

A STUDY ON ADSORPTION AND DESORPTION BEHAVIORS OF ^{14}C FROM A MIXED BED RESIN

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Spent resin waste containing a high concentration of ^{14}C radionuclide cannot be disposed of directly. A fundamental study on selective ^{14}C stripping, especially from the IRN-150 mixed bed resin, was carried out. In single ion-exchange equilibrium isotherm experiments, the ion adsorption capacity of the fresh resin for non-radioactive HCO_3^- ion, as the chemical form of ^{14}C , was evaluated as 11mg-C/g-resin. Adsorption affinity of anions to the resin was derived in order of $\text{NO}_3^- > \text{HCO}_3^- \geq \text{H}_2\text{PO}_4^-$. Thus the competitive adsorption affinity of NO_3^- ion in binary systems appeared far higher than that of HCO_3^- or H_2PO_4^- , and the selective desorption of HCO_3^- from the resin was very effective. On one hand, the affinity of Co^{2+} and Cs^+ for the resin remained relatively higher than that of other cations in the same stripping solution. Desorption of Cs^+ was minimized when the summation of the metal ions in the spent resin and the other cations in solution was near saturation and the pH value was maintained above 4.5. Among the various solutions tested, from the view-point of the simple second waste process, $\text{NH}_4\text{H}_2\text{PO}_4$ solution was preferable for the stripping of ^{14}C from the spent resin.

KEYWORDS : Ion-exchange Equilibrium, Adsorption and Desorption, Spent resin, ^{14}C Radionuclide, Radioactive Waste Disposal, Stripping Solution

1. INTRODUCTION

In PHWR NPPs (Pressurized Heavy Water Reactor Nuclear Power Plants), due to the ^{17}O in heavy water, ^{14}C radionuclide is generated by the reaction of ^{17}O (n, α) ^{14}C . It is known that about 93% of ^{14}C is generated from the moderator system of a PHWR. Especially in PHWR-type Wolsong NPPs, an ion-exchange process adapting the IRN-150 mixed bed resin is used for the removal of ^{14}C radionuclide [1~4]. Generally, most of the low- and intermediate-level radioactive wastes (LILWs) generated from NPPs can be disposed of at the disposal facility without a problem. However, because the ^{14}C is a β -emission radionuclide with a 5,730-year half life, the waste acceptance criteria (WAC) for waste containing ^{14}C radionuclide are strict. Normally, the spent resin generated from the PHWR-type NPPs contains more ^{14}C radionuclide than allowed by the regulation. Thus, it cannot be disposed of without further treatment [5, 6].

Under the current status, at Wolsong NPPs, the spent resin waste has been stored with other media generated from different parts of the plant for a long period of time. At this point, expanding the storage by reducing the resin

consumption is important. However, development of technology for the separation of ^{14}C from the resin is ultimately required. If ^{14}C can be removed from the resin, the majority of the volume of the resin could be disposed as one of the LILWs. Of course, a high-performance stabilization technology or an option for the utilization of the residual ^{14}C concentrate should be developed independently. Fortunately, many researchers have recently investigated various technologies to separate ^{14}C from the spent resin [7~13].

This paper comprises the results of a fundamental study conducted to suggest disposal alternatives for the spent resin waste containing high concentrations of ^{14}C radionuclide. Diverse chemical species of ^{14}C , for instance $^{14}\text{CO}_2$, $\text{H}_2^{14}\text{CO}_3$, $\text{H}^{14}\text{CO}_3^-$, and $^{14}\text{CO}_3^{2-}$, exist depending on the actual pH condition of the solution [14]. Under the pH condition of the PHWR moderator coolant, the HCO_3^- ion form is the governing chemical species. All of the experiments were executed by making use of the HCO_3^- ion, and the adsorption affinity and the adsorption capacity of the resin were evaluated through ion-exchange (hereafter assumed as adsorption) equilibrium isotherm experiments. The thermal degradation

effect on the adsorption isotherm was evaluated by making use of the resins dried at temperatures of 70°C and 110°C respectively. Meanwhile, the mutual competitive adsorption characteristics were also evaluated between candidate desorption ions of NO₃ (NaNO₃) and H₂PO₄ (NH₄H₂PO₄) of HCO₃⁻ ion in the resin. Finally, HCO₃⁻ desorption characteristics were evaluated by making use of various stripping solutions.

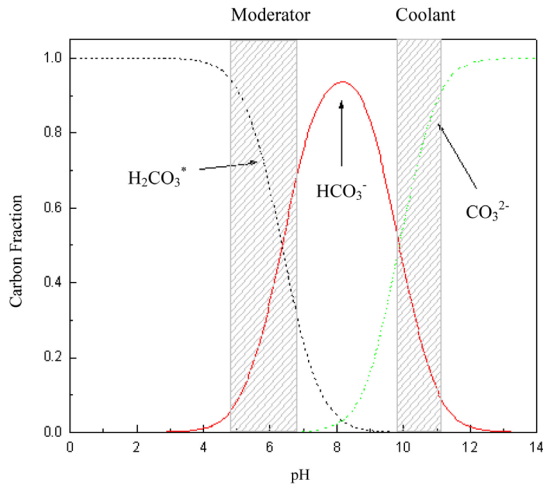


Fig. 1. Chemical Species of the Carbon in the Solution with The Change of pH [14] ($H_2CO_3^* = [CO_2] + [H_2CO_3]$)

2. EXPERIMENTAL SETUP

2.1 Materials for the experiments

All of the experiments in the study were conducted under non-radioactive conditions. The mixed bed resin named Amberlite IRN-150 (hereafter, referred to as simply ‘the resin’) was used for the experiments. The resin is a mixture of the cation-exchange resin (IRN-77) and the anion-exchange resin (IRN-78) with same equivalent ratio. The physical-chemical characteristics of the two resins are shown in Table 1 [17].

