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Study on Sulfate Chemical Erosion Failure Mechanism of Reinforced Concrete Structures

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As a major aspect of concrete durability, the related research on sulfate erosion has a history of more than 100 years. However, due to the differences between experimental simulation methods and actual engineering exposure conditions, it is still considered that the research status of concrete sulfate erosion is a “chaotic”. Starting from reality, this paper systematically analyzes the relationship between actual concrete structures and the external environment and the engineering examples. Aiming at half buried and fully buried in two kinds of exposure methods in actual projects, a series of more practical indoor experiments are designed and carried out. The paper puts forward the corresponding concrete sulfate erosion mechanism.

1. Introduction

The damage degree of concrete depends on the content of sulfate in the environment, the movement of water, the composition of the cement, the property of the concrete and the transport mechanism of the solution in the concrete. With the erosion of sulfate, the hardened cement paste continuously decomposes and loses its strength, eventually causing the collapse of the entire concrete component (Yuan et al., 2016). From 2009, China will build new railways and renovate existing railway networks in the western region, with a total mileage of 20,000 kilometers in the next ten years. It is estimated that by the end of 2020, the total railway mileage in the entire western region will reach 50,000 kilometers (Wang et al., 2018). However, in the vast western region, many types of sulfate are dissolved in the soils and groundwater, such as sodium sulfate, magnesium sulfate, ferrous sulfate and calcium sulfate (Huayan et al., 2016). For example, in the Korla region of Xinjiang Province in China, the sulfate concentration in groundwater is as high as 21,299 m/l and the content of magnesium ion is as high as 3,639 mg/l; the concentration of sulfate in the tunnel drainage ditch of Baijialing tunnel of the Chengdu-Kunming Railway has reached 32,475mg/l (Zhang et al., 2017); Ma Baoguo, et al. has conducted survey sampling and investigation and comprehensive test analysis on the water in the gallery drainage ditch of the Bapanxia hydropower station on the Yellow River in the northwest of China. The test results are shown in Table 1, which indicates that the water also contains a large amount of sulfate.

Table 1: Water sample analysis results

K^{+}+Na^{+}	Ca^{2+}	Mg^{2+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}
12893	1024	534	18976	6675	234

It can be seen from the above analysis that buildings located in the western part of China are facing huge risks of sulfate erosion, such as tunnels, piers, foundations and slope protection. What is worse is that the geological structure is complex in the western region and thus many railway tunnels and bridges need to be built. On the other hand, a large number of existing tunnels, bridges and other concrete projects, especially tunnels, on railway lines have been severely eroded by sulfate (Bylapudi et al., 2017). Figure 1 shows the damage caused by sulfate erosion in a certain tunnel of the Chengdu-Kunming Railway. It can be seen from the figure that some of the concrete surfaces in the tunnel have been exfoliated and crystalloid salt has been formed on some concrete surfaces.

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Figure 1: Reinforced concrete damaged by sulfate erosion

The erosive environment and test methods used in the laboratory research are not based on the analysis of actual damage engineering, which are highly arbitrary and subjective, resulting in many disordered, unpractical (Loghman-Estarki et al., 2015) and contradictory test results and theoretical analysis.

2. Laboratory Research on Concrete Sulfate Attack

Concrete sulfate erosion refers to a series of complex and intersecting physicochemical processes between cement hydration products and the sulfate from external sulfate environment and internal concrete. There are both chemical reactions and physical changes in the sulfate erosion process, which is a very complex process (as is shown in Figure 2).

