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Leaching behavior of ^{60}Co and ^{137}Cs from spent ion exchange resins in cement–bentonite clay matrix

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Abstract

The leach rate of ^{60}Co and ^{137}Cs from two different ion exchange resins: (a) spent cation exchange resins and (b) spent mix bead ion exchange resins in cement–bentonite matrix has been studied. The solidification matrix was a standard Portland cement mixed with 290–350 kg/m^3 spent cation exchange resins, with or without 2–5% of bentonite clay. The leach rates from the cement–bentonite matrix as ^{60}Co: $(4.2–7.3)\times10^{-5}$ cm/d, and for ^{137}Cs: $(3.2–6.6)\times10^{-5}$ cm/d, after 245 days were measured. From the leaching data the apparent diffusivity of cobalt and cesium in cement–bentonite clay matrix with a waste load of 290–350 kg/m^3 spent cation exchange resins was measured as ^{60}Co: $(1.0–4.0)\times10^{-6}$ cm^2/d and for ^{137}Cs: $(0.5–2.6)\times10^{-4}$ cm^2/d after 245 days. These results are part of a 20-year mortar and concrete testing project which will influence the design of radioactive waste management for a future Serbian radioactive waste disposal center.

1. Introduction

Ion exchange may be used most successfully for the removal of radioactive ions from dilute solutions. This process produces deionized water, thus the radioactive ions are removed together with non-radioactive ones. Ion exchangers are resins that are polymers with cross-linking (connections between long carbon chains in a polymer). The resin has active groups in the form of electrically charged sites. At these sites ions of opposite charge are attracted but may be replaced by other ions depending on their relative concentrations and affinities for the sites. Spent cation exchange resins containing ^{60}Co and ^{137}Cs represent a major portion of the solid radioactive waste in nuclear technology.

Cement is used as a solidification material for the storage of intermediate-level radioactive waste. However the retention of radionuclides, especially cesium, in the cement matrix is negligible. The sorption of cesium on cement is low and diffusivity of cesium in the hydrated cement is high [1–3]. Only when the cement is mixed with a material having a significant sorption capacity, normally bead or powdered ion exchange resins, is the leachability of cesium and cobalt from the cement matrix low enough to be acceptable [4–8].

The objectives of immobilization are to convert the waste into forms which are:

- leach resistant, so that the release of radionuclides will be slow even in contact with flowing water;
- mechanically, physically and chemically stable for handling, transport and disposal.

Although cement has several unfavorable characteristics as a solidifying material, e.g. low volume reduction and relatively high leachability, it possesses many practical advantages: good mechanical characteristics, low cost, easy operation and radiation and thermal stability. It is generally assumed that the cement leachability of ^{137}Cs and other radionuclides can be reduced by adding minerals like bentonite, vermiculite and zeolite. Zeolite

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was excluded for reasons of economy and availability; of the above minerals, a natural bentonite is especially preferable from our leaching tests [6,9].

2. Materials and methods

The cement specimens were prepared from a standard Portland cement. The cement was mixed with saturated wet spent cation exchange resins (100 g of dry resins + 100 g of water containing ^{60}Co and ^{137}Cs, both as nitrates, pH = 8.4–8.8), shown in Table 1 (panel A), and bentonite clay (63% SiO_2; 18% Al_2O_3; 4% Fe_2O_3; 2.6% MgO and 3.3% CaO). Also, cement was mixed with saturated wet spent mix bead ion exchange resins, shown in Table 1 (panel B). The mixtures were cast into 50 mm diameter cylindrical molds with a height of 50 mm, approximately 100 g, which were then sealed and cured for 28 days prior to the leaching experiments [5,6].

More then 100 different cement formulations were examined to optimize their mechanical and sorption properties. In this paper we discuss the sixteen best formulations with respect to mechanical characteristics.

3. Experiments

Samples for leachability determination were prepared according to the IAEA standard procedure [1]. The leachant was exchanged and analyzed for radioactivity after: 1, 2, 3, 4, 5, 6, and 7 days, and thereafter every week for one month and after that every month, until the 245th day. After each leaching period the radioactivity in the leachant was measured using EG&G-ORTEC spectrometry system and software. The volume of the leachant in every leaching period was 200 ml.

Preliminary testing of grout compressive strength used a classical method, which is practiced in civil engineering. Cube shaped of grout samples $10\times10\times10$ cm were used. Compressive strength is express in MPa.

4. Mathematical treatment of data

The results are expressed by incremental leaching rates R_n (cm/d):

$$R_n = \frac{\sum a_n}{A_0}\frac{V}{S}\frac{1}{\sum t} \quad (\mathrm{cm/d}), \tag{1}$$

where a_n is the radioactivity of leached constituent during each leaching interval (Bq); A_0, the specific radioactivity initially present in the specimen (Bq); S, the exposed surface area of the specimen (cm^2); V, the sample volume (cm^3); t, the duration of the leaching period (d).