2.2 Experimental method

2.2.1 Experiments on the adsorption isotherm equilibrium of the IRN-150 resin

The ion-exchange capacity (assume as the adsorption capability) is defined as the total exchange capacity of the ion-exchange resin. Normally, the capacity is proportional to the amount or the concentration of the functional group [1, 16]. The capacity unit is expressed in milli equivalent per gram (meg/g). The weight in the unit is the dried weight of a resin sample having the functional group in the structure. Calcareous adsorption experiments were conducted to evaluate the adsorption isotherm of the ion-exchange resin. Fig. 1 shows the distribution of chemical species of the ¹⁴C radionuclide upon variation of the pH by carbonic acid in the solution by making use of a geo-

Table 1. Properties of Each Resin Mixed in the Amberlite IRN-150 Resin

	Cation Resin (Ambelite IRN-77)	Anion Resin(Ambelite IRN-78)
Ionic form	H ⁺	OH ⁻
Degree of Cross-linking	8% Divinylbenzene	6% Divinylbenzene
Functional Group	-SO ₃ H	-CH ₂ N(CH ₃) ₃ OH
True density(wet)	1.2 g/Cm ³	1.1 g/Cm ³
Bulk density	690 g/L (IRN-150)	
Void fraction		32.7 %
Bead(gel) particle size	0.3 - 1.18 mm <0.3 mm: max. 0.2% <1.18mm : max. 3.0%	0.3 - 1.18 mm
Effective size	0.5 mm	0.55 mm
Uniformity coefficient	1.8	1.35
Moisture content	55%	50%
pH range	0 - 14	0 - 14
Maximum operating temp.	120 °C	60 °C
Total exchange capacity	1.9 eq/L or higher (H ⁺)	1.2 eq/L or higher (OH ⁻)
Volume per unit gram	1.25 ml/g-dry	1.51 ml/g-dry

chemical code, PHREEQE [17]. As shown in the figure, the prevalent ion is ^{14}C in a solution with a pH lower than 5 is $\text{H}_2^{14}\text{CO}_3^*$ (mostly volatilized as $^{14}\text{CO}_2$ gas), and $\text{H}^{14}\text{CO}_3^-$ in a solution with a pH between 6 and 8. A small quantity of $\text{H}_2^{14}\text{CO}_3^*$ exists too. The prevalent chemical species in a solution with a pH higher than 10 is $^{14}\text{CO}_3^{2-}$. By the way, the pH value of the cooling water is about 8.3 in the moderator system. However, when the cooling water passes through a mixed ion-exchange tower, the pH value changes to somewhere between 6 and 7 due to the counter ions, such as H^+ and OH^- , discharged from the resin. Therefore, the exact chemical species of ^{14}C absorbed into anion-exchange resin is HCO_3^- ion form. In the study, the ion-exchange isotherm experiments of the resin were performed depending on variation of HCO_3^- ion concentration. The HCO_3^- ion was introduced by the injection of the NaHCO_3 standard reagent into the solution. The C concentration in the solution was measured with a Total Organic Carbon (TOC) analyzer. The concentrations of H_2PO_4^- ion and NO_3^- ion were measured with Ion Chromatography (IC) and Total Nitrogen (TN) analyses. The concentrations of metal cations were measured with ICP-mass analysis.

The evaluation results of adsorption characteristics of metal cations by the resin indicated relatively low concentrations of Cs^+ , Co^{2+} , Na^+ , and NH_4^+ in the disposed liquid wastes. Therefore, the isotherm experiment was executed for verifying ion-exchange capacity at low and high concentration levels actually probable in the waste solution, not for obtaining a perfect isotherm by making use of adsorption experiments of the cation state above by the resin. One gram of resin was added to each of the 100ml batch solutions with $10^{-4} \sim 10^{-2}$ M of initial cation concentrations. To achieve the full isotherm, the batches were agitated continuously and maintained under 30°C for one week.

