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## Expansive Strontium Aluminate Cements

### 1. Expansive cements

Cement hydration is a complex set of exothermic chemical reactions. Each chemical compound may react with water in different ways, each reaction has its own volume stoichiometry, and the reaction (or hydration) products may undergo the transition to different forms. There are several mechanisms by which a cement paste changes its volume (shrinks or swells) during the hydration process under sealed conditions, or without the moisture transfer from paste to the environment. The major mechanisms of total shrinkage include [12,278,673-676]:

- Hydration shrinkage;
- Self-desiccation shrinkage;
- Thermal contraction or expansion;
- Crystallization swelling;
- Shrinkage during the phase transition or expansion.

Autogenous shrinkage is a phenomenon in which cementitious materials shrink at constant temperature without any changes in weight [677]. It is well-known that the volume changes in a cement paste or concrete mentioned above may occur simultaneously. It is the overall shrinkage behaviour that controls the concrete performance [278]. Furthermore, the influence of this phenomenon on total shrinkage depends on the size of specimen [414]. Most chemical shrinkage measurements reported are often performed at short duration and suggested water to cement ratio of 0.40 as required by ASTM C 1608 [678].

Autogenous shrinkage in concrete with low water-cement ratio is the major factor that generates larger shrinkage and early cracking [673,677,679]. A small increase in the chemical shrinkage at “infinite time” was found with increasing water-cement ratio. The influence of temperature was found to be twofold: Increasing temperature caused increasing rate of the development of chemical shrinkage and the decrease of the chemical shrinkage at “infinite time” [680]. The mineral admixtures in concrete affect the concrete shrinkage in different ways. Fly ash and limestone powder can reduce the autogenous shrinkage while silica fume may lead to increased shrinkage [679,681].

At very early age and during the setting, two phenomena are directly responsible for the shrinkage of material in sealed conditions [648]:

1. Capillary depression in the porous space;
2. Le Chatelier's contraction caused by the density difference between hydrates on one hand and cement and water on the other hand.

Drying shrinkage is relatively slow process. The driving force is the loss of water from the pores due to lower humidity prevailing outside the concrete. The diffusion of water through the material depends mainly on its porous structure, on the size and shape of the specimen, on the duration of drying and on prevailing atmospheric conditions [414,682].

The shrinkage can be compensated by several compounds acting through different mechanisms, but the principle remains similar-the incidence of expansion pressure on the setting paste. It can be achieved via the formation of new crystalline phases, predominantly ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ,  $\text{C}_6\text{AS}_3\text{H}_{32}$ , AFt), swelling gel of portlandite ( $\text{Ca}(\text{OH})_2 \cdot \text{CH}$  [12,688]) or brucite ( $\text{Mg}(\text{OH})_2 \cdot \text{MH}$  [12,683-687,690]), or by the osmotic pressure generated by semi-permeable membrane of hydration products on the surface of anhydrous grains under suitable conditions.

The expansion admixture has to produce the expansive stress after the start of setting, at the stage when the paste attains certain rigidity to be able to transfer the expansion stress as a plastic material. If ettringite occurs homogeneously and immediately (within hours) after the start of setting, it does not cause any significant localized disruptive action (early ettringite formation, EEF). In the case of the expansion, which appears after the solidification (Delayed Ettringite Formation, DEF) it reduces the mechanical performance, or in extreme case, it leads to the material failure. DEF occurs when the constituents of concrete provide initial source of sulphates as a result of undesirable heating of the concrete to a temperatures higher than 65-70 °C. It has been found that the expansion time is inversely proportional to the fineness of expansive component and directly proportional to the amount of added sulfate [12,688-691,738,739].

The mechanisms mentioned above are based on the formation of ettringite where the expansion occurs due to the crystallization pressure as well as the swelling pressure which is caused by the selective absorption of ions combined with large number of water molecules on tiny ettringite crystals. The growing mechanism, the size and the shape of ettringite crystals are important factors, once the shrinkage compensation or the expansion effect shall be reached. The needle-like form of ettringite crystals growing on the surface of  $\text{C}_3\text{A}$  grains by the topochemical process after the solidification of cement slurry can convert the resulting strain into the desired volume expansion. In the case that ettringite crystals precipitate from the solution in the pores between grains of clinker phases, the expansion or shrinkage compensation effect does not occur [12].

Three types of expansive cements are defined by ASTM C 845 (Standard Specification for Expansive Hydraulic Cement) – K, M and S type [692]. The main aluminate phase that is responsible for the formation of ettringite varies with the cement type. The Klein's compound

( $3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4$ ,  $\text{C}_4\text{A}_3\bar{\text{S}}$ , so-called “kleinite”) is present in K-type cement [12,693-697], monocalcium aluminate ( $\text{CaO}\cdot \text{Al}_2\text{O}_3$ , CA) in M-type cement [12,693,697] and tricalcium aluminate ( $3\text{CaO}\cdot \text{Al}_2\text{O}_3$ ,  $\text{C}_3\text{A}$ ) in S-type cement [12,693,697].

Gypsum ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ,  $\text{C}\bar{\text{S}}\text{H}_2$ ) [698],  $\alpha$  or  $\beta$  hemihydrates ( $\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$ ,  $\text{C}\bar{\text{S}}\text{H}_{0.5}$ ) [699] and  $\alpha$  or  $\beta$  anhydrites ( $\text{CaSO}_4$ ,  $\text{C}\bar{\text{S}}$ ) [699,370] are used as the sources of  $\text{SO}_4^{2-}$  ions. The decreasing dissolution rate of anhydrite results in the lack of sulphate ions necessary for the formation and stability of ettringite, which is sensible to such factors as temperature, pH,  $\text{Al}(\text{OH})_4^-$  to  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  to  $\text{SO}_4^{2-}$  ratio [700-703].

## 2. Ettringite and analog of ettringite

Ettringite ( $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ , AFt as calcium aluminate or ferrite tri-substituted hydrates of general formula  $3\text{CaO}\cdot (\text{Al,Fe})_2\text{O}_3\cdot 3\text{CaX}_2\cdot n\text{H}_2\text{O}$ ) is formed in hydrated cement at early hydration stage. The AFt designation was first suggested by Smolczyk in 1961 in order to distinguish the high sulfate hydrate phases from the low sulfate phases, which are collectively termed AFm ( $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{CaSO}_4\cdot 12\text{H}_2\text{O}$ ). From its natural occurrences, ettringite has been known since 1874 [637,704-707].

