Evaluation on SGBD demineralizers and Optimized Cation/Anion Resin ratio in PWR NPPs

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Abstract

In PSR on the Kori 3&4 NPP, The low level radioactive waste resin from SGBD demineralizer is more than 65% of total waste resin in NPP. So, it needs to be improved. The secondary cooling water pH control methods are used ammonia-AVT from the first. According to changing ETA which is better than ammonia, SGBD cation load is increased about 2-3 times. Waste resin product is also increased in proportion to the SGBD cation load. To reduce the waste volume, new cation resin exchange criteria is confirmed that demineralizer is almost saturated.

Key word : Reducing LLW, SGBD Demineralizer, Cation/Anion Resin, Exchange Capacity, AVT, Amine

1. Introduction

The secondary cooling water pH control in Korean PWR NPP used ammonia-AVT from the beginning. According to changing ETA which is better than ammonia, SGBD cation load is increased about 2-3 times. Waste resin product is also increased in proportion to the SGBD cation load. Waste resin produced at blowdown demineralizer in NPP purifies the secondary water quality. If the water is not polluted, that is the disposed object itself. But the secondary radiated material by a neutron spreaded at an atomic reactor or resin of blowdown demineralizer by radiated material polluted by unconfirmed leakage at SG from the prime to the secondary is known to a little higher than natural level. After treated SG blowdown flow, exchanged resin is almost disposal object itself as a radiowaste production. But radioactive material is condensed and it is not ease to treat the ash, when waste resin is incinerated in accordance with the Environmental Act. Though blowdown demineralizer waste resin quantity treated by ammonia is 65% of total radioactive waste resin, about 15ton a year, when pH agent at the secondary system is changed into ETA-AVT, the radwaste volume which has to be managed is increased. In thesis, to solve that problem, the possibility of saturated operation is checked, after analyze the operating situation of blowdown demineralizer at SG of PWP NPP and evaluating experiment of saturated operation possibility of ETA, pH agent worked by demineralizer load and the model of removal impurities. It is tried to detect the fittest ratio and the resin exchange criteria.

2. Experimental result of resin capacity

The resin volume is decreased at a mock experiment for the evaluation of resin capacity. To shorten experimental time, the cation volume at SG blowdown demineralizer is 1/80000 of 2.5m^3

which is equal to 30ml of resin capacity and experiment is achieved for resin which is 30times of addicted chemical material at the secondary system. The result is that ion selectivity for resin is $CS^{+} > Na^{+} > ETA^{+} \geq NH_{4}^{+} > H^{+}$. The graphs maintain Figure 1,2.
Selectivity and breakthrough curve for 4 ions shows the appropriateness of ETA's operation level at the secondary system in NPP through experiment.

Table 1. ionic concentration at experimental high concentration

ion	molecular weight	ionic concentration		system concentration (ppm)	raio with system ion concentration
		(ppm)	(meq/l)		
ETA^{+}	61.08	122.16	2	3.5	35
NH_3^{+}	17	34	2	0.2	170
Na^{+}	23	46	2	0.001	46000
Cs^{+}	133	266	2	0	∞
total	101.08	202.16	8	3.701	

