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Mechanism of thaumasite formation in concrete slabs on grade in Southern California

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Abstract

Thaumasite formation has been observed in residential concrete slabs on grade in Southern California. The concrete examined did not contain any carbonate bearing aggregates or fillers. Microstructural analyses showed a carbonated layer with calcite and gypsum at the bottom of the concrete. Above the carbonation layer, deposits of intermixed gypsum and thaumasite were observed. Further into the concrete towards the upper surface, deposits of thaumasite alone or in combination with ettringite were observed. Most of the thaumasite deposits were observed in air voids. SEM–EDS analysis showed deposits of ettringite, thaumasite and intermediate phases within the same air voids. The formation of thaumasite, ettringite and gypsum was caused by ingress of sulfate and carbonate ions from ground water. The presence of thaumasite, ettringite and intermediate phases in the same air void indicates that ettringite is first formed followed by thaumasite with a series of solid solutions. In this reaction process the pH of the local environment and the balance between sulfate, silicate and carbonate ions are important parameters.

Keywords: Thaumasite; Ettringite; Gypsum; Carbonation; SEM

1. Introduction

Thaumasite form of sulfate attack in concrete is well recognized [1]. In conventional sulfate attack, ettringite and/or gypsum are the deleterious minerals formed in the concrete due to the ingress of sulfates into a concrete structure by water containing soluble sulfates. In the thaumasite form of sulfate attack, thaumasite is present in the deteriorated concrete in addition to ettringite and/or gypsum. The chemical formula of thaumasite, $Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2 \cdot 24H_2O$ indicates that the anionic species CO_3^{2-} and $Si(OH)_6^{2-}$ besides SO_4^{2-} are essential. The thaumasite expert group suggests that the conditions required for the formation of thaumasite in concrete are: a source of calcium silicate, a source of sulfate ions, a source of carbonate ions, and a very wet, cold (below 15 °C) environment [1]. Most of the thaumasite form of sulfate attack investigations reported in the literature suggest that the source of carbonate ions for the formation of thaumasite is either the aggregates or ground limestone added into the cement [2–8].

In a recent study, we observed that thaumasite formed in a concrete without an internal source of carbonate ions [9]. This study presents the possible mechanisms of thaumasite formation in a non-carbonate bearing concrete as deduced from microstructural observations. In the present investigation, SEM coupled with EDS and polarized light microscopy (PLM) has been used for identifying deposits of thaumasite.

2. Investigation methodology

2.1. Sample preparation

Concrete cores from a garage floor of a residential home in Southern California were cut into three sections and designated as top, middle and bottom with the top section having a surface exposed to the atmosphere and the bottom section exposed to the ground. The concrete sections were cut into 40 × 40 mm blocks in order to scan large areas of the concrete. Fluorescent epoxy impregnated thin sections were made according to the procedure described by Jakobsen et al. [10]. The thin sections

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were polished and coated with a thin layer of carbon for analysis under SEM.

2.2. SEM–EDS

Microstructures of the specimens were studied using an ASPEX personal scanning electron microscope (PSEM) with EDS capability. Back-scattered electron (BSE) images were acquired for each specimen at 20 keV. Most of the images were acquired as a composite image comprising of (a) an area imaged at lower magnification, (b) an enlarged image displayed to the right of the first image, a sub area of interest, outlined by a square, and (c) an EDS spectrum taken at a point in the higher magnification image with the location marked on the right image with a small square.

3. Results and discussion

The combined attack of sulfates and carbonates from the ground water alters the original cement paste in addition to the precipitation of sulfate minerals. Figs. 1–4 represent the carbonated area at the very bottom of the concrete exposed to the ground water. Figs. 1 and 2 show the formation of discrete calcite particles in a matrix of magnesium silicate gel. Due to the severity of carbonation of the porous concrete with low calcium hydroxide content, the carbonation process is not an ordinary carbonation but rather occurring through bicarbonation [11]. The details of the bicarbonation process are described in a previous publication [11]. The bicarbonation process takes place below pH 11. In this process, not only the calcium hydroxide is consumed but calcium silicate hydrate is also carbonated to produce silica gel. The chemical reactions taking place during this bicarbonation process are presented in the following equations.

$$CO_2 + OH^- \Longleftrightarrow HCO_3^- \tag{1}$$

$$HCO_3^- + Ca(OH)_2 \Longleftrightarrow CaCO_3 + H_2O + OH^- \tag{2}$$

$$Ca_3Si_2O_7 \cdot 3H_2O + 3HCO_3^- + OH^- \Longleftrightarrow 3CaCO_3 + 2H_2SiO_4^{2-} + 3H_2O \tag{3}$$

When sulfates in the form of magnesium sulfate penetrate into porous concrete, gypsum is precipitated in air voids (Figs. 3 and 4). The gypsum deposit is surrounded by calcite crystals. The silica gel further reacts with magnesium hydroxide to produce magnesium silicate hydrate. It is noted that the magnesium silicate gel is rich in aluminum. This occurs due to the instability of calcium sulfoaluminate hydrate in the low pH carbonated paste.

