LEACHING OF ^{137}Cs FROM SPENT ION EXCHANGE RESINS IN CEMENT-BENTONITE CLAY MATRIX

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Abstract

The leaching rate of ^{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^{137}Cs:(3.2-6.6)×10^{-4}(cm/d), after 125 days were measured. From the leaching data the apparent diffusivity of cesium in cement-bentonite clay matrix with a waste load of 290-350 (kg/m^3) spent cation exchange resins was measured for ^{137}Cs: (1,5-26)×10^{-5}(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 radioactive waste disposal center.

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 ^{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.[1,2] 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.[3,4,5,6]

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,
- mechanically, physically and chemically stable for handling, transport and disposal.

Although cement has several unfavorable 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 reasons of economy and availability, out of the above and other minerals, a natural bentonite is especially preferable in our leaching tests.[6,7]

Results and discussion

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,(100gr. of dry resins +100 gr. of water containing ^{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.[5] More then 100 different formulations of mortar form were examined to optimize their mechanical and sorption properties. In this paper we discuss eight representative formulations. Grout composition formulas are shown in Table I.

Table 1. Grout Composition (calculated as grams for 1000 cm^3 of mixtures).

	Formula							
Materials (g)	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8
cation exchange resines	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 (^{137}Cs), $A_o = 8.0\times10^7$ Bq/per sample.

Leachant was exchanged and analyzed for radioactivity after 1,2,3,4,5,6,7 days, and thereafter every week for 1 month and from there on every month. After each leaching period the radioactivity in the leachant was measured by gamma counting. The volume of the leachant in every leaching period was 200 mL.

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

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

where:

a_n - the radioactivity of leached constituent during each leaching interval (Bq)
A_o - 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:

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

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

Testing of compressive strength is a classical method, which is practiced in civil engineering. Cube shaped mortar samples 10×10×10 cm were used. Compressive strength (M) is expressed in MPa. 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 cement matrix was performed with each of the eight samples. Table II gives the results of incremental leach rate R_n(cm/d) and apparent diffusivity D_e(cm^2/d) after 125 days, keeping in mind the decay of ^{137}Cs.

Table 2. Incremental leach rate R_n(cm/d) and apparent diffusivity D_e(cm^2/d) of ^{137}Cs after 125 days.

	Formula							
Radionuclide	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8
R_n ^{137}Cs ×10^4	5.20	5.00	5.10	5.40	3.20	3.60	6.50	6.60
D_e ^{137}Cs ×10^5	14.00	1.50	7.00	7.50	5.20	5.20	24.00	26.00

Conclusion

A significant difference in leaching and in apparent diffusivity of ^{137}Cs in immobilized spent cation exchange resins was observed. Analysis of the results presented in Table II shows that the values are very similar to the literature data[5,7,8,9] 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 10-year grout and concrete testing project, which will influence the design of a radioactive waste management for a future radioactive waste disposal center.

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Povzetek

Določili smo hitrosti izluževanja ^{137}Cs iz utrjenih izrabljenih smol ionskih izmenjevalcev v cementno bentonitnih zmeseh. Za utrditev smo uporabili različne betonske zmesi Portland cementa z ali brez 2 - 5% dodatka bentonita in z umešanimi določenimi količinami izrabljenih smol ionskih izmenjevalcev (290 - 350 kg/m^3-zmesi). Imerjene hitrosti izluževanja (R_n) v izluževalnih testih po 125 dneh so bile za ^{137}Cs: (3,2 - 6,6) x 10^{-4} (cm/dan), in iz teh meritev izračunane difuzivnosti (D_e) za ^{137}Cs: (1,5 - 26) x 10^{-5}(cm^2/dan). Te meritve so del 20 letnega projekta preizkušanja betonskih in maltnih materijalov za utrjevanje radioaktivnih odpadkov in so med drugim podlaga za načrtovanje ravnanja z radioaktivnimi odpadki v bodočem centralnem odlagališču.