Effect of Ethanolamine Injection on Wall Thinning Rate of PWR Carbon Steel Components

Takuya FUKUMURA1,*

1 Institute of Nuclear Safety System, Inc., Sata 64, Mikata-gun, Mihama-cho, Fukui 919-1205, Japan

ABSTRACT

For pH control of PWR secondary system water chemistry, some plants have changed to ethanolamine injection. The purpose of this work was to understand the effect of changing water chemistry on wall thinning rate of the PWR secondary system due to flow accelerated corrosion. For that purpose, evaluations of water chemistry were carried out by a mass balance calculation, wall thinning rate measurement by a rotary disk test and wall thinning rate evaluation based on calculated magnetite solubility. As a result, it was found to be effective to inhibit the wall thinning rate of the PWR secondary system due to flow accelerated corrosion by ethanolamine injection, but it was not sufficiently effect to neglect wall thinning rate due to flow accelerated corrosion. The effect of the wall thinning rate inhibition also varied greatly for each component of the PWR secondary system. It was found that maintenance of the carbon steel used for the PWR secondary system was still required under ethanolamine injection condition.

KEYWORDS

PWR, Ethanolamine, Wall thinning rate, Flow accelerated corrosion, Carbon steel, Water chemistry

ARTICLE INFORMATION

Article history:
Received 19 May 2014
Accepted 20 October 2014

1. Introduction

In the pressurized water reactor (PWR) secondary system, carbon steel is used for some components such as piping. Pipe wall thinning management for plant maintenance is carried out because of flow accelerated corrosion (FAC). For wall thinning due to FAC, many studies have been carried out and much knowledge has been obtained regarding material factors, flow factors and environmental factors of FAC. For environmental factors in particular, temperature dependence, dissolved oxygen concentration dependence and pH dependence have been reported [1-5].

However, most environmental factor data have been gotten under neutral or all-volatile treatment (AVT) conditions. The AVT has been widely used in PWR secondary systems, such as adding hydrazine and ammonia to feed water for the purposes of deoxygenation and pH control, respectively. But recently some plants have changed the PWR secondary system water treatment from AVT to ethanolamine (ETA) injection. The purpose of ETA injection is to lower iron amounts carried in the feed water to the steam generator (SG) by increasing the pH of the feed water. The decrease in the iron concentration level differs for each plant. But iron concentration of feed water down to 10 ppb has been reported [6].

On the other hand, not enough about the PWR secondary system water chemistry for each component is known. This is because substances in the PWR secondary system water have complex variations caused by the liquid-vapor distribution and thermal decomposition in the SG, but analysis points and frequency of water chemistry measurements are limited. Therefore the effect of ETA injection on wall thinning rate due to FAC of the PWR secondary system is not sufficiently known. From this background, this study aimed at evaluating the PWR secondary system water chemistry under AVT and ETA injection conditions and determining the effect of water chemistry on wall thinning rate due to FAC.

The reason for the complex variations of the PWR secondary system water chemistry is considered due to the concentration change caused by the liquid-vapor distribution of volatile

*Corresponding author, E-mail: fukumura@inss.co.jp
substances and ammonia generation caused by thermal decomposition of hydrazine at the SG and moisture separator-and-reheater (MSR) etc. Therefore, first the PWR secondary system water chemistry under representative AVT and ETA injection conditions was evaluated by model calculations considering liquid-vapor distribution and thermal decomposition. Next, the wall thinning rate change between AVT and ETA injection conditions was evaluated experimentally by the rotary disk test under AVT and ETA injection water chemistry which was calculated by the model calculations. Also the wall thinning rate change was evaluated under the model of wall thinning rate due to FAC is proportional to the magnetite solubility and compared to the result of rotary disk test.

2. Model calculations of PWR secondary system water chemistry

2.1. Method

For model calculations of the PWR secondary system water chemistry, an 800MW class 3 loop plant was selected and water chemistry of the PWR secondary system was calculated from feed water chemistry using a mass balance calculation.

