

Characteristics of ETA for pH Control and Full Scale Test at Kori Unit 1

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To reduce FAC of carbon steel on secondary system, water treatment method was converted to ETA control at Kori Unit 1. Full scale tests to determine the optimum concentration of ETA were conducted and the evaluation after one cycle operation with ETA was also performed. The optimum concentration of ETA at final feed water was determined as 1.8 ppm. At this condition, iron concentration was reduced by 69.8 % at final feed water and 69.7% at heater drain compared to ammonia-AVT. The amount of sludge removed from each steam generator was 11.3 kg, which was 88.2 % lower than that of ammonia-AVT. No adverse effects, especially turbine blades, gasket and packing, on secondary system materials were found.

Keywords : ethanolamine (ETA), flow accelerated corrosion (FAC), ammonia-AVT, water treatment, sludge, chemWORKs code

1. Introduction

The Kori Unit 1, which is the first nuclear power plant in Korea, has been in commercial operation since April 1978. Westinghouse provided it and its capacity is 587.5 MWe. This unit has two loop steam generators. The cooling water for the condensers is supplied from the East Sea. The unit has been using ammonia and hydrazine for the secondary water chemistry controls since commercial operation. Specification of major facilities is described in Table 1.

In early 1990s, stress corrosion cracking (SCC) occurred at sludge pile. To prevent the sludge pile-up, a high pH-all volatile treatment (AVT) was adopted[1]. It reduced the corro-

sion of carbon-steel significantly. However, it was not sufficient to prevent corrosion around the wet-steam area, which was susceptible to flow accelerated corrosion (FAC)[2].

In the efforts toward maintaining the long-term integrity of SG in PWR secondary system, the reduction of iron ingress into steam generator(SG) has become one of the most important tasks. Most of such iron is considered to be FAC products of piping and component materials in two phase areas vapor and liquid, such as steam extraction and drain systems. The increase of pH in these areas is one of good practice to lessen FAC[1].

As of mid-1980s, the water treatment method in many foreign PWRs such as U.S and France

Table 1. Specification of major facilities

Facility	Items	Specification
Reactor	Type	W PWR Two-Loop
	Thermal Power(MW(t))	1,723.5
	Coolant Outlet Temperature(°C)	319.3
	Coolant Inlet Temperature (°C)	282.9
	System Pressure(kg/cm ²)	157.3
Steam Generator	Type	Recirculating Vertical U-Tube(W 51 series)
	Tube Material	Alloy 600
	Steam Generation Rate(T/hr) [†]	1,700
	System Pressure(kg/cm ²)	55.6
	Steam Temperature(°C)	270.5
Turbine	Number	2
	Type	Tandem compound three casing four flow exhaust reheat regeneration type
	Capacity(MWe)	587

was shifted from the use of ammonia to morpholine for the pH control of secondary system[3]. Morpholine is less volatile than ammonia, resulting in a more favorable distribution of the pH control agent to the liquid phase throughout the steam cycle. In addition, advanced amines have been also studied in Electric Power Research Institute (EPRI) and full scale tests of selected advanced amines are currently under way[4].

On the other hand, Korea Electric Power Research Institute (KEPRI) has studied the advanced amines as an alternates of ETA for the secondary side[5]. The results of loop and pilot tests of ETA have shown that it has superior properties to ammonia for pH control in nuclear stations. ETA is a stronger amine than ammonia in basicity, both at room temperature and at elevated temperatures found in steam generators and the high temperature drain portions of PWR secondary systems. Furthermore, ETA exhibits favorable distribution to the liquid in two-phase regions of the secondary system. A higher proportion of ETA will partition to the liquid phase than the vapor

phase. ETA partitions are almost to the liquid phases, while ammonia partitions almost completely to the vapor phase. Therefore, ETA will provide more corrosion protection for the high temperature carbon steel portions of the system at a lower concentration than ammonia. ETA injection started on October 1998, following the replacement of SG as a demonstration unit in Korea Electric Power Corporation (KEPCO).

This paper describes the results of a study on optimum concentration of ETA and the assessment on environmental improvement after one cycle of operation with ETA chemistry that conducted as a full scale tests at Kori Unit 1.

