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SOME ASPECTS AND MECHANISMS OF SULPHATE ATTACK

Abstract

Consideration of the concrete durability should take into account sulphate attack which may be significantly various. The destruction of concrete under sulphate attack is particularly related to expansion, however, the dissolution of cement matrix may by considerable. The way of destruction is dependent on the type of salt, its cation and solution pH. The most reactive phases of cement paste are alumunoferrite hydrate phases (AFm) and calcium hydroxide. The expansion is directly connected with formation of gypsum and ettringite. The ultimate product of total destruction of concrete is gypsum. Mechanism of sulphate attack is a subject of discussion and hypotheses. The test results of expansion of mortar immersed in 5% Na_2SO_4 and SEM analysis indicate that ettrinite formed in air pores may not affect the value of the expansion. Ettringite formation inside small pores of the microstructure (eg C-S-H) can cause expansive force and destruction of mortars.

Keywords: sulphate attack, cement paste, mortar, SEM, air entrainment, ettringit

1. Introduction

In order to properly design a concrete structure, it is necessary to take into account the properties of the concrete not only related to conditions of safety – described by the ultimate limit states, which confines itself primarily to the strength of concrete. A durable structure shall meet the requirements of serviceability, strength and stability throughout its design working life, without significant loss of utility or excessive unforeseen maintenance [1]. In the standard PN-EN 206-1, the durability of concrete is defined by exposure class. The strictest requirements are connected with XA3 exposure class. For this class, strength class for concrete not less than C35/45 and w/c ratio not bigger than 0.45 are required. The use of no less than 360 kg/m³ of high sulphate resistant cement (HSR) is also recommended. Thus, the most severe conditions under sulphate attack can be considered.

Factors influencing the durability of the structure can be physical, chemical or mechanical. Mechanical destructions are caused by impact, abrasion, erosion or cavitations. Physical destruction results from effects of high temperatures or the effects associated with differences in thermal expansion of aggregate and hardened cement paste. A special type of destruction of concrete is caused by thawing and freezing cycles. As a result of this kind of destruction internal cracks and surface scaling which is related with the chloride ions occur. Chemical destruction occurs mostly in the interaction of aggressive ions (chlorides, sulphates, or carbon dioxide) as well as various gases and liquids of natural or industrial origin.

The reasons for destruction of concrete are usually complex and occur simultaneously. There are three basic types of destruction of concrete in aggressive environments: dissolution of cement matrix, the formation of non-binding phase and expansion. The process of dissolution and leaching of cement paste components results in slackening of its microstructure. Expansive reactions cause fracture connected with the increase in volume of product in comparison with substrates volume.

A special case of the concrete destruction is sulphate corrosion, which is primarily classified to

the destruction of the expansion. However, the nature of destruction depends on the cation associated with sulphate anions as well [2]. The severity of destruction depends on the solubility of various sulphates and pH of their solutions. Usually it is important to consider hydroxide of the sulphate salt [3].

2. Types of sulphate attack

2.1. Calcium sulphate

Low reactivity of calcium sulfate results from its low solubility (0.23 g/100 gH_2O) and very slight acidity (pH = 6.6 at a concentration of 0.01 mol/dm³). This sulphate is practically neutral. Moreover, this salt has a calcium cation which is common to all phases present in the cement paste. That is why the calcium sulphate attack is an example of chemical synthesis of ettringite i.e. "pure" sulphate attack without cation exchange reaction. The reaction of calcium sulphate is practically only connected with the formation of ettringite from monophases of calcium alumunoferrite hydrates (AFm). Portlandite takes part in the reaction (reaction (1) and (2)) as well. However, it does not react directly alone with calcium sulphate solution.

$$C_3A \cdot CaSO_4 \cdot 12H_2O + 2CaSO_4 + {} \atop + 20H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O \qquad (1)$$

$$C_3A \cdot Ca(OH)_2 \cdot 12H_2O + 3CaSO_4 + {} \atop + 20H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O + Ca(OH)_2 \qquad (2)$$
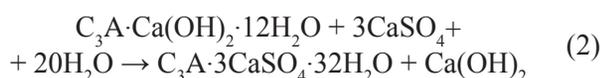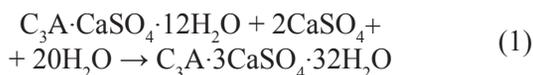
In practical terms it should be noted that in this way the internal sulphate attack on concrete also undergoes when gypsum is present in aggregate.