Twenty-two major components, described later, of the PWR secondary system were selected for the water chemistry calculation. Fig. 1 is a schematic drawing of the modeled PWR secondary system. Some of the temperatures and the amounts of water and vapor used in the model calculation are shown in the drawing.

Hydrazine, ammonia and ETA were considered as the substances in the PWR secondary water chemistry. Hydrazine and ammonia exist under the AVT condition and hydrazine, ammonia and ETA exist under the ETA injection condition. The water chemistry is changed by the plant itself and the plant operating cycle. In this study, 0.1 ppm hydrazine concentration and 0.4 ppm ammonia concentration were assumed as the typical AVT feed water chemistry (pH about 9.2) and 0.1 ppm hydrazine and 9 ppm ETA were assumed as the typical ETA injection feed water chemistry (pH about 9.8) based on reported [6-8] water chemistry; this allowed comparison between the low pH AVT condition and the high pH ETA injection condition.

Water chemistry for each component of the PWR secondary system was calculated as follows. When system A branches to system B and system C, mass balance can be expressed as equation (1). In equation (1), the flow rates of systems A, B, C are \( F_A, F_B, F_C \) and the substance concentrations of systems A, B, C are \( C_A, C_B, C_C \), respectively.

The flow rates were obtained from a heat balance sheet. The downstream water chemistry was
calculated from the mass balance using the typical feed water chemistry assumed before as the initial value, taking into consideration the thermal decomposition and liquid-vapor distribution of substances.

Ammonia in feed water is stable at the plant operating temperature, but hydrazine undergoes thermal decomposition. Additionally, thermal decomposition of ETA is considered to be negligible based on actual plant measurement results of organic substances. Therefore in this study only hydrazine was assumed to experience thermal decomposition, as expressed by equation (2), in the SG which is the highest temperature component in the PWR secondary system.

Hydrazine concentration time-dependence is expressed in equation (3), assuming a general first-order kinetics reaction. In equation (3) \( C_0 \) is the concentration at time 0, \( C(t) \) is the concentration at time \( t \) and \( \lambda \) is the thermal decomposition constant.

Hydrazine, ammonia and ETA are volatile substances and there is a liquid-vapor distribution at the SG and MSR. The liquid-vapor distribution coefficient \( K_D \) is expressed in equation (4), where \( C_{V,X} \) and \( C_{L,X} \) are substance concentrations in vapor and liquid, respectively. \( X \) represents the substance being considered, either hydrazine, ammonia or ETA.

In order to execute the water chemistry model calculations, \( \lambda \) of hydrazine in an actual plant SG and \( K_D \) of hydrazine, ammonia and ETA in an actual plant SG and MSR need to be determined. To determine \( \lambda \) and \( K_D \), the expected range of \( \lambda \) was assumed as 0.3 to 0.4 min\(^{-1}\) and expected ranges of \( K_D \) hydrazine, ammonia and ETA were assumed as 0.1 to 0.4, 1.6 to 4.6 and 0.1 to 0.5, respectively, from literature data and measurements in an actual plant. Water chemistry model calculations of the PWR secondary system were carried out using \( \lambda \) and \( K_D \) as parameters. For this model calculation, feed water chemistry was used as input conditions. The calculated water chemistry results were compared with the actual plant data, specially obtained at different feed water conditions, then parameter fittings of \( \lambda \) and \( K_D \) were carried out.

\[
F_A \times C_A = F_B \times C_B + F_C \times C_C \quad (1)
\]

\[
8\text{N}_2\text{H}_4 \rightarrow 10\text{NH}_3 + 3\text{N}_2 + \text{H}_2 \quad (2)
\]

\[
C(t) = C_0 e^{-\lambda t} \quad (3)
\]

\[
K_D = \frac{C_{V,X}}{C_{L,X}} \quad (4)
\]

2.2. Results of water chemistry model calculations

Optimized values of \( \lambda \) and \( K_D \), shown in Table 1, were obtained as results of the parameter fittings of \( \lambda \) in equation (3) and \( K_D \) in equation (4), by comparing water chemistry calculated by equation (1) and the water chemistry in measured the actual plant.