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

$$SiO_2 + Mg(OH)_2 + H_2O \Longleftrightarrow MgO \cdot SiO_2 \cdot 2H_2O \tag{5}$$

Further into the concrete, deposits of gypsum line air voids associated with thaumasite, Figs. 5 and 6. The paste surrounding the air void is altered, cracked and

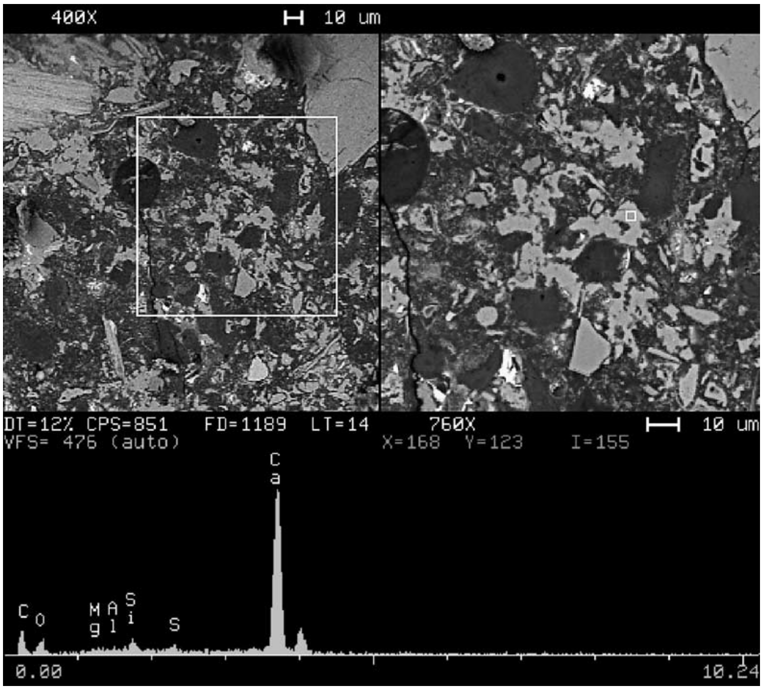

Fig. 1. BSE image showing bright "popcorn" crystals of calcium carbonate in decalcified cement paste.

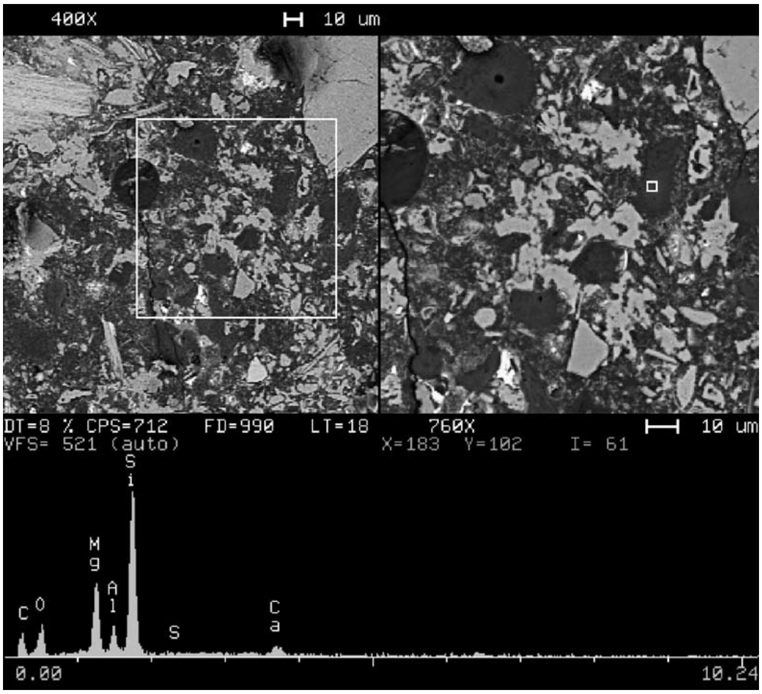

Fig. 2. Same area as Fig. 1. The decalcified cement paste is rich in silica, magnesium and aluminum.

