The Treatment of Boron-containing Radioactive Liquid through Ion Exchange Resin

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1. Introduction

The light water reactor type nuclear power plant(NPP) is treated by adding boric acid to the primary coolant to control the nuclear fission reaction rate of the reactor. This chemical control controls the relatively slow change in reactivity associated with the combustion of nuclear fuel with boron concentration, and the added boron concentration varies from a few hundred ppm to a few thousand ppm. Therefore, the development of technology to effectively separate a large amount of boron generated every year and the derivation of linkage plans with the Liquid Radwaste System(LRS) used in NPPs are essential procedures for treating boron-containing radioactive liquid waste. Therefore, in this study, we would like to develop a small module radioactive liquid waste treatment system including a module that reduces boron. Since this system consists of three modules, each module is divided into a physical removal process, a radionuclide removal process, and a boron removal process. In this presentation, a experiment of boron concentration control for the development of a boron removal process was described.



Fig. 1. Configuration diagram of small modular liquid radwaste system.

2. Methods and Results

2.1 Chemical Properties of Boron

Boron is a metalloid belonging to group 3A in the periodic table and exists mainly in the form of boric acid (H_3BO_3) and borate or borate(boro-silicate) in nature. Boric acid exists mainly in the form of Ortho Boric Acid $[B(OH)_3]$ that is not ionized in an aqueous solution and the ionized Mono-borate Ion $[B(OH)_3^-]$, and the presence ratio of the two chemical species

depends on pH. The main ionic species of boric acid identified in the aqueous solution are present as $B(OH)_4$, $B_3O_3(OH)_4$, and $B_3O_3(OH)_5^{2-}$ as shown in Equations (1) to (3) below. As shown in Figure 2, it is present as $B(OH)_3$ at pH 6 or below, $B(OH)_3$ and $B_3O_3(OH)_{34}$ at pH 7 to 8, $B(OH)_3^-$ at pH 8 to 9, $B_3O_3(OH)_3^-$, $B(OH)_4^-$ at pH 9 to 10, and $B(OH)_3(OH)_3(OH)_5^{2-}$ at pH 10 or higher [2]. Therefore, in order to remove boron by adsorbing the anion exchange resin, the pH of the aqueous solution should be maintained at 10 or higher.

$$B(OH)_{3} + OH^{-} = B(OH)_{4}^{-} \dots \dots (1)$$

$$3B(OH)_{3} + OH^{-} = B_{3}O_{3}(OH)_{4}^{-} + 3H_{2}O\dots (2)$$

$$3B(OH)_{3} + 2OH^{-} = B_{3}O_{3}(OH)_{5}^{2-} + 3H_{2}O\dots (3)$$



Fig. 2. Distribution chart of hydrolyzed species in aqueous boric acid solution

2.2 Manufacturing of simulated waste liquid

Boric acid (H₃BO₃, 99.5%) of Samchun Chemical Co., Ltd. was used to carry out the boron removal experiment, and the concentration of the simulated waste solution was set to 4,000 ppm, which is the maximum boron concentration during planned preventive maintenance.

2.3 Calculation of reactive resin volume

For the boron removal experiment, Amberlite® IRN-78 used as an anion exchange resin in NPPs was used. Figure 3 shows the physical and chemical properties of the Amberlite[®] IRN-78 ion exchange resin. As shown in Figure 6, the total exchange capacity of Amberlite[®] IRN-78 is 1.20 eq/L and the density is 690 g/L, so it can be converted to 1.5 mL/g. Calculated based on this, the amount of anion exchange resin required for boric acid removal of 4,000 ppm is 207.37 g per 4,000 ppm boric acid/L to adsorb all boron.

Physical form Matrix	Yellow spherical beads Styrene divinylbenzene copolymer	Amberlite™ IRN-78
Functional group	Trimethylammonium	
Ionic form as shipped	OH.	
Total exchange capacity [2]	≥ 1.20 eq/L (OH [*] form)	
Moisture holding capacity ⁽¹⁾ Shipping weight Particle size	54 to 60 % (OH' form) 690 g/L_	
Uniformity coefficient [1]	≤ 1.2	
Harmonic mean size [1]	0.580 to 0.680 mm	
< 0.300 mm ^[1]	0.2 % max	
Whole beads	≥ 95 %	
Breaking weight (average)	≥ 350 g/bead	
> 200 g/bead	≥ 95 %	
Ionic conversion [1]	≥ 95 % OH [*]	
	≤ 5 % CO ₃ =	
	≤ 0.1 % Cl [*]	
	$\leq 0.1 \% \text{ SO}_4^=$	

Fig. 3. Physical and chemical properties of Amberlite® IRN-78

2.4 Boron removal according to changes in resin input calculation of reactive resin volume

Since the anion exchange resin used in this study has strong basic properties, it was judged that boron could be completely adsorbed and removed at a pH that could be adjusted by adjusting the input amount of the resin for a certain amount of distilled water. Therefore, a boron adsorption experiment was performed in which pH was adjusted by adjusting the amount of the input resin. Table 1 shows the experimental results of the input resin amount, the adjusted pH, and the boron removal rate according to the pH, and Figure 4 shows the boron removal rate according to the pH. Through this experiment, it was confirmed that boron could be removed by adjusting the input amount of the resin to the primary cooling water containing boron. Table 1 below shows the results of the boron removal experiment by adjusting the amount of resin.

Table 1. Results of boron removal experiment by resin volume control

구분		S-01	S-02	S-03	S-04	S-05	S-06
4,000 ppm Boric acid		100 mL					
Resin input		10 g	13 g	21 g	23 g	40 g	80 g
pH		pH 6	pH 7	pH 8	pH 9	pH 10	pH 11
Boron ppm	Before resin input	3877.02	3877,02	3877,02	3877.02	3877,02	3877,02
	After resin input	1247,97	296,61	88,11	32,82	4,06	3,68
Boron removal rate (%)		67,811	92,350	97,727	99,153	99,895	99,905



Fig. 4. Boron removal rate according to resin volume Through the boron removal experiment using the resin reactor above, the rate of change of the pH value according to the resin input amount and the boron removal rate according to the pH were confirmed, and then the experiment was conducted using the column planned to be applied to the actual module. In a column having a capacity of about 500 mL, 57.5 g of anion exchange resin and 250 mL of boric acid were added, and samples passing through the columns after 0, 20, 40, 60 seconds were collected and measured. As shown in Figure 5, after adding boric acid to the column, more than 97% of the sample flowed immediately without waiting time was removed, and it was confirmed that more than 99% of the sample flowed after 20 seconds was removed.



Fig. 5. Boron removal rate after column passage

3. Conclusions

In this study, an experiment was conducted to remove the boron concentration of the boron-containing simulated waste solution to develop the small modular liquid radwaste system that will be applied in connection with LRS in an emergency situation or planned preventive maintenance at an actual NPPs. The optimum amount of resin required for high removal was calculated and verified through an experiment.

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