textsubscript{2}:

\[
E_{\text{hydrogen electrode}}^{\text{SHE}} = E_{\text{hydrogen electrode}}^{\text{ref}} - \frac{RT}{nF} \ln \frac{f_{H_2}}{a_{H^+}^{n/2}} \quad [\text{Volts}]
\]  

- \( E_{\text{hydrogen electrode}}^{\text{SHE}} \) is the electrochemical potential of the hydrogen exchange reaction vs. SHE (volts)
- \( E_{\text{hydrogen electrode}}^{\text{ref}} \) is the standard potential at unit fugacity and activity (volts) (\( E^\circ = 0 \) in equation [1])
- \( R \) is the universal gas constant (8.314 J/mol·K)
- \( T \) is temperature in Kelvin, K
- \( n \) is the number of electrons transferred in equivalents/mole (\( n = 2 \) in equation [1])
- \( F \) is Faraday’s constant (96,500 coulombs/equivalent)
- \( f_{H_2} \) is the fugacity of H\textsubscript{2} (atmospheres), where \( f_{H_2} = [H_2] \cdot h \)
- \([H_2]\) is the aqueous hydrogen concentration and \( h \) is the Henry’s law coefficient
- \( a_{H^+} \) is the activity of hydrogen ions (where \( a_{H^+} = [H^+] = 10^{-\text{pH}} \), \( \ln a_{H^+} = -2.303 \cdot \text{pH} \))

Equation [1] can be simplified to:

\[
E_{\text{hydrogen electrode}}^{\text{SHE}} = -4.3 \times 10^{-3} \cdot T (\ln ([H_2] \cdot h)) + 4.6 \cdot pH \quad [\text{Volts}]
\]

Table 1 provides the necessary input data for calculating \( E_{\text{corr}} \) via the specimen/component method.

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1. Figure 3 suggests that nickel may behave as a hydrogen electrode at lower coolant hydrogen values than Ni-based alloys.
Table 1. Data Needed for Hydrogen Electrode Calculations

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Temperature (K)</th>
<th>Henry’s Law coefficient, ( H ) atm/sec/kg</th>
<th>Test pressure(^1) (psig)</th>
<th>Calculated pH (at temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>533</td>
<td>( 1.50 \times 10^3 )</td>
<td>1800</td>
<td>6.70</td>
</tr>
<tr>
<td>288</td>
<td>561</td>
<td>( 1.06 \times 10^2 )</td>
<td>1500</td>
<td>6.62</td>
</tr>
<tr>
<td>316</td>
<td>589</td>
<td>( 7.19 \times 10^3 )</td>
<td>3000</td>
<td>6.52</td>
</tr>
<tr>
<td>338</td>
<td>611</td>
<td>( 5.08 \times 10^3 )</td>
<td>3000</td>
<td>6.57</td>
</tr>
<tr>
<td>360</td>
<td>633</td>
<td>( 3.47 \times 10^3 )</td>
<td>3200</td>
<td>6.75</td>
</tr>
</tbody>
</table>

\(^1\) The 288°C testing was performed at a lower pressure than the 260°C testing because it was performed more recently; test pressures were reduced to increase the likelihood of survivability of linear variable differential transformers (LVDTs) and YSZ/iron-iron oxide reference electrodes.

**Henry’s Law coefficients:** The Henry’s Law coefficients (Table 1) are taken from [15]. Unpublished hydrogen permeation data indicate that the existing Henry’s Law correlation, on which these data are based, may be slightly in error; the uncertainty introduced by this issue is on the order of \( \sim 10 \text{ mV} \).

**pH:** The pH values were calculated using a high temperature thermodynamic code. Key parameters in the pH calculations are the concentration of pH additive and pressure used in the calculation, plus the presence/absence of a density correction. It is noted that when ECPs are measured vs. the YSZ/Fe-Fe\(_3\)O\(_4\) RE or calculated versus the Ni/NiO equilibrium [4, 8], the pH term ‘drops out’ since the hydrogen electrode potential, the Fe/Fe\(_3\)O\(_4\) equilibrium, and the Ni/NiO equilibrium all have the same pH dependence (i.e., the same slope on a Pourbaix diagram).

**Sample Calculation:** For the Alloy 600 specimen tested at 120 sec/kg and 338°C (see Figure 3), the hydrogen fugacity is calculated as 0.61 atmospheres using the Henry’s law coefficient in Table 1. Using equation [2] and Table 1, the ECP for the hydrogen electrode is calculated as: \( E_{\text{hydrogen, electrode}}^{\text{SHE}} = -0.781 \text{ V}_{\text{SHE}} \); note that this value is consistent with our previously published data [4].

**Benefits and Drawbacks:** Method (1) is cost-effective, simple, and can be applied in situations where no RE data are available (e.g., plant components or ‘historical’ autoclave test specimens). Method (1) is generally not useful in off-nominal environments (e.g., in the presence of an oxidizer, which may cause the specimen ECP to deviate from hydrogen electrode behavior). Also, this method cannot improve test quality control by detecting inadvertent chemistry changes during a test.

**Method (2): Platinum Electrode Method:** Calculations are performed to determine the potential of a hydrogen electrode at the specified temperature and aqueous H\(_2\) level using the Nernst equation. Then, the measured steady-state voltage difference between the specimen and the Pt electrode is added to the calculated Pt potential to calculate the specimen potential on the SHE scale:

\[
E_{\text{specimen}}^{\text{SHE}} = E_{\text{hydrogen, electrode}}^{\text{SHE}} + (E_{\text{specimen}} - E_{\text{platinum}}) \tag{3}
\]

It is important to electrically isolate the specimen and Pt electrode from all other metals when using methods (1) or (2) (particularly from metals such as zircalpy which do not behave as hydrogen electrodes), using ceramic, teflon (if ≤ 288°C) or thermally-oxidized zirconia [17].

