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Chapter 8

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 (3CaO⋅Al₂O₃⋅3CaSO₄⋅32H₂O, C₆AS₃H₃2, AFt), swelling gel of portlandite (Ca(OH)₂, CH [12,688]) or brucite (Mg(OH)₂, 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 C₃A 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 ettringitevaries with the cement type. The Klein’s compound
(3CaO·3Al₂O₃·CaSO₄, C₄A₆S, so-called “kleinite”) is present in K-type cement [12,693-697], monocalcium aluminate (CaO·Al₂O₃, CA) in M-type cement [12,693,697] and tricalcium aluminate (3CaO·Al₂O₃, C₃A) in S-type cement [12,693,697].

Gypsum (CaSO₄·2H₂O, C₅H₂O) [698], α or β hemihydrates (CaSO₄·0.5H₂O, C·H₂O) [699] and α or β anhydrites (CaSO₄·CS) [699,370] are used as the sources of SO₄²⁻ 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, Al(OH)₄⁻ to SO₄²⁻ and Ca²⁺ to SO₄²⁻ ratio [700-703].

2. Ettringite and analog of ettringite

Ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O, AFt) as calcium aluminate or ferrite tri-substituted hydrates of general formula 3CaO·(Al,Fe)₂O₃·3CaX₂·nH₂O) 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 (3CaO·Al₂O₃·CaSO₄·12H₂O). 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: [Ca₆[Al(OH)]₆×24H₂O]⁶⁺

Channels: [3(SO₄²⁻)×2H₂O]⁶⁻

The columns consist of Al(OH)₆ octahedra alternating with triangular groups of edge-sharing CaO₆ polyhedra. The column alignment is along the c-axis of the trigonal-hexagonal unit cell. Eight oxygens atoms in the polyhedra come from the Ca coordination with four OH ions shared with the Al(OH)₆ octahedra and from the coordination with four H₂O 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 SO₄²⁻ and one by two H₂O 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 Ca²⁺, Al³⁺, SO₄²⁻ and OH⁻. They are listed in Table 1.

Reported analogs of ettringite are listed in Table 2.
Table 1. Ion substitutions in ettringite minerals according to [706].

<table>
<thead>
<tr>
<th>Ion</th>
<th>Name/ formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(OH)$_4^-$</td>
<td>High-boro-ettringite (3CaO·Al$_2$O$_3$·CaB(OH)$_4$·36H$_2$O), B-AFt</td>
<td>[737,713,714]</td>
</tr>
<tr>
<td></td>
<td>Low-boro-ettringite (3CaO·Al$_2$O$_3$·CaB(OH)$_4$·2Ca(OH)$_2$·36H$_2$O)</td>
<td></td>
</tr>
<tr>
<td>HBO$_3^{2-}$</td>
<td>Boro-monophase (4CaO·Al$_2$O$_3$·½ B$_2$O$_3$·12H$_2$O, B-AFm)</td>
<td>[737]</td>
</tr>
<tr>
<td>CrO$_4^{3-}$</td>
<td>Chromate ettringite (3CaO·Al$_2$O$_3$·CaCrO$_4$·nH$_2$O)</td>
<td>[736,715]</td>
</tr>
<tr>
<td></td>
<td>Chromate monophase (3CaO·Al$_2$O$_3$·CaCrO$_4$·15H$_2$O)</td>
<td>[736]</td>
</tr>
<tr>
<td>SeO$_4^{2-}$</td>
<td>Selenate ettringite (Ca$_6$[Al(OH)$_6$]$_2$[SeO$_4$]$_3$·31.5H$_2$O)</td>
<td>[712,716,717]</td>
</tr>
<tr>
<td></td>
<td>Selenatemonophase (3CaO·Al$_2$O$_3$·CaSeO$_4$·xH$_2$O)</td>
<td>[712,718]</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>Carbonate ettringite (Ca$_6$Al$_4$(CO$_3$)$_3$(OH)$_2$·26H$_2$O)</td>
<td>[719]</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>Solid solution of Al- and Fe-ettringite (Ca$_6$<a href="OH">Al$_{1-x}$Fe$_x$</a>$_6$·(SO$_4$)$_3$·26H$_2$O)</td>
<td>[708]</td>
</tr>
</tbody>
</table>

Table 2. Reported analogs of ettringite.
According to the stability field diagram of the system CaO–Al₂O₃–SO₃–H₂O (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 CaO-Al₂O₃-CaSO₄-H₂O (Fig.1(b)) system at 25 °C [721], 50 °C and 85 °C was performed by Damidot and Glasser [722]. The effect of Na₂O and K₂O on the equilibrium state is discussed in works [721] and [723], respectively.

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

- Ettringite (triphase or AFt in cement nomenclature): 3CaO⋅Al₂O₃⋅3CaSO₄⋅32H₂O;
- Monosulfate (monophase or AFm): 3CaO⋅Al₂O₃⋅CaSO₄⋅12H₂O;
- Gypsum: CaSO₄⋅2H₂O;
- Hydrogarnet: 3CaO⋅Al₂O₃⋅6H₂O (other calcium alumina hydrates are also possible but they are metastable with respect to hydrogarnet);
- Portlandite: Ca(OH)₂;
- Gibbsite: Al(OH)₃.

The reaction of cement minerals with sulphate and carbonate ions can lead to the formation of thaumasite (Ca₆[Si(OH)]₆[CO₃]₂(SO₄)₂) 24H₂O or CaSiO₃ CaCO₃ CaSO₄ 15H₂O) 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 Å, a=10.401 Å) with the columns of [Ca₃Si(OH)]₆
and sulfate and carbonate ions in an ordered arrangement in channels between the columns. Si is octahedrally coordinated by oxygen [724-730].

