



Insight on the mechanism of sulfate attacking on the cement paste with granulated blast furnace slag: An experimental and molecular dynamics study

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HIGHLIGHTS

- Sulfate attack causes the decalcification and increases MCL in PC pastes.
- Sulfate ions react with the aluminate and produce the ettringite crystal.
- Sulfate ions carry interface Ca ions into the pore solution and form ionic cluster.
- C-S-H with low Ca/Si ratio has better sulfate resistance.
- GBFS incorporation resists the decalcification by sulfate attack to PC paste.

ARTICLE INFO

Article history:

Received 23 August 2017

Received in revised form 28 January 2018

Accepted 21 February 2018

Keywords:

Sulfate attack

Ca/Si ratio

Hydration degree

Mean chain length

Molecular dynamics simulation

Ionic cluster

ABSTRACT

Sulfate attacking to the marine concrete is detrimental to the material durability. To better understand the sulfate attacking mechanism, ²⁹Si and ²⁷Al MAS NMR spectroscopy combined with SEM-EDS techniques were utilized to investigate the microstructure of Portland cement paste (PC) and PC with granulated blast furnace slag (PC-GBFS) curing in both water and the sulfate sodium solution during 365 d. When the PC hydrated in sulfate sodium solution, the Ca/Si ratio reduces from 2.33 to 1.88 and the mean length of aluminosilicate chains for the C-A-S-H gel is elongated by 27.49%. It means that the sulfate ions de-calcificate the calcium ions in the C-A-S-H gel, enhancing the polymerization of its silicate tetrahedra. Meanwhile, Al[4]/Si ratio decreases from 0.026 to 0.011 and plenty of ettringite was also observed in the cement paste hydrating in sulfate sodium solution. Sulfate ions reacted with the aluminate species in the C-A-S-H gel, producing the ettringite crystal. On the other hand, the incorporation of GBFS in PC paste can reduce the effects of de-calcification and de-alumination significantly, effectively preventing the secondary formation of ettringite, and hence improving the stability of silicate-aluminate skeleton in C-A-S-H gel. Furthermore, molecular dynamics study was carried out to characterize the interaction between sulfate ions and C-A-S-H gel at a molecular scale. The sulfate ions carried interface Ca²⁺ ions into the pore solution to form ionic clusters of Ca-SO₄, leading to the decalcification of C-A-S-H gel. The C-A-S-H structure with intact aluminosilicate chain structure and low Ca/Si ratio in PC-GBFS has more stable Si-O-Ca bonding and the Ca ions can remain in the C-A-S-H gel for longer time.

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1. Introduction

As the ubiquitous construction and building materials, concrete has been widely utilized as the important material for the basic infrastructures. The hydration products and their microstructure are the fundamental units for the concrete materials and

determine the mechanical properties and durability of cement-based materials [29]. When concrete structures serve in the marine environment, they are more probable to be attacked by the detrimental ions [42,28]. For instance, SO₄²⁻, one type of common ions in seawater, can react with hydration products of cement-based material, change the chemical composition of phases and destroy the micro-scale morphology of the material, resulting in concrete degradation and even damage of the structure [13]. In order to elongate the service life of marine concrete and prepare more

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sustainable material, considerable researches have been carried out to reveal failure mechanism of cement-based material due to sulfate attack.

Gollop and Taylor [15] found that when the sulfate ions invaded into the cement-based material, the crystal phases were changed dramatically due to many chemical reactions. It involves the transition from AFm to ettringite, disappearance of calcium hydroxide, decalcification of Calcium-Silicate-Hydrate (C-S-H) gel and precipitation of gypsum. The phase change can further result in the development of micro-cracks, weakening the mechanical performances for the material. Irassar [19] systematically investigated the mechanism of sulfate attacking on cementitious material and divided the sulfate attack process into four stages: (1) SO_4^{2-} diffusion and portlandite leaching; (2) ettringite formation; (3) gypsum formation; (4) decalcification of C-S-H. Also micro-cracking was induced by the localized expansion stress during ettringite formation. Yu C. [43] studied the mechanism of expansion of mortars immersed in Na_2SO_4 solutions, and they proposed that the expansion damage of mortars was caused by transformation of monosulfate crystals embedded in the C-S-H to ettringite. Furthermore, Kunther [24] studied the influence of Ca/Si ratio of C-S-H on the ettringite crystallization pressure. The results showed that lowering Ca/Si ratio of C-S-H can decrease the crystallization pressure with respect to ettringite in the pore solution. The above studies have attributed the swelling failure and microcrack growth to secondary formation of ettringite or gypsum when sulfate ions penetrate into the pastes or mortars. In spite of many studies on the compositional and crystal phase changes due to sulfate attacking, few researches have paid attention to the microstructure evolution of calcium silicate hydrate (C-S-H) gel that is the main binding phase in cementitious pastes. On the other hand, modern cementitious pastes are often prepared with high volume of supplementary cementitious materials (SCMs) to partially substitute the cement. The pozzolanic reaction of these SCMs (such as fly ash and furnace slag) leads to more aluminum substituting into C-S-H gel, ie. C-A-S-H gel. Studies of Hou and Qomi show that C-A-S-H gel has a higher nanomechanical properties [18,36] and a better durability in seawater [12,20] than that of C-S-H gel. Hence, the compositional and microstructural variation of C-A-S-H gel becomes more important for the deterioration of pastes related to sulfate attack. Since there are aluminate phases in almost all the commercial cement clinkers and then aluminum substitution in C-S-H during cement hydration, in the following text, we would use C-A-S-H gel to define the binding phase in hydrated cement materials.