2.2.2 Experiments on desorption characteristics of HCO_3^- ion in spent IRN-150 resin

The desorption characteristics of HCO_3^- ion were analyzed by making use of NaOH , $\text{Na}_3\text{PO}_4(\text{PO}_4^{3-})$, $\text{NaNO}_3(\text{NO}_3^-)$, and $\text{NH}_4\text{H}_2\text{PO}_4(\text{H}_2\text{PO}_4^-)$ solutions. 0.2 grams from the resin absorbed 12mg-C were taken for each experiment. The concentration of each solution ranged between 0.005 and 0.1N, and the effects upon the variation of solution volume were simultaneously evaluated. After the desorption experiment, the resin and the solution were separated, and the desorption rate of HCO_3^- was calculated by comparing the total quantity of C in the resin prior to desorption and the total quantity of C in the solution after desorption.

$$\text{Desorption rate} = \frac{\text{Total C components in the solution after desorption (C concentration} \times \text{solution volume)}}{\text{Total C components in the resin before desorption [absorbed quantity (mg-C/g-resin)]} \times \text{resin quantity(g)}} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Characteristics of HCO_3^- adsorption isotherm in IRN-150 resin

Fig. 2 shows the results of the experiments on the adsorption rate of HCO_3^- ion to the resin. To analyze the adsorption characteristics of the resin, the variation of the adsorption rate of HCO_3^- ion over time was measured. 0.005N of the initial NaHCO_3 solution (60ppm-C) was used to set the ratios of the solution volume over the resin quantity to 2L/30g and 2L/40g respectively. The concentrations of C in the solution over the adsorption time were measured under constant temperature. As shown in the figure, five hours were sufficient for achieving a full adsorption isotherm. Fig. 3 shows the results of the experiments on the isothermal adsorption characteristics of HCO_3^- to the fresh IRN-150 resin. In addition, the thermally-treated resins were tested to secure alternatives to ^{14}C desorption for the future. In the experiments, the rates between the consumed quantity of resin and the volume of solution were kept between 0.5 and 2g/L. The solution was agitated continuously under a constant temperature of 30°C . As shown in the figure, the adsorption quantity of the resin was approximately 11 mg-C/g-resin. This value is about 10% lower than the theoretical value (12mg-C/g-IRN150 resin) [15]. Due to the loss of moisture in the resin during thermal treatment, the weight of the tested resin increased, but the absolute amount of HCO_3^- adsorption did not increase in proportion to the weight of the resin. According to this result, if both the stripping and the thermal treatment are applied

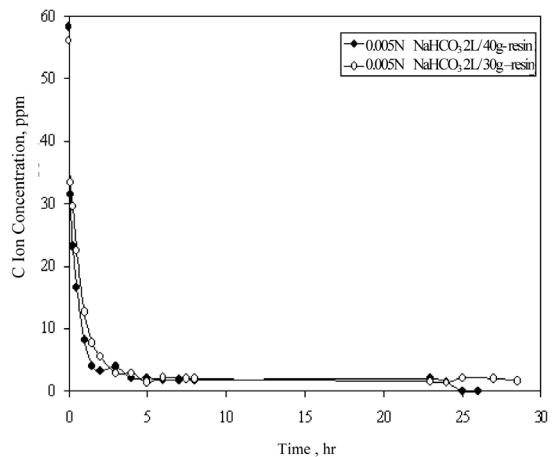


Fig. 2. Adsorption Behavior of HCO_3^- Ion in the IRN-150 Resin with Elapsed Time (Initial C Concentration : 60ppm C)

simultaneously, a more efficient desorption of HCO_3^- can be expected.

Fig. 4 shows the experimental results regarding the isothermal adsorption isotherm in a single system. The experiments were executed to analyze the competitive adsorption characteristics between the candidate desorption ions, such as NO_3^- and H_2PO_4^- , with HCO_3^- . As shown in the figure, the adsorption affinity order of each ion to the resin was identified as $\text{NO}_3^- > \text{HCO}_3^- > \text{H}_2\text{PO}_4^-$. The values nearly matched the reported adsorption affinity of each ion each ion [15, 18].

Figs. 5 and 6 show the competitive adsorption isotherms conducted at the binary systems. The candidate anions selected for the experiments are the mutual com-

petition ions in the stripping solution. Fig. 5 shows the experiment results of the $\text{NO}_3^- - \text{HCO}_3^-$ system, and Fig. 6 shows the $\text{NO}_3^- - \text{H}_2\text{PO}_4^-$ system. The adsorption affinity of a NO_3^- ion is higher than that of a HCO_3^- ion or H_2PO_4^- ion. The order of the adsorption affinity was evaluated to be nearly the same as the results of the single system.

Generally, both the cations and the anions in the waste solution are removed by ion-exchange with H^+ (or Na^+) and OH^- attached to each functional group in the resin structure, respectively. The probability of ion-exchange can be predicted depending on the following factors: (1) the valence of exchanged ions (electric charge), (2) the concentration of ions in the water or solution, and (3) the physical and chemical properties of the ion exchanging

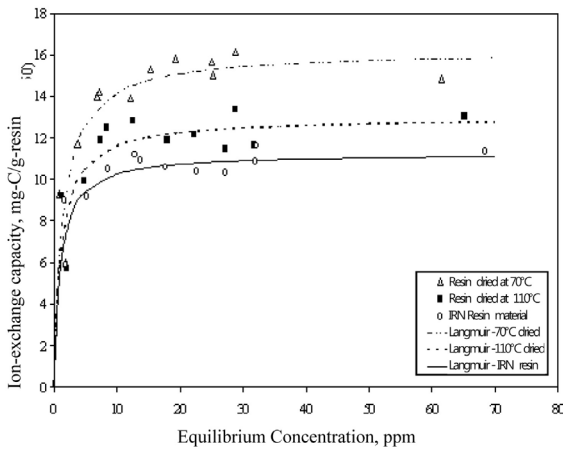


Fig. 3. Adsorption Isotherms of HCO_3^- Ion in the Fresh IRN-150 Resin and in the Thermally Treated Resins under Constant Temperature of 30°C