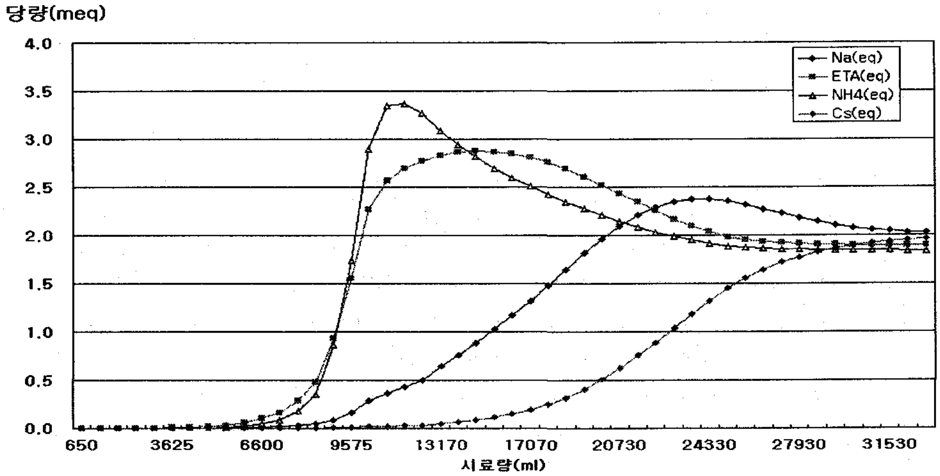

Figure 1. character of classified ion of H-type resin

3. ETA saturated operation system water quality and demineralization capacity

FSAR and EPR related to the SG water quality are the secondary water chemistry guiding principle. It should be achieved the system water quality by the change of blowdown demineralizer's exchange criteria and mixture ratio satisfies authorization and ALARA of water management.
The first, normal and expected excessive operation should follow the SG secondary water quality level. The second, when SG is leaked, DF capacity is ensured to remove radioactive material.

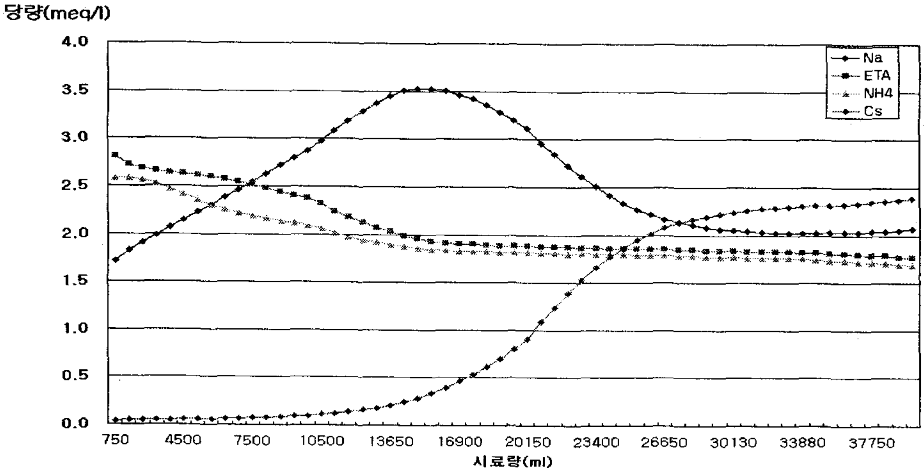

Figure 2. Cs exchange response of saturated resin of ETA, NH_4^+, Na

Table 2. SG Steam side and Feedwater AVT Chemistry Guidelines (FSAR)

Chemistry Parameters	Cold/Hydro/ Cold wet Layup	Hot Functional Shutdown/ Standby	Startup From Hot Standby		Normal Power Operation	
	Blowdown	Blowdown	Feedwater	Blowdown	Feedwater	Blowdown
pH at 25℃	> 9.8	>9.0	9.0-10.0	9.0-10.0	9.0-9.6	9.2-9.8
cation conductivity, μmhos/cm	NA	<2.0	NA	< 7	NA	< 2.0
Na, ppb	< 100	< 100	NA	< 100	< 100	< 20
Cl, ,ppb	< 100	< 100	NA	< 100	< 100	< 20
SO_4, ppb	< 100	< 100	NA	< 100	< 100	< 20
ETA, NH_3, ppm	As pH requires	NA	1-5	> 1.5	NA	> 1.5
Hydrazine, ppm	75~500	NA	> 8 $[O_2]$	NA	> 8 $[O_2]$	NA
Dissolved Oxygen , ppb	< 5	NA	< 5	NA	< 5	NA

The the secondary system water management is changed from ammonia-AVT to ETA-AVT in 2002. The water management result is showed at Table 4. pH is increased from 9.2 to 9.6, and ETA is maintained about 3,500ppb instead of ammonia concentration decreased to about 1/3. The other impurities concentration is similar to before and after water management change.

