

Supplementary Information

Effect of ion exchange resin particle size on homogeneity and leachability of Cs and Co in polymer waste form

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Experimental Section

1. Materials

Nuclear grade mixed bed IERs (TULSION MB-106) were supplied by Thermax and the detailed information for these IERs is shown in Table S4. A liquid bisphenol-A type epoxy resin (YD-128H) and a cycloaliphatic amine modified hardener (IPDA) were purchased from Kukdo Chemical. A polymer-based defoamer (BYK-1790) was obtained from BYK Additives & Instruments. Reagent grade cobalt chloride (CoCl_2 , anhydrous) and cesium chloride (CsCl) from Alfa Aesar and Sigma-Aldrich, respectively, were used without further purification.

2. Preparation of epoxy polymer waste forms

In a typical synthesis, IERs were added into the 30 mM CsCl and 30 mM CoCl_2 solution at a solid to solution ratio of 1 kg/10 L and the resultant mixture was stirred for 3 days (d) at room temperature. After reaction, the spent IERs were filtered and dried in an oven at 60 °C for 3 d. Simulated spent IERs (200 g) were ground by a planetary ball mill (ProPM2L, Pronextech), using a 500 mL stainless steel grinding jar with SUS balls of Φ 6 mm (60 ea), 10 mm (40 ea), and 20 mm (5 ea), at 500 rpm for 5 hours (h) and used as ball mill ground IERs.

Before making polymer waste form with 50-wt% IERs loading, epoxy resin was stored in an oven at 60 °C to increase workability. Approximately 120 g of simulated IER waste was added to 100 g of epoxy resin, 20 g of hardener, and 1 mL of defoamer; the resulting content was mixed and poured into a 5 cm \times 10 cm cylindrical metal mold. The epoxy polymer was cured for 1 d at room temperature, taken out from the metal mold, and aged in an oven at 60 °C for an additional 1 d. The epoxy polymer waste form prepared using the ball mill ground IER powder is referred to as BG polymer, and the epoxy polymer waste form prepared using granular IER without grinding is referred to as NG polymer.

3. Analytical methods

The average particle size of IERs was measured by the Mastersizer 2000 (Malvern Panalytical). The Co and Cs distribution in the IERs of BG and NG polymer were investigated by LIBS, a powerful atomic emission spectroscopy and one of the most useful techniques developed in the past few years, which can be efficiently applied for hetero/homogeneity analysis of solid matrix surfaces and also for elemental analysis.¹ The advantages of LIBS analysis are that it does not require sample pretreatment and can detect almost all elements, including light

elements, and simultaneously analyze multi-elements.²⁻⁴ Several studies have reported the application of LIBS for quantitative elemental analysis using calibration curve method.⁵⁻⁷ It provides a wide range of analysis options (e.g., detectors, collection/excitation optics, wavelength, pulse duration, energy), which can be set and used as per the need of sample analysis.

In this experiment, a nanosecond Nd: YAG Laser with 100-mJ laser pulse energy at 1,064 nm was used to generate the plasma with J200 (Applied Spectra). The detection range was 190 to 1,040 nm, and the intensities of Co 345.35 nm and Cs 894.35 nm were used to process the data. To evaluate the vertical and radial homogeneity, polymer waste forms were divided equally into three sections; top, middle, and bottom (each section has 1cm width). Each section was analyzed at five different locations using 5 mm × 5 mm sized samples: center, top; bottom, right, and left. SEM-EDS images were obtained using the JSM-7800F PRIME (JEOL) at an acceleration voltage of 20 kV. Samples were coated with Pt before SEM-EDS analysis. XRF analysis was performed with the S4 EXPLORER (Bruker) for Cs and Co contents.