2. The history of water chemistry and retrofit

The Kori Unit 1 experienced a lot of leakages of seawater in the early stage of commercial operation. Several types of corrosion occurred in the tube of steam generator. Improvement of water chemistry and retrofit of system were made to alleviate those kinds of corrosion effectively. They are summarized in Table 2.

In 1985, the main corrosion type was pitting.

Table 2. The summary of history of water chemistry and retrofit

Date	Contents	Water treatment
1978. 4.29 10.25 - 12.30	<input type="checkbox"/> Commercial operation started <input type="checkbox"/> O/H - Detection of SG tube denting - Replacement of SS tube with cupronickel at air removal zone of condenser	AVT
1979. 1.27 1979. 1.28 - 1980. 7. 1	<input type="checkbox"/> Boric acid treatment started <input type="checkbox"/> Boron soaking(1st-5th)	Boric Acid & AVT Treatment
1982. 7.20	<input type="checkbox"/> CPP operation started and boric acid treatment stopped	
1984. 7. 7 - 10. 1	<input type="checkbox"/> Replacement of condenser tube(lower of A1,B1)	
1985. 1.14 8.14 - 11. 1	<input type="checkbox"/> Huge seawater leakage with condenser tube rupture <input type="checkbox"/> O/H for nuclear fuel replacement(6th) - Replacement of condenser tube(at B2 bottom) - Replacement of MSR tube A/B	
1988. 1.15 - 7.15	<input type="checkbox"/> O/H for nuclear fuel replacement(8th) - Replacement of all condenser tubes(Al bronze→Ti tube) - Replacement of each HTR tube (#1,2,3,5,6 HTR cupronickel → SS)	
1989. 3.28	<input type="checkbox"/> First implement of HORT(Hide-out return test)	
1990.11. 3 - 11. 4	<input type="checkbox"/> Chemical cleaning for SG A/B (Removal of the hard sludge at tube sheet of secondary side)	
1991. 1.14 2. 1	<input type="checkbox"/> High concentration of hydrazine operation started <input type="checkbox"/> SGBD recovery system installation and operation	
1994.11. 8 - 1995. 1. 2	<input type="checkbox"/> O/H(SG tube leak by ODSCC) <input type="checkbox"/> Crevice cleaning/hydrazine soaking('94.12) <input type="checkbox"/> Nitrogen purge for condensate storage tank when start up	AVT
1995. 1. 2 - 1996. 1.14	<input type="checkbox"/> Implement of molar ratio control(0.5 ± 0.1) <input type="checkbox"/> Reduction of power output(85%)	
1995. 6. 1 - 1997. 12.11	<input type="checkbox"/> CORS(Catalytic Oxygen Removal System) operation	
1996. 1.15 - 3. 31	<input type="checkbox"/> O/H for nuclear fuel replacement(14th) - SG lancing - Crevice cleaning/hydrazine soaking('99.3) - Dry treatment for HTR(using Heater Fan)	
1996. 4. 1 - 1998. 6.18	<input type="checkbox"/> Molar ratio control(0.7 ± 0.1)	
1997. 3.30 - 6. 8	<input type="checkbox"/> O/H for nuclear fuel replacement(15th) - SG HORT - SG sludge lancing(using CECIL) - Crevice cleaning/hydrazine soaking - Replacement of TBN rotor	
1998. 6.19 - 9.16	<input type="checkbox"/> O/H for nuclear fuel replacement(16th) - Replacement of SG	

* O/H : Over-haul

It was caused by sludge piles in the region of tube sheet of SG and oxidizing environmental conditions. The main countermeasures were replacement of condenser tube material from copper alloy to titanium. The other materials (moisture separator & reheater, heater) made of copper bearing material were also replaced with stainless steels. High concentration of hydrazine was employed to reduce environmental conditions.

In 1990, the main corrosion type was primary water stress corrosion cracking (PWSCC). It was caused by high temperature of metal in the region of sludge pile. The main countermeasures were performance of chemical cleaning to remove sludge pile and installation of condensate polishing plant (CPP) to remove corrosion product.

In 1994, the main corrosion types were PWSCC and outer diameter stress corrosion cracking (ODSCC). They were caused by alkalinized environment in the region where sludge was piled up and also has a high corrosion potential due to the copper sludge. The main countermeasures were the reduction of corrosion potential with hydrazine soaking and operation with high concentration of hydrazine. The reduction of power output was also conducted and the power output decreased to 85%. It was observed that the hot-leg temperature (T_{hot}) was decreased 5°C. TiO_2 was also injected as an inhibitor.