2.2. Sodium sulphate

The solubility of sodium sulphate (for $Na_2SO_4 \cdot 10H_2O$: 44 g/100 gH_2O) is much higher than that of calcium sulphate. Therefore, sodium sulphate attack on concrete is much more severe. However, sodium sulfate as a salt of a strong base has a relatively high pH (pH = 7.7 at a concentration of 1 mol/dm³). Formation of gypsum from portlandite under attack of Na_2SO_4 is an exchange reaction (3). It results in the formation of calcium sulfate which precipitates and crystallizes in cement paste microstructure contributing to expansion. The sodium hydroxide is a by-product of the reaction.

$$Ca(OH)_2 + Na_2SO_4 \cdot H_2O \rightarrow {} \atop \rightarrow CaSO_4 \cdot H_2O\downarrow + 2NaOH \qquad (3)$$
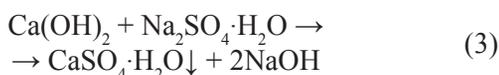
Due to formation of hydroxide NaOH the relatively high pH is maintained which reduces the solubility of portlandite in pore solution retarding formation of gypsum. When sulphate ions concentration increases locally close to gypsum and monosulphate (AFm) the precipitation of ettringite and expansion will follow (reactions (4) and (5)).

$$C_3A \cdot Ca(OH)_2 \cdot 12H_2O + 3Na_2SO_4 + 2Ca(OH)_2 + {} \atop + 20H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O + 6NaOH \qquad (4)$$

$$C_3A.CaSO_4.12H_2O + 2Na_2SO_4 + 2Ca(OH)_2 + {} \atop + 20H_2O \rightarrow C_3A.3CaSO_4.32H_2O + 4NaOH \qquad (5)$$
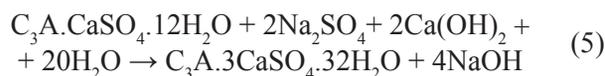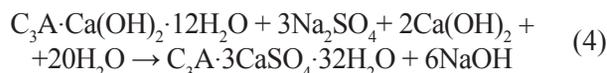
Due to occurrence of hydroxide NaOH and relatively high pH of pore solution the dissolution of ettringite is retarded. That is why a significant amount of ettringite (in comparison with gypsum) in cement paste occurs under Na_2SO_4 attack. Also the ultimate disintegration of C-S-H phase is delayed. However, numerous microcrackings occur and cracks which follow the expansion. They are a prime reason of cement paste and concrete failure usually.

2.3. Magnesium sulphate

The pH of the magnesium sulfate solution is acidic (pH = 5.7 at a concentration of 1 mol/dm³). Solubility of this salt is relatively high (30.8 g/100 gH_2O). The impact of magnesium sulfate on concrete is a double chemical attack because each of the ions SO^{2-} and Mg^{2+} forms its usual product. Therefore, magnesium sulfate attack is dangerous for cement composites. As a result of $MgSO_4$ solution influence, the main products (ettringite, gypsum) of sulphate attack and hydroxide $Mg(OH)_2$ in exchange reaction with Ca^{2+} ions (reaction (6), (7)) are formed.

$$C_3A \cdot CaSO_4 \cdot 12H_2O + 2MgSO_4 + 2Ca(OH)_2 + {} \atop + 20H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O + {} \atop + 2Mg(OH)_2\downarrow \qquad (6)$$

$$C_3A \cdot Ca(OH)_2 \cdot 12H_2O + 2Ca(OH)_2 + 3MgSO_4 + {} \atop + 20H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O + 3Mg(OH)_2\downarrow \qquad (7)$$
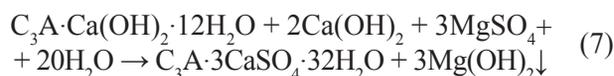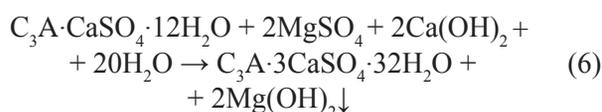
Due to the lower solubility of $Mg(OH)_2$ as compared to $MgSO_4$, magnesium hydroxide gel is precipitated in all reactions of magnesium sulphate with calcium hydroxide and other calcium phases. Gel $Mg(OH)_2$ and then brucite is formed on the sample surface or in large pores. It may affect the progress of the attack. The compact cover of brucite may retard the attack a little. However, it means that cation Mg^{2+} leaves solution lowering its pH value. Thus, the acidity of solution is sustained and it results in acceleration of calcium ions dissociation in the solution and formation of gypsum.