<table>
<thead>
<tr>
<th>( \lambda ), min(^{-1})</th>
<th>SG</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.3</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( K_D ) (Hydrazine)</th>
<th>SG</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.3</td>
<td>0.12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( K_D ) (Ammonia)</th>
<th>SG</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.9</td>
<td>3.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( K_D ) (ETA)</th>
<th>SG</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.36</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Fig. 2 shows the relationship between measured values in the actual plant and calculated values (explained in 2.1) of hydrazine, ammonia and ETA concentrations in the PWR secondary system. The calculated and measured values showed a good correlation, and it was confirmed that the PWR secondary system water chemistry can be calculated successfully using these model calculations.

![Graph showing the relationship between measured and calculated values of hydrazine, ammonia, and ETA in the PWR secondary system.](image)

**Fig. 2 Relationship between measured and calculated values of hydrazine, ammonia and ETA concentrations in the PWR secondary system**

(Values of hydrazine, ammonia and ETA are normalized by 0.4ppm, 0.2ppm and 10ppm, respectively)

Table 2 shows the calculated water chemistry and pH at the 22 major components of the PWR secondary system; the input feed water conditions were: 0.1 ppm hydrazine + 0.4 ppm ammonia for the AVT condition; and 0.1 ppm hydrazine + 9 ppm ETA for the ETA injection condition. In Table 2, liquid phase water chemistry is shown for the two phase flow part and at the operating temperature pH. It was found that water chemistry varies at each component of the PWR secondary system and ETA injection causes high pH throughout the PWR secondary system.

<table>
<thead>
<tr>
<th>Component</th>
<th>Hydrazine (ppm)</th>
<th>Ammonia (ppm)</th>
<th>pH</th>
<th>ETA (ppm)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensate pump</td>
<td>0.10</td>
<td>0.40</td>
<td>8.9</td>
<td>0.10</td>
<td>5.7</td>
</tr>
<tr>
<td>LP-Preheater1</td>
<td>0.10</td>
<td>0.40</td>
<td>8.0</td>
<td>0.11</td>
<td>6.5</td>
</tr>
<tr>
<td>LP-Preheater2</td>
<td>0.09</td>
<td>0.42</td>
<td>7.4</td>
<td>0.10</td>
<td>6.7</td>
</tr>
<tr>
<td>LP-Preheater3</td>
<td>0.09</td>
<td>0.42</td>
<td>7.0</td>
<td>0.10</td>
<td>6.7</td>
</tr>
<tr>
<td>LP-Preheater4</td>
<td>0.09</td>
<td>0.42</td>
<td>6.8</td>
<td>0.10</td>
<td>6.7</td>
</tr>
<tr>
<td>Deaerator in</td>
<td>0.09</td>
<td>0.42</td>
<td>6.8</td>
<td>0.10</td>
<td>6.7</td>
</tr>
<tr>
<td>Deaerator out</td>
<td>0.10</td>
<td>0.40</td>
<td>6.3</td>
<td>0.10</td>
<td>9.0</td>
</tr>
<tr>
<td>HP-Preheater</td>
<td>0.10</td>
<td>0.40</td>
<td>6.0</td>
<td>0.10</td>
<td>9.0</td>
</tr>
<tr>
<td>SG</td>
<td>0.17</td>
<td>0.25</td>
<td>5.7</td>
<td>0.16</td>
<td>25.6</td>
</tr>
<tr>
<td>HP turbine1</td>
<td>0.24</td>
<td>0.23</td>
<td>5.9</td>
<td>0.21</td>
<td>28.0</td>
</tr>
<tr>
<td>HP turbine2</td>
<td>0.27</td>
<td>0.22</td>
<td>6.2</td>
<td>0.25</td>
<td>29.9</td>
</tr>
<tr>
<td>LP turbine1</td>
<td>0.48</td>
<td>0.21</td>
<td>6.9</td>
<td>0.44</td>
<td>41.2</td>
</tr>
<tr>
<td>LP turbine2</td>
<td>0.38</td>
<td>0.22</td>
<td>7.2</td>
<td>0.37</td>
<td>38.5</td>
</tr>
<tr>
<td>LP turbine3</td>
<td>0.31</td>
<td>0.21</td>
<td>7.7</td>
<td>0.32</td>
<td>36.1</td>
</tr>
<tr>
<td>LP turbine4</td>
<td>0.25</td>
<td>0.20</td>
<td>8.1</td>
<td>0.27</td>
<td>32.2</td>
</tr>
<tr>
<td>LP turbine5</td>
<td>0.21</td>
<td>0.18</td>
<td>8.7</td>
<td>0.23</td>
<td>28.8</td>
</tr>
<tr>
<td>MSR drain</td>
<td>0.27</td>
<td>0.22</td>
<td>6.2</td>
<td>0.25</td>
<td>29.9</td>
</tr>
<tr>
<td>HP-Preheater drain</td>
<td>0.06</td>
<td>0.43</td>
<td>6.3</td>
<td>0.06</td>
<td>8.3</td>
</tr>
<tr>
<td>LP-Preheater drain1</td>
<td>0.03</td>
<td>0.45</td>
<td>7.0</td>
<td>0.04</td>
<td>6.0</td>
</tr>
<tr>
<td>LP-Preheater drain2</td>
<td>0.03</td>
<td>0.46</td>
<td>7.3</td>
<td>0.04</td>
<td>6.0</td>
</tr>
<tr>
<td>LP-Preheater drain3</td>
<td>0.03</td>
<td>0.47</td>
<td>7.9</td>
<td>0.03</td>
<td>5.6</td>
</tr>
<tr>
<td>LP-Preheater drain4</td>
<td>0.04</td>
<td>0.47</td>
<td>8.0</td>
<td>0.05</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table 2 Calculated results of water chemistry
3. Wall thinning rate evaluation due to FAC

