Studies on Oxidation Treatment of Spent Ion-Exchange Resins (2) – 17330

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ABSTRACT

Ion-exchange resins used in nuclear power plants adsorb radioactive nuclides, like Co-60, Ni-63 and so on. The large amounts of spent ion-exchange resins must be stored. In Japan, the volume reduction of spent ion-exchange resins, which have been categorized as low-level radioactive waste with relatively high radioactivity (hereinafter called “Level 1”), are required by methods other than incineration. In this study, to reduce the amount of Level 1, a method for the removal of radioactive nuclides involving oxidation with O_3, H_2O_2, and Fe^{2+} ions (hereinafter called “radical oxidation”) was investigated. Radicals generated with O_3, H_2O_2, and Fe^{2+} ions oxidized and dissolved resins and radioactive nuclides in the liquid phase at ordinary pressures and temperatures less than 100 °C. Then the dissolved radioactive nuclides were separated by coprecipitation with iron ions. In this study, using radical oxidation and coprecipitation with iron ions, Level 1 spent ion-exchange resins were separated into a small amount of Level 1 and other comparatively low radioactive wastes.

INTRODUCTION

Spent ion-exchange resins categorized Level 1 are generated from reactor water clean-up systems (CUW), fuel pool cooling and cleanup systems (FPC) [1]. To reduce the amount of radioactive waste, the volume of spent ion-exchange resins categorized Level 1 should be reduced or the radioactive nuclides should be removed from the resins. Ignoring the radioactivity, incineration [2], advanced oxidation processes [3], supercritical water oxidation[4], steam reforming [5], cold crucible induction melting[6], elution[7], etc. have been investigated. Although they have the advantage of high reduction or high elution ratios, they need large quantities of energy or large amounts of chemical reagents.

Using radical oxidation, spent ion-exchange resins can be treated under normal conditions, such as ordinary pressures and temperatures < 100 °C, and by using smaller quantities of energy and chemical reagents.

Basic experimental results from radical oxidation of cation resins have been reported in WM 2016-16083[8]. In this paper, experimental results from radical oxidation of cation and anion mixed resins, effects of Crud, and coprecipitation with iron ions are reported.

EXPERIMENTAL SECTION

Radical oxidation of cation and anion mixed resins

Cation and anion mixed resins are used in CUW and FPC of BWR in JAPAN. To simulate actual conditions, cation and anion mixed resins (cation resin : EBARA Co., EMK-100, anion resin : EBARA Co., EMA-200) were oxidized. Before radical oxidation, the cation resin was immersed in $CoSO_4$ solution so that Co^{2+} ions were adsorbed. The Co ion concentration of the liquid after oxidation was measured by using inductively-coupled plasma atomic emission spectrometry (SII Nano Technology Inc., SPS3520). The Co ion removal ratio (*R* [%]) was calculated by using the following equation:

$$R = \frac{C_a}{C_b} \times 100 \quad [\%] \qquad \text{(Eq.1)}$$

C_a: Co ions dissolved in liquid through oxidation [mmol/g-dry resin]
C_b: Co ions adsorbed in ion-exchange resin before oxidation [mmol/g-dry resin]

Test conditions are shown in TABLE I. A depiction of the radical oxidation process used in the tests is shown in Figure 1.

TABLE I. Test conditions for oxidation of cation and anion mixed resins

Resin	Cation: EMK-100 (Co adsorbed) Anion: EMA-200 Total: 50 g
Liquid phase [cm^3]	500
Time [min]	50
Temperature [°C]	70
O_3 conc. [g/m^3]	130
O_3 flow rate [cm^3/min]	300
H_2O_2 [mass%]	2.5
Fe ions [mg/L]	50