3. Experiment

To assess optimum concentration of ETA at Kori Unit 1, a short term ETA test was conducted under the conditions shown in Table 3, based on the prediction using chemWORKS code designed by EPRI. ETA is provided by Korea polyol Co. It was diluted to 8% through

9.5% and injected at outlet of CPP. Water qualities of the secondary side were analyzed before and after the injections. We analyzed pH, conductivity, Na, Cl, SO_4 , N_2H_4 , ETA, NH_3 , Fe, acetate, formate, and glycolate. Cation and anion were analyzed using Ion Chromatography (Dionex Co., model 2000I).

Corrosion products were collected using integrated sampler, concentrated type sampling apparatus which collects a lot of samples to one place and analyzed to evaluate the performance of pH control. Collected sample was digested with acid and measured using inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu Co., model ICP-1000IV).

The sampling line was very long (about 50-60m). The length of sampling pipe might influence iron concentration because of the possibility of corrosion products deposition in the pipe. Therefore, a new local sampling apparatus was installed, as shown in Fig1. The length is shorter than 5m.

4. Results and Discussion

ETA was injected into the secondary system at the outlet of the condensate polisher. To evaluate the distribution of ETA, pH and various chemical species were analyzed in different parts of the secondary system..

4.1 ETA and pH distribution in the secondary system

Fig. 2 shows the system diagram of Kori Unit 1 and the distribution of ETA concentrations in different areas of the secondary system, when the ETA concentration at final feed water was 2 ppm. The concentrations of ETA in the area of feed water train and blow down are higher than those of condensate region due to the lower volatility of ETA.

Table 3. Experimental conditions of short term ETA test

Experimental conditions	ETA Conc. at FFW(ppm)	Ammonia Conc. At FFW(ppm)	Hydrazine Conc. at FFW(ppm)	Condensate Polisher	Water Treatment
I	0	1.3	110	Partial Flow 13% in-service	AVT
II	1.5	0	110		ETA
III	1.8	0	110		ETA
IV	2.0	0	110		ETA

Table 4. Comparison of pH between ETA and ammonia in different parts of secondary side.

Items		C/D	FW	HTR Drn	SG B/D	M/S	MSR
pH (25°C)	AVT	9.5	9.4	9.5	9.2	9.6	-
	ETA	9.25	9.2	9.2	9.6	9.3	-
pH(T)	AVT	9.5	6.28	6.26	5.95	5.95	5.93
	ETA	9.2	6.37	6.41	6.23	6.23	6.35

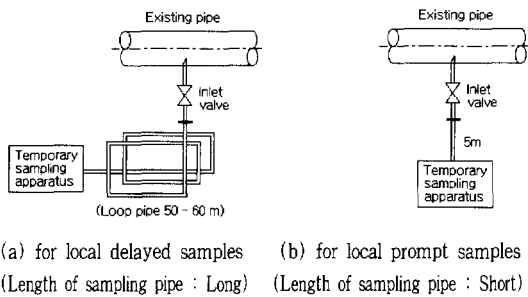


Fig. 1. Sampling line for measurement of corrosion

*condition : ammonia 1.2-1.3ppm(AVT), ETA 2.0ppm(ETA)

