시멘트 경화체중 TSA 현상에 대한 연구

Evidence of TSA in Cement Matrix

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ABSTRACT

TSA(thaumasite sulfate attack) is one of the important and prevailing phenomena to damage concrete structures by sulfate attack. In the present study, the thaumasite ($CaSiO_3 \cdot CaSO_3 \cdot CaSO_4 \cdot 15H_2O$) has been observed by the authors and other researchers in concrete samples in laboratory or field. Microstructural and mechanical observations clearly confirm that the thaumasite formation is greatly associated with sulfate attack indicating mass loss, expansion and spalling in the sample.

This study summarizes the results of observation carried out by the authors and researchers on TSA which thaumasite formation has been identified.

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. Among the causes of concrete deterioration by sulfate attack, the formation of thaumasite is recognized as a difficult problem to analyze and understand effects on concrete performance. In connection with the durability of concrete, thaumasite is thought to be a special kind of sulfate attack during a few decade. However, the formation is commonly investigated in concrete samples all over the world even though concrete structures lie in ambient temperature.

This paper deals with the TSA due to external sulfate attack. It is hoped that further studies would lead to the development of generalized analysis on the thaumasite formation that could be used for concrete deterioration.

2. What is TSA?

In conventional sulfate attack, ettringite, gypsum and/or M-C-S-H are the deleterious minerals formed in the

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concrete due to the ingress of sulfates into a concrete structure by water containing soluble sulfates. Concerning TSA in concrete, it was diagnosed as a symptom and cause of deterioration in concrete in North America and Europe about a decade ago[1,2]. Fig. 1 shows the damage of concrete structure located in Orange Country , Southern California, which has a mild climate over 15 ℃. It has commonly been believed that thaumasite forms during sulfate attack at low temperature (< 5℃). However, numerous studies suggested the possibility of thaumasite formation in ambient temperature.

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 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 (1).

$$3CaO \cdot 2SiO_2 \cdot 3H_2O + 2(CaSO_4 \cdot 2H_2O) + CaCO_3 + CO_2 + 23H_2O \rightarrow 2Ca_3[Si(OH)_6](CO_3)(SO_4) \cdot 12H_2O \quad (1)$$

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

More importantly, thaumasite is often indistinguishable from ettringite due to their nearly identical XRD pattern, as shown in Fig. 2. 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 should be investigated using microstructural techniques. However, it should be keep in mind that the nature of the crystal structure of thaumasite is still a subject of contraversy with respect to the coordination number of the Si in thuamsite.

Fig. 1 Damage by TSA in concrete structure

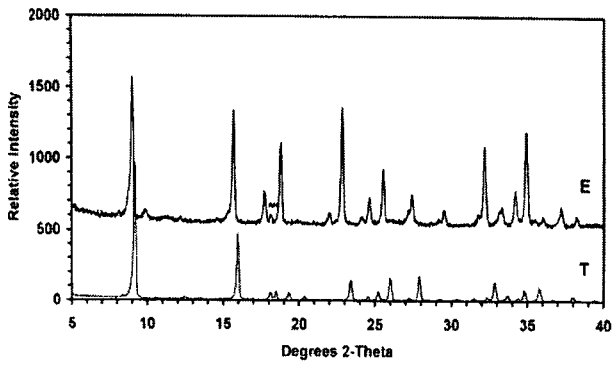

Fig. 2 X-ray patterns of ettringite(E) and thaumasite(T).

3. Studies of the authors about TSA

Lee et al.[4] published a work in association with TSA in high-alumina GGBFS paste exposed to magnesium sulfate solution. Using SEM and DSC techniques, they showed the negative effect of GGBFS

with a high fineness with respect to TSA. Their another work[5] confirmed the roles of thauamsite formation on the damage of mortar samples with recycled fines. Petrographic examination revealed abundant deposits of thaumasite filling in the cement-aggregate interface in the sample. The formation in ITZ may be an important cause of the serious damage of the sample with the recycled fines. This was clearly observed by XRD patterns and EDS profiles.

Author's other works were exhibited in Fig. 3 and 4. The BSE images shows the alternation of microstructure near the surface of the sample. For the high magnification. EDS analysis clearly showed the formation of thaumasite in the cracks indicating the presence of elements of calcium, sulfur and silica. The figures related to the transition mechanism to thaumasite formation from conventional formation by sulfate attack. A great amount of gypsum was formed into air void or cracked zone in cement matrix exposed to sulfate solution. With further exposure, supplies of silica ions by decomposition of C-S-H and of sulfate ions by external sulfate source accelerated the thaumasite formation in the low-density area. This conversion led to the production of the cracks resulting from deterioration in the cement matrix.