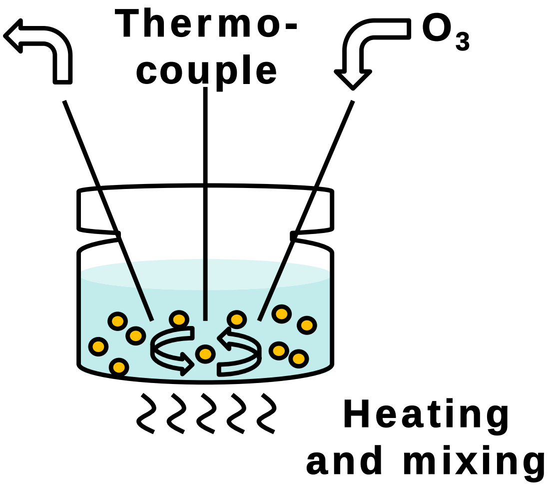

Figure 1. A depiction of the radical oxidation process

The relative amount of hydroxyl radicals (OH radical, or ·OH) produced during radical oxidation was estimated in relation to the amount of CH_3COONa [9], since it is decomposed by OH radicals. The CH_3COONa concentration was determined by using liquid chromatography (SHIMADZU Corp., HPLC CBM-20A) and a total organic carbon meter (SHIMADZU Corp., TOC-L). The effects of pH were evaluated using the conditions summarized in TABLE II.

TABLE II. Test conditions for assessing the effects of pH on OH radical generation

CH_3COONa [mmol/L]	10
Liquid phase [cm^3]	500
pH	1(controlled with H_2SO_4), 5
Time [min]	60
Temperature [°C]	90
O_3 conc. [g/m^3]	130
O_3 flow rate [cm^3/min]	300
H_2O_2 [mass %]	2.5
Fe ions [mg/L]	50

Cation and anion mixed resins were oxidized under pH-controlled conditions, which are summarized in TABLE III. Although the resins in TABLEs I and III were different, all of the resins (EMK-100, EMA-200, PD-3 and PD-1) consisted of polystyrene cross-linked with divinylbenzene. The cation resins had sulfo functional groups, and the anion resins had quaternized ammonium groups. Thus, the difference in the resins did not have a substantial impact on the radical oxidation reaction. In addition, the effects of the temperature between 70 and 90 °C were studied after oxidizing for 50 min [8].

TABLE III. Test conditions for oxidation under pH control

Resin	Cation: PD-3 (Co adsorbed) Anion: PD-1 Total: 50 g
Liquid phase [cm^3]	500
pH	1 (controlled with H_2SO_4)
Time [min]	60
Temperature [°C]	90
O_3 conc. [g/m^3]	130
O_3 flow rate [cm^3/min]	300
H_2O_2 [mass %]	2.5
Fe ions [mg/L]	50

Effects of Crud

CUW of BWR in Japan filter Crud. To confirm the effects of Crud, the relative amount of OH radicals generated during radical oxidation was measured. Test conditions are summarized in TABLE IV.

TABLE IV. Test conditions for assessing the effects of Crud on OH radical generation

CH_3COONa [mmol/L]	10
Liquid phase [cm^3]	500
Crud [g]	1.1
pH	1(controlled with H_2SO_4)
Time [min]	40
Temperature [°C]	90
O_3 conc. [g/m^3]	80
O_3 flow rate [cm^3/min]	490
H_2O_2 [mass %]	2.5
Fe ions [mg/L]	50

Radical oxidation of cation and anion mixed resins including Crud

To simulate actual resins categorized Level 1, cation and anion mixed resins (cation resin: DOW chemical Co., 50wx8, anion resin: DOW chemical Co., 1x8) and Crud were oxidized. Before radical oxidation, the cation resin was immersed in $CoCl_2$ solution, and Co-60 (Co^{2+}) ions were adsorbed. The Co-60 ion concentration of the liquid after oxidation was measured by using a germanium semiconductor detector (CANBERRA Industries Inc., GC4018). The Co ion removal ratio (*R* [%]) was calculated by using eq. 1. Test conditions are summarized in TABLE V.

