Desorption Characteristics of $H^{14}CO_3$ ion from Spent Ion Exchanged Resin by Solution Stripping Technology

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ABSTRACT

Spent ion-exchanged resin generated from various purification systems in CANDU reactor is causing concern due to a limited storage capacity and safe disposal. As a suggestion for a proper treatment technology for the spent ion-exchanged resin containing a high activity of C-14 radionuclide which would be classified as Class A and C wastes, a fundamental study for the development of C-14 removal technology from a spent resin was performed. The adsorption characteristics of the inactive HCO_3^- ion and other ions in a stripping solution on IRN-150 mixed resin was evaluated and the removal technology of the HCO_3^- ion adsorbed on IRN-150 by an alkaline stripping method was proposed.

1. INTRODUCTION

Four CANDU commercial Nuclear Power Plants are in operation at the Wolsong site in Korea. The operation of power reactors produces a large quantity of spent resin waste streams. These resins originate from the clean-up systems and decontamination facilities. The spent resins generated from the moderator and primary heat transfer purification systems comprise of the largest fraction of the radioactive resin waste. They are classified as low and intermediate level waste, largely because of their C-14 content; the moderator resins, in particular, contain elevated levels of C-14 [1]. In general, the spent resins are slurried out of the service columns and then stored in in-station resin storage tanks [2].

The amount of C-14 generated from CANDU nuclear power plants is much higher than those from the reactors of other types [3]. The production of C-14 occurs in the Moderator (MOD), Primary Heat Transport System (PHTS), Annulus Gas System (AGS), and Fuels. Approximately 94 % of the total C-14 production is from the moderator system, about 95 % of that is removed and retained by the liquid purification ion exchange resin in the CANDU Nuclear Power Plant [4]. At present, the untreated ion exchange resin wastes from CANDU power plants are stored at a spent resin storage site in a nuclear power plant facility.

The Nuclear Regulatory Commission (NRC) has required in 10CFR61 that C-14 be measured in nuclear power plant radioactive wastes, and has specified C-14 concentration limits for class A and C wastes. As preliminary steps for a legal disposal of spent resins, C-14 concentration in the spent resins should be evaluated precisely and then a separation of them into anionic and cationic components is necessary for making their preliminary partial decontamination more feasible and less of a hazard.

Especially, spent ion-exchange resins contaminated with the C-14 radioisotope which has a long half-life of 5,730 years influences the strategy for the disposal of the spent resin. It is recommended that the disposal concentration limit of the spent resin loaded with C-14 is 8 Ci/m^3 according to US 10 CFR 61.8. Therefore, the removal of ^{14}C from spent resin and its concentration to solid sorbents become a desirable feature which can be disposed of as conventional low level waste. Acid stripping and thermal stripping methods are under development for the removal of C-14 from spent resins [5, 6].

This paper describes the results of a fundamental study to analyze the characteristics of a C-14 removal from IRN-150 spent ion exchange resin using alkaline solutions. At first, the adsorption characteristics of the inactive HCO_3^- ion and other ions in a stripping solution on IRN-150 mixed resin were evaluated. Based on these results, detailed experiments for a removal of the HCO_3^- ion adsorbed on to IRN-150 by an alkaline stripping solution such as Na_3PO_4 and $NaNO_3$ was carried out. This experiment includes the removal characteristics of the HCO_3^- ion from a mixed resin and the gasification of the HCO_3^- ion to CO_2 using an acidic solution.

2. EXPAERIMENTAL

All experiments were performed using inactive reagents in stead of the C-14 radioisotope, and IRN-150 resin was selected as a starting material for the removal of C-14, which is widely used to purify a coolant circuit at the Wolsung reactor with a mixture form of a stoichiometric equivalent to the strongly acidic cation and the strongly basic anion exchange resins. Table 1 shows the physical and chemical characteristics of the IRN-150 mixed resin.

