EVALUATION OF PH CONTROL AGENTS INFLUENCING ON CORROSION OF CARBON STEEL IN SECONDARY WATER CHEMISTRY CONDITION OF PRESSURIZED WATER REACTOR

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The effect of various pH agents on the corrosion behavior of carbon steel was investigated under a simulated secondary water chemistry condition of a pressurized water reactor (PWR) in a laboratory, and the steel's corrosion performance was compared with the field data obtained from Uljin NPP unit 2 reactor. All tests were carried out at temperatures of 50°C – 250°C and pH of 8.5 – 10. The pH at a given temperature was controlled by adding different agents.
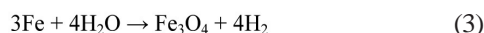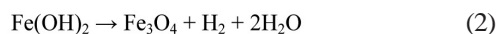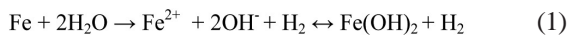
Laboratory data indicate that the corrosion rate of carbon steel decreased as the pH increased under the test conditions and the highest corrosion rate was measured at 150°C. This high corrosion rate may be related to high dissolution and instability of Fe oxide (Fe_3O_4) at 150°C. It was also found that an addition of ethanolamine (ETA) to ammonia was more effectivefor anti-corrosion than ammonia alone, and that mixed treatment reduced 50% of iron or more at pHs of 9.5 or higher, especially in the steam generator (SG) and the moisture separator & re-heater (MSR).

KEYWORDS : PWR Secondary System; pH Agents; Carbon Steel, Corrosion

1. INTRODUCTION

The secondary side of a PWR, a circulatory system of water and steam, is managed to control the water quality by minimizing the incoming corrosion products into the SG. The corrosion products coming into the SG are, in large part, iron oxides generated from flow-accelerated corrosion (FAC).[1]

FAC is affected by water chemistry such as temperature, pH, and ECP, and also by hydraulic properties such as flow rate and the type of metal. Figure 1 shows the schematic drawing of general corrosion of carbon steel in an aqueous environment, showing that the water penetrates into the porous magnetite layer and then reacts with the metal to form ferrous hydroxide, $Fe(OH)_2$, and hydrogen. The ferrous hydroxide, in part, is transformed to magnetite at the nearby high-temperature oxide layer, while some diffuses into the bulk with atomic hydrogen. Above 200°C, magnetite is directly formed at the interface of the metal oxide layer as described by the following three reactions.[2]

$$Fe + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \leftrightarrow Fe(OH)_2 + H_2 \quad (1)$$

$$Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O \quad (2)$$

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad (3)$$

The magnetite layer on the carbon steel surface, being affected by water chemistry conditions, is destined to be dissociated into ferrous hydroxide and ferrous ions, and then to diffuse into the bulk, the rate of which would increase with fluid velocity.[2]

$$1/3Fe_3O_4 + (2\text{-}b)H^+ + 1/3H_2 \leftrightarrow Fe(OH)b^{(2\text{-}b)+}$$
$$+ (4/3\text{-}b)H_2O \ (b=0, 1, 2 \text{ and } 3) \quad (4)$$

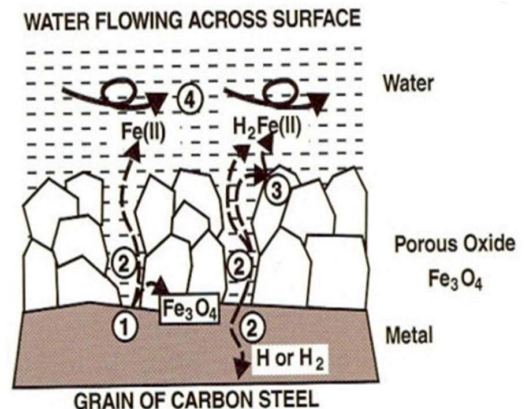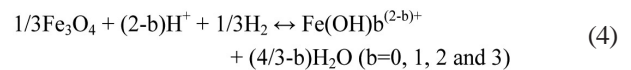$$Fe(OH)_2 \leftrightarrow Fe^{2+} + 2OH^- \quad (5)$$