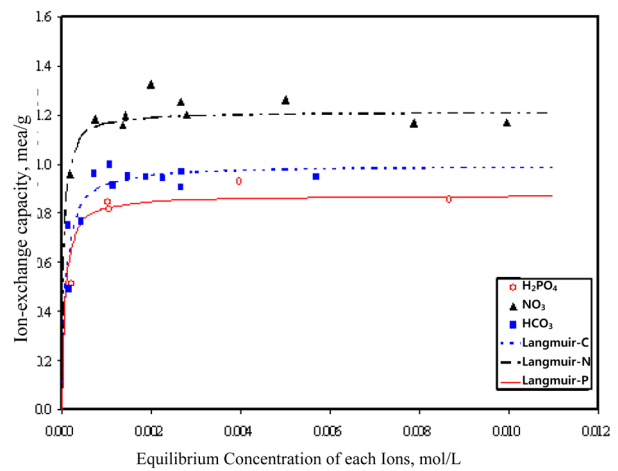


Fig. 4. Adsorption Isotherms of the Various Ions in the IRN-150 Resin under Constant Temperature of 30°C

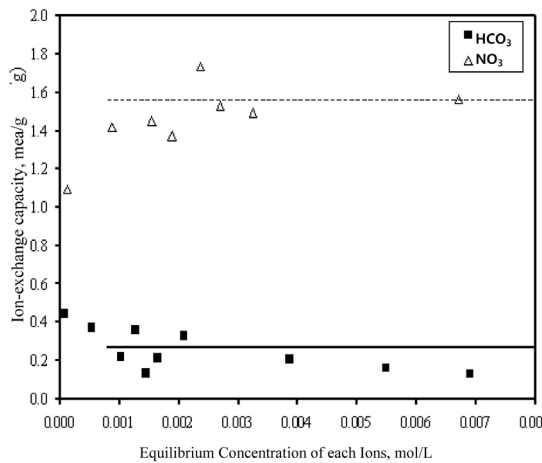


Fig. 5. Adsorption Isotherms of Each Ion in a Binary System of $\text{NO}_3^- - \text{H}_2\text{PO}_4^-$ in the IRN-150 Resin under Constant Temperature of 30°C

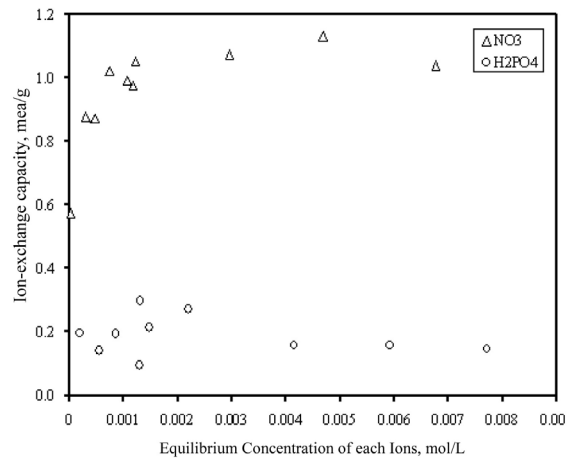
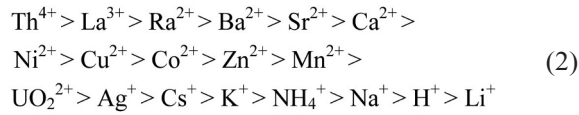
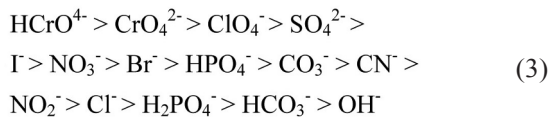


Fig. 6. Adsorption Isotherms of Each Ion in a Binary System of $\text{NO}_3^- - \text{H}_2\text{PO}_4^-$ in the IRN-150 Resin under Constant Temperature of 30°C

substance. The greater the electric charge of exchanged ion and the higher the atom number, the more the ion-exchange affinity grows. For example, the affinity of cations in ion-exchange resin appears as follows [16, 18]:



Therefore, the ion-exchange of radium (Ra) in the cation resin system is expected to be easy, but the ion-exchange of lithium (Li) is expected to be very difficult. Among the cations of interest, such as Cs^+ , Co^{2+} , NH_4^+ , and Na^+ , the ion-exchange capability of Co^{2+} is the strongest and that of Na^+ is the weakest. On other hand, the affinity of the ion-exchange of anions appears as follows [16, 18]:



This ion affinity to the resin is the selection basis of the solutions for desorption of ^{14}C radionuclide (typically as HCO_3^- ions) from the spent resins.

