Influence of the pH and Temperature on Carbon Steel in the Secondary System of Nuclear Power Plants

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1. Introduction

The carbon steel is mainly used piping material in the secondary system of nuclear power plants. Accident of carbon steel piping in the secondary system was issue of nuclear power industry. The main cause of the pipe break accident is a piping thinning phenomenon by FAC (Flow Accelerated Corrosion). The broken pipes events occurred in the Surry unit 2 nuclear power plant in USA at 2004 and the Mihama unit 3 nuclear power plant in Japan at 1986 caused many casualties. It is mainly generated in the carbon steel pipe of the single-phase or two-phase. Also, most important influential factors of the FAC are known to be flow rate of the fluid, flow, pH, temperature, material contents and shape of the piping. The FAC is caused by the interaction of hydraulics factors and water chemistry factors. It can be mitigated effectually by the control of influential factors.

In this study, the corrosion rate influenced by pH and temperature is evaluated in the single-phase by using the secondary system of power plant carbon steel.

2. Methods and Results

2.1 Tafel Extrapolation Method

The Tafel extrapolation method is exploited to measure corrosion rates. More details are as below.

At large polarization, in the results of polarization test, the graphical representation in coordinates for reactions under pure activation control gives straight lines (Tafel lines), and at small polarization, the graphical representation gives curve line. A Tafel behavior means that the potentiodynamic curve represents straight line. At the potentiodynamic curve used by a voltage applying unit (ZIVE MP2A) as in Figure 1, the two straight lines drawn by the cathode and anode potentiodaynamic curve intersect and it makes possible the estimation of the corrosion current density. Corrosion potential is the potential that occurs in the surface of corrosion specimen under open circuit. The measurement of current density by Tafel extrapolation method needs to identify straight line in the range of one dimension for precision. The corrosion current density using Tafel extrapolation method could apply to Faraday's low and calculate corrosion rate. As assuming uniform metal dissolution across the surface, Faraday's laws can be used to convert as a rate of weight loss in g/m^2h or rate of penetration in mm/year.

The Tafel extrapolation method is a faster experimental technique compared to classical weight loss estimation. In addition, it is possible to measure accurately with Tafel extrapolation method even in the situation where the corrosion rate is low.
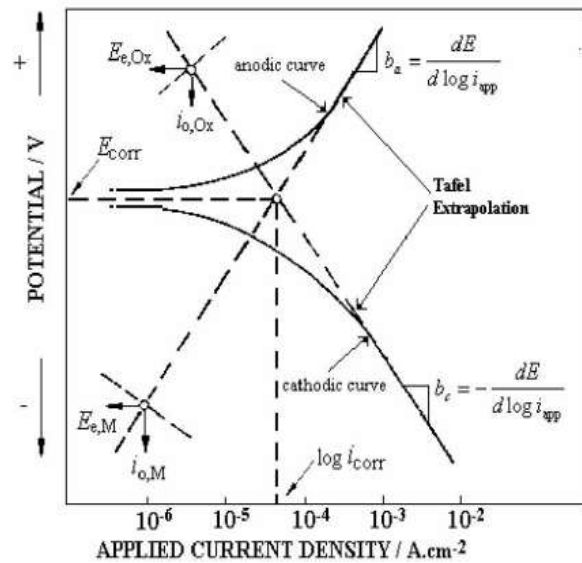

Figure 1. Tafel extrapolation method [4]

2.2 Corrosion Rate

The corrosion rate can induce from the equation of the Faraday's law. In the induce chemistry reaction, the proportional expression in between both of the current(i) and reactant(m) can be written as:

$$m = \frac{a}{nF} \qquad (1)$$

Where F is Faraday's constant (96500C/mol), a is molecular weight (g/mol), n is the number of electrons ions, and t is time (seconds).

If equation (1) is divided by the time and specimen area, the corrosion rate(r) can be shown as follow:

$$r = \frac{ma}{tA} = \frac{ia}{nF} \qquad (2)$$

Where i = I / A, and is defined as the current density. It can be expressed with the unit of penetration per unit time if the equation (2) is divided into the density of the

metal. If the µA/cm^2 is used as the unit of the electric current density (I) and the g/cm^3 is used as the unit about the density (D), then it can be shown as follow:

$$\text{Corrosion Rate(MPY)} = \frac{0.129ai}{nD} \quad (3)$$

2.3 Potentiodynamic Polarization Corrosion Test

2.3.1 Test Condition

Potentiodynamic polarization corrosion tests were performed using a Static-Autoclave. By using ETA which is pH adjusting agent of the nuclear power plant, pH was controlled with the 4 steps (8.5, 9.0, 9.5, 10.0) and the temperature was evaluated on 3 sections (50℃, 150℃, 250℃) with respect to each pH. Table 1 shows the test of water chemistry condition. The SA106.Gr.C was selected as the test material among the power plant piping materials and its chemical compositions are representing in Table 2.

