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Evaluating Deterioration of Concrete by Sulfate Attack

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Abstract: Effects of factors such as water to cement ratio, fly ash and silica fume on the resistance of concrete to sulfate attack were investigated by dry-wet cycles and immersion method. The index of the resistance to sulfate attack was used to evaluate the deterioration degree of concrete damaged by sulfate. The relationship between the resistance of concrete to sulfate attack and its permeability/porosity were analyzed as well as its responding mechanism. Results show that the depth of sulfate crystal attack from surface to inner of concrete can be reduced by decreasing *w*/*c* and addition of combining fly ash with silica fume. The variation of relative elastic modulus ratio and relative flexural strength ratio of various specimens before and after being subjected to sulfate attack was compared.
Key words: sulfate attack; strength; relative dynamic elastic modulus; permeability; concrete

1 Introduction

Generally, there are two sides of physical crystallization and chemical corrosion in the deterioration of concrete caused by sulfate attack. The pure physical crystallization action(not including chemical action) of sulfate in pore of concrete, which often occurs in permeable concrete by dry-wet cycle action and evaporating action, can seriously damage concrete compared with the chemical corrosion of sulfate[1]. Much achievement related to this field has been made[2-11].However, there also exist many questions needed to be further discussed and investigated[12,13],especially in the field of evaluation method and mechanism of sulfate attack as well as the relationship between deterioration of sulfate attack and microstructure of concrete and *etc*. In this paper, the relative dynamic elastic modulus ratio and relative flexural strength ratio and relative compressive strength ratio denoted as index of resistance to sulfate attack were used to investigate the effects of several factors, such as water to cement ratio, fly ash and silica fume, on damage of concrete caused by physical crystallization and chemical corrosion of sodium sulfate. The relationships between deterioration of concrete by sulfate attack and its permeability, and its porosity as well as its mechanism were discussed and analyzed in detail. These studies are of great importance to expound its corresponding mechanism and to find new improving way for the resistance of concrete to sulfate attack.

2 Experimental

2.1 Raw materials and concrete mixture

Grade 42.5 ordinary portland cement was used with a compressive strength of 44.1 MPa at 28 d, produced by Huan Xiangxiang Cement Plant. Fly ash used was from Power Plant of Xiangtan City of Hunan. Its specific area was 600 m^2/g. Silica fume with mean diameter of 0.2 μm used was from Silicon-ferroalloy Plant in Zunyi City of Guizhou Province. The chemical properties of cement, fly ash and silica fume are listed in Table 1. Fine aggregate with a fineness of 2.65 used in concrete mixture was river sand from Xiangjiang River of Hunan Province. Crushed limestone was used as coarse aggregate of concrete, with a size of 5-20 mm and a crushed index of 7.7%. A naphthalene superplasticizer was used to improve the workability of concrete mixture.

The experiment was designed to investigate the effects of water to cement/binder ratio (*w*/*c* or *w*/*b*), amount of fly ash and silica fume on the resistance of concrete to sulfate attack. The compositions of concrete mixture with various *w*/*c* are listed in Table 2. Based on A3 serial concrete mixture sample, samples of cement replacement with fly ash of 15%, 25% and

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35% by weight are denoted as B1 serial, B2 serial and B3 serial, respectively. Samples of cement replacement with silica fume of 5% and 10% by weight are denoted as C1 serial and C2 serial, respectively. Samples of cement replacement with fly ash of 25% and with silica fume of 5% and 10% by weight are denoted as D2 serial and E3 serial, respectively. Slumps of all fresh concrete mixtures ranged from 120 mm to 150 mm.

2.2 Sample preparation and test method

The concrete mixture was mixed by a forcibly mixer. Samples with a size of 100 mm×100 mm×400 mm for flexural strength test and relative dynamic elastic modulus test, with a size of 100 mm×100 mm×100 mm for compressive strength test and with a size of ϕ100 mm×50 mm for permeability test were made. The relative dynamic elastic modulus was obtained from the vibration frequency by resonance method according to Standard GBJ82-85. The specimens were cured in water at 22 ℃ after being demolded for 1 day. The result of strength test of various serials concrete at 28 day age is listed in Table 3.

