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Development of FAC Monitoring System Through Electrochemical Sensors

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Abstract

Degradation of low alloy steel piping due to flow-accelerated corrosion (FAC) phenomenon is one of consequential problems in nuclear power plants including pressurized water reactor (PWR) and CANDU. The development of an *in-situ* condition monitoring system through pertinent sensors is highly required to evaluate the severity of FAC phenomenon in the piping components and to take actions before some grave event should occur. As the results of extensive research during the past two decades, it is now possible to predict the corrosion behavior of metals as function of electrochemical corrosion potential (ECP) and pH. For this purpose, it is necessary to develop reference and pH sensors for condition monitoring and life management of a PWR. We report here the results of sensor development for this purpose. Ag/AgCl external electrode and gold-coated nickel electrode have been employed for condition monitoring of water chemistry and ECP. The water-filled Ag/AgCl reference electrode potential remained stable within ± 10 mV over two weeks period. A thermal cycling to 240 °C and back to 288 °C led to a potential shift not exceeding 15 mV. External Ag/AgCl electrode has a temperature limit due to the use of polymer materials. We developed a gold-plated Ni electrode, which was based on the ceramic-to-metal brazing technology. Therefore, it can be used even in high temperature water at 320 °C. Reliability and stability tests have been made in boron and lithium mixture solution at 320 °C. The electrode potential remained stable within ± 10 mV over two weeks period.

1. Introduction

Degradation of low alloy steel piping due to FAC phenomenon is one of consequential problems in nuclear power plants including PWR and CANDU. The development of an *in-situ* condition monitoring system through pertinent sensors is highly required to evaluate the severity of FAC phenomenon in the piping components and to take actions before some grave event should occur. The corrosion of structural metals in PWR operating water is the primary causes of the degradation and fouling of steam generator (SG), piping, and turbine. As the results of extensive research during the past two decades, it is now possible to predict the corrosion behavior of metals as function of ECP and pH^{1,2}. For this purpose, it is necessary to develop reference and pH sensors for condition monitoring and life management of a PWR. Fig. 1 shows the alloy 600 corrosion mode diagram on potential-pH plot¹. We report here the results of sensor development for this purpose and application method of ECP and pH signal to FAC monitoring.

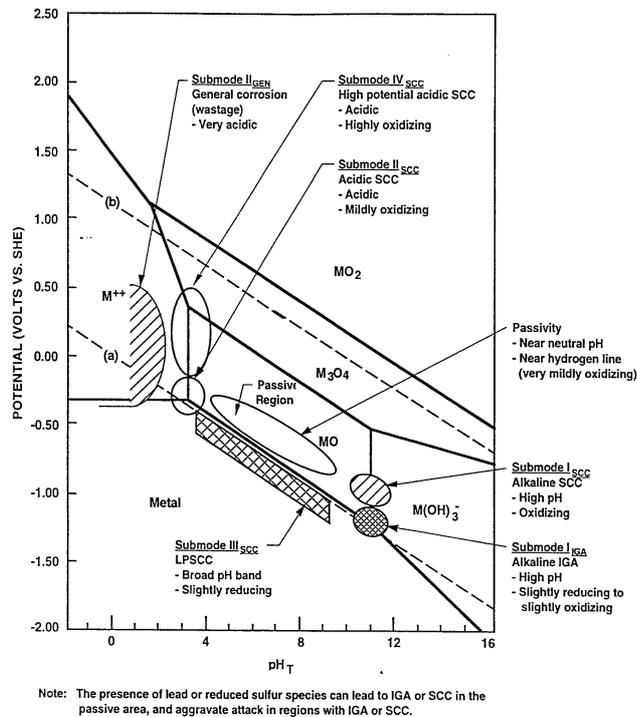


Figure 1. Alloy 600 corrosion mode diagram on potential-pH plot¹.

