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The Process of Sulfate Attack on Cement Mortars

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The process of sulfate attack on cement mortar was studied from influences of interfacial zone between aggregate and bulk paste. The influences are the content of interfacial zone and the structure of interfacial zone. The mortar samples were prepared in accordance to a series of volume fraction of aggregate. To improve the structure of interfacial zone, a pretreated quartz aggregate was used, which is composed of hydraulic surface layer and inert core. The results showed that the interfacial zone was an important influencing factor. The mortar resistance to sulfate attack was reduced with the increase in content of interfacial zone but was enhanced by the improvement of the structure of interfacial zone. ADVANCED CEMENT BASED MATERIALS 1996, 4, 1–5

KEY WORDS: Cement mortar, Interfacial structure, Pretreated aggregate, Sulfate attack

Cement mortars can be attacked by solutions containing sulfate, such as natural or polluted ground waters. Attack leads to strength loss, expansion, cracking, and ultimately, disintegration. The phenomena of sulfate attack have been extensively studied over a long period of time. The expansion of cement mortar attacked by sulfate is generally attributed to the formation of ettringite and gypsum [1]. However, this process of sulfate attack on cement mortar is not well understood, and this results in the lack of methods to improve resistance to sulfate attack [2].

Sulfates attack not only the surface layer of cement mortar but also the inner part. The sulfate media penetrate into the cement mortar though pores and react mainly with hydrated crystals such as calcium hydroxide and calcium sulphoaluminate. The pores and hydrated crystals are unevenly distributed in the structure of cement mortar. Many investigators [3] have revealed that the interfacial zone between cement paste and aggregate has a structure different from that of the paste away from the interface. The structure of this zone is characterized by high porosity and richness in the hydrated crystals. Therefore, this interfacial zone can be expected to be an important factor influencing the resistance of mortars to sulfate attack.

The process of sulfate attack on cement mortar was studied from the influences of interfacial zone. One influence is the content of interfacial zone. Because the contents of interfacial zone are proportional to the volume fraction of aggregate, the influence of content was studied by a comparison of resistance to sulfate attack among mortars that were prepared with different volume fractions of aggregate. The other influence is the structure of interfacial zone. A pretreated aggregate was used to improve the structure of interfacial zone. It was composed of hydraulic surface layer and inert core. Investigations [4,5] had shown that the structure of interfacial zone was substantially improved with the hydration of the surface layer of aggregate. By a comparison of mortars with normal aggregate and with pretreated aggregate, the influence of structure of interfacial zone was studied. Based on the studies of influences of interfacial zone, a hypothesis of sulfate attack on cement mortar has been proposed in this paper.

Experimental

Materials

Type I portland cement (Chinese standard) was used; its properties were similar to that of ASTM type 1 portland cement. The chemical composition is listed in Table 1; the cement is lower in aluminate.

Two kind of aggregates were used. One is a normal quartz sand. It was inert to water and sulfates. The other is a pretreated quartz sand, as shown in Figure 1. It was formed by a calcination of quartz sand and $CaCO_3$ powder. Examinations [5] found the surface layer consisted mainly of mineral β-C_2S, which was 8 ~ 10% of the aggregate, and the inert core is as same as the normal quartz sand. The pretreated quartz sand was

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TABLE 1. Chemical composition of cement

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Total
64.50	21.17	4.97	5.19	1.08	2.30	99.21

hydraulic. The size of both aggregates ranged from 0.15 mm to 0.75 mm in diameter.

Mortar Sample Preparation and Tests

A series of mortar samples was prepared with different volume fractions of aggregate V_a (volume of aggregate over volume of the whole sample). Because the water demand of mortar preparation varied with the increasing of aggregate, specimens have a variable water/cement ratio (w/c). But the fresh mortar were controlled to a similar slump for all the specimens. The mix proportions of mortar specimens are listed in Table 2.

