

Studies on Oxidation Treatment of Spent Ion-Exchange Resin – 16083

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ABSTRACT

Organic ion-exchange resins used at nuclear power plants of light water reactor adsorb radioactive nuclides, ^{60}Co , ^{63}Ni and so on, and the large amounts of spent ion-exchange resins are generated. In this study, to reduce the amount of spent ion-exchange resin, removal of radioactive nuclides through oxidation with O_3 , H_2O_2 , and Fe^{2+} was investigated. Radicals generated with O_3 , H_2O_2 , and Fe^{2+} oxidized and dissolved the resin. The radioactive nuclides and decomposition products (organic acids and some other decomposition products) were dissolved in the liquid phase.

More than 99% of simulated adsorbed radioactive nuclide (non-radioactive cobalt) was removed by selected conditions.

INTRODUCTION

Ion-exchange resins are used in Reactor Water Clean-up systems, Fuel Pool Cooling and Cleanup systems, Condensate Demineralizer systems, and Radioactive Waste Management Facilities for removing ionic impurities from water ^[1]. Spent ion-exchange resins are treated as radioactive waste. To reduce the amount of radioactive waste, the volume of resin should be reduced or radioactive nuclides should be removed from the resin. Thermal treatment using incineration ^[2], advanced oxidation processes ^[3], supercritical water oxidation^[4], steam reforming ^[5], cold crucible induction melting^[6], elution^[7] and some other methods have been investigated. They have the advantage of a high reduction ratio; however, there are some problems, such as the large quantity of energy or large amount of chemical reagent required.

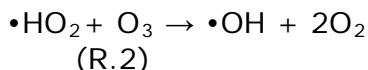
Ion-exchange resins consist of polystyrene cross-linked by divinylbenzene and functional groups (sulfo group, amino group, or some other functional groups). Ion-exchange resins were oxidized and decomposed with O_3 , H_2O_2 and Fe^{2+} . Above Oxidation method has advantage of low secondary waste than other oxidation methods, for example using permanganic acid potassium. Thus, in this study, to reduce the amount of energy and chemical reagent required, an oxidation method with O_3 , H_2O_2 , and Fe^{2+} less than 100°C was investigated.

Experimental

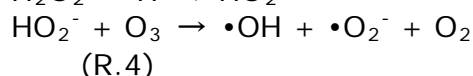
Hydroxyl radical (OH radical), some other radicals and ions were generated from self-decomposition of O_3 , the reaction of O_3 and H_2O_2 , and the reaction of H_2O_2 and Fe^{2+} , which is called the Fenton reaction. These radicals have strong oxidizability, and the ion exchange resin was oxidized. The fundamental reaction formulas are shown below ^{[8]- [11]}.

[O_3 decomposition]





[O₃ and H₂O₂ reaction]



[Fenton reaction]



To accelerate reaction, oxidation with O₃, H₂O₂ and Fe²⁺ in combination was a basic condition in all experiments.

Measurement of OH radical

A relative amount of OH radical with O₃, H₂O₂ and Fe²⁺ in combination was evaluated. The amount of OH radical was calculated by measuring sodium acetate (CH₃COONa)^[12]. CH₃COONa was added to liquid phase which included H₂O₂ and Fe²⁺. O₃ gas was also added to the liquid phase, generating OH radical. CH₃COONa was decomposed by the OH radical, decreasing the concentration of CH₃COONa. The CH₃COONa concentration was measured by the liquid chromatography method (SHIMADZU Corp., HPLC CBM-20A). A relative amount of OH radical was evaluated from the change in the CH₃COONa concentration.

Effective factors on OH radical generation were chemical reagent supply, time and temperature. The chemical reagent supply was from reconnaissance investigation, and time was defined 60min for comparison. Thus, the effect of temperature was examined on amount OH radical. CH₃COONa supply was enough for theoretical OH radical generation. The test conditions are shown in Table 1.

