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The effect of $MgSO_4$ on thaumasite formation

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ABSTRACT

Normally, $MgSO_4$ is considered to promote thaumasite sulfate attack (TSA) due to pH drop of solution caused by insoluble brucite formation. However, some test results indicate that thaumasite formation (TF) should occur in the solution with relatively high pH.

In the current paper, cement, cement + fly ash, cement + limestone powder and high sulfate resisting (HSR) cement pastes were immersed in sealed bottles containing Na_2SO_4:$MgSO_4$ = 0:5, 1:5, 3:5 and 10:30 at 10 °C. The pH was measured and corrosion products were identified by means of XRD. The results indicated that the existence of relatively low content $MgSO_4$ (even 5%) may not cause significant pH drop under non-exposed condition. The pH was still kept at the level of 13.0, while the increase of $MgSO_4$ could promote TF. The pH fell below 10.0 in the solution containing saturated $MgSO_4$, however, gypsum dominated the mechanism of paste deterioration.

1. Introduction

As generally known, $MgSO_4$ not only reacts with calcium hydroxide but also leads to the decomposition of the C–S–H phase, forming not only expansive gypsum but also unbound products of brucite and magnesium silicate hydrate (M–S–H). $Mg(OH)_2$ (brucite) is insoluble and its saturated solution has a pH of 10.5. Thus, generally, it is agreed upon that the damage from $MgSO_4$ attack on concrete is more severe than from Na_2SO_4 attack [1–3].

Thaumasite sulfate attack (TSA) was identified as the major mechanism for the extensive and sensitive deterioration of deeply buried foundation concrete of a number of 30-year-old M5 motorway bridges in Gloucestershire, west England in spring, 1998 [4–9]. Hobbs and Taylor analyzed these field cases of TSA [10]. They indicated that the oxidation of pyrites within the backfill leads to the formation of sulfuric acid, reducing the pH of the groundwater. Magnesium ions and the formation of insoluble $Mg(OH)_2$ also reduce the pH, increasing the degree of chemical attack on the C–S–H, playing a major role in increasing the risk of thaumasite attack [11]. Sharp et al. [12] compared the thaumasite formation (TF) of Portland-limestone cement pastes in different sulfate solutions, the results indicated that the storage in the $MgSO_4$ and Na_2SO_4 mixed solution behaves in a similar scaling manner to simple $MgSO_4$ solution. This suggests that magnesium ions plays a considerable role in the TF due to the generation of low soluble $Mg(OH)_2$, resulting in the drop of pH and the disintegration of C–S–H. In summary, a low pH storage condition due to the existence of $MgSO_4$ favors TF.

However, a number of reports show contrary results. Jallad et al. [13] studied the stability of pure thaumasite samples in solutions with different pH ranging from 6.0 to 13.0. The results indicated that thaumasite reacts with the ions present in the solutions, and some conversions to calcium phosphate, calcium silicate and calcium carbonate are detected at low pH levels ($\leqslant$11.0). At pH level >11.0, minor amounts of calcium carbonate are generated, while only in highly basic conditions (pH = 13.0) thaumasite is stable. Zhou et al. [14] studied the role of sulfuric acid in thaumasite sulfate attack. The results showed that the existence of acid cannot promote TF. TSA occurs in the sulfate solution at pH above 12.0. The pH of acidified solution is maintained between 2.0 and 6.0, gypsum is the dominating reactive phase in the solution. Hagelia pointed out thaumasite decomposes and forms gypsum and calcite at low pH level [15,16]. The experimental results attained by Gaze and Crammond [17] presented that, after 90 days exposure to $MgSO_4$ solution under "non-exposed" condition (separated from atmosphere), calcite and gypsum are the main reaction products although the pH is 12.5. Only in the K_2SO_4 solution with pH of 13.0 thaumasite is the predominant product. Therefore, the above experimental results support that TSA plays a major role in cementitious materials deterioration only in the sulfate environment with high pH close to 13.0.

Obviously, the above two views are conflicting. The former view indicates that the pH drop of solution by $MgSO_4$ favors TF, and the increase of $MgSO_4$ can promote TSA. However, the latter view

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concludes that high pH is an essential factor for TSA. In the current paper, tests were carried out to try to explain the differing views and any possible connection between them.

2. Experiments and raw materials

Concerning the pH of solution, it should be noted that the pH of sulfate solution is controlled by the combined effects of three factors: the Mg^{2+} content, the replace rate of fresh solution and the relative volume ratio of concrete to solution [18]. Also, the storage condition is also an important factor. In the abovementioned report [17], Gaze and Crammond compared the pH of the same $MgSO_4$ solution or K_2SO_4 solution under exposed and non-exposed storage conditions respectively. The results showed that under non-exposed condition the pH of solution remains at a high level (>12.5) during the whole process, but the pH drops to 6.0 or 8.1 if the solution is in contact with air (exposed condition).

Concerning the field experience of M5 motorway bridges, an interesting appearance should not be overlooked that TSA was just found on the top of deeply buried foundation [4,5,7,8]. Combining the relationship between groundwater and foundation [19–21], this means that TSA just occurs in a perched solution formed on the top of concrete foundation, and the perched solution is stagnant and not frequently replaced by fresh solution. The volume of solution is much less than the concrete foundation. The foundations are deeply buried underground and far separated from atmosphere. This can be regarded as a kind of non-exposed storage condition.

