



Analysis of calcium leaching behavior of plain and modified cement pastes in pure water

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ABSTRACT

The calcium ion leaching behavior of cement pastes modified with a high-alkali fine glass powder, silica fume, and fly ash, exposed to deionized water, is reported in this paper. Porosity enhancement in pastes subjected to leaching is attributed both to the dissolution of calcium hydroxide (CH) as well as decalcification of C–S–H gel. A methodology that combines the measured porosity increase along with the CH and C–S–H contents remaining after leaching for a particular duration is developed to separate the porosities created due to CH and C–S–H leaching. In order to quantify the influence of leaching on the amounts of Ca ions remaining in the CH and C–S–H phases, solid–liquid equilibrium curves for calcium are developed for the unleached and leached pastes. Leaching depths are also calculated using the CH contents of the leached and unleached specimens. All the modified pastes show better leaching resistance than the plain paste. In addition to the microstructure densification, the lower Ca–Si molar ratio in modified pastes that reduces the equilibrium liquid Ca ion concentration contributes to this observation. For the glass powder modified paste, the presence of higher alkali content in the pore solution further reduces the dissolution of CH due to common ion effect, thus providing it with the highest leaching resistance. Fly ash and silica fume modified pastes demonstrate leaching resistance in between those of the plain and glass powder modified mixtures.

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1. Introduction

Leaching of calcium ions from cement paste matrix is of concern in concrete structures used for radioactive waste disposal, and underground and underwater members that are constantly exposed to low pH environment. Pure or deionized water is one of the strong decalcifying agents of cement based materials [1–3]. Leaching is a combined diffusion–dissolution/precipitation process. The concentration gradients between the pore solution and the pure water cause diffusion of calcium ions from the pore solution to the surrounding ion free water. The reduction in concentration of calcium ions in the pore solution forces the dissolution of calcium hydroxide (CH) and calcium–silicate–hydrate (C–S–H) gel [3–6]. This results in increased material porosity, and consequently increased permeability, and reduced mechanical properties [7–9]. The influence of porosity on leaching, and the changes induced in the pore structure because of leaching are detailed in [10,11]. Models to explain the degradation kinetics and property changes due to leaching either individually or in combination with other chemical processes have been reported [12–15].

The use of silica fume or fly ash as supplementary cementing materials is reported to result in reduced calcium leaching

[16,17]. A recent study [18] has investigated the use of silica nanoparticles to control calcium leaching in cement pastes. Apart from the pozzolanic reaction of nano-silica that reduces the porosity, this study showed that nano-silica modifies the internal structure of the C–S–H gel by increasing the average length of silicate chains, which increases calcium stabilization. Increase in silicate anion chain length of C–S–H gel with increase in dissolution (or reduction in Ca–Si molar ratio of the solid phase) has also been reported in [19]. Some studies [5,20,21] have reported that C–S–H gel begins to dissolve only after complete dissolution of CH, i.e., dissolution reactions do not occur concurrently. However, other authors [19,22] have reported that CH does not have to dissolve completely for C–S–H dissolution to occur, and this is a function of the mass (or volume) ratios of the leachant to the solid. For lower liquid-to-paste mass or volume ratios CH preferentially dissolves, while both CH and C–S–H dissociation are reported to occur in powdered samples of pastes for liquid-to-paste mass ratios (m_l/m_p) higher than 500 [19]. This value will change with surface-to-volume ratios of the sample. The solubility product of the C–S–H gel is also a function of Ca–Si ratio of the gel [23,24].

This paper investigates the influence of two high silica cement replacement materials – a fine glass powder (72.4% SiO₂) and silica fume (93.4% SiO₂) – on the leaching resistance of cement pastes exposed to deionized water and compares the performance of these modified pastes to a plain paste and a fly ash modified paste.

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Table 1
Chemical composition and physical characteristics of the materials used.

Composition (% by mass)/property	Cement	Fine glass powder (GP)	Fly ash (FA)	Silica fume (SF)
Silica (SiO ₂)	20.2	72.5	50.24	93.4
Alumina (Al ₂ O ₃)	4.7	0.4	28.78	0.42
Iron oxide (Fe ₂ O ₃)	3	0.2	5.72	0.52
Calcium oxide (CaO)	61.9	9.7	5.86	1.91
Magnesium oxide (MgO)	2.6	3.3	1.74	–
Sodium oxide (NaO)	0.19	13.7	0.96 ^a	0.25
Potassium oxide (K ₂ O)	0.82	0.1	–	0.79
Sulfur trioxide (SO ₃)	3.9	–	0.51	0.34
Loss on ignition	1.9	0.36	2.8	2.3
Median particle size (μm)	13	20	20	<1
Density (kg/m ³)	3150	2490	2250	2200

^a Equivalent alkalis.

Porosity measurements and thermogravimetric analysis are conducted on unleached and leached specimens. The Ca ion content in CH and C–S–H phases before and after leaching are quantified using equilibrium curves for calcium. Indirect estimation of leaching depths from thermal analysis results is also reported.