The mortar specimens were shaped with 1 × 1 × 4-cm molds, and stainless steel studs were mounted on both ends of the specimen, as shown in Figure 2. The samples were precured for 7 days in water at 40°C; then they were placed in 5% Na_2SO_4 solution at room temperature. The length of specimens was measured every week with a micrometer. At the same time, the sulfate solution was renewed.

After a period of sulfate attack, some specimens were removed from the sulfate solution and prepared for SEM examination. To study the process of sulfate attack, we cut two slices down from each specimen. One was from the surface layer; the other was from the inner part.

TABLE 2. Mix proportions of mortar samples

Quartz sand aggregate			Pretreated quartz sand aggregate		
Sample	V_a	w/c	Sample	v_a	w/c
MOS1	0.1	0.31	MTQS1	0.1	0.31
MQS2	0.2	0.34	MTQS2	0.2	0.34
MQS3	0.3	0.37	MTQS3	0.3	0.37
MQS4	0.4	0.40	MTQS4	0.4	0.40
MQS5	0.5	0.43	MTQS5	0.5	0.43

Results and Discussion

The Expansion of Mortars

The length change of mortar specimen is shown in Figure 3. Both the specimens with normal quartz aggregate and with pretreated quartz aggregate expanded during the attack, but the expansion rates were different. First, the volume fraction of aggregate greatly influenced the expansion of the specimens. The higher the volume fraction of aggregate, the faster the mortar expanded. Second, the nature of aggregate greatly influenced the expansion of mortar specimens. The specimens (MTQS) with pretreated quartz aggregate expanded significantly less than the specimens (MQS) with normal quartz aggregate.

The Content of Interfacial Zone and Its Influences

Only cement paste was attacked by sulfates in the structure of mortar. It can be divided into interfacial zone (interfacial paste) around aggregate and bulk paste away from aggregate. As previously mentioned, the structure of interfacial zone is affected by the aggregate and characteristics of high porosity and richness in hydrated crystals. It was believed to be a weak part to sulfate attack. The thickness of interfacial zone was verified to be a constant (about 25–70 μm) [6]. With increased aggregate, the content of interfacial zone increased although the cement paste decreased. However, the structure of bulk paste was little affected by the aggregate and was similar to the structure of hardened cement paste. It was believed to be a dense part and performed high resistance to sulfate attack [7]. Because the aggregates did not react with sulfates, the influence of volume fraction of aggregate on the expansion of the mortars can be explained with the variations of content of interfacial zone. The influence of content of interfacial zone was discussed with sample MQS as follows.

Assuming that the aggregates were spheres with a diameter equal to the average aggregate particle size (D = 0.45 mm) and distributed with a body-centered cubic arrangement in the specimen, the variation of the nearest distance (d) between aggregates with increasing volume fraction of aggregate (V_a) was calculated and listed in Table 3.

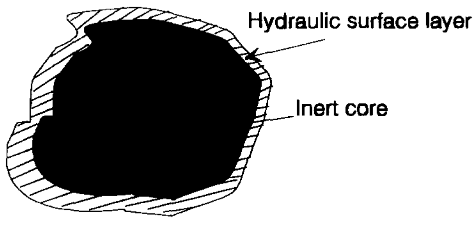

FIGURE 1. Sketch of pretreated aggregate.

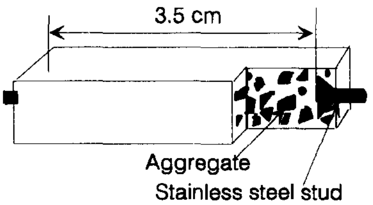

FIGURE 2. Sketch of mortar sample.

