Mechanism and Process of Sulfate Attack on Roller Compacted Concrete with MgO Expansive Agent

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Abstract: The mechanisms and processes of sulfate attack on roller compacted concrete (RCC) with MgO expansive agent are proposed by investigating the microstructure and hydration products in specimens immersed in 5% sodium sulfate solution for one year with the optical micrograph, scanning electron microscopy (SEM) and scanning electron microscopy-energy dispersive spectrometer (SEM-EDS). The results show that the deterioration of concrete due to the sulfate attack is mainly loss of stiffness, strength and adhesion, and expansion cracking is mainly caused by the formation of gypsum and ettringite. In the presence of MgO expansive agent, the microstructures of RCC can be improved by hydration and un-hydrated products, the large pores and permeability are reduced, and the resistance to sulfate corrosion of concrete and durability of hydraulic structure are improved slightly.

Key words: sulfate attack; concrete; expansive agent; microstructure

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0 Introduction

Sulfate attack is a main cause of concrete deteriorations which decreases the durability of hydraulic structure. The sulfate-related deterioration of concrete is mainly due to the formation of ettringite, gypsum and thaumasite, which arise from the reaction of sulfate ions with calcium hydroxide and calcium aluminate hydrate in concrete[1,2]. The sulfate ions in solution, which come from the soil, ground water, and seawater, are combined with other ions such as sodium, potassium, magnesium and calcium ions[3]. Destruction of concrete structures caused by sulfate attack has been found in China[4,5].

There has been no fundamental remedial method for the destruction caused by sulfate attack to concrete. It is well known that the principal methods available to prevent sulfate attack are to reduce the permeability by restricting the ratio of water to cementitious materials, to control the amount of tricalcium aluminate (C_3A) in cement, or to introduce a pozzolan such as fly ash into the concrete mixture[6,7]. Since roller compacted concrete (RCC) has fine and discontinuous pore structure, low cement and high fly ash content, it will show a better resistance to the sulfate attack when properly designed and well cured. As the amount of calcium hydroxide and calcium aluminate hydrate in RCC is very low, the sulfate attack on concrete may be reduced[8].

In order to reduce the cracks in concrete dam caused by temperature and autogenous shrinkage stress, high magnesium cement and MgO type expansive agent were used to concrete in China[9,10]. They may produce a delayed expansive stress to compensate the shrinkage of concrete and decrease cracking, and the resistance to sulfate attack of concrete may be improved. However, excessive dosage of high magnesium cement and MgO type expansive agent may cause exces-

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sive expansion of concrete, and the cracks would occur. Thus, the sulfate attack to concrete will be increased. A higher or lower expansion caused by hydration of MgO into $Mg(OH)_2$ may lead to the micro-structural change of concrete, produce cracking and form magnesium sulfate, and decrease the resistance of concrete to sulfate attack[11].

The previous studies about sulfate attack on mortars or concretes are mainly on non-restrained concretes in 50 000 mg/m^3 Na_2SO_4 exposure related to cement type, W/C and the presence of fly ash [12,13], and few discussions in restrained concrete which are widely used in engineering projects widely. No detailed studies about the restrained concrete with high magnesium cement and expansive agent immersed in 5% sodium sulfate solution have been reported. In the paper, the sulfate attacks on the restrained concrete are investigated.

1 Experimental Procedure

The study is carried out on restrained concretes with or without a MgO-type expansive agent. Cement used is low in C_3A, such as ASTM Type V Portland cement (ISO 42.5 with high MgO), and the mineral composition of it is as follows: C_3S, 50.77%; C_2S, 21.57%; C_3A, 3.06%; C_4AF, 16.28%. The MgO-bearing expansive agent, which is prepared by calcining two mineral materials at different temperatures and the main chemical compositions are MgO, C_2S and CaO. Fly ash is from Guizhou Province Power Plant. The chemical compositions of these materials are shown in Table 1.

The fine aggregate is graded silica sand with a fineness modulus of 2.5. The superplasticizer is a retard naphthalene water reducing agent, from Zhejiang Province.

The linear expansions of the concrete specimens are measured in accordance with ASTM C-1012 and China National Standard JC476-2001, and the specimens are immersed in 5% Na_2SO_4 solution (by mass, 33 800 ppm SO_4^{2-}) for one year. Three concrete specimens are 75 mm × 75 mm × 280 mm, and the mix proportions of these specimens are shown in Table 2.