At H\(_2\) levels \( \geq 5 \) to 10 sec/kg, the difference between Methods (1) and (2) is negligible. However, if one considers the Alloy X-750 AH data point in Figure 3 at 0.7 sec/kg H\(_2\) and 338°C, where the measured potential between Alloy X-750 AH and Pt is \(-47 \text{ mV}\), the calculated Pt potential (i.e., hydrogen electrode potential) is \(-0.646 \text{ V}_{\text{SHE}}\), while the calculated specimen potential is \(-0.693\).
A 47 mV difference may represent an appreciable error, and this example shows why Method (2) is the more accurate and preferred method at H2 levels below ~ 5 to 10 scc/kg.

**Evaluation of Pt as a Hydrogen Electrode:** Figure 5 shows the Ecorr of Pt versus Fe/Fe3O4 as a function of aqueous H2 level at 316°C. The data follow the trend for the theoretical hydrogen electrode quite closely, with an offset of ~ 15 to 20 mV. Agreement within ± 10 mV has been termed ‘excellent’ for potentials measured using a high temperature RE [18]. The 15 to 20 mV offset is believed to be due to uncertainties in the thermodynamic values for the Fe/Fe3O4 equilibrium used to calculate the theoretical hydrogen electrode line. The offset in Figure 5 indicates that there is a systematic bias in either: (a) the ECP measurements or (b) the thermodynamic properties used to calculate the theoretical hydrogen potential. It is judged that (b) is much more likely, since the ECP measurements versus the YSZ/Fe-Fe3O4 electrode are relatively straightforward and are not subject to any evident bias (it is shown later in this paper that the impedance of the YSZ/Fe-Fe3O4 probe does not introduce a bias to the measurements).2 As shown in Figures 6 to 9 and in Tables 4, 5, 7 and 8, similar data to those in Figure 5 and Table 6 (316°C) have been obtained at 260, 288, 338 and 360°C.

Figure 10 shows a semi-logarithmic plot of the Ecorr of Pt versus Fe/Fe3O4 as a function of the logarithm of aqueous H2 level from 260 to 360°C. The evident linearity in the E vs. log [H2] data for each temperature indicates that the RE is behaving in a Nernstian manner. In fact, linearity is evident for more than two orders of magnitude in aqueous H2 concentration at 338 and 360°C. The Nernst equation predicts that a larger negative slope for the E vs. log [H2] data should be observed as the temperature increases (Equation [2]). Figure 10 shows that the slopes at 260, 288, 316, 338 and 360°C are − 0.041, − 0.044, − 0.050, − 0.052 and − 0.059, respectively: this trend is consistent with theoretical expectations. Further, a quantitative comparison can be made between the slopes of the E vs. log [H2] data and the theoretical slopes derived from the Nernst equation. The theoretical slope is equal to the coefficient in equation [2] (i.e., − 4.3 × 10−5 · T), multiplied by 2.303 to account for the conversion between natural and base-ten logarithms. Figure 10 shows that the agreement with theory is reasonable, with errors of 23, 21, 14, 16, and 6% at 260, 288, 316, 338 and 360°C, respectively.

**Method (3): YSZ/Iron-Iron oxide RE Method:** This method requires only that the temperature and the pH be known, since the Fe/Fe3O4 equilibrium does not depend on the aqueous H2 level. The measured potential is converted to the SHE scale using thermodynamic data for iron and iron oxide. A schematic diagram of the YSZ/Fe-Fe3O4 electrode is shown in Figure 11. The iron/iron oxide electrode is built by mixing Fe and Fe3O4 powder and placing the mixture into a closed-end ceramic (YSZ) tube which is then immersed in the autoclave. An equilibrium develops between Fe and Fe3O4 (i.e., Fe3O4 + 8 H+ + 8 e− ↔ 3 Fe + 4 H2O) which produces a constant potential on an iron or stainless steel wire immersed in the powder, at a given pH and temperature [12]. This concept can be

2 Further, it is not uncommon for there to be some inaccuracies in high temperature thermodynamic metal/metal oxide calculations. For example, the theoretical Ni/NiO equilibrium calculated using thermodynamic data has been shown to be somewhat different than the experimentally measured Ni/NiO phase transition [7].

3 General Electric has used the YSZ-based RE primarily in the Cu/Cu2O form. In the present work, Cu/Cu2O was not used due to concern that the autoclave would be contaminated with copper if the ceramic tube were to fracture near its tip.

4 The ceramic tube provides a sheath for the Fe + Fe3O4 powder which prevents the mixture from becoming wet. It also serves as an oxygen ion conductor, which allows an equilibrium to develop between Fe, Fe3O4, H2O and H+. At the inner surface of the tube, the following equilibrium is established: Fe3O4 + 4 V" + 8 e− ↔ 3 Fe + 4 O2 (V" represents oxygen ion vacancies in the ceramic and O2 represents oxygen ions in the ceramic). The equilibrium at the outer tube surface is: 8 H+ + 4 O2 ↔ 4 H2O + 4 V", yielding a net reaction of: Fe3O4 + 8 H+ + 8 e− ↔ 3 Fe + 4 H2O (these reactions are based on those described for the YSZ/Hg-HgO electrode in [9]).
visualized in terms of the Fe Pourbaix diagram in Figure 2. The diagonal line labeled '13' corresponds to the equilibrium between Fe and Fe₃O₄. If the pH of the environment is essentially constant and reasonably well-known (as is the case for high temperature hydrogenated water), the Fe/Fe₃O₄ reaction exhibits a unique (and calculable) electrode potential on the SHE scale.