2. Rationale & Approach

The potential and pH are essential parameters in the condition monitoring of passive components. The FAC phenomenon of steel piping also is related to the ECP of steel and pH of surrounding solution. The temperature range of the FAC occurrence in a PWR secondary system is from 100 to 250 °C. To perform *in-situ* condition monitoring, first of all, the electrodes should survive in such high temperature and have a reliable performance. Stable and long-lived reference and pH electrodes need to be developed. Then, to predict the FAC

rate with the ECP and pH signals, the measured results should be combined with the developed models. The FAC model can be newly developed but there are various mechanistic or empirical FAC models. To verify the accuracy of the ECP and pH monitoring method, an independent *in-situ* thickness monitoring method can be introduced, such as ultrasonic technique, acoustic emission, or vibration monitoring technique.

3. Electrode Development

3.1 EREP

Pressure-balanced external Ag/AgCl electrode has been extensively used for PWR environment^{3,4}. The use of KCl-based buffer solution often becomes the source of electrode potential drift due to Cl⁻ ion leakage through its porous plug, typically made of zirconia (ZrO₂). To solve the leakage problem fundamentally and improve the life and stability of the electrode, high purity water was used as the filling solution in which Cl⁻ ion activity can be

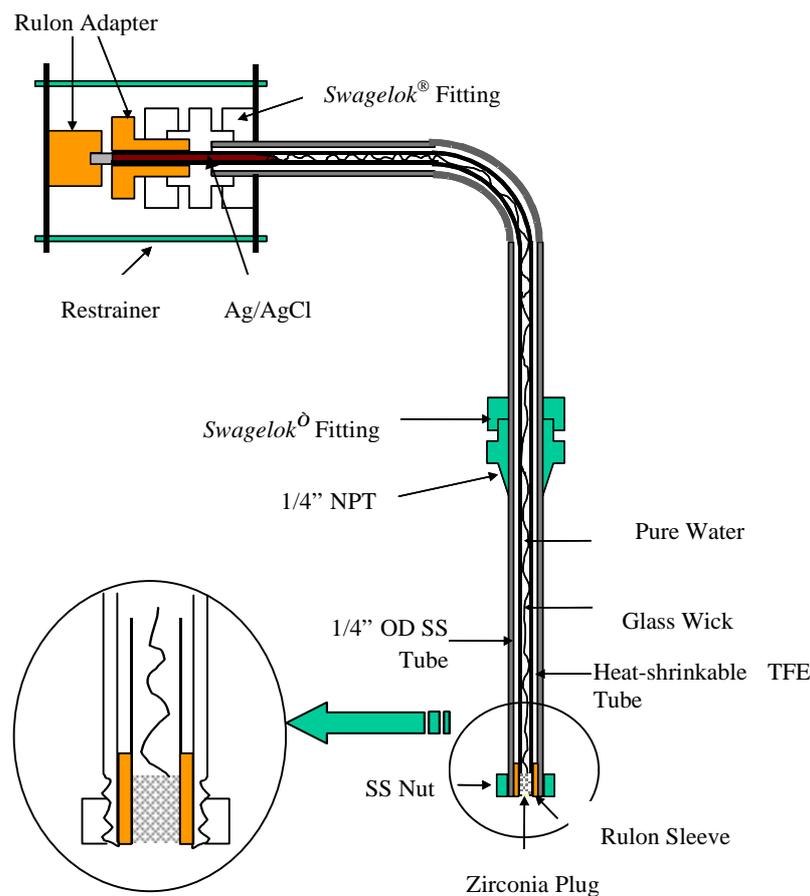


Figure 2. Schematic of developed water-filled Ag/AgCl reference electrode, EREP.