*pH(T) : calculated by EPRI chemWORKs code

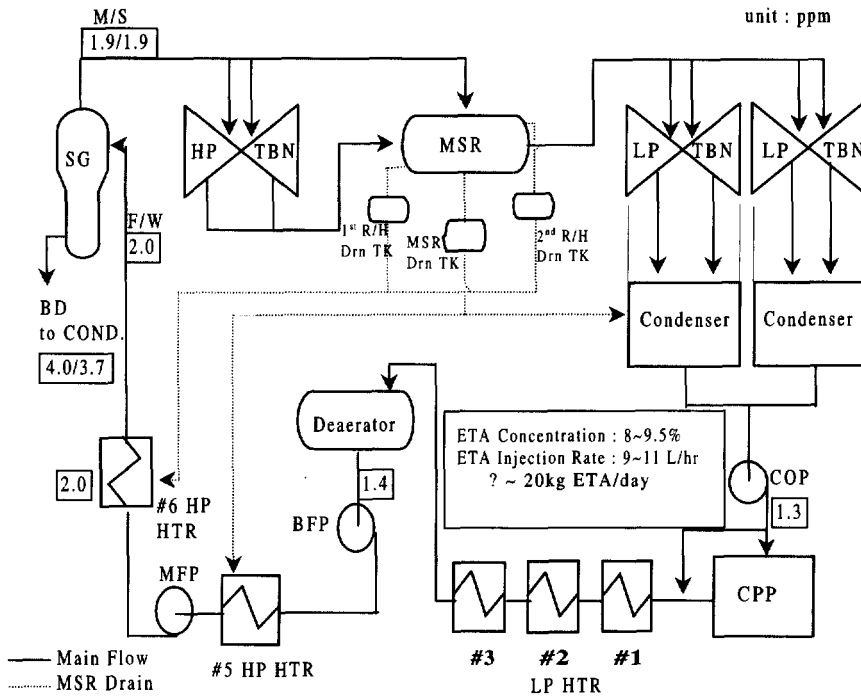


Fig. 2. Distribution of ETA in different parts of the secondary system at Kori Unit 1.

Table 4 shows the distribution of pH in different part of the secondary side between ETA and existing ammonia conditions. With injection of ETA, pH increased to 6.35 at moisture separator & reheater (MSR) and 6.41 at heater drain (HTR Drn). It will be effective to prevent corrosion in the wet and steam areas which are especially susceptible to FAC.

4.2 Profile of iron concentration during transition period

Iron transport trend has been monitored as a control factor of water chemistry. The typical concentration of iron at Kori Unit 1 were approximately 6.1 ppb. These values varied with the status of the units. Start ups, shut downs, or significant power changes usually affect the iron transport values, as it still does today. Profile of iron concentration during the transition period is shown in Fig. 3. Since the water chemistry has changed from ammonia to ETA, the reduction of iron transport values was observed in all parts of system. The iron concentration at final feed water (FFW) decreased from 6.1 ppb to 1.84 ppb and at heater drain system from 6.1 ppb to 1.85 ppb. Because pH in the feed water system increased significantly compared to ammonia chemistry. These results show that pH affects the rate of FAC[6]. An

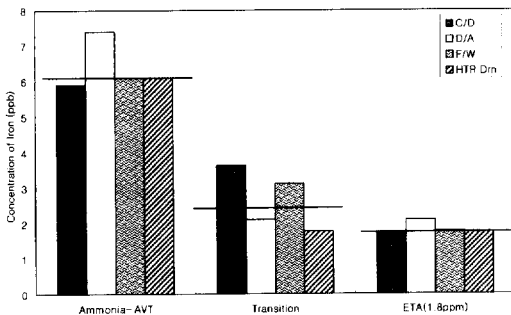


Fig. 3. Profile of iron concentration dependent on water chemistry

increase in the cold pH induces a decrease in FAC, which can be related to the hot pH or the equilibrium iron solubility.

4.3 Optimum concentration of ETA

Fig. 4 shows iron concentration at final feed water relative to ETA concentration. Initial concentration was 2.0 ppm. As shown in Fig. 4, iron concentration decreased significantly. However, as shown in Table 4, ion load of blow down demineralizer increased rapidly. To lessen ion load, ETA concentration was adjusted to 1.5 ppm. But concentration of iron at FFW was higher than the previous ETA concentration. Therefore, the concentration of ETA was finally adjusted to 1.8 ppm with considering both iron concentration of FFW and ion load of blow down demineralizer.

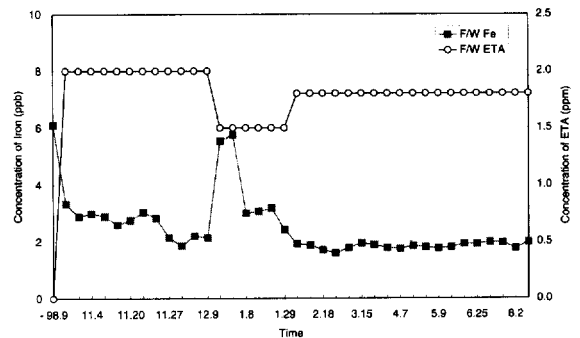


Fig. 4. Iron concentration at FFW as a function of ETA concentration

Table 5. The amount of organic substance in different areas after ETA injection

(unit : ppb)				
Location	Acetate	Glycolate	Formate	Total
S/G	8.7	13.2	6.3	28.2
M/S	12.0	1.6	5.6	19.2
F/W	10.2	1.4	2.4	14.0
C/D	7.1	0.6	0.6	8.3