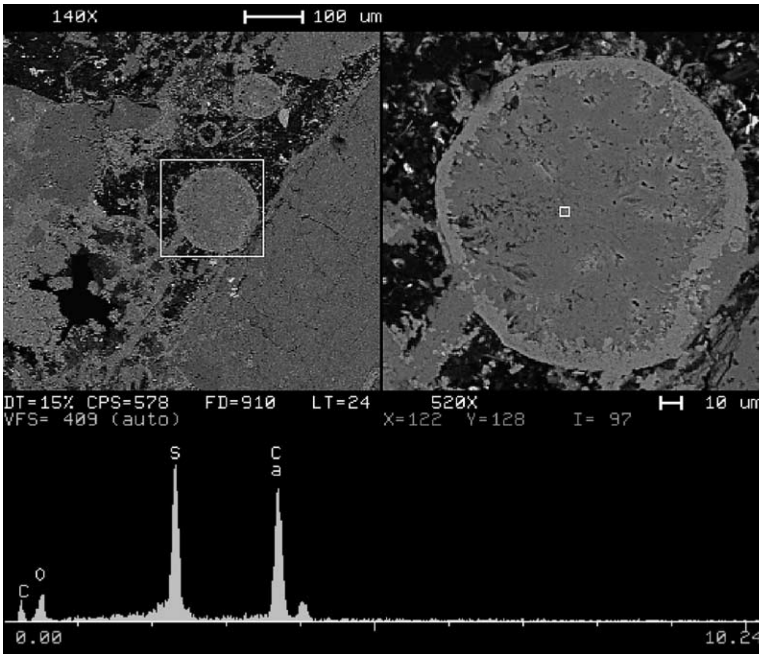

Fig. 3. BSE image showing an air void filled with gypsum.

deposits of ettringite rich in silica are observed, Figs. 7 and 8.

A few millimeters further into the concrete, deposits of pure thaumasite or thaumasite in association with ettringite are observed within air voids, Figs. 9–13. A common feature observed is the presence of thaumasite deposits in the center of air voids. EDS analysis away from the center indicates that a gradual increase in aluminum content is observed in the crystal fibers. The analyses of crystals in proximity to the wall of the air void show the presence of pure ettringite.

Above these features towards the upper surface of the concrete, a layer of pure ettringite is observed as deposits in air voids and within the cement paste, Fig. 14.

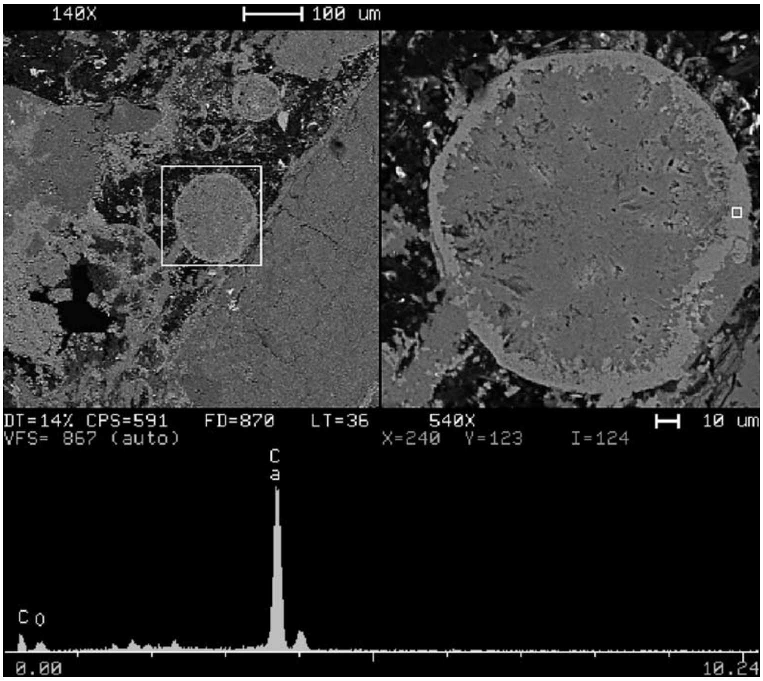

Fig. 4. Same area as Fig. 3. The light gray mineral rimming the air void is calcium carbonate.