3.2 Adsorption characteristics of the metal cations in IRN-150 resin

Normally, a portion of the active ion-exchange sites remain empty in the spent resin. If the quantity of NH_4^+ ions in the solution is smaller than the number of empty sites, the desorption possibility of metal ions from the

resin may be lowered. On the contrary, if the quantity of NH_4^+ ions is larger than the number of empty sites, the desorption may proceed depending on the selectivity of ions to the resin. In this regard, to evaluate the selective desorption probability of ^{14}C radionuclide from the spent resin, the desorption characteristics for the ions of interest, such as Cs^+ , Co^{2+} , Na^+ , and NH_4^+ , were evaluated in the single system. Furthermore, the characteristics of the ion selectivity of the resin were evaluated in the binary-systems as well.

Figs. 7 and 8 show the adsorption isothermal curves and the change of pH measured during experiments on the adsorption isotherm, respectively. In the figures, the ion-exchange adsorption capacity was reduced in order of $\text{Co}^{2+} > \text{Cs}^+ > \text{Na}^+ > \text{NH}_4^+$. Even at a high concentration level, the adsorption of Na^+ and NH_4^+ failed to reach the saturation capacity of the resin. However, Cs^+ and Co^{2+} were adsorbed to capacity. This means that Co^{2+} and Cs^+ maintain an affinity for ion-exchange resin that is relatively higher than those of the two cations. However, is not reasonable to assume the low Cs^+ desorption from the resin based only on the results from HCO_3^- isotherm adsorption experiments in single-system. The ion-exchange process is significantly affected by pH, and the pH itself is changed by the counter ions discharged from the resin. In addition, both the characteristics of the anion-exchange and the cation-exchange varied depending on the concentration. Thus, the quantities of H^+ and OH^- discharged from the resin to the solution differed accordingly. Fig. 8 shows the change of pH depending on the progress of adsorption in the single system. As shown in the figure, no specific change appeared in the initial pH value of 6.85 at a low concentration range. However, the final pH changed to 3 ~ 4 at an initial concentration higher than 0.007 mol/L. In particular, the pH reduction appeared in the order of $\text{Co}^{2+} \approx \text{NH}_4^+ > \text{Na}^+ > \text{Cs}^+$. When

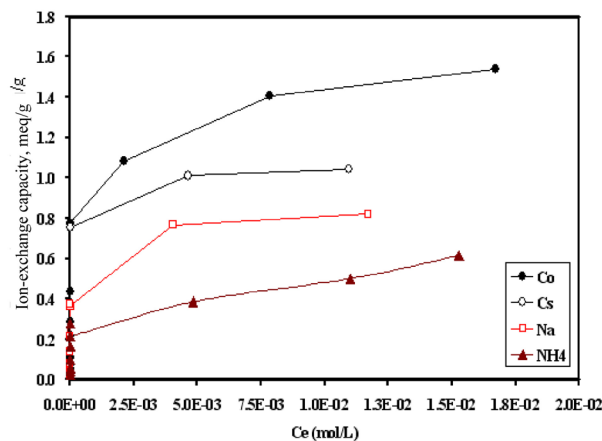


Fig. 7. Adsorption Isotherms of Cs^+ , Co^{2+} , Na^+ , NH_4^+ Ions in the IRN-150 Resin under Constant Temperature of 30°C

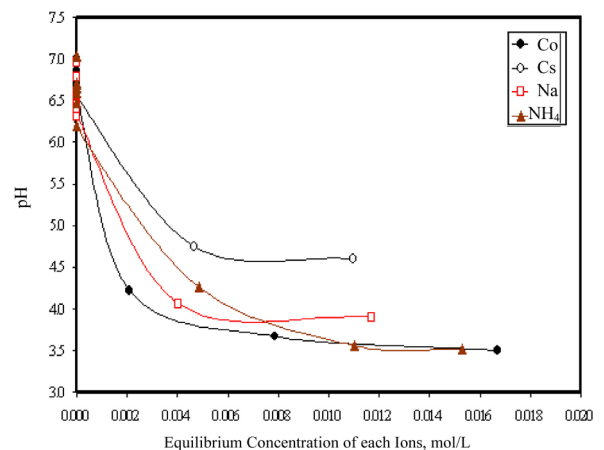


Fig. 8. Solution pH Variation with Equilibrium Concentration of Each Ion after Adsorption Equilibrium of Each Anion in the IRN-150 Resin