Table 1 Chemical composition of materials %

Item	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss on ignition	Σ
Cement	20.90	4.57	5.35	60.91	3.81	2.59	1.48	99.61
Fly ash	46.53	27.69	16.52	2.56	1.45	0.80	3.82	98.57
EA (MgO-type expansive agent)	14.29	2.54	1.05	39.46	38.31	0.05	3.02	98.72

Table 2 Mix proportions of concrete specimens

Item	Cement/g	Fly ash/g	Sand/g	Aggregate/g	*W*/*B*	Expansive agent/%	Superplasticizer/%
C1	100	100	800	1 448	0.44	0	0.8
C2	100	100	800	1 448	0.44	8	0.8
C3	100	100	800	1 448	0.44	6	0.8

The concretes are mixed and moulded by vibration under the vibrating conditions of frequency 50 Hz and surcharge mass 20 kg. After being placed in a fog room 20 ℃, 90% RH for 48 h, the specimens are demoulded and cured in lime water at (20±2)℃ for 26 d, then the specimens are stored in two different solutions: Saturated lime water solution (control, L0) and 5% Na_2SO_4 solution for one year after measured the lengths of them (L1) at different ages. The expansion ratios of the concrete specimens in 5% Na_2SO_4 solution are L1/L0.

The mechanism and process of sulfate attack on RCC with MgO-bearing expansive agent in lime water and 5% Na_2SO_4 solution for one year are elucidated by investigating the microstructure features with optical micrograph, mercury intrusion porosimetry (MIP) and scanning electron microscope(SEM). SEM and MIP testes are performed on small-cored samples taken out from the beams in order to generate relevant information about the morphology and the pore system characteristics of the concrete. The procedure of the test is described in details somewhere else[14], and the small cores are dried in an oven at 105 ℃ for 24 h and stored in a desiccator until testing.

2 Results

2.1 Expansion ratios of concrete

Fig. 1 shows the expansion ratios of the concrete with or without expansive agent in 5% Na_2SO_4 solution at different time, respectively.

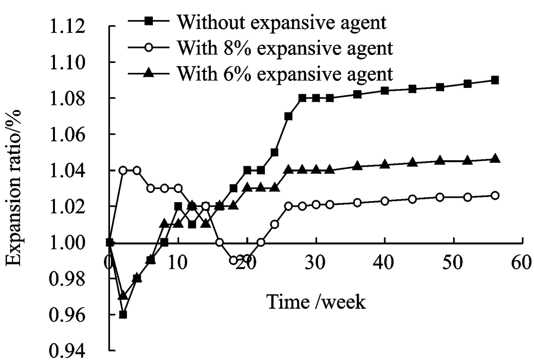

Fig. 1 Expansion ratios of RCC in Na_2SO_4 solution at different immerged time

In the first 14 weeks, the expansion ratios of the concrete without expansive agent in 5% Na_2SO_4 solution are lower than those of concrete with expansive agent. After 14 weeks, the expan sion ratios of the concrete without expansive agent increase and are higher than those of concrete with expansive agent, and tend to be steady after 26 weeks. The results indicate the expansion ratios of concrete without expansion agent increase with the immersion time, but those of concrete with expansive agent have almost increase with time in early age.

Excessive expansions of concrete with MgO expansive agent are not found. The results show that the expansive agent may improve the resistance of concrete to sulfate attack and no magnesium sulfate is produced.

2.2 Porosity and pore size distribution

The influence of the expansive agent on the pore size distribution of concrete without and with 8% expansive agent cured in lime water or 5% Na_2SO_4 solution at 20 ℃ for 90 d is investigated by MIP, and the porosity and pore size distributions are listed in Table 3.

Table 3 Porosity and pore size distribution of pastes cured in lime water and Na_2SO_4 solution at 20 ℃ for 90 d

Item	Porosity/%	Pore size distribution /%		
		<20 nm	20—100 nm	>100 nm
Without expant agent in lime water	12.41	29.76	63.88	6.36
With expant agent in lime water	15.36	29.15	65.51	5.34
Without expant agent in Na_2SO_4 solution	12.02	32.86	58.57	8.57
With expant agent in Na_2SO_4 solution	13.94	41.74	51.17	7.09

It is generally appreciated that the durability of concrete is greatly affected by the penetrability of aggressive solution into concrete. With respect to the threshold value of pore diameter affecting the permeability of concrete, Mehta, et al. pointed out that a good correlation was found between the water permeability of paste and the volume of pore with diameter greater than 100 nm[9,15]. In the comparison of pore size distribution between the pastes with and without MgO-type expansive agent in Table 3, it is clear that the volume of pores with diameter greater than 100 nm is decreased when the expansive agent is added, although the porosity of paste increases. When the MgO-type expansive agent is introduced, more medial pores (20—100 nm) appear, and less large (>100 nm) and small pores (<20 nm) emerge.