By using the spot welding, the specimens were fixed on stainless steel wire. The working electrode with the specimens is installed in the autoclave using conax fitting. The specimen area is 4.5cm^2 and the molecular weight is 55.84g and density 7.09g/cm^3.

Table 1. Water chemistry condition of test

pH	Temp (℃)	Pressure (bar)	Dissolved oxygen (ppb)	Hydrazine (ppb)
8.5 – 10.0	50 - 250	40	≤ 5.0	80 ≤

Table 2. Chemical composition of test specimens

	Chemical Composition								
	C	Mn	P	S	Si	Cr	Mo	Ni	Cu
SA106 Gr.C	0.25	1.07	0.012	0.003	0.23	0.08	0.03	0.14	0.14

2.3.2 Test Method

The corrosion behavior of carbon-steel was evaluated in the test condition of pH for 8.0 to 10.0 with various range of temperature (50~250℃). The dissolved oxygen (DO) and pH in the test solution were controlled by degassing system using high purity Ar gas and ETA (Ethanolamine) solution. The oxygen concentration in the test solution was maintained to be below 5ppb, and the residual oxygen was removed using hydrazine. The room temperature sensing part of electrochemical analysis system consists of DO-electrode, pH-electrode and conductivity-electrode. The high temperature sensing part of the system consists of Ag/AgCl-electrode (0.1N KCl). Figure 2 shows the autoclave and reference electrode.

The potentiodynamic curve was measured using a voltage applying unit (ZIVE MP2A) at scan rate of 1mV/sec.

The current density values were calculated using the potentiodynamic curve values. Then, corrosion rate was calculated using the equation (3) and current density values.
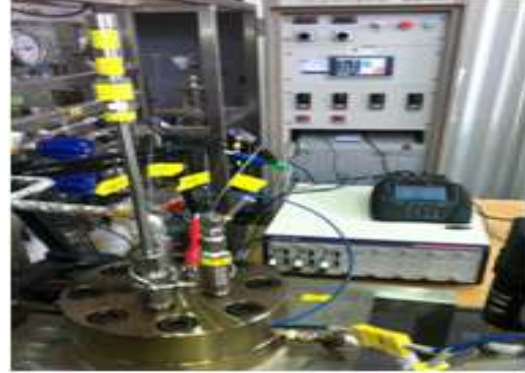
(a) Test autoclave

(b) Carbon specimen

Figure 2. Test facility and Carbon specimen

2.4 Test Results

The corrosion rate and current density values were determined using Tafel-extrapolation at various pH and temperature test conditions. The lowest values of corrosion rate and Icorr at pH 8.5 and 50℃ of temperature in the test condition were respectively 3.29 mils/year and 6.486E^{-06} A/cm^2. The highest values of corrosion rate and Icorr for 150℃ at pH 8.5 were 17.65 mils/year and 3.483E^{-05} A/cm^2. Other testing results for various testing conditions are shown in Table 3.

Figure 3 shows the results of potentiodynamic polarization test. The corrosion rate of carbon steel-specimens under the same temperature condition were tended to decrease with increasing the pH of the test solution. The corrosion rate of carbon steel was showing a tendency to be highest at 150℃ temperature condition and it tended to decrease if the test solution temperature condition is higher than 150℃.

Table 3 Results of potentiodynamic polarization test

| pH	Temp(℃)	Icorr(A/cm^2)	Corrosion rate (mils/year)
8.5	50	6.486E-06	3.29
	150	3.483E-05	17.65
	250	1.462E-05	7.41
9.0	50	5.702E-06	2.89
	150	1.671E-05	8.47
	250	1.164E-05	5.90
9.5	50	5.058E-06	2.56
	150	1.472E-05	7.46
	250	8.035E-06	4.07
10.0	50	4.775E-06	2.42
	150	9.226E-06	4.67
	250	7.943E-06	4.02