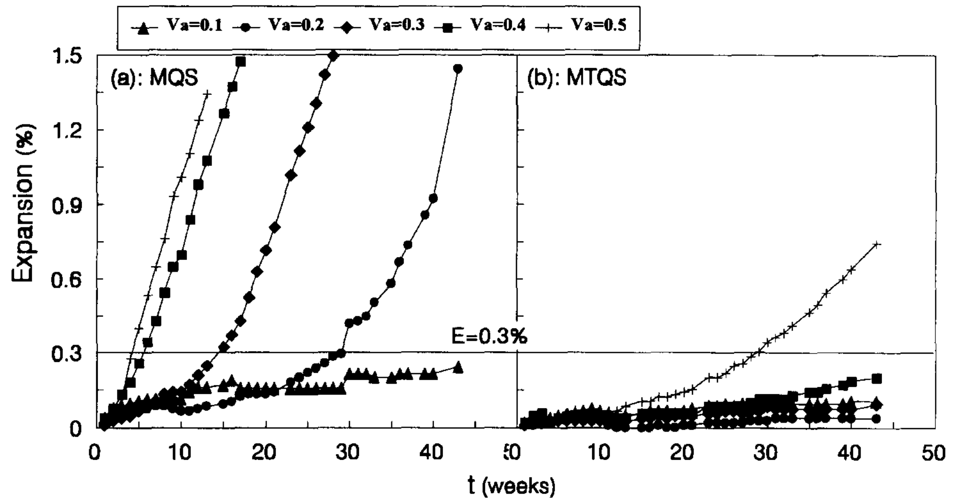

FIGURE 3. Expansion of mortars attacked by 5% Na_2SO_4 solution. Samples were precured for 7 days in water at 40°C.

In the specimens MQS1 and MQS2, half the distance between aggregates was much larger than the thickness of interfacial zone. The aggregates and interfacial zone around them were isolated by bulk paste. Because of the denser structure, the bulk paste would block the sulfate media penetrating into the inner part of specimens. Thus, the specimens expanded slowly. In the specimens MQS4 and MQS5, half the distance between aggregates was shorter than the thickness of interfacial zone. The interfacial zones around aggregates were connected and formed a network. Because the interfacial zone is porous and rich in hydrated crystals, sulfate media easily penetrated into the specimens through the network and reacted with the calcium hydroxide and calcium monosulphoaluminate in the interfacial zone. This reaction caused large and quick expansion of the specimen. In the specimen MQS3, half the distance between aggregates was a little larger than the thickness of interfacial zone. Therefore, the rate of expansion of the specimen was between the fast and slow expanding.

The Influence of Structure of Interfacial Zone

Other investigations [4,5] have revealed that the structure of the interfacial zone is improved in mortars containing pretreated quartz aggregate. By the hydration effect of the hydraulic surface layer of pretreated quartz aggregate, the porosity of the interfacial zone was reduced like the bulk paste [8] and its composition contained more silicate hydrates. The improvement of structure of interfacial zone greatly enhanced the resistance of mortar to sulfate attack. The expansion of specimen MTQS4 was not only less than the expansion of specimen MQS4 but also less than the expansions of specimen MQS3 and MQS2 which were prepared with smaller volume fractions of aggregate and lower w/c ratios, as shown in Figure 3b.

A comparison was made between specimen MQS5 and MTQS5. These two specimens were made with the same mix proportions and subjected to the same curing and attacking conditions. But the structure of interfacial zone in specimen MTQS5 was improved with pretreated quartz aggregate, and the structure of interfacial zone in the specimen MQS5 was not. Taking 0.3% as a critical value for expansion [2], the period of attack to reach this level of expansion was 4 weeks and 30 weeks, respectively. The ability of specimen MTQS5 to resist sulfate attack was 6–7 times higher than that of specimen MQS5.

TABLE 3. The distance between aggregates

V_a	0.1	0.2	0.3	0.4	0.5
d(μm)	493	266	172	104	58

The SEM Examination

Having been attacked for 14 weeks, some specimens were removed from sulfate solution and were prepared for SEM examination. To study the sulfate attack process, the surface layer and inner part of the specimens were examined, separately.

