THE DAMAGE OF CALCIUM SULFOALUMINATE CEMENT PASTE PARTIALLY IMMERSED IN NA_2CO_3 SOLUTION

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Abstract: In the presented paper, the tests were designed to offer indirect evidences for the *physical sulfate attack on ordinary concrete*. The calcium sulfoaluminate (CSA) cement paste was partially exposed to 10% Na_2CO_3 solution under condition of 20°C and RH 60%. The microanalysis results showed that Na_2CO_3 crystallization did not occur in the CSA cement paste and the Na_2SO_4 crystallization, the product of chemical reaction between CSA cement paste and Na_2CO_3, caused the cracks formation at the edge of specimens. The Na_2CO_3 crystallization occurred after the chemical reactions disappeared. As comparison, it can be confirmed that the physical sulfate attack or sulfate crystallization also cannot occur in the ordinary concrete due to the chemical reactions between Portland cement paste and sulfate.

1 INTRODUCTION

Sulfate attack on concrete is considered as a typical chemical corrosion of cement, causing the decomposition of cement hydration products. However, when the concrete element is partially exposed to sulfate environment, the similar slat weathering of porous materials occurs that the upper part of concrete in contact with air is severely damaged but with the sound part of concrete surrounded by sulfate ions. People generally indicates that the concrete is damaged by physical sulfate attack or sulfate salt crystallization distress causing the structures failure not the decomposition of hydration products. Therefore, there is viewpoint that the physical sulfate attack cannot be regarded as sulfate attack on concrete.

However, according to author's previous researches [1], it seems that the main reason causing concrete damage is not the physical sulfate attack but still the chemical sulfate attack. In the paper [2], author indicated that the sulfate salt crystallization cannot occur if there is chemical reaction between sulfate and hydration products of cement. When Portland cement paste was partially exposed to 10% Na_2SO_4 solution under the condition of 20°C and RH 60%, the specimens were damaged after 5months' exposure. The micro-analysis results showed that the ettringite and gypsum were identified as the evidences of chemical sulfate attack [3-4]. However, the similar test results showed that the CSA cement paste specimens were quickly damaged just after 7 days exposure. Na_2SO_4 could be clearly identified as the evidence of sulfate salt crystallization [5]. The reason for the quick failure is that the hydration products of CSA cement are stable in the Na_2SO_4 solution.

The hydration products of CSA cement contain rich ettringite, C-S-H and Al gel. 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 [6-7]:

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2 = 3CaCO_3 + 3(CaSO_4 \cdot 2H_2O) + Al_2O_3 \cdot xH_2O + (26-x)H_2O \quad (1)$$

If CSA cement paste is immersed in Na_2CO_3 solution, the chemical reaction cannot be avoided. However, a test can be designed as following: the CSA cement paste specimens are divided into two parts, (1) one part will be immersed in the 10% Na_2CO_3 solution at 40°C until the finish of chemical reaction between CSA cement paste and Na_2CO_3. Then, the paste specimen will be partially immersed in 10% Na_2CO_3 solution again under the exposure condition of 20 °C and 60% RH, (2) as reference, the other uncontaminated CSA paste specimens will be also partially exposed to 10% Na_2CO_3 solution under the same exposure condition. The comparison between the above two concrete performances can offer more evidences to disclose the so-called physical sulfate attack on concrete from a different perspective.

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 cement is given in Table 1. Paste specimens were exposed to a 10% Na_2CO_3 solution by mass.

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

	CaO	SiO_2	Fe_2O_3	MgO	Al_2O_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

Plain cement paste with a W/C ratio of 0.45 was mixed. The fresh paste were cast in a mould with size of 10*40*150 mm covered with a plastic sheet in a moist room for 24 h. The specimens were demoulded and stored in water at 20 ± 1 °C. At the age of 7 days, all specimens were dried in a climate box at 20 ± 3 °C and 60 ± 5% RH for 7 days. After drying, the CSA cement paste specimens are divided into two parts, (1) three specimens were immersed in the 10% Na_2CO_3 solution at 40°C until the finish of chemical reaction between CSA cement paste and Na_2CO_3. Then, the specimens were partially immersed in 10% Na_2CO_3 solution again under the exposure condition of 20 °C and 60% RH, (2) the other three uncontaminated CSA paste specimens were partially exposed to 10% Na_2CO_3 solution under the same exposure condition.