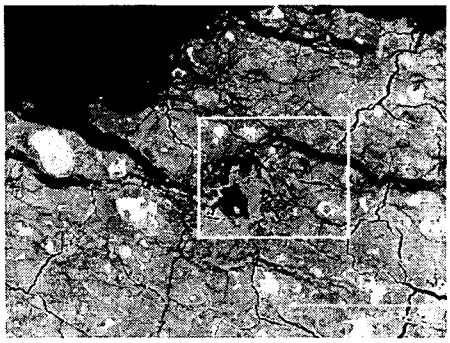

Fig. 3 BSE image of cement paste exposed to sulfate solution

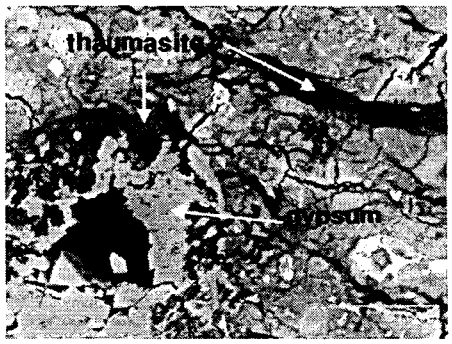

Fig. 4 BSE image showing thaumasite in assosiation with gypsum formation (high magnification)

4. Studies of researchers about TSA

In the UK, TEG(Thaumasite Expert Group) has reported a discovery of advanced TSA affecting buried concrete elements supporting some bridges that raised the concern with respect to TSA. It suggested the following risk factors related to the TSA: 1) presence of a source of sulfate including sulfide that may decay to sulfate, 2) presence of mobile water, 3) presence of carbonate, and 4) low temperature.

Romer et al.[6] reported an another interesting work in their literature. They found that the shotcrete lining in Swiss tunnel structures had been severely damaged by TSA because of flowing underwater. Additionally they emphasized the importance of 'thumasite performance test' to understand the exact mechanism.

Canadian researchers investigated the evidence of thauamsite in field concrete suspected of being affected by sulfate attack using optical and electron microscopy techniques. Fig. 5 and 6 show the presence of thaumasite both within air void and in the vicinity of ITZ of concrete sample with fly ash. It is interesting that the sample was exposed to the seawater attack for 10 years. Thaumasite has been found in marine-exposed concrete by other workers. Generally, a common feature of thaumasite formation, whether in

marine environment, acidic condition or sulfate-contaminated groundwater, is that the concrete contains a source of carbonate ions, as previously mentioned above.

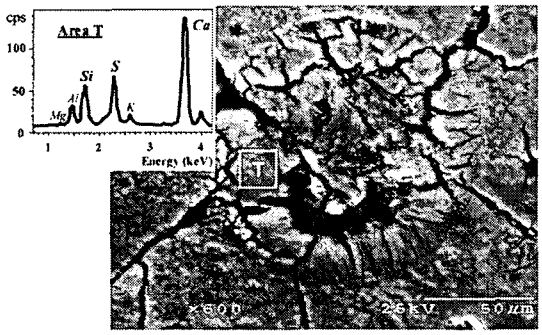

Fig. 5 BSE image and EDS profile showing thaumasite in air void in concrete.

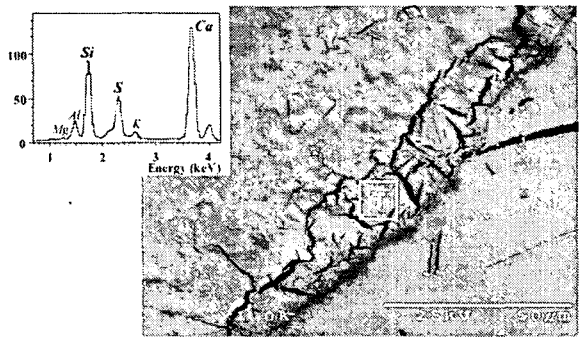

Fig. 6 BSE image and EDS profile showing thaumasite in ITZ in concrete.

5. Concluding remarks

TSA in cement matrix is not a special phenomena any more in concrete durability. A great amount of efforts have been carried out to establish the deterioration mechanism and testing methods in association with thaumasite formation. The works by the authors and researchers will give helpful information to analyze and understand the characteristics of thaumasite formation.

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