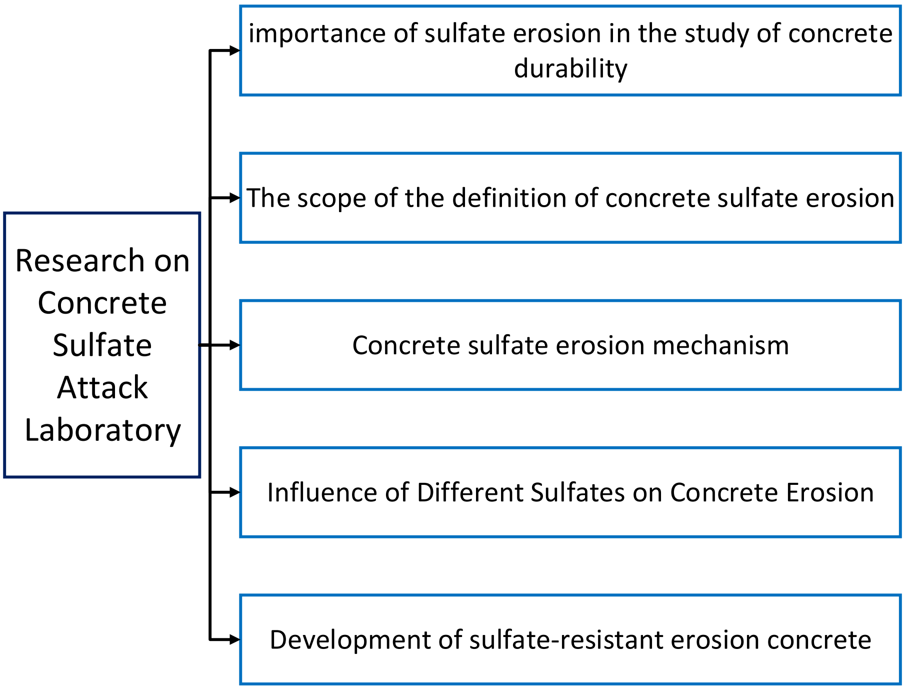

Figure 2: Research on Concrete Sulfate Attack Laboratory

2.1 The Importance of Sulfate Erosion in the Study of the Durability of Concrete

As the sulfate erosion of concrete is a long-term process, it is impossible to carry out experimental research entirely at the erosion site. Therefore, in order to accelerate the test process, more severe test conditions such as high concentration of sulfate solution, drastically changing drying and watering cycle, small test pieces and the use of neutral sulfate solution (pH value=7) are often adopted in laboratory researches. However, due to the use of these harsh test conditions, many scholars believe that the accelerated laboratory research does not correctly reflect the actual process of sulfate erosion deterioration process in the actual engineering, but causes an anxiety of groundless among people.

2.2 The Definition Scope of Concrete Sulfate Erosion

Researches on concrete sulfate erosion have focused on the second concept all the time, and the related mechanism for the chemical reaction between sulfate ions and cement hydration products have been obtained (Qian et al., 2016). The "physical erosion" of concrete sulfate mainly occurs in semi-buried concrete, but it has only received corresponding attention in recent times. Superficially, the bone of contention is the definition scope of concrete sulfate erosion. However, it is essentially a controversy over the mechanism of sulfate erosion. Whether it is the chemical erosion of sulfate or the physical erosion of sulfate leads to the deterioration of the corresponding concrete.

2.3 Mechanism of Concrete Sulfate Erosion

It is well known that the main cement hydration products are hydrated calcium silicate (C.S.H), calcium hydroxide (CH), calcium aluminum hydrate (C.A.H), ettringite (AFT) and monosulfide hydrated calcium aluminate sulfate (AFT). However, three of these hydration products cannot stably exist in the sulfate environment and the following chemical reactions will take place, producing chemical erosion products:

$$Ca\left(OH\right)_2 + C - S - H + SO_4^{2-} \rightarrow CaSO_4 \cdot 2H_2O \tag{1}$$

$$\begin{aligned} & 3CaO \cdot Al_2O_3 \cdot Ca\left(OH\right)_2 \left(12-18\right) H_2O + SO_4^{2-} \cdot 2H_2O + H_2O \\ & \quad \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \end{aligned} \tag{2}$$

The main chemical reaction products are: gypsum, ettringite, thumasite, magnesium hydroxide and silica gel. Gypsum and ettringite are two of the most common chemical erosion products in sulfate erosion. Magnesium hydroxide and silica gel are the products of magnesium sulfate erosion. If C03 exists in the reaction process, the thumasite may be formed.
The chemical reaction of calcium hydroxide to produce gypsum is as follows,

$$Ca\left(OH\right)_2 + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2OH^- \tag{3}$$

The pH value and sulfate concentration in the external erosion environment (Lei et al., 2015), especially the pH value, play an important role in the concrete sulfate erosion products and erosion mechanism. The boundary conditions of the erosive environment concentration and pH value for the formation of gypsum, ettringite and thumasite are shown in Table 2.

