

# Influence of Cement Types and Mineral Admixtures on the Resistance of Mortar to Thaumasite Form of Sulfate Attack

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**Abstract:** Mortar prisms made with different cements or mineral admixtures plus 30% mass of limestone filler were stored in 2% magnesium sulfate solution at  $5\pm 1^\circ\text{C}$  for 1 year and their visual appearance, strength development were measured at intervals. The formation of thaumasite was checked and confirmed by XRD and FTIR. The results show that the relative resistance to thaumasite form of sulfate attack of the cements is outlined below, from best to worst: sulphoaluminate cement, sulfate resisting Portland cement, OPC. The resistance to thaumasite form of sulfate attack of mortar is remarkably improved by the addition of silica fume or ground granulated blastfurnace slag (SL), and the better the resistance to thaumasite form of sulfate attack, the more the addition of SL is. The thaumasite form of sulfate attack is decreased to a certain degree by a lower replacement of cement with fly ash, but it is accelerated by the addition of a higher amount of fly ash due to its lower reactivity.

**Key words:** sulfate attack; thaumasite; cement type, mineral admixture

## 1. Introduction

In recent years, it has become a common practice to incorporate fine limestone powder as an additional constituent in the cement production [1]. A high volume of limestone filler is also used frequently to increase the content of fine particles and optimize the particle packing in self-compacting concrete (SCC) mixes [2]. In addition, calcareous aggregates are extensively used in many countries. The formation of thaumasite ( $\text{CaSiO}_3\cdot\text{CaCO}_3\cdot\text{CaSO}_4\cdot 15\text{H}_2\text{O}$ ) as a result of sulfate attack at lower temperature, however, has been widely reported to be associated with the use of limestone in cements and concretes [3-6]. Recent researches [6-7] show that ordinary Portland cement is susceptible to the thaumasite form of sulfate attack at  $5^\circ\text{C}$  after only a few months exposure to sulfate solutions. The formation of thaumasite can damage the cement concrete by destroying the strength bearing C-S-H phases, therefore the attacked concrete lose its strength quickly and has to be changed or renovated just after a much shorter service lifetime than that expected.

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The replacement of ordinary Portland cement by mineral admixture or different type of cement influences the hydration products and the microstructure of cement paste, contributing to a difference in resistances to thaumasite form of sulfate attack, but there are some unclear or conflicting viewpoints on that [8-9]. Accordingly it is difficult to choose the cementitious material to improve the resistance of concrete to thaumasite form of sulfate attack. The paper presents experimental results related to the effect of mineral admixture and cement types on the resistance to thaumasite sulfate attack of mortar containing limestone filler.

## 2. Experimental details

Three types of cements were used: ordinary Portland cement (OPC) from Huaxin Cement Co. LTD in Hubei province; sulfate resisting Portland cement (SRC) from Yongdeng Cement Company of Lanzhou city; sulphoaluminate cement (SAC) from Fenghuang Cement Company of Xiaogan city. They have the same strength grade of 42.5. Three mineral admixtures are: fly ash (FA), with grade II according to Chinese Standard GB1596-91; ground granulated blastfurnace slag (SL) with specific surface area of 400m<sup>2</sup>/kg (Blaine); silica fume (SF) with specific surface area of 23 000m<sup>2</sup>/kg (Blaine). The chemical composition of cements and mineral admixtures are shown in Table 1. The limestone from Huangshi City was ground to a specific surface area of 400m<sup>2</sup>/kg (Blaine). A quartz sand was used with a fineness modulus of 2.6 and density of 2.65g/cm<sup>3</sup>. Synthetic MgSO<sub>4</sub> was used to prepare the sulfate solutions.