2.3. Visual observation, XRD, IC

The damaged specimens were visually observed and analyzed by XRD analysis. The samples were vacuum dried with silica gel at 20 °C. The specimens did not touch solution and water any more after removal from the solution. The SO_4^{2-} concentration was measured by IC (Ion Chromatography) The substance on the surface of the specimens was cleaned by a soft brush or a thin blade.

3. RESULTS AND DISCUSSION

3.1 CSA cement paste exposed to 10% Na2CO3 solution

After 3 months exposure to 10% Na_2CO_3 solution, the CSA cement paste specimen observation is shown in Figure 1. It can be found that the evaporation zone of specimen was covered with white crystals. Several cracks occurred at the edge of specimen, and small pieces of paste can be easily taken off from the specimen. After the paste parts in the solution and evaporation zone were broken off respectively, two different zones in the section were observed the outer zone with light color and the inner zone with dark color. The products of small pieces of paste and white crystals were identified by XRD analysis (shown in Figure 2). The products of outer zone (shown in Figure 3) and inner zone (shown in Figure 4) were also identified by XRD analysis.

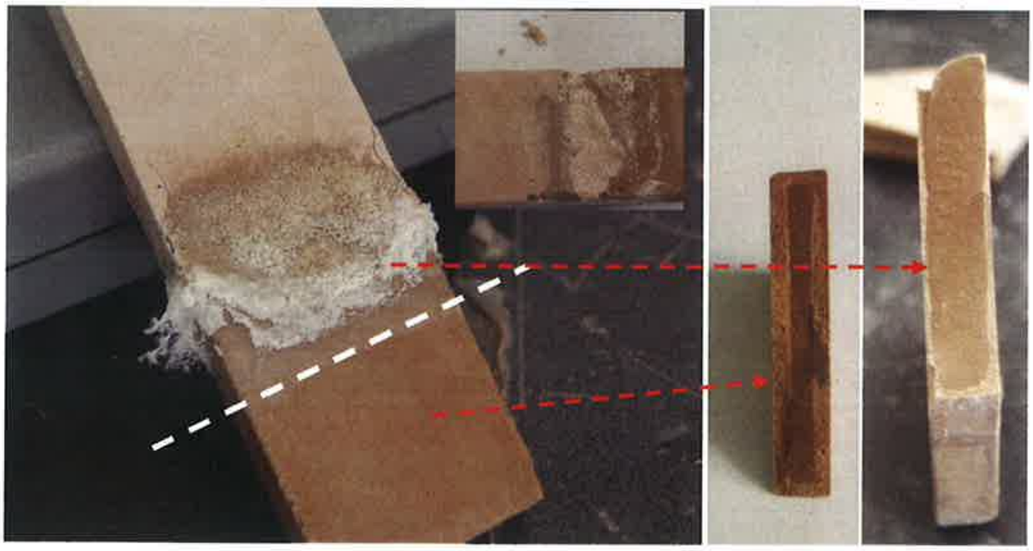

Figure 1: Visual observation of CSA paste specimen partially immersed in Na_2CO_3 for 3 months