The penetrability of sulfate solution into concrete with expansive agent is less, which corresponds to the small amount of expansion caused by the formation of gypsum, ettringite and brucite. A decrease of large and continuous pores in concrete with high magnesium cement and expansive agent may result in an improved resistance to sulfate attack. The result indicates the effects of expansive agent on the improvement of sulfate resistance of concrete can be explained by the micro-structural change associated with the number decrease of large pores as well as the lower content of brucite formation. This may result in a slight improvement in the resistance of concrete to sulfate attack.

2.3 Microstructure observation

Fig. 2 shows the optical micrograph of concrete with the MgO-bearing expansive agent cured in 5% Na_2SO_4 solution for one year.

The micro cracks may be found near the edge of the specimen (Fig. 2). The sulfate solution intrudes into the cracks of specimen and forms a typical gypsum vein. A gypsum area that forms in the air voids of the specimen is observed.

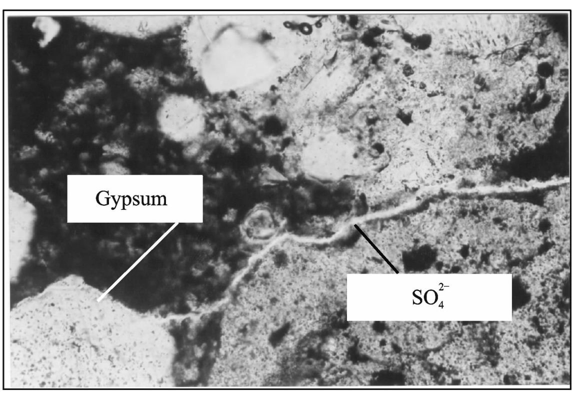

Fig. 2 Optical micrograph of RCC with 5% Na_2SO_4

By investigating the reaction products in the cracks of RCC (See Fig. 2), we find a white strip, in which hydration products of cement, and hydrated and un-hydrated expansive agent are found by SEM image observation (See Fig. 3). By SEM-EDS, we find gypsum and ettringite[16], and do not find Mg in the white strip (See Fig. 4). In addition, the hydrated and un-hydrated MgO type expansive agent adhering to the interface of ettringite and calcium hydroxide can be found (See Fig. 5).

If the cracks near the edge of specimen are connected through the air voids in specimen, the Na_2SO_4 solution may quickly enter the air voids of concrete and form gypsum and ettringite with calcium hydroxide in air voids. The formation of