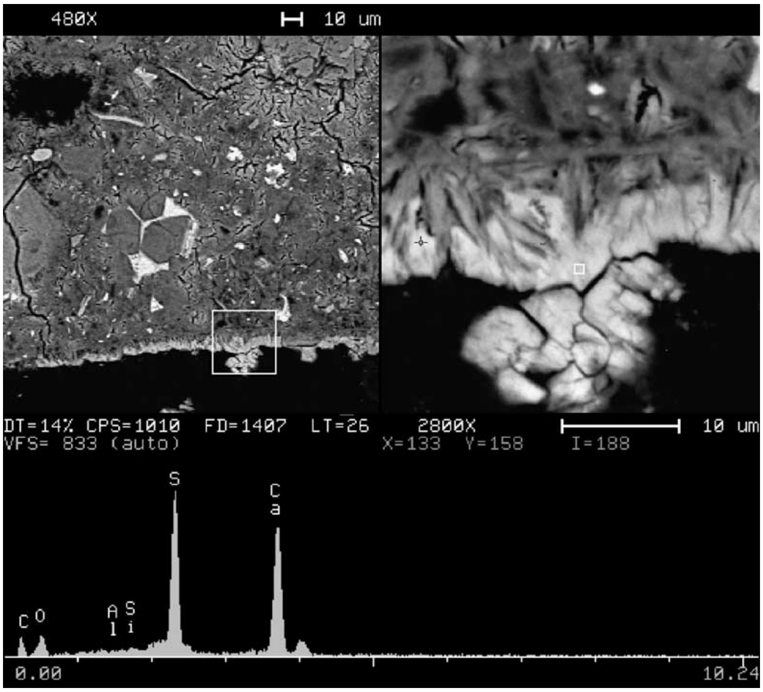

Fig. 5. BSE image and EDS of gypsum rimming a large air void.

However, this ettringite zone disappears where carbonation from the top of the concrete is present.

The microstructural observations suggest that ettringite first formed in the air voids. When carbonate and silicate ions were available in the system, formation of thaumasite started from the center. This raises a question; “why does the formation not start from the pore wall as the required chemical species are supplied through the wall?” One possible explanation of this phenomenon is that thaumasite forms at a narrow pH range of about 10–11. Thaumasite may be stable at higher pH, but the formation is a compromise between

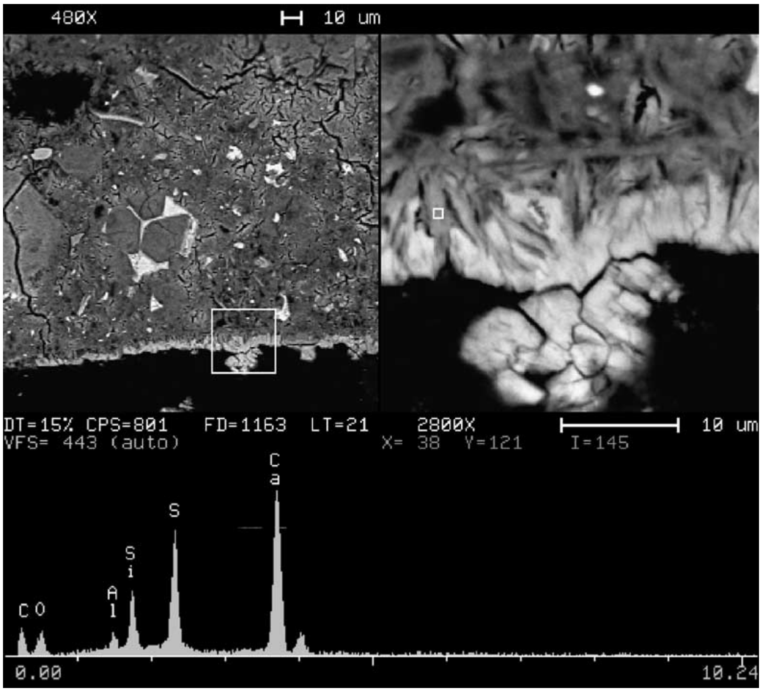

Fig. 6. Same area as Fig. 5. Thaumasite is present. Gypsum is growing on thaumasite.

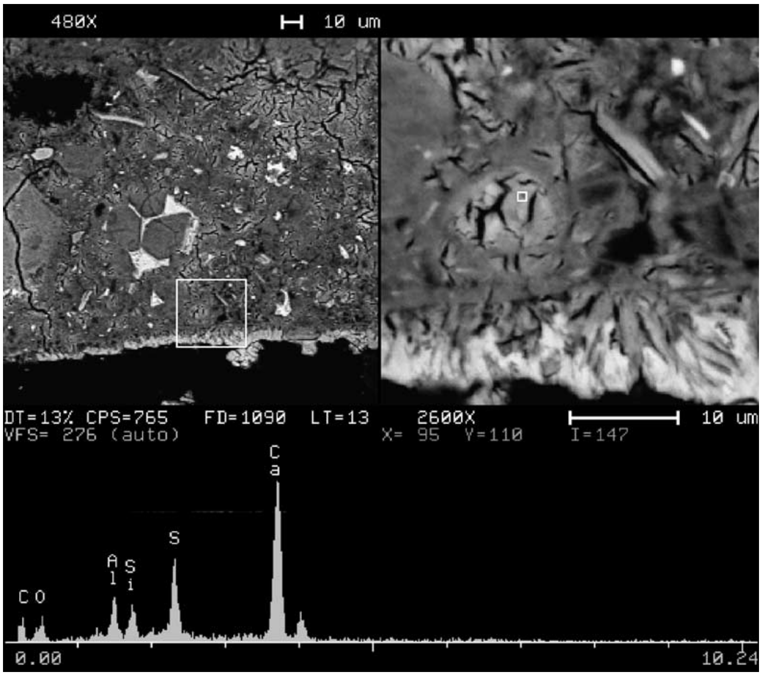

Fig. 7. Same general area as Figs. 5 and 6. Silica-rich ettringite is present in a former cement grains.