Table 1. Test conditions for assessing the effect of temperature on OH radical generation

| No. | CH ₃ COONa [mmol/l] | liquid phase [cm ³] | Time[min] | Temperature[°C] | O ₃ [g/Nm ³] | O ₃ [cm ³ /min] | H ₂ O ₂ [%] | Fe[mg/l] |
|-----|--------------------------------|---------------------------------|-----------|-----------------|-------------------------------------|---------------------------------------|-----------------------------------|----------|
| 1 | 10 | 500 | 60 | 50 | 130 | 400 | 3 | 50 |
| 2 | 10 | 500 | 60 | 70 | 130 | 400 | 3 | 50 |
| 3 | 10 | 500 | 60 | 90 | 130 | 400 | 3 | 50 |

Assessment of effects of temperature

Powdered cation-exchange resin (EBARA Co., PD-3) was immersed in Co(SO₄) solution, and Co²⁺ was adsorbed. To confirm the effects of temperature, O₃, H₂O₂ and Fe²⁺ were added under the conditions shown in Table 2. Some decomposition products from ion-exchange resin were generated on oxidation. To examine the oxidation process of the ion-exchange resin, a lower organic acid (formic acid, acetic acid, propionic acid, butyric acid, and valeric acid) concentration was measured by liquid chromatography method. The test conditions are shown in Table 2, Nos. 2–5.

The Co concentration of the liquid after oxidation was measured by inductively-coupled plasma atomic emission spectrometry (SII Nano Technology Inc., SPS3520). The Co removal ratio: R [%] was calculated by the following equation:

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

C_a : Co dissolved in liquid through oxidation [mmol/g-dry resin]

C_b : Co adsorbed in ion-exchange resin before oxidation [mmol/g-dry resin]

Table 2. Test conditions for assessing the effect of temperature

| No. | resin [g-dry] | liquid phase [cm ³] | Time[min] | Temperature[°C] | O ₃ [g/Nm ³] | O ₃ [cm ³ /min] | H ₂ O ₂ [%] | Fe[mg/l] |
|-----|---------------|---------------------------------|-----------|-----------------|-------------------------------------|---------------------------------------|-----------------------------------|----------|
| 1 | 22 | 500 | 60 | 50 | 130 | 400 | 3 | 50 |
| 2 | 22 | 500 | 60 | 60 | 130 | 400 | 3 | 50 |
| 3 | 22 | 500 | 60 | 70 | 130 | 400 | 3 | 50 |
| 4 | 22 | 500 | 60 | 80 | 130 | 400 | 3 | 50 |
| 5 | 22 | 500 | 60 | 90 | 130 | 400 | 3 | 50 |

Removal ratio improvement

To improve the Co removal ratio, the amounts of O₃, H₂O₂ and Fe²⁺ were increased. From this experiment, the effect of O₃, H₂O₂ and Fe²⁺ was examined. The test conditions are shown in Table 3.

Table 3. Test conditions for removal ratio improvement

| No. | resin [g-dry] | liquid phase [cm ³] | Time[min] | Temperature[°C] | O ₃ [g/Nm ³] | O ₃ [cm ³ /min] | H ₂ O ₂ [%] | Fe[mg/l] |
|-----|---------------|---------------------------------|-----------|-----------------|-------------------------------------|---------------------------------------|-----------------------------------|----------|
| 1 | 22 | 500 | 60 | 90 | 130 | 400 | 3 | 50 |
| 2 | 22 | 500 | 60 | 90 | 130 | 1,200 | 3 | 50 |
| 3 | 22 | 500 | 60 | 90 | 130 | 400 | 8 | 50 |
| 4 | 22 | 500 | 60 | 90 | 130 | 400 | 3 | 150 |

RESULTS AND DISCUSSION

Measurement of OH radical

Fig. 1 shows the effect of temperature on the relative amount of OH radical. OH radical was generated higher at high temperature than at low temperature. The observed tendency of OH radical was because the reaction rates of (R.1) to (R.5) were presumed to be higher at high temperature than at low temperature. Moreover, OH⁻ generated from the Fenton reaction (R.5) seemed to accelerate the O₃ and H₂O₂ reaction (R.3) and O₃ decomposition (R.1), and thus, a large amount of OH radical was generated in the presence of O₃, H₂O₂ and Fe²⁺. However, the self-decomposition of O₃, the reaction of O₃ and H₂O₂, and the reaction of H₂O₂ and Fe²⁺ are complicated reactions [13]. It will be necessary to continue to investigate the oxidation process in more detail.

