Doctoral Thesis

The influence of calciumsulfoaluminate as accelerating component within cementitious systems hydration, microstructure, strength development, and sulfate resistance of the cement-based mixtures

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The Influence of Calciumsulfoaluminate as Accelerating Component within Cementitious Systems

Hydration, Microstructure, Strength Development, and Sulfate Resistance of the Cement-based Mixtures

A Dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY

for the Degree of

Doctor of Technical Science

Presented by

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2000
A Maria, Silvio, Rosanna, Lara e Barbara

La sola infinita forza é amare

Grazie
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Zusammenfassung


Abstract

In the present work the influence of alkali-free, calciumsulfoaluminate-based accelerators on cementitious systems was investigated. Particular attention was paid on the relationship between the strength and the microstructural development. A general comparison with an alkali-rich accelerator was also matter of concern. Moreover, the exposition in 5% Na₂SO₄ solutions of the alkali-free and alkali-rich accelerated systems allowed to gain in depth knowledge of the mechanisms by which they were attacked and thereby the correspondent resistance of the mixtures against sulfates. The addition of calciumsulfoaluminate as activator for a burnt oil shale-based cementitious system was also investigated with the aim of clarifying its high early strength development.

The addition of the alkali-free, calciumsulfoaluminate-based admixtures caused the crystallization of ettringite prisms which contributed to the fast setting. These chemical admixtures did not influence the main hydration behavior of the calciumsilicatehydrate gel, which developed to a dense compact mass with time. On the other hand, the dissolution and the homogenization of these admixtures within the cementitious mass was decisive for the strength development. A good dissolution of the admixtures caused the ettringites to be homogeneously distributed within the mass, thus acting as crack arrester and enhancing the strength. The calciumsulfoaluminate promoted this latter structure-mechanical feature. On the contrary, an inhomogeneous distribution of the admixtures resulted in the formation of high voluminous ettringite enrichments which adversely affected the strength. The addition of the alkali-based admixture caused a delay in the hydration of the calciumsilicatehydrate gel and in its growing process. Consequently, a general high porosity persisted over time, resulting in the greatest strength decreases.
The resistance to sulfates was adversely affected by the aluminum and sulfate ions added throughout the accelerators, since the sulfate ions act as reactant and the aluminate ions promote the reaction to ettringite. The free calciumhydroxide availability controlled the extent of the calcium-silicatehydrate gel disintegration, which was promoted by a free calciumhydroxide depletion. This disintegration increased the porosity resulting in a further penetration of the sulfate solution which partially contributed to the expansion of the specimens. This explained the lack of a direct relationship between ettringite formation and expansion. Moreover, the calciumsilicatehydrate gel disintegration, typical for magnesium sulfate attack, also took place with sodium sulfate solutions. The damage was related to the distribution of the accelerator within the cement matrix. A temperature increase influenced the extent of the damage by both a homogeneous and an inhomogeneous accelerator distribution. The extent of the damage was related to the free calciumhydroxide availability, the aluminate distribution and the ettringite rearrangements. Moreover, qualitative investigations of the sulfate susceptibility of the cementitious material revealed a possible trustworthy prediction of the long-term sulfate resistance on site.

The high early strength attained by mixing calciumsulfoaluminate and burnt oil shales as main components of a cementitious system was caused by the simultaneous formation of ettringite and a dense amorphous calciumsilicatehydrate gel. The free calciumhydroxide concentration of the pore solution simultaneously influenced the hydration kinetics of the $\beta$-dicalciumsilicate of the burnt oil shales to calciumsilicatehydrate gel, and the ettringite formation from the calciumsulfoaluminate component. The ettringites, in turn, exhibited a strong dependence on the free calciumhydroxide concentration of the pore solution with regards to their formation mechanism. The calciumoxide-rich burnt oil shale component greatly delayed the hydration of the two-phase system and caused the formation of expansive ettringite crystals. This led to lower early strengths compared to the system with calciumoxide-depleted burnt oil shale as a component.
### Abbreviations

**General cement nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>C: CaO</td>
<td>Calcium oxide</td>
</tr>
<tr>
<td>S: SiO₂</td>
<td>Silicium dioxide</td>
</tr>
<tr>
<td>A: Al₂O₃</td>
<td>Aluminum oxide</td>
</tr>
<tr>
<td>S: SO₃</td>
<td>Sulfur trioxide</td>
</tr>
<tr>
<td>F: Fe₂O₃</td>
<td>Iron trioxide</td>
</tr>
<tr>
<td>C: CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>H: H₂O</td>
<td>Water</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S:</td>
<td>Tricalcium silicate (Alite) 3 CaO. SiO₂</td>
</tr>
<tr>
<td>C₂S:</td>
<td>Dicalcium silicate (belite) 2 CaO. SiO₂</td>
</tr>
<tr>
<td>C₃A:</td>
<td>Tricalcium aluminate 3 CaO. Al₂O₃</td>
</tr>
<tr>
<td>C₄AF:</td>
<td>Tetracalcium ferroaluminate 4 CaO. Al₂O₃. Fe₂O₃</td>
</tr>
<tr>
<td>C₅₂S₁₆AM:</td>
<td>Calcium magnesium alumosilicate 54 CaO. 16 SiO₂. Al₂O₃. MgO</td>
</tr>
<tr>
<td>CSA (C₄A₃S):</td>
<td>Calcium sulfoaluminate 4 CaO.3 Al₂O₃. SO₃</td>
</tr>
<tr>
<td>C₂AS:</td>
<td>Gelehnite 2 CaO. Al₂O₃. SiO₂</td>
</tr>
<tr>
<td>C₁₂A₇:</td>
<td>Calcium aluminate 12 CaO. 7 Al₂O₃</td>
</tr>
<tr>
<td>CA:</td>
<td>Monocalcium aluminate CaO. Al₂O₃</td>
</tr>
<tr>
<td>CA₂:</td>
<td>Calcium dialuminate CaO. 2 Al₂O₃</td>
</tr>
<tr>
<td>CSH₂:</td>
<td>Gypsum CaO. SO₃. 2 H₂O</td>
</tr>
<tr>
<td>CS:</td>
<td>Anhydride CaO. SO₃</td>
</tr>
</tbody>
</table>

**AFm:** Hexagonal calcium ferro-aluminate hydrate

\[ [\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]_x^+ (Y^{a^-} \cdot x \text{H}_2\text{O}) \]

\[ Y^{a^-} = \text{SO}_4^{2-}, \text{OH}^-, \text{CO}_3^{2-}, \text{HCO}_3^-, \text{Cl}^- \]

(AFm₁₁: C₄A₇H₁₁)

(AFm₁₂: CA₀.₅H₁₂)

**Ettringite:** Trigonal calcium ferro-aluminate hydrate

\[ [\text{Ca}_3(\text{Al,Fe})(\text{OH})_6\cdot12\text{H}_2\text{O}]_y^{3+} (3Y^{a^-} \cdot x \text{H}_2\text{O}) \]

\[ Y^{a^-} = \text{SO}_4^{2-}, \text{OH}^-, \text{CO}_3^{2-}, \text{HCO}_3^-, \text{Cl}^- \]
CH: Portlandite CaO.H₂O, commonly Ca(OH)₂
CSH: Calciumsilicatehydrate gel x CaO. y SiO₂. z H₂O
AH₃: Aluminumhydroxide Al₂O₃. 3 H₂O
OPC: Ordinary Portland Cement (CEM I)

Other shortenings

SEM: Scanning electron microscopy
XRD: X-ray diffraction
TG: Thermogravimetry
DTA: Differential thermal analysis

ASR: Alkali-silica reaction
DEF: Delayed ettringite formation
Mean Std: Arithmetic mean of the standard deviations

CSA (Calciumsulfoaluminate) / accelerators

N: Cement I
ST: Cement I / 1% plasticizer
NQ: Cement I / 1% plasticizer / 7.5% silica fume

AF: Cement I / 1% plasticizer / 6%
alkali-free accelerator I (wet mixed)
RF: Cement I / 1% plasticizer / 1.6%
technical calciumsulfoaluminate (CSA)
AS: Cement I / 1% plasticizer / 3.98%
aluminumsulfate
L 50: Cement I / 1% plasticizer / 8%
alkali-free accelerator II
L 20: Cement I / 1% plasticizer / 4.5%
alkali-rich accelerator
CSA / burnt oil shale-based cement