low pH where calcium carbonate is more soluble and high pH where silica is more soluble. Thaumasite growth, therefore must be partially controlled by a balance between two nearly mutually exclusive reactions as stated by Hunter [12]. This condition is readily available in the center and a relatively higher pH condition is prevailing near the wall due to supply of calcium hydroxide from the cement paste. The presence of pure thaumasite at the center and pure ettringite near the wall of the air void and proportionately changed

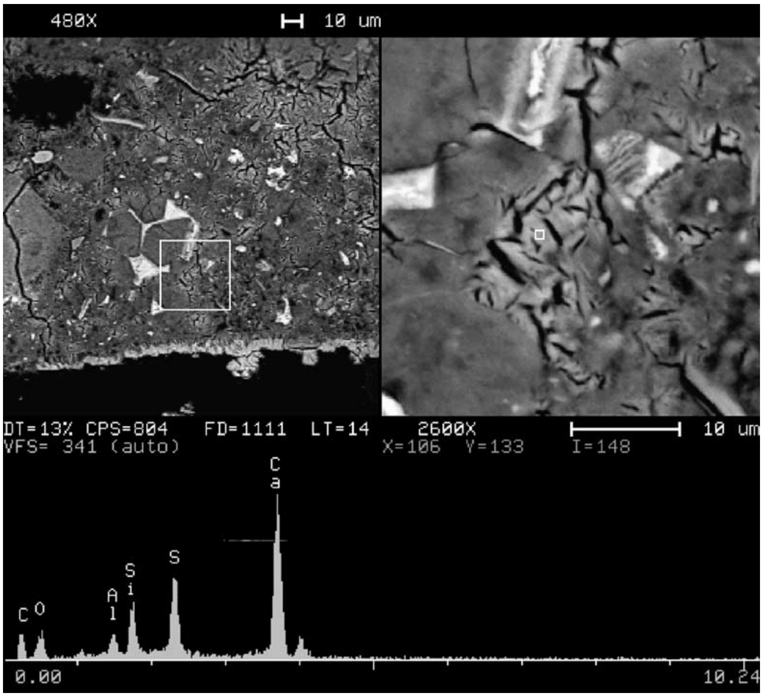

Fig. 8. Same general area as Fig. 7. The composition of the precipitate is closer to thaumasite. Some aluminum is still present.

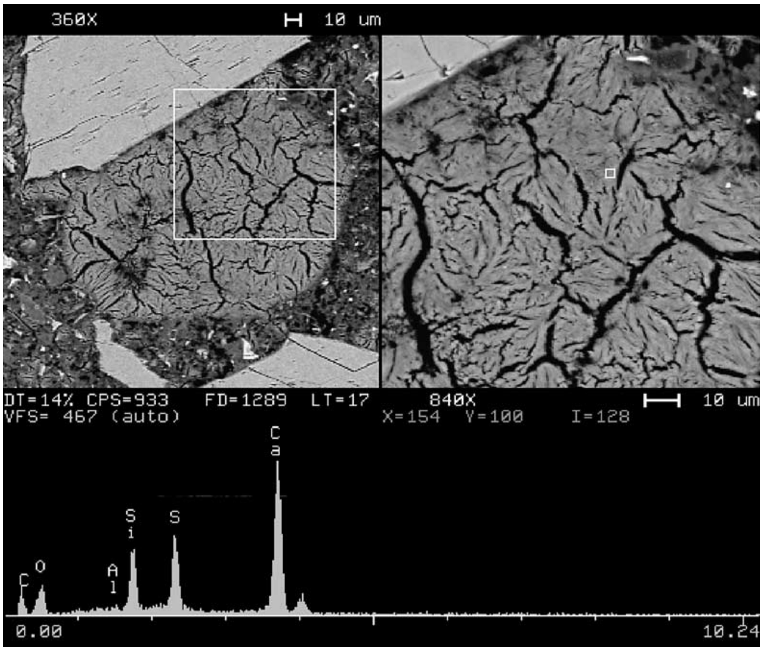

Fig. 9. BSE image and EDS of pure thaumasite in a former air void. Note the absence of aluminum.

ratio between silica and aluminum of the crystals suggests a presence of solid solutions between ettringite and thaumasite. The presence of a series of solid solution between the ettringite and thaumasite has been reported previously [13,14]. The reactions taking place during the formation of thaumasite can be represented in the following equation.

$$\begin{aligned}&Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O + 2HCO_3^- \\ &\quad + 2H_2SiO_4^{2-} \Longleftrightarrow Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2 \\ &\quad \cdot 24H_2O + 2Al(OH)_4^- + SO_4^{2-} + 2OH^- \qquad (6)\end{aligned}$$

