

THAUMASITE NON-SULPHATE ATTACK AT AMBIENT TEMPERATURE AND PRESSURE

Barbara SŁOMKA-SŁUPIK ^{a*}, Adam ZYBURA ^b

^a Assistant Prof., PhD; Faculty of Civil Engineering, Silesian University of Technology, Akademicka 5, 44-100 Gliwice, Poland

*E-mail address: *barbara.slomka-slupik@polsl.pl*

^b Prof.; Faculty of Civil Engineering, Silesian University of Technology, Akademicka 5, 44-100 Gliwice, Poland

Received: 25.06.2017; Revised: 10.08.2017; Accepted: 14.09.2017

Abstract

One of the products of concrete sulphate corrosion, besides gypsum and ettringite, is thaumasite. The thaumasite is a very dangerous, non binding crystalline phase, which is forming at the expense of C-S-H phase. There was a conviction that the conditions required for the formation of thaumasite in concrete are: source of calcium silicate, sulfate ions, carbonate ions and a very wet, cold (below 15°C) environment. The corrosion of concrete caused by the external source of sulphate ions during which thaumasite is formed was called thaumasite sulphate attack (shortly TSA). While the TSA is recognized, the thaumasite non-sulphate attack (T n S A) must be highlighted, because is also possible. The purpose of this work is to show that thaumasite, or solid solutions of Ett-Th (ettringite with thaumasite) are able to form in hardened cement paste without external source of sulphate ions, at ambient temperature and pressure ($25 \pm 2^\circ\text{C}$ (298.15 K) and 102 ± 1 kPa). The experiment appeared on thaumasite formation in corroded specimen made of CEM I (Portland cement) and of CEM III (slag cement) after 4 days of immersion in saturated water solution of NH_4Cl .

Streszczenie

Jednym z produktów korozji siarczanowej betonu, obok gipsu i ettringitu jest thaumasyt. Thaumasyt jest bardzo niebezpieczną, niewiążącą krystaliczną fazą, która powstaje kosztem fazy C-S-H. Uważa się, że warunkiem utworzenia thaumasytu w betonie jest działanie na krzemian wapnia jonów siarczanowych i węglanowych w bardzo wilgotnym i chłodnym środowisku (poniżej 15°C). Mechanizmy i skutki thaumasytowej korozji siarczanowej betonu spowodowanej zewnętrznym źródłem siarczanów (w angielskim skrócie TSA) są dobrze rozpoznane. Jednak thaumasytowa korozja betonu może być wywołana także wewnętrznym źródłem siarczanów (w angielskim skrócie TnSA). Ten typ korozji betonu jest w mniejszym stopniu znany. Celem tej pracy jest wykazanie, że thaumasyt lub jego roztwór stały z ettringitem (w skrócie Ett-Th) są w stanie wykrystalizować w stwardniałym zaczynie cementowym bez zewnętrznego działania jonów siarczanowych, w temperaturze otoczenia i w warunkach ciśnienia atmosferycznego ($25 \pm 2^\circ\text{C}$ (298.15 K) and 102 ± 1 kPa). Przeprowadzone badania doświadczalne potwierdziły tworzenie się thaumasytu w skorodowanych próbkach wykonanych z cementu portlandzkiego (CEM I) oraz z cementu hutniczego (CEM III) po 4 dniach immersji w nasyconym wodnym roztworze chlorku amonu (NH_4Cl).

Keywords: Ammonium chloride; Concrete corrosion; Portland cement; Slag cement; Thaumasite formation; TSA.