OSF: Burnt oil shales stored for 1 day at 23°C and 65% relative humidity
OSA: Burnt oil shales stored for 3 months at 23°C and 65% relative humidity

SC OSF: Blend with OSF as component
SC OSA: Blend with OSA as component
SC OSA CO₂: Blend with OSA cured in a CO₂ saturated atmosphere as component
SC OSA (CaO, CH): Blend with OSA and CaO, CH as components
CSA (RF): Technical calciumsulfoaluminate

Sulfate attack (5% Na₂SO₄ solution)

S/ST: Cement I / 1% plasticizer / 23°C
ST/ST: Cement I / 1% plasticizer / 65°C

S/AF: Cement I / 1% plasticizer / 6%
alkali-free accelerator I (dry mixed) / 23°C
ST/AF: Cement I / 1% plasticizer / 6%
alkali-free accelerator I (dry mixed) / 65°C

S/AF2: Cement I / 1% plasticizer / 6%
alkali-free accelerator I (wet mixed) / 23°C
ST/AF2: Cement I / 1% plasticizer / 6%
alkali-free accelerator I (wet mixed) / 65°C

S/L50: Cement I / 1% plasticizer / 8%
alkali-free accelerator II / 23°C
ST/L50: Cement I / 1% plasticizer / 8%
alkali-free accelerator II / 65°C

S/L20: Cement I / 1% plasticizer / 4.5%
alkali-rich accelerator / 23°C
ST/L20: Cement I / 1% plasticizer / 4.5%
alkali-rich accelerator / 65°C
Publications


Curriculum Vitae


1997-2000  Ph. D and teaching assistant at the Institute of Building Materials, Material Chemistry and Corrosion at the Swiss Federal Institute of Technology, Zurich (ETH-Zurich) in collaboration with the Admixture Department, Central R&D, SIKA AG Zurich.

1999  Literature search on Sulfate Attack on Concrete Structures for the Alptransit base tunnels for the Expert Commission (Beton-Zulassungsprüfungskommission).

Major: Geological Engineering, Mineralogy and Petrography
Diploma Thesis title: "Structural and Petrographic Investigation along the South Margin of the Malenco Ultramafic Intrusion (Italy)."


1977-1986  Primary and secondary schools in Lugano and Bellinzona.
1. Introduction

1.1 General overview

The acceleration of the chemical reactions within cement systems is a matter of considerable concern and at the centre of a number of investigations. The accelerated set and hardening of the cementitious systems become decisive within the first 14 hours and generally influences the long-term mechanical properties.

The acceleration of the chemical reactions may be attained throughout the addition of special set and hardening accelerating admixtures [1]. The acceleration of the setting becomes especially important in shotcrete applications where concrete (shotcrete) or mortar (gunite) are sprayed onto the tunnels walls for immediate temporary support following excavations in unstable ground [2]. In this context, different requirements such as for instance rapid set, early strength, and a good satisfactory adhesion to the substrate [3] must be attained.

In general, accelerators, commonly calcium chloride, sodium carbonate, silicate and aluminate [4], enhance the mechanical properties of the shotcrete in particular at early stages, but their use often results in strength decrease at later stages [4-8]. These reductions in the strength appear to be most pronounced when flash setting is promoted [5, 8]. Additional technological requirements such as for instance the rebound, the permeability, the causticity of the fast set-agents and the related health risks [9] promoted the development of new admixtures.

In this context, alternative alkali-free, calciumsulfoaluminate-based accelerating admixtures were developed in order to substitute the alkali-rich-based accelerators. In spite of the general improved performances, the alkali-free admixtures developed, also had the disadvantage of leading to slight strength decrease at later stages.
With regards to the durability, the use of accelerators in shotcrete or gunite usually appears to have adverse effects [4, 6, 10]. Therefore, as the accelerated shotcrete mixtures are used in tunnel applications and thereby exposed to circulating sulfate-rich waters, the sulfate resistance of the concretes must be carefully considered.

Accelerated cementitious systems may also be attained with the use of very rapid hardening blends. These special blends are mainly used for construction or repair works, where high early minimum strength values are required (5 MPa for structural elements; 15 MPa for airfield, highways, precast tunnel elements; >25 MPa for structural elements under high load) [11].

The cements of which these blends are often composed of, mainly consist of special manufactured high reactive aluminate-rich clinkers, such as \( \text{C}_11\text{A}_7\cdot\text{CaF}_2 \) (regulated set cements), CA (Ciment Fondu) and \( \text{C}_4\text{A}_3\overline{\text{S}} \) (calciumsulfoaluminate cements). Mixtures of these cements with anhydride, ordinary portland cements (OPC), other hydraulic binders, and chemical admixtures also result in high early strengths [4, 11]. The formation of calcium aluminate hydrates and ettringite appears to be the main strength supporting phase of these high strength systems. As an alternative to these ettringite-based strength supporting systems, chemically modified OPC were also developed [11].

The use of these special concretes allows to accomplish constructional works within remarkably shorter times, thus leading to considerable cost reductions.

As part of the latter category, a very rapid CSA / burnt oil shale, high early strength composite cement was developed. This special blend exhibits strength of up to 25 MPa at 3-5 hours with a considerable workability (30-40 minutes) [12, 13]. Nevertheless, the use of CaO-rich burnt oil shales shows a delay in the early strength development, which could be correlated to the free CaO content of the burnt oil shales.
1.2 Thesis objectives

The aim of the present work was at the one hand to investigate the influence of alkali-free, calciumsulfoaluminate-based shotcrete accelerators on the setting and the strength development of cementitious mixtures.

The main goal was to characterize the rapid setting and to explain the reasons for the strength decrease taking place at later stages. A comparison with the alkali-rich accelerated mixtures was also matter of concern (chapter 4.1).

On the other hand, the durability of these accelerated mixtures was also investigated (chapter 4.2). Mechanisms of attack and damage, resulting from the interaction with Na₂SO₄ solutions were analyzed at 23 °C and at 65°C. Particular attention was paid to the role played by the supplementary enrichment of aluminates caused by the addition of the admixtures.

Moreover, the accelerating behavior of calciumsulfoaluminate in a rapid hardening cement must also be studied (chapter 4.3). In this system calciumsulfoaluminate was added to a burnt oil shale-based cement and high early strength was achieved. The hydration products responsible for the high early strength, and the influence of both the CaO content and the hydration products formed during the storage of the burnt oil shales were characterized in order to find out the reasons for the delayed strength development of the blends.
2. Literature

2.1 General introduction

In the present work, the calcium sulfoaluminate (CSA), is investigated as alkali-free accelerating component of the setting and to improve the strength of shotcreting applications. In this concern, a comparison with the alkali-rich accelerated mixtures and the sulfate resistance is also considered. At the other hand, the calcium sulfoaluminate is added as activator within a burnt oil shale-based blend in order to obtain a very rapid hardening concrete.

Thus the influence of the accelerators, in particular the alkali-rich and alkali-free admixtures, on the mechanical properties of the shotcrete is reviewed. Moreover, a gain in knowledge in the ettringite formation from the CSA (C₄A₃S) and its stability also assumes a central role. In fact, depending on the conditions, the crystallization of ettringite crystals as setting and strength determining factor as well as from the reaction of sulfate solutions with cementitious phases, greatly affect the mechanical properties of the cementitious mixes.

Furthermore, the features of the oil shales and their burnt ashes, base component of the rapid hardening calcium sulfoaluminate activated blend, are described.

2.2 Shotcrete

2.2.1 Cementing materials, additives, aggregates

The main commercial cements are used in shotcrete applications [14, 15], although in several cases, alumina cements are used in refractory shotcrete constructions [16], and sulfate-resisting cements in remedial works subjected to sulfate exposure [14]. The cement dosages are usually high [17] and range between 250 and 450 Kg / m³ [15] or higher.
Additives such as pozzolanic materials (e.g. fly ash and silica fume) are often added (< 15%) [14, 18] to improve the mechanical parameters of the shotcrete. The main benefits are depicted in Tab. 2.1 for wet shotcrete [14].