Table 1 Chemical composition of the raw materials (wt.%)

No.	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	R <sub>2</sub> O	IL
OPC	61.27	21.04	6.94	2.36	1.32	1.94	0.97	3.76
SRC	63.52	22.75	4.12	4.37	2.19	2.01	0.68	0.33
SAC	41.53	8.10	30.32	3.41	3.60	11.93	—	0.65
FA	3.20	56.25	27.87	5.26	1.05	—	—	6.00
SL	40.30	38.20	11.00	0.32	7.35	—	—	—
SF	0.33	90.54	0.77	1.77	1.68	0.40	—	2.78

Mortar prisms (40×40×160 mm) were cast according to the mixture proportions presented in Table 2. After 24 hours in a moist cabinet, they were removed from the mould and cured in water at room temperature (20±2°C). After 27 days curing in water, the mortar specimens were stored into 2% MgSO<sub>4</sub> solutions with temperature of 5°C (with a fluctuation of ±1 °C). The sulfate solution was replaced every 2 months and the volume ratio of solution to mortar specimens was kept at about 2:1. The visual examination and strength measurement of mortar specimens were performed at regular intervals up to 1 year. Samples were selected from

the surface of prisms after strength testing at different immersion ages. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were used to analyze these samples and distinguish the degraded products of cement mortar after sulfate exposure at lower temperature.

Table 2 Mortar mixture proportions (kg)

No.	Cement*	SF	FA	SL	Sand	Limestone	Water
OPC	1.0	0	0	0	2.2	0.3	0.6
SRC	1.0 SRC	0	0	0	2.2	0.3	0.6
SAC	1.0 SAC	0	0	0	2.2	0.3	0.6
SF8	0.92	0.08	0	0	2.2	0.3	0.6
FA20	0.8	0	0.2	0	2.2	0.3	0.6
FA40	0.6	0	0.4	0	2.2	0.3	0.6
SL30	0.7	0	0	0.3	2.2	0.3	0.6
SL60	0.4	0	0	0.6	2.2	0.3	0.6

\*The cement is OPC if there is no special marking.

The XRD analysis was conducted using an automated Japan D/MAX-III A X-ray diffractometer operating at 35 kV and 30 mA using  $\text{CuK}_\alpha$  radiation. Data was collected between  $5^\circ$  and  $60^\circ 2\theta$  using a step-size of  $0.02^\circ$  and a count time of 0.6 s per step. Fourier transform infrared (FTIR) spectroscopy was carried out using a Nicolet 60 SXB FTIR Spectrophotometer. Samples were prepared for analysis by grinding a known mass of solid with dried KBr. The resulting powder was then pressed at 2000 psi for 5 min to produce a pellet for analysis. The wavenumber ranges from  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ .

### 3. Results and discussion

#### 3.1 Visual inspection

A visual inspection of the mortar specimens was carried out monthly. After the initial 27-day curing under water, a little of white precipitate was present in the sample containers, and particularly on the top surface of the specimens. This material is attributed to the CH leaching-out from the mortar and a little of carbonate in water. During the first several months of immersion in sulfate solution, such white mass exudation continued and it seemed to have no negative influence on the mortar mechanical performance. After 4 months, some signs of deterioration were firstly found on the surfaces and edges of the OPC mortar and the mortar with fly ash. A longer time of 6 months was required for other mortars when visible sign of attack were firstly observed on the specimen surfaces. In most of cases, the first sign of attack was some pitting on the undersurface and small cracking along the edges. Progressively, expansion and spalling took place on all the surfaces and edges of the specimen.

Fig. 1 shows the visual appearances of specimens after 1 year exposure to sulfate solution at 5 °C. Obvious signs of deterioration were observed in all the specimens except for the mortar containing 60% SL, and a white soft substance formed on the surfaces or was precipitated on the container bottom due to the spalling specimen surfaces. From the visual inspection, it was found that different mineral admixtures have different influences on the resistance to sulfate attack at lower temperature. And less degradation occurred on mortar FA40, OPC, FA20, SL30, SF8 and SL60, in ascending order. Both sulfate resisting Portland cement mortar and sulphoaluminate cement mortar showed improved resistances to sulfate attack, and the latter is better.