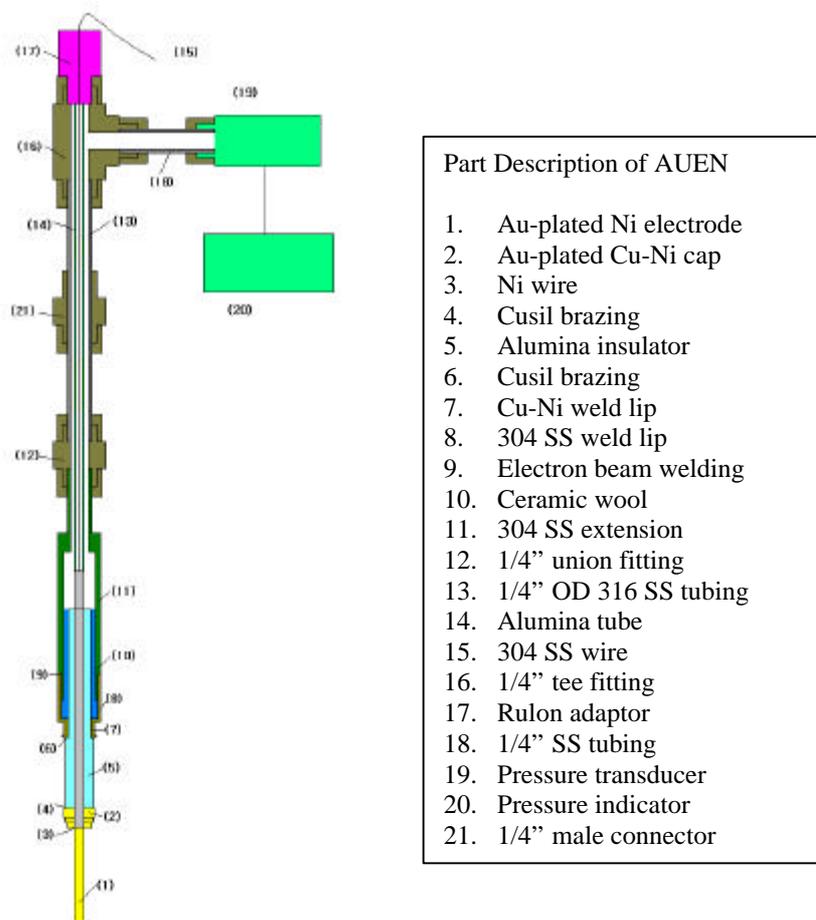


Figure 3. Schematic diagram and part description of Au-plated Ni electrode, AUEN.

established and maintained at the solubility of AgCl even with the sustained leakage for a long period. The Ag/AgCl electrode was called as external reference electrode-PTFE (EREP). EREP potential remained stable within ± 10 mV over two weeks period. A thermal cycling to 240 °C and back to 288 °C led to a potential shift not exceeding 15 mV. Experimental results and analysis for EREP has been published in detail⁵. Figure 2 shows the schematic diagram of developed water-filled Ag/AgCl reference electrode.

3.2 AUEN

Fig. 3 shows the schematic diagram and part description of gold-plated nickel electrode. The developed electrode was called as Au electrode-non PTFE (AUEN), which was made of a conventional feedthrough conductor used in a high temperature vacuum system. To make the surface of Ni conductor serve as hydrogen electrode, Ni conductor and Cu-Ni cap were gold-plated with the thickness of 10 μm . Ni electrode serves as hydrogen electrode, if a surrounding environment contains hydrogen, and we can determine the concentration of dissolved hydrogen or pH, if one of two parameters maintains a constant value. Oxidation-

reduction potential (ORP) can be measured by using AUEN in an environment without hydrogen. To extend the length of AUEN with maintaining the pressure boundary, a 316 SS tube was welded to Cu-Ni weld lip by using electron beam welding technique. A 304 SS signal wire passed through the Rulon[®] adaptor at the end of AUEN, as described in Fig. 3. The Rulon[®] adaptor prevented the water leakage from AUEN to an ambient environment. The inner pressure of AUEN was continuously monitored with a pressure transducer to recognize the leakage. The ceramic-to-ceramic and ceramic-to-metal brazed parts in AUEN were considered as the weakest point in a high temperature aqueous environment. Therefore, the corrosion resistance test of the brazed parts was an essential test, as well as potential stability and reproducibility tests of AUEN.