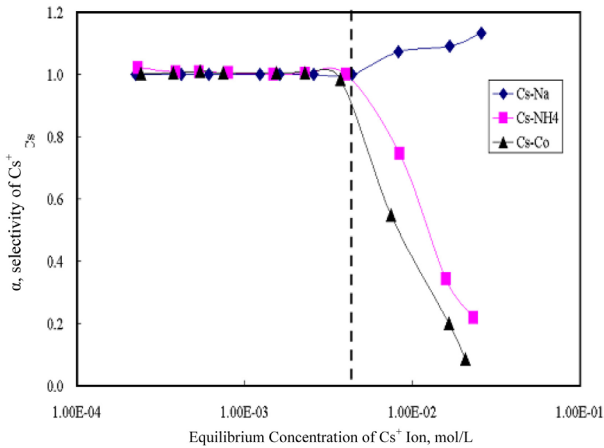


Fig. 9. Selectivity of Cs⁺ into the IRN-150 Resin in the Binary Systems of Cs⁺-Na⁺, Cs⁺-Co²⁺, Cs⁺-NH₄⁺

assuming that anion concentrations were kept at the same level in the initial solutions, the pH reduction means that the adsorption of the cation occurred to a greater extent than that of the anion. In particular, the adsorption of Co²⁺ at a high concentration range resulted in the highest pH reduction. This indicates that ion-exchange of Co²⁺ can be made effectively at a final pH level of 3. In the case of Cs⁺, the adsorption showed the lowest reduction of pH, and at around a pH level of 4.5, the capabilities of saturation and maintaining a stable state are shown as well. On the other hand, the final pH levels of Na⁺ and NH₄⁺ were 3 ~ 4, and the adsorption equilibrium had not reached saturation capacity. When considering that the adsorption capability increases slowly depending upon the growth of isotherm concentration, the result can be comprehended by considering that there is a relatively competitive relationship between H⁺ and other ions (Na⁺, NH₄⁺).

Figs. 9 and 10 show the experimental results of the binary systems. Firstly, Fig. 9 illustrates the selectivity of Cs⁺ dependent upon the change in the initial concentrations of each ion in the binary systems consisting of Cs⁺-Na⁺, Cs⁺-NH₄⁺, and Cs⁺-Co²⁺. The selectivity of Cs⁺ in each binary system was calculated with the following equation after calibrating the initial concentration rate of heterogeneous components:

$$\alpha = \frac{\text{(Amount of Cs in Ion-exchanger, mol)}}{\text{(Amount of M in Ion-exchanger, mol)}} \quad (4)$$

As shown in Fig. 9, when the initial concentration of the cation was lower than 0.004 mol/L, the selectivity of Cs⁺ was in the vicinity of 1. When the concentration is higher than that and NH₄⁺ and Co²⁺ are present, the se-

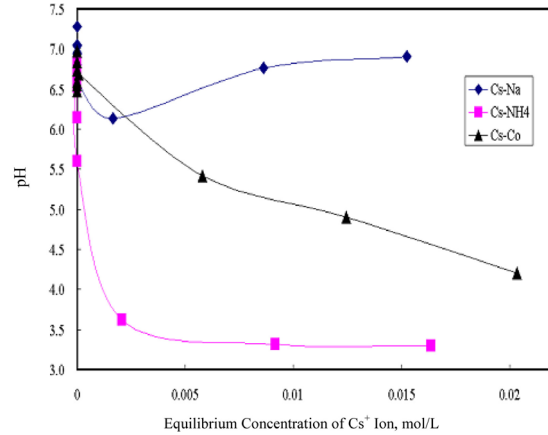


Fig. 10. pH Variation with Equilibrium Concentration of Cs⁺ in the IRN-150 Resin in the Binary Systems of Cs⁺-Na⁺, Cs⁺-Co²⁺, Cs⁺-NH₄⁺

lectivity of Cs⁺ over each ion rapidly decreases below 1. On the contrary, if Na⁺ is present, the selectivity of Cs⁺ increases slowly. The rapid decrease of Cs⁺ selectivity to lower than 1 at the initial concentration above 0.004 mol/L confirms the high probability of Cs⁺ desorption by other metal cations. As in the single-ion experiment, the adsorption of Co²⁺ and Cs⁺ nearly reached the saturation capacity of ion-exchange resin, even in the low concentration range. Therefore, at a low concentration range of cation in waste solution, excepting at an extremely low concentration, the number of empty active ion-exchange sites in spent resin is assumed to be relatively low. So, during the removal of HCO₃⁻ from anion-exchange resin, the probability of desorption of Cs⁺ by other cations in stripping solution always should be considered. In particular, isotherm pH should be considered together with the total amount of cation.

Fig. 10 shows the final pH in the binary system of Cs⁺-Co²⁺ decreasing down to 4. And, as shown in Fig. 9, because the affinity of Cs⁺ to the resin is relatively lower than Co²⁺ in the single system experiments, the selectivity of Cs⁺ appears low in the high concentration range. As for the Cs⁺-NH₄⁺ system, if considering the characteristics obtained from the single system adsorption, the selectivity of Cs⁺ should be relatively high. However, in the binary system of Cs⁺-NH₄⁺, the selectivity of Cs⁺ is lower than 1, and this is lower than that for NH₄⁺. In the single system, the isotherm pH of Cs⁺ in a high concentration range was about 4.7, and the final pH in the Cs⁺-NH₄⁺ system was about 3.5. It was relatively lower in the binary system. From these results, both for the efficient removal of HCO₃⁻ and for the minimization of Cs⁺ desorption from the resin, maintaining the pH of the stripping solution above 4.5 is desirable. Based on the experiment results of the single and binary systems, for

Table 2. Characteristics of ^{14}C Desorption from the Resin with the Concentration of the Stripping Solutions