The aluminates produced in this reaction process are slowly removed from the air voids. This indicates that

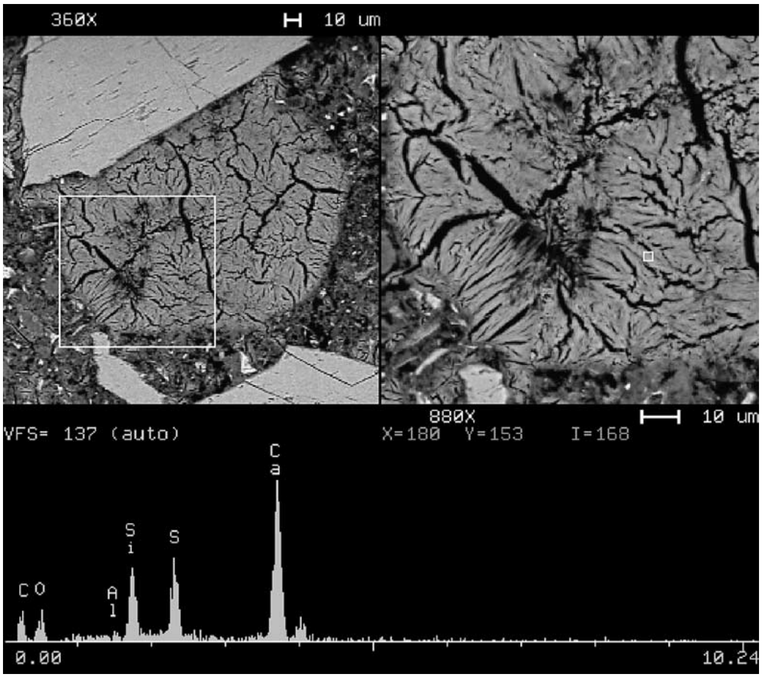

Fig. 10. Same area as Fig. 9. Pure thaumasite is found.

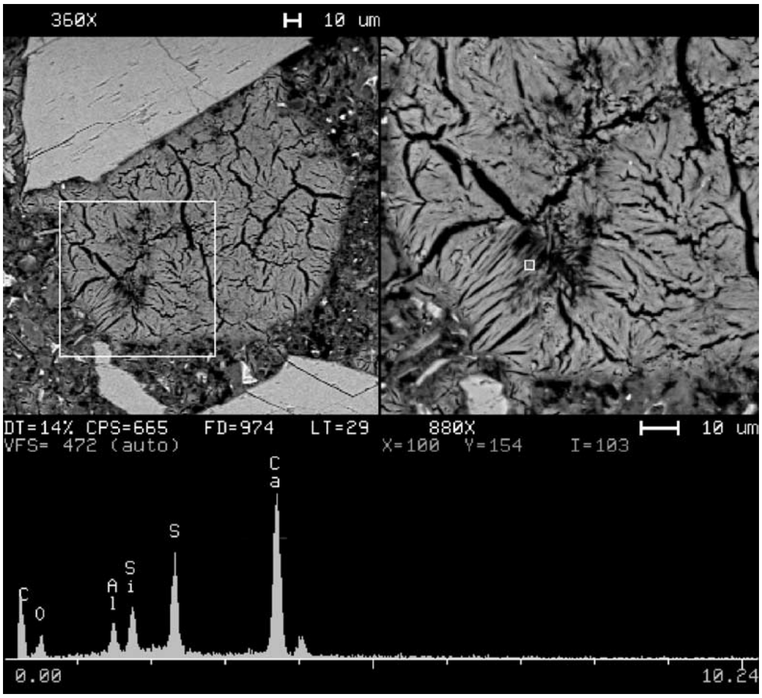

Fig. 11. Same area as Fig. 10. Closer to the wall of the air void silica-rich ettringite is found.

released $Al(OH)_4^-$ can further participate in ettringite formation. The available sulfates from this reaction can either participate in ettringite or gypsum formation. When ettringite is intermixed with calcium silicate hydrate or deposited as small crystals in the paste, thaumasite can form directly from C–S–H. The reaction presented below is adapted from a publication by Bensted [15]. The reactants: $CaCO_3$, CO_2, xH_2O in the equation creates an environment of bicarbonation process in the system.