TABLE V. Test conditions for oxidation of cation and anion mixed resins including Crud

Resin	Cation: 50wx8 (Co-60 adsorbed) Anion: 1x8 Total : 50 g
Liquid phase [cm^3]	500
Iron cladding [g]	1.1
pH	1(controlled with H_2SO_4)
Time [min]	60
Temperature [℃]	90
O_3 conc. [g/m^3]	80
O_3 flow rate [cm^3/min]	490
H_2O_2 [mass %]	2.5
Fe ions [mg/L]	50

Coprecipitation of Co-60 ions with iron ions

To confirm radioactive nuclide separation, a coprecipitation experiment involving Co-60 ions was conducted. A few methods for separating Co-60 ions, such as adsorption, electrodeposition and coprecipitation, have been investigated. From a standpoint of waste volume and use of energy, coprecipitation with iron ions is considered to be better than other methods are. The Co-60 ion concentration of the liquid after oxidation was measured by using a germanium semiconductor detector. The Co ion coprecipitation ratio (R_c [%]) was calculated by using the following equation:

$$R_c = \frac{C_2}{C_1} \times 100 \ \ [\%] \qquad \text{(Eq.2)}$$

C_2: Co ions removed from liquid through coprecipitation [Bq]
C_1: Co ions dissolved in liquid before coprecipitation [Bq]

Test conditions are summarized in TABLE VI. The setup for the radical oxidation experiment is shown in Figure. 2.

TABLE VI. Test conditions for coprecipitation of Co-60 ions with iron ions

Liquid phase	After radical oxidation of cation and anion mixed resins including Crud
Liquid phase [cm^3]	50
Temperature [°C]	Ambient temp.
NaOH [mol/L]	1
Fe ions [mg/L]	50–230

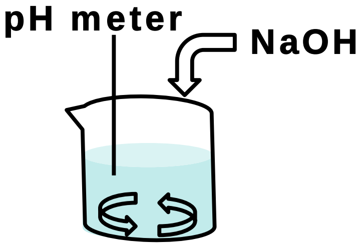

Figure 2. Experimental setup for coprecipitation of Co-60 ions with iron ions

RESULTS AND DISCUSSION

Effects of cation and anion mixed resins

1. Radical oxidation of cation and anion mixed resins

Figure 3 shows the *R* value for the the oxidation of the cation resin and mixed resins. The *R* value for the cation resin oxidation was over 60%, whereas that for mixed resins oxidation was less than 0.1%. In other words, Co ions adsorbed on the cation resin could not be removed.

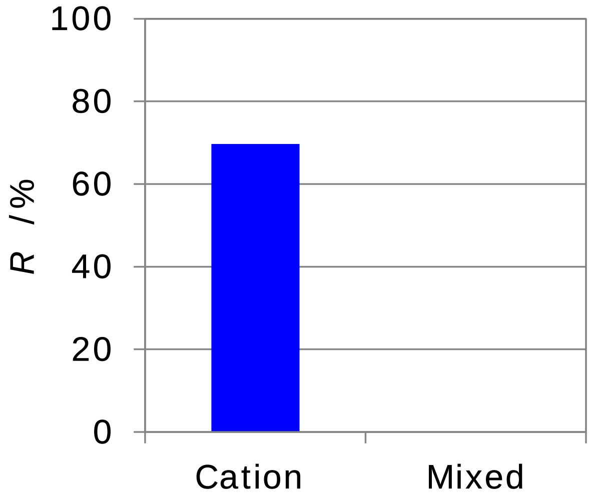

Figure 3. Comparision of oxidation of the cation and mixed resins

The pH values for the cation resin and mixed resins oxidations were different, because of the OH^- from the anion resin. The pH of the solution for the cation resin oxidation was about 1.0, and that for the mixed resin oxidation was 4–5. The difference in pH was considered to be due to the difference in the amount of the OH radicals generated. Thus, effects of pH on OH radical generation were studied.

2. Effects of pH on OH radical generation

Figure 4 shows the effects of pH on the relative amount of OH radicals generated during radical oxidation. The change in the CH_3COONa concentration at pH 1 at 60 min was defined as 1.0 for standardization. During radical oxidation, OH radicals are generated by O_3, H_2O_2 and Fe^{2+} [10]–[13]. O_3 solubility increases at lower pH.The Fenton reaction is also promoted at lower pH. Fe^{2+} ions and O_3 react to generate OH radicals as shown below [14]. Thus, at lower pH, the relative amount of OH radicals generated via radical oxidation is high.