<table>
<thead>
<tr>
<th>Silica Fume</th>
<th>Fly Ash</th>
</tr>
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<tbody>
<tr>
<td>Adhesion, cohesion, reduced rebound</td>
<td>Workability, pumpability with harsh aggregates</td>
</tr>
<tr>
<td>Thickness of the build-up layer, reduction of the accelerator</td>
<td>Reduce alkali-aggregate reaction</td>
</tr>
<tr>
<td>Compressive, flexural strength and durability</td>
<td>Sulfate resistance</td>
</tr>
</tbody>
</table>

Tab. 2.1: Shotcrete benefits with the addition of silica fume and fly ash [14].

The aggregates generally correspond to the those employed in conventional concrete. Because of the reduced rebound and the increased adhesion, fine-sized aggregate-rich mixtures are often used [15, 18].

2.2.2 Accelerators

Shotcrete accelerators mainly consist of calcium chloride, sodium carbonate, silicate, aluminate [4], alkali metal hydroxide and organic chemicals [2], and are used to increase the build-up in a single pass (productivity enhancement) and to reduce the initial setting and increase the early strength development (24 hours) [14].

The setting of OPC is usually attributed to the crystallization of ettringite, CSH and CH during the acceleratory period. A recrystallization of microcrystalline ettringite to well developed crystals [2, 19] and ettringite with a stubby rod morphology are also assumed to cause the setting [20, 21]. Being the setting a mechanical process, these hydrates do not necessarily need to be largely present. In fact, the moderate presence of cohesion points is sufficient for the setting [2, 4, 22-24].
On the other hand, the accelerating admixtures promote the $C_3A$ hydration, resulting in the precipitation of insoluble calcium salts, partly derived from the admixture itself. The ettringite formation taking places with the addition of aluminates appears to be the main cause of the accelerated setting [25]. The addition of admixtures and the resulting increase in the temperature may also promote the hydration of $C_3S$, which support the early strength through the formation of CSH gel [2] with a tobermorite structure [26]. The hydration of the $C_3S$ phase mostly appears to take place with a congruently dissolution of the material [27-30]. The addition of soluble salts changes the rate of ions release from $C_3S$ at very early stages, where the CH delays the $C_3S$ hydration [31].

The accelerating admixtures exhibit different technical features such as causticity, toxicity, transport, storage and have a direct influence on the performance, working safety, and generally on the economic aspects [32]. Increasing requirements on the mechanical parameters, working conditions, safety, lower environmental impact and easier maintenance of existing tunnel facilities promoted the development of alternative technologies in order to substitute the alkali-rich aluminate and silicate admixtures used since present [32, 33]. These technologies consists in the use of alkali-free accelerators as well as shotcrete with a shotcrete-bindner without addition of an accelerator. This latter technology, although succesfully used for some time, revealed its high production and transportation costs [33]. Thus, the low shotcrete performance such as for instance the strength development, the ecology, and the unfavorable working conditions [32, 33] attained with the use of the alkali-rich accelerators was increasingly improved with the development of the alkali-free accelerators [32-34] as depicted in Tab. 2.2 [32, 33].

The development of alkali-free accelerators was based on amorphous aluminum hydroxide combined with reactive sulfates, which resulted in the early strength of the shotcretes [34]. The dosage of the admixtures normally ranges between 3 and 6 % referred to the cement weight [18, 34].
2.2 Shotcrete

### Parameters

<table>
<thead>
<tr>
<th></th>
<th>Alkali-free accelerators</th>
<th>Alkali-rich accelerators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working environment</td>
<td>less dust, reduced chemical burns</td>
<td>intense dust formation, risk of chemical burns</td>
</tr>
<tr>
<td>Mountain water</td>
<td>less leaching, same pH as normal concrete</td>
<td>high pH value, high leaching</td>
</tr>
<tr>
<td>Tunnel drainages</td>
<td>less scale deposit</td>
<td>scale deposit</td>
</tr>
<tr>
<td>Technological features</td>
<td>less rebound, increased strength, water impermeability</td>
<td>extremely fast setting, high rebound, strength reduction, high porosity, low structural density</td>
</tr>
<tr>
<td>Average alkali-content</td>
<td>&lt; 0.2%</td>
<td>&lt; 25 %</td>
</tr>
<tr>
<td>pH</td>
<td>4 - 6</td>
<td>11 - (&gt; 13</td>
</tr>
</tbody>
</table>

Tab. 2.2: Comparison between alkali-free and alkali-rich accelerators. Table modified from Huber [33].

As it can be seen from Tab. 2.2, these new admixtures indicate various technical advantages other than the strength and offset the higher materials costs compared to the alkali-aluminate accelerated shotcrete [33]. In particular, the obstruction of tunnel drainage systems is reduced [32, 34]. In fact, during the leaching process, hydroxides, mostly Ca(OH)₂ are washed out from the shotcrete through the mountain water, which, in contact with CO₂, air or H₂CO₃ aggressive waters, precipitate to limestone, thereby clogging the drainages. When additional soluble alkalis such as KOH, NaOH are washed out (alkali-rich accelerators), the Ca(OH)₂ solubility decreases and the precipitation of limestone is favored [32, 34].
2.2.3 Strength

Generally, the strength of cementitious systems is related to different factors such as porosity [35-41], specific surface area [42, 43], main clinker minerals proportions [44-53], particle size distribution [43, 54-56], clinker microstructure [57-66], and SO$_3$ content [54, 67]. The effect of minor components such as alkalis [68, 69] and MgO [44, 68, 70] appears to be not uniform or insignificant, whereas the CaO content affects the strength mainly by inducing unsoundness, volume instability and cracking. Moreover, the different components of the concrete such as cement paste, aggregates and its heterogeneous nature may overshadow the role of the interfacial zone (cement paste-aggregate) [2]. Cohesion is often attributed to the interlocking of needle-like particles, although attractive forces between adjacent CSH layers or other phases are probably more important [4].

Concrete deforms plastically after the maximum load is exceeded and appears to fail progressively [71], whereas hardened cement pastes fail suddenly with a brittle behavior. In this context, the features of the microstructure that promote high local stress or act as crack arrester become very important [4]. The anhydrous material [72], the porosity [4, 73, 74], the crack propagation [75], CH crystals [76], and the structure-mechanical heterogeneities within OPC pastes [77, 78] influence the fracture development.

The fracture behaviour of brittle materials like cement paste, is described with the non-linear fracture mechanic, which assumes a stress release on the crack front when a critical tensile strength value is reached [79]. The fracture of cement pastes is preceded by a zone of micro-cracking (fracture zone or process zone) after the crack front and is characterized by a stress decrease with increasing microcracking and increasing deformation. The stress distribution indicates a zero value on the crack front, and reaches a maximum values in the vicinity of the micro-cracks zone. Failure starts, when microcracks gradually change into more or less visible cracks, whilst in some cases the paste still can carry some stress [80].
During the tensile test to complete separation, energy is adsorbed inside and outside the fracture zone. The general adsorption of energy in a crack describing a simplified fracture zone is depicted in equation (2.1).

\[ A \int_0^{\infty} \sigma \, d\varepsilon = AG_f \]  

(2.1)

A: cross sectional area
wl: (deformation) w-value for \( \sigma = 0 \)
\( \sigma \): stress
\( G_f \): specific fracture energy (area below the \( \sigma - \varepsilon \) curve)

\( G_f \) thus describes the adsorbed energy per unit crack area for the complete separation of the crack surfaces, namely the specific fracture energy [80].

2.2.4 Strength of the accelerated mixtures

The acceleration of the early reaction attained with the addition of accelerating admixtures, greatly affect the microstructure. In fact, the high early strength at early ages, is generally followed by a strength decrease at later ages [4]. This fact must be considered in particular for underground tunnel construction where a shotcrete must set quickly with an early strength development in order to support the surrounding strata of the tunnel. Two different processes are distinguished during shotcrete applications: "dry" process, where the accelerator is dispersed as a powder and intermixed with the dry components before they are conveyed to the nozzle or added as a liquid with the mixing water at the nozzle, and "wet" process, where the concrete is premixed with water prior to pumping to the nozzle. In "wet" processes the accelerator is added in liquid or powder form to the stream of compressed air at the gun [2]. Traditionally, because of the higher water demand in wet-mix shotcrete they were considered inferior to dry-mixes with respect to strength. However, with the advent of superplasticizers and silica fume, this is no more true [14].

