

Thaumasite Formation in a Newly Built Concrete Structure in Northeastern Algeria

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Abstract: Severe damages such as expansion, cracking, spalling, have been observed in a public facility (communal library) recently built in the northeastern region of Algeria. Microstructural examination of the concrete samples extracted from different structural elements revealed an abundant presence of thaumasite in association with ettringite and/or gypsum. The thaumasite was found within cavities at the interfaces aggregates/cement as well as in the high dolomitic cement matrix. The deterioration of the concrete studied was attributed to the thaumasite sulphate attack (TSA) supported by the alkali dolomite reaction (ADR). With regard to the semi-arid nature of Algerian climate, it appears that the condition of low temperature (less than 5 °C) required for the formation of thaumasite reported in the literature seems to be not necessarily true.

Keywords: concrete, expansion, sulfate, thaumasite.

I. Introduction

The durability and serviceability of concrete structures is known influenced by sulfate attack. The formation of thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$), ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has been recognized for many years in laboratory studies, [1, 2]. However, only a few cases of sulfate attack involving the formation of thaumasite have been discovered in site concrete structure [3-7]. Different theories about the formation mechanisms of thaumasite have been published, [1, 8]. It is widely discussed whether it forms at the expense of C-S-H or by nucleation from ettringite. As far as we know, ettringite is a normal product of cement hydration and the thaumasite form of sulfate attack always starts with the formation of small quantities of thaumasite, which may gradually develop into large deposits. The nature of the crystal structure of thaumasite is still a subject of controversy with respect to the coordination number of the Si in thaumasite. According to the literature, [9-11], the conditions needed for thaumasite formation in concrete are generally believed to be the presence of calcium carbonate combined with wet conditions and low temperatures.

Nevertheless, the importance of cement composition and the role of carbonate are still unclear. It has already been reported that there are two mechanisms of thaumasite formation the ettringite conversion and the solution reaction, [1]. The formation of thaumasite requires a source of calcium silicate, i.e. C-S-H; sulfate, carbonate and humidity [12, 13]. Furthermore, it has been suggested in the literature that thaumasite is more stable at lower temperatures (preferably at 0 - 5 °C and certainly below approximately 10 °C) since silicon tends to adopt the octahedral co-ordination found in thaumasite more easily at lower temperatures, [14,15]. Nonetheless, thaumasite is formed also at temperatures around 20 °C and above as reported for buildings in Southern California [16] and Italy [6]. Thaumasite has indeed been extensively studied before, but mainly outside of Algeria, such as in the USA and in Europe and particularly the UK [4].

This paper reports a case of deterioration in a recently constructed public facility, where the formation of the sulfate-bearing mineral thaumasite associated with dolomitic cement matrix have been identified.

II. Case study and analyses conducted

The damaged building investigated was a public facility (communal library) constructed using reinforced concrete, Fig 1. This structure was built during the period 2005-2007 in an important urban area, located in north eastern part of Algeria.



Fig. 1. Damaged public facility in northeastern of Algeria,

A careful visual inspection of the structure was conducted. This investigation was completed by microscopical observations on samples extracted from the affected structural elements, in order to identify the causes of the pathology. The

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samples analyzed in this study were cored from damaged structural elements, Fig 2. Cores (with approximately 75 mm in diameter) were slabbed to prepare thin sections for scanning electron microscopy SEM/EDS analysis.

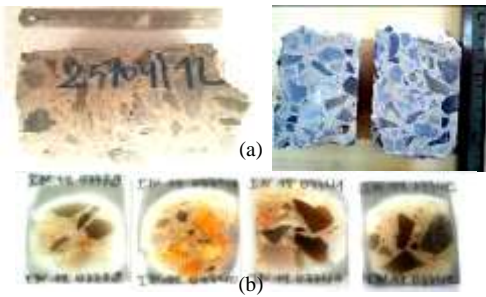


Fig. 2. a) Samples cored; b) Thin sections prepared

In order to detect the presence of eventual products resulting from chemical attack, thin sections were analyzed by means of an optical microscopy combined with SEM coupled with energy dispersive X-ray spectroscopy (EDS).

III. Results and discussion

A. Visual inspection

The visual observation conducted revealed various damages such as expansion, cracks, spalling etc., affecting the concrete and mortar, as shown by the Fig. 3 (a, b, c and d) below. These damages include sub-parallel cracks filled with white haloes occurring around aggregate pieces and sometimes cement paste matrix transformed into a mush. The observed damage phenomena have attributed to the sulfate attack associated with the alkali dolomite reaction.



Fig. 3. Damages observed in situ: a) cracks and large expansion of mortar; b) concrete spalling with white coating; c) expansion of concrete and materials loss; d) concrete transformed into mush

B. Analysis and discussions

The microscopic observation on thin sections showed large pores and voids abundantly distributed in the dolomitic paste, Fig 4 (a and b). Petrographic analyses of the thin sections revealed clearly the thaumasite deposits present in association with gypsum and ettringite. The thaumasite bands were concentrated in isolated areas of the cement paste and the paste-aggregate transition zone. Some of them passed through the siliceous aggregate particles. The source of carbonate for thaumasite formation was probably calcite due to the carbonation of the cement paste or carbonate ions in the ground water and certainly the very low carbonate aggregate.