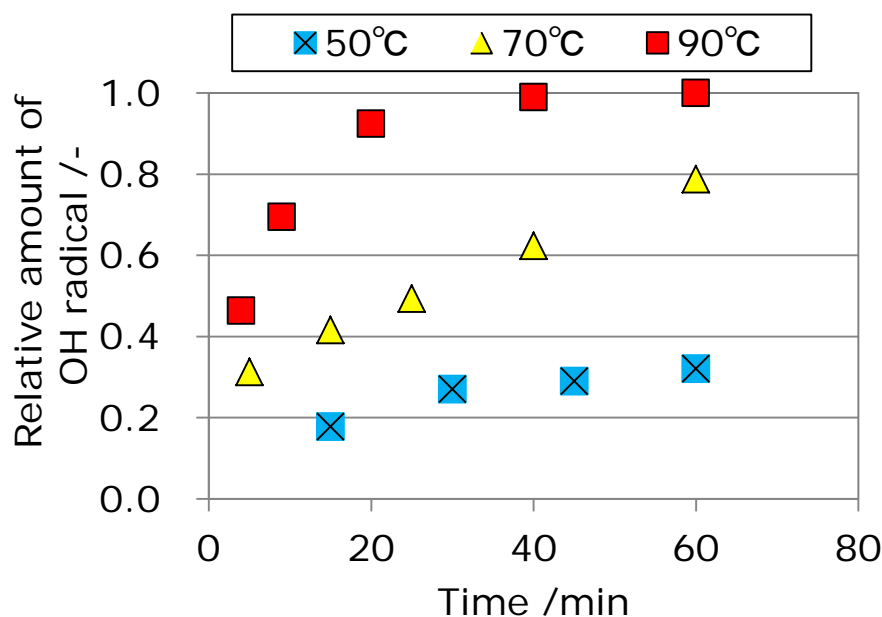


Fig. 1 Effect of temperature on OH radical generation

Assessing the effect of temperature

Fig. 2 shows formic acid generation. From the measurement of low molecular weight organic acid, only formic acid was measured. Formic acid concentration increased gradually. The ion-exchange resin was decomposed gradually, and high molecular decomposition products, for example sodium polystyrene sulfonate, were generated in the initial stage. The high molecular decomposition products were presumed to be decomposed gradually, and some organic matters, for example, benzenesulfonic acid-sodium salt, were presumed to be generated. Thus, low molecular weight organic acids, for example formic acid, were generated in the late stage.