3.1. Procedure for the rotary disk test

The rotary disk test is one type of corrosion rate measurement; a disk type specimen is rotated at high speed in order to simulate the high flow condition. In order to evaluate the wall thinning rate due to FAC, the rotary disk test was executed using carbon steel specimens under PWR secondary system water chemistry.

Table 3 shows the chemical composition of the carbon steel tested. Low chromium (0.02 wt%) carbon steel was used because its wall thinning rate susceptibility was thought to be high. The specimen diameter and thickness were 275 mm and 3 mm, respectively. The rotation speed was 35 m/s at the outermost edge of the specimens. A high rotation speed was selected to simulate a high wall thinning rate due to FAC under a turbulent flow condition, although flow rate of the single phase of the actual plant is as low as 6 m/s. Fig. 3 shows a schematic drawing of the rotary disk test system. The PWR secondary system simulated water was discharged outside the system to avoid the influence of dissolved iron after passing through the system once. The PWR secondary system simulated water was made up to the required water chemistry in the chemical control tank, and it was heated to the desired temperature using a heater. Then it was supplied to the test part at a flow rate of 5 dm$^3$/h. This flow rate was selected as sufficient based on the volume of the test section being about 2 dm$^3$.

The wall thinning rate due to FAC ($J$) was calculated using the weight loss, that is the difference between the pre-test specimen weight ($W_0$) and the after test specimen weight ($W$) divided by the specimen surface area ($S$) and test time ($t_{test}$) as shown in equation (5). The test time was fixed at 100 hours.

$$J = \frac{W_0 - W}{S \times t_{test}}$$

Eight representative components of the PWR secondary system were selected for testing the water chemistry calculated in section 2.2. The numbers in parentheses correspond to the number of each component in Table 2. The components were: Condensate pump (1); LP-preheater 2(3); LP-preheater 4(5); Deaerator out (7); HP-preheater (8); SG (9); HP-turbine 1 (10); and MSR drain (17).

Table 3 Chemical composition of carbon steel test material

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Ni</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.02</td>
<td>0.002</td>
<td>Tr.</td>
<td>0.05</td>
<td>0.004</td>
<td>0.0025</td>
<td>0.01</td>
<td>0.01</td>
<td>Bal.</td>
<td></td>
</tr>
</tbody>
</table>
3.2. Results of rotary disk test

Fig. 4 shows some photos of the outer appearance of the post-test specimens. The specimens were covered with black magnetite oxide film and partially worn. The wear situation differed depending on the water chemistry and temperature. The AVT condition showed more severe wear than the ETA injection condition for the LP-preheater 4 and Deaerator out. In the AVT condition, no remarkable wear was observed at 274°C, but remarkable wear was observed at 180 and 142°C. Furthermore, observations by scanning electron microscope showed fish-eye type wear which is common in FAC.