$$Fe^{2+} + O_3 \rightarrow Fe^{3+} + O_3^- \qquad \text{(R. 1)}$$

$$O_3^- + H^+ \rightarrow \cdot OH + O_2 \qquad \text{(R. 2)}$$

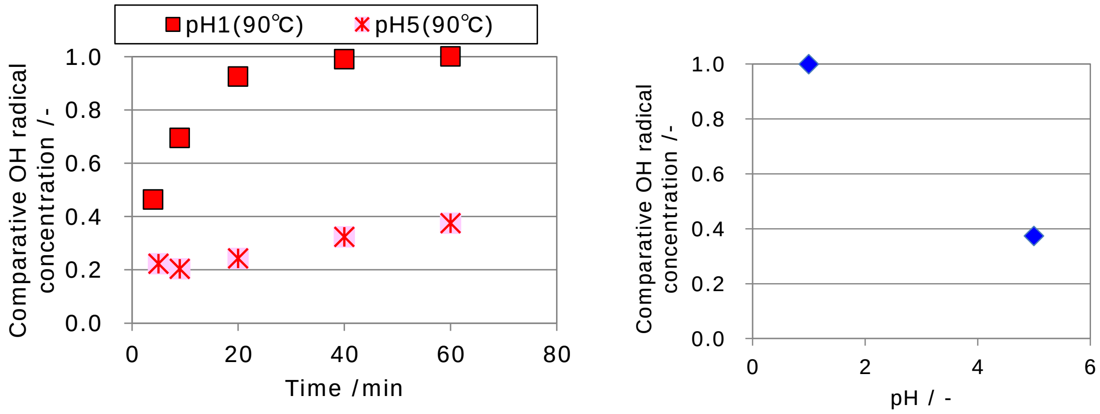

Figure 4. pH effects on OH radical generation during radical oxidation
(L: time dependent change, R: comparison at 60 min)

3. Radical oxidation of cation and anion mixed resins under pH-controlled conditions

Figure 5 shows the *R* value for the oxidation of the mixed resins under pH-controlled conditions. The pH was controlled at 1 with H_2SO_4. Since SO_3^- was removed from the cation resin by radical oxidation, H_2SO_4 was used to control the pH. In Figure 5, *R* was improved by controlling the pH. In other words, the pH affects the radical oxidation of resins.

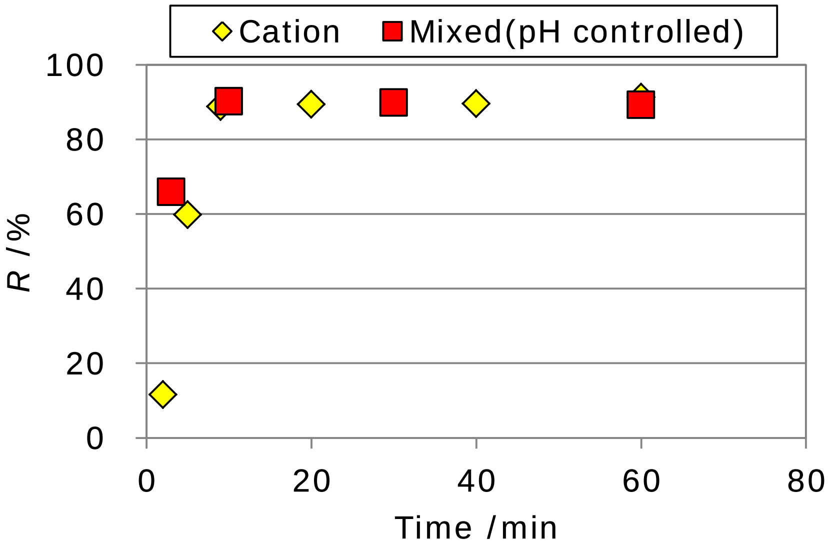

Figure 5. Co removal ratios during mixed resin oxidation under pH controlled conditions

Effects of Crud

Figure 6 shows the effects of Crud on the relative amount of OH radicals generated during radical oxidation. The change in the CH_3COONa concentration with Crud at 40 min was defined as 1.0 for standardization. Crud had no effect on the amount of OH radicals generated. OH radicals are generated by O_3, H_2O_2, and Fe^{2+} ions in the solution. Since only a small amount of Crud dissolved in the liquid phase, it scarcely affected OH radical generation, which is a liquid-liquid reaction. However, radical oxidation of ion-exchange resins is a solid-liquid reaction. So, the effects of Crud on radical oxidation of ion exchange resins was investigated in the next section.