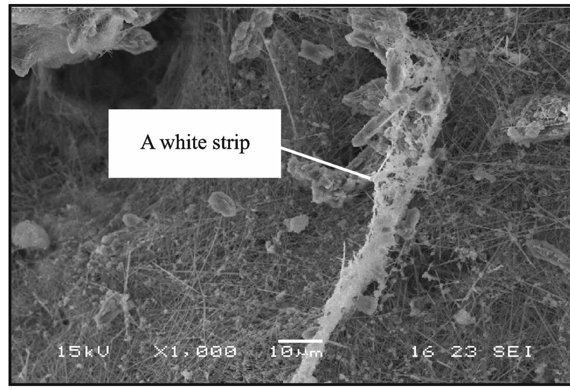

Fig. 3 SEM image of RCC with 5% Na_2SO_4

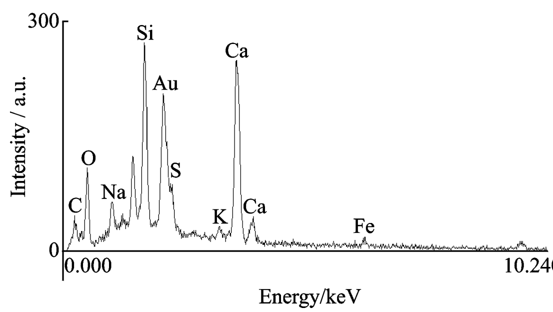

Fig. 4 SEM-EDS of a white strip in crack of Fig. 3

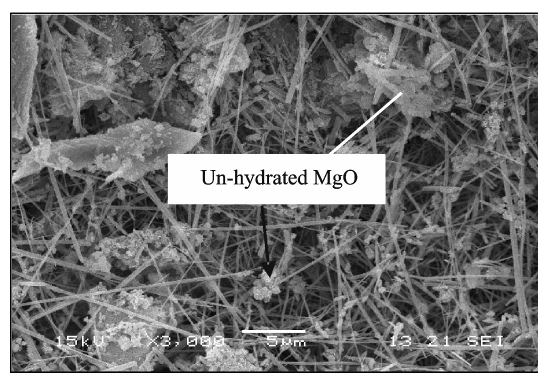

Fig. 5 Morphology of corroded specimen

the gypsum and ettringite in RCC may produce a great pressure in concrete. The external forces make SO_4^{2-} get into other cracks or air voids in specimen and form gypsum again, so the cohesion of cementitious materials with aggregate is lost, the widths of cracks increase, and the structure of concrete are damaged. The sulfate attack may play an important role in the process of deterioration of concrete.

3 Discussion

As RCC has low W/C, less cement, higher fly ash content and is well compacted, the formation of the crystalline compounds gypsum and ettringite produced by sulfate attack on the cementitious matrix of the paste in concrete may be decreased. These may cause the deterioration mechanisms and process of sulfate attack on concrete different from that on conventional concrete. From the study on the reaction in specimens immersed in Na_2SO_4 solution, the following sequence of reaction may be proposed.

When specimens are immerged in the Na_2SO_4 solution, the calcium hydroxide in the surface of specimens reacts with Na_2SO_4 and forms gypsum, and SO_4^{2-} in solution may diffuse into the specimen through the interface between aggregate and matrix of the paste to form gypsum and ettringite that make the surface of specimen loose.

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3SO_4^{2-} + 3Ca(OH)_2 + 25H_2O \rightarrow 6OH^- + 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$$

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2Na^+ + 2OH^-$$

When cracks exist in concrete, Na_2SO_4 solution may run into the crack and react with the calcium hydroxide around the crack and form diagonally gypsum /ettringite veins along the crack. In the area, a lot of gypsum and a few of ettringite grow up to a large bundle of lath—As crystals in the range from 5 μm to 10 μm in one year exposure time as shown in Fig. 3. The formation of the large amount of gypsum may contribute to the crack increasing of concrete, and subsequently accelerate the deterioration of concrete due to the sulfate attack. As high fly ash content is used in concrete, only a small amount of ettringite are observed in the cracks, which appears to be harmless to concrete.

The replacement of a portion of the Portland cement with fly ash may decrease the total amount of crystalline tricalcium aluminate (C_3A) in concrete, which reduce the expansion caused by the ettringite formation due to the tricalcium aluminate reaction. Fly ash may produce pozzolanic reaction with the calcium hydroxide and form a refined calcium silicate hydrate binder matrix. Thus, the porosity and permeability decrease, and the excess calcium is consumed and renders unavailability of the expansive formation of ettringite and gypsum. The pores and cracks decreased in concrete with high fly ash content may result in an excellent resistance to the sulfate attack. For the lower C_3A and higher fly ash content, the formation of ettringite is lower, so the deterioration caused by ettringite decreases. The sulfate attack through gypsum formation is a main factor of deterioration in concrete. It can result in smaller expansion, and loss of stiffness, strength and adhesion.

Using MgO expansive agent in concrete dams may produce delayed expansive stress to compensate the temperature and autogenous shrinkage stress, but may also bring unsoundness problem of concrete. A higher expansive stress caused by overdose of MgO may change the microstructure of concrete, and then decrease the resistance of sulfate.

4 Conclusions

MgO type expansive agent may improve the resistance of concrete to sulfate corrosion and not produce magnesium sulfate corrosion. The effects of expansive agent on the improvement of sulfate resistance of concrete may be due to the microstrutural change associated with the number decrease of large pores as well as the small content of brucite formation. CaO may offset the early shrinkage and provide $Ca(OH)_2$ to react with excessive fly ash in concrete.

SO_4^{2-} diffuses into the specimen from outside, and causes the deterioration of concrete. SO_4^{2-} runs into the cracks and air voids and forms the expansive products, enlarges the cracks and causes the deterioration of concrete structure. The deterioration of concrete due to the sulfate corrosion is mainly the formation of gypsum and ettringite, which results in the loss of stiffness, strength and adhesion of concrete.

When the expansive agent is added into the concrete, the hydration product of expansive agent, $Mg(OH)_2$ which has low solubility may fill into the space of pores and micro-cracks, protect it against further attack, and improve the resistance to sulfate corrosion and durability of hydraulic concrete structure.

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