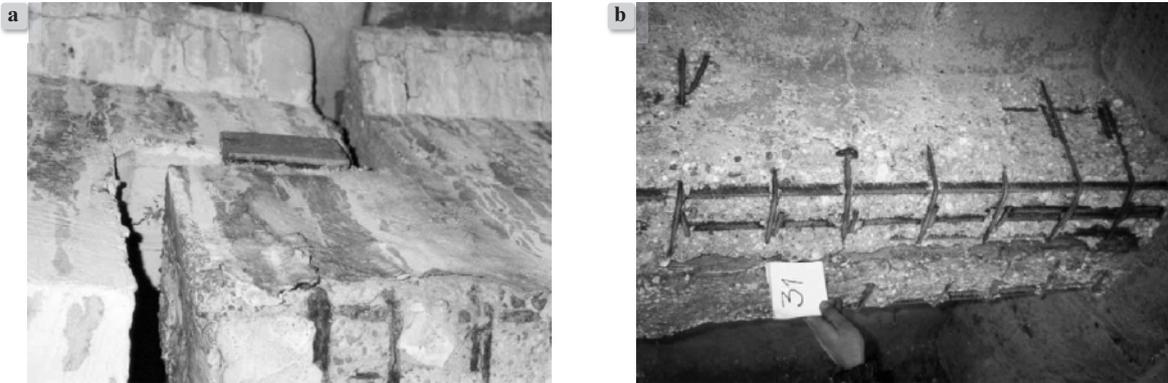


Figure 1. Corroded reinforced concrete elements from Ferenc Puskás Sports Stadium – a) mushy concrete, b) exhibited steel bars [4]

1. INTRODUCTION

In conventional sulphate attack, diffusing into concrete sulphate ions react with calcium aluminate phases and calcium hydroxide in hardened cement pastes to form either ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$) or gypsum ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$). The effects are usually expansion, cracking and spalling. Formation of thaumasite ($\text{CaSiO}_3\cdot\text{CaCO}_3\cdot\text{CaSO}_4\cdot15\text{H}_2\text{O}$) does not need aluminate phases, but necessary is the source of carbonate ions, SO_4^{2-} ions, SiO_3^{2-} and water, as well. The calcium silicate hydrates (C-S-H gel) are attacked by external sulphates. Replacement of C-S-H by thaumasite results in the softening of the cement paste matrix into a white, mushy incohesive mass, what destroys the cementitious binding ability [1, 2, 3, 4, 5]: In addition

- the strength of the concrete started to gradually and significantly decrease (Fig.1)
- the cross section of concrete construction was reduced due loss of cover with exposition of reinforcement.

Many works indicate, that the formation of thaumasite prefers wet and cold conditions. This kind of corrosion appeared mainly in buried construction, where groundwaters containing dissolved sulphates can lead to chemical attack on concrete. It was observed in concrete foundations, columns, pillars, tunnels, slabs of foundations of buildings, sewer pipes, road pavements, drainage construction, concrete anchors, in a grout in a mine, in the base of slab-on-grade pavement, in historical buildings, water dams [2, 3, 5, 6, 7, 8]. For example, the structural concrete of the largest Hungarian Ferenc Puskás Sports Stadium in Budapest suffered significant damages due to carbonation and sulphation causing thaumasite crystallization. This construction was under the

effect of waste gases from the nearby railway station and rubber plant [4] – Fig. 1. But, the thaumasite form of sulphate attack have come to light on the M5 motorway in Gloucestershire, UK [2, 5, 6, 9]. Moreover, the first case of thaumasite occurrence in concrete products in the United States were identified in the 1960s [8].

During microscopic observation, thaumasite easily can be confused with ettringite. Morphologically, both appear as needle-like and sometimes columnar crystals and can overgrowth with each other. Also the X-ray diffraction patterns of both phases are quite similar. The main peak of ettringite is by the angle of $9.091^\circ 2\theta(\text{Cu})K\alpha$, and the main peak of thaumasite is by the angle of $9.242^\circ 2\theta(\text{Cu})K\alpha$ [1, 8, 10, 11, 12].

Examinations presented in this work are not concerning conventional sulphate corrosion. During decalcification caused by ammonium chloride penetrated into cement paste and its reactions with hydrated phases, pH of cement matrix was lowered. Due pH changes, stability of different pristine and not pristine hydrated cement phases was disturbed, some of them started to dissolve, and other started to crystallize, depending on substrate accessibility [13, 14, 15]. Portlandite, as the first one, starts to react with ammonium and chloride ions and releases calcium free ions necessary to reactions in further transformations of phases. The formation of thaumasite needs also source of carbonate which can be supplied from the limestone contained in the cement, from carbonate contained in aggregates, ground waters, soils or the air, from monocarbonate ($\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot11\text{H}_2\text{O}$) or calcite. According to Schmidt et. al. [16], thaumasite is forming from pH 12.5 and is leaching at low pH levels, below 8.0. Then gypsum became the dominant sulphate phase and the amount of thaumasite is decreasing.