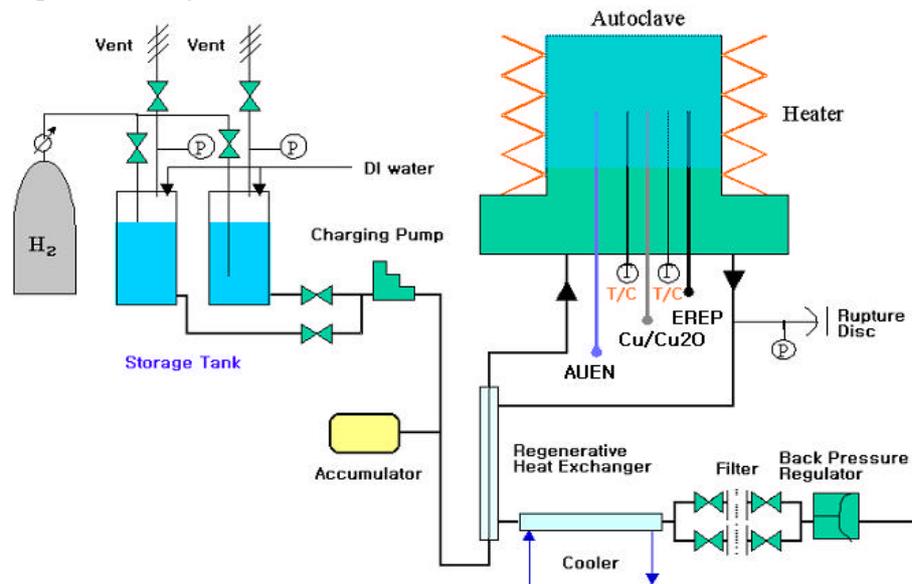


Figure 4. Schematic diagram of the experimental system for AUEN testing.

Fig. 4 shows the schematic diagram of the experimental system for AUEN testing. To protect the penetration seals from high temperature, the autoclave was turned upside down. A refreshed water system was used with a charging/bleeding rate of about 1 L/hr for the loop of which an estimated water volume was about 4 L. Overall flow diagram for the test loop is shown in Fig. 4. Two solution storage tanks made of Ti with the volume of 200 L made it possible to conduct long-term experiments. The autoclave made of 316L SS with the volume of 1 gallon was used and the electric heater with the maximum power of 4 kW heated up the autoclave to control solution temperature. To maintain a PWR primary water environment, the solution supply tank was pressurized by pure hydrogen gas at 10-12 psig. The corresponding dissolved hydrogen concentration at 10-12 psig is about 2.653-2.868 ppm⁶. The test solution was made of 1000 ppm boron as boric acid (H₃BO₃) and 2 ppm lithium as lithium hydroxide (LiOH). The pH of test solution was calculated as a function of temperature by MULTEQ-REDOX[®] Ver. 2.22⁷. The temperature of test solution was 320 °C and the pressure was controlled within 145±5 kg_f/cm². Two AUEN and Cu/Cu₂O/ZrO₂ electrode were installed with thermocouples. To estimate the potential difference between each AUEN, two AUEN were installed in the test cell. Cu/Cu₂O/ZrO₂ electrode has been

used as a reference electrode in BWR environment⁸ or a pH electrode in other environments^{9,10}. In this experiment, Cu/Cu₂O/ZrO₂ electrode was used as a reference electrode with respect to AUEN assuming that pH of test solution maintained constant.

Fig. 5 shows the potential variation results of AUEN as a function of time. From the results, 'AUEN #1' and 'AUEN #2' showed a very good stability within ± 15 mV over all testing times of 350 hours. The potential transients were observed when 100 and 200 hours elapsed. The reason of these transients could be considered as the results of temperature transient, hydrogen overpressure variation, or pH transient caused by solution tank change. The potential difference between each AUEN was estimated as less than 10 mV. The potential difference became smaller with time.