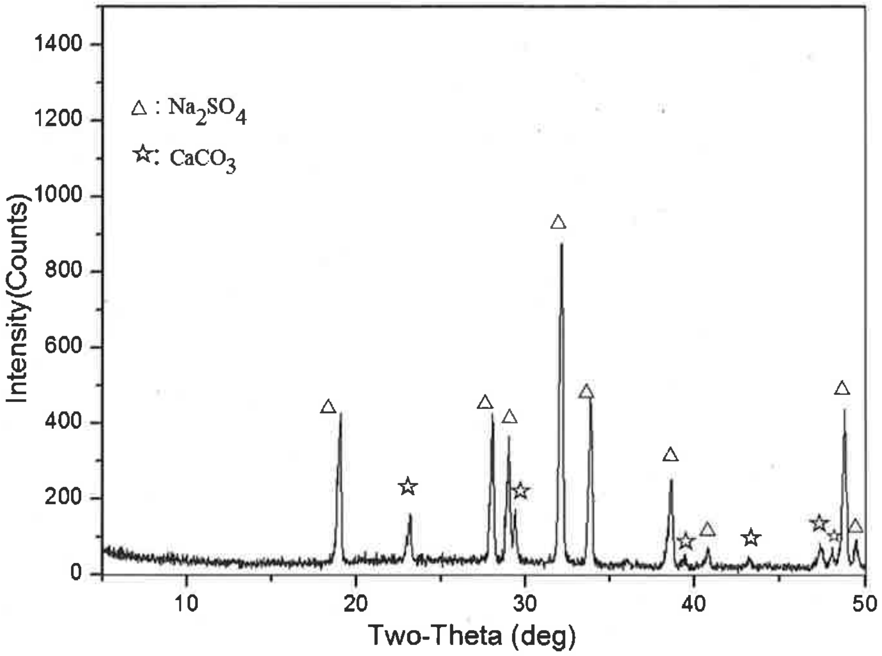

Figure 2 XRD pattern of small pieces of paste and white crystals (T:

It is very interesting to find that the white crystals were $Na_2SO_4 \cdot 10H_2O$ although the CSA cement paste was partially immersed in Na_2CO_3 solution. $CaCO_3$ was the main product in the small paste pieces.