Table 1.
Chemical and phase composition of cements, mass %

cement	component												
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	K ₂ O	Na ₂ O	MgO	C ₃ A	C ₄ AF	C ₃ S	slag	
B: CEM I 42.5 R	62.63	19.03	5.60	2.89	3.14	0.98	0.16	-	10.0	8.8	59.56	-	
C: CEM III/A 32.5 N-LH/HSR/NA	51.95	27.87	5.55	1.63	2.56	0.71	-	4.21	5	4	30	50	

The purpose of this work was to highlight thaumasite formation in hydrated cement paste in non-sulphate-bearing environment – in saturated water solution of NH₄Cl, after very short, because 4 days, of immersion in normal (temperature and pressure) conditions.

2. MATERIALS AND METHODS

The samples made of cement paste, which is the most reactive component of concrete, were used for experiments. Samples were separately produced from two industrial cements. The first one was CEM I 42.5R (Portland cement), and two specimens named “B” was made from it. Also 2 specimens from slag cement CEM III/A 32.5 N-LH/HSR/NA with low heat of hydration, marked as “C”, prepared. Both with w/c = 0.4. Chemical compositions of cements and theirs phases composition, according to Bogue’s method, are presented in Tab. 1.

The paste samples of dimensions 60×250×250 mm were cured for 2 weeks in moulds, in laboratory conditions, and after demoulding – 3 months in lime-saturated water, in temperature 20±2°C. Afterwards one sample of each cement: B and C, was immersed in saturated water solution of ammonium chloride, of pH equal to 5. To keep on constant level the concentration of NH₄Cl in the solution, the salt addition was in excess to saturation and remained undissolved on the bottom of the container, in which the samples were immersed. Hydrated cement samples were taken away from the solution after 4 days and designated as B-4 and C-4. Reference samples (B-0 and C-0) were also prepared. They were cured during 3 months in saturated solution of Ca(OH)₂ to avoid leaching effects. Before examination, samples were dried in laboratory conditions – in air, during 2 days. The changes of phases content with reference to the pH and microstructure are discussed in this article. For this purpose specimens to examination under SEM and XRD were collected as fractures, polished sections and powders. Fractures were used to determine corrosion fronts, roughly, and to microscopic observations with a Zeiss Supra 25 high-resolution

scanning electron microscope with smartSEM and Leo32 software. Several specimens were collected by abrasion from consecutive layers of thickness: 0.5; 1.0; 1.5 or 2.0 mm with known distance from external surface of suitable sample. Powder specimens were stored in hermetically closed glass containers. Granulation of powder samples was in correct range for X-ray analysis: 2–10 µm. X-ray patterns were collected using Cu-Kα radiation (45 kV, 35 mA) with PANalytical X’PERT PRO MPD diffractometer. For peaks identification, the HighScore software package of the PANalytical and PDF4+(2008) ICDD database was used. In order to investigate the changes of contents of main phases in the consecutive layers collected from the outer surfaces of samples, the intensity of strongest peaks was measured. In addition, after one minute from mixing of powder with distilled water (in mass relation: p/w = 1/100), the pH measurement was also carried out using an pH electrode for wastewater.

3. RESULTS AND DISCUSSION

In Fig. 2 presented the XRD patterns illustrating crystalline phases changes of samples exposed to the NH₄Cl attack (B-4 and C-4) together with the reference (B-0 and C-0) samples. The localization of particular layers of powdered paste are indicated, as well. In Tab. 2 compiled the presence of phases in various layers.