Table 2: Influence of pH and Concentration of Liquid on Formation of Gypsum, Vermiculite and Carbon-Carbinite

	pH	Concentration
Gypsum	<12.9	>1400mg/l
Ettringite	>11.5-12	--
Thaumasite	>10.5	--

2.4 Impact of Different Sulfates on Concrete Erosion

Groundwater contains a large amount of sulfate ions combined with basic ions (Na+, K+) or Ca2+, and also a large amount of M92+ can be found in some waters. Due to the extensive use of chemical fertilizers in agriculture, the ammonium sulfate may also be found in some places (Yang et al., 2016). Only a small amount of groundwater may contain sulfate reward. Sodium sulfate and magnesium sulfate are two of the most common sulfates and they are also the focus of researches on concrete sulfate erosion.
As is shown in Figure 3, the major products between sodium sulfate and cement hydration products are gypsum and ettringite.

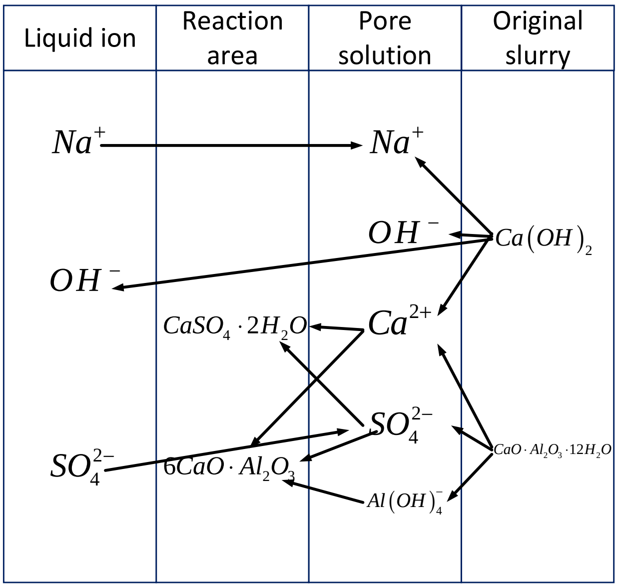

Figure 3: Chemical reaction between sodium sulfate and cement hydration products

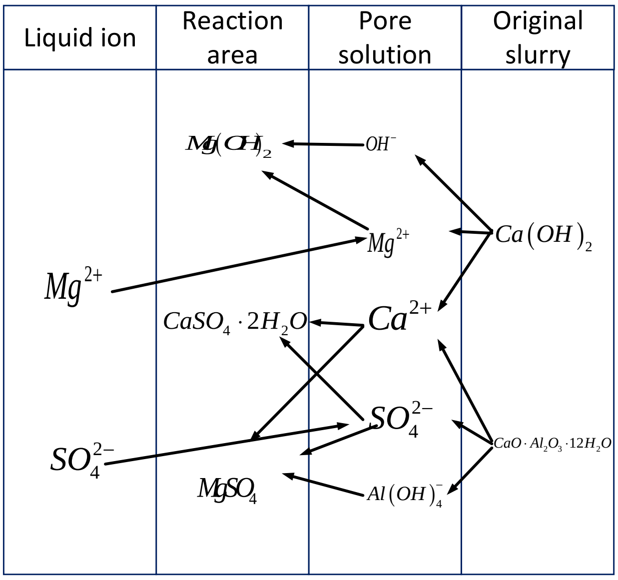

Figure 4: Chemical reaction between magnesium sulfate and cement hydration products