<table>
<thead>
<tr>
<th></th>
<th>ETA injection</th>
<th>AVT</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP-preheater 4</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>Water chemistry 142°C</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>Deaerator</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>Water chemistry 180°C</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
</tr>
<tr>
<td>SG water chemistry 274°C</td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image10" alt="Image" /></td>
</tr>
</tbody>
</table>

**Fig. 3** Schematic drawing of the rotary disk test system

**Fig. 4** Specimen surface appearances after rotary disk test
Fig. 5 shows measurement results of wall thinning rate due to FAC obtained by the rotary disk test. The wall thinning rates due to FAC of the condensate pump and SG were almost the same under AVT and ETA injection conditions, but for other components wall thinning rates due to FAC under the ETA injection condition were reduced remarkably compared to the AVT condition.

![Graph showing FAC rates in AVT and ETA injection conditions for the rotary disk test](image)

3.3. Wall thinning rate evaluation procedure based on magnetite solubility

The difference of wall thinning rate due to FAC between the AVT and ETA injection conditions was evaluated from the viewpoint of magnetite solubility.

A carbon steel surface which contacts with high temperature deaerated water as in the PWR secondary system, is covered with magnetite (Fe$_3$O$_4$) oxide film which is formed by the Schikorr reaction expressed in equation (6).

\[
\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + \text{H}_2
\]

\[
3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2
\]  

FAC is a phenomenon in which dissolution of magnetite produced on the carbon steel surface is promoted by the fluid flow. On the magnetite surface, magnetite and iron ion are in equilibrium and the iron ion concentration on the magnetite surface is equal to the magnetite solubility. The FAC model of FAC rate is proportional to the concentration difference between surface and bulk iron ion concentrations expressed in equation (7), where $C_S$ is magnetite solubility, $C_b$ is iron concentration of bulk water and $k$ is mass transfer coefficient. In this model, wall thinning rate due to FAC becomes higher when magnetite solubility is high. Fig. 6 shows a schematic of this model. Furthermore equation (7) can be approximated as equation (8) when $C_b$ is sufficiently smaller than $C_S$. 

\[
\text{FAC rate} = \frac{C_S - C_b}{k}
\]

\[
\text{FAC rate} \approx \frac{C_S}{k}
\]
In order to determine the magnetite solubility, equations (9) to (15) were taken into consideration as the main dissolution reactions of magnetite.

\[
\begin{align*}
\text{Fe}_3\text{O}_4 + 6\text{H}^+ + \text{H}_2 & \rightarrow 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \quad (9) \\
\text{Fe}_3\text{O}_4 + 3\text{H}^+ + \text{H}_2 & \rightarrow 3\text{Fe(OH)}^+ + \text{H}_2\text{O} \quad (10) \\
\text{Fe}_3\text{O}_4 + 5\text{H}_2\text{O} + \text{H}_2 & \rightarrow 3\text{Fe(OH)}_3^+ + 3\text{H}^+ \\
& \quad \rightarrow 3\text{HFeO}_2^2^- + 3\text{H}^+ + \text{H}_2\text{O} \quad (11) \\
\text{Fe}_3\text{O}_4 + 5\text{H}_2\text{O} + \text{H}_2 & \rightarrow 3\text{FeO}_2^{2-} + 6\text{H}^+ + \text{H}_2\text{O} \quad (12) \\
\text{Fe}_3\text{O}_4 + 9\text{H}^+ & \rightarrow 3\text{Fe}^{3+} + 4\text{H}_2\text{O} + \frac{1}{2}\text{H}_2 \quad (13) \\
\text{Fe}_3\text{O}_4 + 6\text{H}^+ & \rightarrow 3\text{Fe(OH)}_2^+ + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2 \quad (14) \\
\text{Fe}_3\text{O}_4 + 3\text{H}^+ + 2\text{H}_2\text{O} & \rightarrow 3\text{Fe(OH)}_2^+ + 1/2\text{H}_2 \quad (15)
\end{align*}
\]

