



The stability of bound chlorides in cement paste with sulfate attack



Jian Geng^{a,b,*}, Dave Easterbrook^b, Long-yuan Li^b, Li-wei Mo^a

^a Research Center of Green Building Materials and Waste Resources Reuse, Ningbo Institute of Technology, Zhejiang University, China

^b School of Marine Science and Engineering, University of Plymouth, UK

ARTICLE INFO

Article history:

Received 10 July 2014

Accepted 25 November 2014

Available online 27 December 2014

Keywords:

Sulfate attack (C)

Bound chlorides (D)

Stability (C)

Fly ash (D)

Ground granulated blast-furnace slag (D)

ABSTRACT

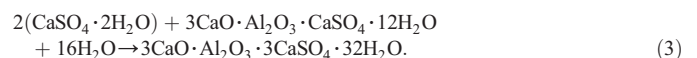
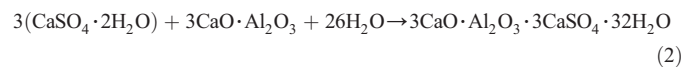
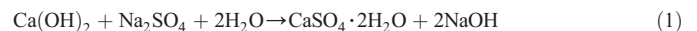
This paper presents an experimental investigation on the stability of bound chlorides in chloride-contaminated cement pastes with and without FA/GGBS when subjected to Na₂SO₄ and MgSO₄ attack. It is shown that bound chlorides were released in the chloride-contaminated pastes when exposed to Na₂SO₄ or MgSO₄ solution. This is mainly attributed to the decomposition of Friedel's salt (FS), where Cl⁻ bound in FS is replaced by SO₄²⁻. However there were fewer released chlorides found in the pastes exposed to MgSO₄ solution than in those exposed to Na₂SO₄ solution. This is partly due to the low pH in the pore solution and partly due to the blocking effect of brucite on ionic transport caused by MgSO₄. The inclusion of FA/GGBS in concrete can increase the decomposition of FS and thus the release of bound chlorides. However, it also resists the penetration of Na₂SO₄ and thus reduces the attack of Na₂SO₄.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The corrosion of reinforcing steel in concrete structures, due to chloride ion contamination, is one of the main reasons for the deterioration of concrete structures. There are two forms of chloride ions in concrete. One is free chlorides and the other is bound chlorides. It is well-known that the corrosion of reinforcing steel is mainly induced by the free chlorides, so reducing free chlorides by increasing bound chlorides will be beneficial to the durability of concrete structures. According to the binding mechanism, chloride ions can be bound through chemical reactions and physical absorption. In the former, chloride ions are mainly bound in Friedel's salt (FS) (3CaO·Al₂O₃·CaCl₂·10H₂O) through hydration reactions between chloride ions, tricalcium aluminate (C₃A) and its hydration products. In the latter, chloride ions are mainly absorbed by calcium silicate hydrate (C–S–H gel). It was reported that the formation of bound chlorides could be affected by a multitude of factors such as the quantity of C₃A in cement, supplementary cementitious materials (SCM), alkalinity of pore solution, Ca/Si and Ca/Al of hydration products, chloride salt type, and service condition of concrete structures [1–5]. In summary, the chloride binding capacity of concrete can be improved by using SCM or cement with high C₃A content. However, many researchers have identified that the stability of bound chlorides, especially of FS, can be affected by pH, carbonation, and chemical erosion [6–9].

Sulfate attack is another problem for the durability of concrete structures. The attack of sodium sulfate (Na₂SO₄) and magnesium sulfate (MgSO₄) on concrete is a common phenomenon. The mechanisms of Na₂SO₄ and MgSO₄ attack on concrete are different, mainly due to the solubility of phases formed with sodium and magnesium ions [10–12]. With regard to Na₂SO₄ attack, the deterioration of concrete is attributed to the formation of expansion products such as gypsum (CaSO₄·2H₂O) and secondary ettringite (Aft) (3CaO·Al₂O₃·3CaSO₄·32H₂O) according to the following equations:

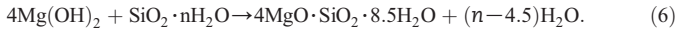
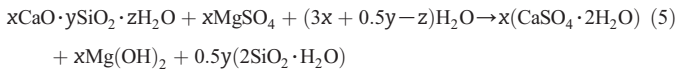
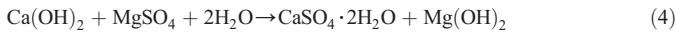


Whereas for MgSO₄ attack, the transformation of the cementitious C–S–H gel to the non-cementitious magnesium silicate hydrate mush (M–S–H), which has very little strength, is the main reason for the deterioration of concrete, although gypsum and secondary Aft are also formed during the attack. In addition, brucite, i.e. Mg(OH)₂, will form when magnesium is present in the pore solution, which has low solubility and could densify the pore system and thus affect the transport of

* Corresponding author.

E-mail address: gengjian@whut.edu.cn (J. Geng).

ions in the cement paste. The mechanism of MgSO_4 attack occurs according to the following equations:



In fact, sulfate attack and chloride contamination are often found to coexist in concrete structures which are exposed to marine and saline environments. The effects of the sulfate and chloride on a concrete structure's durability are multifaceted. On the one hand, the existence of sulfate, especially of Na_2SO_4 , inhibits the formation of FS and reduces the quantity of bound chlorides [13–15]. On the other hand, the existence of chloride ions is beneficial for the resistance of concrete to Na_2SO_4 and MgSO_4 attack [15–18]. However, Baghabra argued that the effect of chloride ions on MgSO_4 attack was slight because the transformation of cementitious C–S–H gel to non-cementitious M–S–H was not affected by chloride ions [19].