Figure 4 shows the main reaction and products between magnesium sulfate and cement hydration products. Compared with the products of sodium sulfate and cement hydration products, the magnesium hydroxide, M. S. H(3MgO·2Si02·2H20) and amorphous silicon dioxide (Si02"2H20) are also produced by the reaction between magnesium sulfate and cement hydration products in addition to gypsum and ettringite (Fouad et al., 2017). Since magnesium hydroxide is a slightly soluble base, its production will reduce the content of OH in the solution, thereby lowering the pH value of the entire solution and further leading to severe decalcification reaction that causes the decomposition of the C.S.H gel. In addition to the reaction of ettringite and gypsum, the other main reactions are:

$$Mg^{2+} + SO_4^{2-} + Ca(OH)_2 + 2H_2O \rightarrow Mg(OH)_2 + CaSO_4 \cdot 2H_2O \tag{4}$$

$$xMg^{2+}+SO_4^{2-}+xCaO\cdot 2SiO_2\cdot aq+2H_2O \rightarrow 2x\left[2-CaSO_4\cdot 2H_2O\right]+x\mathrm{Mg}\left(OH\right)_2+SiO_2\cdot aq \tag{5}$$

Due to the existence of both C.S.H decalcification and production of swelling products in the erosion process of magnesium sulfate, it is generally believed that the erosion effect of magnesium sulfate on concrete erosion is greater than that of sodium sulfate.

3. Development of Sulfate Erosion Resistance Concrete

Based on the above analysis, it is generally believed that the erosion effect of magnesium sulfate on concrete erosion is greater than that of sodium sulfate. However, there are many trials showing the opposite phenomenon: A long-term experiment conducted by EW. Brown showed that the deterioration depth of sulfate erosion resistance concrete with O.45 water-cement ratio after immersed in the 3000 ppm magnesium sulfate solution for 23 years was about 7mm, but the deterioration depth of concrete in the same concentration of sodium sulfate solution reached 22mm.

$$2xMg^{2+}+2xSO_4^{2-}+2x\left[2-xCaO\cdot 2H_2O\cdot aq\right]+xH_2O \rightarrow 3MgO\cdot 2SiO_2\cdot 2H_2O+2x\left[2-CaSO_4\cdot 2H_2O\right]+\left(2x-3\right)Mg\left(OH\right)_2 \tag{6}$$

For concrete with admixtures, whether fly ash, slag or silica fume, the concrete exposed to air is subjected to more severe erosion damage compared with normal concrete.
The standard definition of for chemical erosion of concrete sulfate in the United States is shown in Table 3.

Table 3: ACI C 317-08 standard in USA

Exposure level	In water	Water-soluble sulfate ion in soil
Negligible	<150	<0.10
Moderate erosion	150-1500	0.10-0.20
Severe erosion	1500-10000	0.20-2.00
Very severe erosion	>10000	>2.00

The standard definition of for chemical erosion of concrete sulfate in Europe is shown in Table 4.

Table 4: European Standard EN206．I 16

Exposure level	In water	In the soil	Magnesium ion concentration in water
Slight erosion	200-600	2000-3000	300-1000
Moderate erosion	600-3000	3000-12000	1000-3000
Severe erosion	3000-6000	12000-24000	3000

The standard of China is shown in Table 5.

Table 5: China Standard GB ／T50476．2008

Exposure level	SO_4 in water	SO_4 in the soil	Mg in water	pH	Air CO2 content in water
V-C	200-1000	300-1500	300-1000	5.5-6.5	15-30
V-D	1000-4000	1500-6000	1000-3000	4.5-5.5	30-60
V-E	4000-10000	6000-15000	>3000	<4.5	60-100

It can be seen from the comparison of data in the above three standards, the basic framework is the same regardless of different boundary values of each standard. However, as Nevill has pointed out, "We have no way of knowing whether these levels of erosion are correct, because these values have not been strictly calculated or verified."

4. Conclusions

This paper firstly proposes two types of concrete sulfate erosion in accordance with actual engineering examples according to the exposure model of concrete components in the sulfate environment. Then, on the basis of the actual engineering examples of sulfate erosion damage, the logical analysis is conducted on the proposed concrete sulfate erosion. Meanwhile, combined with previous relevant laboratory researches, the corresponding relationship between laboratory researches and engineering examples are explored and finally the corresponding erosion mechanism is proposed. Relevant simulation experiments are carried out to prove the proposed erosion mechanism based on this.

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