^{14}C Removal Technology for the Treatment of Spent Resin from Nuclear Power Plants : A Review

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1. Introduction

There are four CANDU commercial Nuclear Power Plants in Wolsong site in Korea. The operation of the power reactors produces a large quantity of spent resin waste streams. These resins originate from clean-up systems and decontamination facilities. The spent resins generated from the moderator and primary heat transfer purification systems comprise 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 moved out of the service columns as a slurry type and then stored in in-station resin storage tanks [2]. Especially, spent ion-exchange resins contaminated with C-14 radioisotope which has long half-life of 5,730 years influences the strategy for the disposal of spent. It is recommended that disposal concentration limit of spent rein 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 [3, 4]. This paper describes the results from a program undertaken to analyze C-14 in the spent resins produced from the nuclear operations of Wolsong Nuclear Power Plant. Total 72 resin samples were sampled from the in-station storage tank at Wolsong Nuclear Power Plant Unit 1. Resin samples were collected from both man-hole (68 samples) and test-hole (4 samples). They were separated into liquid, activated carbon, zeolite, and spent resins which were oxidized and analyzed for C-14. The average concentration of C-14 in the mixed exchange resin (cation and anion exchange resin) was determined. A comparison of the C-14 concentrations in mixed and anion exchange resin was obtained. Fundamental study was focused to analyze the characteristics of C-14 removal from IRN-150 spent ion exchange resin using alkaline solutions. In first, adsorption characteristics of inactive HCO_3^- ion and other ions in stripping solution on IRN-150 mixed resin was evaluated. Based on these results, detailed experiments for removal of HCO_3^- ion adsorbed on IRN-150 by alkaline stripping solution such as Na_3PO_4 and $NaNO_3$ was carried out. This experiment includes removal characteristics of HCO_3^- ion from mixed resin and gasification of HCO_3^- ion to CO_2 using acid solution.

2. Methods and Results

In this section some of the techniques used to resin sampling, ^{14}C analysis, and ^{14}C removal from spent resin are described.

2.1 Resin Sampling Technique

Commercially available grain samplers were referred for resin sampling. The sampler (see Fig.1) was consisted of main control part, finger, and four extension stainless steel tubes: they were connected and disconnected with bolts. The largest of the sampler connected of all is approximately 6 m long. The finger which was opened or closed by take-up of the inner wire has a conical tip to facilitate penetration. For sampling spent resins from the in-station storage tank 2 at Wolsong Nuclear Power Plant Unit 1, an overall length of approximately 5.5 m was required. The 15 cm finger was, therefore, equipped with four extensions each approximately 1.5 m long. Concrete caps of manhole and test-hole were first removed from the in-station storage tank structure to sample the spent resin. The finger was assembled with the extension pieces, and then, the sampler being lowered through the manhole or test-hole into the in-station storage tank. The maximum dose rate, in contact with the resin sampler, was about 8mR/h and the tritium level in the room was about 2.9 DAC during sampling. Lead blankets were used to minimize dose uptake during sampling.

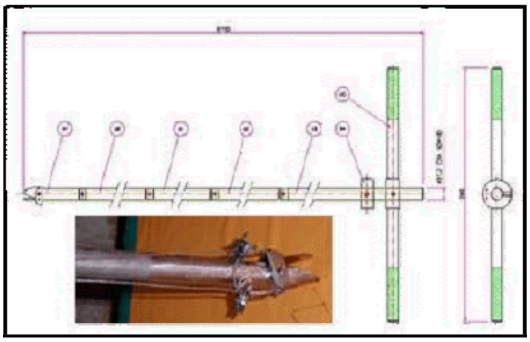

Fig. 1. Spent Resin Sampler for in-station storage tank within Wolsong NPP.

2.2 Carbon-14 analysis

The distribution of C-14 concentration with elevation in the Wolsong NPP's spent resins sampled from manhole is shown in Fig. 2.