As a consequence, the decalcification of C-S-H phase or conversion into M-S-H phase follows, which has no binding properties (reaction (9)).

2.4. Ammonium sulphate

Ammonium sulphate solution is highly soluble salt. Its solubility is 75.4 g/100gH$_2$O. Water solution of the sulphate is acidic (pH = 4.62 at a concentration mol/dm³). Therefore, its reaction with the calcium phases are similar to the reaction of sulfuric acid and attack of sulphate salt. Ammonium sulphate attack on concrete causes overlapping dissolution process (typical for acid) and expansion (typical for a salt). Solution of $(NH_4)_2SO_4$ reacts with calcium hydroxide rather rapidly. Gypsum precipitates and ammonia is volatilized. The by-product is ammonium hydroxide which decomposes into ammonia in gaseous form. Ammonium sulphate also reacts with AFm phase and calcium hydroxide. It results in formation of ettringite and expansion of hardened cement paste follows. In all reactions between $(NH_4)_2SO_4$ and calcium phases, ammonium cations NH_4^+ leave solution. Volatilization of ammonia in gaseous form occurs as well. That is why low pH value of solution is sustained and dissociation of calcium phases is accelerated. In consequence that results in rather rapid decrease in strength and hardness of concrete. Therefore, the product observed in the cement paste under ammonium sulphate attack is primarily gypsum. Lowering of pH in pore solution and simultaneous dissociation of calcium ions affect accelerated decomposition of ettringite possibly soon after reaction.

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3(NH_4)_2SO_4 \rightarrow$$
$$\rightarrow 6(CaSO_4 \cdot 2H_2O) + 2Al(OH)_3 + 6NH_3\uparrow + 20H_2O \quad (8)$$
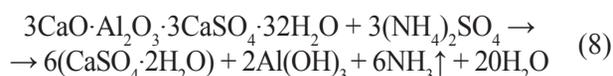
Long term attack of all sulphate solutions with exception of calcium sulphate will result in the dissociation of portlandite and formation of gypsum and decrease in pH value of pore solution in hardened cement paste. Finally the decalcification and ultimate decomposition of all cement paste phases will follow. Also the most durable C-S-H phase and ettringite formed under sulphate attack originally will be decomposed as well (reaction 9). The ultimate product of sulphate attack is gypsum alone [7].

$$3CaO \cdot 2SiO_2 \cdot 3H_2O + n[0.5Mg, Na, NH_4]SO_4 +$$
$$+ nH_2O \xrightarrow{pH} 3(CaSO_4 \cdot 2H_2O) + \quad (9)$$
$$+ n[0.5Mg, Na, NH_4]OH + 2(SiO_2 \cdot nH_2O)$$
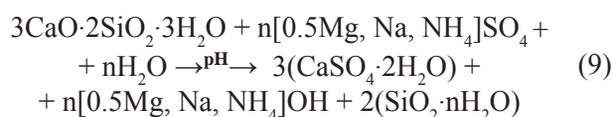
3. The mechanisms of sulphate attack

Mechanism of sulphate expansion is still a subject of numerous discussion and hypotheses. The hypothesis of Lafuma [4] deals with topochemical formation of ettringite directly on the site of AFm phase, without dissolving and precipitation reactions. Mehta [5] suggests that ettringite could absorb water and, thus, cause expansion due to swelling – this hypothesis was rejected by Brown and Taylor [1]. They stated that the crystal structure of ettringite makes it unlikely that ettringite attracted water more strongly than the phase of the C-S-H. The two most discussed concepts in recent decades say that the expansion occurs due to the additional volume generated by ettringite. However, a direct relationship between the quantities of ettringite formed and the size of the expansion has been undocumented – neither the origin of stresses which are necessary to effect expansion. Furthermore, an additional volume of ettringite and gypsum is usually smaller than the available space in the free pores. Ettringite formation seem to be a necessary condition for expansion, but it is not sufficient. Ping, Flatt, Steiger and Scherer [9] found that the expansion is caused by the crystallization pressure, due to formation of ettringite from supersaturated solution in the small pores. The theory of crystallization pressure has been explained in a detailed manner by the most recent observations of the research team from Switzerland under the leadership of Karen Scrivener [10]. She argues that the expansion does not depend on how much ettringite formed but primarily of where it has been formed. According to Scrivener's hypothesis of 2013 if gypsum and monosulphate occur locally at the same place in cement paste, and the solution is supersaturated with respect to ettringite then ettringite formation inside small pores of the microstructure (eg CSH) can cause expansive force. Also the authors [8] have observed that it is not necessary to formate of large amounts of ettringite, for occurrence of high expansion.