Table 1 Chemical composition of cement, fly ash and silica fume

	Chemical composition/%						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LL
Cement	24.3	4.8	3.8	55.3	4.2	2.2	2.4
Fly ash	52.7	25.8	9.7	3.7	1.2	0.2	5.0
Silica fume	92.4	-	0.66	-	-	-	-

Table 2 Mix proportion of concrete samples

Serial number	Cement /(kg/m³)	Water (w/c) /(kg/m³)	Superplasticizer /%	Sand /(kg/m³)	Crushed stone /(kg/m³)	Slump /mm
A1	327	180(0.55)	0.5			150
A2	378	170(0.45)	0.8	685	1135	140
A3	460	161(0.35)	1.1			150

Table 3 Results of strength test of various serials concrete at 28 day age

Serials	Splitting strength /MPa	Splitting to compressive strength ratio	Senials	Splitting strength /MPa	Splitting to compressive strength ratio
A1	3.67	1/10	B3	3.79	1/12
A2	4.29	1/11	C1	4.06	1/16
A3	5.21	1/11	C2	4.52	1/17
B1	4.79	1/11	D2	4.05	1/14
B2	4.34	1/12	E2	4.30	1/15

Na_2SO_4 solution was selected as the experimental sulfate solution to research the resistance of concrete to sulfate attack. 1 litre tap water and 350 gram pure Na_2SO_4 were mixed to prepare Na_2SO_4 saturation solution with a density of 1.151-1.174 g/cm^3 at of 25 ℃.

At 28 d age, two experimental treatment ways of immersing and dry-wet cycle in Na_2SO_4 saturation solution at 22 ℃ were selected to investigate the damage of concrete caused by the physical crystallization and chemical corrosion of sulfate attack. The dry-wet cycle regime was 14 h immersing time and 10 h dry time at 60 ℃ and 24 h as a dry-wet cycle. And other concreted samples continued to cure in water at 22 ℃. The total dry-wet cycles of sample were 90 cycles. And the total immersing time in Na_2SO_4 saturation solution was 120 days. The relative strength or dynamic elastic modulus ratio between immersing or dry-wet cycle samples in Na_2SO_4 saturation solution and curing in water with corresponding age were used to evaluate the resistance of concrete to sulfate attack, respectively.

The permeability of concrete denoted as the amount of transporting charge within 6 h was measured according to ASTM C 1202 method. Thr porosity of concrete was tested by 'content of evaporable water method' referred to document[12]. The porosity of concrete in this paper can be obtained by testing the water loss between saturation concrete and dry concrete dried at 105 ℃ to constant weight and apparent density of concrete. The SEM images of microstructure of samples were obtained by a KYKY-2800 scanning electron microscope.

3 Results and Discussion

3.1 Depth of Na_2SO_4 attack by physical crystallization

The sulfate physical crystallization attack is characterized by the denudation damage of concrete from surface to inner, which results from the crystallization of Na_2SO_4 in concrete. In present paper, the ingressive depth of Na_2SO_4 crystal was measured from four sides to inner of sample according to the crystal salt aspect in cross section of concrete sample treated by 90 dry-wet cycles, respectively. And the

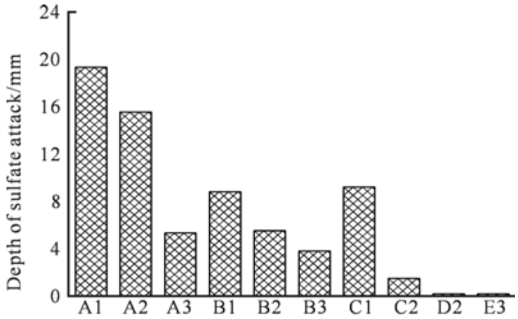


Fig.1 Depth of Na_2SO_4 attack in conrete after 90 dry-wet cycles

average value of four depth values corresponding to four sides of each concrete represents the depth of Na_2SO_4 attack for each concrete sample. Fig.1 gives the experimental results of the depth of Na_2SO_4 attack for all samples.

