

## Concrete Deterioration under Alternate Action of Carbonation and Sulfate Attack

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**Abstract:** By micro- and macro-observations, the study reveals the deterioration mechanisms of concrete under alternate action of carbonation and sodium sulfate solution attack (C-SA) compared with the single sodium sulfate solution attack (SA). The studies indicate that in both cases, the main attack product is ettringite, some gypsum is checked only in the first layer of case SA, the thaumasite form of sulfate attack is not initiated in case C-SA. Compared with the single sodium sulfate solution attack, although the carbonation layer mitigates the extent of sulfate attack in limited exposure period, the alternate action of carbonation and sulfate attack still leads to strength degradation to some extent. The effect of carbonation on sulfate attack for longer exposure period deserves further research.

**Keywords:** Attack product, concrete, carbonation, strength, sulfate, sulfate-ion content

### INTRODUCTION

Deterioration of cementitious systems exposed to sulfate salts is the result of sulfate ions transport through the pore system, chemical reaction with the hydration product, generation of stress due to the creating of expansive reaction products and the mechanical response (typically spalling and cracking) of bulk material due to the stresses (Ferraris *et al.*, 2006). Recently, many researches about sulfate attack on concrete only consider single affecting factor and few researches considering action of multi-factors were reported. In practice, when suffered from sulfate attack, the concrete will often be subjected to some actions of other factors and there are mutual effects between them. It is necessary to do some researches on deterioration mechanism of sulfate attack on concrete under actions of multi-factors.

Our researches depend on the following background to investigate the multi-factors action cases: some concrete structures lying in fluctuation region of sulfate-rich water discharged from chemical plant suffer from carbonation when no water, which is referred as the action of both carbonation and sulfate attack. Based on the previous researches have finished discussing concrete deterioration mechanisms under single carbonation action (Li *et al.*, 2006), the study studies the mechanisms of concrete under alternate action of carbonation and sulfate attack compared with the single sulfate attack.

### MATERIALS AND METHODS

**Raw materials:** The cement is P.O. 42.5 with chemical composition listed in Table 1. The fine aggregate is

river sand with fineness modulus of 2.71. The coarse aggregate is mixed by two grades crushed limestone with maximum grain size of 10 mm and 20 mm in mass proportion 1:1. The tap water is adopted as mix water.

**Proportion of concrete and specimen fabrication:** The proportion of concrete corresponding to strength grade of C40 is given in Table 2. The specimens are cubes with dimension of 100 mm. After natural curing for 24 h, the specimens are demoulded and then shifted into the standard curing room with temperature of (20±3) °C and relative humidity of 95% for 28 d. After that, start the attack experiments.

**Test method:** Sulfate attack on concrete can be divided into four types such as ordinary sulfate attack, magnesium salt attack, thaumasite form of sulfate attack (TSA) and crystallization attack. The ordinary sulfate attack is considered in the experiment, the sodium sulfate solution is chosen as attack solution. The mass fraction of attack solution is 10% corresponding to the sulfate-ion content of 73000 mg/L. The experimental observations consist of micro- and macro-ones. Micro-observations include the analysis of attack products by thermal analysis method and the determination of sulfate-ion content from surface to interior by chemical titrating method (modified barium sulfate gravimetric method). Macro-observations mainly include the mechanical behaviors such as compressive strength and splitting strength. Two experiment cases are designed as follows.

**Single sodium sulfate Solution Attack (SA):** To reflect one-dimensional sulfate attack regularity, only one surface is attacked and the other five surfaces are

Table 1: Chemical composition of cement

Chemical composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	f-CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Alkali
Weight percent (%)	31.43	12.43	3.34	41.28	0.76	4.25	3.22	0.80	0.43	0.97

Table 2: Mix design of concrete

Constituent	Cement	Fine aggregate	Coarse aggregate	Water
Weight (kg/m <sup>3</sup> )	457	591	1201	201

sealed by paraffin wax. The specimens are stored in sodium sulfate solution for continuous immersion. During experiment, the solution is sealed by plastic membrane to prevent evaporation and refreshed once every month to keep solution concentration constant. The experiment is conducted in the room and the air-conditioner is installed to keep temperature of 20°C and relative humidity of 70% almost invariable. The micro- and macro-observations are finished at exposure period of 30 d, 90 d, 180 d, 270 d and 360 d respectively.