The final strength of shotcrete is adversely affected by the use of accelerators [2, 4-8, 14]. The higher the dosages and the consequently shortened setting times, the higher the strength decrease at later stages [2, 5, 8]. The strength decrease is mostly accounted for by the textural changes resulting from the shotcreting procedure [18], or for the fast crystallization of hydration products as well as for the addition of foreign ions such as alkali-ions
throughout the admixtures [15]. Strength decrease may therefore not be directly caused by the accelerating admixture itself, but also by the application technique, which may influence the texture, adhesiveness, rebound and compaction of the mixtures [18]. Generally, compared to the powdery admixtures, the use of liquid ones allows a better mixing with the concrete, thus reducing the final strength losses [15].

2.2.5 Resistance to sulfate attack

2.2.5.1 General considerations

Compared with the conventional concrete, shotcrete exhibits comparable general durability [17, 81], but the application in different sprayed layers avoid a continuous capillary porosity through the material and sometimes reduce its permeability [15, 81]. Nevertheless, concretes are attacked by sulfate solutions. The sulfate ions react with compounds present in the cement damaging it [2]. Sulfate attack was often described as the reaction between the solid phases in the cement paste and dissolved compounds within the attacking solution, such as Na$_2$SO$_4$ or MgSO$_4$. The phases in the cement which are mostly susceptible to sulfate attack are CH, unhydrated C$_3$A, aluminate hydrates such as C$_4$AH$_n$, C$_3$AH$_6$, C$_3$A.CaSO$_4$.H$_{12}$ and their solid solutions C$_3$A (CH, CaSO$_4$, CaCO$_3$)H$_n$. The most resistant phase amongst the aluminate hydrate phases are more resistant [82], and significant improvements against sulfate attack were achieved by replacing C$_3$A with C$_4$AF [2]. It was reported that competing reactions take place within the pore solution of cements. This is the reason why, for instance, Na$_2$SO$_4$ solutions may cause both sulfate attack and alkali-silica reaction (ASR) [83, 84], and MgSO$_4$ solutions reactions forming brücke [4].

Attempts were made to predict the potential resistance of cements by measuring the initial ratio of the different oxides such as SO$_3$, Na$_2$O [85]. Despite the number of correlations found with different oxides and phases within the cement, the C$_3$A content in the cement showed the most direct relationship with the chemical resistance and a general threshold value between 3.5 and 5.5 % was established for sulfate resistant cements [2, 4]. In sulfate resistant cements smaller quantities of Al$_2$O$_3$ are present, and the potential of forming C$_6$A$\bar{S}$$_3$H$_{32}$ is, therefore, reduced [86].
Low W/C improves sulfate resistance to both external and internal sulfate attack. Reduced porosity is more important in the case of external attack since it prevents sulfate ion penetration [87]. Low W/C can be achieved with plasticizers, which decrease the porosity and increase the properties of the mortars, although W/C around 0.4 can occasionally show water separation, causing locally very porous hardened paste [91]. In most cases, a correlation between permeability, sulfate ion penetration and resistance was found [4], even though the strength of the solution and the composition of the cement bare an important influence on the rate of the attack [2].

Depending on the SO$_3$ content, soils and waters are known to attack concrete structures. Despite differences within European countries, values from the UK (Table 2.3) are taken as an example to classify the severity of the exposure conditions [2].

<table>
<thead>
<tr>
<th>Severity of exposure conditions</th>
<th>Total SO$_3$ (%)</th>
<th>SO$_3$ in 1:2 soil/water extract (g/L)</th>
<th>g/L Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate</td>
<td>0.2-0.5</td>
<td>1.0-1.9</td>
<td>0.3-1.2</td>
</tr>
<tr>
<td>Severe</td>
<td>0.5-1.0</td>
<td>1.9-3.1</td>
<td>1.2-2.5</td>
</tr>
<tr>
<td>Very severe</td>
<td>1.0-2.0</td>
<td>3.1-5.6</td>
<td>2.5-5.0</td>
</tr>
<tr>
<td>Extreme</td>
<td>&gt;2.0</td>
<td>&gt;5.6</td>
<td>&gt;5.0</td>
</tr>
</tbody>
</table>

*Tab. 2.3: Classification of the severity of exposure for concrete structure exposed to sulfates. British standard 8110 [2].*

Two main forms of attack are usually described: the first is of an external type, occurring when cement mixtures are exposed to a sulfate-rich environment; the second is of an internal type due to the presence of sulfate-rich constituents in the cement-based mixtures. The internal form of attack is mainly caused by gypsum rich aggregates [87], or by a too high gypsum dosage in the cement [88]. Gypsum normally reacts with cement alkalies to form CH through a topochemical reaction, whereas sulfate ions enter the solution triggering ettringite forming reactions.
Compared to the external attack, in which sulfate ions must penetrate into the matrix prior to initiating reactions, leading to expansion and cracking, which in turn further accelerates sulfate ion penetration, in the internal attack the amount of sulfate ions decreases as the chemical reaction proceeds. In this case the rate of attack tends to slow down with matrix age. The cement dosage [87] and type [89] are also of importance in the internal attack. The sulfate liberated during the hydration of sulfate-bearing clinkers, for instance C$_2$S (0.83 SO$_3$%), must also be taken into account (chapter 2.2.5.6) [90].

The main form of sulfate attack was often caused by the penetration of sulfate solutions into the cement. Calcium, magnesium, sodium and potassium sulfates are found throughout the world in clays and in different soils, frequently in considerable quantities [2]. Solutions consisting of magnesium, sodium and potassium sulfate were often used to explain the reaction mechanisms involved between soluble sulfate and the cement matrix.

### 2.2.5.2 Reaction mechanisms with Na$_2$SO$_4$ solutions

Whilst calcium sulfates react only with the hydrated aluminates to form calciumsulfoaluminate, sodium sulfates react with hydrated aluminates and CH to form ettringite and gypsum. The two main reactions are highlighted in the equations (2.2) (2.3)[2].

$$Na_2SO_4 \cdot 10H_2O + CH \leftrightarrow C\tilde{S}H_2 + 2NaOH + 8H_2O \quad (2.2)$$

$$C_4AH_19 + 3C\tilde{S}H_2 \leftrightarrow C_6A\tilde{S}_3H_{32} + CH + 9H_2O \quad (2.3)$$

Experiments conducted at 25°C with different sulfate concentrations, assuming gypsum in equilibrium with a 0.125 M sodium sulfate solution, give the indicative ettringite stability domains depicted in Fig. 2.1.
Fig. 2.1: *Evolution of the ettringite stability domains during the addition of sodium*
[92].

Ettringite is stable over a wide range of sulfate concentrations. The presence of sodium modifies the ettringite stability domain but ettringite remains stable even at high sodium concentration, although the stability domain is displaced to lower calcium, but to higher aluminum concentrations [92]. The sulfate concentration of the solutions and the availability of the aluminate seems to determine the phase formation. For instance, low sulfate concentration in the solution < 0.12 % (8.45 mM SO$_4^{2-}$) and high C$_3$A content promote ettringite formation [93], whilst higher sulfate concentrations and lower C$_3$A content seems to promote gypsum formation [93].

Under normal pH conditions of the cement pore solution (pH = 13-13.5) calcium silicate hydrate gel is stable. Furthermore, the exchange Ca$^{2+}$ = Na$^+$ does not appear possible, mainly because of the ion diameter difference. Nevertheless, initial CSH decalcification was already observed [94]. Sulfate concentrations higher than 0.15 M attack not only C$_3$S pastes but β-C$_2$S pastes as well, possibly resulting in gypsum formation [83]. The CH dissolution and the CSH decalcification release a quantity of OH$^-$ equivalent to the SO$_4^{2-}$ taken up in ettringite and gypsum. If the cations in the attacking solution are Na$^+$ or K$^+$, OH$^-$ remains in the solution, and this can cause ASR if the aggregate is reactive [4, 95].
2.2.5.3 Reaction mechanisms with MgSO₄ solutions

Magnesium sulfate has a more severe action than other sulfates and decomposes the hydrated calcium silicates in addition to reacting with hydrated aluminates and calcium hydroxide [2]. The Mg²⁺ reacts with OH⁻ ions from the pore solution, giving brucite according to equation (2.4).

$$\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2$$ \hspace{1cm} (2.4)

Because of its low solubility, it can form a dense skin on the mortar surface and this tends to hinder further penetration of the solution [96]. On the other hand, the hydrated calcium silicates react according to equation (2.5).

$$3\text{CaO} \cdot 2\text{SiO}_2\text{aq} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \leftrightarrow 3\text{CSH}_2$$

+ $3\text{Mg(OH)}_2 + 2\text{SiO}_2\text{aq}$ \hspace{1cm} (2.5)

The reason why this reaction proceeds to completion, in contrast to sodium sulfate, is due to the low solubility of the Mg(OH)₂ and the resulting low pH value of its saturated solution (pH = 10.5). Under these pH conditions, hydrated calcium silicates are not stable. The silicates liberate lime to the solution to establish their equilibrium pH, but when magnesium sulfate is present, the lime reacts with it, forming magnesium hydroxide thus reducing the pH value to 10.5 once again. As a consequence, more lime goes into solution to re-establish the pH, driving the reaction further [2, 97]. At pH around 10.5 ettringite is also unstable and decomposes to gypsum, aluminate and calcium carbonate.