From the results given in Fig.1, it can be seen that the ingressive depth of Na_2SO_4 crystal increases with increasing *w*/*c*. The depth of Na_2SO_4 crystal attack is about 5 mm for sample with *w*/*c* of 0.35 and the one is about 20 mm for sample with *w*/*c* of 0.55. At the same time, one can find that the ingressive depth of Na_2SO_4 crystal of samples decreases with the increment of the amount of fly ash or silica fume in samples. The most noteworthy is that the depth of Na_2SO_4 crystal attack is almost zero when fly ash together with silica fume was added into sample. This result agrees well with the denudation of appearance of corresponding concrete sample. The reduction of *w*/*c* or addition of fly ash and silica fume greatly decreases the porosity, especially the capillary pore of concrete. The reduction of porosity of concrete results in hindering rapid transportation of ion in Na_2SO_4 solution and, therefore, improving the resistance of concrete to sulfate attack.

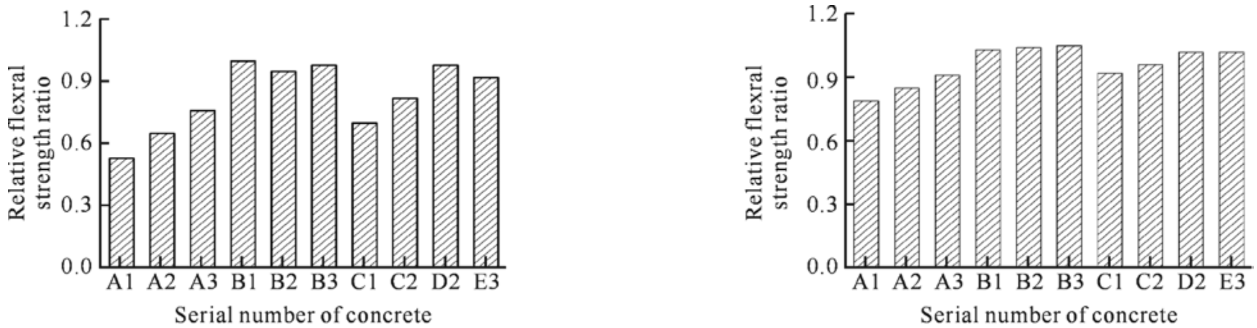
3.2 Variation of resistance to sodium sulfate

After finishing the dry-wet cycle or immersion in Na_2SO_4 solution experiment, the relative flexural/compressive strength ratio and relative dynamic elastic modulus ratio of concretes between samples suffering from 90 dry-wet cycles or 120 d immersion in Na_2SO_4 solution and specimens cured at 22 ℃ in water with corresponding age were calculated to evaluate the resistance of various concretes to sulfate attack, respectively. Fig.2 show the corresponding results.

It can be seen that, from results given in Fig.2, the relative flexural strength ratio of various concrete differs from each other. However, compared with samples suffering from 120 d immersing in Na_2SO_4 solution, the corresponding relative flexural strength ratio of concretes suffering from 90 dry-wet cycles in Na_2SO_4 solution is less and differs greatly from each other. This indicates that the damage of concrete caused by physical crystallization of Na_2SO_4 solution is much larger than that by chemical corrosion of Na_2SO_4 solution. In addition, on can find that the resistance to sulfate attack of serial A1, A2, A3, C1 and C2 concrete samples are all worse than those of other concrete samples whether under 90 dry-wet cycles or 120 d immersion in Na_2SO_4 solution condition. The result shows that reduction of *w*/*c* can improve to a certain extent the resistance of concrete to sulfate attack but not enough. Further, single addition of silica fume into concrete does not effectively improve the resistance of concrete to sulfate attack. However, combining the reduction of *w*/*c* with the addition of fly ash/silica fume is effective in improving the resistance to sulfate attack of concrete and the corresponding relative flexural strength ration is larger than 0.9. The reason may be the reduction of porosity of concrete caused by decreasing *w*/*c* and/or the addition of fly ash and silica fume. At the same time, the pozzolanic effect of fly ash under Na_2SO_4 solution condition results in a further improvement of concrete microstructure, especially the improvement of microstructure in the interface zone between paste and coarse aggregate[6,10,11]. Though the addition of silica fume can reduce the porosity of concrete, the addition of silica fume into concrete will increase the brittleness of concretesee, which may not benefit for the resistance to denudation caused by sulfate attack and, therefore, result in a worse resistance of concrete to sulfate attack.