Portlandite started to dissolved in external layers. At his expense arose ettringite, thaumasite and vaterite. Gypsum crystallized due ettringite, thaumasite and theirs solid solution (SS) decomposition. Calcite in both samples was present everywhere. Even vaterite occurred in the external layers, probably because of carbonation reaction of atmospheric CO₂ with calcium ions diffusing from decalcified internal parts of samples, or because of thaumasite dissolution.

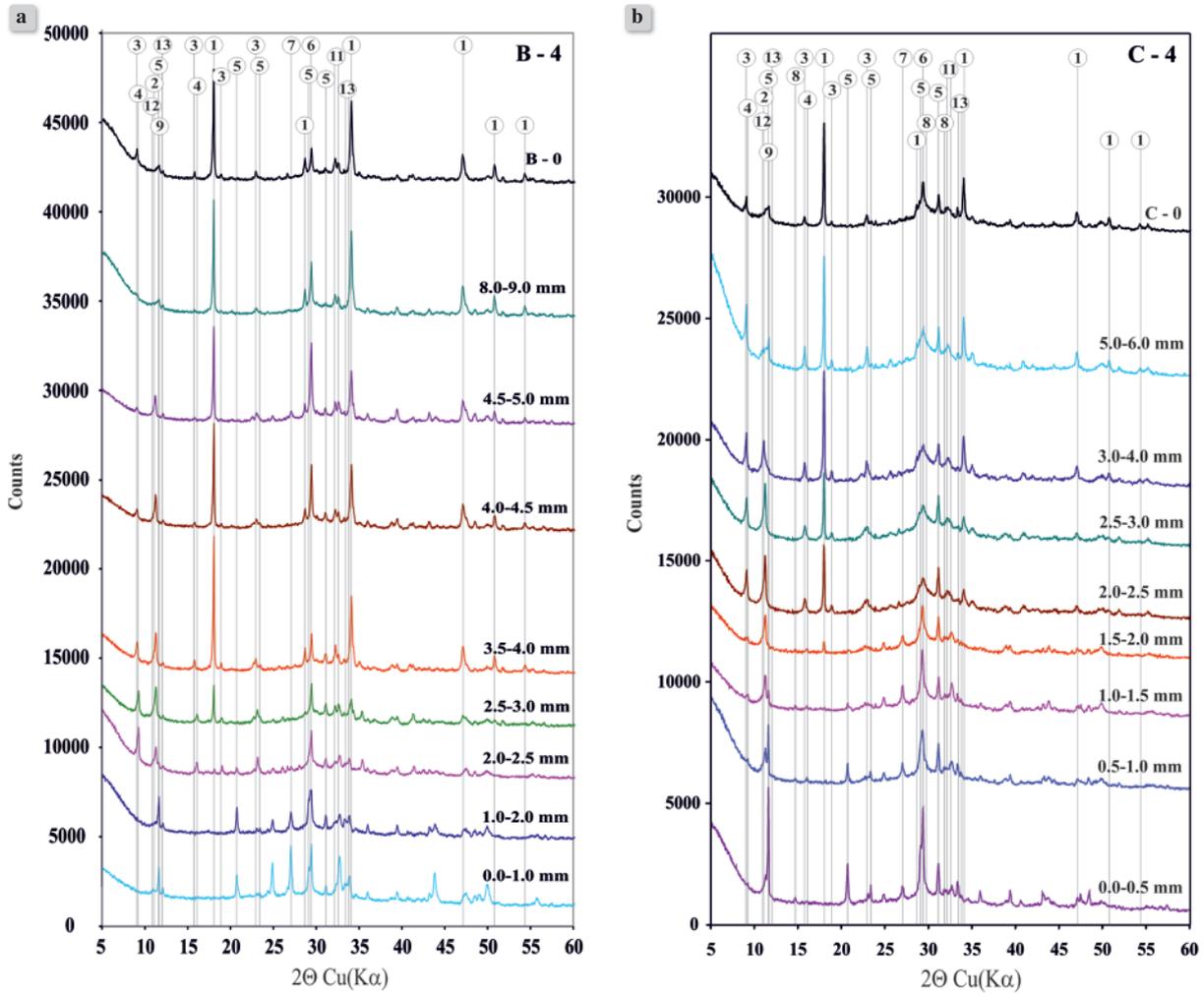


Figure 2. The diffraction patterns of hardened cement pastes: corroded and comparison a) B-0, B-4 and b) C-0, C-4. Notation: 1 – portlandite, 2- Friedel’s salt, 3 – ettringite, 4 – thaumasite, 5 – gypsum, 6 – calcite, 7 – vaterite, 8 – bassanite, 9 – carboaluminate, 11 – belite, 12 – calcium aluminate, 13 – brownmillerite