Procedure: Calculations are performed using the thermodynamics for the iron/magnetite reaction:

\[
Fe₃O₄ + 8 H^+ + 8 e^- \leftrightarrow 3 Fe + 4 H₂O
\]  \[4\]

The Nernst Equation for this reaction is written as:

\[
E_{\text{SHE}}^{\text{Fe/Fe₃O₄}} = E_{\text{Fe/Fe₃O₄}}^o - \frac{RT}{nF} \ln \frac{a_{Fe}^3 \cdot a_{H₂O}^{-4}}{a_{Fe₃O₄} \cdot a_{H^+}^8} \ [\text{Volts}] \]  \[5\]

• \(E_{\text{Fe/Fe₃O₄}}^{\text{SHE}}\) is the electrochemical potential of the iron/iron oxide reaction vs. SHE (volts)
• \(E_{\text{Fe/Fe₃O₄}}^o\) is the standard potential of the reaction at unit fugacity and activity (volts)
• \(R, T, n, \) and \(F\) have been previously defined (note that \(n = 8\) for reaction \[4\]).
• \(a_{Fe}, a_{Fe₃O₄}, \) and \(a_{H₂O}\) are the activity of iron, magnetite, and water [all are assumed = 1]
  • \(a_{Fe} = a_{Fe₃O₄} = 1\) since these are pure solid species; \(a_{H₂O} = 1\) since the environment is dilute

Using this information, equation \[5\] can be simplified to:

\[
E_{\text{SHE}}^{\text{Fe/Fe₃O₄}} = E_{\text{Fe/Fe₃O₄}}^o - \frac{2.303RT}{F} \cdot pH \ [\text{Volts}] \]  \[6\]

Using thermodynamic quantities derived from magnetite testing by Ziemniak [19]:

\[
E_{\text{Fe/Fe₃O₄}}^o = 0.073 - 1.38 \times 10^{-3} \cdot T + 1.47 \times 10^{-4} (T \cdot \ln T) \ [\text{Volts}] \]  \[7\]

Table 2 shows \(E_{\text{Fe/Fe₃O₄}}^o\) values, pH values, and \(E_{\text{Fe/Fe₃O₄}}^{\text{SHE}}\) values as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Temperature (K)</th>
<th>(E_{\text{Fe/Fe₃O₄}}^o) (V)</th>
<th>Calculated pH (at temperature)</th>
<th>(E_{\text{Fe/Fe₃O₄}}^{\text{SHE}}) (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>533</td>
<td>-0.171</td>
<td>6.70</td>
<td>-0.879</td>
</tr>
<tr>
<td>288</td>
<td>561</td>
<td>-0.179</td>
<td>6.62</td>
<td>-0.916</td>
</tr>
<tr>
<td>316</td>
<td>589</td>
<td>-0.187</td>
<td>6.52</td>
<td>-0.949</td>
</tr>
<tr>
<td>338</td>
<td>611</td>
<td>-0.194</td>
<td>6.57</td>
<td>-0.990</td>
</tr>
<tr>
<td>360</td>
<td>633</td>
<td>-0.200</td>
<td>6.75</td>
<td>-1.048</td>
</tr>
</tbody>
</table>

\(^{1}\) The pH calculations were performed using the test pressures shown in Table 1. The pH and \(E_{\text{Fe/Fe₃O₄}}^{\text{SHE}}\) values are similar, but not identical, to the values used previously [4] (a previous pH code was used in that work).

Equation \[6\] and Table 2 can be used to convert the measured specimen potential vs. Fe/Fe₃O₄ to SHE:
\[ E_{\text{sHE}}^{\text{specimen}} = E_{\text{iron/iron oxide}}^{\text{sHE}} + (E_{\text{specimen}} - E_{\text{iron/iron oxide}}) \text{ [Volts]} \]  

**Sample Calculation:** Figure 5 (a) and Table 6 show that \( E_{\text{specimen}} - E_{\text{iron/iron oxide}} \) for Alloy 600 at 120 scc/kg H₂ and 316°C is 0.177 V. According to Table 2, the \( E_{\text{iron/iron oxide}}^{\text{sHE}} \) value at 316°C is –0.949 V. Thus, the value of \( E_{\text{sHE}}^{\text{specimen}} \) is –0.772 V, as shown in Figure 5 (b) and Table 6.

**Evaluation of Fe/Fe₃O₄ as a RE in High Temperature Hydrogenated Water:**

**Reasonableness check:** According to Figure 2, the difference between the Fe/Fe₃O₄ equilibrium line and the standard hydrogen line (which corresponds to a fugacity of 1 atmosphere) is on the order of ~150 to 200 mV at 250°C. The best available comparison in the present study is at 260°C and 67 scc/kg H₂ (which corresponds to ~1 atmosphere according to the Henry’s law coefficient in Table 1); however, there are no available Pt vs. YSZ/Fe-Fe₃O₄ data at this condition (Figure 6 (a)). It can be stated, though, that the Pt \( E_{\text{corr}} \) data are consistently located ~15 to 20 mV active to the theoretical hydrogen electrode line (e.g., see Figure 5 (a)). Since the theoretical hydrogen electrode potential vs. the YSZ/Fe-Fe₃O₄ electrode at 260°C and 67 scc/kg H₂ is ~173 mV (Figure 6 (a)), it is expected that the potential of Pt vs. the YSZ/Fe-Fe₃O₄ electrode at 260°C and 67 scc/kg H₂ would be on the order of ~153 to 158 mV. Thus, the potentials measured in this study appear to be consistent with the values expected from the Pourbaix diagram.

**Evaluation versus a hydrogen electrode:** Earlier in this paper, several different types of data were used to show that Pt appeared to behave as a hydrogen electrode in the present testing. Since all of the diagnostics used to prove this point rely upon data measured versus the YSZ/Fe-Fe₃O₄ electrode, the consistency of the measured platinum data with expected hydrogen electrode behavior implies that the YSZ/Fe-Fe₃O₄ electrode is truly functioning as a useful RE in this environment.

