The role of $\text{Ca}(\text{OH})_2$ in sulfate salt weathering of ordinary concrete

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Abstract: In the present paper, a micro-analysis of sulfate salt weathering of calcium sulfoaluminate (CSA) cement paste and concrete was conducted to offer reference values and to elucidate the *sulfate salt weathering of ordinary concrete*. The test results showed that Na_2SO_4 crystals could be clearly identified in CSA cement paste and concrete, causing the failure of the paste and concrete in the evaporation zone. Based on the surface physicochemical theory of crystallization in a pore, a solution film between the pore wall and the salt crystal causes crystal growth and can be formed due to the inert relationship between sulfates and CSA cement hydration products without the effect of $\text{Ca}(\text{OH})_2$. However, after the inevitable chemical reaction between the sulfates and hydration products of Portland cement due to the existence of $\text{Ca}(\text{OH})_2$, the solution film is not formed, and Na_2SO_4 crystallization cannot occur in the Portland cement concrete.

Keywords: $\text{Ca}(\text{OH})_2$, sulfoaluminate cement, sulfate salt weathering, sulfate attack

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1. Introduction

Salt weathering is widely recognized as one of the primary agents that leads to deterioration of historical masonry through the production of physical stress that results from the crystallization of salts in pores [1]. When ordinary concrete elements are partially exposed to a sulfate environment, sulfate salt weathering distress is also regarded as the damage mechanism for the concrete part in contact with relatively dry air near the earth's surface, in addition to the pores (defined as the evaporation zone in this paper [2]).

However, whether ordinary concrete suffers sulfate salt weathering has been questioned in detail in an extensive discussion on the contradictions between concrete damage performance and the classic theory of salt weathering of porous materials in a review paper [3]. The controversy focuses on if crystallization in cement paste pores can occur during the chemical reactions between the sulfates and hydration products of Portland cement. Supersaturation is a well-known threshold for crystallization in pores, and this state can only be reached by cooling, evaporation or drying and wetting [4]. However, the chemical reactions in the pore solution can occur at any sulfate concentration. If sulfate crystallization can occur in an easier chemical reaction is questioned.

$\text{Ca}(\text{OH})_2$, ettringite and C-S-H are the main hydration products of Portland cement. When cement paste is in contact with sulfate ions, (1) $\text{Ca}(\text{OH})_2$ reacts with sulfate ions to form gypsum and causes expansion, (2) $\text{Ca}(\text{OH})_2$ reacts with sulfate ions and Al to form ettringite and causes expansion, (3) the pH value of the pore solution is influenced by the $\text{Ca}(\text{OH})_2$ concentration and controls the stability of ettringite and C-S-H[5]. The source of the chemical sulfate attack on concrete seems to be $\text{Ca}(\text{OH})_2$. In previous papers by the authors of this present contribution [6,7], the micro-analysis results of stimulating tests of *sulfate salt weathering of Portland cement*

concrete showed that no trace of sulfate crystals could be identified in damaged concrete, and this finding is the most powerful and direct evidence of the same salt crystallization in pores as found in rocks[8]. Meanwhile, gypsum and ettringite, the chemical reaction products, could be clearly identified.

Consequently, if a hydraulic cementitious material has hydration products that are similar to Portland cement, except the exclusion of $\text{Ca}(\text{OH})_2$, what performance will this material exhibit when subject to sulfate salt weathering? Will the test results help scientists and engineers to further understand *sulfate salt weathering of ordinary concrete*?

Fortunately, Calcium sulfoaluminate (CSA) cement meets this purpose. The hydration products of this cement contain rich ettringite, C-S-H and Al gel but do not include the $\text{Ca}(\text{OH})_2$ phase [9]. Micro-analysis tests similar to previous research [6-7] were performed on CSA cementitious materials.

2. Experiments

2.1 Raw materials

Low alkalinity sulfoaluminate cement, complying with JC/T 659—2003, was used in the experimental program. The chemical composition of this cement is given in Table 1. Gravel with sizes ranging from 5–10 mm was used as the aggregate. The mixing water for concrete was tap water. Paste specimens were exposed to a 10% by mass Na_2SO_4 solution. Concrete specimens were exposed to a 10% sodium sulfate solution.