The general mechanism of attack appears to be dependent on the sulfate concentration of the attacking solutions: at sulfate concentrations < 0.48 % (39.89 mM SO₄²⁻) the attack is dominated by ettringite formation, whereas with concentrations ranging between 0.48 and 0.75 % (39.89 - 62.33 mM SO₄²⁻) the mechanism is controlled by a combined ettringite-gypsum formation. At higher concentrations, magnesium attack occurs when magnesium sulfate and hydrated calcium silicates react in solution to form gypsum, Mg(OH)₂, and silica gel. Subsequently, magnesium hydroxide can
react with the silica gel to form water and hydrated magnesium silicates according to equation (2.6).

\[ Mg(OH)_{2} + SH \rightarrow M_{4}SH_{8.5} + xH_{2}O \quad (2.6) \]

The phase \( M_{4}SH_{8.5} \) is non-cementitious [98] and results by the complete replacement of \( Ca^{2+} \) with \( Mg^{2+} \) [99]. In some cases poorly crystalline serpentine (\( M_{3}S_{2}H_{2} \)) is also formed [100]. These hydrated magnesium silicates represent the final stage in the deterioration of concrete attacked by magnesium sulfate solutions, although in practice it may only be reached after long periods of time [2].

### 2.2.5.4 Damaging mechanisms

The main type of damage caused by sulfate attack are cracking or spalling of the concrete or softening and disintegration.

Reaction products such as ettringite and gypsum, formed under sulfate solution attack, have a greater volume compared to the initial phases needed for their formation, as can be seen in Tab. 2.4.

<table>
<thead>
<tr>
<th>Initial phase</th>
<th>Reaction product</th>
<th>Amount needed for the conversion Kg/Kg IP SO₃ SO₄ Solution</th>
<th>Volume change (%)</th>
<th>Additional formed volume l/Kg IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>Gypsum</td>
<td>1.1</td>
<td>200</td>
<td>0.4</td>
</tr>
<tr>
<td>C₃A_H₆</td>
<td>AFm</td>
<td>0.2</td>
<td>250</td>
<td>0.6</td>
</tr>
<tr>
<td>C₃A_H₆</td>
<td>AFt</td>
<td>0.7</td>
<td>480</td>
<td>1.5</td>
</tr>
<tr>
<td>AFm</td>
<td>AFt</td>
<td>0.3</td>
<td>230</td>
<td>0.7</td>
</tr>
</tbody>
</table>

*Tab. 2.4: Mass and volume proportions of the main phases formed during the attack of sodium sulfate [88].*

When insufficient pore space is available to accommodate the hydrates formed during the penetration of the attacking solution, expansion forces result, mainly due to ettringite formation. The pressure build-up during the
crystallization is mainly caused by confined crystal growth, and occurs if the activity product of the reactants in the pore solution is greater than the solubility product of the solid product [101,102]. Hydrated calcium aluminates immersed in gypsum saturated solutions may cause pressures around 0.63 N/mm² after 4 days [88]. It is sometimes difficult to estimate the expansion caused during the formation of the ettringite crystals. However, it was reported that ettringite formed from a topochemical reaction contribute to a greater extent to the expansion compared to those ettringites crystallized from a saturated pore solution [2]. It appears that a decrease in the hydroxil ion concentration and an increase in the sulfate ion concentration in the environment lowers the stiffness of the cement paste and increases the water-adsorption capacity of the ettringite [103]. Although the contribution of gypsum to the expansion remains unclear [2], Metha [103] proposed that, as a result of gypsum formation and sulfate adsorption by CSH, some reduction in the stiffness of hydrated cement paste is proceeded by a large expansion due to ettringite. SEM investigations often show ettringite enrichment in the interface zone between cement and aggregate [4], but because of the different reaction mechanisms involved (chapter 2.2.5.2; chapter 2.2.5.3), a direct relationship between ettringite amount and expansion was not, as yet, found [4, 93, 104, 105].

It can also generally be stated, that the decalcification of the CSH gel is more accentuated with MgSO₄ solutions compared to Na₂SO₄ solutions and the samples tend to soften and disgregate through the formation of a non-cementitous MSH gel [93, 96, 98, 106, 107]. Softening and disintegration were also attributed to gypsum formation [108]. Ettringite, on the contrary, tends to cause expansion and the subsequently formation of cracks [96].

The different processes leading to damage can often not be distinguished from one another, due to the different reaction mechanisms simultaneously involved [105]. They also are dependent on the Al₂O₃ content of the cement [93, 100] and on the type of the attacking sulfate solution. Furthermore, additional processes which act directly or indirectly such as ASR, various chemical and bacterial attack, and leaching, which causes the dissolution of CH, hydrated aluminate and silicate phases, can promote different types of damage. The chemical and physical conditions of the environment influence the type of processes that take place and makes it difficult to associate a particular damage to one specific reaction only.
2.2.5.5 Influence of the additives

Granulated blast furnace slag, pulverised fly ash, silica fume

Partial replacement of cement by pozzolanic active additives, can often increase the resistance against Na$_2$SO$_4$ attack and to a lesser extent against MgSO$_4$ [109]. The additives react with the CH formed during the cement hydration, to generate CSH gel (pozzolanic reaction). A certain length of time is required for the pozzolanic reaction to occur, therefore the curing time of the samples should be long enough for the pozzolanic "effect" to be achieved [4, 84]. Thanks to the latter reaction, the interface zone between cement and the aggregate is densified and the sulfate ions penetration is therefore reduced. Furthermore, additives reduce the concentration of ions like Ca$^{2+}$ and SO$_4^{2-}$ in the pore solution with respect to the formation of ettringite or gypsum [110], and this is always a beneficial effect for the increased sulfate resistance [2, 101].

The effectiveness of the additive on the resistance, depends on properties and proportions of the different slags [4]. Good results on the resistance are reached when the water requirement [111] and sulfide content of the slags [96] are low. The Al$_2$O$_3$ content must also be taken into account: contents of 11% or 17.7% appear not to have a negative influence on the resistance if the slag content of the composite cement reaches at least 65%; in contrast, with a lower slag content, the Al$_2$O$_3$ amount should be maintained low [112]. Substitution of 22% pulverised fly ash, 9% silica fume and 80% granulated blast furnace slag showed to improve the resistance [113]. In general low calcium content is reported to slightly improve the resistance, whilst the slag size to have a variable influence [96, 111, 4]. The ratio between CaO and aluminates into the amorphous phases of fly ashes was often used to estimate their potential resistance, although their SiO$_2$ content should not be too high because of the possible accelerated formation of non-cementitious M$_4$SH$_{8.5}$ during MgSO$_4$ attack [114].

Gypsum, Mg(OH)$_2$, M$_4$SH$_{8.5}$ and M$_3$S$_2$H$_2$ are the main phases formed during MgSO$_4$ attack of blended cements and the main damage was found to occur tendentially through the weakening of the CSH matrix, causing disintegration of the samples. CSH decalcification can, however, also occur with Na$_2$SO$_4$ solutions [96]. Destruction of CSH is favored by low or zero content of CH which is consumed through the pozzolanic reaction. If sufficient CH is available, it acts as the preferred source of Ca$^{2+}$ ions and,
thus tends to protect the CSH from attack [115]. Furthermore, it was suggested that CSH gel, formed through the pozzolanic reaction, is attacked more by MgSO₄ solution, compared to CSH, formed through the C₃S hydration [116, 117].