TABLE 1. Physical and Chemical Characteristics of IRN-150 Mixed Resin Used in This Study

	IRN-77(Cation IX resin)	IRN- 78(Anion IX resin)
Ionic form	H^+	OH-
Degree of Cross-linking	6% DVB*	
True density(wet)	1.1 g/㎤	
Void fraction	32.7 %	
Particle size	0.4 ~ 1.2 mm	0.4 ~ 1.2 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 ℃	60 ℃
Total exchange capacity	1.75 meq/ml	1.1 meq/ml

Adsorption data of the HCO_3^- ion on the IRN-150 is needed to identify the desorption characteristics of this ion adsorbed on the same resin. Also, the competitive adsorption characteristic of other ions in a stripping solution as for a removal of the HCO_3^- ion from the IRN-150 is necessary. Standard $NaHCO_3$ reagent was used for the C-14 surrogate. Ion types for the adsorption isotherm experiments were selected. Typical anions were HCO_3^-, NO_3^-, $H_2PO_4^-$ and cations for Cs, Co, Na^+ and NH_4^+. The ratio of the resin mass to the solution volume (m/V) ranged from 2 to 20 g/L. Shaking method in a water bath at 30°C was used for an adsorption equilibrium. C content on the IRN-150 was obtained from HCO_3^- concentration before and after the adsorption experiment. Based on the adsorption experiments, IRN-150 adsorbed HCO_3^- ion was used for the removal experiment of this ion by using an alkaline stripping solution such as Na_3PO_4 and $NaNO_3$, HNO_3 solution was used for a reference as an acidic stripping. Concentration range of this stripping solution was in the range of 0.005 ~ 0.1N. Analytical instruments for a determination of the ions concentration involve TOC, TN, and IC, ICP-Mass, gas chromatography.

3. RESULTS AND DISCUSSION

3.1. ADSORPTION CHARACTERISTICS OF THE HCO_3^- AND OTHER IONS ON IRN-150

Adsorption isotherm of the HCO_3^- ion on thermally treated IRN-150 resin is shown in Fig. 1. Maximum adsorption amount of the HCO_3^- ion onto a raw resin was about 11 mg-C/g-resin. This value agrees with the theoretical adsorption amount calculated by the physical property data shown in Table 1. Thermally treated resins which were dried at 70°C and 110°C have a maximum adsorption amount of 13 ~ 16 mg-C/g-resin, respectively. On considering the resin weight after a removal of the moisture in a raw resin, this adsorption amount was slightly lower than the theoretical value due to the effect of a thermal degradation.

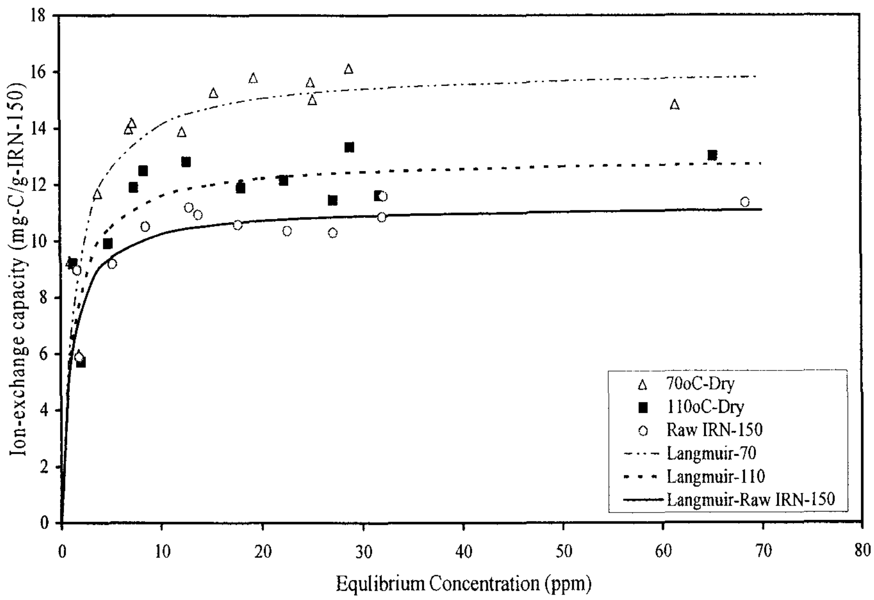

FIGURE 1. Adsorption Isotherms of the HCO_3 ion on Raw and Thermally-treated IRN-150 at 30°C.

Fig. 2 represents the competitive adsorption characteristics of the two ions used for the stripping solution for the removal of the HCO_3 ion from IRN-150. This result comprises of a high selectivity of the stripping solution when compared to the HCO_3 ion on IRN-150. Based on the adsorption amount of various ions, it was confirmed that the candidate stripping solutions for the removal of the C-14 from spent the resin were $NaNO_3$, Na_3PO_4 and $NH_4H_2PO_4$.