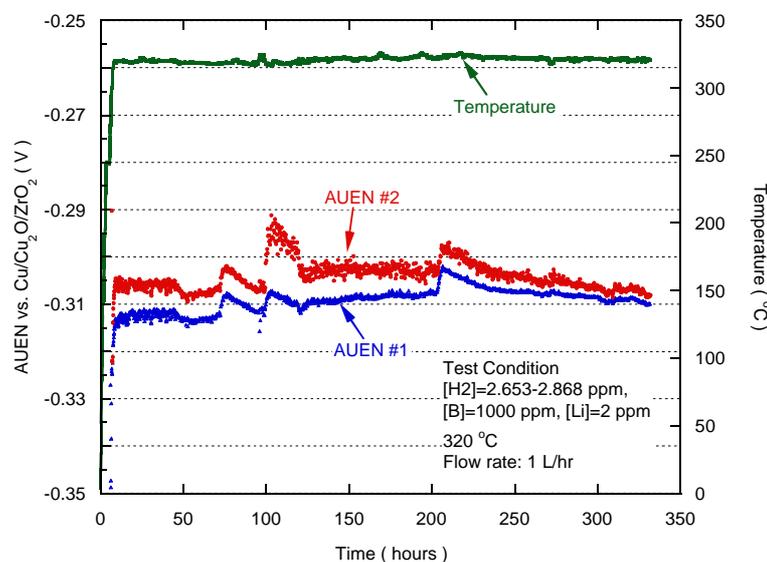


Figure 5. Potential variation results of AUEN as a function of time.

Fig. 6 shows the potential stability results of AUEN in comparison of a round robin test. Five of the world's best laboratories at performing stress corrosion cracking (SCC) studies – ABB Atom AB (Sweden), AEA Technology (UK), GE Corporate Research & Development Center (USA), Studsvik Material AB (Sweden), and VTT Manufacturing Technology (Finland) – were selected to participate in a round robin to evaluate the quality and reproducibility of testing conditions and resulting stress corrosion crack growth rates in sensitized Type 304 SS in 288 °C water¹¹. The results of Pt potential monitoring in the round robin were plotted in Fig. 6. Internal-type Ag/AgCl (Water) electrode of ABB, external-type Ag/AgCl (0.1 M KCl) electrode of AEA, Cu/Cu₂O/ZrO₂ electrode of GE, external-type Ag/AgCl (0.01 M KCl) electrode of Studsvik, and Ni/NiO/ZrO₂ of VTT were installed in the same environments and Pt electrode potential was measured with respect to these electrodes at 288 °C. Under 150 ppb hydrogen environment, ABB, GE, and VTT's electrodes showed the approximate potential to theoretical value. As compared with ABB, GE and VTT's electrodes, AUEN showed a comparable potential stability.

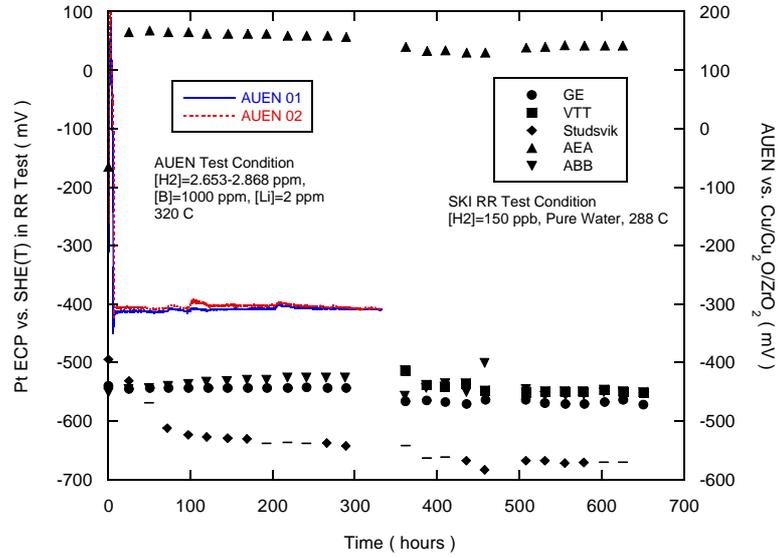


Figure 6. Potential stability results of AUEN in comparison of SKI round robin test.

To calculate the potential of AUEN theoretically, the hydrogen fugacity and pH of solution as a function of temperature should be known. The hydrogen fugacity can be calculated by using Henry's law constant for hydrogen⁶. Assuming AUEN serves as hydrogen electrode, the theoretical potential of AUEN with respect to standard hydrogen electrode at temperature (SHE(T)) can be formulated as follows;

$$\begin{aligned}
 E_{Au(H_2/H^+)} &= E_{Au(H_2/H^+)}^o - 2.303 \frac{RT}{2F} [\log f_{H_2} + 2pH] \\
 &= -2.303 \frac{RT}{2F} [\log(H_{H_2} \cdot x) + 2pH] \text{ vs. SHE(T)}
 \end{aligned} \tag{1}$$