**Alternate action of carbonation and sodium sulfate solution attack (C-SA):** The carbonation is conducted in CCB-70A Carbonation Chambers with CO<sub>2</sub> concentration of 20%, temperature of 20°C and relative humidity of 70%. At the exposure period 0, 30, 90, 180, 270 d, respectively, all specimens first are carbonated for 7 d and then shifted into sodium sulfate solution for continuous immersion (similar to case SA). The micro- and macro-observations are the same as case SA.

## RESULTS AND ANALYSES

**Main attack products:** The main attack products and their loss of weight from surface to interior of the attacked concrete can be determined by STA 409 PC Simultaneous Thermal Analyzer to generate typical TG/DSC figures. According to the decomposition temperature corresponding to heat absorption peak in the DSC curves, the attack product is determined, the loss of weight of which is shown simultaneously in the TG curves. The attacked specimens with exposure period of 270 d are chosen as analyzing objects. The measured slice with thickness from surface layer to interior layer is the first one of 1.5 mm, the second of 2 mm, the third and more of 5 mm. Results of thermal analysis of the attacked concrete in both cases are listed in Table 3.

All DSC curves have three obvious heat absorption peaks which lie in temperature stages of 74.1, -101.0, 429.6, -448.0 and 742.0, -791.8°C respectively. In terms of many related researches (Kresten and Berggren, 1975; Shu and Lu, 2007; Xie and Wang, 1997; Zou *et al.*, 1995), the three temperature stages stand for dehydration and decomposition of ettringite, decomposition of portlandite and decomposition of calcite respectively. On the DSC curve of the first layer in case SA, one more obvious heat absorption peak occurs at 132.8°C, which indicates some amount of gypsum is produced.

In the other layers of case SA and in case C-SA, no obvious gypsum is checked, which can be attributed to large amount of Al<sub>2</sub>O<sub>3</sub> (12.43% by weight) in cement used that can lead to much C<sub>4</sub>AH<sub>13</sub> by hydration which consumes gypsum produced by reaction of sulfate and portlandite to form ettringite. In case C-SA, although with alternate action of carbonation and sulfate attack, no thaumasite is found. According to the researches on effect of temperature on thaumasite formation in carbonated mortars (Blanco-Varela *et al.*, 2006) and the role of CO<sub>2</sub> in the formation of thaumasite (Collett *et al.*, 2004), the thaumasite can be formed only below 15°C and more readily at 5°C. The similar conclusion is also drawn by Thomas *et al.* (2003). In case C-SA, the temperature is kept 20°C invariable, so the thaumasite is hard to be formed. Furthermore, the thaumasite form of sulfate attack will generate white halo on the concrete surface, but with careful observations to the specimens attacked for 360 d, no evidence about white halo is found.

According to the loss of weight shown in Table 3, the ettringite content in the first layer is highest in case SA, but the ettringite content in first layer is lowest in case C-SA due to carbonation consuming some portlandite. Within the first layer of case SA, the portlandite is exhausted and because of alternate action of carbonation and sulfate attack, the portlandite is used up within the first three layers of case C-SA. Due to carbonation producing some calcite, the calcite content in the first three layers of case C-SA is obviously greater than that in case SA in which the calcite is mainly from coarse aggregate or powder carried by coarse aggregate and the content is relatively stable.

**Sulfate-ion content distribution regularity:** Sulfate-ion content from surface to interior is determined by chemical titrating method (modified barium sulfate gravimetric method) (JTJ 270-98, 1998; Zhang *et al.*, 2003; Zhao *et al.*, 2008). The sample preparation is just like that of thermal analysis. Because the cement used contains some amount of gypsum and SO<sub>3</sub>, before the concrete suffers from external sulfate attack, the concrete itself contains some amount of initial sulfate ions about 0.78% (calculated according to SO<sub>3</sub> content) by measurement. Figure 1 shows the sulfate-ion content distribution regularity from surface to interior in both cases.

