A comparable study on the deterioration of concrete under sodium sulfate and magnesium sulfate attack

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Abstract: The deterioration mechanisms and corrosion of concrete exposed to Na2SO4 and MgSO4 solution were investigated in the present study. The damage of concrete specimen was evaluated by multi-scale observation, change of mass and relative dynamic modulus. Quantitatively analyse of the compositions for corrosion products during sulfate attack was applied in this study. The concrete was mainly cracked and spalling at the edges and corners when immersed in sodium sulfate solution. But pitting corrosion was formed on the surface of concrete under magnesium sulfate attack, and the powder peels off into a honeycomb hollow structure.

1. Introduction

The effect of sulfate is one of the most important factors in the deterioration of concrete structures. The sulfate ions in groundwater, soil, and sea water can penetrate into concrete by means of diffusion or capillary suction and cause serious damage[1,2]. The sulfate ions react with the ions of the pore solution, i.e. Ca2+, Al3+, corrosion products, such as secondary ettringite and gypsum are formed, and results in volume expansion, cracking and spalling of concrete, which subsequently causes the surface to become weak, reducing durability[3-5].

Sulfate ions are mostly existing in the forms of Na2SO4 and MgSO4 in practice, and the corresponding attacks take place as and mainly in three types: (1) reaction with calcium hydroxide in hydration products to form gypsum; (2) further reaction of the generated gypsum with C3A to produce ettringite; (3) what’s more, Mg2+ replaces Ca2+ in C-S-H gel forming magnesium silicate hydrate (M-S-H) with low cementitious performance[6-9].

In this work, the comparable study of sodium sulfite and magnesium sulfate on the deterioration of concrete specimens has been investigated. Accelerated tests were conducted in the laboratory by increasing the concentrations of the solutions. Macro-cracks and micro-cracks were observed by means of appearance inspection, stereoscopic microscope and backscattered electron (BSE), respectively. Mass change and elasticity modulus (Erd) change were tested to quantify the degree of degradation of concrete. Mineralogy of corrosion products in concrete were calculated by X-ray diffraction (XRD), and thermo gravimetric analysis (TGA).
2. Materials and methods

2.1. Materials and preparation

The mixture of concrete was given in Table 1. The materials used in the experiments were Type 42.5 Ordinary Portland Cement (OPC). The packing density accounts of sand was 1516 kg/cm³. The coarse aggregates used were granite stones with the continuous grading of 5-20 mm. The cement content was 430 kg/m³ and the water-to-cement ratio was 0.42. To get good workability, superplasticizer (SP) based on polycarboxylic ethers was added. Table 2 gives the chemical composition of cement.

Specimens were cast in cubes with a size of 100 mm × 100 mm × 100 mm. After 24 h, they were demoulded and cured in lime water at 20 ℃ until the age of 28 days. To investigate the influence of the corrosive solution on concrete, four surfaces of each sample were sealed by paraffin, leaving two opposite sides exposed to the corrosive solution.

| Table 1 | Mixture of concrete. |
|---------|----------------------|
| Cement  (kg/m³) | Water (kg/m³) | Sand 0/5 (kg/m³) | Aggregate 5/10 (kg/m³) | Aggregate 10/16 (kg/m³) | SP (%) |
| 430     | 180                 | 615               | 590                 | 590                 | 5      |

| Table 2 | Chemical composition of cement (wt %). |
|---------|--------------------------------------|
| SiO₂    | Al₂O₃      | Fe₂O₃    | CaO    | MgO    | K₂O    | Na₂O    | SO₃    | LOI   |
| 21.86   | 4.45       | 2.35    | 63.51  | 1.67   | 0.55   | 0.26    | 2.93   | 1.89  |

LOI: Loss on ignition

2.2. Exposure conditions

After sealed by paraffin, all specimens were respectively transferred to several air-tight tanks filled with 1 mol/L Na₂SO₄ and MgSO₄ solutions until testing for different age. All tanks were stored in laboratory at constant 20 ℃, and the solutions were renewed every 3 months to maintain its concentration constant. Conventionally, three specimens were prepared for each test, and the mean values of data were used as the final results.

