

## Alternation of physicochemical properties of cation exchange resins by gamma irradiation

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### 1. Introduction

Most commercially produced cation exchange resins contain sulfonic acid ( $-\text{HSO}_3$ ) and polystyrene (PS) based ion exchange resins cross-linked with divinylbenzene (DVB) are available. The radiation stability of PS-DVB cation exchange resins is determined by the amount of cross-linked DVB, and it is generally known that higher cross-linking results in greater resistance to decomposition by radiation. Cation exchange resins are known to be more radiation-resistant than anion exchange resins, but continuous exposure to high levels of radiation can cause sulfonic acid groups to decompose, resulting in a decrease in ion exchange capacity [1-3]. Moreover, when exposed to a high radiation dose in an atmosphere with high oxygen and humidity, decomposition of sulfonic acid and the PS-DVB backbone accelerates, leading to changes in chemical and thermal properties. However, research on the changes in characteristics of cation exchange resins due to high radiation exposure is still insufficient [4,5]. The cation exchange resins used in nuclear facilities are typically strongly acidic ion exchange resins in which styrene and DVB are copolymerized and then sulfonated. These resins are reported to have excellent thermal stability for adsorption functional groups and can be used even at temperatures as high as  $120^\circ\text{C}$ , exhibiting high chemical and thermal stability. However, research on the changes in properties of these resins due to radiation exposure is still limited [6].

In this study, the changes in the chemical structure and thermal decomposition properties of cation exchange resins under high-dose gamma ray irradiation were investigated.

### 2. Methods and Results

#### 2.1 Gamma ray irradiation of cation exchange resin

To evaluate the thermal degradation characteristics through gamma ray irradiation, we purchased Amberlite IRN77, a nuclear grade cation exchange resin sold by Rohm & Haas. The physicochemical properties provided by the vendor are shown in Table 1. Ion exchange resin loaded with nuclides and organic complexing agents was irradiated with gamma rays from a  $^{60}\text{Co}$  source (Nordion, Canada) at room temperature and atmospheric pressure. The radiation dose rate was

$10 \text{ kGy hr}^{-1}$  and irradiation was carried out at doses of 0, 300, 500, and 700 kGy.

#### 2.2 IR Spectra

The IR spectrum changes of cation exchange resin according to gamma-ray irradiation are shown in Fig. 1. Ion exchange resins stored in nuclear facilities are generally exposed to air for a long time, causing decomposition and cross-linking reactions of ion exchange resins by gamma-ray and oxygen. When gamma-rays are irradiated on ion exchange resins, it can be seen that the decomposition reaction is dominant over the cross-linking reaction up to 500 kGy, but at 700 kGy, the cross-linking and decomposition reactions occur to a similar extent.

#### 2.3 XPS analysis

The alterations in elemental composition as determined by EDS analysis of ion exchange resin are shown in Fig. 2. Notably, the elemental ratios of carbon, oxygen, and sulfur - the key components of the ion exchange resin - underwent discernible changes by gamma ray irradiation. Specifically, as the irradiation dose increased from 0 to 700 kGy, the carbon content declined from 69.6% to 67.1%, while the oxygen content concurrently increased from 23.8% to 26.9%. The results suggest that the elemental composition of the ion exchange resin is sensitive to gamma radiation, with cross-linking and degradation reactions occurring similarly with increasing irradiation dose.

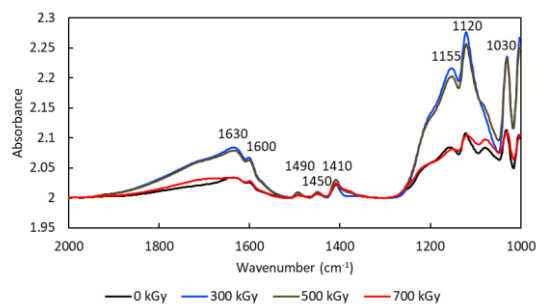


Fig. 1. IR spectrum changes of cation exchange resin according to gamma-ray irradiation.