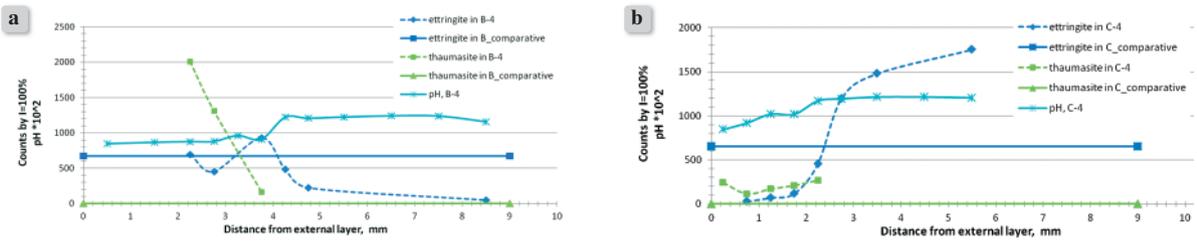


Figure 3. The comparison of pH, thaumasite and ettringite content in: a) B-4 and b) C-4 specimen as a number of counts by the peaks of the highest intensity, based on XRD patterns

In corroded specimen made of CEM I (B-4) thaumasite was identified mainly as solid solution with ettringite in layers at the depth of 2.0 to 4.0 mm from external surface of the specimen, while in C-4 (cor-

roded specimen made of CEM III) thaumasite was found as a separate phase (in layers from 0 to 2.5 mm) and in solid solution with ettringite (in layers from 1.0 to 1.5 mm), as well – Tab. 2. The thaumasite

Table 2.
Selected phases identified in the layers of the B-4 and C-4 specimens

specimens	Depth [mm]	Phases					pH	
		Gypsum CaSO ₄ ·2H ₂ O	Thaumasite	Thaumasite-SS-Ettringite	Ettringite	Vaterite CaCO ₃		Portlandite Ca(OH) ₂
B-4	0.0 – 1.0	+				+	8.48	
	1.0 – 2.0	+				+	8.68	
	2.0 – 2.5	+	+	+	traces	+	8.78	
	2.5 – 3.0		+	+	traces		+	8.81
	3.5 – 4.0			+			+	9.12
	4.0 – 4.5				+		+	12.21
	4.5 – 5.0				+		+	12.08
	8.0 – 9.0				+		+	11.58
C-4	0.0 – 0.5	+	traces			+	8.45	
	0.5 – 1.0	+	traces		traces	+	9.20	
	1.0 – 1.5	+	+	traces		+	10.20	
	1.5 – 2.0	+	+		+		10.19	
	2.0 – 2.5	traces	+		+		traces	11.70
	2.5 – 3.0				+		+	11.93
	3.0 – 4.0				+		+	12.13
	5.0 – 6.0				+		+	12.05

