Short communication

Sorption of radionuclides by cement-based barrier materials

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ABSTRACT

This paper investigates the sorption of radionuclide ions, $^{137}Cs^+$ and $^{90}Sr^{2+}$, by cement-based barrier materials for radioactive waste disposal. A mortar with ternary binder is prepared and powder samples are ground from the hardened material following a predetermined granulometry. After pre-equilibrium with an artificial pore solution, the sorption behaviors of powder samples are investigated through single sorption and blended sorption. The results show that: (1) no systematic difference is observed for single and blended sorptions thus the interaction between $^{137}Cs^+$ and $^{90}Sr^{2+}$ sorptions must be weak; (2) the sorption kinetics is rapid and all characteristic times are less than 1d; (3) the sorption capacity is enhanced by C–A–S–H hydrates and the measured K_d values can be predicted from C–S–H sorption data with Ca/Si ratio equal to Ca/(Si + Al) ratio.

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1. Introduction

The disposal of radioactive wastes (radwaste) from nuclear power plants has constantly been a high-lightened technical issue in the past decades [1]. Cement-based materials are used both in low-level and intermediate-level radwaste disposal as engineered barriers [2,3] and in high-level radwaste (geological) disposal as facilities or buffer materials [4]. The safety assessment of these facilities is usually related to the radionuclide migration through water-percolated pore structure of materials [5,6]. For this purpose, systematic modeling has been proposed for multi-barrier structures of disposal [7,8], while other authors investigated the long term evolution of pore structure and pore chemistry, e.g. by leaching, on the radionuclide migration process [9,10].

For safety assessment, the sorptivity of radionuclides by cement-based barrier materials is one key parameter. Compared to geotechnical materials, sorption data for cement-based materials are relatively in dearth [11–13]. The sorption behaviors of cement-based materials differ from geotechnical materials in that the pore solution provides a high alkaline environment and the hydrates show very different sorption capacity according to their mineral composition [14–16]. For mortar and concrete, the $^{137}Cs^+$ ions can be sorbed onto both hardened cement paste (HCP) and aggregates [17]. The calcium silicate hydrates (C–S–H) are judged to be the main absorbent in HCP, and other minerals show very low sorption capacity [14,18]. The Cs sorption by C–S–H is regarded as an ion-exchange process between Cs^+ and alkaline ions (Na^+, K^+) on negatively charged sites [19], or acidic silanol (Si–OH) sites [20]. The sorption of $^{90}Sr^{2+}$ by cement-based materials is attributed to HCP and the incorporated aggregates, and C–S–H hydrates are also judged as the only efficient absorbent through ion-exchange processes [21]. For

both Cs^+ and Sr^{2+} ions, the sorption capacity of C–S–H is found to be determined by the Ca/Si ratio and ion strength in pore solution: larger Ca/Si ratio and high ion strength tend to decrease the sorption capacity of C–S–H hydrates [22]. An extensive review of sorption mechanisms of cement-based materials of radionuclides can be found in [14].

This paper investigates experimentally the sorption behaviors of a typical cement-based barrier material with respect to the radionuclides of $^{137}Cs^+$ and $^{90}Sr^{2+}$. Both the sorptivity and the sorption kinetics are studied and compared to the literature sorption data, and peculiar attention is given to the difference between the single radionuclide sorption ($^{137}Cs^+$ or $^{90}Sr^{2+}$) and the sorption of blended radionuclides ($^{137}Cs^+$ and $^{90}Sr^{2+}$).

2. Experimental procedure

2.1. Materials and samples

A mortar used as barrier material for near surface disposal of radwaste is investigated in this study. The binder of mortar contains 30% Portland cement, 65% slag (GGBS) and 5% silica fume (SF). The cement is PI type [23], equivalent to CEM I in European Standards [24]. A quartz sand is used as aggregates according to ISO standard [25] with the size range of 0.08–2.0 mm. The chemical composition for the raw cementitious materials is given in Table 1 and the mix proportioning is given in Table 2. The mortar is cast into cubic molds of 4 cm × 4 cm × 4 cm, cube specimens are demoulded at age of 1d and put into standard curing conditions (20 °C and humidity above 95%) and cured to the age of 56d. Then cube specimens are crushed and ground into powder, the powder is sieved, and the grain size between 0.076 mm and 1.25 mm is retained for sorption tests. The granulometry of sieved powder is: mass ratio of 12.57% for particle size between 0.076 mm and 0.16 mm, 24.18% for 0.16–0.4 mm, 13.31% for 0.4–0.56 mm, 23.34% for

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Table 1
Chemical composition of raw materials of the mortar.