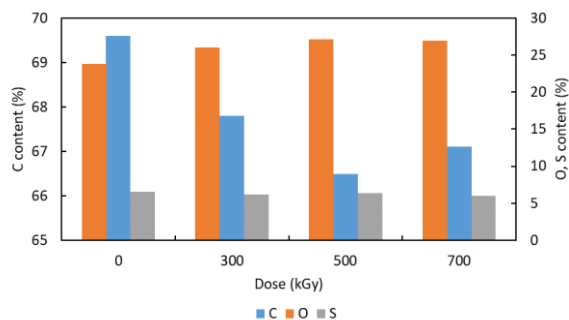


Fig. 2. Alterations in elemental composition as determined by EDS analysis of ion exchange resin.

#### 2.4 TGA analysis

Thermogravimetric analysis conducted on cation exchange resin under ambient conditions is presented in Fig. 3. The ion exchange resin examined in this study possesses a PS-DVB structure and  $-SO_3H$  functional group. The sulfone group was observed to decompose at 250-350°C, and the PS-DVB structure decomposed at 400-600°C, resulting in a clear change in the thermal degradation characteristics of the resin. The degradation onset temperature of cation exchange resin is shown in Table 1. The decomposition temperature of the sulfonic group reduced with increasing irradiation dose, reaching 274.0, 263.2, 259.7, and 258.1°C at 0, 300, 500, and 700 kGy, respectively. This shows that the degradation of the ion exchange resin by gamma irradiation is expedited. The residue change of the cation exchange resin by gamma irradiation is presented in Table 2. The residue declined to 16.3%, 15.5%, and 12.2% at 0, 300, and 500 kGy, respectively, as a result of 80-90% decomposition of PS-DVB at 600°C, whereas it slightly increased to 17.8% at 700 kGy. These results are consistent with the degradation and crosslinking reactions induced by gamma irradiation, signifying that the residues are produced due to chemical alterations rather than thermal property changes.

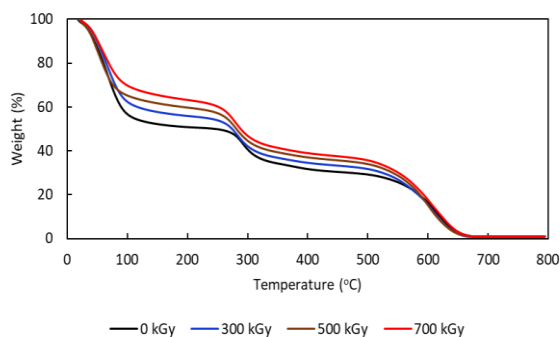


Fig. 3. Thermogravimetric analysis conducted on cation exchange resin under ambient conditions

Table 1: Change of degradation on-set temperature after gamma irradiation

	Dose (kGy)			
	0	300	500	700
-HSO <sub>3</sub>	274.0	263.2	259.7	258.1
PS-DVB	564.1	556.0	553.4	548.3

Table 2: Residue change of cation exchange resin after gamma irradiation

Temperature (°C)	Dose (kGy)			
	0	300	500	700
600	16.3	15.5	15.2	17.8
700	0.9	0.7	1.1	0.8
800	1.0	0.7	1.1	0.8

### 3. Conclusions

Cation exchange resins used in nuclear power generation facilities were irradiated with high doses of gamma radiation to investigate changes in the chemical and thermal properties of ion exchange resins. The carbon content was reduced by gamma irradiation up to 500 kGy. The carbon content was reduced up to 500 kGy, but slightly increased at 700 kGy. Unlike the changes in chemical characteristics, the sulfonic groups of PS-DVB and PS-DVB decreased with increasing irradiation dose. The onset temperature of decomposition of sulfonic groups and PS-DVB decreased with increasing irradiation dose, showing a decrease in thermal stability. However, residue formation with increasing temperature was consistent with IR and EDS changes.

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