Despite the work on the interaction of sulfate and chloride in concrete mentioned above, there is very little work on the effect of sulfate attack on the stability of bound chlorides in concrete. Brown and Badger investigated the distributions of bound sulfates and chlorides in field concrete cores exposed to mixed NaCl, Na_2SO_4 and MgSO_4 attack. They found that there was extensive Aft in the absence of a gypsum zone for some concrete cores [20]. Xu et al. obtained similar results, i.e. that sulfate attack could lead to the release of bound chlorides [21]. Both studies suggested the transformation of FS to Aft due to sulfate attack, but the mechanism of FS transform to Aft and the stability of bound chlorides absorbed by C–S–H gel under sulfate attack were not discussed in depth.

It is well known that the use of fly ash (FA) and ground granulated blast-furnace slag (GGBS) in concrete can not only improve the chloride binding capacity of concrete, but also the resistance of concrete to sulfate attack [22,23]. Hence, it would be interesting to know how they affect the stability of bound chlorides when the concrete is under sulfate attack. The purpose of this paper is to report the experimental investigation on the stability of bound chlorides in cement paste under Na_2SO_4 and MgSO_4 attack, and the corresponding influence of FA and GGBS on the stability of bound chlorides. The stability of bound chlorides in cement paste was examined by analyzing the change of a dimensionless index, R_{cl} , which represents the mass ratio of bound chlorides to initial total chlorides in the sample after it was exposed to a 5% Na_2SO_4 solution or a 5% MgSO_4 solution for 28, 56 or 90 days. The mechanisms of the release of bound chlorides are discussed based on the results of X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and differential thermo-gravimetric analysis (DTG).

2. Experiment

2.1. Materials

The materials used in the experiments were Type 42.5 Ordinary Portland Cement (OPC), grade II FA and GGBS. The chemical compositions of OPC, FA and GGBS are listed in Table 1. The potential phase compositions of OPC, calculated from chemical analysis by Bogue, are given in Table 2. All other chemical reagents used in the experiments, but not listed in the tables, are analytically pure.

Table 1

Chemical composition of main materials (data presented by mass %).

	SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	SO_3	Ignition loss
OPC	19.67	60.43	4.56	4.20	5.70	2.30	2.54
FA	43.10	6.30	0.24	7.26	38.20	0.70	2.04
GGBS	23.50	52.80	6.50	0.70	11.80	1.65	0.78

2.2. Methods

In order to reduce the experimental running time but still able to achieve good and representative results, chloride binding was achieved by using 0.5 mol/L NaCl solution as the mixing water for the casting of samples. The mass ratio of the mixing water to the binder (cement and SCM) was 0.5, which was the same for all samples. The influence of single and combined use of FA and GGBS on the stability of bound chlorides was also investigated. The replacement of cement with SCM was 30% by weight, and the proportions of FA to GGBS in the combined samples were either 1:1 or 7:3. The detailed mix proportions of the samples tested are listed in Table 3.

A total of 106 samples were tested. All samples were of a size of 40 mm × 40 mm × 160 mm. There were three groups of samples. The first group (2 × 5 × 7 samples) were cured at a standard curing condition (20 ± 2 °C and 95% RH) for periods of 1,3,7,14,28,56 and 90 days for the investigation of the effect of curing time and SCM on the evolution of bound chlorides in the cement paste. The second group (2 × 5 × 3 samples) were examined for the effect of Na_2SO_4 attack on the stability of bound chlorides. In this group, all samples, after the 56 days standard curing, were dried at a room temperature (20 ± 2 °C and 60% RH) for 1 day. Then, for each sample its five surfaces were sealed by paraffin wax and one 40 mm × 40 mm surface was left untouched. After then, all samples were immersed in a covered plastic container (575 mm × 400 mm × 275 mm) of 5% Na_2SO_4 solution for 28, 56 and 90 days at the standard curing condition (20 ± 2 °C and 95% RH). The third group (2 × 1 × 3 samples) were for the samples only with OPC, which were cured as the same as those done in the second group. The only difference is that they were immersed in a similar covered container of 5% MgSO_4 solution for 28, 56 and 90 days at the standard curing condition (20 ± 2 °C and 95% RH) for the examination of the effect of MgSO_4 attack on the stability of bound chlorides. The volume of the sulfate solutions used in the immersion tests was 25 L and the storage solutions were not renewed during the immersed tests.

In the second and third groups, when the attack time reached 28, 56, and 90 days, the samples were dried at room temperature for 1 day, and then were sliced into four pieces parallel to the exposed surface (starting from the exposed surface) and each piece is one cm thick. Afterwards, each piece was broken into small blocks, which were then immersed in anhydrous ethanol for 7 days to terminate hydration. These small blocks were ground into fine powder by passing through a sieve of 0.15 mm mesh aperture size, which was then stored in a desiccator with silica gel and soda lime at 11% RH to minimize carbonation before it was used in the tests for chloride content titration and other material characterization analyses.

The initial total chloride content (C_t) of the sample cured at the standard curing condition can be calculated based on the mixing water of

Table 2

Potential phase composition of OPC (data presented by mass %).

Potential phase composition	OPC
C_3S	51.58
C_2S	17.77
C_3A	8.01
C_4AF	12.77
CS	3.91

Download English Version:

<https://daneshyari.com/en/article/1456249>

Download Persian Version:

<https://daneshyari.com/article/1456249>

[Daneshyari.com](https://daneshyari.com)