Blended cements attacked by Na₂SO₄ or MgSO₄ solutions generally tend to soften and disintegrate rather than to expand with the consequent cracks formation [96].

**Carbonate**

The addition of small size CaCO₃ to OPC composites slightly improves the sulfate resistance, thanks mainly, to the formation of the more resistant phase amongst the aluminate hydrates, namely C₃A.CaCO₃.H₁₂ instead of C₃A.CaSO₄.H₁₂ (Monosulfate) [82]. On addition of CaO and SiO₂ (from CSH) and carbonates, ettringite, which is formed from the C₃A under the influence of sulfate-rich waters, converts into thaumasite, Ca₃Si(OH)₆(SO₄)(CO₃).12H₂O. An additional ettringite phase containing SiO₂ and CO₂ was recognized as woodfordite 6CaAl₁.₅(SO₄SiO₃CO₃)(OH)₁₀.₅.₁₅H₂O [118]. The thaumasite formation is favored at constant pH conditions, temperatures around 4 - 6 °C, and by sufficient supply of H₄SiO₄ and CO₃²⁻ ions [119]. Its unit cell occupies 45% of the volume of the ettringite unit cell, and it therefore give rise to smaller expansion compared to ettringite [88, 120]. Thaumasite mainly causes a disgregation and a weakening of the cement matrix [4].

Coarse limestone aggregate favors a tighter and stronger transition zone between the grain and the bulk paste, resulting in a lower degree of orientation of portlandite and ettringite crystals [121]. In some cases topochemical growth of CH upon CaCO₃ crystals might occur, leading to a facilitated access of sulfate ions and to the formation of gypsum [110]. Destructive expansion was observed in concrete containing dolomite as aggregate caused by the so-called dedolomitization reaction depicted in equation (2.7) [4].

\[ CaMg(CO₃)₂ + 2OH^- \rightarrow CaCO₃ + Mg(OH)₂ + CO₃^{2-} \] (2.7)
Under, as yet, unclear conditions, ettringite is reported to form via the reaction between monosulfate and calcite according to equation (2.8).

\[ 3C_4A\tilde{S}H_{12} + 2\tilde{C}C + 18H_2O \rightarrow 2C_4A\tilde{C}H_{11} + C_6A\tilde{S}_3H_{32} \] (2.8)

although it is still not clear if this reaction may really cause expansion in concrete [122].

The carbonation process of surface layer generally improves the response to sulfate attack, reducing the permeability of the samples. This positive effect seems to occur for both OPC and composite cements [123, 124].

### 2.2.5.6 Influence of elevated temperature

Temperature is known to influence the external sulfate attack rather than the internal one [89]. Increasing the temperature (\( \leq 40^\circ C \)) has a deleterious effect on the resistance of OPC cements, mostly due to an acceleration of the main reactions. This temperature effect appears to be less harmful in composite cements. This seems to be a general feature, although more pronounced with MgSO\(_4\) solutions [113, 117].

At higher temperatures (\( \geq 40^\circ C \)) the capillary and volumetric water absorption are reduced, thus lowering the diffusion rate of sulfate ions [117]. The solubility of CH is reduced and the solubility products of ettringite and gypsum are modified [101]. Sulfates and aluminate ions are adsorbed with a reversible process on the CSH surface. The mechanism remains partially unclear, but it is known that, a higher pH of the solution promotes the ion adsorption, and it is believed that ions are held more tightly if the curing temperatures are high. It was also suggested that sulfur-to-alumina ratio of the CSH close to three, can cause expansive stress [90, 125]. When the temperature is decreased, the adsorbed ions pass into the solution and delayed ettringite formation (DEF) may restart. In all cases, a rather long induction period is required for the ions to migrate to the nucleation site and cause expansion [2]. DEF may occur if the concrete temperature during curing or in service reaches a temperature high enough to decompose ettringite, or if the clinker contains a substantial amount of slowly soluble sulfate (clinker sulfate levels may be as low as 1.5 % to cause DEF). Depending on the cement composition, the critical temperature to cause DEF may be as low as 60 °C [90], although some authors suggested 60 and 75°C [91] or 70°C for UK-cements [126]. At higher temperatures (90°C)
expansion increases with cement grain size, C₃A content, C₃S content, MgO and alkali content (Na₂O eq.)[126].

It is common to find secondary ettringite (DEF) in association with alkali-silica gel. Ettringite formation is more favorable in solutions low in alkali, therefore locally lowered alkali concentrations in the solution, due to alkali silica reaction, could lead to a situation in which ettringite formation is preferentially favored especially because of the locally low pH and of low alkali / hydroxile concentrations. Alkali and more important, hydroxil ion consumption through the formation of alkali silica gel, seems to facilitate the formation of delayed ettringite. Secondary ettringite occurs at specific locations of low pH, and this correspond to sites where ASR take place, namely the paste-aggregate interface. Ettringite formation takes up a significant amount of water, thereby elevating the alkali concentration of the solution which is again reduced by further ASR. The kinetics of ASR appears to be qualitatively linked with the rate of ettringite formation [127, 128].

The stability domain of ettringite in deionized water reaches temperatures between 100 and 130 °C [129, 130]. The presence of alkalies considerably reduce the domain of thermal stability of ettringite [125, 130]. The main decomposition reactions occur already between 60 and 80 °C according to equation (2.9).

\[
C₆ÅS₃H₃₂ + 4(Na,K)OH \rightarrow C₄ÅSH₁₂ + 2(Na,K)₂SO₄ + 2CH + 20H₂O \tag{2.9}
\]

whereas at temperatures around 80°C and at higher hydroxide concentrations, the reactions (2.10) and (2.11) were observed.

\[
C₆ÅS₃H₃₂ + 6(Na,K)OH \rightarrow C₄AH₁₃ + 3(Na,K)₂SO₄ + 2CH + 19H₂O \tag{2.10}
\]

\[
C₆ÅS₃H₃₂ + 6(Na,K)OH \rightarrow C₃AH₆ + 3(Na,K)₂SO₄ + 3CH + 26H₂O \tag{2.11}
\]
A general increase in the OH⁻ concentration forces the intermediate CaSO₄, formed through the decomposition of ettringite, to react giving CH and Na₂SO₄ according to the equation (2.12).

\[ CaSO_4 + 2(Na,K)OH \leftrightarrow Ca(OH)_2 + (Na,K)_2SO_4 \]  

(2.12)

At room temperature the reaction is shifted towards CaSO₄ and consequently towards ettringite formation [130].

### 2.3 Rapid hardening CSA-based cements

#### 2.3.1 Manufacturing and composition

CSA (Klein’s compound: C₄A₃S) is an important mineral phase for rapid hardening of sulphoaluminate cement. Its formation from molar mixes of the oxides of calcium aluminum and sulphur derived from synthetic pure chemicals or commercial natural raw materials such as limestone, bauxite, gypsum or phosphogypsum is in the temperature range between 950 °C and 1350 °C. The sulfates and alumina required for the manufacture of these cements can not only be derived from commercial or raw materials, but also from industrial process wastes, such as fly ash, blast furnace slag etc. [131]. These cements belongs to the energy saving low temperature cements. For the production of ordinary portland cement (OPC) the theoretical energy required is 1756 kJ/kg; most of this energy is spent in the calcination process and formation of the high lime containing phase C₃S at 1450°C. The high lime containing phases C₃S and C₃A of OPC were suitably replaced by two low lime sulfate phases CSA (C₄A₃S) and C₅S, which are responsible for the setting and hardening properties of this cement. The total lime requirement to produce such a modified cement is about 15% (weight) less compared to OPC cements. Hence, the total theoretical heat requirement is about 1337 kJ/kg of clinker [132]. Although CSA (C₄A₃S) starts to form at 830 °C, it is only in the temperature interval between 950 °C and 1100°C that the main CaAl₂O₄ is formed and consumed according to the reaction (2.13).

\[ 3CA + CaSO_4 \rightarrow C_4A_3S \]  

(2.13)
At temperatures above 1100°C, the amount of CA decrease rapidly due to increasing formation of sulfoaluminates [133].