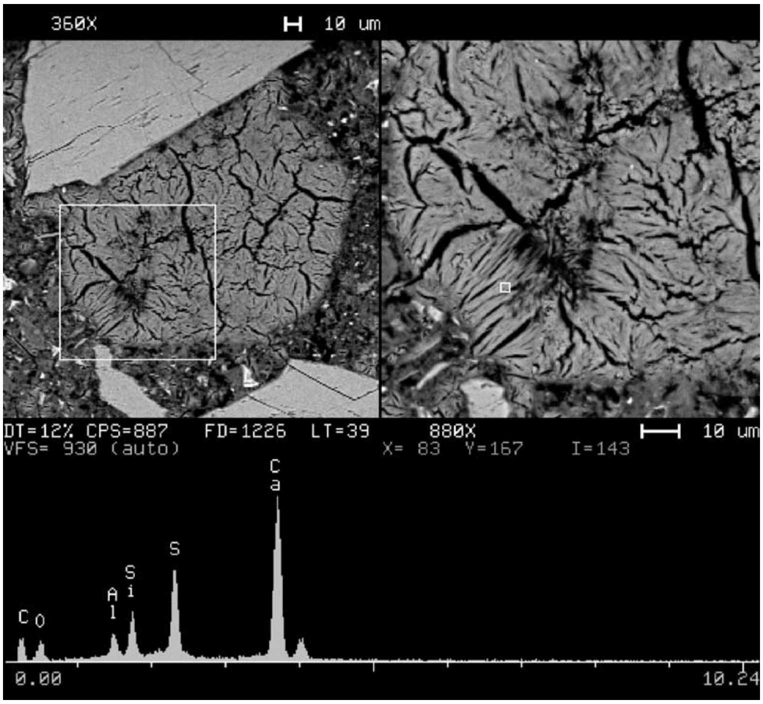

Fig. 12. Same area as Fig. 11. The presence of silica rich ettringite is confirmed.

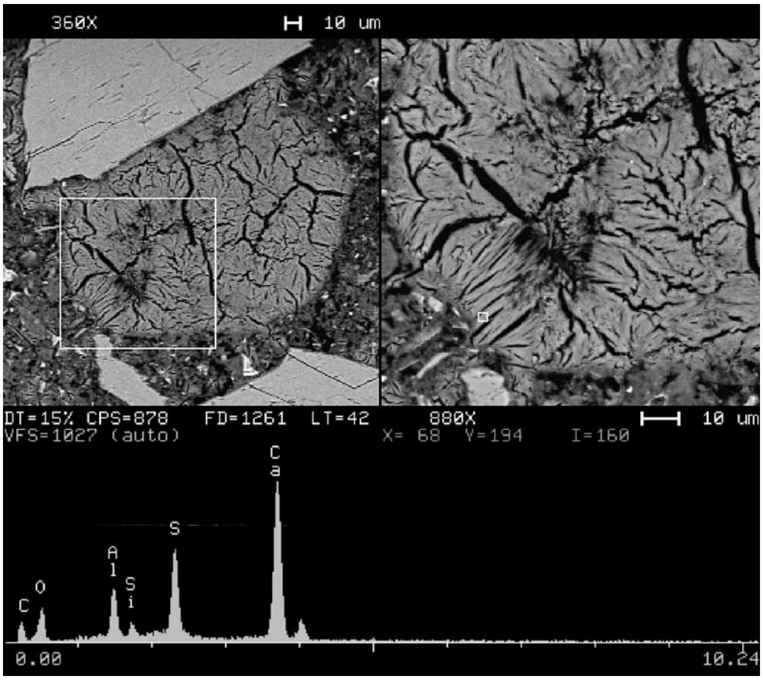

Fig. 13. Same area as Fig. 12. The ettringite crystals closer to the wall of the air void are lower in silica.

$$\begin{aligned}&Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O + Ca_3Si_2O_7 \cdot 3H_2O\\&\quad + CaCO_3 + CO_2 + xH_2O \Longleftrightarrow Ca_6[Si(OH)_6]_2\\&\quad \cdot (CO_3)_2(SO_4)_2 \cdot 24H_2O + CaSO_4 \cdot 2H_2O\\&\quad + Al_2O_3 \cdot xH_2O + Ca(OH)_2 \qquad (7)\end{aligned}$$

The observations of the mode of thaumasite formation suggest that ettringite acts as precurser for the thaumasite formation. This mode of mineral deposition suggests that at the very bottom of the concrete slab is a region of slightly acidic to slightly basic condition, pH 6–8. In the region, where thaumasite and gypsum are coexisting, a