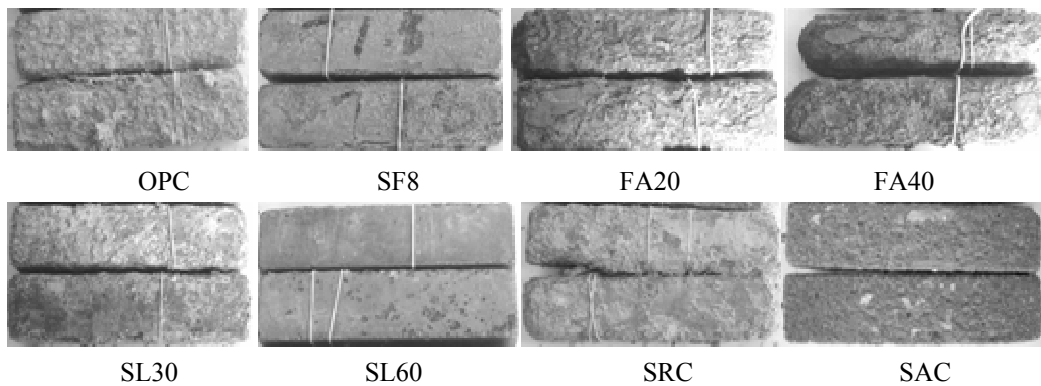


Fig. 1 Visual appearance of mortars after 1 year exposure to sulfate

### 3.2 Strength development

Fig.2 presents the strength development of mortars with different types of cements immersed in sulfate solution. Every mortar showed a significant loss of strength after a long time exposure to sulfate attack. With the increasing time of exposure to sulfate solution, the strength loss of mortars increased evidently. After 1 year of immersion, OPC, SRC and SAC mortars showed 72.3%, 53.6% and 35.6% of compressive strength loss and 45.6%, 35.1% and 25.0% of flexural strength loss respectively. Though sulfate resisting Portland cement mortar shows a less strength loss than OPC mortar, it doesn't behave as good as expected for the traditional sulfate attack. Sulphoaluminate cement shows a much better resistance to sulfate attack at lower temperature than OPC mortar. These results are consistent with the above visual inspection.

Influence of mineral admixture on strength development of mortar is shown in Fig. 3. Most of mortars, except for mortars containing SL, showed strength loss due to sulfate attack, and the strength loss increased with the increasing time of exposure to sulfate. Here the strength loss of mortar after 1 year is just discussed. The addition of 8%

silica fume obviously reduced the compressive and flexural strength loss of mortar to 22% and 10.8% respectively. The mortar with 20% fly ash showed 56.3% of compressive strength loss and 33.3% of flexural strength loss which are less than those of the OPC mortar. But more addition of fly ash seemed to have no advantage. Mortar FA40 showed a more strength loss than the OPC mortar, and it is attributed to the more badly deterioration as observed from the visual appearance. The mortars containing SL showed obviously less strength loss than OPC mortar, and the more the addition of SL is, the less the strength loss is. The mortar with 60% of SL showed no notable strength loss after 1 year of exposure to sulfate because pozzolanic reaction of SL increased the mortar's strength during the first several months. According to the strength loss, the improvement of mineral admixture on resistance to sulfate attack at lower temperature is outlined below, from best to worst: 60% SL, 8% silica fume, 30% SL, 20% fly ash, no admixture and 40% fly ash.

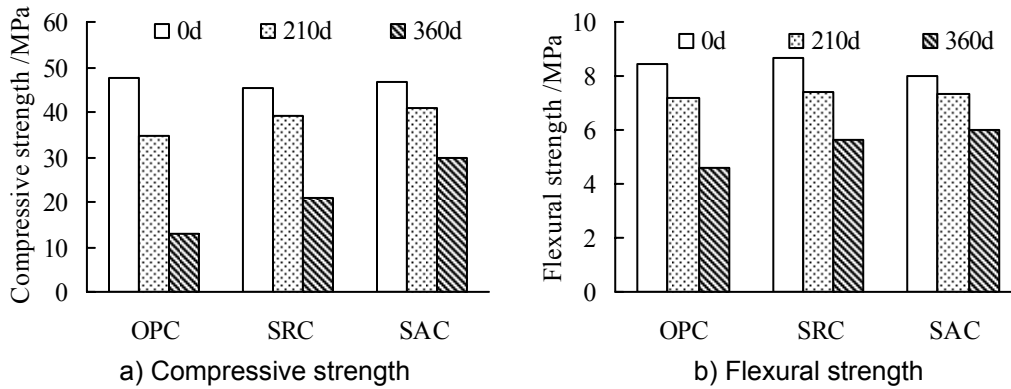


Fig. 2 Strength development of mortars with different types of cement exposed to sulfate attack at lower temperature