Figures 4a and b show the morphology of the surface layer and the inner part of specimen MQS4. A large amount of needle-shaped products were found in both parts. It was verified to be gypsum ($CaSO_4 \cdot 2H_2O$) by energy dispersive X-ray analysis (EDXA) and X-ray diffraction (XRD) analyzers [5] and was the product of sulfate attack. The SEM examination showed that both the surface layer and the inner part were attacked by

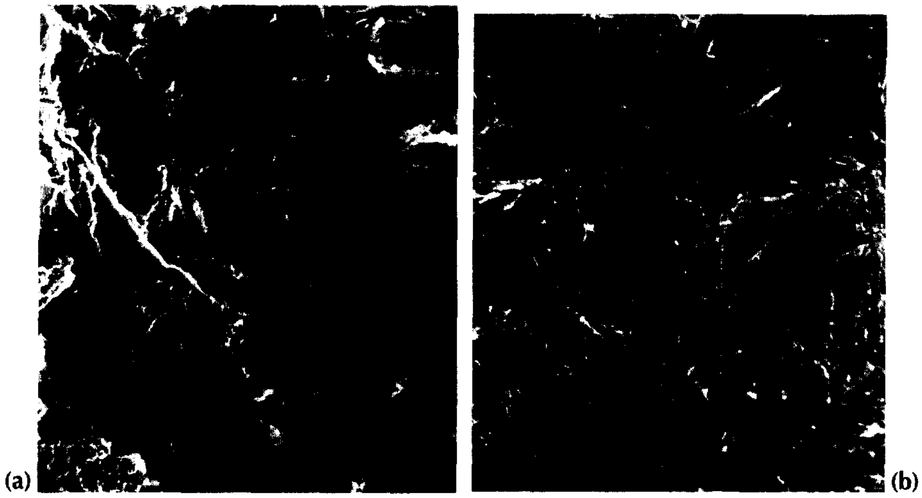

FIGURE 4. Morphology of specimen MQS4 attacked by 5% Na_2SO_4 solution for 14 weeks. (a) Morphology of the surface layer; (b) morphology of the inner part.

sulfates; this can explain the high expansion (shown in Figure 3a).

Figure 5a shows the morphology of the surface layer of specimen MQS1. The sulfate-attacked products (needleshaped) were found in the interfacial zone around the aggregate. Figure 5b shows the morphology of the inner part of specimen MQS1. The sulfate-attacked products were not found, although the interfacial zone was porous. The SEM examination showed significant sulfate attack on the surface layer of specimen MQS1 but hardly any attack on the inner part. Therefore, specimen MQS1 expanded only 0.03%. Long-term observations [5] of similar specimens also showed that the damage of specimen MQS1 attacked by sulfate was limited to a peeling surface layer. Compared to specimen MQS4, specimen MQS1 displayed a higher resistance to sulfate attack.

Figures 6a and b show the morphology of the surface layer and the inner part of specimen MTQS4. The interfacial zone appears compact, and sulfate-attacked products can hardly be found in the surface layer; meanwhile, the calcium hydroxide in the inner part did not react with sulfates. The SEM examination showed that both the surface layer and the inner part of specimen MTQS4 were hardly attacked by sulfate, thus the small expansion (0.05%) observed. Compared to specimen MQS4, specimen MTQS4 performed better during sulfate attack. Mortar resistance to sulfate attack was enhanced by the improvement of interfacial structure.