The objective of this paper is to investigate C-A-S-H microstructure evolution and aluminate hydrates transition in Portland cement (PC) paste and cement paste modified by Granulated Blast Furnace Slag (GBFS), as immersed in water and sodium sulfate solution. The microstructure of the cement hydrates were characterized by means of Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) and Scanning Electron Microscope Energy Dispersive Spectrometer (SEM-EDS). Furthermore, molecular dynamics simulations were also performed in order to have a better understanding of the mechanism for sulfate attack on C-A-S-H gel.

2. Experimental and computational procedure

2.1. Experimental procedure

2.1.1. Materials

The Portland Cement (PC) and Granulated Blast Furnace Slag (GBFS) used in this experiment are P.I 52.5 cement produced by Huangshi Huaxin cement Co. LTD, China and GBFS produced by Jiangnan grinding Co. LTD, China, respectively. The PC and GBFS

used have a specific surface of $374 \text{ m}^2/\text{kg}$ and $454 \text{ m}^2/\text{kg}$, respectively, with their chemical compositions given in Table 1.

2.1.2. Sample preparation

Pure cement paste and cement paste with 30 wt% of GBFS replacement were prepared at the water to binder ratio of 0.35. The fresh pastes were cast in plastic tubes, sealed in polyethylene bags and cured for 24 h in water before hardened and removed from plastic tubes. Then the hardened pastes were placed in pure water or 5 wt% Na_2SO_4 aqueous solution for 3 d, 28 d, 180 d and 365 d. After different time of exposure, the samples were cut into little cubes of the size of about $1 \text{ cm} \times 1 \text{ cm} \times 1 \text{ cm}$, which were quickly treated with absolute ethanol to stop the hydration process. The little cubes were then dried at 20°C in desiccator, then crushed and ground to fine powder for NMR measurements.

2.1.3. NMR measurements

The solid-state ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (^{29}Si and ^{27}Al MAS NMR) experiments were performed on Bruker Avance III 400 MHz spectrometers (magnetic field 9.4 T; larmor frequency of 79.5 MHz for ^{29}Si , 104.3 MHz for ^{27}Al) using a magic angle spinning (MAS) chemagnetics probes with 7 mm and 4 mm o.d. zirconia rotors for ^{29}Si and ^{27}Al , respectively. The NMR experiments used a pulse width of $1 \mu\text{s}$, pulse delay of 5 s, spinning speed of about 6 kHz and 2048 scans for ^{29}Si , and a pulse delay of 1 s, spinning speed of about 12 kHz and 2048 scans for ^{27}Al . Chemical shifts for ^{29}Si were referenced with respect to the downfield resonance of tetrakis(trimethylsilyl)silane (TTMS) at -9.8 ppm , for ^{27}Al were referenced with respect to Al (NO_3) $_3 \cdot 9\text{H}_2\text{O}$ at 0 ppm. The spectra were fitted using the Peakfit software with the line shape of Lorentz distribution, detailed deconvolution methods are described in Ref. [21].

Generally, the local chemical environment difference of silicon atoms can cause corresponding various chemical shift in the NMR spectra [27]. To differentiate the polymerization degree of silicate tetrahedral in cementing material, they are defined as $\text{Q}^n(\text{mAl})$ [25], where a Si tetrahedron is connected to n neighboring Si/Al tetrahedron in which m neighboring AlO_4 tetrahedron is included. In anhydrous cement clinker, such as alite and belite, silicate tetrahedron are isolated by calcium ions in the lattice, thus all of them are categorized into Q^0 species [30]. On the other hand, as the clinker hydrated and C-S-H precipitates, separated silicate tetrahedral gradually polymerizes to “dreierketten” chains, where Q^1 (dimers), Q^{2B} (bridging groups) and Q^{2P} (pairing groups) exists [9]. In the presence of Al atoms, they can partially enter the bridging position and promote the polymerization of aluminosilicate chains. Simultaneously, pairing silicate tetrahedron that connect with a bridging AlO_4 tetrahedron can produce a different chemical shift in the spectra [3], making this part of AlO_4 indirectly detectable and quantifiable from the ^{29}Si NMR spectra. Therefore, after the quantification of the Q species, the hydration degrees of the blends, mean chain length (MCL) and aluminate tetrahedra to silicate tetrahedra (Al[4]/Si) ratio of C-A-S-H gel in the pastes can be calculated by the following equations [14,38]:

$$\text{Hydration degree of the pastes} : \alpha_c = 1 - \frac{\text{Q}^0}{\text{Q}_0^0} \quad (1)$$

Mean Chain length of C – A – S – Hgel :

$$\text{MCL} = \frac{\text{Q}^1 + \text{Q}^2 + 1.5\text{Q}^2(1\text{Al})}{0.5\text{Q}^1} \quad (2)$$

Al[4] to Si ratio of C – A – S – H gel :

$$\text{Al[4]/Si} = \frac{0.5\text{Q}^2(1\text{Al})}{\text{Q}^1 + \text{Q}^2 + \text{Q}^1(1\text{Al})} \quad (3)$$

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