CSA (C₄A₃S) is a member of the sodalite family, a class of compounds with the general formula M₈(T₁₂O₂₄)X₂, composed of tetrahedral buildings blocks, TO₄, where T= Si, Al, Be, Fe³⁺, linked at the vertices via oxygen sharing to form a framework. The latter forms open cages that contain cations, typically Cl⁻, S²⁻ but also SO₄²⁻ etc. Although the structural distortions may be relatively minor, they may have a considerable influence on the reactivity [134]. Strontium sulfoaluminate was also synthesized [135].

Calciumsulfoaluminate cements are defined of primary or secondary use: primary use requires that the cement be used as the bonding material with sand or stone to form mortar or concrete; secondary uses are various, and include mixtures with OPC, where the sulfoaluminate is intended to reduce shrinkage or to increase early strength. Careful attention to bulk chemistry, mixing and burning are essential to obtain a desirable phase balance comprising mixtures of belite and CSA (C₄A₃S) [136]. Sulphoaluminate belite cement clinkers contain C₂S and CSA (C₄A₃S) as the major phases and essentially belong to the five component oxide system CaO - SiO₂ - Al₂O₃ - Fe₂O₃ - SO₃ [137]. The presence of a limited amount of free lime seems to be necessary to promote a rapid strength development, and conditions such that all the SO₃ is bound as CSA (C₄A₃S) is required to avoid atmospheric pollution. The phase composition is given as: C₄A₃S, 54%; C₂S, 32%; C₄AF, 5%; free lime, 9%. The clinker is normally interground with the by-product anhydrite. The optimum SO₃/Al₂O₃ ratio seems to be 1.3-1.9 (20-25% SO₃)[4].

A new calciumsulfoaluminate cement, known as Rockfast cement was developed and used in the production of coal mining roadway supports [138]. The Rockfast clinker is C₃S and C₂S free and contains low amount of CaO and SO₃, so that wet slurries of cement can be pumped for 24 h with little detectable ettringite (C₆A₅S₃H₅₂) formation. The ettringite reaction can be initiated by mixing the mixture with slurries containing gypsum and hydrated lime as activators. Additional varieties of rapid hardening, shrinkage compensating cements were obtained by blending the ground Rockfast clinker with OPC and anhydrite. These cements are in general not suitable in reinforced concrete because of the lack of CH consumed during ettringite formation.
A comparison between the calciumsulfoaluminate-Rockfast clinker and the calciumsulfoaluminate-type K clinker highlighting the main phase differences is shown in the Table 2.5.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Rockfast</th>
<th>Type K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4A_3S$</td>
<td>57</td>
<td>10</td>
</tr>
<tr>
<td>CA</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>$C_{12}A_7$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C$S$</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>$C_2AS$</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>CT</td>
<td>4</td>
<td>0.2</td>
</tr>
<tr>
<td>$C_2S$</td>
<td>0</td>
<td>61</td>
</tr>
<tr>
<td>$C_3S$</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>CaO</td>
<td>0.3</td>
<td>8</td>
</tr>
</tbody>
</table>

Tab. 2.5: Comparison between Rockfast clinker and type-K clinker [11].

### 2.3.2 Hydration and hydraulic properties

The properties of calciumsulfoaluminate cements are mainly influenced by CSA ($C_4A_3S$) which forms ettringite according to the reactions (2.14) and (2.15).

\[
C_4A_3S + 8CS + 6C + 96H \rightarrow 3(C_6A\bar{S}H_{32}) \quad (2.14)
\]

\[
C_4A_3S + 2CS + 38H \rightarrow C_6A\bar{S}H_{32} + 2AH_3 \quad (2.15)
\]

Ettringite produced by the reaction depicted in (2.14) is expansive and this property is exploited in shrinkage-resistant and self-stressing cements [139]. Ettringite formed in the absence of lime, as depicted in (2.15) is non-expansive and generates high early strength in cementitious systems [140]. Hydrates, which are formed in the system, composed by CSA ($C_4A_3S$) - CaSO$_4$ - CaO - H$_2$O by $C_4A\bar{S}H_x$, by $C_6A\bar{S}H_{32}$ and solid solutions of $C_3A$, 0.5 CH, 0.5 C$S$. H$_x$ coexist with hydrates like CH, C$S$H$_2$, AH$_3$ and $C_3AH_6$ in 8 four-phase assemblages. These constituents are closely related to the formation and stability of hydrated products by setting and hardening of hydraulic cement mixture based on a sulphoaluminate clinker. The stability
field of these hydrate assemblages depends on the ratio of CaO/SO$_3$ and Al$_2$O$_3$/SO$_3$. The concentration limits for the phase stability of ettringite were ascertained as $1 < \text{CaO/SO}_3 < 4$ and $0.25 < \text{Al}_2\text{O}_3/\text{SO}_3 < 1$. In the subsystem $\text{C}_4\text{A}_3\overline{\text{S}}-\text{H}_2\text{O}$ the hydration of CSA ($\text{C}_4\text{A}_3\overline{\text{S}}$) proceeds with the formation of $\text{C}_4\text{A}_3\overline{\text{S}}\overline{\text{H}}_{12}$, whereas in the subsystem $\text{C}_4\text{A}_3\overline{\text{S}} - \text{CS} - \text{H}_2\text{O}$, the stoichiometric mixture $\text{C}_4\text{A}_3\overline{\text{S}} / 2\text{CS}$ gave ettringite and aluminum hydroxide as hydrated products, according to the equation (2.15) [141]. Finally, in the subsystem $\text{C}_4\text{A}_3\overline{\text{S}} - \text{CSH}_2 - \text{CH} - \text{H}$ the reactions proceed according to the general scheme highlighted in the equation (2.16)[142].

$$a\text{C}_4\text{A}_3\overline{\text{S}} + b\text{CSH}_2 + c\text{CH} + n\text{H}_2\text{O} \leftrightarrow d\text{C}_4\text{A}_3\text{S}H_x + e\text{C}_6\text{A}\overline{\text{S}}_3\text{H}_{32} + f\text{AH}_3 + g\text{C}_3\text{A} \cdot 0.5 \cdot \text{CS} \cdot 0.5 \cdot \text{CH} \cdot \text{H}_{15} \tag{2.16}$$

When $a = 1, b = 8, c = 6, e = 3, d = f = g = 0$ the subysystem reacts according to the equation (2.17).

$$\text{C}_4\text{A}_3\overline{\text{S}} + 8\text{CSH}_2 + 6\text{CH} + 74\text{H}_2\text{O} \leftrightarrow 3\text{C}_6\text{A}\overline{\text{S}}_3\text{H}_{32} \tag{2.17}$$

The hydraulic activity of the calcia-sulfoaluminate cement clinker is mainly due to the presence of CSA ($\text{C}_4\text{A}_3\overline{\text{S}}$) [142]. Clinker phase compositions control the reactivity and the dimensional stability. In general, sulfoaluminate formulations with added lime, gypsum and calcium aluminates are expansive, but those consisting of CSA ($\text{C}_4\text{A}_3\overline{\text{S}}$) and belite, hydrate rapidly and give rise to dimensionally stable products [143]. Depending on both the rate of formation and the microstructure of ettringite, calcia-sulfoaluminate-based cements can be employed as shrinkage-resistant, self-stressing and high early strength cements. Rapid-hardening is due to the instantaneous formation of non-expansive ettringite which develops relatively large crystals able to provide high mechanical strength at early ages. Satisfactory performance at early or later stages was achieved with cements containing 30-40% CSA ($\text{C}_4\text{A}_3\overline{\text{S}}$) [144]. The main hydration products are ettringite ($\text{C}_6\text{A}\overline{\text{S}}_3\text{H}_{12}$) and calcium silicate hydrates. Mixture of CSA ($\text{C}_4\text{A}_3\overline{\text{S}}$), $\beta$-$\text{C}_2\text{S}$ and $\text{CS}$ (1.5-1-1 weight ratio) hydrate rapidly to ettringite and develop high early 1 day strength; the addition of blast furnace slag or fly ash and slag to the above composition reduces the quantity of ettringite, and consequently, the 1 day strength [131]. Mortars made with sulfoaluminate belite cements containing 20% SO$_3$ developed compressive strengths of 27 MPa at 3 h, 49 MPa at 1 day and 59
MPa at 28 days. The strength development at later stages was attributed to C₂S hydration [4]. A noteworthy feature is the high reactivity of the belite phase compared to the belite phase of OPC cements [143]. The specific surface area of the anhydrite particles and an optimum particle size fraction could play an important role in the mechanism of ettringite formation and in the gaining of the high initial strength [145]. The surface areas of the different sulfoaluminate clinker phases, such as C₂S, CSA (C₄A₃S) and C₅S, can control the concentrations of different ions in the non-equilibrium liquid phase, and therefore determine the mechanism of formation of hydrated products in the system [146](chapter 2.3.4).