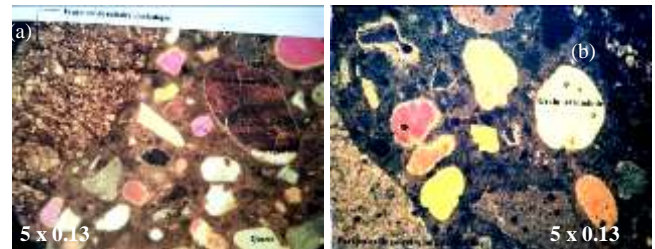


Fig. 4. Dolomitic cement matrix contain thaumasite deposits present in association with gypsum and ettringite

The Fig. 5 illustrates an SEM micrograph of the concrete, in which there are large amounts of needle-like crystals. According to the traditional theory of sulfate attack in cementitious materials, the needle-like crystals should be ettringite associated with gypsum.

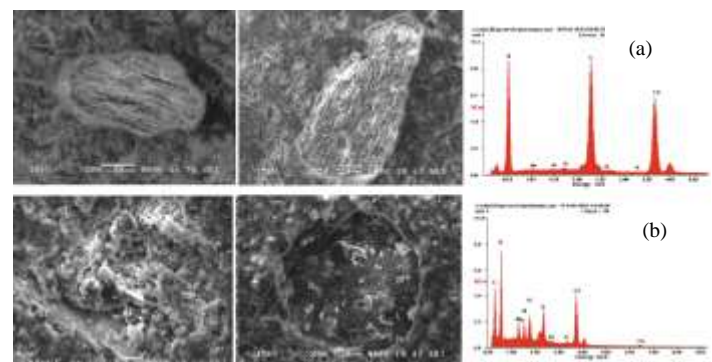


Fig. 5. SEM photograph of ettringite and thaumasite formation on the concrete communal library structure; (a) abundance presence of gypsum; (b) the EDS spectrum shows that the height peaks for Si, S, Ca and Al, typical for thaumasite presence

However, it should be noted that the ettringite crystals normally should contain Al^{3+} in it, but the EDS analysis conducted showed that the product includes also Ca, S and Si, and Al. Therefore, the crystals are not expected only to be ettringite. In our case, beside ettringite, gypsum was also observed, as shown in Fig 5. This could explain the high concentration of sulfate solutions in the sample analyzed, [20]. In the micro-observations, gypsum was formed initially since

the formation of thaumasite was kinetically very slow. Gypsum acted as a source of sulfate for the precipitation of additional thaumasite. This mineral was found to be the last phase forming during sulfate interaction [21-23].

With regard to the obtained results of micro-analytical investigations and examination of the deterioration features, it seemed possible that the thaumasite in concrete structure was formed both by the routes of solution reaction and ettringite conversion. On the one hand, it is thought that the $\text{Ca}(\text{OH})_2$ in concrete reacted with SO_4^{2-} to produce gypsum which reacted in its turn with CaCO_3 and C-S-H to form thaumasite. On the other hand, due to the C3S, a content of the Portland cement, the formation of secondary ettringite was expected to be possible, [22, 23]. This could be yielded by the expansions and deterioration of the structure material. Furthermore, the ettringite could be transformed to thaumasite by the “indirect” route.

Results of scanning electron microscopy (SEM) and Energy Disperse X-ray (EDX) are supported by the analysis of the concrete composition and the geotechnical conditions of the site soil, where the library was funded. Indeed, in addition to the salts contained in the foundation soil, it was also discovered that limestone and dolomite aggregates, extracted from a career located in the vicinity of the building site, were used in the concrete composition. These two facts could explain the sulfate attacks observed [14, 22, 24, and 25].

iv. Conclusion

The microstructural analyses of concrete samples highlighted clearly thaumasite minerals associated with gypsum deposits in the highly carbonated and severe dedolomitized pastes, as well as at the interface around aggregate grains. The formation of this thaumasite has led to the complete destruction of the cement paste and the loss of cohesiveness by transforming it into mush (consumption of the C–S–H binder). The formation of thaumasite and ettringite, could be reflected by several form of damages including expansion, cracking, spalling, loss of strength and adhesion, as observed in this case study. The observed symptoms (thaumasite, ettringite and gypsum) were found consistent with concrete suffering from external (soil) and internal (dolomite aggregate as sources of carbonates) sulfate attack.

The admitted general notion that thaumasite formation occurs only in cold environments (less than 5 °C) seems to be not necessarily true. The case reported here showed that the thaumasite could also form in the warm climatic conditions of Algeria.