Ettringite, like other AFt phases, forms hexagonal prismatic or acicular crystals. The crystals have two distinct structural components:

Columns:  $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \times 24\text{H}_2\text{O}\}^{6+}$

Channels:  $\{(\text{SO}_4^{2-})_3 \times 2\text{H}_2\text{O}\}^{6-}$

The columns consist of  $\text{Al}(\text{OH})_6$  octahedra alternating with triangular groups of edge-sharing  $\text{CaO}_8$  polyhedra. The column alignment is along the c-axis of the trigonal-hexagonal unit cell. Eight oxygen atoms in the polyhedra come from the Ca coordination with four OH ions shared with the  $\text{Al}(\text{OH})_6$  octahedra and from the coordination with four  $\text{H}_2\text{O}$  molecules. The hydrogen atoms from the molecules of water form the cylindrical surface of the columns. The channels contain four sites per formula unit of the column structure which contains six calcium atoms. Three of these sites are occupied by  $\text{SO}_4^{2-}$  and one by two  $\text{H}_2\text{O}$  molecules [706-709].

Both calcium sulfoaluminate hydrates (AFt and AFm) have the ability to combine with a number of cations and anions, which makes them important with regard to the waste immobilization in cementitious matrices [710-712]. Ions available for the substitution in the ettringite structure are  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$  and  $\text{OH}^-$ . They are listed in Table 1.

Reported analogs of ettringite are listed in Table 2.

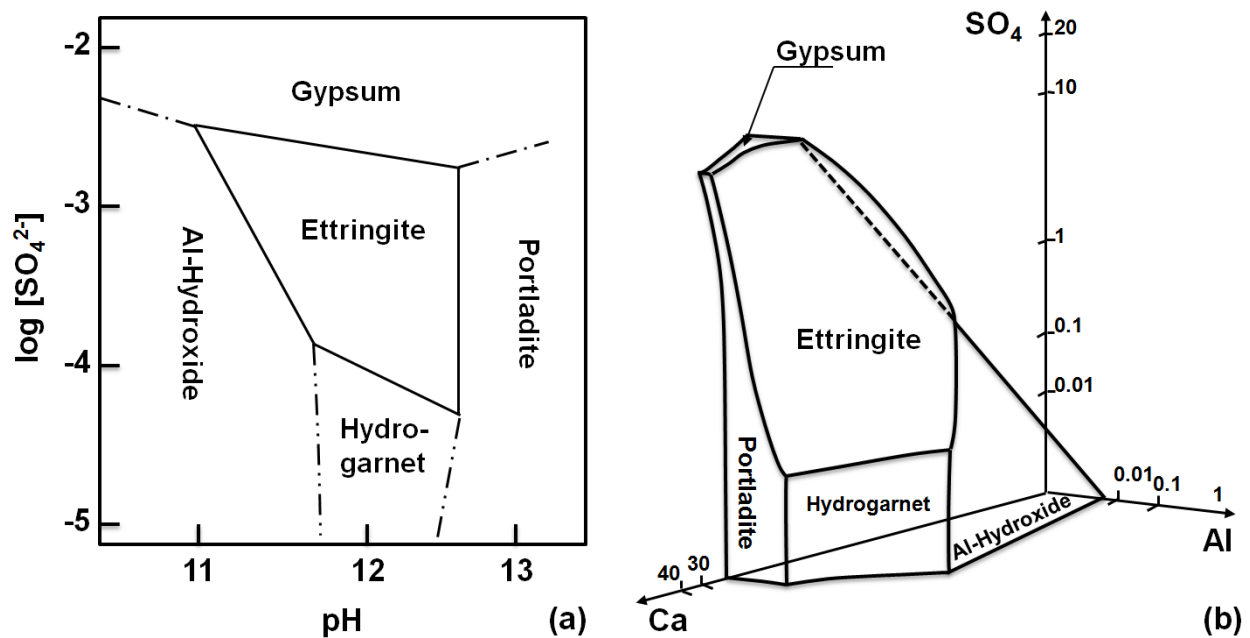
Site	Ion size [Å]	Site	Ion size [Å]	Site	Ion size [Å]	Site	Ion size [Å]
Ca <sup>2+</sup>	1.12	Al <sup>3+</sup>		SO <sub>4</sub> <sup>2-</sup>		OH <sup>-</sup>	
Sr <sup>2+</sup>	1.26	Cr <sup>3+</sup>		B(OH) <sub>4</sub> <sup>-</sup>		O <sup>2-</sup>	
Ba <sup>2+</sup>	1.42	Si <sup>4+</sup>		CO <sub>3</sub> <sup>2-</sup>			
Pb <sup>2+</sup>	0.90 – 1.42	Fe <sup>3+</sup>	0.42 – 0.76	Cl <sup>-</sup>			0.62 – 1.38
Cd <sup>2+</sup>		Mn <sup>3+</sup>		OH <sup>-</sup>			
Co <sup>2+</sup>		Ni <sup>3+</sup>		CrO <sub>4</sub> <sup>2-</sup>	0.62 – 3.71		
Ni <sup>2+</sup>		Co <sup>3+</sup>		AsO <sub>4</sub> <sup>3-</sup>			
Zn <sup>2+</sup>		Ti <sup>3+</sup>		SeO <sub>4</sub> <sup>2-</sup>			
				VO <sub>4</sub> <sup>3-</sup>			
				BrO <sub>3</sub> <sup>-</sup>			
				NO <sub>3</sub> <sup>-</sup>			
				MnO <sub>4</sub> <sup>-</sup>			
				CrO <sub>3</sub> <sup>-</sup>			
				SO <sub>3</sub> <sup>2-</sup>			
				IO <sub>3</sub> <sup>-</sup>			

Table 1. Ion substitutions in ettringite minerals according to [706].