For every exposure period of case SA, sulfate-ion content is decreased obviously with increasing depths. When attacked to 360 d, the sulfate-ion content in the fourth layer (11 mm away from the attacked surface) is 0.79% closing to the initial content 0.78%. At the fixed depth, the content in the first layer is relatively high which increases from 3.05% of 30 d to 6.47% of 360 d,

Table 3: Results of thermal analysis of the attacked concrete

Case	Sample layers	Peak temperature from DSC curves (°C)				Loss of weight from TG curves (%)			
		1	2	3	4	1	2	3	4
SA	1	95.3	132.8	-	742.0	8.36	4.11	-	11.70
	2	88.0	-	429.6	763.2	3.86	-	1.02	15.81
	3	91.2	-	440.7	775.4	3.71	-	1.63	13.03
	4	89.2	-	439.3	770.6	3.71	-	1.61	13.56
C-SA	1	101.0	-	-	776.2	1.52	-	-	17.25
	2	94.0	-	-	791.8	1.69	-	-	21.93
	3	89.1	-	-	775.5	1.67	-	-	21.53
	4	86.1	-	436.2	756.7	3.17	-	1.29	13.94
	5	88.5	-	448.0	770.6	3.87	-	1.61	11.46
	6	74.1	-	439.3	765.2	4.07	-	1.83	11.72
	7	86.9	-	443.9	778.7	3.58	-	1.74	10.90
	8	81.5	-	444.1	768.8	3.63	-	1.88	11.37

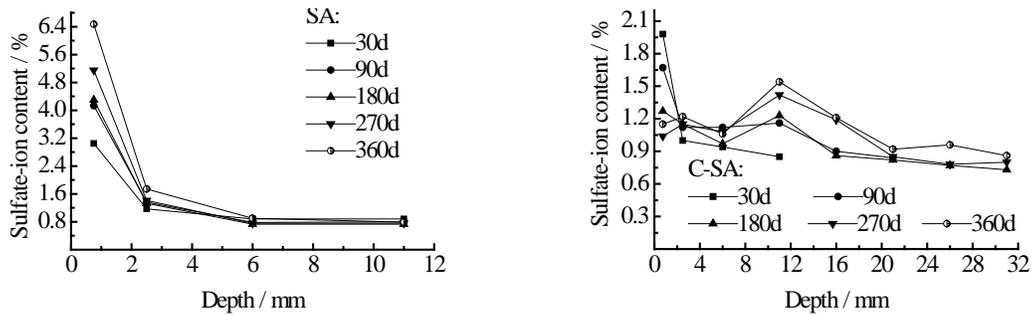


Fig. 1: Sulfate-ion content distribution in attacked concrete

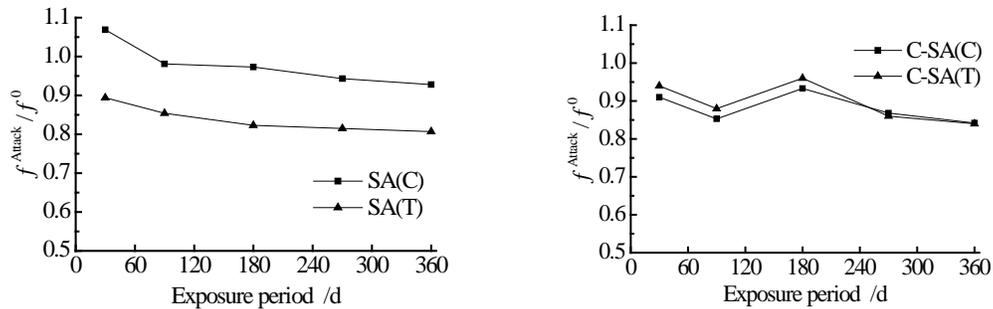


Fig. 2: Strength degradation of attacked concrete

but the content in the second layer expresses a sharp drop and only 1.74% when attacked to 360 d. The content difference between the first layer and the second one proves that most of ettringite precipitate in voids and microcracks of the first layer. The expansive ettringite can fill the voids and microcracks, which hinders sulfate ions diffusing inwards. From the TG curves of 270 d, within 74.1°C -101.0°C, the loss of weight of the first layer and the second one is 8.36% and 3.86% respectively. There is also an obvious drop, which accords with sulfate-ion content distribution regularity.