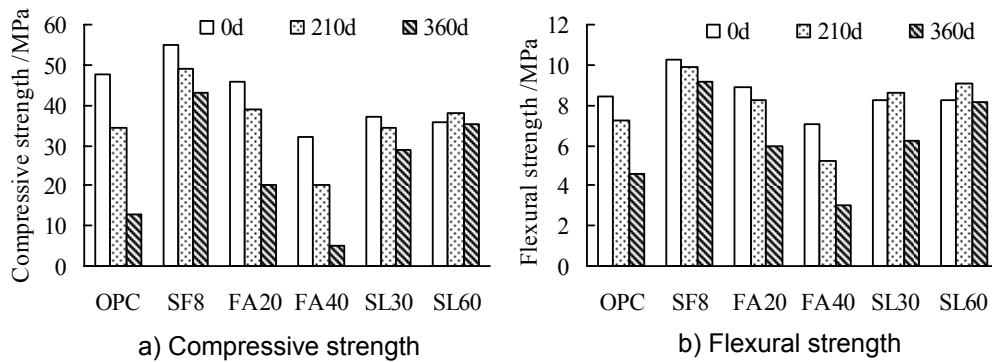


Fig. 3 Strength development of mortars with different mineral admixtures exposed to sulfate attack at lower temperature

### 3.3 Mineralogy

The samples were selected from mortars after the initial 27 days curing in

water and XRD patterns of them are shown in Fig. 4. In all samples, there are obvious peaks corresponding to quartz ( $\text{SiO}_2$ ) from the sand and calcite ( $\text{CaCO}_3$ ) from the limestone filler. As expected, a mass of portlandite ( $\text{Ca}(\text{OH})_2$ ) formed in all the mortars with OPC, and its quantity decreases with the replacement of cement by mineral admixture. The formation of less portlandite is attributed to the reduced amount of cement and the pozzolanic reaction of mineral admixture. Monocarboaluminate ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ ) formed as one of hydration products of  $\text{C}_3\text{A}$  from OPC and limestone filler. And the less monocarboaluminate formed, the more cement is replaced by mineral admixture. When the mortar is immersed into sulfate solution, sulfate ions penetrate into the mortar and react with portlandite, monosulfoaluminate, CSH gel to form ettringite, gypsum and thaumasite [10]. The formation of these products leads to the swelling, cracking, and finally decomposition of the mortar. So the reduced formation of portlandite and monosulfoaluminate by the addition of mineral admixture results in the improved resistance of mortar to sulfate attack at lower temperature. On the other hand, the pozzolanic reaction of mineral admixture increases the density of mortar, and this is another reason of the alleviated deterioration of mortar with mineral admixture. However, the severer attack on the mortar with 40% fly ash maybe is attributed to the much reduced strength and density because fly ash has a low pozzolanic reactivity during the initial curing period.