The compressive strengths of the polymer waste forms were determined with the MTS 815 (MTS Systems Corporation) according to ASTM C39 methods at a loading rate of 0.3 MPa/s.⁸ Leaching tests were performed using deionized (DI) water according to ANSI/ANS-16.1.⁹ The ratio of the leachant volume to the surface area of the sample was fixed at 10 and the leachant was replaced by a new leachant 10 times at 2 h, 7 h, 1 d, 2 d, 3 d, 4 d, 5 d, 19 d, 47 d, and 90 d. The concentrations of Co and Cs in the leachate were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) with NexION 300D (PerkinElmer). The leaching tests were performed in duplicate, and the average concentration of the leached target elements was used to calculate the effective diffusivity. The effective diffusivity and leachability index were calculated by the following equations (Eqs.1–2):

$$D_{i,n} = \pi \left[\frac{a_n}{A_0} \right]^2 \left[\frac{V}{S} \right]^2 T \dots (Eq.1)$$

where $D_{i,n}$ is the effective diffusivity coefficient of element i during interval n (cm^2/s), a_n is the quantity of an element released from the specimen during interval n , A_0 is the total quantity of a given contaminant (Cs or Co) in the specimen, $(\Delta t)_n$ is $t_n - t_{n-1}$, the duration of the n^{th} leaching interval (s), V is the volume of the specimen (cm^3), and S is the geometric surface area of the specimen (cm^2). T , calculated as $[(t_n^{1/2} + t_{n-1}^{1/2})/2]^2$, is the mean time of the leaching interval (s).

$$LI_i = \frac{1}{10} \sum_{n=1}^{10} \left[\log \left(\frac{\beta}{D_{i,n}} \right) \right]_n \dots (Eq.2)$$

where LI_i is the leachability index of element i , and β is a defined constant (1.0 cm²/s).

The cumulative fraction leached (CFL) was determined by the following equation (Eq.3):

$$CFL = \frac{\sum a_n}{A_0} \times 100 (\%) \dots (Eq.3)$$

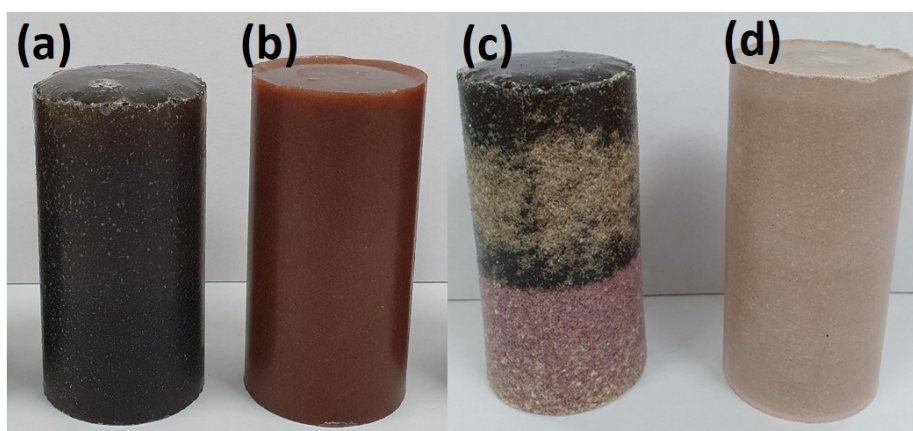


Figure S1. Photographs of the polymer waste forms before and after leaching tests: (a) and (b) represent NG and BG polymer waste forms, respectively, before leaching; (c) and (d) reflect NG and BG polymer waste forms, respectively, after leaching tests.