As shown in Figure 4, the corrosion rate of carbon steel at below 9.0 of pH was more than twice compared to the cases of pH 9.5 and pH 10.0. And also, it was founded that the corrosion rate for above pH 10.0 was more than twice compared to the case of that for below pH 10.0.
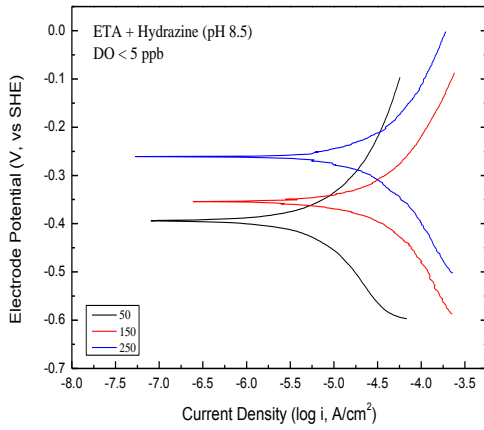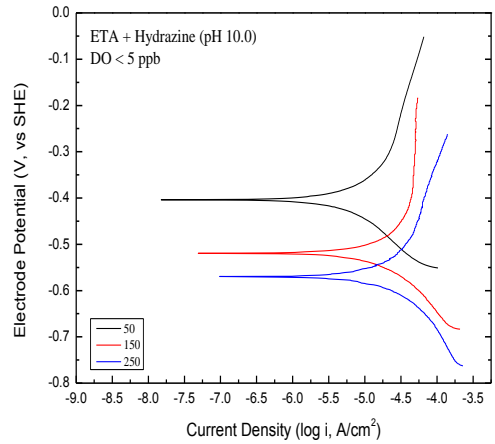

(a) pH 8.5 of test solution condition
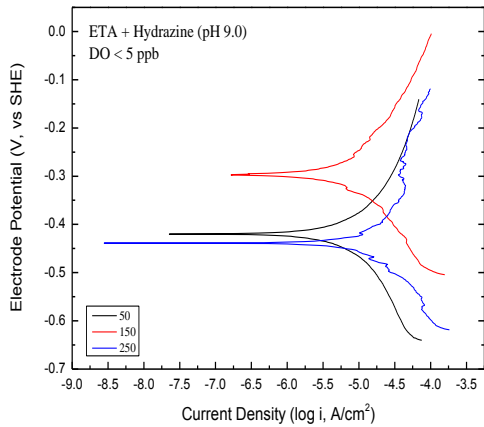
(b) pH 9.0 of test solution condition
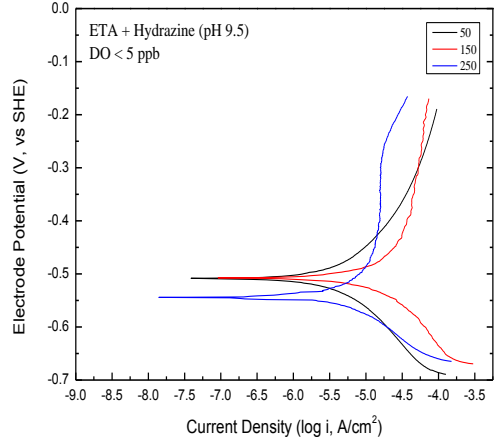
(c) pH 9.5 of test solution condition

(d) pH 10.0 of test solution condition

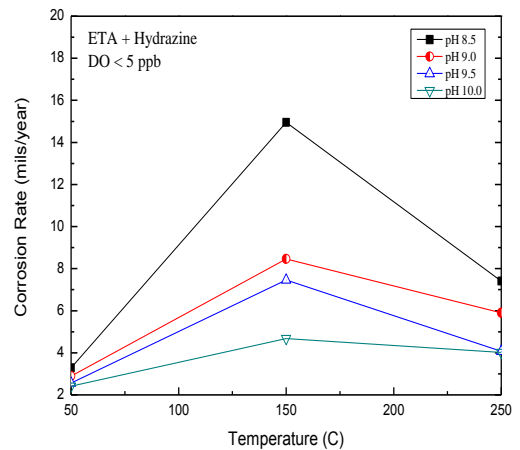Figure 3. The results of Potentiodynamic curve in pH 8.5, 9.0, 9.5 and 10.0

Figure 4. Corrosion rate of specimens in changed pH and temperature

3. Conclusions

In this study, the pH and temperature effects on the carbon steel used in nuclear power plant secondary system were evaluated. Generally, it is known that the corrosion rate of carbon steel reveals the highest values under the condition of lower pH value and 150℃ temperature. Most effective factor on the corrosion rate is a solubility of magnetite and hematite produced by reaction between carbon steel and oxygen. The solubility of magnetite and hematite decreases for increasing pH, and it shows the highest value at 150℃ temperature condition and decreases for higher temperature condition than 150℃.

In this study, the experimental tests were performed for nuclear power plant operating condition of high temperature water chemistry environment using carbon steel specimen and static autoclave. The test results are showing consistent with the magnetite solubility trend. The static autoclave test is not able to consider the FAC phenomenon completely. However, in this study, it is confirmed that the corrosion rate of carbon steel material can be controlled by pH and temperature condition, which are effective factors on FAC.

ACKNOWLEDGMENTS

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