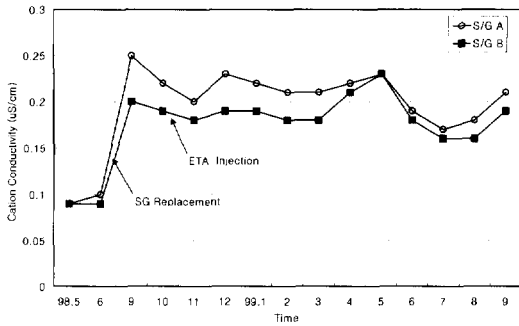


Fig. 5. The variation of cation conductivity at steam generator blow down

4.4 Organic acid production and variation on cation conductivity

Organic acids (formic acid, acetic acid, glycol acid), which are the thermal decomposition products of ETA, may contribute to a pH drop in the system, causing adverse effects on turbine dry-wet portions. Therefore, it is important to control the concentration of these organic acids. The amount of organic substance in different areas of the secondary system is shown in Table 5.

It was found that the concentrations of formic, acetic and glycol acids at SG blow down increased in proportion to ETA concentration at the feed water. We found that acetic acid increased to 8~11 ppb from 1~3 ppb.

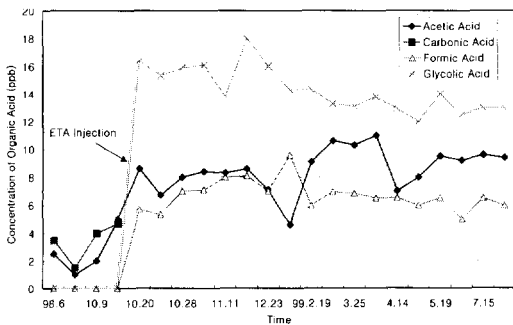


Fig. 6. The variation of organic acids at steam generator blow down

formic acid 5~10 ppb, and glycol acid 14~18ppb when 1.8 ppm was injected at FFW, while formic and glycol acid did not appear under the ammonia AVT. Consequently, total amounts of organic acids produced in the secondary side were about 30 ppb. They are lower than those of foreign plants experienced before[7]. It may be due to the new SG, which has less sludge piles and less copper contents. It is known that sludge contained copper accelerates the thermal decomposition of ETA.

The profile of cation conductivity and the amount of organic acids at blow down were shown in Fig. 5 and 6. The cation conductivity is increased by 0.1µs/cm.

4.5 Impurity concentration

No significant increase in impurity concentration of the secondary side was observed between before and after ETA injection. However, as shown in Table 6, the impurity composition at SG blow down was changed. Concentration of sulfate ion increased while sodium and chloride ions decreased. The decrease in sodium concentration might be due to the high sodium selectivity on cation resin under ETA chemistry. Na+ selectivity with ETA is 1.73, while that of ammonia is 0.81. The decrease in chloride concentration might be due to the high purity of ETA. Some investigation on the high concentration of sulfate is currently under way. Profile of impurities at SG blow down is shown

Table 6. Impurity concentration of the secondary side before and after ETA injection.

Impurities	(unit : ppb)	
	AVT	ETA
Na ⁺	0.7	0.35
Cl ⁻	1.5	0.47
SO ₄ ⁻²	1.3	3.16

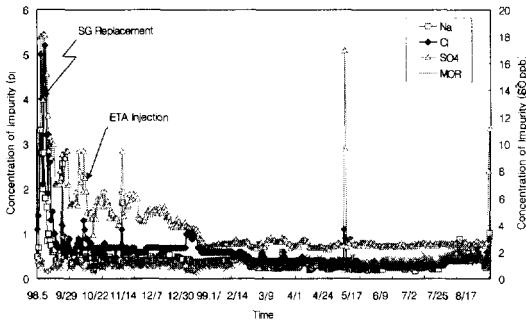


Fig. 7. Profile of impurities at SG blow down

in Fig. 7.