A reaction constant $K$ is defined for each reaction. For example, the reaction constant $K_1$ is shown as equation (16). $[\text{Fe}^{2+}]$ and $[\text{H}^+]$ are concentrations of Fe$^{2+}$ and H$^+$, respectively. $P_{\text{H}_2}$ is partial pressure of hydrogen. The relationship between the Gibbs free energy $\Delta G^0$ and the reaction constant $K$ is established in equation (17) from thermodynamics. In equation (17), $R$ is the gas constant and $T$ is absolute temperature. Regarding equation (16), $\text{Fe}^{2+}$ concentration is shown in equation (18), using $pH = -\log[\text{H}^+]$ and equation (17). Only the partial pressure of dissolved hydrogen, the pH at the temperature of interest and $\Delta G^0$ need to be known. The reaction constant can be determined using the concentration of Fe$^{2+}$ calculated in equation (18).

\[
K_1 = \frac{[\text{Fe}^{2+}]^3}{[\text{H}^+]^6 \cdot P_{\text{H}_2}} \quad (16)
\]

\[
\Delta G^0 = -RT \ln K \quad (17)
\]

\[
\log[\text{Fe}^{2+}] = -\frac{1}{3} \cdot \frac{\Delta G^0}{2.3026RT} - 2pH + \frac{1}{3} \log P_{\text{H}_2} \quad (18)
\]

Regarding equations (10) to (15), this reaction constant can also be determined. The partial pressure of dissolved hydrogen can be shown as equation (19) from Henry’s law. In equation (19) $\chi$ is dissolved hydrogen mole fraction and $K_H$ is a proportionality constant. Regarding equation (9), $\Delta G^0$ is expressed by equation (20), where $G_1^0, G_2^0, G_3^0, G_4^0, G_5^0$ are Gibbs free energies of Fe$^{2+}$, H$_2$O, Fe$_3$O$_4$, H$^+$, H$_2$, respectively. The Gibbs free energy at specific temperature $T$, $\Delta G^0(T)$ is shown in equation (21), where $C_p^0(T)$ is specific heat at constant pressure. Regarding the ion species for which specific heat is not known, it was calculated by equations (22), (23) and (24) based on a Criss-Cobble corresponding theory[10].
In equations (22) to (24), $S_{\text{abs}}^0(T)$, $S_{\text{conv}}^0(T)$, $Z$ are absolute entropy, entropy and valence of ion, respectively. $A(T)$ and $B(T)$ are constants determined by the ion species. Because of the lack of $A(T)$ and $B(T)$ values at high temperature, the linear relationship in equation (23) was assumed for temperatures over 473K.

3.4. Results of wall thinning rate evaluation based on magnetite solubility

Fig. 7 shows magnetite solubility obtained using the calculation procedure described in section 3.3 and water chemistry under the AVT and ETA injection conditions shown in Table 2. Under the ETA injection condition, magnetite solubility in the PWR secondary system was decreased compared to the AVT condition.

Fig. 8 compares the FAC reduction rates under the AVT and ETA injection conditions obtained from: solubility of magnetite (equation (25)) and the rotary disk test (equation (26)). $RS_{E TA/ AV T}$ is based on the model of FAC rate being proportional to magnetite solubility. In equation (25), $C_{E TA}$ and $C_{AV T}$ are the magnetite solubility under the ETA injection condition and AVT condition, respectively.
From the results of the magnetite solubility calculation, FAC rate is expected to be lowered from about 0.1 to 0.3 by ETA injection. $RR_{ETA/AVT}$ was evaluated by the FAC rate measured from the rotary disk test described in section 3.2. In equation (26), $J_{ETA}$ and $J_{AVT}$ are FAC rates of the ETA injection condition and AVT condition. Regarding the SG and condensate pump, $RR_{ETA/AVT}$ differs remarkably from $RS_{ETA/AVT}$.