Table 1: Chemical composition of low alkalinity sulfoaluminate cement (% by mass)

	CaO	SiO ₂	Fe ₂ O ₃	MgO	Al ₂ O ₃	SO ₃	TiO ₂
Cement	41.51	6.30	4.26	0.80	28.07	13.26	2.20

2.2. Specimens preparation, curing and testing

Concrete was made with only cement and coarse aggregate to highlight that the interfacial transition zone (ITZ) had the same role in the test as in a previous paper [6]. The cement/aggregate ratio was 0.4 and the water/cement ratio (W/C) was 0.45. Plain cement paste with a W/C ratio of 0.45 was mixed.

Fresh concrete and paste were cast in a 10*40*150 mm mold covered with a plastic sheet in a moist room for 24 h. The specimens were demolded and stored in water at 20 ± 1 °C. At an age of 7 days, all the specimens were dried in a climate box at 20 ± 3 °C and $60 \pm 5\%$ RH (shown in Fig. 1) for 7 days. After drying, the specimens were partially immersed in containers with 10% Na_2SO_4 in the abovementioned climate box.

Fig. 1 Climate box and specimen immersion

2.3. Visual observation, XRD, SEM, ESEM and EDS analysis

The damaged specimens were visually observed and analyzed by means of XRD, ESEM and EDS as the same as the previous papers [6,7].

3. Visual Observations

The damage observed on the paste and concrete specimens is shown in Fig. 2 and Fig. 3, respectively. Compared with performance of the Portland cement paste and concrete specimens in the previous papers [6-7]:

1. The parts of CSA cement above the solution deteriorated after just 7 days of exposure. For Portland cement, the paste and concrete specimens were severely damaged until after 5 months;
2. Successive paste layers had detached in the damaged CSA cement paste. A core was formed after the successive paste layers detached. This appearance was similar to the typical salt weathering of porous rock [8]; The Portland cement paste specimen was split in several pieces along the shrinkage cracks due to expansive ettringite crystals [7].
3. In the evaporation zone as defined in the literature [19], the aggregates and pastes along the ITZ were completely separated and similar in appearance to Portland cement concrete [6].

Fig. 2 Damage observed to CSA cement paste exposed to the Na_2SO_4 solution

Fig. 3 Damage observed to CSA cement concrete exposed to the Na_2SO_4 solution

According to the different damage performances of Portland cement and CSA cement described above, the following conclusions can be deduced:

1. The damage mechanisms for these two cements should be different.
2. $\text{Ca}(\text{OH})_2$ played a key role in the observed differences.

3. Analyzing the damage mechanism for CSA cementitious materials can offer a reference to further understand the damage mechanism for Portland cementitious materials.

4. Micro-Analysis Results

4.1 Paste specimens

According to Fig. 2, a small piece of the paste layer was dried and analyzed by means of ESEM, EDS and XRD. The products on the surface of the paste core were analyzed by means of ESEM and EDS. The products in the core paste were identified by means of XRD.

Fig. 4 shows the ESEM image and EDS result for products on the surface of the paste layer. A large bunch of crystals were generated on the surface of the paste layer, and could be identified as Na_2SO_4 crystals by EDS analysis.

Fig. 4 ESEM image and EDS analysis of products in successive layers

Fig. 5 shows the ESEM image and EDS result of the products on the surface of the paste core. The surface of the paste core was almost covered by a layer of white crystals. These crystals can also be identified as Na_2SO_4 according to EDS analysis.

Fig. 5 ESEM image and EDS analysis of the products on the surface of the paste core

Based on the observation in Fig. 2, the paste core can be regarded as the last layer of successive paste layers after 7 days of exposure. A reasonable assumption is that the paste core would become smaller due to new layers detaching after 8 days of exposure. Obviously, Na_2SO_4 crystallization in

the pores is the mechanism causing the CSA cement paste damage.

To verify the damage mechanism, the products in different parts of the paste specimen were identified by XRD.