Material	Composition (%)							SSA	Density
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O (eq.)	(m^2/kg)	(g/mL)
Cement	22.02	4.00	3.48	62.12	2.58	2.72	0.53	343	3.10
GGBS	32.86	16.38	0.97	36.31	9.37	2.28	–	449	2.78
SF	95.00	0.30	0.80	0.40	0.30	0.50	0.90	20,000	2.20

0.56–0.90 mm, and 26.61% for 0.9–1.25 mm. The powder samples are then sealed into a container to limit the possible carbonation.

Meanwhile, crushed particles of 5 mm are prepared for the pore structure characterization through mercury intrusion porosimetry (MIP). The MIP results are provided in Table 2 for porosity, apparent density and pore specific surface. From parallel tests the MIP results for HCP at the same age are also presented. To better quantify the sorption behaviors of mortar, the hydration characteristics of the blended binder are also provided, including the overall hydration extent and the composition of calcium silicate hydrates (C–S–H). The results are obtained from a hardened cement paste with the same blended binder and w/b ratio. The hydration extent is quantified from cement hydration extent and slag hydration extent through EDTA selective dissolution method [26]. The relative content of low density C–S–H (LD–CSH) and high density C–S–H (HD–CSH) is determined through nano-indentation tests [27], and the Ca/Si and Ca/(Si + Al) ratios are quantified by EDX method associated with the SEM observation [26]. The Ca/Si and Ca/(Si + Al) ratios are average results of EDX analysis on about 30 sites on Al-incorporated C–S–H hydrates. Later, these data are used to evaluate the radionuclide sorptivity of mortar samples.

2.2. Sorption tests

The sorption tests begin with the equilibrium treatment of the powder samples with the pore solution of mortar. An artificial pore solution is retained for the equilibrium treatment with composition as follows: Na^+ 1600 mg/L, K^+ 6300 mg/L, Ca^{2+} 40 mg/L and OH^- 3963 mg/L, and the pH value of solution is 13.4. This composition is considered representative for mortars incorporating slag in binder, and has been used to study the sorption of $^{137}Cs^+$ ions [28]. Totally 1600 mL of artificial pore solution is prepared for the pre-equilibrium treatment. The treatment consists of two phases: (1) powder sample of 10.0 g is put into 100 mL pore solution and encapsulated in one plastic bottle, seven bottles are prepared in total; then the powder samples are kept in equilibrium with the pore solution for 7d, and the pore solution is stirred for 15 min per day; (2) the powder samples are filtered out

Table 2
Mortar mixture, pore structure and hydration characterization.

Composition/characterization		Mortar
Mixture	Cement PI (kg/m^3)	187
	Slag (kg/m^3)	406
	Silica fume (kg/m^3)	31
	Water (kg/m^3)	281
	Water to binder ratio (−)	0.45
	Quartz sand (kg/m^3) (0.08–2.0 mm)	1325
MIP results	Porosity/Mortar (−)	19.5%
	Bulk density/HCP (g/cm^3)	2.23
	Bulk density/mortar (g/cm^3)	2.51
	Pore surface area/HCP (m^2/g)	109.64
	Pore surface area/mortar (m^2/g)	44.34
Hydration (90d)	Hydration extent (−)	0.51
	LD–CSH content (−)	0.13
	HD–CSH content (−)	0.33
	CSH Ca/Si ratio (−)	1.31
	CSH Ca/(Si + Al) ratio (−)	1.18

and put into equilibrium with fresh pore solution again for a second period of 14d.