Fig. 1. Schematic of General Corrosion of Carbon Steel in Aqueous Environment[2]

Figure 2 shows a solubility curve in ammonia solution as a function of temperature and pH. In a deoxygenated, basic solution , dissolution of iron reduced with pH increase, and it grew with temperature, marking a peak at 150ºC, and decreased afterwards.[2]

The secondary side of a PWR is classified into states of 'aqueous', 'gaseous', and 'moisture and steam.' In fact, FAC in the secondary side of a PWR frequently occurs in aqueous phases and moisturized steam areas. Generally, in those areas containing more than 5% of moisture, the thinning rate of a carbon tube would be higher than anywhere else, as it is known to be affected by factors like the size of water drops, liquid film thickness on tubing surfaces, diffusion rates for liquid film and moisture, and locally dissolved iron concentration.[2]

In order to suppress FAC, pH agents and hydrazine are fed into the secondary system, which consequently maintains a weakly basic pH, depletion of dissolved oxygen, and a reductive environment (see Equations. 6-10).[3]
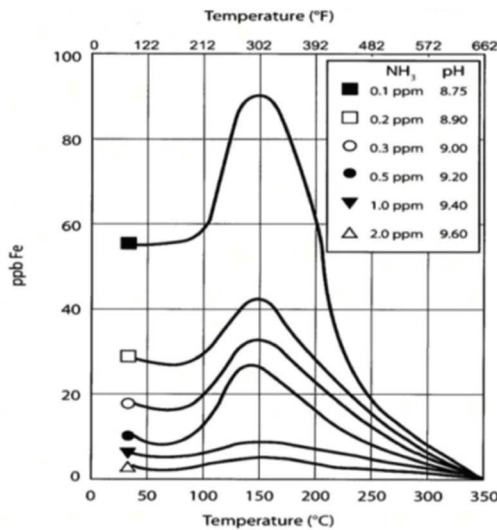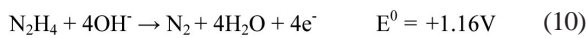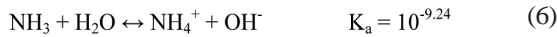
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \qquad K_a = 10^{-9.24} \qquad (6)$$

$$ETA + H_2O \leftrightarrow ETAH^+ + OH^- \qquad K_a = 10^{-9.50} \qquad (7)$$

$$H^+ + OH^- \leftrightarrow H_2O \qquad K_w = 10^{-14} \qquad (8)$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \qquad (9)$$

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \qquad E^0 = +1.16V \qquad (10)$$

Fig. 2. Iron Solubility Versus Temperature with pH and NH₃[2]

It is noted that phosphates were used as early pH controllers, and then in the 70's they were replaced with ammonia for buffering pH, which was called AVT (all volatile treatment). Now a variety of amines are used according to tube type and operation characteristics.[4-5] In terms of corrosion, optimal pH agents are acknowledged to be of 1.0 distribution coefficient, to be basic, and to be diffused poorly

The purpose of this work is to investigate the corrosion behavior of carbon steel under a simulated water chemistry condition of the secondary system of a PWR in the presence of various pH agents such as ammonia and ETA. Further field tests at Uljin NPP were conducted to investigate the effectiveness of additives by controlling the input composition and subsequent environmental parameters.

2. EXPERIMENTAL PROCEDURES

2.1 Corrosion Test at Laboratory
2.1.1 Specimen Preparation
The test carbon steel specimens were prepared in the form of 1cm(W)x1cm(D)x0.2cm(H) samples. They were cleaned with acetone and subsequently with demineralized water. The specimens were then spot-welded to 304 stainless steel (SS), insulated with polytetrafluoroethylene (PTFE), and installed in a Conax fitting.