Stripping solution	Concentration (N)	0.01	0.02	0.05	0.07	0.1
NaOH	Specimen weight (g)	0.122	0.12	0.12	0.122	0.121
	C concentration before desorption (ppm)	14.27	19.72	33.27	40.93	49.31
	C concentration after desorption (ppm)	18.22	24.41	38.09	45.03	54.85
Na_3PO_4	Specimen weight (g)	0.121	0.12	0.121	0.122	0.121
	C concentration before desorption (ppm)	14.27	16.85	22.6	26.56	29.90
	C concentration after desorption (ppm)	15.47	21.82	27.29	31.07	35.44
Calculated C concentration after desorption (ppm)		16*				

* Note: Concentration of C in Solution after Entire Separation of HCO_3^- from the Spent Resin

Table 3. Characteristics of ^{14}C from the Resin with Simultaneous Variations of the Concentration and the Volume of the Stripping solutions

Stripping solution	Concentration (N) - Solution volume (ml)	0.01-50	0.02-25	0.05-10
NaOH	Specimen weight (g)	0.2	0.2	0.2
	Initial C concentration (ppm)	4.22	8.93	11.49
	C concentration after desorption (ppm)	9.93	19.89	53.08
Na_3PO_4	Specimen weight (g)	0.21	0.2	0.21
	Initial C concentration (ppm)	8.31	10.96	14.47
	C concentration after desorption (ppm)	14.14	27.52	62.56
Calculated C concentration after desorption (ppm)		16	32	80

the minimization of the desorption of other metal cations, the summation of metal quantity in spent resin and the cations in the stripping solution should be adjusted close to the saturation adsorption capacity of the resin and the pH of the stripping solution should be kept higher than 4.5 simultaneously.

3.3 Characteristics of HCO_3^- desorption from IRN-150 resin

In this study, Na^+ , NH_4^+ , and NO_3^- , Cl^- , and H_2PO_4^- were considered as the candidate cations and anions, respectively. In this regard, the desorption characteristics of HCO_3^- ions from the resin were evaluated in the alkali solutions of NaNO_3 , Na_3PO_4 , NaOH, in the weak acid solution of $\text{NH}_4\text{H}_2\text{PO}_4$, and in the acid solutions of HNO_3 and HCl.

3.3.1 Desorption characteristics of HCO_3^- by NaOH and Na_3PO_4 solutions

A study on HCO_3^- desorption from IRN-150 resin us-

ing 0.005N Na_3PO_4 solution was conducted by KHNP-CRI [19]. In connection with this research, the desorption characteristics of HCO_3^- were evaluated under two conditions. One experiment was executed in accordance with the concentration changes of NaOH and Na_3PO_4 in each solution. Table 2 shows the changes of C concentrations in the stripping solutions measured before and after desorption. The concentrations of each initial solution were set between 0.001N and 0.1N. About 0.12g of resin with an adsorption ratio of 4mg-C/g-resin was used for the desorption experiments, and the volumes of the solutions were about 50ml each. The weight of adsorbed C in the resin specimen before desorption was about 0.48mg, and the concentration of C in solution after entirely stripping HCO_3^- from the resin was about 16ppm. The other experiment with the simultaneous variation of the concentration and the volume of the stripping solutions focused on secondary waste minimization, but the quantity of PO_4^{3-} in the solution was equivalent in each experiment. Table 3 illustrates the change of C concentration in the solution measured before and after the ex-

periment. The quantity of C in resin prior to desorption was 0.8mg-C, and C concentration in solutions after the complete stripping of HCO₃⁻ from the resin ranged from 16 to 80ppm.

In Tables 2 and 3, the initial C concentration in the stripping solutions was measured to be higher than zero, probably due to the CO₂ absorption from the air environment. The results of the experiments illustrate that CO₂ absorption raises the concentration of C in the stripping solution, and this has a significant adverse effect on the stripping of ¹⁴C from the spent resin and on the minimization of the waste volume. Therefore, the handling of NaOH and Na₃PO₄ stripping solutions should be performed in a glove box providing an inert gas environment. Accordingly, this condition is apparently unfavorable for the development of a ¹⁴C stripping process for the spent resin.

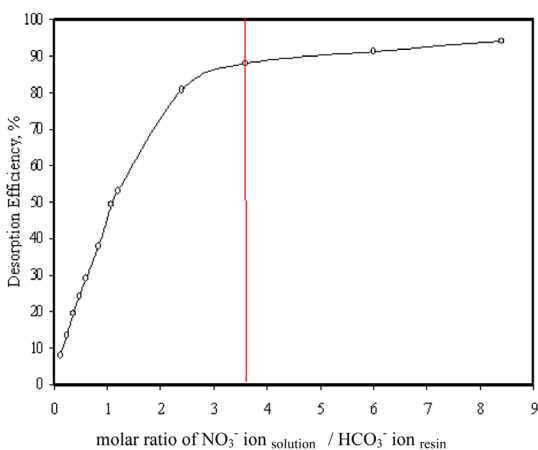


Fig. 11. Desorption Efficiency of HCO₃⁻ with the Mol Ratio of the NO₃⁻ in Solution over the HCO₃⁻ in IRN-150 Resin