The effect of carbonation on the stability of CSA cement paste is a problem, and ettringite decomposes to gypsum, calcium carbonate, and alumina gel after carbonation, as described in the following equation [10-11]:

In Fig. 6, the products from the surface paste and inner paste of the top part of specimens in contact with air, but not immersed in the Na_2SO_4 solution, were identified by XRD analysis. The XRD Pattern 1# can be regarded as the reference pattern that was isolated from the sulfate solution and atmosphere. In Pattern 1#, the main phases were ettringite and unhydrated $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$. However, Pattern 2# indicated that ettringite diminished when accompanying the formation of gypsum and calcium carbonate, and this result occurred even in the absence of the sulfate solution.

Fig. 6 XRD patterns of the surface paste and the inner paste of the top part. (1)- the inner paste of the top part; (2)-the surface paste of the top part (B-Bassanite: $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$; C-calcite: CaCO_3 ; E-Ettringite: $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$; G-Gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Y-Yeelimite: $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$)

The paste of the specimen in the sulfate solution (Pattern 3#) was also compared with the reference pattern, as shown in Fig. 7. The products in the paste were the same as the products after carbonation of ettringite as described in the literature [10]: calcium carbonate in the form of aragonite and gypsum. No new phase was generated in the paste in contact with the sodium sulfate solution.

Fig. 7 XRD patterns of the paste in the sulfate solution and the inner paste of the top part. (1)- the inner paste of the top part; (3)-the paste in the solution (A-Aragonite: CaCO_3)

Combining the results in Figs. 6 and 7, the phase changes in the CSA cement paste immersed in the sodium sulfate solution should be influenced by carbonation but not sodium sulfate.

Fig. 8 shows the XRD patterns of the successive paste layers (Pattern 4#) and paste core (Pattern 5#).

Fig. 8 XRD patterns of the successive paste layers and the paste core in the evaporation zone. (4)- the successive paste layers; (5)- paste core. (A-Aragonite: CaCO_3 ; Gl-Glauberite: $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$; N-Sodium Sulfate: Na_2SO_4)

These results can be described as follows:

1. Compared to Pattern 3#, Patterns 4# and 5# contained gypsum and aragonite, but ettringite had diminished;
2. Compared with Pattern 1# and 3#, no other new phases were formed in Patterns 4# and 5# except for the sodium sulfate and double salt of glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$).
3. The formation of glauberite indicated that the formation of gypsum was not influenced by the sodium sulfate solution and that sodium sulfate could stably accumulate in the CSA cement paste;
4. The appearance of glauberite in the evaporation zone of the damaged paste seems strange because sodium salts could not be found in the paste directly exposed to the sodium sulfate solution. The solution transport mechanisms in the different pastes were the key factors to answer this question. We know that ions penetrated into the paste when the paste was immersed in the solution, as the Na_2SO_4 concentration of the pore solution in the paste was far lower than the concentration of the external Na_2SO_4 solution. However, due to the wicking action, the concentrations of the ions in the pore solution in the evaporation zone reached super-saturation [12], causing sodium sulfate crystallization in the paste and the formation of successive paste layers. The damaged paste evidently aggravated the carbonation-induced decomposition of ettringite, causing a large amount of gypsum to form. In the pore solution with the higher concentration of sodium sulfate and gypsum, the double salt of glauberite was generated.

4. 2 Concrete specimens

According to the images in Fig. 3, the products on the surface of the paste and aggregate of ITZ in the evaporation zone were analyzed by means of ESEM and EDS.

Fig. 9 ESEM image and EDS analysis of products on the surface of the aggregate. (a), EDS analysis of the needle crystals labeled by a short line; (b) EDS analysis of needle crystals labeled by a cross

Fig. 9 shows the products on the surface of the aggregate. The surface of the aggregate is covered by a large amount of needle-like crystals similar to a hedgehog, and the tips of the needles are bonded to white crystals. According to the EDS analysis, the needle crystals should be ettringite [13] and the white crystals should contain Na_2SO_4 .

Fig. 10 ESEM image and EDS analysis of products on the surface of the CSA cement paste. (a) EDS analysis of

needle crystals is labeled as the short line; (b) EDS analysis of needle crystals is labeled as the cross

Fig. 10 shows the products on the surface of the paste. The needle crystals are composed of the same elements as the ones in Fig. 9. Patches of white crystals cover the needle crystals. According to the EDS analysis, the white crystal is Na_2SO_4 .

