

Carbonation-induced weathering effect on cesium retention of cement paste

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ARTICLE INFO

Article history:

Received 12 October 2017

Received in revised form

11 April 2018

Accepted 11 April 2018

Available online 12 April 2018

Keywords:

Radioactive waste disposal

Engineered barrier

Cement

Weathering

Adsorption

ABSTRACT

Carbonation is inevitable for cement and concrete in repositories over an extended period of time. This study investigated the carbonation-induced weathering effect on cesium retention of cement. Cement paste samples were exposed to accelerated carbonation for different durations to simulate the extent of weathering among samples. The extent of carbonation in cement was characterized by XRD, TG and NMR spectroscopy, while the retention capacity for cesium was investigated by zeta potential measurement and batch adsorption tests. Though carbonation led to decalcification from the binder gel, it negatively charged the surface of cement hydrates and enhanced their cesium adsorption capacity.

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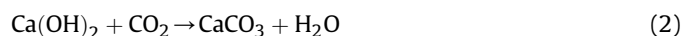
1. Short communication

The role of cement pastes in a radioactive waste repository is vital. Cement is used to produce cemented waste forms for the immobilization of low- and intermediate-level radioactive waste [1–3], cementitious backfill [4–6], and engineered barriers in repositories [7,8]. Cement pastes effectively act as multiple barriers and has a multifunctional role by preventing the release of radionuclides, isolating disposed radioactive waste and preserving the entire structural integrity of the repository. However, these performances of cementitious materials can significantly be affected by the external environment over time [9]. The carbonation of cement is one of the chemical degradation phenomena that cement generally is subjected to in a repository environment [10]. Carbonation of cement pastes naturally occurs in atmospheric conditions because CO₂ dissolves in the interstitial solution of the pores of a hardened cement matrix shown by Eq. (1) [11].

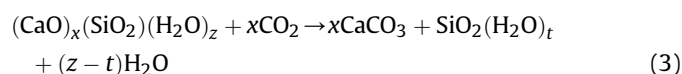


In the presence of portlandite, the carbonation reaction of this

phase occurs as shown in Eq. (2) [12,13], prior to the main binding phase, such as calcium silicate hydrate (C-S-H), and the secondary phases, such as AFt and AFm.



Furthermore, the decalcification of C-S-H can occur after the carbonation of portlandite is complete, because the stability of C-S-H is highly associated with the alkalinity of the pore solution [12,13]. The carbonation reaction of C-S-H can cause decalcification from the silicate chain and precipitate CaCO₃ shown in Eq. (3) [12,13].



The carbonation reaction of cement pastes can be considered in terms of two contrasting aspects. The removal of Ca(OH)₂ and the precipitation of CaCO₃ essentially densify the microstructure and significantly reduce the pore network, decreasing the permeability of a cement matrix [14,15]. This aspect was seen to be effective for the immobilization of radionuclides in a solidified waste form made of carbonated cement [16,17]. On the other hand, continuous carbonation of cement pastes leads to the decalcification of C-S-H, inducing a significant increase in the porosity and weakening the

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structural integrity of the cementitious matrix [18,19]. This can be a serious concern because transport through the cementitious matrix becomes easier due to the increased permeability [18,19]. Consequently, the performance of hardened cement for retention of radionuclides can vary depending on the extent of carbonation.

Another issue surrounding the use of cement in a repository is its low retention capacity for key radionuclides such as cesium. For instance, the effective diffusion coefficient of cesium solidified in Portland cement paste is significantly higher than that in alkali-activated cements [1]. Meanwhile, one may consider that the half-life of Cs is relatively short (~30 years) in relation to the rate of cement carbonation, and hence, carbonation-induced effect can be neglected when dealing with the release of radionuclides from hardened cement. However, radioactive Cs requires safe isolation in a solidified matrix for more than 300 years for its radioactive decay [20]. Moreover, the penetration rate of the carbonation front into ordinary Portland cement concrete can be as high as a millimeter per year in a natural carbonation condition [21,22]. The extent of carbonation significantly alters the pore solution chemistry, i.e., a pH of 12.5 while portlandite is present and <10.6 when C-S-H is fully carbonated [23]. Therefore, the overall chemical properties relating to the performance of cementitious materials for the retention of radionuclides such as sorption can be affected. In this context, the aim of the present study was therefore to assess the cesium retention performance of Portland cement in relation to the carbonation-induced structural changes occurring in the binder gel.