3.3.2 Desorption characteristics of HCO₃⁻ ion by NaNO₃ solutions

It is known that NaNO₃ solution absorbs no CO₂ from the air, even at a high concentration, and this is a favorable characteristic for the ¹⁴C stripping process. In this regard, an experiment on the desorption characteristics of HCO₃⁻ from the resin was carried out depending on the variation of NaNO₃ concentration. Prior to the experiment, HCO₃⁻ was adsorbed to the resin at a ratio of 12mg-C/g-resin. As shown in Fig. 11, a 90% desorption rate was observed when the ratio between the mol number of NO₃⁻ in the solution to the mol number of HCO₃⁻ in the resin was 3.5. Consequently, it was recognized that the mol quantity of NO₃⁻ ion in the stripping solution should be at least three times the mol quantity of C in the resin to achieve greater than 90% of ¹⁴C desorption from the spent resin.

3.3.3 Desorption characteristics of HCO₃⁻ ion by NH₄H₂PO₄ solutions

Based on the aforementioned affinity of ions and the results observed in former experiments, an experiment on HCO₃⁻ desorption characteristics from the resin was finally executed by making use of NH₄H₂PO₄ solution. About 0.2 grams of the resin containing HCO₃⁻ at a rate of 4mg-C/g-resin and 50mL of NH₄H₂PO₄ solution were used for each stripping experiment. The concentration of C was measured after every desorption experiment conducted, depending upon the concentration change of the stripping solution. Table 4 shows the results of the experiments.

As shown in the table, all the C concentrations measured before and after the HCO₃⁻ desorption were zero. Because the NH₄H₂PO₄ solution cannot absorb CO₂, the value of 'zero' measured before desorption can be clearly

Table 4. Variation of C Concentration in Stripping Solution with a Concentration Change of NH₄H₂PO₄ Solution

Concentration (N)	0.001	0.002	0.005	0.007	0.01	0.02	0.05	0.07	0.1
pH prior to injection of specimen	5.71	5.56	5.39	5.33	5.25	5.19	5.01	4.98	4.84
pH after injection of specimen	4.13	3.45	3.4	3.21	3.16	2.99	3.25	3.33	3.35
Specimen weight (g)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Initial C concentration (ppm)	0	0	0	0	0	0	0	0	0
C concentration after desorption (ppm)	0	0	0	0	0	0	0	0	0

understood. However, the 'zero' measured in each HCO_3^- desorption can be misunderstood to mean that no desorption was made from the resin at all. But the latter 'zero' could be interpreted to mean, from the viewpoint of the aforementioned ion affinity order, that the desorption of HCO_3^- was made but later it was volatilized to CO_2 because of the acid side pH condition of the stripping solution. The $\text{NH}_4\text{H}_2\text{PO}_4$ solution may have a lower HCO_3^- desorption rate than the NaNO_3 solution. However, since the HCO_3^- ion is converted to CO_2 gas immediately after desorption, the secondary waste treatment process after the ^{14}C desorption could be simplified more than would be possible with NaNO_3 solution.

4. CONCLUSION

To suggest a viable disposal alternative for spent resin containing ^{14}C radionuclide higher than the WAC, we conducted a fundamental study. From the experiment results, the maximum adsorption capacity of HCO_3^- ion in the resin was evaluated to be about 11 mg-C/g. The anion adsorption affinity to the resin was derived in order of $\text{NO}_3^- > \text{HCO}_3^- \geq \text{H}_2\text{PO}_4^-$ through experiments on the adsorption isotherm of the single system. Thus, the competitive adsorption affinity of NO_3^- at the binary system appeared far higher than that of HCO_3^- or H_2PO_4^- ions, and the selective HCO_3^- desorption from the resin seemed very effective. From the observation of the adsorption isotherm experiments of metal cations, the ion-exchange capacity was reduced in order of $\text{Co}^{2+} > \text{Cs}^+ > \text{Na}^+ > \text{NH}_4^+$. This means that Co^{2+} and Cs^+ maintain a relatively higher affinity for ion-exchange resin than other cations in the stripping solution. Thus, to minimize the desorption of metal cations in the resin, the summation of the metal quantity in the spent resin and the cation introduced for stripping should be adjusted close to the saturation adsorption capacity of the spent resin. In addition, the pH value should be kept higher than 4.5 as well. On one hand, the HCO_3^- desorption characteristics are evaluated under various conditions of the stripping solutions. In the case of Na_3PO_4 solution, the desorption of HCO_3^- was effective at low concentration, but because of CO_2 absorption from the air, the actual application in the field looks somewhat difficult. In the case of NaNO_3 solution, more than 90% of HCO_3^- stripping from the resin was obtained when the ratio of the mol number of NO_3^- in the resin to the mol number of C in the resin was higher than three. In the case of $\text{NH}_4\text{H}_2\text{PO}_4$ solution, the concentrations of C were all measured as zero. We interpreted this to mean that HCO_3^- is removed from the resin and gasified immediately before measuring. So, if the $\text{NH}_4\text{H}_2\text{PO}_4$ solution is used for the ^{14}C stripping, the post-process for the waste treatment could be minimized.

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