

황산염 침식과 성능저하 모드

Sulfate Attack and Its Deterioration Modes

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ABSTRACT

Until now, sulfate attack is not completely understood. The purpose of this study is to provide a fundamental data to understand deterioration mechanism by sulfate attack. Chemical processes for products formed by sulfate attack were explained in this study. ASTM C1012 test and microstructural observations such as XRD and BSE analysis were carried out to manifest behavior and role of the products formed during sulfate attack. Regarding the dominant causes of sulfate attack, the main deterioration modes could be divided into 3 types; (1) expansive type, (2) onion-peeling type, and (3) acidic type.

1. Introduction

There are many causes of hardened cement-based materials' degradation such as exposed to carbonation, AAR, F-T cycles, DEF, seawater attack and sulfate attack. Deterioration of concrete structural components exposed to soils and groundwater contaminated with sulfate salts is a serious problem in durability of concrete. A number of hypotheses have been proposed to describe the mechanisms responsible for sulfate deterioration of concrete.^(1,2)

Most importantly, it is necessary to recognize the reactants (e. g. ettringite, gypsum, thaumasite) caused by ingress of sulfate ions to prevent or at least to mitigate sulfate attack. This paper deals with the deterioration modes due to external sulfate attack. It is hoped that further studies would lead to the development of generalized models that could be used for concrete performance prediction.

2. Reactants formed by sulfate attack

2.1 Ettringite formation

Ettringite is generally formed by the reaction of sulfate ions with AFm or ferroaluminate phase. It has been recognized that the product primarily leads to massive expansion on cement matrix. However, the exact mechanism of ettringite formation and subsequent expansion has been a matter of controversy between researchers for a long time. Until now there are two major theory to

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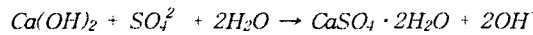
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explain the mechanism of ettringite formation; the crystal growth and the swelling theory.

Many researchers tried to elucidate effects of ettringite formation on deterioration of concrete. The damage caused by the product leads to an increase of permeability of concrete and subsequently may accelerate the ingress of deleterious species. In particular, the formation of ettringite significantly depends on the concentration of external sulfate solution and cation type accompanying sulfate ions. Fig. 1 clearly shows the effect of concentration of sulfate ions on the sulfate deterioration. With an increase in concentration of sulfate ions, there are remarkable increase in both ultimate expansion value and critical time for expansion.

2.2 Gypsum formation

It has been generally accepted that gypsum is formed during sulfate attack as a results of the reaction between sulfate ions originated from sulfate solution and calcium hydroxide liberated by hydration process. The chemical reaction process is as follows.

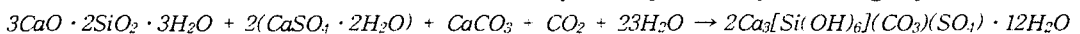


As gypsum results from substitution reaction of calcium hydroxide, the role of calcium hydroxide on the sulfate attack is significantly dependent on the amount and localization of it. Thus, it is evident that further studies are necessary to understand the deterioration mechanism and modes associated with gypsum formation and calcium hydroxide.

Due to the deposits of gypsum crystal on the interfacial transition zone, the porosity of cement matrix subsequently increases in the region. Damage in the surface of cement matrix is attributable to the gypsum formation in parallel to the ingress front of sulfate ions. Consequently, the formation of gypsum leads to the softening effect due to the topochemical reaction. When the concentration of sulfate solution is as high as 5000 ppm SO_3 , sulfate attack process is driven by the formation of gypsum formation. Using XRD analysis, it could be found that the deterioration of cement matrix is greatly related to the gypsum formaton formed in surface part of cement matrix. Fig. 2 clearly shows the gypsum formation by sulfate attack. As expected the gypsum formation were prevailing at around 11.7, 20.7 and 29.0° 2θ . More importantly, there was no evidence of the presence of portlandite because of entire consumption of it by sulfate attack process. However, until now there has been no clear documentation which gypsum formation associated with sulfate attack leads to expansion. Thus, it needs more data and studies to clearly establish the mechanism related to the expansion due to gypsum faromation.

2.3 Thaumasite formation

Many researchers have reported that thaumasite form from reaction of calcium carbonate, sulfate ions and C-S-H. It should be noted that thaumasite formation needs a sufficient amount of Si ions in the pore solution. Actually, the decomposition of C-S-H due to appears to be the source of Si and this is available in the pore solution to react with dissolved atomospheric CO_2 or CO_3^{2-} from aggregate and sulfate ions supplied from the external solution to form thaumasite. The general reaction for the formation of thaumasite may be expressed by following equation.



Namely, the formation of thaumasite directly involves C-S-H with supply of a sulfate source and a carbonate source.