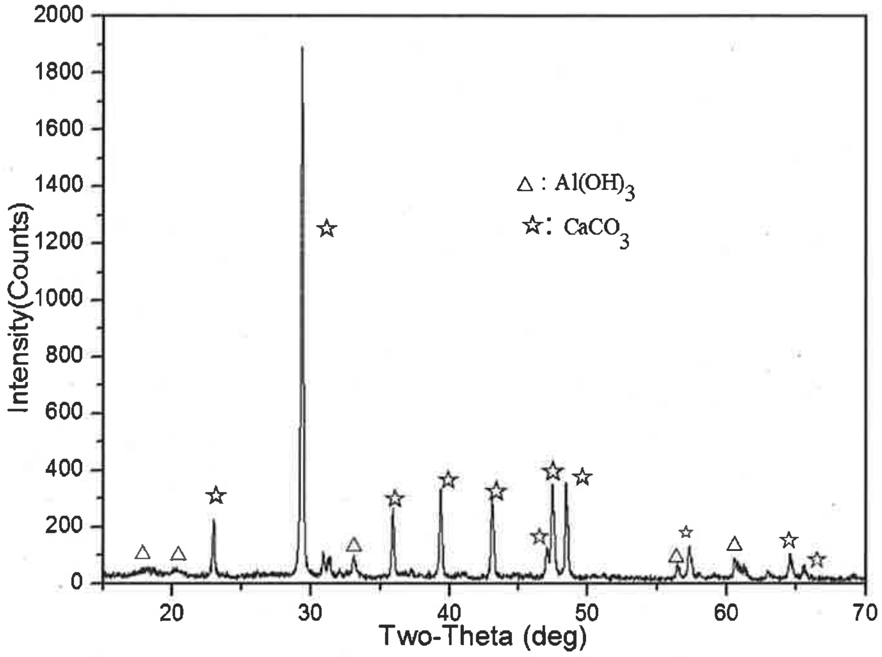

Figure 3 XRD pattern of outer layer of CSA paste in the solution

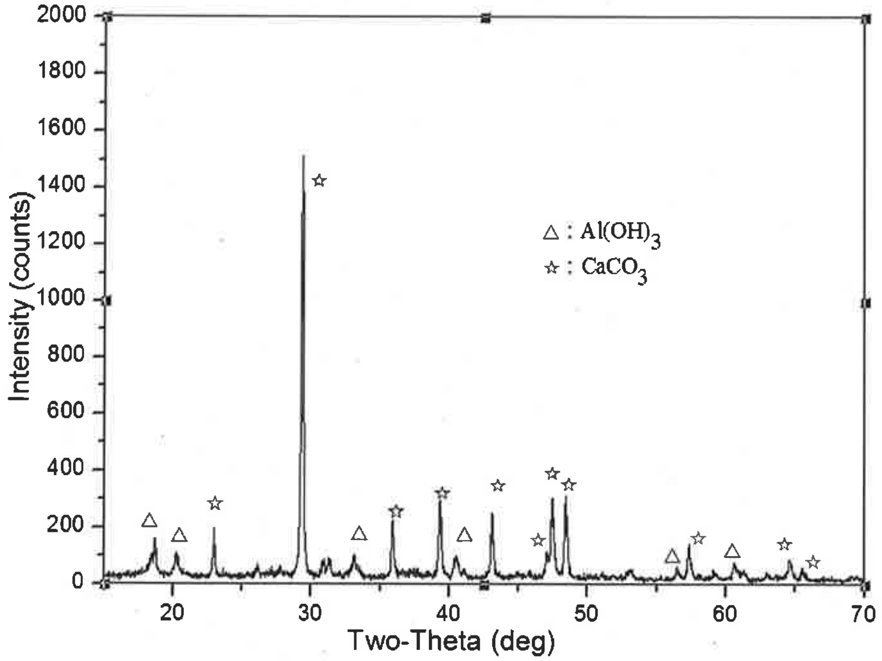

Figure 4 XRD pattern of outer layer of CSA paste in the evaporation zone

Figures 3 and 4 show the XRD patterns of products in the outer zones of paste in the solution and evaporation zone. Obviously, the products in the two zones were the same, containing rich $CaCO_3$ and $Al(OH)_3$.

Based on the results shown in Figures 2, 3 and 4, it can be conformed that (1) Na_2CO_3 crystallization did not appear in the evaporation zone paste, (2) in the evaporation zone the same chemical reaction between Na_2CO_3 solution and hydration products of CSA cement paste occurred as in the solution as following:

$$3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O + 6Na^+ + 3CO_3^{2-} = 3CaCO_3 + 3Na_2SO_4 + Al_2O_3\cdot xH_2O + (32-x)H_2O \qquad (2)$$

(3) $CaCO_3$ is more indissolvable than $CaSO_4$, therefore $CaCO_3$ was the final generation in the solution compared to the carbonation reaction shown in equation 1. the concentration of SO_4^{2-} reached 51.67g/l (about 7.6% Na_2SO_4) in the solution after 3 months exposure according to the IC analysis result. (4) the crystallization distress of the Na_2SO_4 caused the cracks shown in Figure 1. (5) the peaks of $Al(OH)_3$ in Figure 4 are higher than them in Figure 3. The reason is that the Na_2CO_3 concentration of pore solution in the evaporation zone was higher than 10% due to wick action [8].

The above results support that Na_2CO_3 crystallization cannot occur in the porous CSA cement paste due to the chemical reactions between it and the hydration products. Another experiment was designed that the CSA cement paste was fully immersed in the Na_2CO_3 solution until the chemical reaction finish. Then, the paste was partially immersed in Na_2CO_3 solution again to check if Na_2CO_3 crystallization can occur in the paste.

3.2 CSA cement paste after chemical reaction exposed to 10% Na_2CO_3 solution

According to the observation in Figure 1, the light color part means the chemical reaction occurrence in the paste. After the color of paste section totally became light, the specimens were partially immersed in 10% Na_2CO_3 solution again. It is interesting to found that the specimen was damaged just after 10 days exposure shown in Figure 5. The successive paste layers were formed at the top of specimen. This appearance is a typical crystallization distress on porous materials. The XRD analysis on damaged paste clearly proved that the Na_2CO_3 crystallization distress was the mechanism for the formation of successive paste layers.