4. Experimental results and discussion

The changes in the microstructure of air entrained composites were presented. The air entrained and non-air entrained mortars from two various OPCs were immersed in 5% sodium sulphate solution. The longitudinal strains of mortar samples were measured to determine their expansion. Microstructure of cement mortars was examined with scanning electron microscope. The regions of ettringite formation were identified in the AE and nAE mortars and their

expansion was compared. It was checked if the ettringite crystals formed in air pores had affected the expansion of the mortars.

In the non-air entrained mortar (made of OPC containing 11.5% C_3A), there are ettringite crystals (Fig. 1), which are loosely arranged in the capillary pores but also the ones embedded in the microstructure of the C-S-H phase. Moreover, the crystals of ettringite were fairly big. This study was carried out when the mean expansion of mortar samples reached 4.6‰. It was a half of the total expansion which resulted in the ultimate destruction of mortar samples.
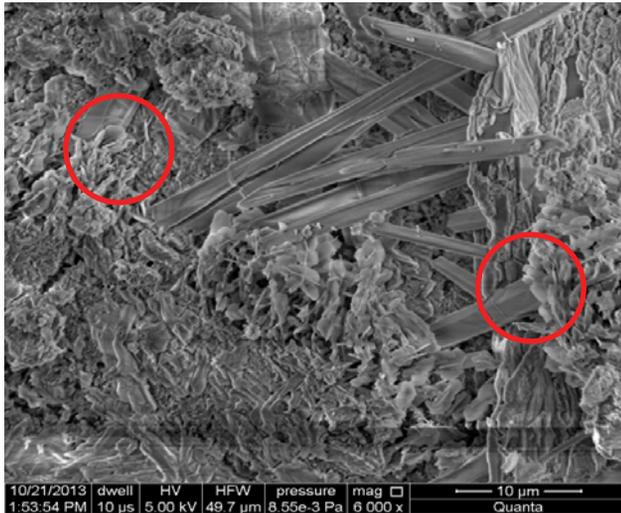
Fig. 1. Microstructure of nAE OPC mortar immersed in the solution of 5% Na_2SO_4 for 12 weeks (SEM 6000x). The mean expansion of specimen was 4.6‰. (C_3A = 11.5%)
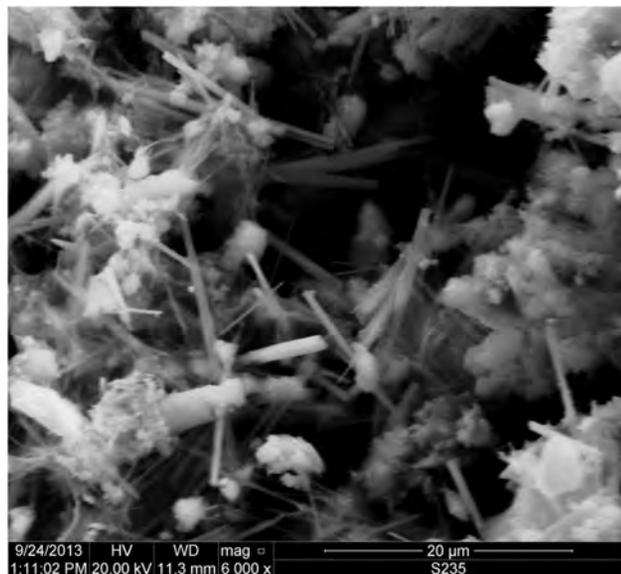
Fig. 2. Microstructure of nAE OPC mortar immersed in the solution of 5% Na_2SO_4 for 64 weeks (SEM 6000x). The mean expansion of specimen was 5.7‰. (C_3A = 6.3%)

In microstructure of non-air entrained mortar (Fig. 2) from OPC containing 6.3% C_3A, the crystals of ettringite were primarily observed in the capillary pores and slightly loose microstructure of C-S-H. The ettringite crystals were relatively small. No ettringite embedded in compact structure of C-S-H was found. The expansion of the samples proceeded slowly. The mean longitudinal strains of samples were 5.7‰. No cracks or scaling occurred on the surface of samples during testing.