Ion	Name/ formula	Reference
B(OH) <sub>4</sub> <sup>-</sup>	High-boro-ettringite (3CaO·Al <sub>2</sub> O <sub>3</sub> ·Ca(B(OH) <sub>4</sub> ) <sub>2</sub> ·Ca(OH) <sub>2</sub> ·36H <sub>2</sub> O), B-AFt)	[737,713,714]
	Low-boro-ettringite (3CaO·Al <sub>2</sub> O <sub>3</sub> ·Ca(B(OH) <sub>4</sub> ) <sub>2</sub> ·2Ca(OH) <sub>2</sub> ·36H <sub>2</sub> O)	
HBO <sub>3</sub> <sup>2-</sup>	Boro-monophase (4CaO·Al <sub>2</sub> O <sub>3</sub> ·½ B <sub>2</sub> O <sub>3</sub> ·12H <sub>2</sub> O, B-AFm)	[737]
CrO <sub>4</sub> <sup>2-</sup>	Chromate ettringite (3CaO·Al <sub>2</sub> O <sub>3</sub> ·CaCrO <sub>4</sub> ·nH <sub>2</sub> O)	[736,715]
	Chromate monophase (3CaO·Al <sub>2</sub> O <sub>3</sub> ·CaCrO <sub>4</sub> ·15H <sub>2</sub> O)	[736]
SeO <sub>4</sub>	Selenate ettringite(Ca <sub>6</sub> [Al(OH) <sub>6</sub> ] <sub>2</sub> (SeO <sub>4</sub> ) <sub>3</sub> ·31.5H <sub>2</sub> O)	[712,716,717]
	Selenatemonophase (3CaO·Al <sub>2</sub> O <sub>3</sub> ·CaSeO <sub>4</sub> ·xH <sub>2</sub> O)	[712,718]
CO <sub>3</sub> <sup>2-</sup>	Carbonate ettringite (Ca <sub>6</sub> Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O)	[719]
Al <sup>3+</sup>	Solid solution of Al- and Fe-ettringite (Ca <sub>6</sub> [Al <sub>1-x</sub> Fe <sub>x</sub> (OH) <sub>6</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·26H <sub>2</sub> O)	[708]

Table 2. Reported analogs of ettringite.

According to the stability field diagram of the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SO}_3-\text{H}_2\text{O}$  (Fig.1(a)) established by Hampson and Bailey [720], high sulphate concentrations stabilize gypsum and only when its concentration is low, then ettringite becomes the stable phase [735]. The thermodynamic investigation of the  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaSO}_4-\text{H}_2\text{O}$  (Fig.1(b)) system at 25 °C [721], 50 °C and 85 °C was performed by Damidot and Glasser [722]. The effect of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  on the equilibrium state is discussed in works [721] and [723], respectively.



**Figure 1.** Ettringite stability in alkaline environments [720] (a) and three-dimensional representation of  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaSO}_4-\text{H}_2\text{O}$  system [721] (b).

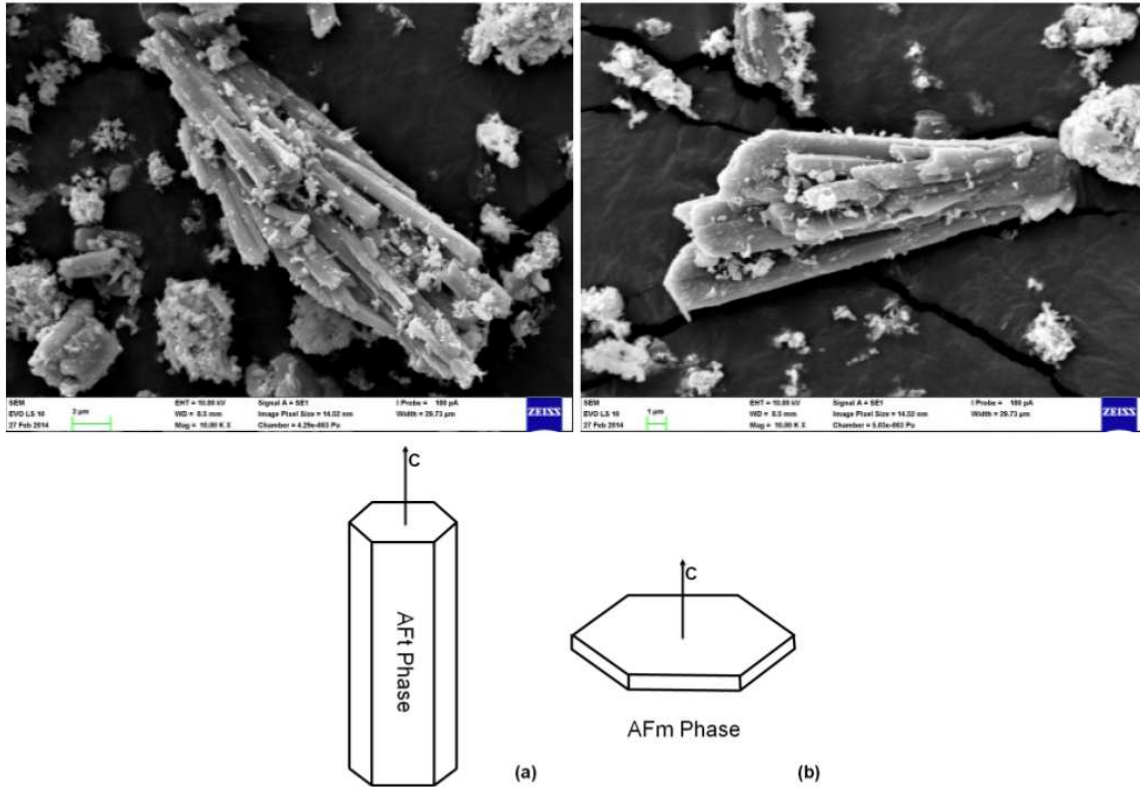
The following solid phases are possible in this system [721]:

- Ettringite (triphase or AFt in cement nomenclature):  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ;
- Monosulfate (monophase or AFm):  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ ;
- Gypsum:  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ;
- Hydrogarnet:  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  (other calcium alumina hydrates are also possible but they are metastable with respect to hydrogarnet);
- Portlandite:  $\text{Ca}(\text{OH})_2$ ;
- Gibbsite:  $\text{Al}(\text{OH})_3$ .