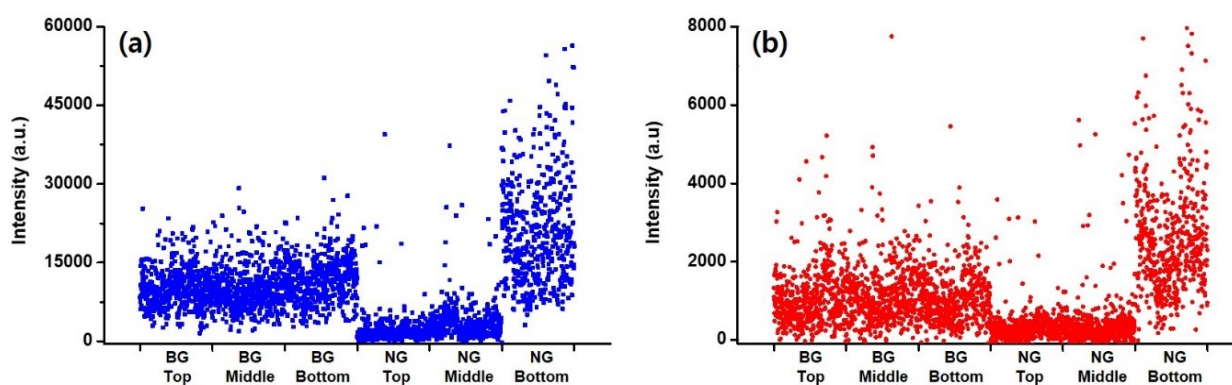


Figure S2. LIBS distribution charts for (a) Cs intensity and (b) Co intensity for the NG and BG polymer waste forms in different sections (top, middle, and bottom)

Table S1. XRF analysis data of the polymer waste forms for Cs and Co contents (wt%) in NG and BG polymers in different sections (top, middle, and bottom).

Selected section	NG polymer (wt%)		BG polymer (wt%)	
	Cs ₂ O	CoO	Cs ₂ O	CoO
Top	L.O.D.*	L.O.D.*	4.66	3.827
Middle	L.O.D.*	0.652	4.71	3.913
Bottom	8.5	6.897	4.95	4.158

* L.O.D.* stands for “limit of detection” because of low concentrations below detection limit.

Table S2. Compressive strength of NG and BG polymer waste forms before and after leaching tests.

Compressive strength	NG polymer		BG polymer	
	Before*	After**	Before*	After**
MPa	111	50	100	72

*Averaged value of triplicates; ** Single measurement.

Table S3. Leachability index (*LI*) and effective diffusivity coefficients (*D_i*) of Cs and Co in NG and BG polymer waste forms.

Properties	NG polymer		BG polymer	
	Cs	Co	Cs	Co
<i>LI</i> *	10.49	14.44	11.13	15.18
<i>D_i</i> [cm ² /s]	4.56 × 10 ⁻¹¹	4.33 × 10 ⁻¹³	7.76 × 10 ⁻¹²	4.23 × 10 ⁻¹⁵

**LI* is the unit less parameter.

Table S4. Properties of TULSION MB-106* ion exchange resins.

Resin name	TULSION T-46 H	TULSION A-33 OH
Type	Strong acid cation exchange resin	Strong base anion exchange resin
Matrix structure	Cross-linked polystyrene	Cross-linked polystyrene
Functional group	Sulphonic acid	Quaternary ammonium type I
Ionic form	Hydrogen	Hydroxide
Total exchange capacity	1.8 meq/ml min. of 99% in H ⁺ form	1.0 meq/ml min. of 90% in OH ⁻ form & max. 1% in Cl ⁻ form
Moisture content	52 ± 3 %	70 ± 3 %
Particle size	0.3–1.2 mm	0.3–1.2 mm
Temperature stability (max.)	120 °C	80 °C
Volume ratio	1	2

*TULSION MB-106 ion exchange resins are the mixture of TULSION T-46 H and TULSION A-33 OH.

References

- 1 V. Unnikrishnan, R. Nayak, V. B. Kartha, C. Santhosh, M. Sonavane, R. Yeotikar, M. Shah, G. Gupta and B. Suri, *AIP Advances*, 2014, **4**, 097104.
- 2 S. Sheta, G. Di Carlo, G. Ingo and M. Harith, *Surface and Interface Analysis*, 2015, **47**, 514-522.
- 3 F. Y. Yueh, J. P. Singh and H. Zhang, *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*, 2006.
- 4 D. W. Hahn and N. Omenetto, *Applied spectroscopy*, 2012, **66**, 347-419.
- 5 C. Aragon, J. A. Aguilera and F. Penalba, *Applied spectroscopy*, 1999, **53**, 1259-1267.
- 6 G. Galbacs, I. Gornushkin, B. Smith and J. Winefordner, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2001, **56**, 1159-1173.
- 7 A. K. Rai, F.-Y. Yueh and J. P. Singh, *Applied optics*, 2003, **42**, 2078-2084.
- 8 A. Standard, *ASTM C39*, 2010.
- 9 R. D. Spence and R. L. Cox, *MRS Online Proceedings Library Archive*, 1989, **176**.