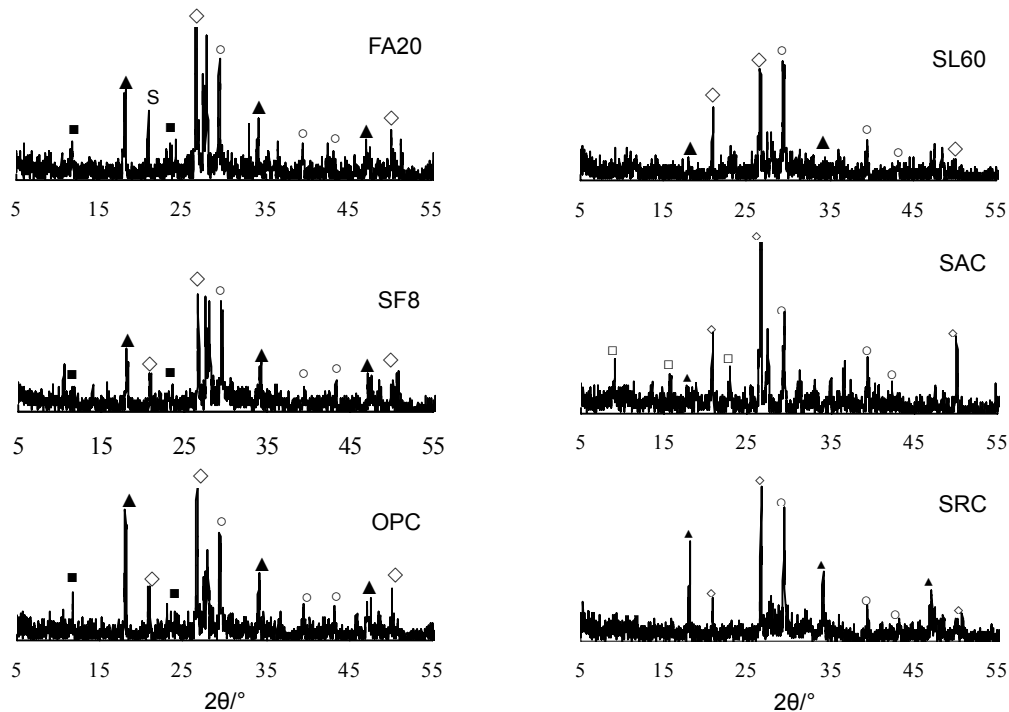


Fig. 4 XRD patterns of mortar before immersion into sulfate solution  
 ◇ Quartz; ○ Calcite; ▲ Portlandite; ■ Monocarboaluminate; □ Ettringite

No detectable monocarboaluminate was found in the sulfate resisting Portland cement mortar which containing much less  $C_3A$ , and the mortar suffered from a slighter attack attributed to ettringite formation. Other composition in SRC is similar to OPC, so the SRC mortar also suffered from the formation of gypsum and thaumasite and it showed a limitedly better resistance to sulfate attack at low temperature than the OPC mortar. The main minerals of sulphoaluminate cement are  $C_4A_3\bar{S}$ ,  $C_2S$  and  $C_{12}A_7$ , and their hydration products mainly contain ettringite, CSH gel,  $Al(OH)_3$  [11]. Very strong peaks corresponding to ettringite and weak peaks attributed to portlandite can be found in the XRD pattern of the SAC mortar. On the one hand, there is no enough portlandite, unstable aluminates such as monocarboaluminate or monosulfoaluminate to form gypsum and ettringite. On the other hand, there is less CSH gel for thaumasite sulfate attack in the SAC paste than in the OPC paste. Therefore, the SAC mortar behaves much better than the OPC mortar.

The identification of products formed as a result of sulfate attack was based on XRD and FTIR measurements. In ordinary Portland cement mortars (with or without mineral admixture) which suffered from cracking and spalling, the soft, white material covering the specimen surface was found to contain mainly thaumasite, gypsum and a little of ettringite [12]. The silica fume mortar and the mortar with 60% SL mortar suffered from a slight degradation and the formation of these products was undetectable. The amount of such sulfate-bearing substances formed corresponds to, to a certain extent, the degradation degree of mortar.

Fig. 5 presents the XRD patterns of samples selected from the surfaces of mortars with different types of cements after 1 year immersion. In all samples, even no detectable trace of portlandite can be seen. And a great deal of sulfate-bearing substances including ettringite/thaumasite and gypsum formed in the samples. According to the relative intensities of major peaks at around  $9.1^\circ$  and  $11.6^\circ$   $2\theta$ , there is more sulfate bearing substances formed in OPC mortar than SRC and SAC mortars which suffered from a slighter deterioration.