References

- [1] A. Neville, “The confused world of sulfate attack on concrete”, *Cement and Concrete Research* 34, 2004, 1275–1296
- [2] J. Bensted, M. Santhanam, M.D. Cohen, and J. Olek, “A-discussion-of-the-review-paper-Sulphate-attack-research-whither-now, by M. Santhanam, M.D. Cohen, and J. Olek”, *Cement and Concrete Research* 32, 2002, 995–1000
- [3] M. Collepardi, “Thaumasite formation and deterioration in historic buildings”, *Cement and Concrete Composites* 21, 1999, 147-154
- [4] M.A. Eden, “The laboratory investigation of concrete affected by TSA in the UK”, *Cement and Concrete Composites* 25, 2003, 847–850
- [5] V. Corinaldesi, G. Moriconi, and F. Tittarelli, “Thaumasite evidence for incorrect intervention in masonry restoration”, *Cement and Concrete Composites* 25, 2003, 1157–1160
- [6] F. Veniale, M. Setti, C. Rodriguez-Navarro, S. Lodola, W. Palestra, A. Busetto, “Thaumasite as decay product of cement mortar in brick masonry of a church near Venice”, *Cement and Concrete Composites* 25, 2003, 1123–1129
- [7] M. Floyd, M.A. Czerewko, J.C. Cripps, D.A. “Spears, Pyrite oxidation in Lower Lias Clay at concrete highway structures affected by thaumasite, Gloucestershire, UK”, *Cement and Concrete Composites* 25, 2003, 1015–1024
- [8] Th. Schmidt, “Sulfate attack and the role of internal carbonate on the formation of thaumasite”, these N° 3853 (2007). Federal Polytechnic School of Lausanne, Suisse 2007.
- [9] E. Ciliberto, S. Ioppolo, and F. Manuella, “Ettringite and thaumasite: A chemical route or their removal from cementitious artefacts”, *Journal of Cultural Heritage* 9, 2008, 30-37
- [10] E.F. Irassar, V.L. Bonavetti, M.A. Trezza, and M.A. Gonz Alez, “Thaumasite formation in limestone filler cements exposed to sodium sulphate solution at 20 °C”, *Cement and Concrete Composites* 27, 2005, 77–84
- [11] D. Heinz, L. Urbonas, “About thaumasite formation in Portland limestone cement pastes and mortars effect of heat treatment at 95 °C and storage at 5 °C”, *Cement and Concrete Composites* 25, 2003, 961–967
- [12] P. Hagelia, R.G. Sibbick, “Thaumasite sulfate attack, popcorn calcite deposition and acid attack in concrete stored at the «Blindtarmen» test site Oslo, from 1952 to 1982”, *Materials Characterization* 60, 2009, 686– 699
- [13] A. Skaropoulou, G. Kakali, S. Tsivilis, “Thaumasite form of sulfate attack in limestone cement concrete-The effect of cement composition, sand type and exposure temperature”, *Construction and Building Materials* 36, 2012, 527-533
- [14] S.J. Barnett, M.A. Halliwell, N.J. Crammond, C.D. Adam, A.R.W. Jackson, “Study of thaumasite and ettringite phases formed in sulfateblast furnace slag slurries using XRD full pattern fitting”, *Cement & Concrete Composites* 24, 2002, 339–346
- [15] R.G. Sibbick, N.J. Crammond, and D. Metcalf, “The microscopical characterisation of thaumasite”, *Cement & Concrete Composites* 25, 2003, 831–837

- [16] S. Sahu, S. Badger, N. Thaulow, “Evidence of thaumasite formation in southern California concrete”, *Cement and Concrete Composites* 24, 2009, 379–384
- [17] S.A. Hartshorn, J.H. Sharp, and R. N. Swamy, “The thaumasite form of sulfate attack in Portland limestone cement mortars stored in magnesium sulfate solution”, *Cement and Concrete Composites* 24, 2002, 351–359
- [18] W. Brown, “Thaumasite formation and other forms of sulfate attack”, *Cement and Concrete Composites* 24, 2002, 301–303
- [19] T. Sibbick, D. Fenn, and N. Crammond, “The occurrence of thaumasite in modern construction a review”, *Cement and Concrete Composites* 25, 2003, 1059–1066
- [20] I. Sims, and S.A. Huntley, “The thaumasite form of sulfate attack breaking the rules”, *Cement and Concrete Composites* 26, 2004 837–844
- [21] J. Bensted, “Thaumasite background and nature in deterioration of cements, mortars and concretes”, *Cement and Concrete Composites* 21, 1999, 117-121
- [22] S. Sahu, D.L. Exline, and M.P. Nelson, “Identification of thaumasite in concrete by Raman chemical imaging”, *Cement and Concrete Composites* 24, 2002, 347–350
- [23] Linglin Xu, Peiming Wang, Guofang Zhan, “Formation of ettringite in Portland cement/calcium aluminate cement/calcium sulfate ternary system hydrates at lower temperatures”, *Construction and Building Materials* 31, 2012, 347-352
- [24] E.F. Irassar, V.L. Bonavetti, M. GonzaLez, “Microstructural study of sulfate attack on ordinary and limestone Portland cements at ambient temperature”, *Cement and Concrete Research* 33, 2003, 31-41
- [25] J. Bensted, “Thaumasite-direct, woodfordite and other possible formation routes”, *Cement and Concrete Composites* 25, 2003 873–877.