According to the results shown in Fig. 9 and Fig. 10, two possibilities could cause the separation of the cement paste and aggregates. One possibility is the growth of needle crystals composed of ettringite, whereas the alternative is the formation of white crystals of Na_2SO_4 . However, ettringite is the original hydration product in the ITZ [13], so forming this material cannot be the reason. Therefore, the mechanism causing concrete damage can only be Na_2SO_4 crystallization during the process of salt weathering.

Compared with the Portland cement concrete in the previous paper of the present authors [6], Na_2SO_4 crystals could be found on the surface of aggregate in the ITZ, although gypsum was the main product on the surface of the cement paste. The damage mechanism was the formation of gypsum due to chemical action between portlandite and sodium sulfate in the ITZ causing the separation of the cement paste and aggregate. Then, sodium sulfate crystallization occurred on the surface of the aggregate.

4.3 Discussion

CSA cement and Portland cement are both hydraulic cementitious materials with similar hydration products except for $\text{Ca}(\text{OH})_2$. However, the performances of these two cement pastes and concretes are quite different upon damage. In the case of *sulfate salt weathering of Portland cement paste and concrete*, Na_2SO_4 crystals could not be identified in the damaged paste or concrete. Instead, chemical sulfate attack products of ettringite and gypsum crystals were present. In the case of sulfate salt weathering of CSA cement paste and concrete, the Na_2SO_4 crystals could be clearly observed and the failure of the paste and concrete was attributed to this salt. Obviously, $\text{Ca}(\text{OH})_2$ plays a vital role in *sulfate weathering of Portland cement concrete*.

As discussed in the introduction, $\text{Ca}(\text{OH})_2$ is the source cause of the chemical sulfate attack on concrete. The hydration products of CSA cement contain rich ettringite, C-S-H and an Al gel, but do not include the $\text{Ca}(\text{OH})_2$ phase. When CSA cement paste is immersed in the Na_2SO_4 solution, (1) the stability of ettringite is isolated from SO_4^{2-} ; (2) even the high Na^+ concentration cannot cause decomposition of ettringite [14]; (3) the pH value of the pore solution in the CSA cement paste will not be changed by the Na_2SO_4 solution and C-S-H will remain stable; (4) the Al gel can react with Ca^{2+} and SO_4^{2-} to form ettringite in an alkaline solution [15], and the stability of the Al gel will not be influenced by Na_2SO_4 . In other words, without the effect of $\text{Ca}(\text{OH})_2$ no chemical reactions occur between the hydration products of CSA cement and Na_2SO_4 . This limited reactivity is the reason that CSA cement concrete fully immersed in the Na_2SO_4 solution exhibits excellent sulfate attack resistance [16].

In summary, in the Na_2SO_4 solution, the $\text{Ca}(\text{OH})_2$ – ettringite – C-S-H – Al gel system is unstable due to the chemical reaction between $\text{Ca}(\text{OH})_2$ and Na_2SO_4 . However, the ettringite – C-S-H – Al gel system can exist in the Na_2SO_4 solution due to the absence of the chemical reaction between $\text{Ca}(\text{OH})_2$ and Na_2SO_4 . In the first case, chemical sulfate attack is the failure mechanism in the evaporation zone of concrete, whereas in the latter case, physical sulfate attack (sulfate crystallization) is the damage mechanism in the evaporation zone of concrete. These

results indicate that if chemical reactions occur between sulfates and cement hydration products, sulfate crystallization in the pores will not occur and cause concrete damage.

To explain the effect of the relationship between sulfate salts and cement hydration products on the deterioration mechanism for cementitious materials, the theory of crystal growth in a pore should be reviewed. Before the important paper by Carl W. Correns was published in 1949, this author had written other papers to explain the theory of crystallization [17]. In 1926, he attempted to explain the relationship between interfacial tension and growth pressure: if a crystal C is detached from the support S , the liquid L will be pulled between the supporting and the loading surface and work must be carried out. An interface of size ϖ and interfacial tension γ_{cs} disappears in this process. At the same time, two new equally sized interfaces are created, which have the interfacial tensions γ_{cl} and γ_{sl} . If the crystal is elevated, including the weight added during growth, then the work required is:

$$A = \varpi \cdot (\gamma_{cs} - \gamma_{cl} - \gamma_{sl}) \quad (2)$$

Where: ϖ is the interface size, γ_{cs} is the interface tension between the crystal and support; γ_{cl} is the interface tension between the crystal and liquid; and γ_{sl} is the interface tension between the liquid and support.