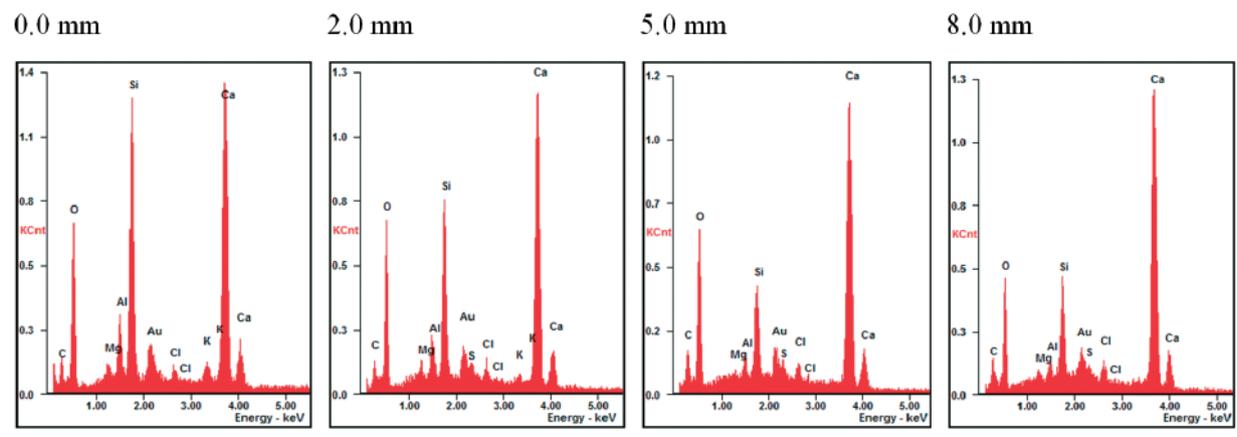


Figure 4.
X-ray microanalysis of the fracture at a certain distance from the surface of B-4 sample

dissolution, during pH lowering, is accompanied with the release of carbonate ions. Carbonate ions formed calcite with the free calcium ions derived from phases decalcification, also thaumasite. The changes in the amount of ettringite and thaumasite, compared to pH values showed in Fig. 3.

After portlandite dissolution, calcium ions released from the subsequent phases, to maintain the balance of calcium content in liquid pore solution and in the solid phase, acc. to Carde and François [17]. Finally, the C-S-H phase dissolution occurred, because the Ca/Si ratio in solid phase also depends on the calcium ions concentration in pore solution remaining in equilibrium with this phase. On the basis of the dis-

continuity in this molar ratio, three kinds of C-S-H phases can be distinguished [18, 19]. The results of changes in the content of particular elements in C-S-H phase, presented in Fig. 4., show the relation: as the distance from the B-4 sample surface increased, the ratio of Ca/Si also increased. This is the evidence of C-S-H decalcification in the external layers after 4 days of NH₄Cl water solution action.

By carrying out a chemical analysis of the micro-area of a crystallized phase located at a distance of 2.2 mm from the surface of the B-4, the presence of thaumasite in solid solution with ettringite has been confirmed – Fig. 5.

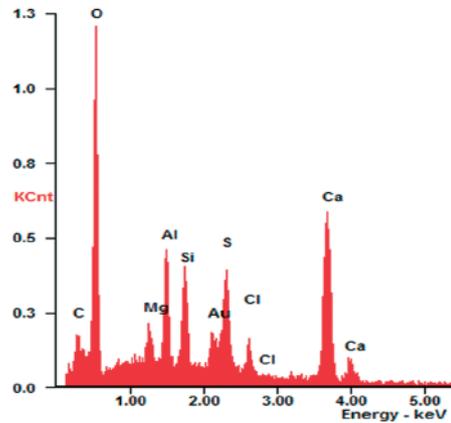
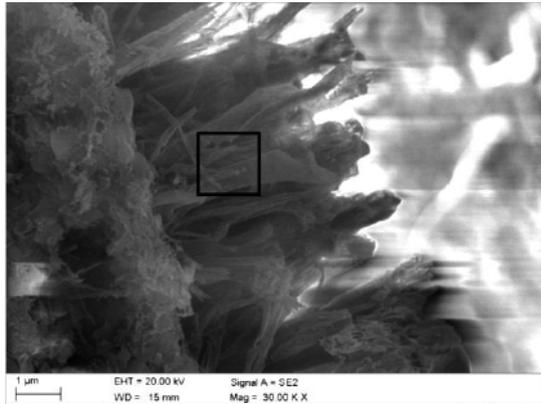


Figure 5. Solid solution of thaumasite with ettringite in a pore in the depth of 2200 μm from external layer of B-4 sample with X-ray microanalysis in selected area