In Eq. (1), H_{H_2} denotes the Henry's law constant for hydrogen and x represents the dissolved hydrogen concentration. Cu/Cu₂O/ZrO₂ electrode potential with respect to SHE(T) can be formulated as follows¹²;

$$\begin{aligned}
 E_{Cu/Cu_2O/ZrO_2} &= E_{Cu/Cu_2O/ZrO_2}^o - 2.303 \frac{RT}{F} pH \\
 &= 0.62262 - 0.00056175T(K) + 1.938 \times 10^{-7} T(K)^2 \\
 &\quad - 2.303 \frac{RT}{F} pH \text{ vs. SHE(T)}
 \end{aligned} \tag{2}$$

By using Eqs (1) and (2), the potential difference between AUEN and Cu/Cu₂O/ZrO₂ electrode can be theoretically calculated. Fig. 7 shows the theoretical values in comparison of experimental results for the potential of AUEN vs. Cu/Cu₂O/ZrO₂ electrode. As shown in Fig.

7, the maximum difference was about 20 mV but, if the uncertainty of high temperature pH and physical and chemical properties are considered, the difference is reasonably acceptable.

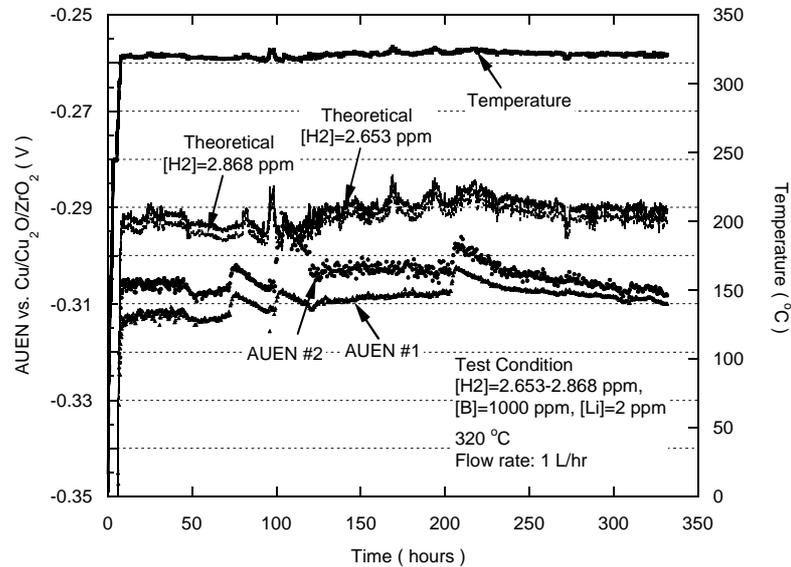


Figure 7. Theoretical potential of AUEN vs. Cu/Cu₂O/ZrO₂ electrode in comparison of the measured results.

4. Application to FAC Monitoring

FAC of carbon steels has been studied world-wide for more than twenty years and is now well understood^{13,14}. The influence of several parameters like water chemistry (i.e. pH and oxygen content), temperature, hydrodynamic or mass transfer conditions (i.e. flow velocity, geometry, steam quality ..) and steel composition on the corrosion kinetics has been demonstrated both theoretically and experimentally. In earlier work, Bouvier et al. investigated the effect of a reducing environment and variable redox conditions to FAC phenomena¹⁵. They observed the good correlation between FAC and electrochemical potential at 180 °C and 235 °C. The FAC phenomenon was stopped when the electrochemical potential was higher than around $-0.45 V_{SHE}$ at 180 °C and $-0.65 V_{SHE}$ at 235 °C. These transition behaviors were interpreted as the result of the oxide transition from magnetite (Fe₃O₄) to hematite (Fe₂O₃). Fig. 8 and 9 show the potential-pH diagram for iron-water system at 180 °C and 235 °C, respectively. The diagrams were plotted by using HSC Chemistry[®] Ver. 4.0, which could compute Gibbs energy, entropy, heat capacity, etc. as a function of temperature and pressure¹⁶. The comparison between ECP measurement and calculated potential-pH diagram is not so direct. The main reason can be a fact that the accuracy of KCl-filled Ag/AgCl reference electrode potential is not so high and the electrode potential drifts with time, as described in SKI round robin results¹¹ and Fig. 6. Precise ECP measurement is needed with a more stable and reliable reference electrode. In Bouvier's experiment, there was no quantitative correlation between the FAC rate and the ECP value for

values lower than the transition¹⁵. It was only an indication of the FAC process existence or not. Additional studies for the quantitative effect of the ECP are needed.