The reaction of cement minerals with sulphate and carbonate ions can lead to the formation of thaumasite ( $\text{Ca}_6[\text{Si}(\text{OH})_6]_2(\text{CO}_3)_2(\text{SO}_4)_2 \cdot 24\text{H}_2\text{O}$  or  $\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$ ) at temperatures below 15 °C. This reaction can destroy the C-S-H matrix and result in the disintegration of concrete (thaumasite sulfate attack, TSA). Ettringite and thaumasite have very similar crystal structures. Thaumasite is hexagonal ( $a=11.54 \text{ \AA}$ ,  $c=10.401 \text{ \AA}$ ) with the columns of  $[\text{Ca}_3\text{Si}(\text{OH})_6]$



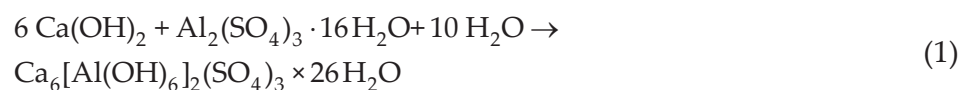
$12\text{H}_2\text{O}]^{4+}$  and sulfate and carbonate ions in an ordered arrangement in channels between the columns. Si is octahedrally coordinated by oxygen [724-730].



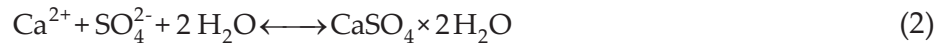
**Figure 2.** SEM image of ettringite crystals prepared by the saccharate method and characteristic crystal morphologies of AFt (a) and AFm (b) [737].

Most synthesis experiments reported in literature are based on the “saccharate” method reported originally by Carlson and Berman [731]. A CaO supersaturated, 10 % sucrose solution is mixed with  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$  in the stoichiometric amounts. Sodium sulfate can be replaced by oxyanion salt to obtain substituted ettringite [713,732]. The same process without the addition of sucrose is referred to as the “paste reaction” method [713].

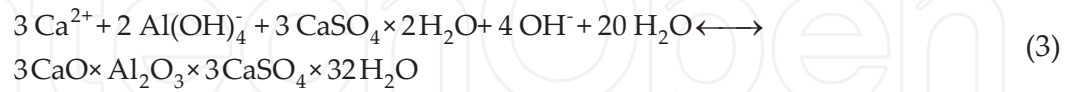
Ettringite can be also synthesized by mixing the calcium hydroxide slurry and the aluminium sulphate solution [733,734]:



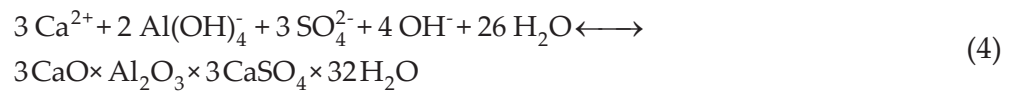
At high sulphate concentrations, gypsum initially controls the maximum concentration of sulphate in solution by the reaction [375]:



At elevated pH (~12) the dissolution of gypsum is promoted while ettringite remains stable. Gypsum is used afterwards as a source of sulphate in the synthesis of ettringite according to the reaction given by:

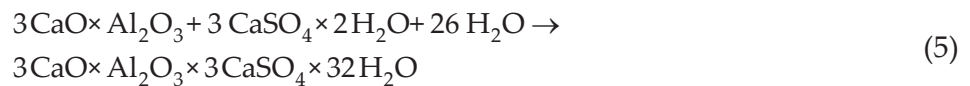


At low sulphate concentrations the ettringite synthesis proceeds following the reaction given by the equation:



The reaction of tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is known to be rapid and complete at room temperature (within 30 to 60 min) [705].

Ettringite appears as a hydrate phase of Portland cement in the first stage of hydration process. In stage one, the aluminate phase reacts with water in the presence of calcium sulfate to form ettringite [706]:



Ettringite can also be formed through the reaction of ferrite hydrate phase. Ettringite is formed within minutes after the start of cement hydration. Its concentration increases to a maximum within about 1 day and then it begins to decrease and may even approach zero. As ettringite disappears, mono-sulfate (AFm) hydrate phase takes its place due to lower sulfate concentration in the pore solutions. The ettringite produced in this first hydration stage tends to be in the form of stubby, prismatic crystals close to the aluminate surface as well as away from these surfaces. Depending on the cement composition and availability of  $\text{CO}_3^{2-}$  ettringite either persists or is converted into monosulfate [7,12,706,736,737]:



Structurally, AFm phases are similar to the mineral hydrocalumite, the crystals of which are morphologically recognizable as thin hexagonal plates (Fig.2). Basal spacing in AFm crystal



structure depends on the type of anion, such as  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , within the interlayer region.

There are two different types of DEF-related damages depending on the sulfate source [738-740]:

- 1. External (ESA) sulfate attack, which occurs when environmental sulfate (from water or soil) penetrates into a concrete structure. It can be avoided or reduced by using impermeable concrete.
- 2. Internal (ISA) sulfate attack, which occurs also in sulfate free-environment by late sulfate ions release from either cement or gypsum contaminated in aggregates. The ISA-induced damage caused by the late sulfate release from the cement can be related either to the thermal decomposition of “primary” ettringite or to sulfate release from C-S-H.

Several forms of ettringite phase which may be formed during the hydration of Portland cement are listed in Table 3.