2.1.2 Water Chemistry Control
For simulation of the water chemistry in the secondary system of a PWR. the water loop was comprised of glass columns, a high-pressure pump, pre-heater, condenser, back-pressure regulator (BPR), sensors (pH, DO, and conductivity), and a metering pump, as shown in figure 3.

First, high purity demineralized water was continuously supplied into the glass columns at 250cc/min, and it was then deaerated with N₂ gas. The pH of the high temperature water was adjusted with additions of NH₃, ETA, or NH₃/ETA before reaching the autoclave. The well-controlled test solution was recycled through the condenser, BPR, sensors (pH, DO, and conductivity), and glass columns. Table 2 shows the water chemistry conditions used in this experiment.

2.1.3 Measurement of Polarization Curve and Corrosion Rate
In order to measure the anodic polarization curve of carbon steel in a given test environment, an Ag/AgCl(1M

Table 1. Chemical Composition of Test Material (wt%)

C	Mn	P	S	Si	Cr	Mo	Ni	V	Cu
24	1.08	0.13	0.003	0.26	0.11	0.04	0.13	0.004	0.13

Table 2. Water Chemistry Conditions

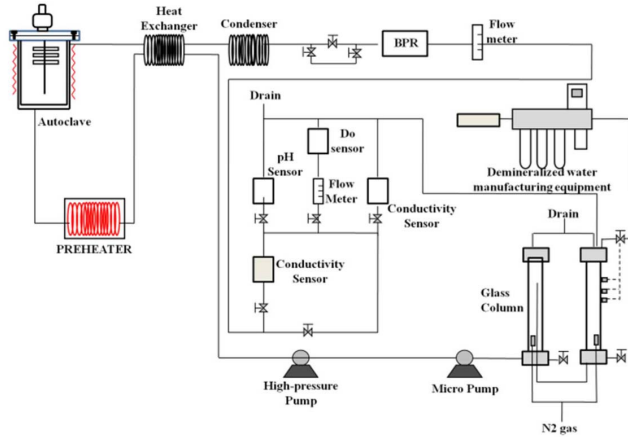| pH Agent	pH (25°C)	Pressure(psi)	Temperature(°C)
NH$_3$	8.5, 9, 9.5, 10	2500	50, 100, 150, 2 00, 250
ETA			
NH$_3$+ETA			

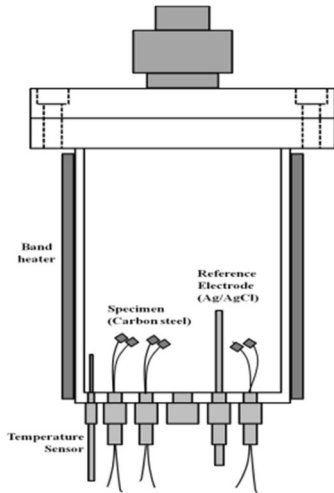Fig. 3. Schematic Diagram of Experimental Set-up and Water Loop

Fig. 4. Arrangement of Test Specimens in the Autoclave

KCl) reference electrode was used, with the autoclave serving as the counter electrode. All polarization measurements were carried out using an AMETEK Solartron (Model 1470E) and Multistat software (see Figure 4. The Conax fitting was positioned at the lower end of the autoclave.

2.2 Field Test at Uljin NPP Unit 2

2.2.1 Composition and Injection Stages for NH$_3$ and ETA
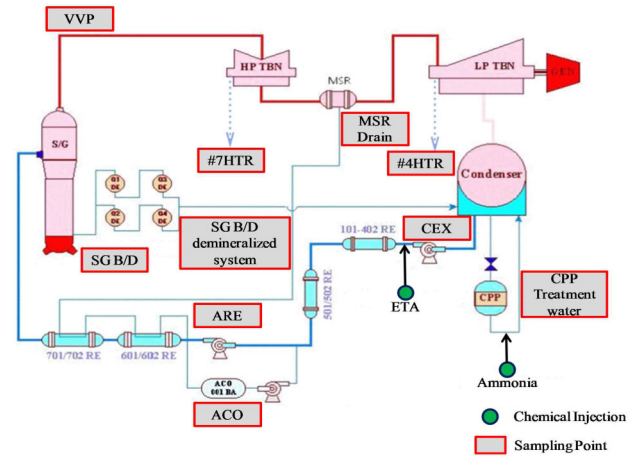
Ammonia and ETA were used as model pH agents in