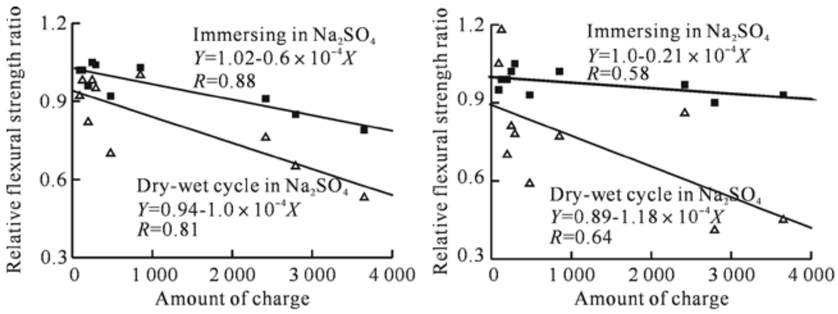
3.3 Relationship between resistance of concrete to sulfate attack and its permeability

Fig.3 gives experimental results of relationship between relative flexural/compressive strength ratio and permeability (tested by amount of transporting charge within 6 hours) of concrete. From the results shown in Fig.3(a), one can see that there exists a good linear relation between the relative flexural strength



(a) Dry-wet cycle in Na_2SO_4 solution (b) Immersing in Na_2SO_4 solution

Fig.2 Relative flexural strength ratio of various concretes ratio and the amount of charge. Moreover, under 90 dry-wet cycles condition the slope of line is larger than that under 120 d immersion in Na_2SO_4 solution condition. The relative flexural strength ratio increases with reducing the amount of charge transporting within 6 h. This result is reasonable. Because the reduction of the amount of charge transporting within 6 h means a decrease of the permeability of concrete and, therefore, results in a lower transporting velocity of ion in solution. So, the resistance of concrete to sulfate attack is improved. There also exists a linear relation between the relative compressive strength ratio and the amount of charge of concrete from results shown in Fig.3(b). But its pertinency is worse compared with that of relative flexural strength ratio and amount of charge of concrete. What's more, under 120 d immersion in Na_2SO_4 solution condition the slope of line between the compressive strength ratio and the amount of charge is less than that of line between the flexural strength ratio and the amount of charge of concrete. The relationship between the relative flexural strength ratio and the amount of charge is closer than that between the relative compressive strength ratio of concrete and the amount of charge. However, under 90 dry-wet cycles in Na_2SO_4 solution condition the slope of line between the compressive strength ratio and the amount of charge is larger than that of line between the flexural strength ratio and the amount of charge of concrete. The reason responsible for this may be that the deduction of loss area caused by the denudation in side and the angle of concrete due to sulfate attack are not carried out during the calculation of the compressive strength of concrete.



(a) Relative flexural strength ratio (b) Relative compressive strength ratio

Fig.3 Relationship between permeability and deterioration of concrete by sulfate attack

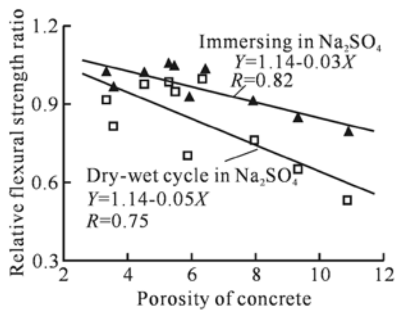
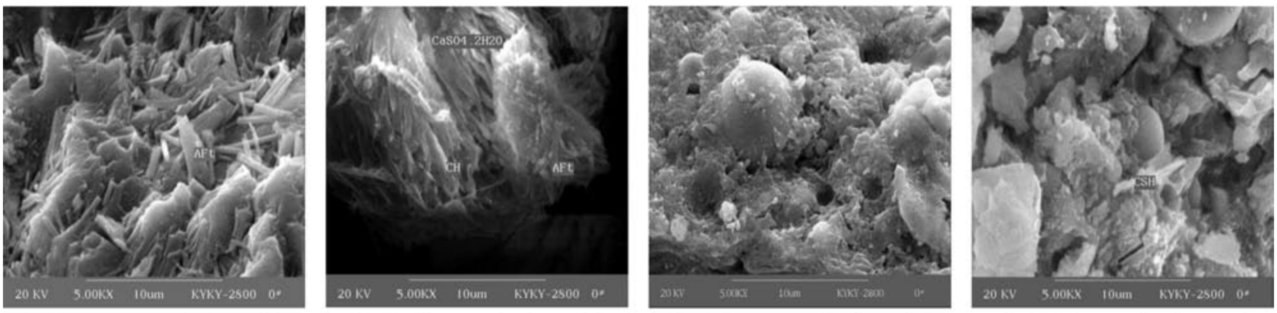