In this study, Type I Portland cement was used because it is widely appreciated for use in radioactive waste repositories on a real scale. Its chemical composition and physical properties are as follows: CaO = 62.5%, SiO₂ = 21.0%, Al₂O₃ = 5.9%, Fe₂O₃ = 3.2%, SO₃ = 2.1%, total alkali content = 0.8%, minor elements (MgO, Mn₂O₃, TiO₂, etc.) = 4.5%, density = 3.15 g/cm³ and Blaine fineness = 3300 cm²/g. Paste samples were fabricated with a constant water-to-cement (W/C) ratio of 0.5. The W/C of concrete used in a repository can vary significantly according to its application, while majority cases requires high flowability (i.e., cementitious grouts, backfill, etc.), hence, relatively high W/C ratio was employed in this study. Three curing regimes were adopted to manipulate different extents of carbonation in the paste samples. 'Sound' samples were kept in a sealed condition for 56 days to exclude the effect of natural carbonation. 'Partially carbonated' samples were cured in a condition identical to the sound samples for 28 days until a high degree of hydration was reached in the samples [24]. These samples were thereafter placed in an accelerated carbonation chamber for exposure to 10% CO₂ at 20 °C and 65% R.H. for a further 28 days. 'Fully-weathered' samples were carbonated for a longer duration, i.e., they were placed in the accelerated carbonation chamber at 1 day after the fabrication and exposed for 56 days. This curing regime was reported to accelerate hydration and carbonation of both unreacted clinkers and hydrates, leading to formation of phases (i.e., silica and alumina gel, and calcium carbonate) expected to be present in severely carbonated cement [25]. This was to ensure that severe extent of carbonation is simulated in the fully-weathered sample in a relatively short duration in a laboratory scale. The duration of the accelerated carbonation was intended to simulate various extents of carbonation (i.e., partial or severe carbonation) among the samples. All the samples were powdered to pass a 64 μm sieve before placing them into the carbonation chamber to ensure uniformity in the carbonation of the samples. At 56 days, all the samples were treated with acetone for 24 h and desiccated to arrest any further chemical reaction for chemical analysis. To simulate radioactive Cs, a stable isotope of cesium chloride (CsCl, 99% reagent grade, Duksan Pure Chemicals Co., Ltd., South Korea) was used. CsCl was dissolved in water to produce a solution with a Cs concentration of 100 ppm for a sorption test.

The experimental programs were systematically designed to (1) provide structural information of the samples, (2) characterize the samples produced by the various carbonation regimes, and (3) evaluate their performance for the retention of Cs. X-ray diffraction (XRD), thermogravimetry (TG) and solid-state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy were conducted for the first two objectives, while zeta potential measurements and batch adsorption experiments were conducted for the third objective.

XRD was conducted using an X'pert APD (PHILIPS, at KBSI Daegu Center) operated at 40 kV and 30 mA with an LFF Cu anode. The scan range and step size were 5–65° 2θ and 0.02, respectively. Phase identification was performed using the International Center for Diffraction Data (ICDD) PDF database. TG analysis was conducted using a TA Instruments Q600 device (PH407, KBSI Pusan Center). The samples were heated up to 800 °C at a rate of 10 °C/min in a N₂ environment. The solid-state MAS NMR spectroscopy was conducted using an Advance III HD instrument (9.4 T, Bruker, at KBSI Western Seoul Center). The solid-state ²⁹Si MAS NMR spectra were collected at a Larmor frequency of 79.51 MHz using a spinning rate of 11.0 and 6.0 KHz, respectively. A HX-CPMAS probe with a 4 mm o. D. zirconia rotor was used for both spectrometry. A pulse width of 1.6 μs and a relaxation delay of 20 s were used. The chemical shifts were referenced to tetra-methyl silane. The ²⁹Si MAS NMR spectra are the accumulation of at least 4000 scans. The solid-state ²⁷Al MAS NMR spectra were collected at 104.296 MHz with a spinning speed of 14.0 kHz. A HX-CPMAS probe with a 4 mm low-Al zirconia rotor was used. A pulse width of 1.2 μs and a relaxation delay of 2 s were used. The chemical shifts were referenced to an external sample of aqueous AlCl₃ at 0 ppm. The ²⁷Al MAS NMR spectra are the accumulation of 1200 scans. All NMR spectroscopy was conducted at room temperature.

The zeta potential of the samples was measured using an ELS-Z2 (Otsuka Electronics). 1.25 g of the samples were suspended in 500 mL of deionized water (DW), i.e., a solid-to-solution ratio of 2.5 g/L. For the batch adsorption tests, a stock solution with a Cs⁺ concentration of 500 ppm was prepared by dissolving 0.317 g of CsCl into 500 mL of DW. Solutions with a Cs⁺ concentration of 100 ppm were prepared by diluting the stock solution in DW. 0.5 g of each sample and 500 mL of solution were mixed in a polypropylene vessel with a volume of 1000 mL. The container was stored at 20 °C, and shaken twice a day. The solutions were sampled 90 h after the placement of the mixture in the container, i.e., when equilibrium was reached [26]. The Cs⁺ concentration in the sampled solution was measured by inductive coupled plasma mass spectrometry using an NexION 300D instrument (PerkinElmer). The Cs⁺ concentration of the starting solutions was also measured. The obtained result was used to calculate the adsorption capacity q_e (mg/g, expressed in Eq. (4) [27]) of each sample with the different extents of the carbonation.

$$q_e = \frac{(c_0 - c_e)V_s}{m_s} \quad (4)$$

Here, c_0 and c_e are the concentrations of Cs⁺ in the sampled solution at $t = 0$ and when the equilibrium is reached; V_s is the volume of the solution, and m_s is the mass of the powdered sample [27]. The distribution factor K_d (L/kg) was computed by Eq. (5) as follows [28].

$$K_d = \frac{(c_0 - c_e)}{c_e} \times \frac{V_s}{m_s} \quad (5)$$

The XRD patterns of the cement paste samples with various degrees of carbonation-induced weathering are shown in Fig. 1. The XRD pattern of the sound sample showed peaks corresponding to

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