The air entrained mortars (Fig. 3 and Fig. 4) were presented less enlarged (500x, 800x) than the non-ain entrained mortars because on this size entire pore and the corosion products like ettringite are shown. In air entrained mortar (made of OPC containing 11.5% C_3A) the air pores are partially filled (Fig. 3) with a fairly densely arranged big crystals of ettringite. The SEM image (500x) suggests that the individual ettringite crystals partially pass into the microstructure of cement paste surrounding air pore. The mean expansion of specimens was 8.8‰.
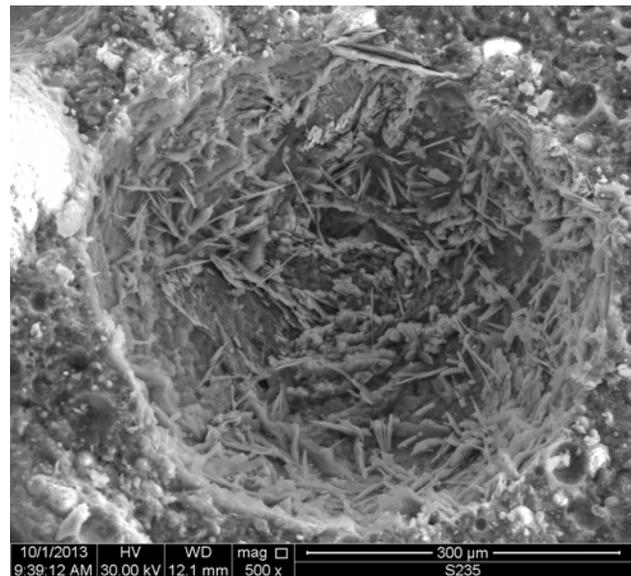
Fig. 3. Microstructure of AE OPC mortar immersed in the solution of 5% Na_2SO_4 for 12 weeks (SEM 500x). The mean expansion of specimens was 8.8‰. (C_3A = 11.5%)

The SEM analysis of air entrained mortar from OPC containing 6.3% C_3A was carried out after 64 weeks of immersion in sulphate solution, when the mean expansion was 5.9‰, and the samples were not destroyed. In some air pores, rather loosely arranged ettringite crystals were detected. They are primarily radially stuck at pore walls. In the microstructure of cement paste distant from air pores, no ettringite was detected.
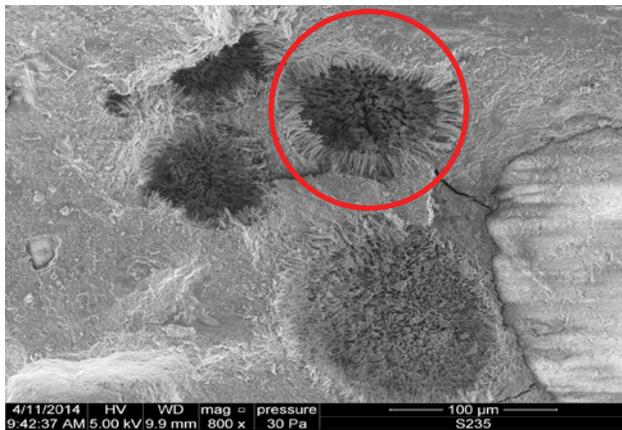
Fig. 4. Microstructure of AE OPC mortar immersed for 64 weeks in the solution of 5% Na_2SO_4 (SEM 800x). The mean expansion of specimens was 5.9‰. ($C_3A = 6.3\%$)

5. Conclusions

1. In non-air entrained mortars made of cement containing 11.5% C_3A, ettringite crystals were observed in a solid microstructure of C-S-H.
2. In non-air entrained mortars made of cement containing 6.3% C_3A, ettringite crystals were visible primarily in the loose microstructure and capillary pores.
3. In the air entrained mortars ($C_3A = 11.5\%$), ettringite crystals were visible mainly in the air pores. Individual crystals of ettringite were partially included in the microstructure of the surrounding paste. In the mortars ($C_3A = 6.3\%$) ettringite crystals were only indentified in the air pores.