In order to simulate such field exposure conditions, in the current paper the specimens were orderly organized in prismatic plastic bottles with two covers. Sulfate solutions just enough to cover the surfaces of specimens were irrigated into the bottles respectively, and not replaced during the whole progress. The pH of solutions was measured and corrosion products were identified by means of XRD.

Table 1 gives the chemical composition of ordinary Portland cement, high sulfate resisting cement (HSR), fly ash (FA) and limestone powder (LP) used in this study. Four pastes with different porportions were made (Table 2). Four solutions with different proportions of Na_2SO_4 to $MgSO_4$ (Na_2SO_4:$MgSO_4$ = 0:5, 1:5, 3:5 and 10:30 by mass) were used. The exposure temperature was kept at 10 °C.

Firstly, specimens were cast and demolded after 24 h, then cured in water at 20 °C for 28 days. The specimens were then dried in a climate room at 20 ± 2 °C and 60 ± 5% RH for 1 week, and moved into four plastic bottles with two tight-fitting lids. Sulfate solutions were irrigated into bottles. At last, the sealed bottles were placed in a refrigerator at 10 °C.

Specimens were taken out for visual observation and XRD analysis at the exposure ages of 1, 3 and 6 months. The outer layer of the specimen was cut off by a knife and grinded to pass a 53 μm sieve; the powder was dried in a vacuum container with silica gel for XRD analysis. The pH of the exposure solution was measured.

Table 1
Chemical composition of cement, fly ash and limestone powder.

Code (%)	C(I) CEM I 52.5	C(III) (HSR) CEM I 42.5 NHSR LA	Fly ash (FA)	Limestone powder (LP)
SiO_2	19.60	19.94	53.31	0.86
Al_2O_3	4.90	3.13	26.43	0.08
Fe_2O_3	3.10	4.76	7.53	0.34
CaO	63.60	61.56	4.46	56.3
MgO	0.90	–	2.54	0.58
K_2O	0.77	0.66	3.58	0.05
Na_2O	0.41	0.24	1.15	0.08
SO_3	3.30	2.54	0.90	–
LOI	2.10	5.45	4.10	42.0

Table 2
Mixture proportions of cement paste.

	Cement	Fly ash (FA)	Limestone power (LP)	W/C
Cement	1(C I)	–	–	0.5
Cement + FA	0.75(I)	0.25	–	0.5
HSR	1(C III)	–	–	0.5
Cement + LP	0.75(I)	–	0.25	0.5

3. Results

3.1. Visual observation

Figs. 1–3 show the visual appearance of pastes after 6 months immersion. In Fig. 1, after 6 months immersion in the Na_2SO_4:$MgSO_4$ = 3:5 solution it can be found that: (1) the HSR pastes looked sound; and (2) the outer layers of cement, cement + FA and cement + LP were both softened and white substance was formed on the surfaces.

Compared with Fig. 1, after 6 months exposure to 5% $MgSO_4$ solution it can be observed in Fig. 2 that: (1) the HSR pastes were still sound; (2) there was not a significant change of cement + LP; and (3) the edges of cement and cement + FA specimens were severely eroded. Large mass loss could be found, with cement + FA likely showing the most severe loss.

In Fig. 3, in the Na_2SO_4:$MgSO_4$ = 10:30 mixed solution it can be found that: (1) the HSR paste, which showed the best performance in Figs. 1 and 2, was severely damaged. A layer of gel-like and soft substance was formed around the core; (2) soft blister material was formed on the surface of the cement paste and cement + FA paste specimens; and (3) cement + LP specimens exhibited the best visual appearance.

3.2. XRD analysis

3.2.1. Exposure for 1 and 3 months

The XRD patterns of ettringite and thaumasite show similarities, with just small differences in the d-spacings of the two major peaks, at around 9.1 and 16.0° 2θ. It can be difficult to distinguish

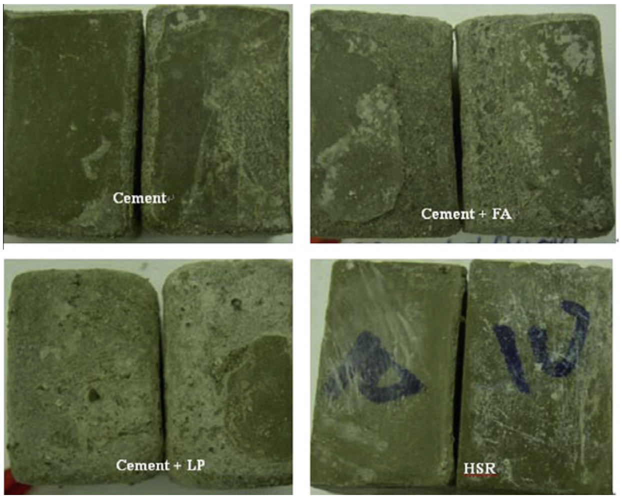

Fig. 1. Visual appearance of pastes exposed to Na_2SO_4:$MgSO_4$ = 3:5 solution for 6 months.