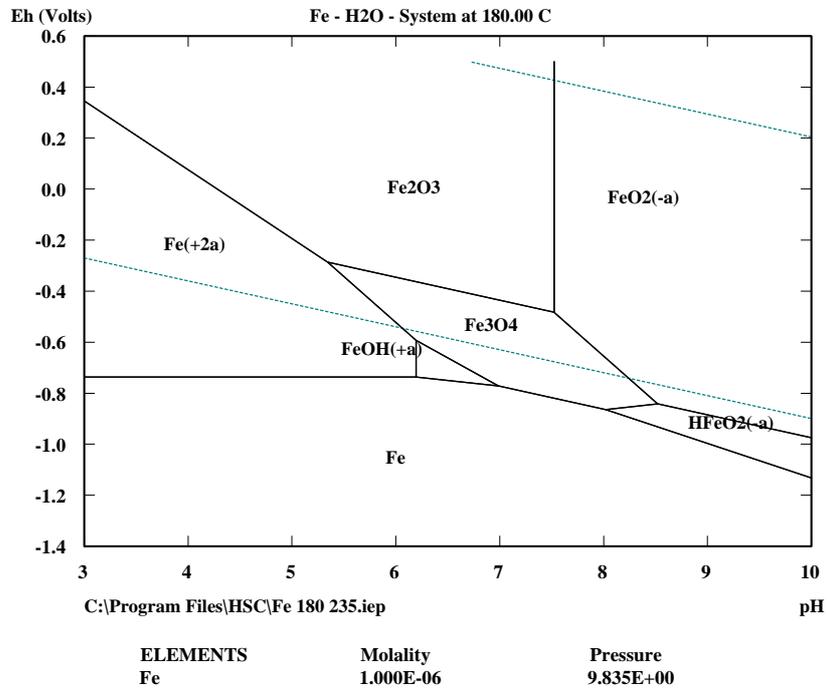


Figure 8. Potential-pH diagram for Fe-H₂O systems at 180 °C.

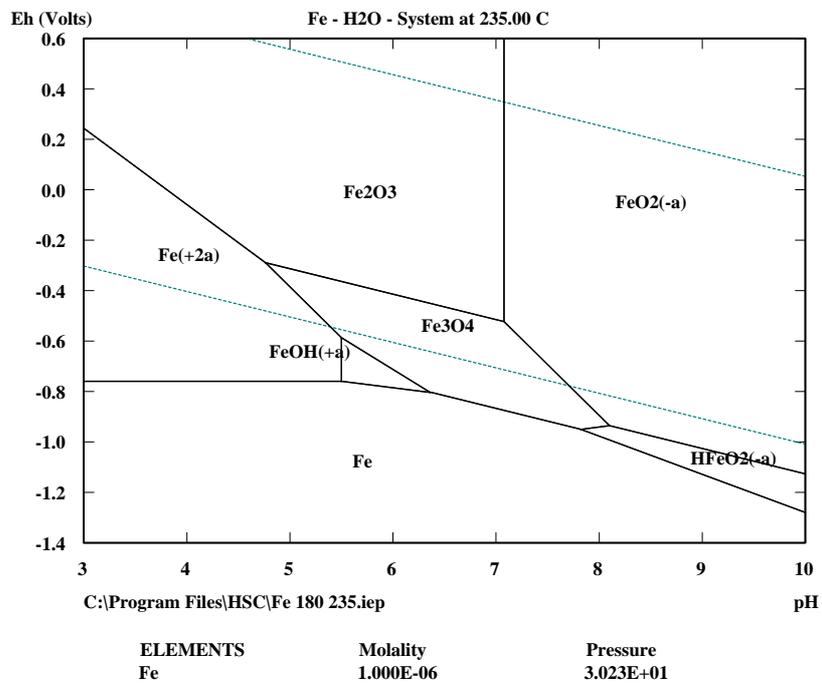


Figure 9. Potential-pH diagram for Fe-H₂O systems at 235 °C.