**Reproducibility:** Measurements versus the YSZ/Fe-Fe₃O₄ probe exhibit good reproducibility to date. Figure 12 shows the \( E_{\text{corr}} \) of Pt and Ni versus YSZ/Fe-Fe₃O₄ at 338°C, for different aqueous H₂ levels. This test has six phases: (A) 40 scc/kg H₂, (B) 19 scc/kg H₂, (C) 15 scc/kg H₂, (D) 10 scc/kg H₂, (E) 15 scc/kg H₂, and (F) 19 scc/kg H₂. The Pt and Ni \( E_{\text{corr}} \) values in phases (C) and (E) are very similar (i.e., within ~2 mV). The Ni \( E_{\text{corr}} \) values in phase (B) are similar to the values in phase (F); a similar comparison cannot be made for Pt since the \( E_{\text{corr}} \) data for Pt did not have enough time to reach a steady-state value in phase (F). Additionally, different probes provide reproducible results. For example, \( E_{\text{corr}} \) values for Ni and Pt at 40 scc/kg H₂ are 0.203 and 0.206 V vs. Fe/Fe₃O₄, respectively, in one test conducted at 316°C. In a subsequent 316°C test with a different electrode, \( E_{\text{corr}} \) values for Ni and Pt at 40 scc/kg H₂ are 0.205 and 0.209 V vs. Fe/Fe₃O₄, respectively (Table 6).

**Response time:** The potentials measured versus the YSZ/Fe-Fe₃O₄ electrode show rapid response to changes in the aqueous hydrogen level. As an example, in Figure 12 the aqueous hydrogen level is changed at 67, 114, 234, 283 and 453 hours. The ECP response for both the platinum and nickel is evident on the subsequent data point (data taken ~every 10 minutes) in most cases.

**Impedance:** The impedance of a RE must be low relative to the input impedance of the voltmeter, to prevent measurement errors due to ‘loading’ of the voltmeter. Because conductivity in the YSZ/Fe-
Fe₃O₄ electrode depends on oxygen ion transport through the ceramic membrane, its impedance tends to be greater than that of traditional high temperature RES such as the Ag/AgCl electrode (whose conductivity depends on ion diffusion through water). Thus, the results of impedance measurements (Table 3) are compared to the input impedance of the voltmeters, as discussed below.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Impedance between Fe/Fe₃O₄ electrode and the autoclave (kΩ)</th>
<th>Impedance between Fe/Fe₃O₄ electrode and a Pt wire (kΩ)</th>
<th>Impedance between Fe/Fe₃O₄ electrode and a Ni wire (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>282</td>
<td>120.5</td>
<td>110.7</td>
<td>106.1</td>
</tr>
<tr>
<td>338</td>
<td>17.8</td>
<td>25.4</td>
<td>25.5</td>
</tr>
</tbody>
</table>

As expected, the impedance values (Table 3) are higher at 282°C than at 338°C. The values are reasonably consistent with previously reported values [20], in which resistances of 100 and 88 kΩ were reported at 250°C. All voltmeters used for ECP measurements in this study have an input impedance of ≥ 10 GΩ (i.e., ~ 10⁵ X greater than the impedance of the YSZ probe at 282°C). These results provide confidence that probe impedance is not adversely affecting the ECP measurements.

**Benefits:** Method (3) is useful in off-nominal environments, the aqueous H₂ level does not have to be known, and the measured potentials are pH-independent since the Fe/Fe₃O₄ equilibrium has the same pH dependence as the hydrogen equilibrium. Also, the YSZ/Fe-Fe₃O₄ electrode is often sensitive to inadvertent chemistry changes during a test, since its potential is not sensitive to changes in oxidizing or reducing conditions. Measurement of potential versus the YSZ/Fe-Fe₃O₄ electrode may therefore show a response if there is inadvertent ingress of an oxidizing agent, for example.

**Drawbacks:** The YSZ/Fe-Fe₃O₄ RES suffer from durability limitations, since the ceramic tube is inherently brittle and is thus susceptible to fracture, particularly at locations of metal-to-ceramic contact. Differential thermal expansion and/or misalignment can cause stress at these contact locations, which can lead to fracture of the ceramic either during assembly or in the autoclave. An example of the ECP-time trace observed due to RE failure in an autoclave is shown in Figure 13. In this test (360°C, 90 scc/kg H₂ from 0 to 161 hours), the RE was functioning effectively until ~40 to 60 hours, at which point the absolute value of the measured Ecorr began to decrease. It is believed that water in-leakage to the ‘active area’ of the RE disrupts the equilibrium between Fe and Fe₃O₄ if the powder becomes wet.⁶

Recent design modifications have improved the durability of the RE. The new design employs a teflon sealant (Figure 14), which eliminates the metal-to-ceramic contact within the sealant region. Historically, teflon sealants have been used successfully in tests conducted in simulated BWR environments [13], which are typically conducted at ~288°C. However, there has always been concern for using teflon sealants at higher temperatures such as those tested in the present study (i.e., up to 360°C), since in order to use teflon, the sealant region must be kept to less than ~93°C. Recent testing has shown that such concerns are legitimate, but that this problem is not intractable. For example, to counteract the increase of sealant temperature, the REs are always placed through a bottom penetration of the autoclave. Also, the use of a ‘stand-off’ (i.e., a 25.4 mm long tube fitting) to move the sealant further away from the autoclave has been successful in reducing the sealant temperature. If the temperature of the sealant increases, the Conax™ housing can be periodically re-

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⁶ Specifically, it is believed that wetting of the powder and the wire creates a mixed potential on the wire which is intermediate between the Fe/Fe₃O₄ potential and the hydrogen equilibrium potential associated with hydrogenated water.
torqued to counteract the extrusion of the teflon (note that the use of the stand-off has minimized the need for re-torque after autoclave cooldown).