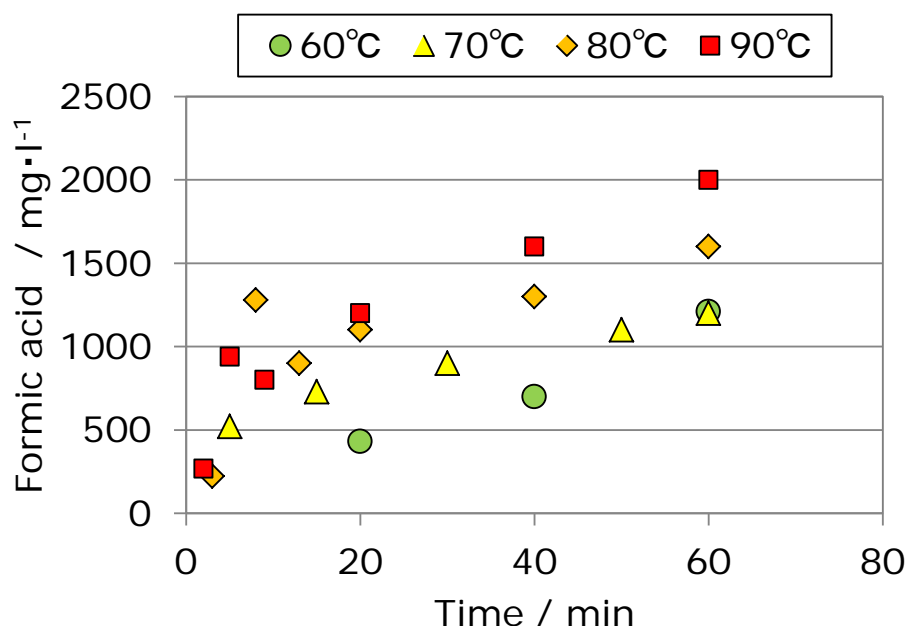


Fig. 2 Effect of temperature on formic acid generation

Fig. 3 shows the effect of temperature on the Co removal ratio. From this result, Co removal with oxidation was confirmed. The Co removal ratio was higher at high temperature than at low temperature. The tendency of the Co removal ratio and amount of OH radical at 90°C was similar. However, the different tendency between Co removal ratio and OH radical, at 70°C, was presumed that OH radical was consumed by decomposition products.

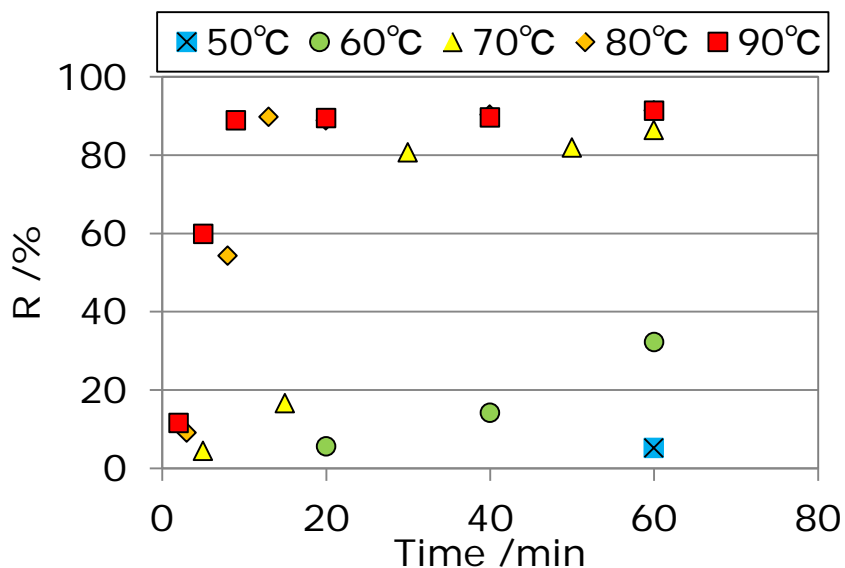


Fig. 3 Effect of temperature on Co removal ratio

Removal ratio improvement

From Figs. 1 and 3, Co removal was due to OH radical oxidation. An increase in the amount of OH radical was presumed to improve the Co removal ratio. Thus, increase of O_3 , H_2O_2 and Fe^{2+} was calculated to improve Co removal ratio. Optimum temperature of oxidation was 90 °C. Moreover, increase of O_3 was better from the decrease of chemical reagent. Fig. 4 shows the effect of increasing the amounts of O_3 , H_2O_2 and Fe^{2+} . From (R.1) to (R.4), increases of O_3 and H_2O_2 resulted in an increase in OH radical. From (R.5), an increase of Fe^{2+} resulted in increases of OH radical and OH^- . The increase of OH^- accelerated both O_3 decomposition (R.1) and the reaction of O_3 and H_2O_2 , and OH radical was increased. Thus, the Co removal ratio was improved to 99%.