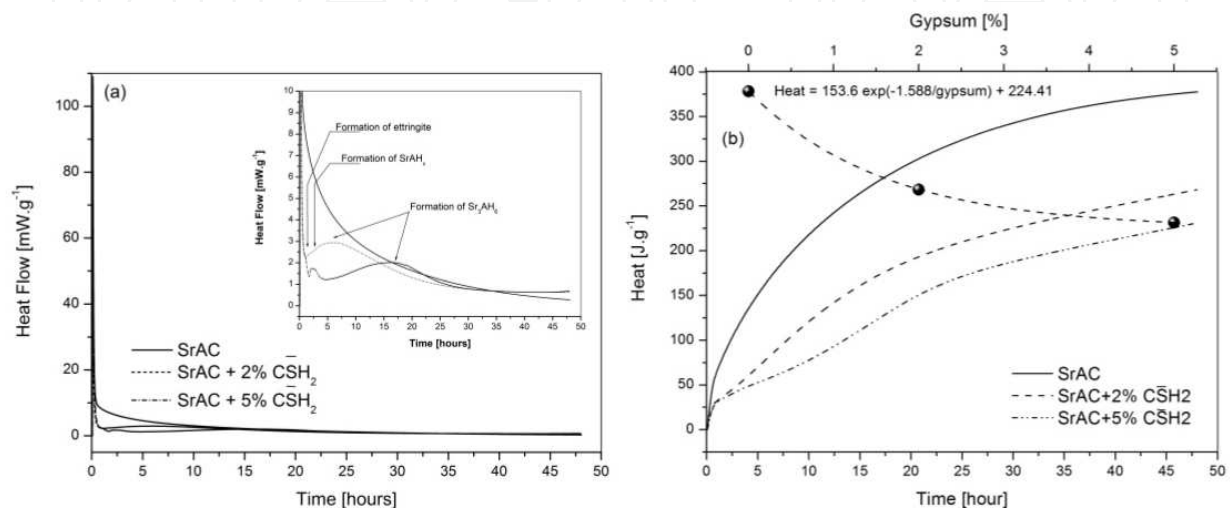
Ettringite	Time of formation	Conditions of formation	$\text{Al}_2\text{O}_3$ source	Texture	Expansive behaviour
Early primary	First hour of hydration	Normal conditions of hydration	$\text{C}_3\text{A}$	Microcrystalline	no
Late primary	First days or weeks of hydration	Excessive amount of gypsum is cement	$\text{C}_3\text{A}$	Microcrystalline	yes
External	Any time	Migration of $\text{SO}_3$ from outside	Mono-sulphate	Microcrystalline	yes
Delayed	Months after thermal curing	After curing at temperatures $>70^\circ\text{C}$	Mono-sulphate	Microcrystalline	yes
Secondary	Months after thermal curing	Recrystallization of ettringite in formed cracks upon wetting and drying	Ettringite	Microcrystalline	No (?)

Table 3. Forms of ettringite [741].

The formation of ettringite, which induces swelling, may also cause failures in stabilization of soil, where within the mechanical treatment  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$  or cement are used. Ettringite shows very high water retention potential. Therefore, as ettringite grows in stabilized soil, its presence enhances the water retention of soil, causing that the sample exerts more force in order to take in the water-sulfate solution from lower soil strata [742]. Although lime treatment can be effective in stabilizing gypseous soils and in enhancing their mechanical properties, the amount of added lime must be adjusted according to the mineralogical composition and the gypsum content of soil [743].

### 3. Expansive strontium aluminate cements

The additions of sulfate bearing phases such as anhydrite to strontium aluminate cement can be performed in order to prepare expansive cements based on strontium aluminate. The effect of gypsum onto the hydration of SrAC was investigated by isothermal calorimetric experiment using the blend of strontium aluminate cement with 2% and 5% of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Fig.3).



**Figure 3.** Effect of gypsum on the hydration of strontium aluminate cement.

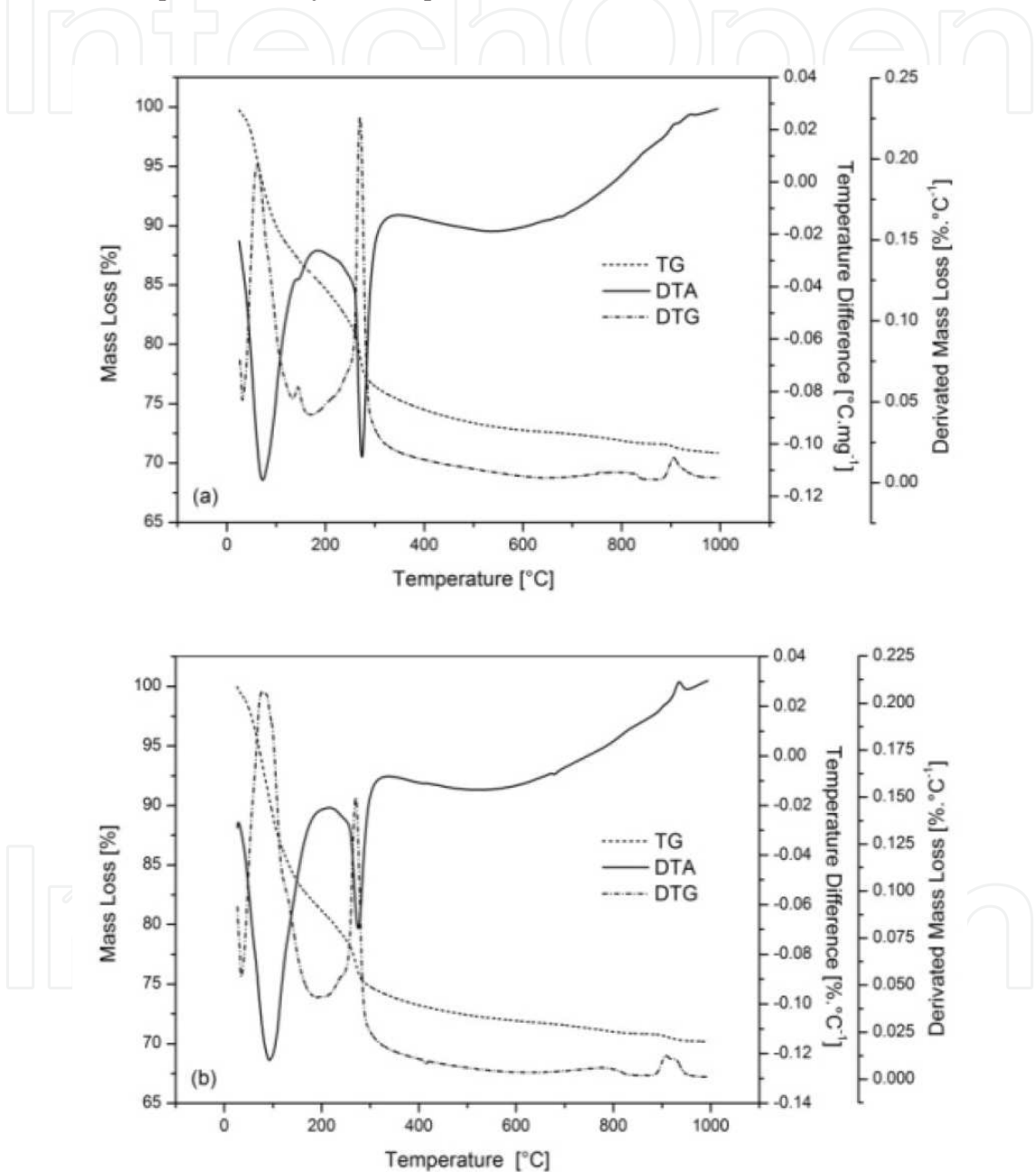
In comparison with pure SrAC, the changes of heat flow indicate that gypsum has a significant effect on the course of hydration of strontium aluminate cement. The calorimetric data indicate the changes in the mechanism of hydration process and those caused by the formation of ettringite (Figs.5, 7 and 8). Fast precipitation of ettringite leads to the deficiency of  $[\text{Al}(\text{OH})_4]^-$  ions and  $\text{Sr}^{2+}$  ions which substitute for  $\text{Ca}^{2+}$  ions in the structure of  $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}^{6+}$  columns. That explains the formation of  $\text{SrAH}_x$  (Fig.5(b)) and the absence of gibbsite. It is obvious that the intensity of effect related to the formation of  $\text{SrAH}_x$  increases with the amount of gypsum added to SrAC. The addition of gypsum changes the main hydration products at least during initial stages of hydration.