An additional new design feature is that the annular gap between the outer diameter of the ceramic tube and the inner diameter of the Conax™ housing has been enlarged, such that more lateral displacement of the ceramic tube is permitted before metal-to-ceramic contact occurs. Thicker wall ceramic tube is also being used in some of the newer REs, which is expected to provide some increase in tube fracture resistance. Note that the standard size tube used in this work has a wall thickness of 0.81 mm, an outside diameter of 6.35 mm and a length of 279.4 to 304.8 mm. The thicker wall ceramic presently under evaluation has a wall thickness of 1.27 mm.

The YSZ/Fe-Fe₃O₄ electrode has a cost of ~ $650 per new electrode, primarily due to the price of custom-built Conax™ fittings required for the electrode pressure boundary, and to the yttria-stabilized zirconia tube. The cost of a replacement electrode is ~ $400, since the Conax™ housing can be reused (a new sealant and a new ceramic tube are needed for each replacement probe). Note that the time to assemble the probe is ~ 1 hour.

Hydrogen Fugacity Measurements using a Silver/Palladium Tube: Data from four tests are shown in Figure 15 (a). The steady-state pressure is a function of the aqueous H₂ concentration, as expected. The calculated pressures on the right side of Figure 15 (a) were determined using the Henry’s Law coefficient from Table 1 (i.e., 0.015 atm/(scc/kg)). Good agreement was obtained between the measured and calculated values, as shown in Figure 15 (b).

DISCUSSION: Converting Corrosion Potentials to the ECP vs. Ni/NiO scale

As described previously [2-7], a maximum in SCC growth rate for nickel-based alloys occurs near the measured Ni/NiO phase transition, as shown in Figures 1 and 16. Thus, the ECP of a specimen or component versus the ECP of the Ni/NiO transition is believed to be the correct parameter for describing aqueous H₂ effects on PWSCC [3, 4, 8]. The following section describes how to determine this “ECP difference” (i.e., \( ECP_{Ni-alloy} - ECP_{Ni/NiO} \) or, alternatively, \( ECP_{Ni/NiO} - ECP_{Ni-alloy} \)).

**Using Method 1:** As shown earlier, nickel-based alloys essentially behave as hydrogen electrodes at \( \geq 5 \) to 10 scc/kg H₂. Thus, the respective aqueous H₂ levels for the environment of interest and the Ni/NiO transition, \([H_2]_{environment}\) and \([H_2]_{Ni/NiO}\), respectively, can be related to ECP via the Nernst equation. Therefore, the ECP of the specimen can be calculated using equation [2]:

\[
ECP_{Ni-alloy}^{SHE} = -\frac{RT}{nF} \left\{ \ln\left( [H_2]_{environment} \cdot H \right) + 4.6 \cdot pH \right\} \text{[Volts]} \tag{9}
\]

and the ECP of the Ni/NiO transition can be calculated using the Nernst equation for a hydrogen electrode at the aqueous H₂ level of the transition (i.e., \([H_2]_{Ni/NiO}\)):

\[
ECP_{Ni/NiO}^{SHE} = -\frac{RT}{nF} \left\{ \ln([H_2]_{Ni/NiO} \cdot H) + 4.6 \cdot pH \right\} \text{[Volts]} \tag{10}
\]

\[\text{In a Pourbaix diagram, the Ni/NiO phase transition (single line) and hydrogen electrodes (multiple lines as a function of H₂ level) have the same slope. These lines are common at the H₂ concentration of the Ni/NiO transition. The aqueous H₂ levels for the measured Ni/NiO transition at 288, 316, 338 and 360°C are 4.7.5. 13.8 and 25 scc/kg H₂, respectively [7].}\]
The “ECP difference” (i.e., $\Delta ECP$) between the specimen and the Ni/NiO phase transition is:

$$\Delta ECP = ECP_{Ni/NiO}^{SHE} - ECP_{Ni-alloy}^{SHE} = 4.3 \times 10^{-5} \cdot T \left\{ \ln \left( \frac{[H_2]_{environment}}{[H_2]_{Ni/NiO}} \right) \right\} [Volts] \quad [11]$$

Note that the terms involving $H$ (Henry’s law coefficient) and $pH$ have dropped out, and that $R/nF$ equals $4.3 \times 10^{-5}$ in Volts/Kelvin, for this reaction. Equation [11] is simply the difference between two hydrogen electrodes, and only the temperature, aqueous $H_2$ level of the environment, and the aqueous $H_2$ level of the Ni/NiO phase transition [7] are needed to determine the “ECP difference”.

**Using Method 2:** The ECP difference using this method can be written as:

$$\Delta ECP = ECP_{Ni/NiO} - ECP_{Ni-alloy} = \left\{ ECP_{Ni/NiO}^{SHE} - ECP_{Ni-alloy}^{SHE} \right\} - \left\{ ECP_{Ni-alloy} - ECP_{Pt} \right\} [Volts] \quad [12]$$

Assuming that the Pt behaves as a hydrogen electrode, the term in the first brackets is simply:

$$ECP_{Ni/NiO} - ECP_{Pt} = 4.3 \times 10^{-5} \cdot T \left\{ \ln \left( \frac{[H_2]_{environment}}{[H_2]_{Ni/NiO}} \right) \right\} [Volts] \quad [13]$$

and the second term is the measured steady-state voltage between the Ni-alloy and the Pt electrode (i.e., $ECP_{Ni-alloy} - ECP_{Pt}$). This term in the second brackets of equation [12] corrects for the extent that the specimen ECP departs from that of a true hydrogen electrode. This value is subtracted from equation [13], to calculate the final ECP difference:

$$ECP_{Ni/NiO} - ECP_{Ni-alloy} = 4.3 \times 10^{-5} \cdot T \left\{ \ln \left( \frac{[H_2]_{environment}}{[H_2]_{Ni/NiO}} \right) \right\} - \left[ ECP_{specimen} - ECP_{Pt} \right][Volts][14]$$

As shown in Figure 3, this correction becomes appreciable only at low $H_2$ levels ($< \sim 5$ to 10 scc/kg).