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 Na₂O Al₂O₃ and Na₂SO₄ 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]:

\[
6 \text{Ca(OH)}_2 + \text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O} + 10 \text{H}_2\text{O} \rightarrow \text{Ca}_6(\text{Al(OH)}_6\text{SO}_4)_3 \times 26\text{H}_2\text{O}
\] (1)

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

**Figure 2.** SEM image of ettringite crystals prepared by the saccharate method and characteristic crystal morphologies of AFt (a) and AFm (b) [737].
Ca\(^{2+}\) + SO\(_4^{2-}\) + 2 H\(_2\)O $\rightarrow$ CaSO\(_4\) × 2H\(_2\)O  \hspace{1cm} (2)

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

\[
3\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 3\text{CaSO}_4 \times 2\text{H}_2\text{O} + 4\text{OH}^- + 20\text{H}_2\text{O} \rightarrow 3\text{CaO} \times \text{Al}_2\text{O}_3 \times 3\text{CaSO}_4 \times 32\text{H}_2\text{O} \hspace{1cm} (3)
\]

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

\[
3\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \times \text{Al}_2\text{O}_3 \times 3\text{CaSO}_4 \times 32\text{H}_2\text{O} \hspace{1cm} (4)
\]

The reaction of tricalcium aluminate (3CaO⋅Al\(_2\)O\(_3\)) with gypsum (CaSO\(_4\)⋅2H\(_2\)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]:

\[
3\text{CaO} \times \text{Al}_2\text{O}_3 + 3\text{CaSO}_4 \times 2\text{H}_2\text{O} + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \times \text{Al}_2\text{O}_3 \times 3\text{CaSO}_4 \times 32\text{H}_2\text{O} \hspace{1cm} (5)
\]

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 CO\(_3^{2-}\), ettringite either persists or is converted into monosulfate [7, 12, 706, 736, 737]:

\[
3\text{CaO} \times \text{Al}_2\text{O}_3 \times 3\text{CaSO}_4 \times 32\text{H}_2\text{O} + 2\left(3\text{CaO} \times \text{Al}_2\text{O}_3\right) + 4\text{H}_2\text{O} \rightarrow 3\left(3\text{CaO} \times \text{Al}_2\text{O}_3 \times \text{CaSO}_4 \times 12\text{H}_2\text{O}\right) \hspace{1cm} (6)
\]

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 CO$_3^{2-}$, OH$^-$, Cl$^-$ and 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.

<table>
<thead>
<tr>
<th>Ettringite</th>
<th>Time of formation</th>
<th>Conditions of formation</th>
<th>Al$_2$O$_3$ source</th>
<th>Texture</th>
<th>Expansive behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early primary</td>
<td>First hour of hydration</td>
<td>Normal conditions of hydration</td>
<td>C$_3$A</td>
<td>Microcrystalline</td>
<td>no</td>
</tr>
<tr>
<td>Late primary</td>
<td>First days or weeks of hydration</td>
<td>Excessive amount of gypsum is cement</td>
<td>C$_3$A</td>
<td>Microcrystalline</td>
<td>yes</td>
</tr>
<tr>
<td>External</td>
<td>Any time</td>
<td>Migration of SO$_3$ from outside</td>
<td>Mono-sulphate</td>
<td>Microcrystalline</td>
<td>yes</td>
</tr>
<tr>
<td>Delayed</td>
<td>Months after thermal curing</td>
<td>After curing at temperatures &gt;70 °C</td>
<td>Mono-sulphate</td>
<td>Microcrystalline</td>
<td>yes</td>
</tr>
<tr>
<td>Secondary</td>
<td>Months after thermal curing</td>
<td>Recrystallization of ettringite in formed cracks upon wetting and drying</td>
<td>Ettringite</td>
<td>Microcrystalline</td>
<td>No (?)</td>
</tr>
</tbody>
</table>

**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 CaO, Ca(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 CaSO$_4$$\cdot$2H$_2$O (Fig.3).

![Figure 3. Effect of gypsum on the hydration of strontium aluminate cement.](image)

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 [Al(OH)$_4$]$^-$ ions and Sr$^{2+}$ ions which substitute for Ca$^{2+}$ ions in the structure of $\{\text{Ca}_6[\text{Al(OH)}_6]^2\cdot24\text{H}_2\text{O}\}$$^{6+}$ columns. That explains the formation of SrAH$_{x}$ (Fig.5(b)) and the absence of gibbsite. It is obvious that the intensity of effect related to the formation of 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 SrAH$_x$ and ettringite while the amounts of formed Sr$_3$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 (Sr₃Al₃H₆) decreases (Chapter 5.1). That indicates that [Al(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°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 cm$^{-1}$ (1250 – 950 and 700 – 580 cm$^{-1}$).

The bands of $\text{CO}_3^{2-}$ anion with $\text{C}_s$ symmetry occur in the spectra of both samples due to the carbonation to SrCO$_3$; the band of antisymmetric stretching $\nu_3$ (1453 cm$^{-1}$), symmetric stretching $\nu_1$ (1071 cm$^{-1}$), out of plane bending $\nu_2$ (857 cm$^{-1}$), in plane $\nu_4$ (699 cm$^{-1}$) and the combination band $\nu_1 + \nu_4$ at 1771 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.](image)

1 Vibration mode is IR active due to the aragonite structure of 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).