It is believed that thaumasite forms during sulfate attack at low temperature ($< 5^\circ C$). However,

numerous studies suggested the possibility of thaumasite formation in ambient temperature. Thaumasite is often indistinguishable from ettringite due to their nearly identical XRD pattern. This can be confirmed by the work carried out by Hartshorn et al.⁽³⁾ SEM analysis with EDS profile could help to detect the presence of thaumasite. Thus, the products formed by sulfate attack were investigated using microstructural techniques. Paste specimen were exposed to 5% sodium sulfate solution for 720 days at room temperature. The BSE images are presented in Fig. 3. and 4. Fig. 3 shows the alternation of microstructure near the surface of the sample. For the high magnification, as shown in Fig. 4, the image shows a great number of micro-cracks. EDS analysis clearly showed the formation of thaumasite in the cracks indicating the presence of elements of calcium, sulfur and silica. It was also observed that gypsum formation gradually converts into thaumasite formation with exposure duration. This conversion led to the production of the cracks resulting from deterioration in the cement matrix.

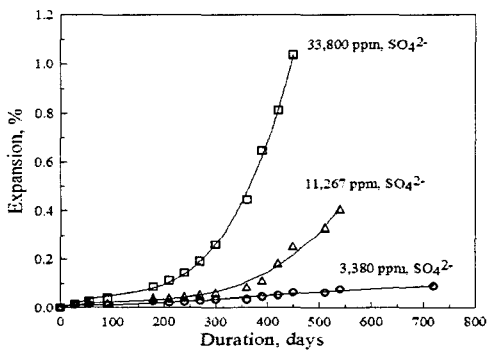


Fig. 1 ASTM C1012 test results with different exposure condition

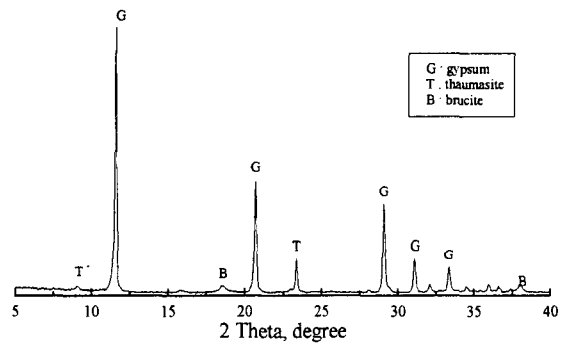


Fig. 2 XRD pattern of cement paste exposed to sulfate attack, gypsum formation.



Fig. 3 BSE image of cement paste exposed to sulfate solution

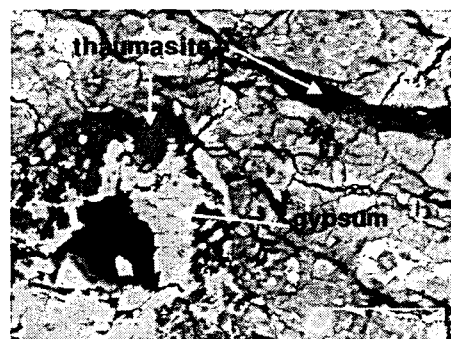


Fig. 4 BSE image showing thaumasite in association with gypsum formation (high magnification)

3. Deterioration modes due to sulfate attack

Fig. 5 shows the deterioration modes of cement matrix associated with sulfate attack. The expansive type, as shown in Fig. 5 (a), represents sulfate damage by the ettringite in presence of

sufficient aluminate phases and sulfate ions, especially from alkali sulfate solution. This mode leads to an increase of cracking and loss of strength and stiffness in the cement matrix. Additionally, it has been reported that the mode is greatly associated with temperature of solution because of the solubility of ettringite.

The second mode of sulfate attack is the onion-peeling type, as shown in Fig. 5 (b). This is characterized by scaling of the surface due to loss of bond in successive layers. The mode is apt to be found in a higher concentration of sulfate solution. The third mode of deterioration (Fig. 5 (c)) results from the loss of cohesiveness between hydrated cement paste and aggregate with the formation of gypsum and/or thaumasite. With a continuous exposure, the surface of cement matrix intends to convert into the mushy and non-cementitious materials.

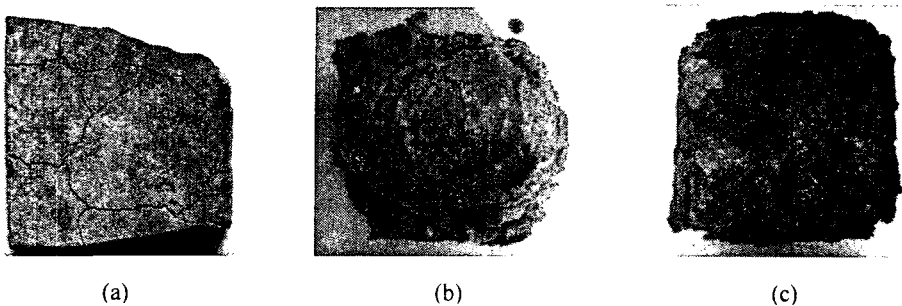


Fig. 5 Various deterioration modes due to sulfate attack, Note: (a) Expansive type, (b) Onion peeling type, and (c) Acidic type

4. Concluding remarks

The products formed by sulfate attack such as ettringite, gypsum and thaumasite are significantly associated with the exposure conditions. In order to establish the deterioration mechanism by sulfate attack it is necessary to understand the chemical reaction processes of the sulfate products with different potentials and characteristics. Further, it is believed that some information on deterioration modes by sulfate attack (Fig. 5) will help to make a countermeasure against sulfate attack.

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