The apparent diffusivity D_e is calculated from equation:

$$D_e = \frac{\pi}{4}m^2\frac{V^2}{S^2} \quad (\mathrm{cm^2/d}), \tag{2}$$

where m is the slope of the straight line, obtained from a plot of $\sum a_n/A_0$ versus $\sqrt{\sum t_n}$ ($d^{-1/2}$).

5. Mechanical characteristics

Compressive strength (M), expressed in MPa, was measured on $10\times10\times10$ cm cubes.

Table 1
Grout composition (calculated as grams of (panel A) spent cation and (panel B) spent mix bead ion exchange resins for 1000 cm^3 of mixtures)

Materials (g)	Formula							
	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8
Panel A								
Spent cation exchange resins	350	350	350	350	290	290	290	290
Portland cement	1270	1280	1315	1270	1340	1335	1380	1340
Water	280	275	260	258	308	320	300	308
Bentonite clay	26	38	15	20	54	66	0	0
	M_9	M_{10}	M_{11}	M_{12}	M_{13}	M_{14}		
Panel B								
Spent mix bead ion exchange resins	327	331	324	327	298	301		
Portland cement	1308	1312	1337	1297	1383	1338		
Water	270	270	284	270	300	308		
Bentonite clay	26	39	53	64	0	0		

Initial activity $A_0 = 8.0 \times 10^7$ Bq per sample (^{60}Co and ^{137}Cs).

Table 2
Incremental leach rate R_n (cm/d) and apparent diffusivity D_e (cm^2/d) ^{60}Co and ^{137}Cs after 245 days, for (panel A) spent cation and (panel B) mix bead ion exchange resins

Radionuclide	Formula							
	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8
Panel A								
R_n ^{60}Co$\times 10^5$	4.72	4.66	5.52	6.82	4.21	4.41	7.03	6.73
R_n ^{137}Cs$\times 10^4$	5.22	5.01	5.12	5.42	3.21	3.61	6.53	6.63
D_e ^{60}Co$\times 10^6$	1.90	1.90	1.80	1.90	1.10	1.20	4.00	4.00
D_e ^{137}Cs$\times 10^5$	14.00	1.50	7.00	7.50	5.20	5.20	24.00	26.00
	M_9	M_{10}	M_{11}	M_{12}	M_{13}	M_{14}	M_{15}	M_{16}
Panel B								
R_n ^{60}Co$\times 10^5$	4.60	4.62	5.50	6.80	4.20	4.38	7.00	6.70
R_n ^{137}Cs$\times 10^4$	5.18	5.00	5.06	5.38	3.20	3.58	6.42	6.48
D_e ^{60}Co$\times 10^6$	1.90	1.88	1.62	1.78	1.00	1.12	3.80	3.82
D_e ^{137}Cs$\times 10^5$	13.00	1.47	6.90	7.40	5.16	5.18	23.20	25.80

Table 3
Compressive strength M (MPa) of samples after 28 days

	Formula							
	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8
Sample 1	26.0	26.5	26.2	26.2	26.7	27.0	29.0	29.0
Sample 2	26.0	26.4	26.1	26.3	26.4	27.1	29.0	29.1
	M_9	M_{10}	M_{11}	M_{12}	M_{13}	M_{14}	M_{15}	M_{16}
Sample 1	28.0	27.5	26.8	26.9	27.0	27.4	29.8	29.8
Sample 2	28.1	27.4	26.9	26.8	27.4	28.1	29.6	29.6

6. Results

The results of the leaching tests of immobilized spent cation exchange resins are given as the incremental leaching rate, R_n (cm/d), after 125 days. Testing of mechanical characteristics of the cement composite was performed with each of the eight samples, by taking arithmetical mean value of tree sample results. Table 2 gives the results of incremental leach rate R_n (cm/d) and apparent diffusivity D_e (cm^2/d) after 245 days, correcting for the decay ^{60}Co and ^{137}Cs.

Table 3 gives compressive strength M (MPa) of eight samples after 28 days.

7. Discussion

This manuscript describes the successful way of immobilization of spent ion exchange resins as a radioactive waste by cement. On the basis of the leaching rate, as the most important characteristic of cement – waste composition, we can predict percentage of leaching during next 300 years (10 half-lives of ^{137}Cs). At the end of this period radioactivity will have decreased more than a thousand times and safety standards will be reached. Although mechanical characteristic is less important, we use it for optimization and selection of sixteen cement-based formulations. Variation in diffusion characteristic is influenced by the amount of bentonite as a sorption material. Contributions of 1–5% bentonite in cement-based formulations are used because higher amounts of bentonite will reduce mechanical characteristic.

Values for diffusion characteristic for ^{60}Co ($1.0–4.0)\times 10^{-6}$ cm^2/d and ^{137}Cs ($0.5–2.6)\times 10^{-4}$ cm^2/d after 245 days, guarantee that only 1–2% of radionuclides will leach into environment.

Results presented in this paper are part of the results obtained in a 20-year grout and concrete testing project, which will influence the design of a future Serbian radioactive waste disposal center.

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