2. Experimental program

2.1. Materials and mixtures

Type I/II ordinary Portland cement conforming to ASTM C 150 was used for all the mixtures described in this study. A Class F fly ash (FA) conforming to ASTM C 618, a dry densified silica fume (SF), and a fine glass powder (GP) were used as partial cement replacement materials. Several replacement levels of these supplementary cementing materials were studied, but in order to keep the discussions succinct, only the results for 10% replacement of cement by mass with fly ash and glass powder, and 6% replacement of cement by mass with silica fume (referred to as GP10, FA10, and SF6, respectively, in the graphs) will be discussed in this paper. The chemical composition and physical characteristics of materials used are given in Table 1. It can be seen that the median particle sizes of glass powder and fly ash are similar, and higher than that of the cement. All the pastes were prepared with a water-to-cementing materials ratio (w/cm) of 0.40.

The cement pastes were cast in prismatic molds of size 150 mm × 50 mm × 25 mm, and cured in saturated limewater for 90 days to facilitate hydration of cement and the replacement materials. After the curing duration, prismatic pieces of size 15 mm × 10 mm × 5 mm were cut from the larger specimens, and immersed in deionized water for leaching. The leaching tests were carried out in sealed containers filled with deionized water from which CO₂ was removed. A m_l/m_p of 1000 was used, and the leachant was not renewed during the duration of the tests.

2.2. Test methods

The unleached specimens (cured for 90 days), as well as those leached in deionized water for 28, 56, or 90 days, were subjected to porosity measurements as per the procedure described in [25]. The 15 mm × 10 mm × 5 mm size specimens were removed from the containers, surface-dried, and kept in an oven at 105 °C for 24 h. After cooling to room temperature, the initial masses (m_1) of the specimens were determined. The specimens were then vacuum dried for 3 h, after which they were saturated under vacuum for another hour, and left to soak in water for 18 h. The masses of saturated surface-dried specimens (m_2) were recorded. The difference between these masses was expressed as a percent of initial mass, then converted into a percent of the initial volume of the specimen, and reported as the porosity.

The unleached and leached specimens were subjected to thermogravimetric analysis (TGA) to determine the CH and C–S–H contents in the specimens. TGA was carried out before and after 28 and 90 days of exposure to deionized water. Any portion of the unleached specimen can be expected to provide the actual CH and C–S–H contents of the pastes in that state. However, in order to obtain the residual CH and C–S–H contents in leached specimens, a representative portion containing both the leached and unleached zones need to be used for TGA. This is accomplished by removing a 6 mm × 10 mm × 5 mm section of the leached specimen as shown in Fig. 1. Five sides of this representative zone are subjected to leaching, and the ratio of the total area of the leached surfaces to the volume of the representative zone is 0.76 mm⁻¹. For the entire specimen, though the leaching is from all six sides, the corresponding ratio is very similar (0.73 mm⁻¹). Similarly, if a leaching depth of 1 mm is assumed uniformly from all sides of the specimen, the ratio of the unleached volume to the total volume of the 15 mm × 10 mm × 5 mm specimen is 0.416. For the representative zone where leaching occurs in five of the six sides, the ratio of the unleached volume to the volume of the representative zone is 0.40. Therefore, from considerations of the surface area to volume ratios, and the unleached to leached volume ratios, the sectioned zone can be considered to be representative of the entire leached sample.

The powdered sample was heated from room temperature up to 1050 °C at the rate of 10 °C per min in a Perkin–Elmer thermogravimetric analyzer. The mass drop in the thermogravimetric curve at temperatures between 400 and 450 °C indicates loss of water from CH. The amount of CH in the specimen (in terms of percentage of mass of the sample at 105 °C) is calculated directly from the thermogravimetric curves using the following equation:

$$\text{CH (\%)} = \text{WL}_{\text{CH}} (\%) \times \frac{\text{MW}_{\text{CH}}}{\text{MW}_{\text{H}}} \quad (1)$$

where WL_{CH} corresponds to the mass loss in percentage attributable to CH dehydration, and MW_{CH} and MW_{H} are the molecular weights of CH and water, respectively.

Different temperature ranges in a thermogravimetric curve are reported to indicate the water loss from C–S–H gel. Previous studies have suggested temperature ranges of 180–300 °C [26], 200–400 °C [27], and from 105 °C until the water loss corresponding to CH dehydration [22]. In this study, the mass loss between 150 °C and the temperature at which CH loss begins (~400 °C) is considered to indicate the loss of water from C–S–H gel. The amount of C–S–H is calculated as:

$$\text{CSH (\%)} = \text{WL}_{\text{CSH}} (\%) \times \frac{\text{MW}_{\text{CSH}}}{2.1 * \text{MW}_{\text{H}}} \quad (2)$$

where WL_{CSH} corresponds to the mass loss in percentage that occurs during C–S–H dehydration, and MW_{CSH} and MW_{H} are the molecular

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