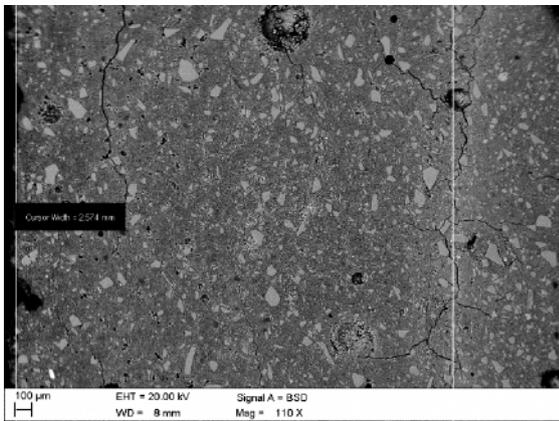


Figure 6. SEM-BSE image of the microstructure of C-4 sample near external layer, with the microcracks at 2570 μm and 500 μm depth

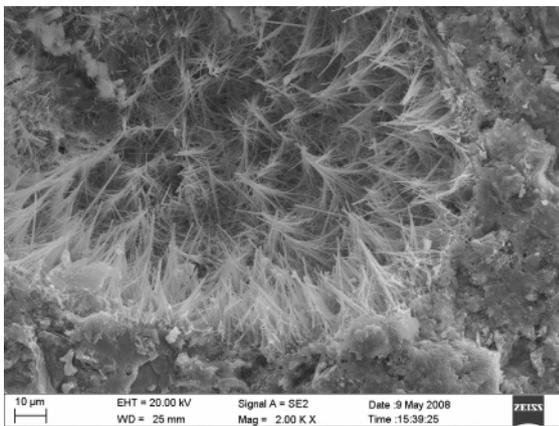


Figure 7. Gypsum crystals on the pore wall. Sample C-4, x = 500 μm

In Fig. 6 is shown the SEM-BSE image of the polished section of C-4 specimen with measured distance from external surface to the microcrack equal to 2.57 mm. There is a suspicion that occurred microcrack is the boundary between external zone – rich and internal zone – lack of thaumasite. At this depth also a boundary of ettringite amount appeared, above and under its comparative line. Ettringite formation can lead to increase in the volume of reaction products from 0.48 to 2.83 times even – during formation from tricalcium aluminate and portlandite [20], what probably caused crack at this depth, as well.

From sulphate ions releasing during thaumasite dissolution, gypsum crystallized. It was observed at a small depth of 0.5 mm from the external surface of C-4 sample, on the pore wall in form of needle-like crystallites – Fig. 7. The reaction of gypsum formation from thaumasite decreases the volume of sulphate products [14], and this dependence probably caused the microcrack formation at the depth of 0.5 mm – Fig. 6.

4. CONCLUSIONS

The diffusion of aggressive ions into and pristine cement ions out of the concrete accompanied chemical reactions, which lead to dissolution and precipitation of solids or even to mechanical damage. Obtained results confirmed that ettringite is unstable, in lower pH underwent dissolution. Thaumasite and gypsum formed from released sulphate ions. Moreover, the formation of thaumasite in specimen attacked by non sulphate medium can cause an astonishment, also the way of thaumasite formation is a little surprising. It seems, thaumasite was formed from solid solution in case of Portland cement paste, but in case of slag cement paste it crystallized directly at the expense of C-S-H phase. Combination of slag with cement (to produce CEM III) extended the scope of thaumasite presence. Whereas in Portland cement sample thaumasite crystallized in a greater amount, but in smaller width of the depth. Thaumasite is stable at a certain pH range, but this is not the only important factor. As can be seen, in case of the sample B-4 (CEM I) thaumasite was noticed from 8.78–9.12 pH and in sample C-4 (CEM III) thaumasite was durable from 8.45 to 11.70 pH. Very important was also presence of portlandite, which was consumed in favor of thaumasite formation. The formation of thaumasite accompanied the drop of pH value, more significant in case of Portland cement sample after 4 days of NH_4Cl aggressive immersion.

This article has shown that thaumasite corrosion of concrete is possible even if the corrosive medium is not a sulphate salt solution, in normal conditions. Has also shown that many factors contribute to corrosion effects that need to be adequately determined prior to construction. A new term: “thaumasite non sulphate attack”, shortly **TnSA**, was introduced in this article.