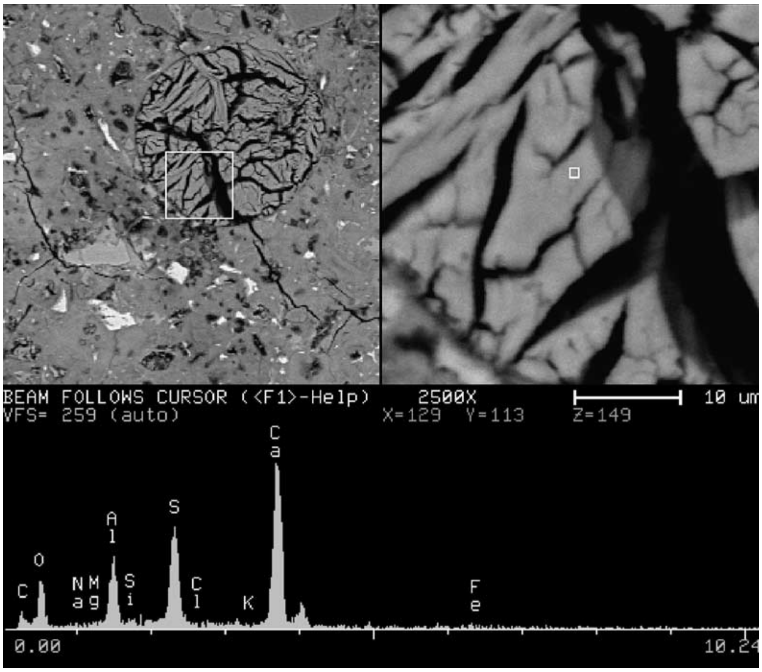

Fig. 14. BSE image with EDS in an uncarbonated area. Pure ettringite is present in a former air void.

pH of 10–11 is suggested. Above this zone, where thaumasite and ettringite coexist, a pH of 11–12 is likely to exist. The zone containing ettringite only has presumably a pH of greater than 12.

4. Conclusion

The concrete examined did not contain any carbonate bearing aggregates or fillers. The required carbonate and sulfate ions for thaumasite formation are derived from the ground water. Thaumasite deposits are observed in air voids alone or in association with gypsum and/or ettringite. SEM–EDS analysis showed deposits of ettringite, thaumasite and intermediate phases within the same air voids. The presence of thaumasite, ettringite and intermediate phases in the same air void indicates that ettringite is first formed followed by thaumasite with a series of solid solutions. In this reaction process the pH of the local environment and the balance between sulfate, silicate and carbonate ions dictates the type of mineral assemblages.

References

[1] Report of the thaumasite Expert Group. The thaumasite form of sulfate attack: risks, diagnosis, remedial works and guidance on new construction. Department of Environment, Transport and the Regions (now, the Construction Industry Directorate of the Department of Trade and Industry), London, 1999.

[2] Hobbs WD, Taylor MG. Nature of the thaumasite sulfate attack mechanism in field concrete. Cem Concr Res 2000;30:529–33.

[3] Crammond NJ, Halliwell MA. Assessment of the conditions required for the thaumasite form of sulfate attack. In: Scrivner KL, Young JF, editors. Mechansims of chemical degradation of cement based systems. E & FN Spon; 1997. p. 193–200.

[4] Crammond NJ, Halliwell MA. The thaumasite form of sulfate attack in concretes containing a source of carbonate ions. In: 2nd Symposium Advances in Concrete Technology ACI SP 154-19, 1995, p. 357–80.

[5] Rogers C, Thomas M, Lohse H. Thaumasite from Manitoba and Ontario, Canada. In: Proceedings of 19th ICMA, 1997, p. 306–19.

[6] Ludwig U, Meher S. Destruction of historical building by the formation of ettringite and thaumasite. In: Proceedings of 8th International Congress on the Chemistry of cement, Rio de Janeiro, vol. V, 1986, p. 181–8.

[7] Hartshorn SA, Sharp JH, Swamy RN. Thaumasite formation in Portland-limestone cement pastes. Cem Concr Res 1999; 29(8): 1331–40.

[8] Barker AP, Hobbs DW. Performance of limestone cements in mortar prisms immersed in sulfate solution at 5 °C. Cem Concr Comp 1999;21(2):129–37.

[9] Sahu S, Badger S, Thaulow N. Evidence of thaumasite formation in Southern California concrete. Cem Concr Comp 2002;24:379–84.

[10] Jakobsen UH, Laugesen P, Thaulow N. Determination of water–cement ratio in hardened concrete by optical microscopy, ACI, SP-191, 2000, p. 27–42.

[11] Thaulow N, Lee RJ, Wagner K, Sahu S. Effect of calcium hydroxide content on the form, extent, and significance of carbonation. In: J Skalny, J Gebauer, I Older (Eds.), Materials Science of Concrete, Special volume, Calcium Hydroxide in Concrete. American Ceramic Society; 2001. p. 191–202.

[12] Hunter D. Lime induced heave in sulfate bearing clay soils. J Geotech Eng 1988;114(2):150–67.

[13] Lukas W. Betonzerstörung durch SO3-angriff unter bildung von thaumasit und woodfordit. Cem Concr Res 1975;5:503–18.

[14] Barnett SJ, Adam CD, Jackson ARW. Solid solutions between ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ and thaumasite, $Ca_3SiSO_4CO_3(OH)_6 \cdot 12H_2O$. J Mater Sci 2000;35:4109–14.

[15] Bensted J. Thaumasite—background and nature in deterioration of cements, mortars and concretes. Cem Concr Comp 1999;21(2):117–21.