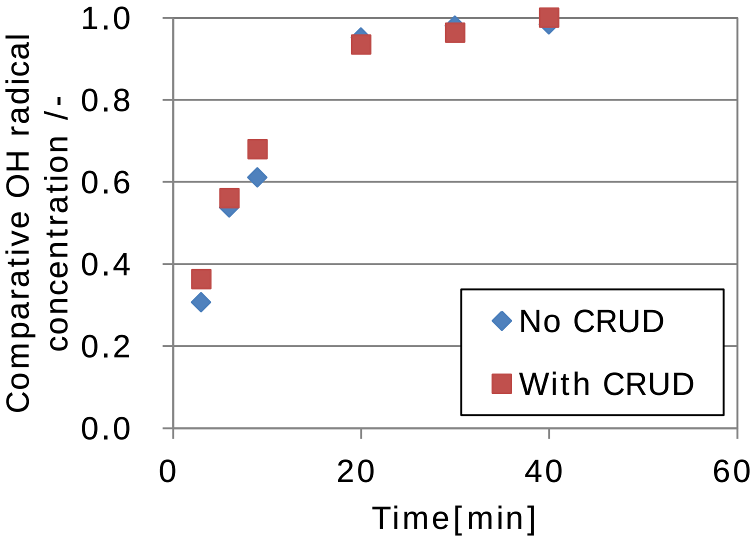

Figure 6. Effects of Crud on OH radical generation

Radical oxidation of cation and anion mixed resins containing Crud
Figure 7 shows the results of the radical oxidation of cation and anion mixed resins including Crud. The results indicated that adsorbed Co-60 ions were removed from cation and anion mixed resins including Crud, meaning that the removal behaviors of Co-60 and Co ions were similar. OH radicals randomly oxidize the bonds of the resins. Thus, the concentration of the adsorbed nuclides is not affected. However,

in inactive tracer experiments, the chemical concentration of Co ions was much larger than that of Co-60 experiment, indicating that Co ions diffused deep into the ion-exchange resins. Radical oxidation started at the surface of the ion-exchange resins, and thus, the Co ions absorbed deep in the ion-exchange resins were considered not to be removed.

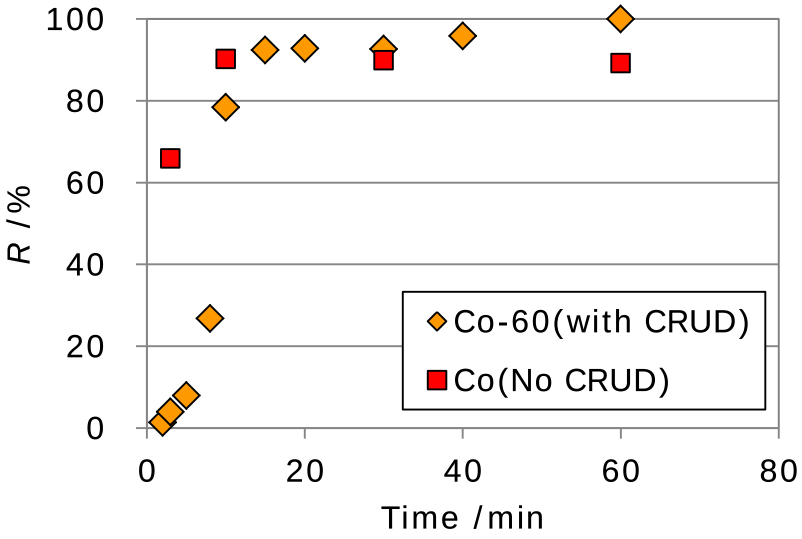

Figure 7. Radical oxidation of cation and anion mixed resins including Crud

Coprecipitation of Co-60 ions with iron ions

Figure 8 shows the coprecipitation of Co-60 with iron ions. The precipitation occurred at around pH11 after adding NaOH. More than the 90% of Co-60 ions coprecipitated with iron ions.