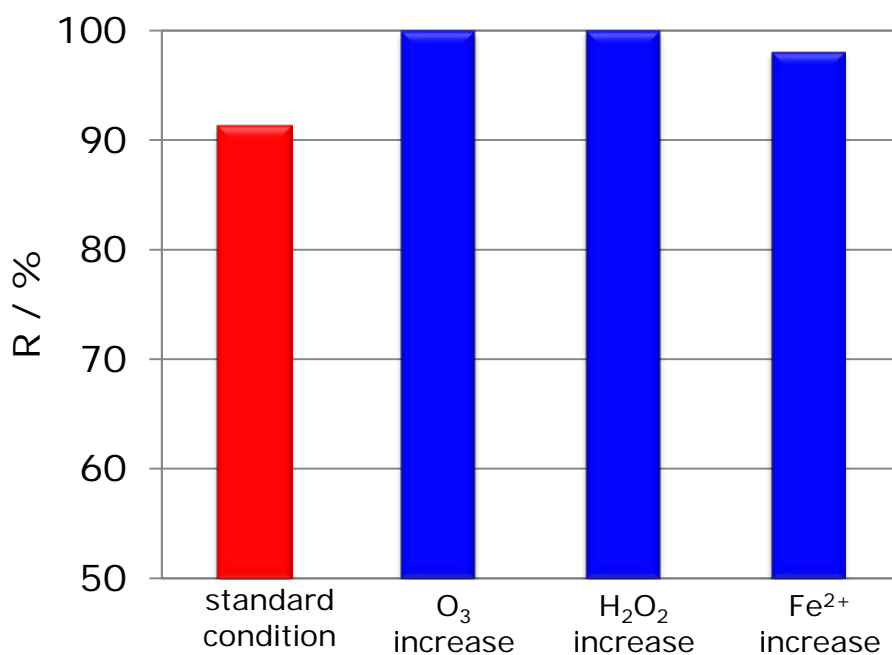


Fig. 4 Effect of increased amounts of O_3 , H_2O_2 and Fe^{2+}

OH radical Oxidation treatment flow of spent ion-exchange resin

Fig. 5 showed the OH radical Oxidation treatment flow. The spent ion-exchange resin was oxidized by O_3 , H_2O_2 and Fe^{2+} . The radioactive nuclide was dissolved in liquid phase. Organic materials were separated from liquid phase. Radioactive nuclide was separated and condensed, thus radioactive waste was decreased.

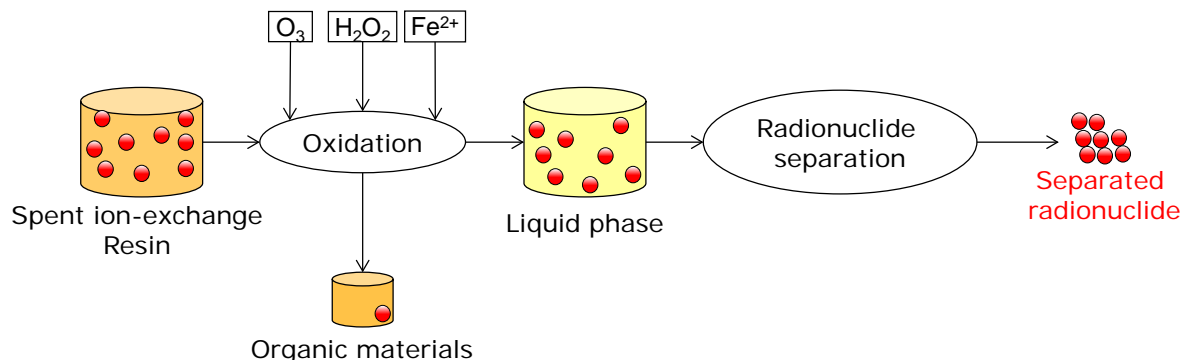


Fig. 5 OH radical Oxidation treatment flow

Conclusion

We examined Co removal through oxidation by OH radical from O_3 , H_2O_2 and Fe^{2+} . OH radical generation was measured, and a high temperature was found to be effective for increasing OH radical generation and Co removal. The amount of low molecular weight organic acid (one of the decomposition products) was increased through oxidation. The Co removal ratio was improved to 99% due to the increased amounts of oxidants or reductant, O_3 : $130g/Nm^3$ and $1,200cm^3/min$, H_2O_2 : 3% and Fe^{2+} : 50mg/l.

We will continue to investigate the optimization of oxidation to reduce the amounts of chemical reagents. We will also calculate the quantity of spent ion-exchange resin waste generation from the solidification experiment of the resin after oxidation.

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