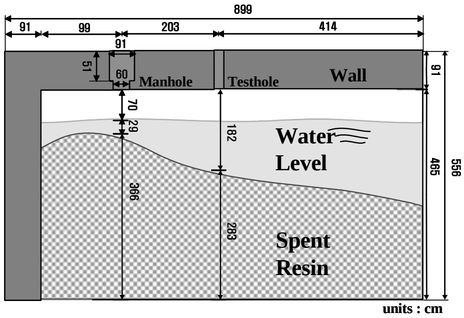

Fig. 2. Schematic of Wolsong NPP Units 1 and spent resin storage tank 2.

The distribution of C-14 concentration with elevation in the Wolsong NPP's spent resins sampled from manhole is shown in Fig. 3. The concentration of C-14 at the bottom of tank was about 170GBq/m^3 for the cation/anion mixed resin. The C-14 concentration at the elevated level from 20 to 40cm was 380GBq/m^3, which was the highest. The concentration of C-14 was generally decreased with elevation.

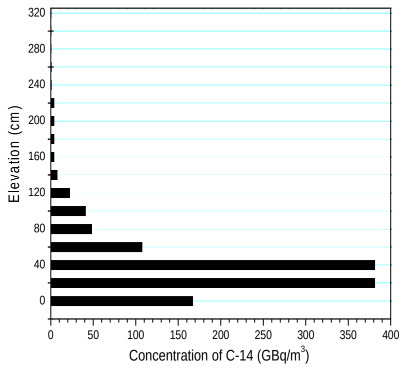

Fig. 3. Concentration of C-14 in the Wolsong NPP's spent resins sampled from manhole.

A comparison of the C-14 concentrations of the cation/anion mixed resins sampled from manhole and test-hole is given in Fig. 4. The average concentration of C-14 was 460GBq/m^3 from test-hole and 53.1GBq/m^3 from man-hole. The differences in the results obtained by two sampling suggest some inhomogeneity exists in the resin storage tank. It is possible that resins from test-hole were originated in the higher proportion of C-14 in the system.

The concentrations of C-14 for the cation/anion mixed and anion resins are given in Fig. 5. The average concentration of C-14 was 546GBq/m^3 for cation/anion mixed resin and 1,431GBq/m^3 for anion resin. The concentration of C-14 for the anion resins was higher than those found for the cation/anion mixed resins; the C-14 concentration in anion resin was approximately 2 times higher than in the cation/anion mixed resin.

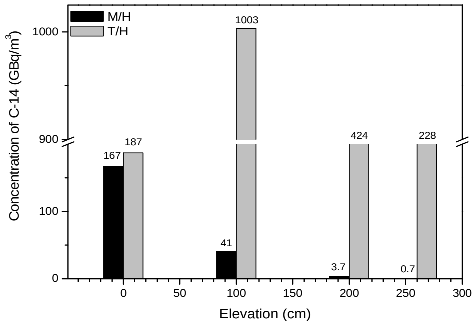

Fig. 4. Concentration of C-14 in the Wolsong NPP's spent resins sampled from man-hole and test-hole.

This explains that most of the C-14 is in the anion resin because cation-to-anion ratio of Wolsong NPP's spent resin is almost 1: 1.

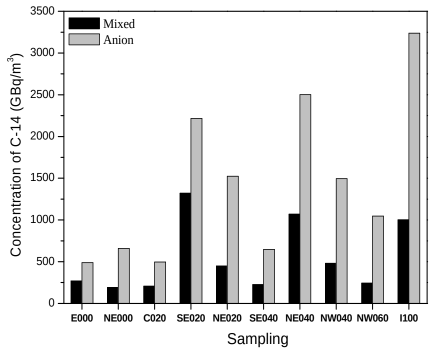

Fig. 5. Concentration of C-14 in the Wolsong NPP's spent resin; mixed resin and anion bead fraction.

2.3 Removal characteristics of C-14

One of technologies for management of spent resin is acid stripping using HNO_3 solution. IRN-150 resin is a mixture form of a stoichiometric equivalent of the strongly acidic cation and the strongly basic anion exchange resins. Therefore, adsorption characteristic of cation on IRN-150 was evaluated as shown in Fig. 6. These cations include Cs, Co as radionuclide in coolant and Na^+, NH_4^+. The degree of adsorption capacity or selectivity on resin showed Co>Cs>Na>NH_4. Cobalt has a favorable adsorption selectivity on IRN-150 compared to Cs ion.