The diffusion barrier formed on the surface of strontium aluminate phase leads to a broad hydration effect where the time and temperature related to the maximum of released heat decreases with increasing content of gypsum. Increasing amount of added gypsum leads increased formation of  $\text{SrAH}_x$  and ettringite while the amounts of formed  $\text{Sr}_3\text{AH}_6$  and gibbsite decrease. Fig.3(b) shows that the heat released during the first 50 hours of hydration of strontium aluminate cement decreases exponentially with increasing content of gypsum. This behavior can provide the explanation for the hydration of the blend of strontium aluminate cement with SrAC (please see the discussion related to Fig.7 in Chapter 7).

The hydration of the samples after the calorimetric assessment was stopped by repeated washing of ground samples in acetone in order to remove water followed by the evaporation

of solvent and drying upon silica-gel in desiccator. The storage of sample in the desiccator also restricts the course of carbonation [409,744,745].

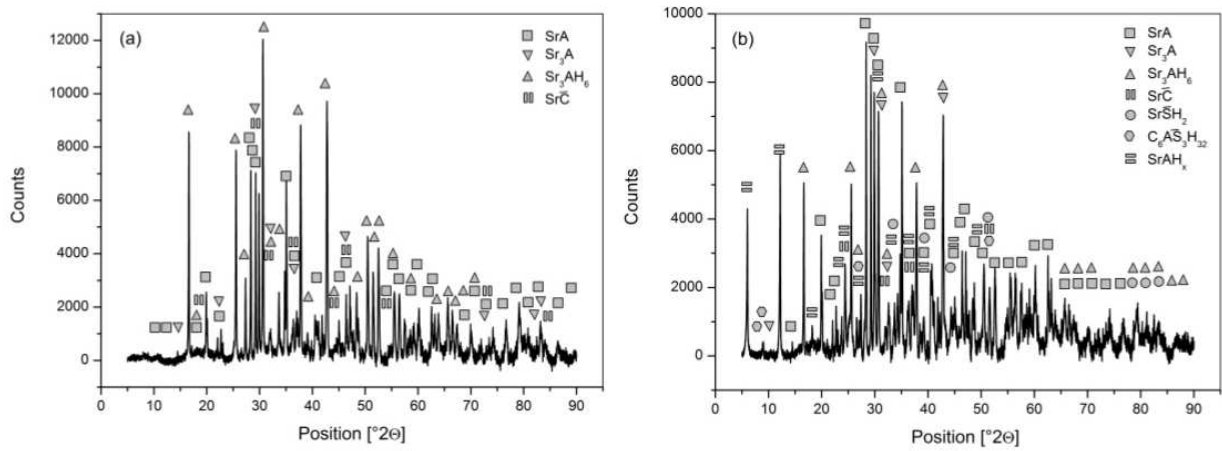
The composition of hydrated cement stone was further investigated by thermal analysis, X-ray diffraction analysis, infrared spectroscopy and scanning electron microscopy in order to explain the effect of gypsum on the course of hydration and to evaluate the changes in the equilibrium composition of hydration products of SrAC.



**Figure 4.** DTA of hardened cement stone prepared from the mixture containing 2 % (a) and 5 % (b) of gypsum.

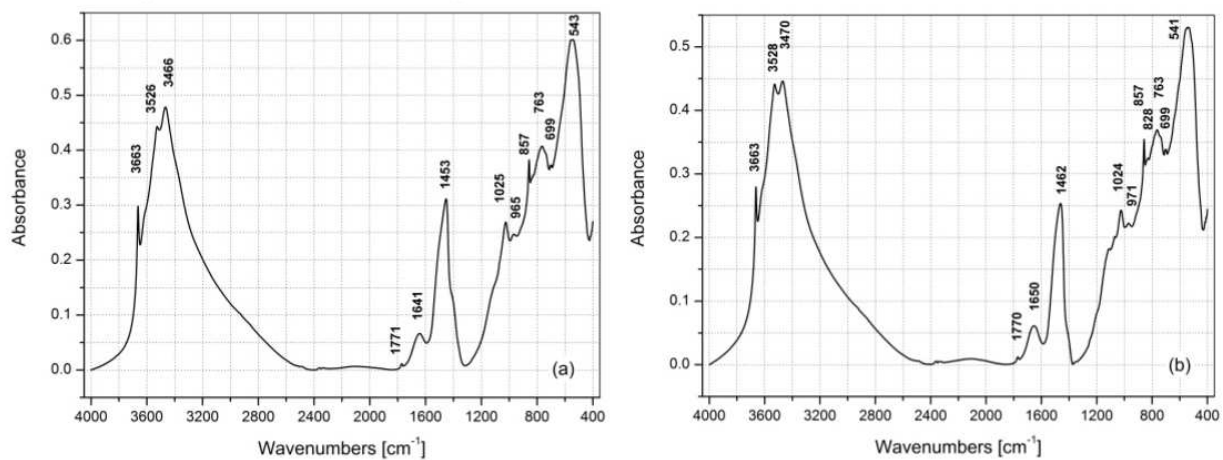
The TG-DTA results are shown in Fig.4. They reveal higher weight change in the first step of thermogravimetric curve for the sample with 5 % of gypsum. The intensity of the effect related