Table 3. the parameters of radioactive equilibrium concentration at the secondary system

Parameters	Design Basis
Condensate demineralizer DF	
Anions	10
Cs, Rb	2
Other nuclides	10
Blowdown demineralizer DF	
Anions	100(10)*
Cs, Rb	10(10)*
Other nuclides	100(10)*
Tritium balance parameters, 1b mass/h	
Main steam leaks	1,700
Condenser leakage	0
Condenser evacuation system and gland seal losses	0

Table 4. the secondary water quality level and water quality exchange before and after ETA treatment

Chemistry Parameters	normal operation level of water quality		B unit operation (NH_3 Cycle) average		B unit operation(ETA+NH_3 Cycle) average	
	FW	BD	FW	BD	FW	BD
pH at 25℃	9.0-9.6	9.2-9.8	9.4	9.2	9.4	9.6
cation conductivity, μmhos/cm	NA	< 2.0	0.1	0.1	0.09	0.1
Na, ppb	< 100	< 20	0.2	0.3	0.1	0.2
Cl, ,ppb	< 100	< 20	0.8	0.7	-	0.3
SO_4, ppb	< 100	< 20	-	0.3	-	0.2
NH_3, ppm	NA	NA	0.420	0.665	0.221	0.250
ETA, ppm	NA	> 1.5	-	-	1.800	3.485
Hydrazine, ppm	> 8 [O_2]	NA	60	36	67	38
Dissolved Oxygen, ppb	< 5	NA	0.4	0.0	0.4	0.0

To do blowdown demineralizer's ETA saturation operation, it is necessary to evaluate the principal parameters of water quality. The result should follow the chemistry Guidelines and the ALARA water quality should be achieved.

Na is concentrated at the SG inside crevice and the concentration is strong base(more than pH 10). Na minimum concentration is 2,300ppb by NaOH and pH of Table 5. The SG water quality level is less than 20ppb and Na concentration is 0.2ppb which is about 1/100 of the limited value at B unit SG blowdown operation. If Na is not condensed to 110,000 times(2300ppb÷0.2ppb) at SG crevice, Na will be less than pH 10. So, alkali corrosion isn't. Therefore, Na^+ exits with Cl^-, SO_4^{-2} and organic acid, Na^+ is neutralized. In case of saturated operation of ETA, the Na^+ concentration at SG blowdown demineralizer outlet is a little increased by resin polluted by Na^+. Leaked Na is mixed with condensator and is diluted. When the Na passed CPP demineralizer, Na is removed.

Table 5. relationship between NaOH concentration and pH

NaOH concentration (ppb as Na)	pH @ 25	note
0.1	7.01	demineralizer blowdown flow concentration level
1.0	7.09	SG blowdown flow concentraion level at operation
5	7.40	EPRI the secondary water quality guideline (R 5) the 2nd step level
20	7.94	correct action the first step level
50	8.33	EPRI the secondary water quality guideline (R 5) the 2nd step level
100	8.63	correct action the first step level
250	9.03	EPRI the secondary water quality guideline (R 5) the 2nd step level
500	9.33	correct action the first step level
2300	10.00	alkali range

4. The resin exchange criteria of SG blowdown demineralizer

The establishment of the capacity deterioration or exchange criteria of SG demineralizer is when SG water quality is not improved. Leaked Na showed the symptom of ion exchange resin's loss of removal. Na leakage of early using demineralizer is occurred by Na which is impurities in resin. Therefore, that is quite different form Na saturated by the demineralizer water quality.