Fig. 5. Locations in the Secondary Side for Injection and Sampling

Table 3. Composition of NH$_3$ and ETA Injected during Field Test

Stage	Concentration(ppm)	
	NH$_3$	ETA
Base	1.3	0
Test 1	0.8	1.6
Test 2	0.9	1.6
Test 3	1.0	1.8
Test 4	1.2	1.8

this work. The concentrations for the two chemicals in the feed stream at designated stages are listed in Table 3. Injection points were at the rear end of the condensate polishing plant for ammonia and that of the condensate pump for ETA as illustrated in figure 6. 'Base' stage means sole injection of ammonia while 'Test #' stages represent 'mixed, but differently composed' injections.

2.2.2 Sampling and Analysis

Samples of the pH agents were taken at 10 locations - steam generator A/B/C (S/G), feedwater (ARE), condensate (CEX), extract of HP steam (#7 HTR), extract of LP steam (#4 HTR), moisture separator & reheater (MSR), condensate of wet steam (ACO), and main steam (VVP) (see Figure 5).

The pH and concentrations of N$_2$H$_4$ were measured using a pH meter (Orion) and a UV-Vis spectrometer (Calorimetric Method). NH$_3$ and ETA were analyzed via Ion Chromatography (DIONEX Cation-IC) while Fe and Cu, byproducts of the corrosion, were quantified through inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.2.3 Setting Mass Balance in PWR Secondary System

In order to quantify the amount of corrosion byproducts generated, or flue in each PWR unit, a material balance in the volumetric flow rate was applied to the entire secondary system (see Figure 6) [6].

3. RESULTS AND DISCUSSION

3.1 Corrosion Behavior of Carbon Steel with Water Chemistry Conditions

After measuring the anodic polarization curves of carbon steel under different test conditions, the Tafel extrapolation method was used to estimate the corrosion current density (I_{corr}) as shown in Figure 7, and the corrosion rate in mils per year(MPY) was calculated by Equation 11.[7]

The parameters used in Equation 11 are given in Table 4.

$$MPY \left(\frac{mile}{year}\right) = 0.129 \times 10^6 \times \frac{I_{corr} \times M}{|z| \times D} \qquad (11)$$

Figure 8 shows the effect of temperature on the potentio-dynamic polarization of carbon steel in ETA and NH_3 solution of pH 9.5.Table 5 shows the effect of temperature on the corrosion current density of carbon steel in ETA and NH_3 solution of pH 9.5. The highest corrosion current density was measured at 150ºC

In addition, the corrosion rates of carbon steel in both

chemicals (NH_3 and ETA) at pH 9.5 were shown to be the highest at 150ºC (see Figure 9). Since the corrosion behavior of carbon steel can be affected by liquid diffusion into the inner oxide film and iron solubility, the corrosion rate is expected to decrease due to the lower diffusion rate at temperatures below 100ºC and subsequently by the reduction of iron solubility at temperatures above 200ºC This test result is in good agreement with the literature, as illustrated in Figure 2.[2] Furthermore, it was shown that the corrosion rate of carbon steel in ETA solution was lower than the one measured in NH_3 solution, and this low corrosion rate in ETA solution may result from the lower diffusion coefficients and electrical conductivities.[9]
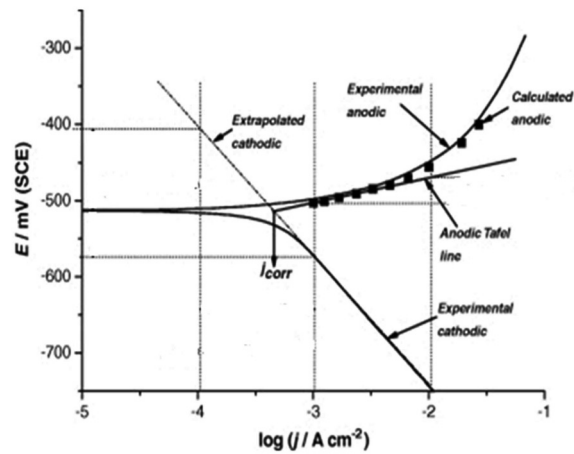