The seven bottles are labeled according to their respective sorption tests: A1 and A2 are for single Cs sorption, B1 and B2 for blended (Cs + Sr) sorption tests, C1 and C2 for single Sr sorption, and D the backup bottle for powder sample in equilibrium. After the pre-equilibrium treatment, 250 mL clear solution is extracted from the bottles, i.e. 25 mL from each of A1, A2, C1 and C2 bottles, and 50 mL from each of B1, B2 and D bottles. Then the radionuclide sources (in glass flacons) of $^{137}Cs^+$ and $^{90}Sr^{2+}$ are diluted and washed by the collected pore solution, giving 104 mL solution for $^{137}Cs^+$ and 104 mL solution for $^{90}Sr^{2+}$. Then liquid sample of 2 mL is taken from each radionuclide solution to determine the initial radionuclide concentrations through radioactivity measurement. Then 25 mL of diluted $^{137}Cs^+$ solution is put back into each bottle of A1, A2, B1 and B2, and 25 mL of diluted $^{90}Sr^{2+}$ solution is put back into each bottle of B1, B2, C1 and C2. This procedure ensures the same radionuclide concentrations in single sorption tests (A1, A2, C1, C2) and in the blended sorption tests (B1, B2).

Note this instant as starting time for sorption tests. Liquid samples of 2 mL are extracted from the six bottles (A1/2, B1/2, C1/2) for time instants of 6 h, 1d, 7d, 42d and 90d. During the sorption tests the bottles are stirred for 30 min per day. The whole sorption tests are performed with the ambient temperature controlled to 25 °C. Totally 32 liquid samples, including 2 samples for initial concentrations and 30 samples during sorption tests, are measured for the radioactivity of $^{137}Cs^+$ and $^{90}Sr^{2+}$. The radioactivity analysis method for $^{137}Cs^+$ is gammaspectrometry with the measurement error within 1%. The radioactivity analysis for $^{90}Sr^{2+}$ is effectuated through liquid scintillation method and the measurement error is within 4.2%.

3. Sorption behaviors

3.1. Radionuclide sorption

The concentrations of radionuclides in artificial pore solution during the sorption tests are given in Fig. 1. The concentrations are given both in terms of radioactivity (Bq/L) and molar concentration (mol/L). The curves represent the average of results of two samples in each sorption group (A1/2, B1/2, C1/2) and the dispersion between the two samples in each sorption group is represented by the error bar in the curves. The initial concentration for $^{137}Cs^+$ is around 0.84×10^{-9} mol/L while the initial $^{90}Sr^{2+}$ concentration is about 0.28×10^{-9} mol/L. The sorption for both radionuclides, through the decrease of radionuclide concentration in pore solution, evolves rapidly. The powder samples are observed to have a larger sorption capacity for $^{90}Sr^{2+}$ than for $^{137}Cs^+$, i.e. the sorption of samples reduces $^{137}Cs^+$ concentration just from 0.84×10^{-9} mol/L to 0.73×10^{-9} mol/L but this decrease is from 0.28×10^{-9} mol/L to 0.004×10^{-9} mol/L for $^{90}Sr^{2+}$ at the end of 90d.

On the same figure, one can further compare single sorption with blended sorption. For $^{137}Cs^+$, the concentration in single sorption is slightly higher than the concentration in blended sorption in terms of average concentration of two samples (A1/2, B1/2). This difference is quantified as 1.3%–1.7% for 7d, 42d and 90d, and this relative difference is very near to the radioactivity measurement error for $^{137}Cs^+$, 1%. For $^{90}Sr^{2+}$, this difference is evaluated as 1%–3.5% for average concentrations, always within the radioactivity measurement error 4.2%. That is, no systematic difference is measured for single and blended Sr sorptions in this study.

3.2. Sorption coefficients and kinetics

To quantify further the sorption behaviors, the concentration change of radionuclides is converted to the quantity of radionuclides sorbed by powder samples with time, cf. Fig. 2. On the figure, the sorption of radionuclides is denoted both by unit mass of solid sample (mol/kg) and by