Hypothesis

Actual cement mortar or concrete are often rich in aggregates and the distance between aggregates is about

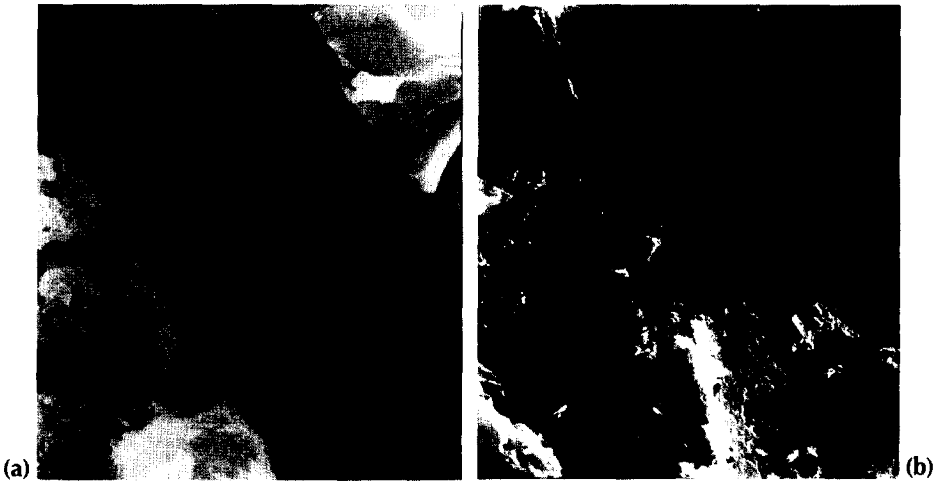

FIGURE 5. Morphology of specimen MQS1 attacked by 5% Na_2SO_4 solution for 14 weeks. (a) Morphology of the surface layer; (b) morphology of the inner part of the mortar.

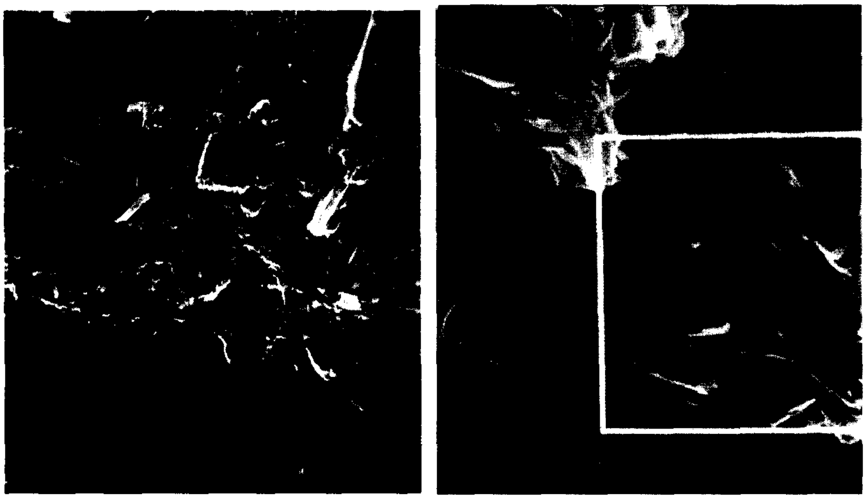

FIGURE 6. Morphology of specimen MTQS4 attacked by 5% Na_2SO_4 solution for 14 weeks. (a) Morphology of the surface layer; (b: crystal $Ca(OH)_2$in bulk paste.

100 μm [9]. These short distances mean that the interfacial zones were connected and indicate that the interfacial zone might play a key role in the process of sulfate attack on mortars. From the previous results and discussions, the process involves three stages:

1. Sulfate media penetrated into mortars mainly through interfacial zone.
2. Sulfate reacted with calcium hydroxide and calcium monosulphoaluminate in the interfacial zone and caused expansion and cracking.
3. Cracks developed from interfacial zone to bulk paste and resulted in the disintegration of cement mortar.

Conclusions

The main results of the study can be summarized as follows:

1. The resistance of mortars to sulfate attack was clearly influenced by the content of the interfacial zone. The higher the content of interfacial zone, the faster the cement mortar expanded.
2. The resistance of mortar to sulfate attack was largely enhanced by improving the structure of the interfacial zone. The resistance was raised as much as 6–7 times when aggregate of pretreated quartz sand was used to improve the structure of the interfacial zone.

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