2.3. Experimental methods

To investigate the effect of multiple ions on concretes, appearance inspection, stereoscopic microscope and backscattered electron, mass change and elasticity modulus (E₀) change were studied. Stereoscopic microscope was used to check the deterioration and cracking of the samples in more detail. Changes in mass and elasticity modulus were recorded at regular intervals. The mass and elasticity modulus were tested by three prism samples as well.

X-ray diffraction (XRD), and thermogravimetric analysis (TGA) were used to calculate the corrosion products. Internal standard approach was selected for absolute phase quantification and estimation of the amorphous or non-identified phase content by XRD analysis. A 15 wt% ZnO internal standard was added to the obtained powder. Samples were measured in θ/2θ geometry over an angular range of 5-90°. German Zeiss EV018 Scanning Electron Microscope was used to observe the microstructure of various phases of concrete after erosion. TGA was carried out in a Netzsch STA409 thermal analyzer, with a heating rate of 20 ℃/min at the range of 25-1000 ℃ in N₂ atmosphere. Samples for all tests coming from the deteriorated part of the specimens.

3. Results and discussion

3.1. Multi-scale observation of damage for concrete

In order to study the corrosion failure pattern of concrete in sulfate solution in detail, a comparative study was made on concrete samples of different ages from macroscopic and microscopic aspects.
Figure 1 shows the macroscopic appearance morphology of concrete immersed in Na$_2$SO$_4$ solutions taken by digital camera at different ages. After 4 months of corrosion, there was no obvious damage trace on the concrete surface, slight peeling damage and visible fine cracks appeared at the edges. When the corrosion age reached 8 months, the edge and corner of the specimen appeared very obvious cracking and peeling, and a small amount of white salt frost also appeared on the surface of the specimen. After 12 months of corrosion, the corrosion damage was further aggravated, the macro cracks were further increased, and gradually expanded from the corners and edges to the center of the concrete surface. The spalled concrete was small blocks, and a large amount of salt frost appeared on the surface. After 20 months, the edges and edges of the concrete were completely cracked and peeled off, and a large amount of coarse aggregate was exposed.

![Fig.1](image1.png)

As shown in Fig.2, the cracking place of concrete was further observed with stereomicroscope. After 4 months, there were subtle cracks in the edge of the concrete. When the corrosion age reached 8 months, the cracks expanded further, became coarser and longer, and the micro-cracks began to migrate to the middle position. At the same time, salt crystals were found in the cracks. After 12 months of corrosion,
the concrete further cracked, and the cracks gradually connected, the concrete damage showed serious cracking condition, and the corners of the concrete completely broken at 20 months.

Fig.2 shows that, when immersed in the sodium sulfate solution, the internal cracks of concrete are formed at the interface between slurry and aggregate first, and the microcracks are perpendicular to the surface of aggregate. Those cracks expanded and connected in the slurry. With the progress of corrosion, the microcracks increased and expanded continuously, forming coarse connected cracks and microcrack network structure between aggregates, and finally completely results in the separating between aggregate and slurry.

Fig.3 shows that, when immersed in the sodium sulfate solution, the internal cracks of concrete are formed at the interface between slurry and aggregate first, and the microcracks are perpendicular to the surface of aggregate. Those cracks expanded and connected in the slurry. With the progress of corrosion, the microcracks increased and expanded continuously, forming coarse connected cracks and microcrack network structure between aggregates, and finally completely results in the separating between aggregate and slurry.
Fig. 3 indicated that there was no obvious damage trace on the concrete surface, but very slight white powdery salt crystals on the surface after 4 months immersed in magnesium sulfate solution. After 8 months, the concrete surface and edge showed corrosion and peeling, the concrete surface showed visible point corrosion raised fish scale corrosion spots, and easily peeled into powdery sand, white powdery salt crystallization increased significantly. When 12 months, the corrosion and peeling of the concrete edge increased significantly, and a large number of erosion pits appeared on the whole concrete surface. The concrete in the erosion pits was soft and low-intensity, and the whole concrete surface was slightly milky white. When 20 months, the whole concrete surface is completely loose and porous, the aggregate is obviously exposed, the concrete surface is easy to peel off into powdery sand soil under the action of external force.