Figure 5: Visual observation of reacted CSA paste specimen partially immersed in Na_2CO_3 for 10 days

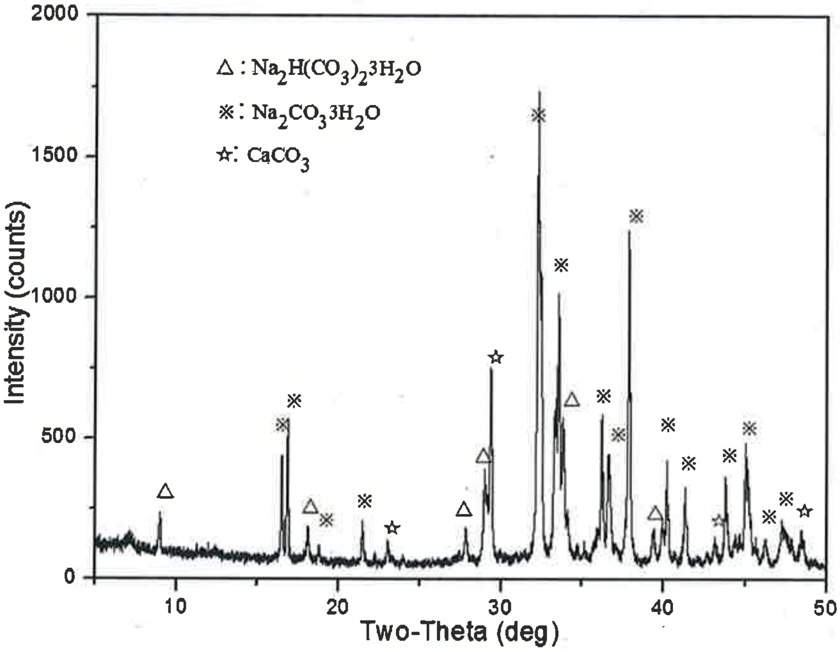

Figure 6 XRD pattern of paste layers

Combined with the above two tests' results, the viewpoint, that the salt crystallization distress cannot occur in the cement paste if there is chemical reaction between paste and salt, can be further confirmed. Therefore, when the Portland cement concrete element is partially buried in the sulfate environment, the mechanism for the failure of concrete in the evaporation zone cannot be simply attributed to sulfate crystallization distress due to the chemical reaction between sulfate and hydration products.

5 CONCLUSIONS

The conclusions can be deduced as follows:

(1) Na_2CO_3 crystallization cannot occur in the CSA cement paste partially immersed to Na_2CO_3 solution.

(2) The paste damage is caused by Na_2SO_4 crystallization that is one of the chemical reaction products between CSA cement paste and Na_2CO_3.

(3) Na_2CO_3 crystallization can occur in the paste only when the chemical reactions disappear.

(4) Compared to ordinary concrete partially buried in sulfate environment, the failure of concrete in the evaporation zone cannot attributed to the physical sulfate attack or sulfate crystallization distress. It should be still the chemical sulfate attack.

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REFERENCES

[1] Liu, Z., Deng, D. and De Schutter, G. Does concrete suffer sulfate salt weathering? *Constr. Build. Mater.* 2014, 66(1): 692-701.

[2] Liu, Z., Deng, D. and De Schutter, G. The role of Ca(OH)2 in sulfate salt weathering of ordinary concrete, submitted to *Constr. Build. Mater.*

[3] Liu, Z., Deng, D. and De Schutter, G. Micro-analysis of the role of interfacial transition zone in "salt weathering" on concrete, *Constr. Build. Mater.* 2010, 24(11): 2052–2059.

[4] Liu, Z., Deng, D. and De Schutter, G. Micro-analysis of "salt weathering" on cement paste, *Cem. Concr. Compo.* 2011, 2011; 33(1):179-191.

[5] Liu, Z., Deng, D. and De Schutter, G. The comparison between sulfate salt weathering of portland cement paste and calcium sulfoaluminate cement paste, *International Conference on the Regeneration and Conservation of Concrete Structures, Proceedings.* 2005 (6):1-11.

[6] Nishikawa, T., Suzuki, K. and Ito, S. Decomposition of synthesized ettringite by carbonation, Cem. Concr. Res. 1992, 22(1): 6-14.

[7] Chen, X., and Zou, R. Kinetic study of ettringite carbonation reaction, Cem. Concr. Res. 1994, 24(7): 1383-1389.

[8] Liu, Z., Deng, D. and De Schutter, G. Chemical sulfate attack performance of partially exposed cement and cement + fly ash paste, *Constr. Build. Mater.* 2012, 28(1): 230-237.