As an example, consider an Alloy 600 specimen tested at 338°C and 120 scc/kg $H_2$. The measured value of $[ECP_{specimen} - ECP_{Pt}]$ was $\sim 2$ mV in this test (Figure 3). At 338°C, the measured Ni/NiO phase transition is located at 13.8 scc/kg $H_2$ [7]. Thus, the “ECP difference” is:

$$\Delta ECP = ECP_{Ni/NiO} - ECP_{Ni-alloy} = 4.3 \times 10^{-5} \cdot 611 \left\{ \ln \left( \frac{120}{13.8} \right) \right\} - [-2] = 0.059 \text{ Volts} = 59 \text{ mV} \quad [15]$$

Figure 16 shows that the ECP difference for the 120 scc/kg $H_2$ point at 338°C is located at 59 mV.

**Using Method 3:** In this case, the ECP difference (i.e., $ECP_{Ni/NiO} - ECP_{Ni-alloy}$ or $\Delta ECP$) is:
\[ ECP_{Ni/NiO} - ECP_{Ni-alloy} = \{ECP_{Ni/NiO}^{SHE} - ECP_{Fe-Fe_2O_4}^{SHE}\} - \{ECP_{Ni-alloy} - ECP_{Fe-Fe_2O_4}\} \text{ [Volts]} \]

The term in the first brackets can be determined by subtracting equation [6] from equation [10], and the term in the second brackets is the measured steady-state voltage between the test specimen and the YSZ RE. This equation can be simplified to:

\[ \Delta ECP = \frac{RT}{2F} \ln([H_2]_{Ni/NiO} \cdot H) - E^0_{Fe/Fe_2O_4} - \{ECP_{Ni-alloy} - ECP_{Fe-Fe_2O_4}\} \text{ [Volts]} \]

A graphical method for determining this difference can also be used, by employing Figure 17 [7], which shows the Ni/NiO transition measurements in ECP space. Figure 17 shows that ECP measurements vs. the YSZ/Fe-Fe_{2}O_{4} RE can discern whether a given environment is located in the Ni or NiO stability regime, and can quantify the ECP distance from this phase transition.

CONCLUSIONS

- Three methods are used to measure and calculate the electrochemical corrosion potential of nickel-base alloys in hydrogenated water (e.g., ~1 to 150 scc/kg H₂) at 260 to 360°C.
  - The first method assumes that the specimen or component behaves as a hydrogen electrode, and its \( E_{\text{corr}} \) is calculated using the Nernst equation. The present work has shown that this method is valid for aqueous H₂ levels ≥ 5 to 10 scc/kg H₂. This method provides the simplest approach for calculating \( E_{\text{corr}} \) for plant components or historical test specimens.
  - The second method utilizes a voltage measurement between the specimen or component and a Pt electrode, with the Pt assumed to behave as a hydrogen electrode. This method is valid even at H₂ levels < ~5 to 10 scc/kg, as long as the aqueous H₂ level is known. This method is judged to provide the best available approach for \( E_{\text{corr}} \) measurements in most cases.
  - The third method uses a voltage measurement versus a YSZ/Fe-Fe_{2}O_{4} electrode. This work shows that the electrochemical performance of this electrode supports its viability as a RE in high temperature hydrogenated water. This method is the best approach if the H₂ level is unknown, or in off-nominal chemistries. Recent design modifications have improved the durability of the RE, though some of the REs do fail prematurely due to water in-leakage.

- Limited test data using a Ag/Pd tube at 260°C show that measured autoclave hydrogen pressures were consistent with the expected pressure values based on Henry's Law.
- Combining the three ECP methods described above with a Ag/Pd tube for measuring autoclave hydrogen pressures appears to provide an optimal method for environmental definition.
- Relating ECP to the Ni/NiO phase transition by the methods described above is advantageous for evaluating the SCC behavior of Ni-based alloys.

ACKNOWLEDGEMENTS

Thanks to Dr. James Orr, John Schisano and Nelson Schwarting. Also, the idea for using the iron/iron oxide probe as a reference electrode was adopted from Leonard Niedrach of GE-CRD.
REFERENCES

Table 4. Electrochemical Corrosion Potential (ECP) Data at 260°C for Pt and Alloy X-750 Condition AH (AH) [4].

<table>
<thead>
<tr>
<th>[H₂] (sec/kg)</th>
<th>Measured Ecorr of Pt vs. Fe/FeO₄ (V)</th>
<th>Measured Ecorr of Pt vs. SHE (V)</th>
<th>[H₂] (sec/kg)</th>
<th>Measured Ecorr of AH vs. Fe/FeO₄ (V)</th>
<th>Measured Ecorr of AH vs. SHE (V)</th>
<th>[H₂] (sec/kg)</th>
<th>Theoretical Ecorr hydrogen electrode vs. Fe/FeO₄ (V)</th>
<th>Theoretical Ecorr hydrogen electrode vs. SHE (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>0.306</td>
<td>-0.573</td>
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<tr>
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<td>0.206</td>
<td>-0.673</td>
<td>5</td>
<td>0.190</td>
<td>-0.689</td>
<td>5</td>
<td>0.232</td>
<td>-0.647</td>
</tr>
<tr>
<td>20</td>
<td>0.189</td>
<td>-0.690</td>
<td>20</td>
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<tr>
<td>106</td>
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<td>-0.723</td>
<td>15</td>
<td>0.207</td>
<td>-0.672</td>
</tr>
</tbody>
</table>

1. Data measured vs. the YSZ/Fe-Fe₃O₄ electrode (i.e., Fe/FeO₄) were converted to the SHE scale by subtracting 0.879 V (Table 2).
2. A slightly different SHE conversion (0.880 Volts) was employed in [4], where the AH and Pt data were initially reported. All data points reported in the present document were converted using the updated Fe/FeO₄-to-SHE conversion (i.e., 0.879 V at 260°C).
3. Theoretical hydrogen electrode values vs. SHE were converted to the Fe/FeO₄ scale by adding 0.879 V (Table 2).
4. Theoretical hydrogen electrode values on the SHE scale were calculated using Equation [2] and Table 1.