A. the resin exchange criteria of cation resin

It is very difficult to remove Na impurities of the secondary system at cation resin. So, exchange criteria of Na comprises that of capacity deterioration of cation resin. When the Na concentration is increased at system, specially, Na increase of SG water quality is leak of seawater, chemicals impurities, leakage from resin polluted by high content Na and the leakage from tube crevice(Hideout & Return). So, Na increase caused resin DF to deteriorate. Therefore, the DF selection of SG blowdown demineralizer is various.
Because Na leakage of SG blowdown is polluted Na, demineralizer resin has removal capacity. When exchange criteria is decided wrong, new exchanged resin used ETA and chemical volume is increased. So, chemical impurities flows to SG.
When ETA is saturated, even the Na concentration is increased at outlet, leaked Na is removed at CPP. There is no the effect capacity deterioration of SG demineralizer resin and CCP established at feed water system is the second defense function. The resin exchange criteria is similar to ALARA of the water management, so, the result will be various from the existing state of things. Cation resin absorbs Na more than ETA.
When ETA is leaked, Na at outlet is not an Na influx to demineralizer but from polluted Na. A cation impurities pushes out ETA or polluted Na. The demineralizer exchange criteria is selected as follow rules.
- ETA of the secondary feed water system is not removed at demineralizer and circulated.
- The Na leakage at new resin does not need to control, therefore that is excluded at

demineralizer exchange criteria
- Even impurities by outside influx is suddenly increased, the impurities concentration should be decreased in proportion to circulating volume as time passes. Impurities concentration should be decreased.

The removal impurities at operation, prevention of SG influx at seawater leakage, and removal radioactive material at SGTR, impurities removal capacity by Hide-out Return are necessary at stop operation. 30% of generation power has an effect on Na leakage by impurities. So, DF 10 is not accurate. DF Na of SG blowdown demineralizer should be less than 10 at all operation except 30% of generating mode.

Table 6. SG blowdown flow water quality

operation	operation mode	Na criteria (ppb)	Cl criteria (ppb)
Reactor shutdown	reactor power operation→hot standby(mode 1-3)	≤ 100	≤ 100
	hot shutdown→reload(mode 3-6)	≤ 1000	≤ 500
startup operation	reload→cold standby(mode 6-5)	≤ 100	≤ 100
	hot shutdown(mode 4)	≤ 100	≤ 100
	hot standby(mode 3)	≤ 100	≤ 100
	startup operation(mode 2)	≤ 100	≤ 100
reactor power operation	reactor power (5 ~ 30%)	≤ 100	≤ 100
	reactor power (more than 30%)	≤ 20	≤ 20

The improvement of cation resin SG blowdown demineralizer exchange criteria is as follows.

○ Na concentration should be less than 100ppb at maximum or stop operation. If the limited concentration at the second step is less than Na 100ppb, the concentration at Na DF 10 should be 10ppb.

○ DF 10 of Na limited value(20ppb) is 2ppb and maximum concentration of Na is 3ppb at operation more than 30% generation. Therefore sum of them is less than 5ppb.

The water quality level is less than Na concentration(5ppb), therefore improvement of cation resin change criteria is that the Na concentration outlet is resonable to select less than 5ppb.

B. The anion resin Exchange criteria

Anion resin includes Cl. NO_3, SO_4^2 like cation resin. The anion resin exchange criteria is also reasonable to monitor management anion item of the secondary which is small selectivity at outlet.

Cl^- which is the smallest selectivity at the secondary management item is reasonable to be select.ed. demineralizer vessels concentration of Cl^- is reasonable to be more than 5ppb so that exchange criteria may be proportion to Na cation, because pH exchange of flow water is very small.

Though SO_4^{-2} detected at SG is removed, SO_4^{-2} selectivity is stronger than that of other

anions. Cation resin is detected at SG blowdown demineralizer after flux at SG. Anion resin will be polluted by sulfuric acid ion as cation resin polluted by Na. Therefore, demineralizer exchange criteria is not reasonable by sulfuric acid ion rather than Cl.
To prevent SG water quality deteriorated by resin influx at NPP, SO_4 concentration is controlled. Therefore demineralization criteria is selected mainly. The SO_4^{-2} concentration of blowdown demineralizer outlet is resonable to be 5ppb.
The water quality factor which monitors the concentration at anion is cation conductivity (C.C). Therefore C.C shows concentration exchange of Cl^-, F^-, $HSiO_3^-$, SO_4^{-2}, organic acid. C.C value is a good indicator to check water impurities formerly. But evaluate of anion resin capacity is reasonable to measure the demineralizer inlet and outlet concentration directly. If the resin exchange criteria of SG blowdown water is decided, the limited water quality of condensate system is resonable to be more than 0.3uS/cm.