The alleviation of corrosive environment of SG was observed with the improvement of molar ratio(MOR) due to low sodium ion concentration. The MOR $,Na^+/Cl^-+SO_4^{2-}$, was adjusted to 0.6~0.8 with injection of ammonium chloride before ETA chemistry. But after changing to ETA, the MOR is 0.8 without injection of ammonium chloride.

4.6 Assessment of the impact on the condensate polisher

The Condensate Polishing Plant was installed in 1982. There are four service vessels installed on each unit. They cover thirteen percent of total flow of condensate water and its normal flow through each service vessel is approximately 400 ton per hour. Each service vessel currently contains 6,020L of resin, 4,010 L of cation resin and 2,010 L of anion resin. The cation resin is Ambersep 252 and the anion resin is Ambersep 900 produced by Roam & Haas. It is MR type. The resin was replaced in July 1998 just before the water treatment was changed to ETA. The regeneration system in use at Kori Unit 1 consists of anion regeneration, cation regeneration and resin mix tanks.

The effect on the condensate polisher was assessed by comparing the results of impurity analysis at the outlet of CPP. No increase of

Table 7. Cycles of CPP and BD demineralizer

(unit : days/cycle)

ETA (ppm)	0	1.5	1.8	2.0
CPP	4.3	8.8	7.7	6.4
B/D	178	80	75	50

*BD demineralizer flow : 10 m³/hr(S/G A, B)

Table 8. Measured gross exchange capacity of condensate polisher resins

(unit : meq/ml)

Items	Ammonia AVT	ETA	Remarks
Cation resin	1.7	1.7	no change
Anion resin	1.0	1.0	no change

impurities was observed, meanwhile, the ion load on resin increased due to the presence of ETA. As shown in Table 7 cycles of CPP increased but cycles of blow down (BD) decreased significantly due to the relatively low volatility of ETA. As shown in Table 8, no change was observed in capacity of resin between before and after ETA injection.

5. Assessment on ETA effect after one cycle operation

ETA injection was continued through one cycle based on the results of component inspection during annual maintenance outage and other data, the effectiveness of ETA was reviewed.

5.1 Comparison of removed sludge and material compatibility

The ETA control has been assessed with analyzing the concentration of iron in the secondary system during the operation. And it was also evaluated, based on the amount of the sludge removed from the tube plate and the

sludge collector in SG during annual maintenance outage. Table 9 shows the amount of sludge removed from SG during the outage between before and after the ETA. The amount of sludge removed from SG was much less than those of previous water chemistry. The sludge amount removed from the SG during inspection was 11.4 kg per SG, while it was 96 kg with ammonia-AVT. It is concluded that the sludge piled-up in SG decreased by about 88 %. However, it is difficult to assess the effect of ETA, based only on the sludge amount removed from the tube sheet parts of SG and sludge collector for one cycle, therefore the amount of removed sludge will be monitored for several more cycles in the future to evaluate ETA effect.

No adverse effect on plant system materials was found, in crack inspection on low-pressure turbine blades and visual inspection of gasket and packing. In conclusion, increase in pH of the system water caused by ETA did not result in any adverse effect on materials in the secondary system.

5.2 The evaluation on resin performance of CPP

Resin testing was performed to evaluate the resin properties including sulfate kinetics testing after switching from ammonia to ETA. R&H analyzed resin samples regularly from 1998 to 1999. The results are shown in Table 10. In the

Table 9. The amount of sludge removed from SG before and after ETA injection

Items	amount of sludge removed(kg)		Remarks
	S/G A	S/G B	
15th Cycle (AVT)	97.1	94.7	Sludge of upper TS
17th Cycle (ETA)	11.9	10.9	Sludge of upper TS + sludge of collector

early stage of switching to ETA, test results showed the anion kinetics to be deteriorated in the transition area, while physical properties did not changed. Being in the transition area means that the resin is degrading, although water quality of CPP effluent may appear to perform satisfactorily on a daily basis, the resin may not perform when challenged by a significant condenser leak. It has been getting better, dependent on number of regenerations performed during that time period. Other utilities have reported fouled anion resin after changing to ETA chemistry in as little as one fuel cycle. The anion resin has been identified as fouling due to a build up of organic on the surface of the resin. The reason might be as follows:

a. Since changed to ETA control, ETA behaves as a solvent in the initial stage. It removes an oily/slimy substance from the valve and internal of towers.