Fig. 7. Potention-dynamic Polarization and Tafel Extrapolation
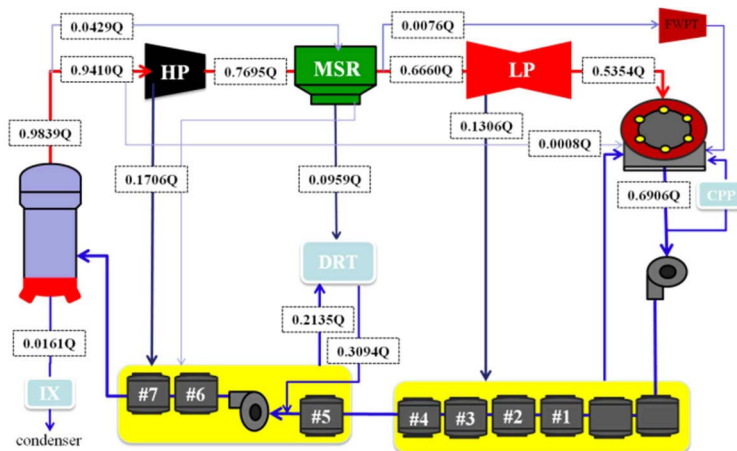

Fig. 6. Mass Balance in PWR Secondary System

Table 4. Electric and Physicochemical Properties of Iron for Equation 11. [8]

Metal	Element/Oxidation state ($|z|$)	Density(D)	Equivalent Weight(M)
Fe	2	7.87 g/cm³	27.92 g

Figure 10 shows the effect of pH on the corrosion rate of carbon steel at 150ºC in two different chemicals. In both solutions, the corrosion rate decreased as the pH increased. It is interesting to note that a monotonic decrease in corrosion rate was clearly observed by shifting the pH from 8.5 to 10. This unique phenomenon may benefit from the corrosion reaction facilitated by highly concentrated hydroxide ions with higher pH that eventually consume more protons. A high pH solution also catalyzes the formation of an oxidation layer on metal surfaces and the layer subsequently blocks transport of electrons and intrusion of impurities, which leads to less corrosion.

3.2 Field Test Result

3.2.1 Concentration of NH₃, ETA and N₂H₄

Figure 11 shows the distribution of concentrations of ammonia, ETA, and hydrazine sampled from given points

at different stages (Table 4). ETA was found to be higher at MSR and SG than ammonia due its low relative volatility

Table 5. Corrosion Current Density of Carbon steel in NH_3 and ETA Solution(pH 9.5) at Different Temperatures