In case C-SA, sulfate attack concentrates in the first layer and the attack extent inside is mild (but the fourth layer has some abnormality). The main reason is that carbonation brings about calcite generated which will fill the void and microcracks to hinder sulphate-

ions diffusing inwards. As far as the first layer is concerned, the sulfate-ion content is 1.98 % when attacked to 30 d but decreased to 1.0% when attacked to 360 d and from the TG curves data of 270 d, within 74.1°C -101.0°C, the loss of weight of the first layer is only 1.52%, much less than that of case SA. This is resulted from alternate action of carbonation and sulfate attack. When attacked to 30 d, the concrete is only carbonated for 7 d prior to sulfate attack and has a carbonation depth of 3.7 mm according to our previous researches (Li *et al.*, 2006). To maintain portlandite phase (pH) balance in the carbonated layer, the  $Ca^{2+}$  and  $OH^-$  in the uncarbonated layer diffuse outwards and once they meet with the  $SO_4^{2-}$  diffusing inwards from the attack solution and the hydration products of  $C_3A$  in the concrete, the ettringite-generated reaction takes place. But when attacked to 360d, the concrete has been

carbonated for total 35d and the carbonation depth has reach 10.9 mm (Li *et al.*, 2006) and now the free  $\text{Ca}^{2+}$  and  $\text{OH}^-$  in the uncarbonated layer is hard to reach the first layer which is carbonated completely and has a pH of 7. According to the researches by Xi (1993), when pH is less than 10.6, the ettringite becomes unstable and begins to decompose and is easy to leach under action of pore water, which results in sulfate-ion content decreases with increasing exposure period. Compared with case SA, the carbonation layer mitigates the extent of sulfate attack. The similar conclusion is also drawn by Brown *et al.* (2004). But the case for longer exposure period deserves further research.

**Concrete strength degradation regularity:** In Fig. 2, the abscissa stands for the exposure period and the ordinate stands for strength ratio between every exposure period strength  $f^{\text{Attack}}$  and standard curing period strength  $f^0$  (C is for compressive strength and T is for splitting strength).

In case SA, when attacked to 30 d, the compressive strength ratio is 1.07. The strength increment is also attributed to the filling and compaction by ettringite. With the increase of exposure period, more ettringite is formed, once the pores are completely filled, additional ettringite formed will result in expansion stress to destroy the pore structures to create new micro-cracks. As a result, when attacked to 360 d, the compressive strength ratio is decreased to 0.95. Different from the compressive strength, the splitting strength tends to decrease. The splitting strength ratio is 0.89 while attacked to 30 d, but decreased to 0.81 while attacked to 360 d. Generally speaking, the splitting strength appears to be more susceptible to the damage resulted from sulfate attack (Boyd and Mindess, 2004).

In case C-SA, the degradation of compressive strength and splitting strength reverse within 270 d. When attacked to 360 d, both strength ratios are close to 0.84. Although the carbonation layer mitigates the extent of sulfate attack as mentioned above, the alternate action of carbonation and sulfate attack still leads to strength degradation. On the one hand, some C-S-H at the solid-liquid interface are carbonated to  $3\text{CaCO}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$  which does not have cementitious properties (Zhang *et al.*, 2003). On the other hand, the alternate action of carbonation and sulfate attack consumes great amount of portlandite and makes pH of pore solution decrease. According to the researches by Xi (1993), when pH is less than 12.5, the C-S-H gel will dissolve and recrystallize, the  $\text{CaO}/\text{SiO}_2$  of which will decrease from 2.12 with pH being 12.5 to 0.5 with pH being 8.8, as is also the cause of strength degradation.

## CONCLUSION

In both cases, the main attack product is ettringite, some gypsum is checked only in the first layer of case SA and the thaumasite form of sulfate attack is not

initiated in case C-SA. In case SA, the expansion stress due to additional ettringite formed is not very serious, which brings the sulfate ions enriched in the surface layer and the relative mild strength decreased. Compared with single sodium sulfate solution attack, although the carbonation layer mitigates the extent of sulfate attack in limited exposure period, the alternate action of carbonation and sulfate attack still leads to strength degradation to some extent. The effect of carbonation on sulfate attack for longer exposure period deserves further research

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