Table 5. ECP Data at 288°C for Pt and Nickel (Ni).

<table>
<thead>
<tr>
<th>[H₂] (sec/kg)</th>
<th>Measured Ecorr of Pt vs. Fe/FeO₄ (V)</th>
<th>Measured Ecorr of Pt vs. SHE (V)</th>
<th>[H₂] (sec/kg)</th>
<th>Measured Ecorr of Ni vs. Fe/FeO₄ (V)</th>
<th>Measured Ecorr of Ni vs. SHE (V)</th>
<th>[H₂] (sec/kg)</th>
<th>Theoretical Ecorr hydrogen electrode vs. Fe/FeO₄ (V)</th>
<th>Theoretical Ecorr hydrogen electrode vs. SHE (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
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<td>-0.680</td>
<td>3</td>
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<tr>
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</table>

1. Data measured vs. the YSZ/Fe-Fe₃O₄ electrode (i.e., Fe/FeO₄) were converted to the SHE scale by subtracting 0.916 V (Table 2).
2. The theoretical hydrogen electrode values vs. SHE were converted to the Fe/FeO₄ scale by adding 0.916 V (Table 2).
3. Theoretical hydrogen electrode values on the SHE scale were calculated using Equation [2] and Table 1.
<table>
<thead>
<tr>
<th>[H] (M)</th>
<th>Measured E&lt;sub&gt;0&lt;/sub&gt; vs. SHE (V)</th>
<th>Measured E&lt;sub&gt;0&lt;/sub&gt; vs. Fe/FeO&lt;sub&gt;2&lt;/sub&gt; (V)</th>
<th>Theoretical E&lt;sub&gt;0&lt;/sub&gt; vs. SHE (V)</th>
<th>Theoretical E&lt;sub&gt;0&lt;/sub&gt; vs. Fe/FeO&lt;sub&gt;2&lt;/sub&gt; (V)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-0.704</td>
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</tr>
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Table 6. ECP Data at 31°C for Pt, Ni, and Alloy 600 (A600) (from the present study and [4]).

<table>
<thead>
<tr>
<th>[H] (M)</th>
<th>Measured E&lt;sub&gt;0&lt;/sub&gt; vs. Ni or AH (V)</th>
<th>Measured E&lt;sub&gt;0&lt;/sub&gt; vs. Pt (V)</th>
<th>Theoretical E&lt;sub&gt;0&lt;/sub&gt; vs. Ni or AH (V)</th>
<th>Theoretical E&lt;sub&gt;0&lt;/sub&gt; vs. Pt (V)</th>
</tr>
</thead>
<tbody>
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<td>-0.619</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>30</td>
<td>0.511</td>
<td>0.515</td>
<td>0.514</td>
<td>0.514</td>
</tr>
</tbody>
</table>

Table 7. ECP Data at 33°C for Pt, Ni, and Alloy X-750 Condition AH (AH) (from the present study and [4]).

[1] Data measured vs. the YSZ/Fe<sub>2</sub>O<sub>3</sub> electrode (i.e., Fe/FeO<sub>2</sub>), which was converted to the SHE scale by subtracting 0.059 V (Table 2).
[2] The theoretical hydrogen electrode values vs. SHE were converted to the Fe/FeO<sub>2</sub> scale by adding 0.059 V (Table 2).
[3] The theoretical hydrogen electrode values on the SHE scale were calculated using Equation 2 (Table 1) and Equation 3 (Table 1).
Table 8. ECP Data at 360°C for Pt, Ni, and Alloy X-750 Condition HTH (HTH) (from the present study and [4]).

<table>
<thead>
<tr>
<th>[H₂] (scc/kg)</th>
<th>Measured E_&lt;sub&gt;corr&lt;/sub&gt; of Pt vs. Fe/Fe₂O₃ (V)</th>
<th>Measured E_&lt;sub&gt;corr&lt;/sub&gt; of Ni or HTH vs. Fe/Fe₂O₃ (V)</th>
<th>Measured E_&lt;sub&gt;corr&lt;/sub&gt; of Ni or HTH vs. SHE (V)</th>
<th>[H₂] (scc/kg)</th>
<th>Measured E_&lt;sub&gt;corr&lt;/sub&gt; of Pt vs. Fe/Fe₂O₃ (V)</th>
<th>Measured E_&lt;sub&gt;corr&lt;/sub&gt; of Ni or HTH vs. Fe/Fe₂O₃ (V)</th>
<th>Measured E_&lt;sub&gt;corr&lt;/sub&gt; of Ni or HTH vs. SHE (V)</th>
<th>[H₂] (scc/kg)</th>
<th>Theoretical E&lt;sub&gt;hydrogen electrode&lt;/sub&gt; vs. Fe/Fe₂O₃ (V)</th>
<th>Theoretical E&lt;sub&gt;hydrogen electrode&lt;/sub&gt; vs. SHE (V)</th>
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[1] Data measured vs. the YSZ/Fe-Fe₂O₃ electrode (i.e., Fe/Fe₂O₃) were converted to the SHE scale by subtracting 1.048 V (Table 2).
[2] A slightly different SHE conversion (1.068 Volts) was employed in [4], where the HTH and Pt data were initially reported. All data points reported in this document were converted using the updated Fe/Fe₂O₃-to-SHE conversion (i.e., 1.048 V at 360°C).
[3] The theoretical hydrogen electrode values vs. SHE were converted to the Fe/Fe₂O₃ scale by adding 1.048 V (Table 2).
[4] Theoretical hydrogen electrode values on the SHE scale were calculated using Equation [2] and Table 1.
Figure 1. Normalized stress corrosion crack growth rate (SCCGR) for several nickel-based alloys at 338 and 360°C, plotted as a function of electrochemical potential (ECP) relative to the ECP of the Ni/NiO phase transition [8]. Crack growth rates are normalized to the minimum growth rate measured for each material (i.e., ~0.64 μm/hr for Alloy X-750 in the AH heat treatment at 338°C, ~0.34 μm/hr for Alloy X-750 HTH at 360°C, and ~0.16 μm/hr for Alloy 600 at 338°C).
Figure 2. Pourbaix diagram for iron (Fe) at 250°C [EPRI].
Figure 3. Electrochemical corrosion potential ($E_{corr}$) of nickel and several types of Ni-based alloy specimens versus a platinum electrode as a function of aqueous hydrogen concentration at 260, 288, 316, 338, and 360°C.
Figure 4 (a). Schematic Evans diagram for Pt in hydrogenated water. The intersection of the reaction rate curves for the H₂ oxidation and H⁺ reduction reactions corresponds to the ECP of a hydrogen electrode. The Pt ECP is that of a hydrogen electrode.