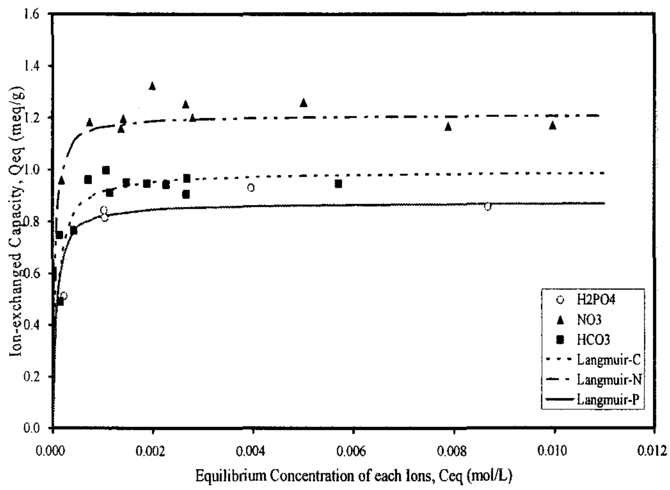

FIGURE 2. Adsorption Isotherms of Various Ions Used for Stripping Solution on IRN-150 at 30°C.

As mentioned before, the IRN-150 resin is a mixture form of a stoichiometric equivalent of the strongly acidic cation and the strongly basic anion exchange resins. Therefore, the adsorption characteristic of the cation on the IRN-150 was evaluated as shown in Fig. 3. These cations include Cs, Co as radionuclide in a coolant and Na^+ and NH_4^+. The degree of the adsorption capacity or selectivity onto the resin was shown as Co>Cs>Na>NH_4. Cobalt has the favorable adsorption selectivity on IRN-150 when compared to the Cs ion.

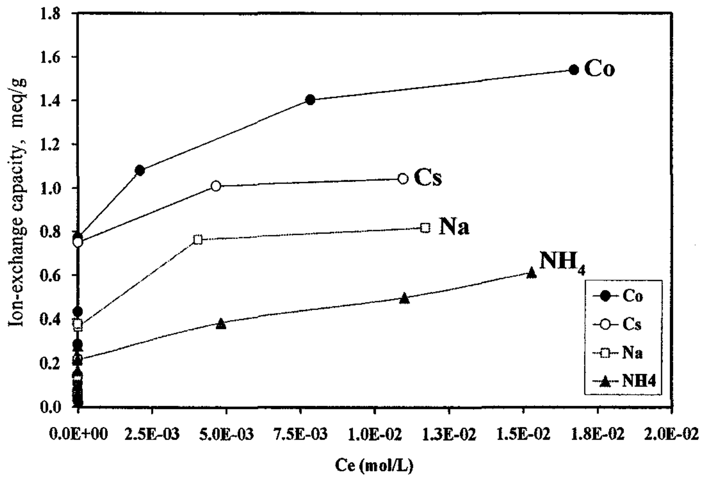

FIGURE 3. Adsorption Isotherms of Various Cations on IRN-150 at 30°C.

3.2. REMOVAL CHARACTERSITICS OF THE HCO_3^- ADSORBED ON IRN-150 BY AN ALKALINE STRIPPING METHOD

One of the technologies for a management of spent resin is an acidic stripping using HNO_3 solution. Total weight of 4 g with an initial C content of 12 mg-C/g-resin was used for this experiment. During a resin-to-acid solution contact by applying a purging with N_2 gas, CO_2 gas was simultaneously generated and sharply increased at an early stripping stage. Non detectable C concentration in the residual solution after a stripping was confirmed. However, the acidic stripping technology has a disadvantage in that it could possibly desorb the Cs and Co anion radionuclide from IRN-77 in a mixed spent resin. Therefore, the total activity of the stripping solution would increase and thus it is necessary to establish a subsidiary treatment of the secondary waste.

The purpose of the alkaline stripping experiments is for an evaluation of the removal characteristics of the HCO_3^- ion from IRN-150. Especially, the effect of the solution concentration on the removal efficiency is necessary for a reduction of the secondary liquid waste. Na_3PO_4 solution has a high removal capacity of the HCO_3^- ion from IRN-150. But due to a high absorption of the surrounding CO_2 gas at a high concentration above 0.01N, an inert atmosphere by using nitrogen gas is needed in an actual operation and it causes a decrease of the $H^{12}CO_3$ concentration in the stripping solution. One of the key parameters for establishing an optimal condition for the alkaline stripping technology is to determine the ratio of the stripping concentration to the C-14 amount for the spent resin to be treated ($N_{addition}/C_{sorbent}$) . Fig. 4 represents that when the $NaNO_3$ solution is used, this ratio should be maintained at over 3 for a high removal capacity of over 90%. This means that the optimal concentration of the alkaline solution should three times higher when compared to the initial total concentration of the C-14 on the resin as the basis of the molar concentration.