$$RS_{ETA/AVT} = \frac{C_{ETA}}{C_{AVT}}$$  \hspace{1cm} (25)

$$RR_{ETA/AVT} = \frac{J_{ETA}}{J_{AVT}}$$  \hspace{1cm} (26)

Fig. 7  Calculated magnetite solubility under ETA and AVT conditions in the PWR secondary system
4. Discussion

4.1. Model calculations of the PWR secondary system

Model calculations were carried out regarding evaluation of the PWR secondary system water chemistry. The evaluation was based on the mass balance calculation taking into consideration the thermal decomposition constant of hydrazine in the SG and the liquid-vapor distribution coefficient of volatile substances in the SG and MSR which were determined by parameter fitting. The calculated and measured water chemistry showed a good correlation as noted earlier (Fig. 2), and water chemistry of the PWR secondary system is considered to be able to provide an evaluation with sufficient accuracy.

Fig. 9 compares pH, FAC rate and magnetite solubility under the ETA injection and AVT conditions. As seen there and in Table 2, the pH at each component under the ETA injection condition increases compared to the AVT condition. The ETA injection is considered to be effective for increasing the pH value of the PWR secondary system. Furthermore in the two phase condition such as at the SG, the concentration of ammonia, which is used to adjust the pH, is decreased under the AVT condition, while the concentration of ETA, also used for pH adjustment, is increased under the ETA injection condition as shown in Table 2. The behavior of pH adjustment compounds in the PWR secondary system differs depending on the actual compound used such as ammonia and ETA. The water chemistry of the PWR secondary system can be changed dramatically by changing water chemistry of the feed water. It is important to understand the effect of water chemistry change.
4.2. Evaluation of wall thinning rate due to FAC by rotary disk test

Regarding measurement of wall thinning rate due to FAC by the rotary disk test, it is thought to have been measured successfully because fish-eye type wear was observed on the specimens (Fig. 4); such wear is commonly seen for FAC in this test. In Fig. 4, the surface appearances of the posttest specimens are different, depending on water chemistry and temperature condition. The degree of oxide film peeling of the specimen surface under the ETA injection condition is less than that under the AVT condition, so that the inhibitive effect of FAC due to ETA injection can be seen. Furthermore under the AVT condition, the degree of oxide film peeling of the specimen surface at 142°C is more remarkable than at the other temperatures, so that the effect of temperature can be seen, although it is necessary to pay attention to the fact that water chemistry is slightly different.

Comparison of the wall thinning rates of the rotary disk test between ETA injection and AVT conditions indicates that the wall thinning rate due to FAC under the ETA injection condition is lowered to a fraction of the value under the AVT condition except at the SG and condensate pump as shown in Fig. 5. At the SG and condensate pump, the wall thinning rate due to FAC under the ETA injection condition is nearly the same as under the AVT condition. As shown in Fig. 9 and Table 2, each pH value at the components of the PWR secondary system is increased by ETA injection; the inhibitive effect on FAC rate by ETA injection can be seen for some components, but the degree of the FAC inhibitive effect is a fraction at most, and it is not a sufficient enough effect to allow neglect of the FAC. On the other hand there are components where the inhibitive effect cannot be seen despite the increased pH. Therefore maintenance of carbon steel components is considered to be necessary after ETA injection.

In order to consider why the inhibitive effect of the FAC rate differs among components, the FAC rate measured by the rotary disk test was organized by pH and is shown in Fig. 10 and was organized by temperature and is shown in Fig. 11. In Fig. 10, the FAC rate measured by the rotary disk test does not show a simple decrease at high pH, some small FAC rate data like for the SG under the AVT condition are seen. It is considered that FAC rate is not controlled only by pH but also by a temperature effect. Fig. 11 has a bell-shaped temperature dependency for FAC rate. The peak of the FAC rate is at about 180°C under the AVT condition and over 220°C under the ETA injection condition. Under the ETA injection condition, the peak of its FAC rate shifts to higher temperature. It should be noted that no inhibitive effect of FAC rate is seen for the SG at 274°C with ETA. Also no inhibitive effect of the FAC rate is seen for the condensate pump at 33°C with ETA, and it is considered the reaction rate is very small due to the low temperature.
4.3. Evaluation of wall thinning rate due to FAC based on magnetite solubility

As shown in Fig. 7, the magnetite solubility in the PWR secondary system is decreased under the ETA injection condition in a range from a fractional amount to one order of magnitude compared to the AVT condition. The reduction of wall thinning rate by ETA injection is expected considering that the model of wall thinning rate due to FAC is proportional to the magnetite solubility.