Figure 4 (b). Schematic Evans diagram for Ni-based alloys at relatively high aqueous H₂ levels. The total anodic reaction rate is dominated by H₂ oxidation. Thus, the Eₓₗ of the Ni-based alloys (Ni-a) is negligibly different from that of a hydrogen electrode.

Figure 4 (c). Schematic Evans diagram for Ni-based alloys at low aqueous H₂ levels. The total anodic reaction rate is now influenced by metal corrosion. Thus, the Eₓₗ of the Ni-based alloys (Ni-a) is appreciably lower than that of a hydrogen electrode.
Figure 5. Electrochemical corrosion potentials ($E_{\text{corr}}$) at 316°C for platinum, nickel, and Alloy-600 as well as the theoretical hydrogen electrode potential, vs. the iron/iron oxide RE (a) and the standard hydrogen electrode (SHE) scale (b), as a function of aqueous hydrogen concentration. Logarithmic fits to the Pt and Ni data are also included. Logarithmic fits were selected due to the apparent agreement of the data with Nernstian behavior.
Figure 6. Electrochemical corrosion potentials ($E_{corr}$) at 260°C for platinum and Alloy X-750 in the AH heat treatment (X-750 AH) as well as the theoretical hydrogen electrode potential vs. the iron/iron oxide RE (a) and the standard hydrogen electrode (SHE) scale (b), as a function of aqueous hydrogen concentration.
Figure 7. Electrochemical corrosion potentials ($E_{\text{corr}}$) at 288°C for platinum and nickel as well as the theoretical hydrogen electrode potential, vs. the iron/iron oxide RE (a) and the standard hydrogen electrode (SHE) scale (b), as a function of aqueous hydrogen concentration.
Figure 8. Electrochemical corrosion potentials ($E_{\text{corr}}$) at 338°C for platinum, nickel, and Alloy X-750 AH as well as the theoretical hydrogen electrode potential, vs. the iron/iron oxide RE (a) and the standard hydrogen electrode (SHE) scale (b), as a function of aqueous hydrogen concentration.
Figure 9. Electrochemical corrosion potentials ($E_{corr}$) at 360°C for platinum, nickel, and Alloy X-750 in the HTH heat treatment (X-750 HTH) as well as the theoretical hydrogen electrode potential, vs. the iron/iron oxide RE ($E_{Fe/Fe_2O_3}$) and the standard hydrogen electrode (SHE) scale (b), as a function of aqueous hydrogen concentration.
Figure 10. Semilogarithmic plot of the $E_{corr}$ of Pt vs. Fe/Fe$_2$O$_3$ as a function of the logarithm of aqueous H$_2$ level at temperatures from 260 to 360°C. The data for each temperature are linear, as predicted by theory, and the measured slopes are in reasonable agreement with theory. One data point at 260°C is judged to be an outlier since it is the only data point out of 45 which is in clear disagreement with the other data points.

<table>
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<th>T (°C)</th>
<th>Measured Slope (V/decade)</th>
<th>Theoretical Slope (V/decade)</th>
<th>Percent Error</th>
<th>$R^2$</th>
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Figure 11. Schematic diagram of ceramic membrane reference electrode, taken from General Electric Corporate Research and Development Center [12].

Figure 12. $E_{corr}$ for Pt and Ni versus a YSZ/Fe-Fe$_3$O$_4$ electrode at 338°C, for different aqueous hydrogen levels. Note that the nickel specimen was consistently found to respond more rapidly than Pt to changes in aqueous hydrogen levels. This result was unexpected, as prior work on nickel-based alloys suggested that Pt response would be more rapid. This apparent difference between nickel and nickel-based alloys in terms of response time is not understood at present.
Figure 13. ECP versus time trace for a 360°C test which exhibited YSZ/iron-iron oxide reference electrode failure at approximately 40 to 60 hours into the test (note that the aqueous H₂ level was 90 cc/kg from 0 to 161 hours).

Figure 14. One of the new designs being used for the YSZ/iron-iron oxide reference electrode. This design employs a teflon sealant.
Figure 15. Hydrogen pressure measurements in a test autoclave at 260°C, conducted using a silver/palladium tube. Pressure transients are shown in (a) as a function of dissolved hydrogen concentration. In (b), the measured values are compared to values calculated using the Henry’s Law coefficient in Table 1.
Figure 16. Alloy 600 crack growth rate at 338°C [8], plotted versus the aqueous hydrogen concentration (a) and the ECP difference versus the measured Ni/NiO transition (b). The Ni/NiO transition shown in (a) is based on CER and corrosion coupon data in [7], which indicate that the Ni/NiO transition at 338°C is located at 13.8 scc/kg H₂.
Figure 17. Ni/NiO phase transition measurements in ECP space [7]. This plot shows that ECP measurements vs. the YSZ/Fe-Fe₃O₄ RE can discern whether a given environment is located in the Ni or NiO stability regime.