If the crystal is elevated, the following condition should be fulfilled:

$$\gamma_{cs} > (\gamma_{cl} + \gamma_{sl}) \quad (3)$$

On the contrary, if the liquid between the crystal and support disappears, the chemical potential $\gamma_{cs} - (\gamma_{cl} + \gamma_{sl})$ is the barrier. Specifically, a chemical potential proportional to $\gamma_{cs} - (\gamma_{cl} + \gamma_{sl})$ is available to prevent contact, drawing liquid into the gap between the crystal and the support. In other words, the liquid film between the crystal and particle is vital for the crystal to continue growing. The van der Waals force should act as a repulsive force within the film and between the particle or support and crystal. On the other hand, if the particle or support attracts the salt crystal, the chemical potential preventing contact will decrease and even disappear, the liquid film will disappear and the crystal will grow and contact and engulf the particles. Similarly, if the interaction between the salt crystal and pore wall is repulsive, a film between the crystal and the pore wall will form. However, if the pore wall attracts the salt, rather than repels, the salt will absorb on the pore wall. The thinner film disappears, and the crystal growth stops. This mechanism controls stress from salt crystallization [18]: to avoid the damaging crystallization pressure, eliminating the repulsive forces between the growing salt and the pore wall would be sufficient. For this purpose [18], certain polymers capable of anchoring to the pore wall and containing a short chain with a ligand that can strongly adsorb various types of salt can be used to alter the surface chemistry of the pore. Changing the surface chemistry of the pore can switch the interaction between the pore wall and salt crystal from repulsion to adsorption. The crystal would be attracted rather than repelled by the wall. The crystal would grow after contact with the wall, but the growth would then stop without any stress developing.

Therefore, if chemical reactions between sulfates and cement hydration products exist, the pore wall of the cement paste is attractive to the sulfates rather than repulsive, and forming a liquid film between the pore wall and the salt crystal is impossible. Crystal growth would stop without any stress developing. On the contrary, if a chemical reaction does not occur or chemical adsorption disappears between the salt and pore wall, then the thin film between the crystals and pore wall

will be formed and sulfate salt crystallization pressure would perform work. This reason explains the role of $\text{Ca}(\text{OH})_2$ in sulfate salt weathering of Portland cement concrete. In a previous paper by the authors of the present paper [7], the occurrence of sulfate crystallization in the CaCO_3 crystals of the carbonated products of $\text{Ca}(\text{OH})_2$ also attributed to the disappearance of chemical reactions between $\text{Ca}(\text{OH})_2$ and sulfates.

5 Conclusions

In the present paper, a micro-analysis of sulfate salt weathering of CSA cement paste and concrete is performed to offer referential research on *sulfate salt weathering of Portland cement concrete* focusing on the role of $\text{Ca}(\text{OH})_2$ in the damage mechanism. The test results indicates the following conclusions:

(1) The deterioration of the CSA cement paste partially immersed in the Na_2SO_4 solution showed typical salt weathering for porous materials with successive paste layers in the evaporation zone after just 7 days of exposure. The Na_2SO_4 crystals were identified in the damaged paste and attributed to the failure mechanism.

(2) The CSA cement concretes were also severely deteriorated, as shown by the separation of the aggregate and paste along the ITZ in the evaporation zone after 7 days of exposure to the Na_2SO_4 solution. The Na_2SO_4 crystals were also identified on the surfaces of the paste and aggregate and attributed to the failure mechanism.

(3) Compared with Portland cement, the reason that Na_2SO_4 crystals can be identified in the damaged evaporation zone of the paste and concrete is that no chemical reaction occurs between the hydration products of CSA cement and Na_2SO_4 without the presence of $\text{Ca}(\text{OH})_2$.

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