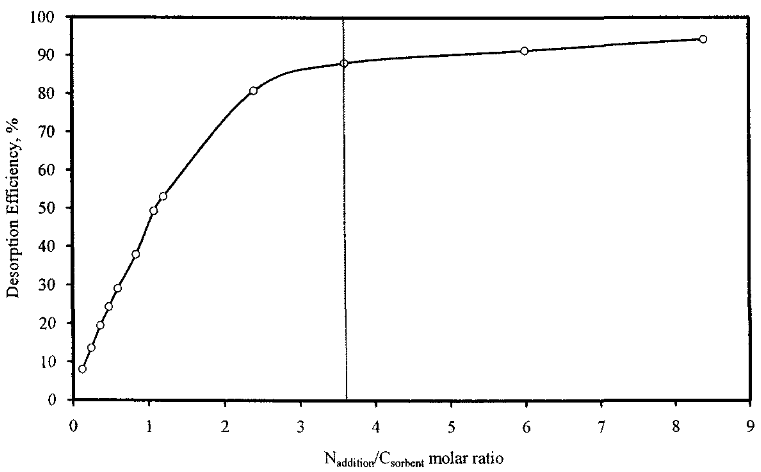

FIGURE 4. Removal Efficiency of the HCO_3 ion from IRN-150 with a Variation of the $NaNO_3$ Concentration.

After the removal of the $H^{14}CO_3^-$ ion into the stripping solution, the C-14 ion in this solution should be treated by a proper technology which produces a minimum secondary waste. One of the possible technologies is a gasification of HCO_3 in a stripping solution to CO_2 gas after a separation of only the stripping solution from the spent resin. Fig. 5 shows the gasification characteristics of the HCO_3 in two kinds of stripping solutions to CO_2 gas by an addition of the HNO_3 solution under a nitrogen gas purging condition. As with the acidic stripping method, the CO_2 gas sharply increased at an early stripping stage. Very low concentration of the HCO_3 in the residual solution after the gasification was confirmed.

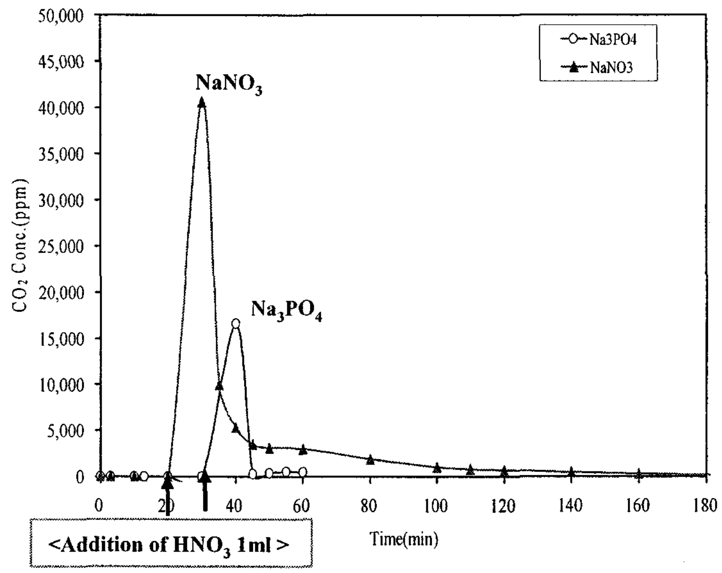

FIGURE 5. Variation of the CO_2 Gas Concentration with the Purging Time During the Stripping with the $NaNO_3$ and Na_3PO_4 Solution.

4. CONCLUSIONS

Maximum adsorption amount of the HCO_3^- ion on raw resin was about 11 mg-C/g-resin. This value agrees with the theoretical adsorption amount calculated by the physical property data. It was confirmed that alkaline solutions such as Na_3PO_4 and $NaNO_3$ would be applicable for an effective removal of C-14 from a spent resin. The minimum concentration of the alkaline solution for an effective removal of C-14 of over 99% should be three times higher as a basis of an equivalent when compared to the initial loading amount of C-14 on the spent resin. It was identified that the Na_3PO_4 and $NaNO_3$ alkaline solutions showed an over 99% removal efficiency of C-14 from the spent resin under the optimal conditions. However, on using the Na_3PO_4 solution, an inert atmosphere should be provided for preventing the CO_2 absorption from the surrounding air gas.

ACKNOWLEDGEMENTS

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