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Wybrane aspekty i mechanizmy korozji siarczanowej

1. Wprowadzenie

Trwałość betonu to jego zdolność do zachowania w założonym czasie użytkowania wymaganych właściwości zapewniających bezpieczeństwo. Przyczyny niszczenia betonu są zwykle złożone i występują równocześnie lub naprzemiennie. Można wyróżnić trzy podstawowe rodzaje niszczenia betonu w środowiskach agresywnych: rozpuszczenie matrycy cementowej, powstawanie faz niemających właściwości wiążących oraz ekspansja. Proces rozpuszczania i wymywania składników zaczynu powoduje rozluźnienie jego mikrostruktury. Reakcje ekspansywne powodują pękanie w wyniku przyrostu objętości substratów. Jedną z najgroźniejszych przyczyn niszczenia kompozytów cementowych jest korozja siarczanowa.

2. Rodzaje agresji siarczanowej

W podrozdziale tym omówiono działanie siarczanu wapnia, sodu, magnezu i amonu na zaczyn cementowy. Podano rozpuszczalność i pH każdego z siarczanów. Pokazano reakcje chemiczne, według których przebiegają poszczególne agresje.

3. Mechanizm korozji siarczanowej

Mechanizm ekspansji siarczanowej jest ciągle przedmiotem wielu dyskusji i hipotez. Dwie najbardziej komentowane koncepcje w ostatnich dekadach to hipoteza Alunno-Rossetti, która mówi, że ekspansja występuje z powodu dodatkowych objętości generowanych przez ettringit oraz hipoteza Ping, Flatt, Scherer i Steiger, którzy stwierdzili, że ekspansja jest spowodowana przez ciśnienie krystalizacji, wywołane tworzeniem się ettringitu z przesyconego roztworu w małych porach. Teoria ciśnienia krystalizacji została w sposób szczegółowy wyjaśniona przez najnowsze obserwacje zespołu badawczego ze Szwajcarii pod przewodnictwem Karen Scrivener, która twierdzi, że ekspansja nie zależy od tego, jak dużo ettringitu powstaje, ale przede wszystkim od tego, gdzie on powstaje. Według hipotezy Scrivener z 2013 roku: jeżeli w zaczynie cementowym gips i monosiarczan występują lokalnie w tym samym miejscu, a roztwór jest przesycony w stosunku do ettringitu to powstawanie ettringitu wewnątrz małych porów struktury (np. C-S-H) może wywoływać siły ekspansywne.

4. Badania

W artykule przedstawiono obserwację zmian w mikrostrukturze kompozytów napowietrzonych pod kątem najnowszej hipotezy. W tym celu wykonane zostały zaprawy nienapowietrzone i napowietrzone z różnych cementów. Poddane one zostały działaniu 5% roztworu siarczanu sodu. Na próbkach prowadzono pomiary odkształceń i wykonywano badania mikrostruktury za pomocą mikroskopu skaningowego. Obserwowano miejsce powstawania ettringitu i porównywano ekspansję. Wykorzystanie zapraw napowietrzonych ma na celu sprawdzenie czy kryształy ettringitu powstają w porach powietrznych i czy ettringit tam powstający może mieć wpływ na ekspansję zaprawy.

5. Wnioski

1. W nienapowietrzonych zaprawach wykonanych z cementu zawierającego 11,5% C_3A, kryształy etryngitu były widoczne w zwartej mikrostrukturze fazy C-S-H.
2. W nienapowietrzonych zaprawach wykonanych z cementu zawierającego 6,3% C_3A, kryształy ettringitu były widoczne przede wszystkim w luźnej mikrostrukturze i kapilarnych porów.
3. W zaprawach napowietrzonych (C_3A = 11,5%), wykryto większą ilość ettringitu, który występo-

pował zarówno w porach powietrznych, jak i w mikrostrukturze zaczynu oddalonego od porów. W zaprawach (C_3A = 6,3%) kryształy ettringitu były widoczne przede wszystkim w porach powietrznych.