b. Anion resin was fouled due to a build up of organics on the surface of the resin. The lack of anion kinetic performance was reported by other utilities using ETA chemistry controls. The testing of an anion bed showed the sulfate kinetics is 0.5 E-4 m/sec or less.

c. However, the following test has shown the kinetics to be slightly improved with increasing number of regenerations. It means that the resin

Table 10. The results of performance test for CPP resin

Sample No.	WB/PB CER	(%) AER	MTC(SO ₄) × 10 ⁻⁴ m/sec	MTC(SO ₄) × 10 ⁻⁴ m/sec
	Sampling date:'99.7.1	Sampling date:'99.7.1	Sampling date:'99.7.1	Sampling date:'99.9.22
1	99.7/99.4	99.2/97.1	0.6	2.1
2	99.2/98.3	98.2/96.4	1.1	1.7
3	99.5/98.3	99.8/99.3	1.3	1.5
4	99.6/98.8	99.3/96.9	1.3	2.2
5	99.1/98.0	98.8/96.4	1.2	1.7

Table 11. Hideout return data

Items		Na	K	Ca	Mg	Cl	SO ₄	SiO ₂	Organic acid	Crevice pH
16th Cycle (NH ₃)	S/G A	11.7	5.4	234.6	20.7	4.2	289.0	1,120.2	-	Neutral (MRC operation)
	S/G B	8.0	4.5	241.6	13.3	3.4	349.6	995.1	-	
17th Cycle (ETA)	S/G A	0.5	0.1	25.7	2.3	0.5	29.0	56.5	0.9	Neutral
	S/G B	0.6	0.2	20.7	1.9	0.5	27.9	47.7	0.9	

(unit: gram)

is restored. And the MR type resin may be effective for ETA-chemistry, as well.

5.3 Hideout return data

It is important to calculate SG hideout return data from the analysis of SG blowdown during plant shut down related to the impact of organic acids on SG crevices. The results of the ETA injection between before and after are shown in Table 11. Both total cation and anion are decreased. This may indicate that impurity ingress was reduced by the injection of ETA. And also there are less sludge pile that impurities can hide in because of new SG.

The amounts of organic acid released from each SG were less than 0.9 g. It is presumed that the ETA injection did not promote the accumulation of organic acids on SG crevices. With calculated crevice pH, which is almost close to the neutral range, the environment is considered to have been far from corrosive.

6. Conclusion

To reduce iron ingress into SG, ETA was injected as a secondary pH control agent at Kori Unit 1. As a result, the iron concentration decreased approximately 69.8% at the feed water and around 69.7% at the heater drains. It was confirmed that ETA is effective to prevent FAC for the two-phase areas in the secondary systems. ETA injection did not have any nega-

tive impacts on water chemistry in terms of impurity concentration. Also, the inspection during annual maintenance outage did not reveal any adverse effects on the condensate polisher and the secondary system component materials. Further studies will be carried out over times to assess the long-term effectiveness of ETA to reduce iron ingress into a SG.

References

1. Electric Power Research Institute, "PWR Secondary Water Chemistry Guidelines," EPRI TR-102134 rev.4, Nov.(1996).
2. Passel, T.O., "Advanced Steam Cycle Water Chemistry Overview," EPRI Workshop, Tampa, Florida, Sept. 25-27(1990).
3. Electric Power Research Institute, "Advanced Studies in Chemistry Control with Morpholine," EPRI TR-100758, July(1992).
4. Millett, P.J., and Passel, T.O., "Qualification Testing of Three Advanced Amines for Secondary-System pH Control in Once-Through Steam Generator Plants," EPRI TR-103098, Mar.(1994).
5. Park, K.K. et al., "Application of ETA Water Treatment for Secondary Chemistry at Kori Unit 1," KEPRI TR97CS13S1999.754, Dec. (1999).

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6. Heitmann, H.G., and Kastner, W., "Proceedings of the International Specialist's Meeting on Erosion-Corrosion of Steels in High Temperature Water and Wet Steam," Les Renardières, France(1982).
 7. Electric Power Research Institute, "Full-Scale Test of ETA at Catawba Nuclear plant Unit 1 and 2," EPRI TR-103042, Palo Alto, CA, Sept.(1994).