to the dehydration of gel phase and of main product of hydration ( $\text{Sr}_3\text{AH}_3$ ) decreases (Chapter 5.1). That indicates that  $[\text{Al}(\text{OH})_4]^-$  ion formed during the hydration is used to form ettringite that slows down the hydration of strontium aluminate cement.



**Figure 5.** X-ray analysis of cement stone after 50 h of hydration: sample with 2 % (a) and 5 % (b) of gypsum.

The results of X-ray diffraction analysis of cement stone after 50 hours of hydration at the temperature of  $25^{\circ}\text{C}$  is shown in Fig.5. Higher intensity of diffraction lines of unreacted strontium aluminate in sample (b) compared to (a) indicates the retardation effect of gypsum on the hydration of strontium aluminate cement. Moreover, both samples still showed the diffraction features of tri-strontium aluminate after 50 h of hydration process, while this compound was not recognized in pure sample of strontium aluminate cement without gypsum (Fig.6). Both samples are slightly carbonated.



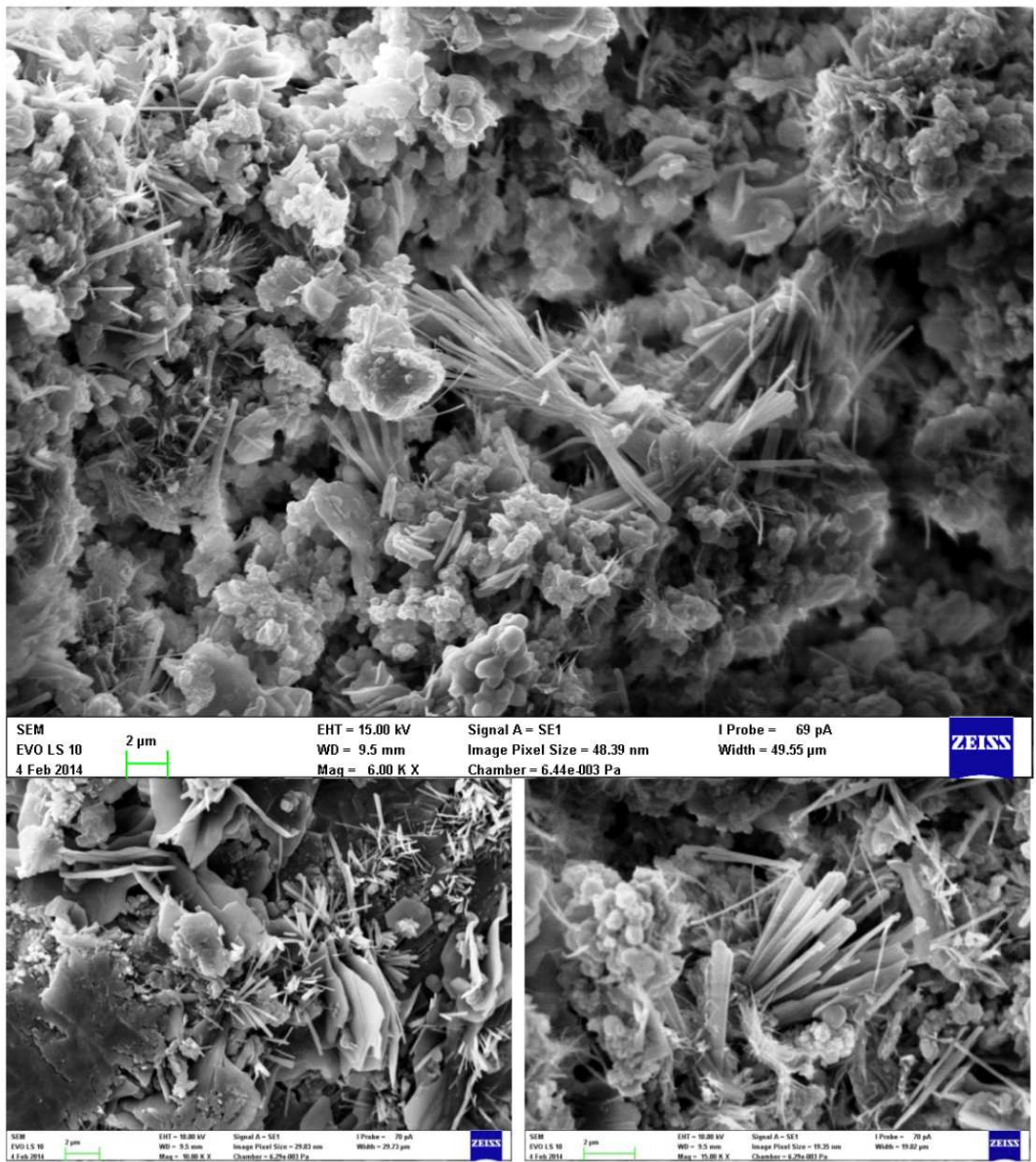
**Figure 6.** Infrared spectrum of hydrated cement stone of sample containing 2 % (a) and 5 % (b) of gypsum.

Infrared spectrum (Fig.6) shows the features typical for hydrated strontium aluminate cement (tri-strontium aluminate hexahydrate and strontium carbonate) which are described in



Chapter 5.1. Fundamental stretching modes of  $\text{SO}_4^{2-}$  ions are located on the left shoulder of multiple band below  $1300\text{ cm}^{-1}$  ( $1250 - 950$  and  $700 - 580\text{ cm}^{-1}$ ).