Because ettringite and thaumasite have similar crystal structures, it can be difficult to distinguish them from XRD patterns when only small amounts are present in a sample [13]. Further investigation was made using FTIR spectra as shown in Fig. 6. The strong peaks at around  $1110\text{ cm}^{-1}$  associated with S-O show that a great deal of sulfate-bearing substances formed in all samples. And the OPC mortar shows a stronger peak, attributed to more sulfate-bearing substances, than the other two samples. The C-O peaks at  $875\text{ cm}^{-1}$  and around  $1400\text{ cm}^{-1}$  are occurring in all the samples as expected, and they are attributable to the presence of carbonates. The obvious peaks at  $499\text{ cm}^{-1}$  and  $669\text{ cm}^{-1}$ , being assigned

to the presence of  $\text{SiO}_6$  bonds [14], indicates a mass of thaumasite or thaumasite-containing solid solution formed in OPC mortar. Weak peaks of  $\text{SiO}_6$  bonds in the other two samples, and the XRD patterns mentioned above, show that SRC and SAC postpone the thaumasite formation.

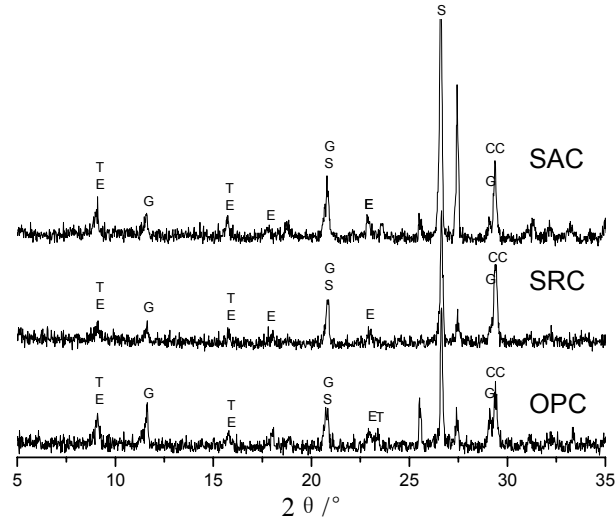


Fig. 5 XRD patterns of mortars after 1 year immersion in sulfate solution  
S—Quartz; CC—Calcite; CH—Portlandite; E—Ettringite; T—Thaumasite; G—Gypsum

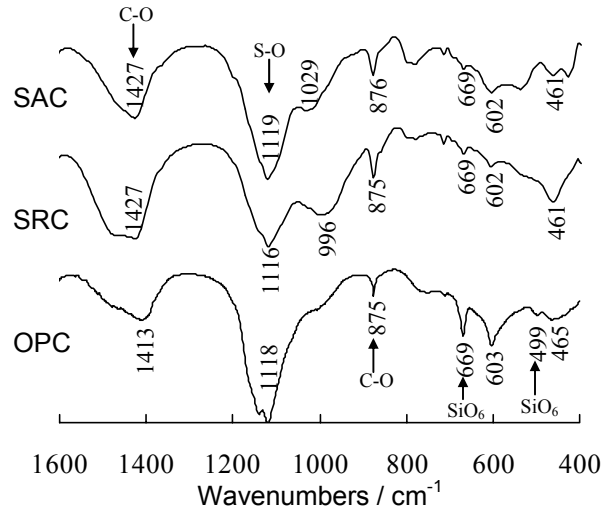


Fig. 6 FTIR spectra of mortars with different types of cements after 1 year exposure to sulfate solution.

#### 4. Conclusions

1) The relative resistance to thaumasite form of sulfate attack of the cements is outlined below, from best to worst: sulphoaluminate cement, sulfate resisting Portland cement and OPC.



2) The resistance to thaumasite form of sulfate attack of mortar is remarkably improved by the addition of silica fume or ground granulated blastfurnace slag (SL), and the higher the resistance to thaumasite form of sulfate attack, the more the addition of SL is. The thaumasite form of sulfate attack is decreased to a certain degree by a lower replacement of cement with fly ash, but it is accelerated by the addition of a higher amount of fly ash due to its lower reactivity.

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