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

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Abstract. The leaching rate of ^{60}Co and ^{137}Cs from the spent cation 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 leaching rates from the cement–bentonite matrix for ^{60}Co : $(4,2–7,0) \times 10^{-5}$ (cm/d) and ^{137}Cs : $(3,2–6,6) \times 10^{-4}$ (cm/d), after 125 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 for ^{60}Co : $(1,1–4,0) \times 10^{-6}$ (cm^2/d) and ^{137}Cs : $(0,5–2,6) \times 10^{-4}$ (cm^2/d), after 125 days. The results presented in this paper are part of the results obtained in a 20-year mortar and concrete testing project which will influence the design of radioactive waste management for a future Serbian radioactive waste disposal centre.

Keywords. Cement; radioactive waste; composite; waste management.

1. Introduction

Ion exchange may be used most successfully for the removal of radioactive ions from dilute solutions. This process produces deionized water, as 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 (Andersson *et al* 1981; Atkinson and Nickerson 1988). Only when the cement is mixed with a material having a significant sorption capacity, normally bead or powdered ion exchange resins, the leachability of cesium and cobalt from the cement matrix is low enough to be acceptable (Hespe 1971; Plecas *et al* 1985, 1990, 1992).

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 though flowing water may contact them and mechanically, physically and chemically stable for handling, transport and disposal.

Although cement has several unfavourable characteristics as a solidifying material, i.e. 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. Whereas zeolite was excluded for economy and availability reasons, out of the above and other minerals, a natural bentonite is especially preferable in our leaching tests (Torstenfeld and Hedin 1988).

2. Materials and methods

The cement specimens were prepared from construction cement which is basically a standard Portland cement. The cement was mixed with saturated wet cation exchange resins (100 g of dry resins + 100 g of water containing ^{60}Co and ^{137}Cs) and bentonite clay (63% SiO_2; 18% Al_2O_3; 4% Fe_2O_3; 2,6% MgO and 3,3% CaO). The mixtures were cast into 50 mm diameter cylindrical molds with a height of 50 mm, which were then sealed and cured for 28 days prior to the leaching experiments (Plecas *et al* 1985, 1990).

More than 100 different formulations of mortar form were examined to optimize their mechanical and sorption properties. In this paper we discuss eight representative

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formulations. Grout composition formulas are shown in table 1.

3. Experimental

Samples for leachability determination were prepared according to the IAEA standard procedure (Hespe 1971). Leachant was exchanged and analysed for radioactivity after 1, 2, 3, 4, 5, 6, 7 days, and thereafter every week for 1 month and from there on every month, until 125th 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 was done using a classical method which is practiced in civil engineering. Cube shaped grout samples of $10 \times 10 \times 10$ cm were used. Compressive strength was expressed in MPa.

4. Mathematical treatment of data

The results are expressed by incremental leaching rate, R_n(cm/d), as

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

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) and t the duration of leaching period (d).

The apparent diffusivity, D_e, is calculated from

$$D_e = \frac{\pmb{p}}{4} m^2 \frac{V^2}{S^2} (\text{cm}^2/\text{d}), \qquad (2)$$

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

5. Results and discusion

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. Although there are experimental results before 125th day, which are not given in this paper, leaching rate of ^{60}Co and ^{137}Cs does not indicate any significant difference in leaching.

Table 2 gives the results of incremental leach rate, R_n (cm/d) and apparent diffusivity, D_e(cm^2/d) after 125 days, keeping in view the decay of radionuclides (^{60}Co and ^{137}Cs). A significant difference in leaching and in apparent diffusivity of ^{60}Co and ^{137}Cs in immobilized spent cation exchange resins, was observed and give us a possibility to extrapolate leachability in next 20 years and more. Analysis of the results presented in table 2 shows that the values are very similar to the literature data and proves that cement–bentonite matrix permits secure preservation of radionuclides for more than 300 years. Results presented in this paper are part of the results obtained in 20-year grout and concrete testing project which will influence the design of a radioactive waste management for a future Serbian radioactive waste storing centre. Testing of mechanical characteristics of cement matrix was performed with each of the eight samples. Table 3 gives compressive strength of 8 grout compositions in MPa.

Table 1. Grout composition (calculated as grams 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
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

Initial activity, $A_0 = 8{,}0 \cdot 10^7$ 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) of ^{60}Co and ^{137}Cs after 125 days.

Radionuclide	Formula							
	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8
R_n ^{60}Co $\times 10^5$	4,70	4,65	5,50	6,80	4,20	4,40	7,00	6,70
R_n ^{137}Cs $\times 10^4$	5,20	5,00	5,10	5,40	3,20	3,60	6,50	6,60
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

Table 3. Compressive strength, *M* (MPa).

Formula							
M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8
28,5	29,0	29,0	29,5	24,0	23,4	25,0	24,0

Acknowledgement

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