5. SG blowdown demineralizer's cation/anion resin mixing ratio

The ion exchange resin of demineralizer is mixture of resin removing impurities. A using term is the inverse proportion of ion concentration of flow water. Ion exchange capacity is the saturating resin volume which is decided by ion concentration included at flow rate.
The mixed ratio is decided by the pH agent (ETA) and ammonia regarding as cation load. According to not regarding as cation load, new ratio cation and anion should be decided.
If it considers ETA load, total cation load will be 115 x 10^{-9} eq/ℓ, if not that will be 3.78 x 10^{-9} eq/ℓ. Anion load not related to ETA is 3.67 x 10^{-9} eq/ℓ. The concentration of organic acid is 7.80x 10^{-9} eq/ℓ.
The ratio of cation resin and anion resin is 30:1, if ETA load is considered. If not, that is 1:2. The mixed ratio of cation and anion resin is 1:2 by ionic strength ignorant ETA. The ionic strength and resin choice of ETA and ammonia is stringer than $H^+$of water. If the elution of ETA is considered, when the factor of elution is 2-6 times, cation resin will need more 1-3 times than anion resin. The mixed ratio of resin of SG blowdown demineralizer is 1~3:1.

Table 7. ion load for water quality of flow water

item / ion	maximum concentration (ppb)	molecular weight (g./mol)	ion load (x 10^{-9} eq/ℓ)	
			ETA considering	ETA not considering
cation				
ETA	5000	61.08	81.86	NA
NH_4^+	500	17.00	29.41	NA
N_2H_4	50	32.00	1.56	1.56
Na^+	20	23.00	0.87	0.87
Fe^{2+}	20	55.85	0.72	0.72
Cu^{2+}	20	63.55	0.63	0.63
		total	115.05	3.78
anion			maximum organic acid x 1	maximum organic acid x 5
Cl^-	20	35.50	0.56	0.56

SO_4^{-2}	20	96.06	0.42	0.42
SiO_2^-	100	60.08	1.66	1.66
Acetic acid	20	60.05	0.333	1.67
Glycolic acid	20	76.05	0.263	1.31
Formic acid	20	46.02	0.435	2.17
total			3.67	7.80

6. Conclusions

O SG blowdown demineralizer's resin phenomena

Exhausted symptom of cation resin is increasing Na ion which is impurities. Former exchange criteria, Na DF≤1 was inappropriateness and had a problem unnecessarily producing a large amount of waste resin. To reduce the waste volume, exchange criteria is Na concentration appeared at demineralizer outlet by Na existed at waste resin itself, but new cation resin exchange criteria is reasonable to select Na≥5ppb as a criteria enable to determine that demineralizer is almost saturated. In anion case, it is reasonable to select Cl which is less selectivity at the secondary water quality control in NPP. It is resonable to select Cl≥5ppb like Na case to be proportion ion content ratio. Cation conductivity and SO_4 ion enable to be selected, as anion resin exchange criteria, Therefore cation conductivity is sum conductivity of other anions, it is unreasonable to be exact good performance or not of anion resin. C.C had better be used to check exchange capacity of anion resin.

If SO_4 concentration is selected by second exchange criteria, SG water quality is SO_4 ≥ 5 ppb like Cl exchange criteria.

The new exchange criteria of blowdown demineralizer inlet and outlet in NPP is as follows.

- exchange criteria of mixed bed : Na, Cl ≥ 5 ppb
- reference exchange criteria : SO_4^{-2} ≥ 5 ppb, C.C ≥ 0.3㎲/㎝

O SG blowdown demineralizer resin ratio of cation and anion

The ratio of cation and anion resin is 10:1 considered ETA load, that is 1:3 excluded ETA load.