Fig.4 Relationship between porosity and relative flexural strength ratio of concrete



(a) 90 dry-wet cycles in Na_2SO_4 solution (A3 concrete) (b) 120 d immersion in Na_2SO_4 solution(A3 concrete) (c) 90 dry-wet cycles in Na_2SO_4 solution (B3 concrete) (d) 120 d immersion in Na_2SO_4 solution (B3 concrete)

Fig.5 SEM images of serial A3 and serial B3

3.4 Relationship between resistance of concrete to sulfate attack and its microstructure

Fig.4 shows the result of relationship between relative flexural strength ratio and the porosity (measured by the content of evaporable water) under 90 dry-wet cycles and 120 d immersion in Na_2SO_4 solution condition. It can be seen, from the result shown in Fig.4, there is a good linear the relation between the relative flexural strength ratio and the porosity of concrete. The relative flexural strength ratio increases with decreasing the porosity of concrete. Moreover, the relationship between the relative flexural strength ratio and the porosity agrees well with that between the relative flexural strength ratio and the permeability of concrete shown in Fig.3. This indicates that reducting the porosity of concrete will upgrade the resistance of concrete to sulfate attack. Obviously, the increment of porosity of concrete results in an increase of permeability and, therefore, causes a high transporting velocity of ion and a more amount of ion ingress concrete, which promotes the deterioration of concrete finally.

It can be seen, from the SEM images of serial

A3(pure cement concrete) and serial B3 concrete(with fly ash) shown in Fig.5, the microstructure of serial A3 concrete differs obviously from that of serial B3 concrete. There are many hydration products of AFt and calcium sulfate in serial A3 concrete due to the reaction between hydration calcium aluminate, CH and Na_2SO_4 transporting into concrete from Na_2SO_4 solution under 120 d immersion in Na_2SO_4 solution condition. The most noteworthy is, under 90 dry-wet cycles in Na_2SO_4 solution condition, there are also many hydration products of AFt within serial A3 concrete except for Na_2SO_4 crystal. This may be that some Na_2SO_4 ingress in concrete, during 90 dry-wet cycles in Na_2SO_4 solution, reacts with hydration products of CH and calcium aluminate. These hydration products will produce a large expansion stress in concrete and, therefore, results in a damage of concrete. However, in SEM image of serial B3 concrete sample there exist many hydration products of CSH and almost no AFt and calcium sulfate exist. The reason responsible for this result is that pozzolanic effect of fly ash under Na_2SO_4 solution condition and therefore restrains the production of AFt and calcium sulfate in concrete, which results in a good resistance of concrete with fly ash to sulfate attack.

4 Conclusions

a) The reduction of *w*/*b* together with the addition of fly ash and silica fume is effective in decreasing the ingress depth of Na_2SO_4 crystal from surface to inner of concrete. The resistance of concrete to sulfate attack can be improved greatly by reducing *w*/*b* and adding fly ash or combination of fly ash and silica fume.

b) The index of the resistance of concrete to sulfate attack expressed by relative dynamic elastic modulus is comparable to that by flexural strength. The parameter of relative dynamic elastic modulus can be used to evaluate the deterioration of concrete by sulfate attack.

c) There is a close relationship between the deterioration of concrete by sulfate attack and its permeability/porosity. The reduction of permeability of concrete is effective in improving the resistance of concrete to sulfate attack.

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