But comparing the FAC reduction rates of the expected value from the calculated magnetite solubility and the measured value from the rotary disk test, it is seen that FAC rates of the SG at high temperature and the condensate pump at low temperature measured by the rotary disk test do not show the reduction expected from the calculated magnetite solubility even though some of the other components showed a good correlation (Fig. 8). This result is considered to show the limitation of
adoption the model of wall thinning rate due to FAC which is proportional to the magnetite solubility at high and low temperature components.

Fig. 12 shows the relationship between calculated magnetite solubility and measured FAC rate of section 3.2. While the observed tendency for the FAC rate is to increase due to increasing magnetite solubility, some low FAC rate data such as for the condensate pump are observed regardless of the magnetite solubility being high under the AVT condition. The reason for the low FAC rate for the condensate pump regardless of the high magnetite solubility is considered to be the small reaction rate due to the low temperature. And therefore the calculated FAC rate is high due to high magnetite solubility, but the measured FAC rate is small due to the small reaction rate at low temperature. And one of the reasons for the low FAC rate for the SG (which is at a high temperature) is considered to be the change the magnetite dissolution reaction due to the changing oxide film property [11] at high temperature.

![Fig. 12 Relationship between calculated magnetite solubility and measured FAC rate](image)

5. Conclusion

For the purpose of evaluating the effect of ETA injection on FAC rate, at first a water chemistry evaluation of the PWR secondary system under AVT and ETA injection conditions was made by model calculations, then FAC rate measurements of some components of the PWR secondary system were made by the rotary disk test, and finally the FAC reduction rate evaluation was carried out from magnetite solubility calculations. The following findings were obtained.

(1) The PWR secondary system water chemistry can be evaluated with suitable accuracy by the mass balance calculation taking into consideration the thermal decomposition of hydrazine in the SG and the liquid-vapor distribution of volatile substances in the SG and MSR.

(2) Because behavior of the PWR secondary system water chemistry varies drastically with the chemical substances present and the components of system, it is necessary to know the effect of water chemistry on each components of PWR secondary system when changing the water chemistry.

(3) ETA injection is effective to increase pH of the PWR secondary system.

(4) The inhibition effect on FAC rate was observed for almost all components of the PWR
secondary system in the rotary disk test under the ETA injection condition, but ETA injection was not
sufficient to allow neglect of the FAC.

(5) There were some components which had a small FAC rate inhibition effect for the ETA
injection condition in the rotary disk test, such as the low temperature condensate pump and high
temperature SG.

(6) There is a limitation to adopting the model of wall thinning rate due to FAC which is
proportional to magnetite solubility for high and low temperature components of the PWR secondary
system.

References

[1] B. Chexal, J. Horowitz, R. Jones et al., Flow Accelerated Corrosion in Power Plants, EPRI TR106611,
Conf. on Water Chemistry of Nuclear Reactor Systems, BNES, Bournemouth, pp.5-18 (1980).
Behavior (Part 1), CRIEPI Q08016, Central Research Institute of Electric Power Industry (CRIEPI) (2009),
[in Japanese].
(2001)
chemistry at Takahama-1," Proc. Int. Conf. Water Chemistry of Nuclear Reactor Systems, Jeju Island,
Japanese].
1998 JAIF Int. Conf. on Water Chemistry in Nuclear Power Plants, Kashiwazaki, Japan, pp.599-602
estropies of the ions up to 200° and the correspondence principle," J. Am. Chem. Soc., 86, pp.5385-5390
(1964).
[CD-ROM].