As shown in Fig. 5, the surface corrosion of concrete observed with stereomicroscope. At 4 months, the concrete surface is loose gradually, there are a few cracks and white salt crystallization. At 8 months, pitting corrosion phenomenon more obvious, the concrete surface was honeycomb scale raised and very easy to peel off, and corrosion center appears pit. At 12 months, there were massive spalling corrosion and aggregate exposure in concrete. When 20 months, the concrete surface completely into a hollow structure.
Fig. 4  Deterioration of concrete exposed to MgSO$_4$ solutions for 4, 8, 12 and 20 months.

Fig. 5  Local cracking of concrete exposed to MgSO$_4$ solutions for 4, 8, 12 and 20 months.
Under the action of magnesium sulfate corrosion, cracks were concentrated in the slurry in Fig.6. Along with the corrosion, these cracks gradually increase and coarsens. Then, a crack network structure connected by a large number of microcracks exhibited in slurry, and some cracks also appeared around the aggregate at the same time. Finally, the whole slurry part were completely scattered and split, and the aggregate were peeled off, and a discrete shape appeared.

3.2. Change of mass and relative dynamic modulus for concrete

As shown in Fig.7, the weight of concrete under the action of magnesium sulfate rose slightly first and then decreased. The loss of weight increased rapidly with the increase of erosion age. In the early stages of erosion, products built up, filling the concrete pore structure but did not caused compressive stress and damage on the pore structure. Concrete became denser, the mass and relative dynamic modulus of elasticity increased. With the continuous corrosion, concrete damage occurred, and mass and relative dynamic modulus of elasticity decreased continuously. The mass loss of concrete in magnesium sulfate solution erosion were greater than that in sodium sulfate solution erosion, but the modulus of elasticity changes were opposite. This is because the concrete under the action of sodium sulfate solution were mainly manifested as crack expansion, resulting in a large number of penetrating cracks. The concrete suffered structural damage directly, and strength decreased rapidly, but the amount of spalling in the early stage was less. The failure mode of concrete in magnesium sulfate solution was pitting corrosion, and the strength of concrete in the local eroded area decreased, result in the formation of raised microcracks and concrete powder peeling, few large penetrating cracks occurred.
3.3. Identification and analysis of sulfate attack products

There was no obvious gypsum in the concrete before erosion in Fig. 8(a). At 4 months, the gypsum content was 3.91% in the range of 0-5mm and 1.85% in the range of 10-15mm from the concrete surface. At 12 months, the erosion depth reached 20-25mm, and the gypsum content was 7.03% in the 0-5mm layer. At 20 months, the gypsum column in the range of 0-5mm was 9.43%, while the erosion depth was still 20-25mm. Gypsum generated by erosion only exist in the periphery of concrete, and there was basically no gypsum in the inner concrete.

The ettringite content in concrete was 1.1% before erosion in Fig. 8(b). At 4 months, ettringite caused by erosion was mainly in the range of 0-5mm, and the content was 7.35%. At 12 months, ettringite content in the range of 0-5mm and 10-15mm were 12% and 9%, respectively. At 20 months, ettringite content from outside to inside were 14.6%, 12.4% and 10.1%, respectively. With the increase of erosion time, ettringite content gradually expanded from surface to interior in the direction of erosion from surface to interior. The distribution of the content of products was consistent with the damage law. As shown in Fig. 9, Compared with sodium sulfate, gypsum content increased and ettringite content decreased for concrete immersed in magnesium sulfate solution at the same age. The content of gypsum and ettringite in the range of 0-5mm were 10.6% and 13.3%, respectively.
4. Conclusion

The damage mode and the distribution law of microcrack were different for concrete immersed in sodium sulfate and magnesium sulfate solutions. The concrete was mainly cracked and spalling at the edges and corners when immersed in sodium sulfate solution. But pitting corrosion was formed on the surface of concrete under magnesium sulfate attack, and the powder peels off into a honeycomb hollow structure. Gypsum content increased and ettringite content decreased for concrete immersed in magnesium sulfate solution compared with sodium sulfate. The main damage of concrete immersed in sodium sulfate solution was cracking and spalling, but the damage of concrete immersed in magnesium sulfate solution due to the reduce of the bonding force of concrete.

Acknowledgements

The research gratefully acknowledges financial support from Science and Technology Foundation of Guangzhou Institute of Building Science Co., Ltd. (No. 2018Y-KJ01) and China Postdoctoral Science Foundation (No. 2020M672584).

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