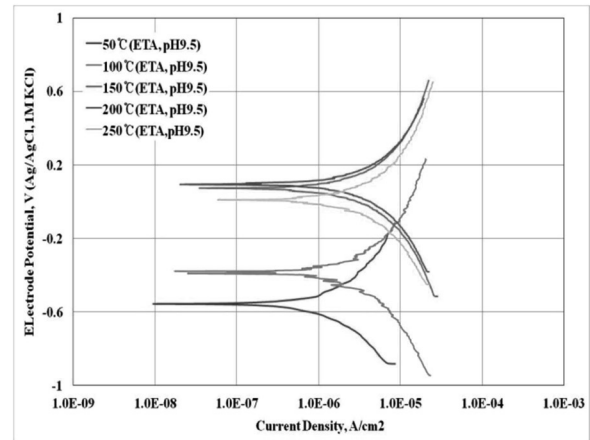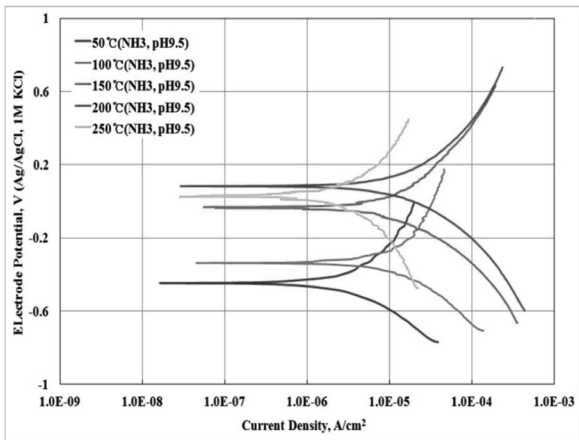| Temperature(ºC)	$I_{corr}(10^{-5}A/cm^2)$	
	NH_3	ETA
50	2.18	1.84
100	3.24	2.86
150	4.02	3.58
200	2.62	2.14
250	1.79	1.70

Fig. 8. Potentio-dynamic Polarization Curves of Carbon steel in NH_3 and ETA Solution(pH 9.5) at Different Temperatures
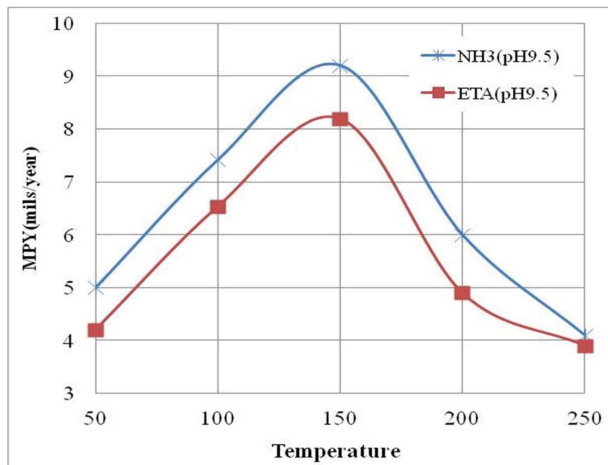

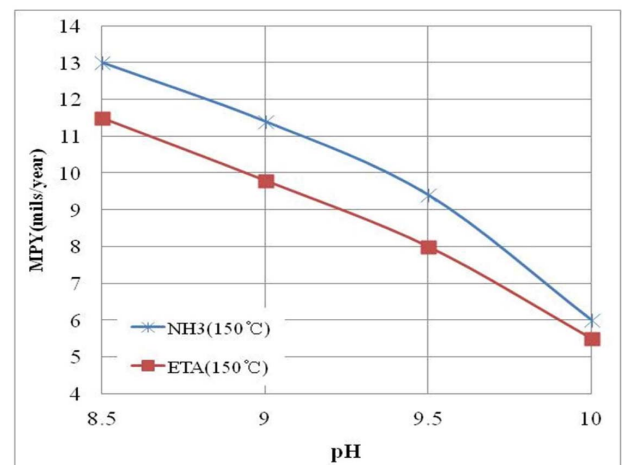Fig. 9. Effect of Temperature on Corrosion Rate of Carbon Steel in Two Different Chemicals at pH 9.5