REFERENCES

- [1] Bensted J. (2007). Thaumasite – part 2: origins, ramifications and discussions related to the thaumasite expert group report. *Cement-Lime-Concrete*, *XII/LXXIV*(5), 245–260.
- [2] Crammond N. J. (2003). The thaumasite form of sulfate attack in the UK. *Cement and Concrete Composites*, *25*(8), 809–818.
- [3] Małolepszy J. & Mróz R. (2006, March-April). Conditions of thaumasite formation. *Cement-Lime-Concrete*, *XI/LXXIII*, 93–101.
- [4] Révay M. & GáveI V. (2003). Thaumasite sulphate attack at the concrete structures of the Ferenc Puskás stadium in Budapest. *Cement and Concrete Composites*, *25*(8), 1151–1155.
- [5] Thaumasite Expert Group (2000). One-Year Review, Prepared by Professor L A Clark and BRE in consultation with The Thaumasite Expert Group.
- [6] Czerewko M. A., Cripps J. C., Reid J. M. & Duffell C. G. (2003). Sulfur species in geological materials – sources and quantification. *Cement and Concrete Composites*, *25*(7), 657–671.
- [7] Maingyu H., Fumei L. & Mingshu T. (2006). The thaumasite form of sulfate attack in concrete of Yongan Dam. *Cement and Concrete Research*, *36*(10), 2006–2008.
- [8] Stark D. C. (2003). Occurrence of thaumasite in deteriorated concrete. *Cement and Concrete Composites*, *25*(8), 1119–1121.
- [9] Wimpenny D. & Slater D. (2003). Evidence from the highways agency thaumasite investigation in Gloucestershire to support or contradict postulated mechanisms of thaumasite formation (TF) and thaumasite sulfate attack (TSA). *Cement and Concrete Composites*, *25*(8), 879–888.
- [10] Edge R. A. & Taylor H. F. W. (1969). Crystal structure of thaumasite, a mineral containing groups. *Nature* *224*(25), 363–364, doi:10.1038/224363a0
- [11] Nielsen P., Nicolai S., Darimont A. & Kestemont X. (2014). Influence of cement and aggregate type on thaumasite formation in concrete. *Cement and Concrete Composites*, *53*, 115–126.
- [12] Słomka-Słupik B. (2009). The changes of phases composition of the paste from cement CEM III/A under the influence of NH_4Cl water solution. *Cement-Lime-Concrete*, *XIII/LXXV*(2), 61–66.
- [13] Biczók I. (1972). Concrete corrosion. Concrete protection, Akadémiai Kiadó, Budapest.
- [14] Słomka-Słupik B. & Zybura A. (2010). Microstructure of decalcified cement paste. *Cement-Lime-Concrete*, *15*(6), 333–339.

- [15] Słomka-Słupik B. & Zybura A. (2015). Corrosion of hardened cement paste in concrete used for building coke wastewater treatment plant tanks. *Pol. J. Environ. Stud.*, 24(3), 1309–1316.
- [16] Schmidt T., Lothenbach B., Romer M., Scrivener K., Rentsch D. & Figi R. (2008). A thermodynamic and experimental study of the conditions of thaumasite formation. *Cement and Concrete Research*, 38, 337–349.
- [17] Carde C. & François R. (1997). Effect of the leaching of calcium hydroxide from cement paste on mechanical and physical properties. *Cement and Concrete Research*, 27(4), 539–550.
- [18] Nonat A. (2010). C-S-H phase and concrete properties. *Cement-Lime-Concrete*, 15(6), 315–326.
- [19] Kurdowski W. (2008, July–August). C-S-H phase – state of the problem. Part 1. *Cement-Lime-Concrete*, III/LXXV, 216–222.
- [20] Sarkar S., Mahadevan S., Meeussen J.C.L., van der Sloot H. & Kosson D.S. (2010). Numerical simulation of cementitious materials degradation under external sulfate attack. *Cement and Concrete Composites*, 32(3), 241–252.