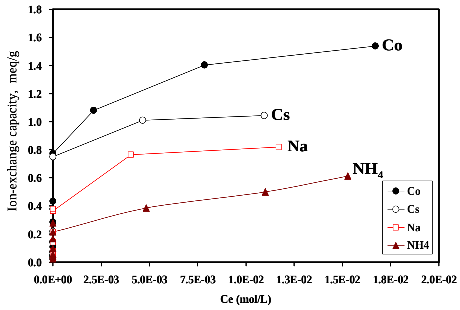

Fig. 6. Adsorption isotherms of various cations on IRN-150 at 30°C.

After removal of $H^{14}CO_3^-$ ion into stripping solution, C-14 ion in this solution should be treated by proper technology which produces minimum secondary waste. One of possible technology is gasification of HCO_3^- in stripping solution to CO_2 gas after separation of only stripping solution from spent resin. Fig. 7 shows gasification characteristic of HCO_3^- in two kinds of stripping solutions to CO_2 gas by addition of HNO_3 solution under nitrogen gas purging condition. As similar to acidic stripping method, CO_2 gas sharply increased at early stripping stage. Very low concentration of HCO_3^- in residual solution after gasification was confirmed.

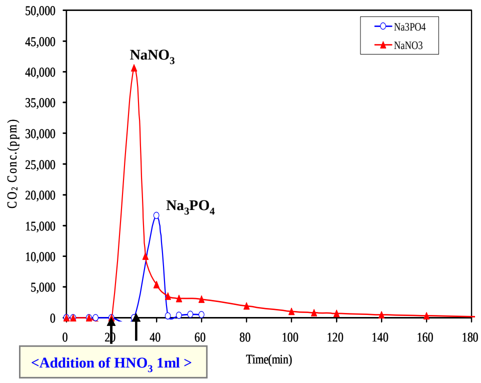

Fig. 7. Variation of CO_2 gas concentration from $NaNO_3$, Na_3PO_4 stripping solution with purging time.

Fig. 8 shows Removal rate of ^{14}C radionuclide from real spent resin stored in Wolsong NPP by using $NH_4H_2PO_4$ and H_3PO_4.

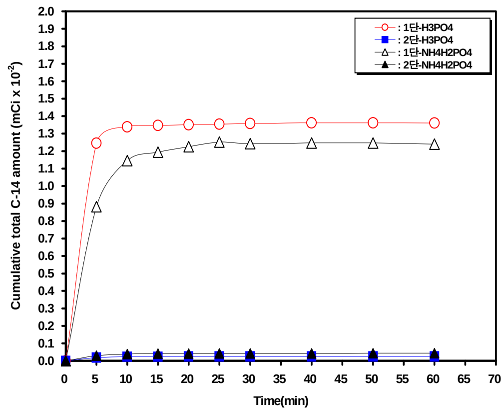

Fig. 8. Removal rate of ^{14}C radionuclide from real spent resin stored in Wolsong NPP by using $NH_4H_2PO_4$ and H_3PO_4.

3. Conclusions

Spent resins were sampled from in-station resin storage tank 2 at Wolsong Nuclear Power Plant Unit 1. Commercially available grain samplers were referred for resin sampling. Resin samples were collected from both man-hole (68 samples) and test-hole (4 samples). The maximum dose rate, in contact with the resin sampler, was about 8mR/h and the tritium level in the room was about 2.9 DAC. Each resin sample was oxidized with sample oxidizer (Perkin Elmer, M307). The average concentration of C-14 in the cation/anion mixed resin was 460 GBq/m^3 from test-hole and 53.1 GBq/m^3 from man-hole. The C-14 concentration in anion resin was approximately 2 times higher than in the cation/anion mixed resin. The C-14 concentration was generally decreased with elevation. In the result, we must separate them into anion and cation resins and then eliminate the C-14 from the anion resins for legal disposal of spent resins.

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

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