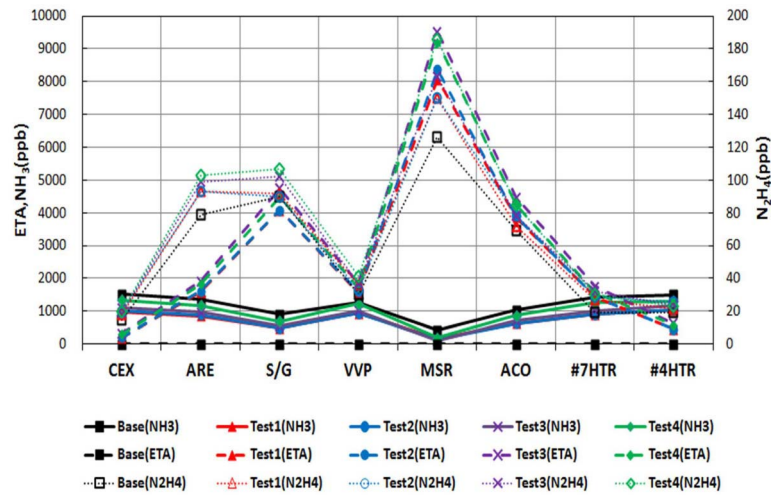Fig. 10. Effect of pH on Corrosion Rate of Carbon Steel in Two Different Chemicals at 150ºC

Fig. 11. Concentration of NH$_3$, ETA, N$_2$H$_4$

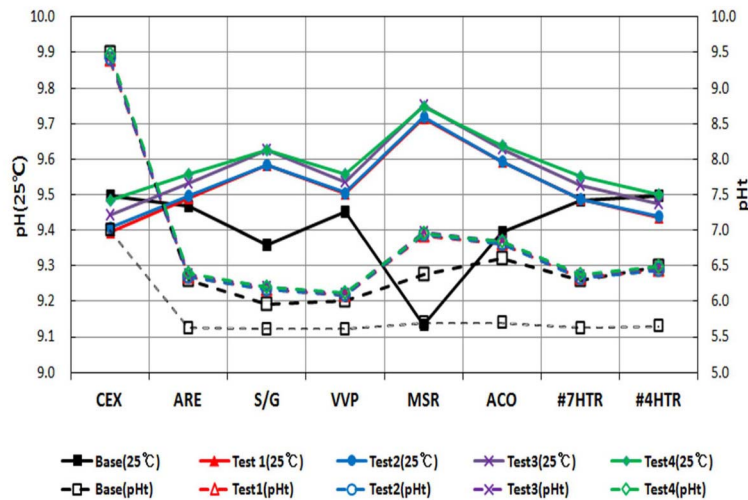

Fig. 12. Values of pH(25℃) and pH(T) at Test Locations

to water. Meanwhile, ammonia was more concentrated than ETA at the terminal units such as condensate (CEX) and extract of LP steam (#4 HTR) owing to its inherently higher relative volatility.

3.2.2 pH(25℃) and pH(T)

Figure 12 shows various values of pH(25℃) and pH(T) at the designated locations of NPP Uljin unit 2. Mixed injection of ammonia and ETA ensures a pH(25℃) above 9.5 at every test location. Increase in pH(25℃) values became strong particularly at MSR and SG when mixed injection was applied. It should be noted that both pH values were much higher at MSR, SG, and Condensate of wet steam (ACO) due to ETA having lower relative volatility.

3.2.3 Concentrations of Fe and Cu

Concentrations of Fe and Cu were collected at select-edcations (Figure 13). Iron concentration at all locations were reduced when mixed injection rather than ammonia only was given because the fluid pH remained above 9.5 owing to the lower volatility of ETA. The iron reduction was most profound at MSR and extract of HP steam (#7 HTR). The concentrations of copper tended to be within a certain limit, overall. Comparison between the tests from #1 to #4 show that Test 3 has the lowest Fe generation at ETA/NH3=1.8,