The bands of  $\text{CO}_3^{2-}$  anion with  $C_s$  symmetry occur in the spectra of both samples due to the carbonation to  $\text{SrCO}_3$ : the band of antisymmetric stretching  $\nu_3$  ( $1453\text{ cm}^{-1}$ ), symmetric stretching  $\nu_1$  ( $1071\text{ cm}^{-1}$ )<sup>1</sup>, out of plane bending  $\nu_2$  ( $857\text{ cm}^{-1}$ ), in plane  $\nu_4$  ( $699\text{ cm}^{-1}$ ) and the combination band  $\nu_1+\nu_4$  at  $1771\text{ cm}^{-1}$  [170,746-748]. The bands of hydration products are described in Chapter 5.1 (please see the discussion to Fig.4).



**Figure 7.** Strontium aluminate cement with 2 wt.% of gypsum.

<sup>1</sup> Vibration mode is IR active due to the aragonite structure of  $\text{SrCO}_3$  (Please see Chapter 2).

X-ray diffraction analysis does not provide the evidence about the formation of ettringite in the sample prepared from the mixture of strontium aluminate cement with 2 % of gypsum. On the other hand, SEM images (Fig.7) show rare and small clumps of needle-like crystals which occur between the plates of the main product of hydration, therefore a very small amount of strontium sulfate or ettringite is probably formed.

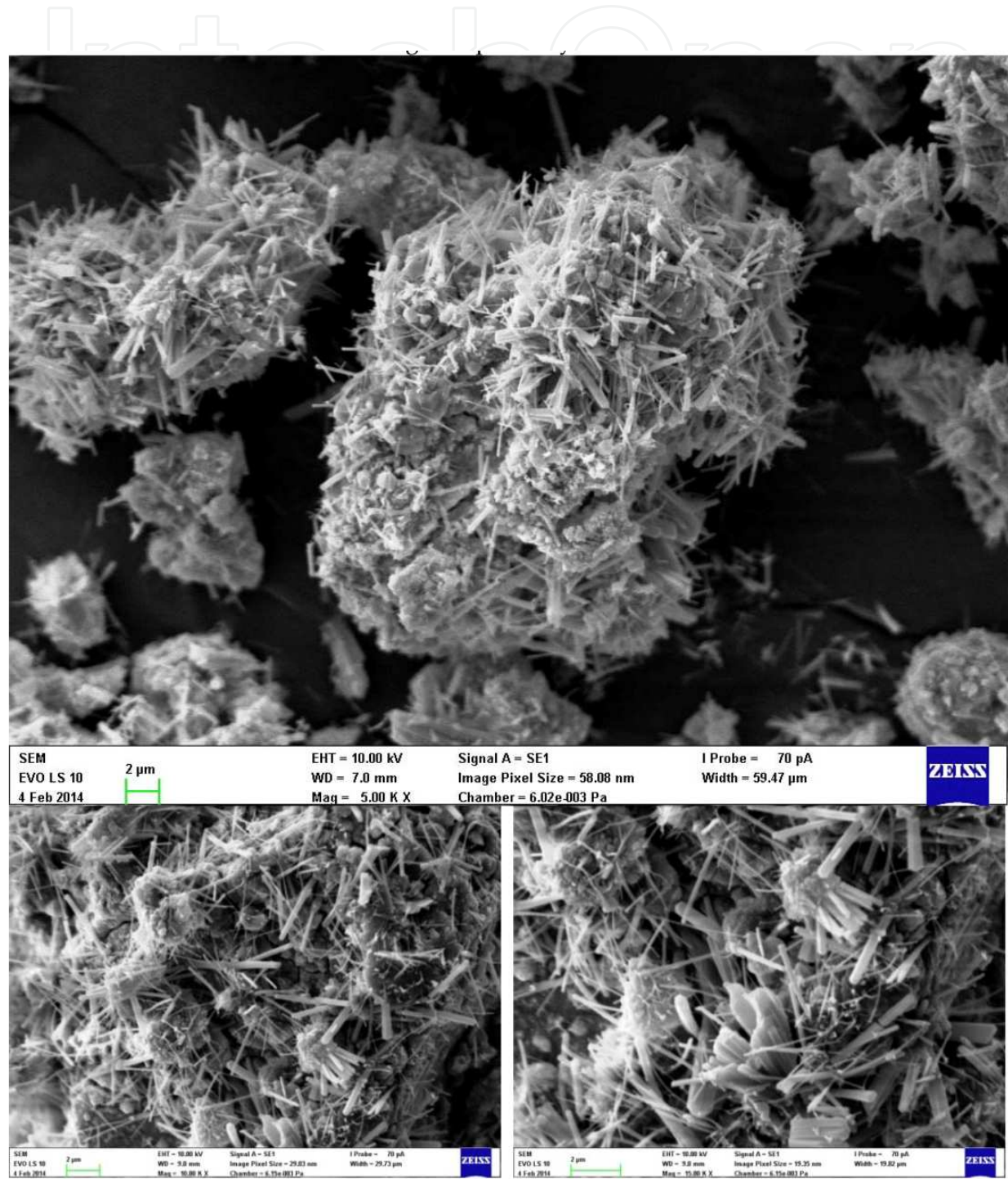


Figure 8. Strontium aluminate cement with 5 wt.% of gypsum.



The sample prepared with 5 % of gypsum shows the diffraction lines of both, strontium sulfate and ettringite. Higher content of sulfate bearing phase, compared to cement with 2 % of gypsum, is also well visible from scanning electron microscopy images, where large amount of needle-like crystals grow on the surface of clusters consisting of partially hydrated grains of strontium aluminate cement.

The comparison of Fig.7 and Fig.8 as well as the results of calorimetry (Fig.3) indicate the change in hydration mechanism from the crystallization to the diffusion. There is a way to prepare expansive strontium aluminate cement, but the control of setting time of the paste is necessary in order to reach required rigidity, which enables to handle the expansion stress. The positive effect was observed for calcined clay (Chapter 7.2).