In a PWR unit, the components affected by FAC are mainly¹⁵:

1. Piping located downstream of the last high pressure feedwater heater,
2. High pressure turbine drain lines,
3. Drains from the moisture separator/reheaters,
4. SG internals made of carbon steel,
5. and potentially Blowdown piping systems.

As a first step, we focus on the drains from the moisture separator/reheaters. To get meaningful ECP and pH signals with electrodes, the testing environments should be a single-phase flow, not two-phase flow, and the relatively low temperature component is selected for the experimental convenience.

The model of Berge et al. assumed the FAC process involved two steps, the soluble iron species production and mass transfer¹⁷. The total FAC rate, V_c is expressed as:

$$V_c = \frac{K_1 K_2}{K_1 + K_2} (C_{eq} - C_\infty) \quad (3)$$

where C_∞ is the soluble ferrous ion concentration at the bulk water, K_1 is the reaction constant which depends on fluid velocity and water temperature, K_2 is the mass transfer coefficient which depends on the Sherwood number ($Sh = \mathbf{a}_1 Re^{\mathbf{a}_2} Sc^{\mathbf{a}_3}$). Re and Sc are the Reynold's number and Schmidt number, respectively and \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 are constants which depend on the pipe component geometry. C_{eq} is the equilibrium soluble ferrous ion concentration at the oxide layer which depends on the pH value and the coolant temperature. In earlier work¹⁸, C_{eq} was expressed as:

$$C_{eq} = \mathbf{a}_4 \exp\left[\frac{-(T - \mathbf{a}_5)^2}{\mathbf{a}_6}\right] + \mathbf{a}_7 \quad (4)$$

Following the Berge's idea, more complex FAC models were developed¹⁹ and an empirical model was also developed by Kastner and Riedle²⁰. The empirical model is expressed as follows.

$$\begin{aligned}
\Delta f_R &= 6.25k_c \left\{ B e^{Bw} \left[1 - 0.175(pH - 7)^2 \right] 1.8e^{-0.118g} + 1 \right\} + f(t) \\
B &= -10.5\sqrt{h} - 9.375 \times 10^{-4} T^2 + 0.79T - 132.5 \\
N &= (-1.29 \times 10^{-4} T^2 + 0.109T - 22.07) \times 0.154e^{-1.2h} \quad \text{for } 0.5 \leq h \leq 5\% \\
f(t) &= 0.9999934 - 0.3356901 \times 10^{-6} t - 0.5624812 \times 10^{-10} t^2 + 0.3849972 \times 10^{-15} t^3
\end{aligned} \tag{5}$$

where Δf_R Material Removal Rate [$\text{mg}/\text{cm}^2\text{hr}$]

k_c Geometrical Factor

w Flow Velocity [m/s]

pH Solution pH

g Dissolved Oxygen [ppb]

h Cr and Mo Contents in Steel [%]

T Temperature [K]

t Operating Time [hr]

In this empirical model, dissolved oxygen was included as one of variables, not ECP. The solution pH was included with the definite form. If this empirical model is used for predicting the FAC rate, dissolved oxygen needs to be correlated with the ECP of steel or other method combining the ECP and pH signal with the present model should be considered.

5. Summary & Conclusions

From the development of electrodes and the analysis of its applicability to FAC monitoring, following conclusions are made.

1. For the FAC monitoring, the ECP of steel components and pH of solution need to be measured at temperature of interest.
2. To monitor the ECP and pH, water-filled Ag/AgCl reference electrode and gold-plated Ni electrode were developed.
3. The water-filled Ag/AgCl reference electrode potential maintained stable value over two weeks period at 288 °C. Reliability and stability tests for gold-plated Ni electrode have been made in boron and lithium mixture solution at 320 °C. The electrode potential remained stable within ± 10 mV over two weeks period.
4. If the empirical model is used for predicting the FAC rate, dissolved oxygen needs to be correlated with the ECP of steel or other method combining the ECP and pH signal with the present model should be considered.

Acknowledgements

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