3.2.4 Mass Balance in Fe

Figure 14 depicts a mass balance for iron occurring in the secondary side of a PWR. It enumerates generations,
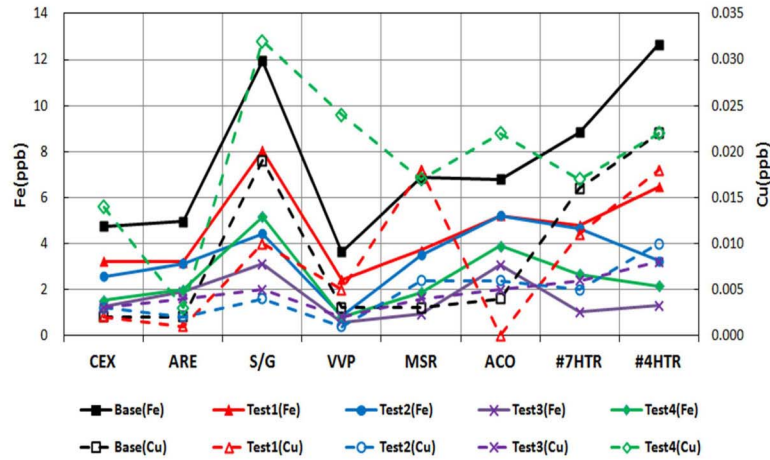
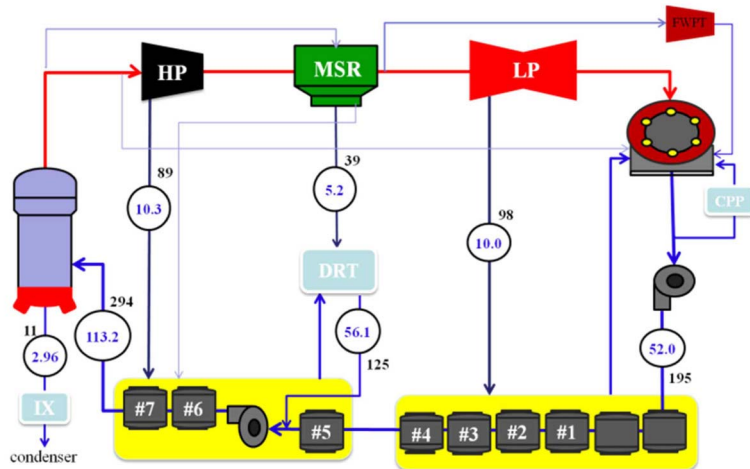Fig. 13. Distribution of Concentrations of Fe and Cu

Fig. 14. Mass Balance Diagram for Corrosion Products in PWR Secondary System. Numbers in Circles Represent the Ammonia Injection Case, While the Outside Numbers Stand for the Mixed Injection Case.

flow-ins, and flow-outs of iron in the mass flow diagram. Two cases are discussed here: ammonia only and mixed injection. At extract of HP steam (#7 HTR) and extract of LP steam (#4 HTR), the mixed injection gives about 10 g/day of corrosion product, at least 90% less than sole injection of ammonia. Its flow-in to SG reduced by more than 50% as well when mixed chemicals were fed. Table 6 summarizes the dramatic decrease in the iron amount found in several important units of the PWR in the case of mixed injection.

Table 6. Iron Generated or Flow-in Through Main Locations(g/day)

	NH$_3$	NH$_3$+ETA
Inflow of Fe in SG	294	113.2
Extract of HP steam	89	10.3
Extract of MSR steam	39	5.2
Extract of LP steam	98	10.0
Condenser pipe	195	52
MSR Drain Tank	125	56.1

4. SUMMARY & CONCLUSIONS

The corrosion behavior of carbon steel was investigated under a simulated secondary water chemistry condition of pressurized water reactor (PWR) in laboratory, and pH controllers' performance was compared with the field data tested at Uljin NPP unit 2 reactor. All tests were carried out in NH$_3$ or ETA solution at temperatures of 50ºC – 250ºC and pHs of 8.5 – 10, and the pH at a given temperature was controlled by adding different agents and additive concentrations.

Laboratory data indicated that the corrosion rate of carbon steel decreased as the pH increased under the test conditions and the highest corrosion rate was measured at 150ºC. This high corrosion rate may be related to high dissolution and the instability of Fe oxide (Fe_3O_4) at 150ºC. It was also found that an addition of ethanolamine (ETA) to ammonia was more effective than ammonia alone, and that mixed treatment reduced 50% of iron or moreat pHs of 9.5 or higher, especially in the steam generator (SG) and the moisture separator & re-heater (MSR).

ACKNOWLEDGMENT

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