Figure 9 shows the radical oxidation process for spent ion-exchange resins. The liquid phase after radioactive nuclide separation is condensed by the existing facility. In this study, we confirmed that radical oxidation and radioactive nuclide separation process occurred as shown in the figure. Thus, radical oxidation can be used to oxidize and separate radioactive nuclides from Level 1 spent ion-exchange resins and other comparatively low-level radioactive wastes.

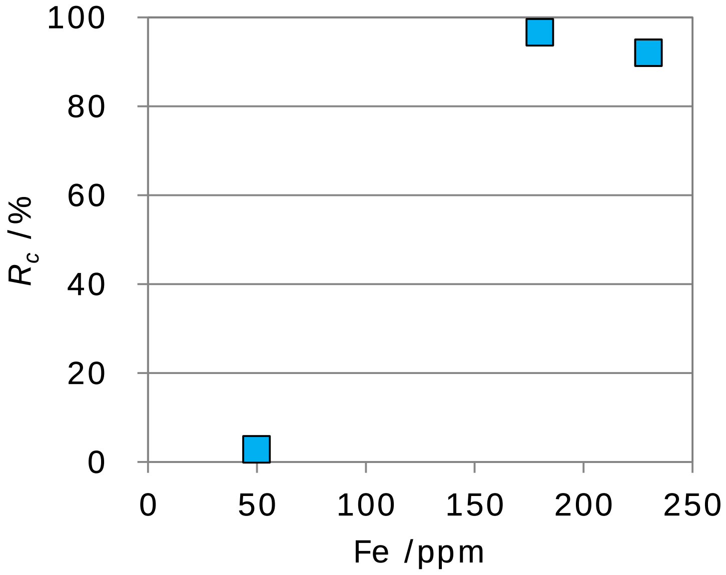

Figure 8. Coprecipitation of Co-60 with iron ions

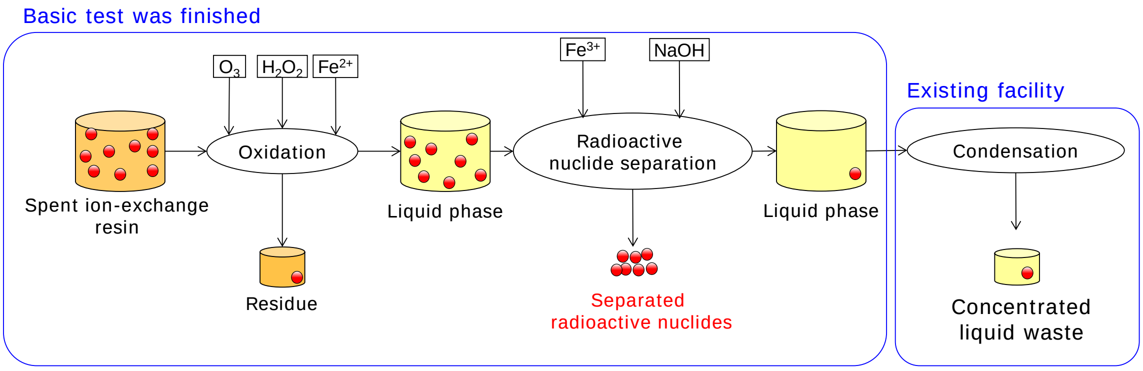

Figure 9. Radical oxidation process for spent ion-exchange resins

CONCLUSION

We studied the removal of Co ions from cation and anion exchange resins including Crud by using radical oxidation. The removed Co ions were selectively separated by using coprecipitation with iron ions. Thus, from Level 1 spent ion-exchange resins, other comparatively low-level radioactive wastes and small amounts of radioactive nuclides can be separated at ordinary pressures and temperatures < 100 °C.

We are currently optimizating the coprecipitation with iron ions. In addition, we are determining the quantity of waste generated during the solidification of the residue, the separated radioactive nuclides and the concentrated liquid waste after radical oxidation.

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