### 2.3.3 Ettringite

#### 2.3.3.1 Composition

Ettringite belongs to the broad group of AFt (Al₂O₃-Fe₂O₃-tri) phases with the general formula (Ca₃(Al,Fe)(OH)₆)X₃. x H₂O, where X represents a formula unit of a double charged anion. The structure of ettringite on the nanometer scale is based on columns composed of (Ca₃Al(OH)₆.12H₂O)₆⁺² running parallel to the c-axis, with SO₄²⁻ and H₂O molecules in the intervening channels. Ettringite is trigonal and it forms prismatic, needle-like crystals or colloidal masses depending on the availability of CH. Slender needles form only if sufficient pore space is available (high W/C) [2]. Substitution of Al³⁺ with Fe³⁺, Mn³⁺, Cr³⁺ or Ti³⁺ ions exist [147]. SiO₂ can also be included in the lattice at the expense of Al₂O₃ [148]. Ettringite become increasingly more stable with increasing SO₄²⁻ content, however, a partial replacement by CO₃²⁻ and OH⁻ has to be taken into account [149].

#### 2.3.3.2 Stability at room temperature

Solubility constants indicate that ettringite should be the stable form of calcium aluminate sulfate hydrate compared to monosulfate, in cement porewater. The variations encountered in the solubility products (Log Ksp) ranging between -39.96 and -44.91, reflect a disordering of the structure. At pH values greater than 13, hydroxy-ettringite is formed as depicted in equation (2.18).
$Ettringite + 4OH^- \rightarrow 2SO_4^{2-} + \text{Hydroxy-Ettringite} \rightarrow$

$Monosulfate + 2Ca^{2+}$

(2.18)

The substitution of $OH^-$ with $SO_4^{2-}$ in ettringite may explain its conversion to monosulfate, although further research is required [150]. In aqueous solutions the pH of the liquid phases generally determines the process of amphoter $Al^{3+}$ ion transfer into solution and therefore, the solubility of the calcium aluminate phases. The pH also influences the crystal structure of the ettringite: at pH around 12.5 for example, the crystal structure becomes disordered and ettringite decreases in its fiber length, compared to that formed for example at pH = 11.5. Drops in pH above 10.7 supports the transfer of ions into the liquid phase causing ettringite to transform into relatively soluble gypsum and aluminum sulfate generally stable at pH below 10.0. The presence of hydrogarnet up to pH 10.0 is also detected. Removal of hydroxyl ions from solution affect the solubility product of ettringite to the $4^{th}$ power, thus resulting in ettringite dissolution. The solubility product also depends on the calcium concentration to the $6^{th}$ power. Thus, lowering the pH and allowing more $Ca^{2+}$ into the solution should promote the formation of ettringite [151, 152]. Furthermore, the concentration of protons in the liquid phase play an important role in the formation and in the general stability of calciumsulfoaluminate hydrates [151].

Because of its low stability it appears unlikely that $3CaO.Al_2O_3.3CaCO_3.32H_2O$ is formed in cements containing calcareous aggregates. With addition of $CaCO_3$ to the cement, calcium aluminate hydrates can react with calcite to form $3CaO.Al_2O_3.3CaCO_3.11H_2O$ as the stable phase [153]. Depending on the partial pressure of $H_2O$ and $CO_2$, carbonation of $3CaO.Al_2O_3.3CaSO_4.32H_2O$ can partially occur, leading to the formation of gypsum, calcium carbonate and alumina gel [154].

2.3.4 Expansion mechanism

2.3.4.1 Microchemistry

It is well known that the expansion in sulfoaluminate-type expansive cements (types K, M and S) is associated with the formation of ettringite. CSA ($C_4A_3S$) in type K, CA and $C_{12}A_7$ in type M and $C_3A$ in type S are the major phases responsible for the formation of ettringite [155]. Pure
aluminum-bearing solid (CSA (C₄A₃S), CA, C₃A, C₄AH₁₃ and C₄A₃S₄) - C₅S₄H₂ - H systems with and without lime were widely investigated [141, 142, 156].

Saturated lime solutions generally decrease the solubility of C₅S₄H₂ and of the aluminate phase and increase the concentration of OH⁻, Ca²⁺ and SO₄²⁻ ions in the solution. As a consequence, ettringite crystals are fine prismatic or granular and form in the close vicinity of the surface of the aluminum-bearing particles. In the absence of lime, sufficient Al(OH)⁴⁻ ions may appear in the bulk solution due to the low concentration of OH⁻ and Ca²⁺ ions in the solution, to combine Ca²⁺, OH⁻ and SO₄²⁻ ions and produce ettringite crystals. These crystals, formed at relatively low supersaturation in the bulk solution, are expected to be large, widely coarse needles and distributed through an extensive region [157]. Depending upon the pH conditions of the liquid phase surrounding the aluminate phases, the mechanism of ettringite formation changes. Low pH values (pH < 10.7) of the solution cause the formation of a liquid interlayer, Y₁, (Y₁ = thickness of the interlayer) with a high content of Al(OH)⁴⁻ ions [146] between the CSA (C₄A₃S) particle and the hydrated product, and increase the rate of transfer of ions into the liquid phase. The rate of formation of the hydrated products is proportional to the volume of the Y₁ interlayer. Solubility of the aluminum phases are higher under these conditions and ettringite is formed with a through-solution mechanism. At higher pH values (pH ≥ 10.7), the interlayer thickness Y₁ is strongly reduced and ettringite forms on the surface of the CSA (C₄A₃S) particle creating a solid layer of hydrated products, which causes a delay in the further hydration. In this case, ettringite is formed by a topochemical mechanism [156].

2.3.4.2 Microstructural features

Ettringite crystals formed on the surface of C₃A are smaller than those formed on CSA (C₄A₃S), because the pH of the liquid phase surrounding C₃A is more than 10.7 (no sulfate present) and ettringite is formed on the surface at higher pH values [156]. This suggests that type "K" expansive cement, with CSA (C₄A₃S) as the main expanding particles, is more efficient in producing expansion, compared to type "S" expansive cement, with C₃A as the main expansive particles. It is important to predict the expansion, time because if it were prolonged, the strength of the cement may drop rendering it unusable. This strength drop due to the mechanical failure of the CSH gel must be avoided [158]. The general conversion of the CSA (C₄A₃S) to
ettringite is associated with a marked increase in volume (by a factor of 9). The presence of lime in sulphoaluminate cements strongly promotes the expansion. With lime saturated solutions growth of a porous layer around the CSA (C₄A₃S) particle is favored [159]. In the presence of CH and, depending on the saturation level of the solution, short prismatic, granular or amorphous colloidal-like ettringite is formed. Colloidal ettringite is able to attract a large number of water molecules which cause interparticle repulsion, thus causing an expansion of the system [160]. Measurements carried out in deionised water systems at 20°C showed that the surface of ettringite had a negative charge leading to a potential of zero charge of -11.6 mV. When the same experiment was carried out in the presence of CH at pH around 10.7, a value of -13.4 was obtained, indicating that the presence of CH plays a role on the potential of zero charge of ettringite. The chemical potential of the adsorbed water is thus lowered and water is easily adsorbed [161, 162]. An increase in the hydration temperature seems to be favorable to the formation of colloidal ettringite [163]. During the hydration, the very small irregular unoriented particles around CSA (C₄A₃S) crystallize and radially arrange. Expansion begins when the reaction zones intersect and continue growing, thus mutually exerting pressure, even though the water adsorption of colloidal like ettringite certainly contributes to the expansion [164]. A generally linear relationship between the degree of linear expansion and CSA (C₄A₃S) degree of hydration for CSA (C₄A₃S) - C₅S - C - H systems was proved. Expansion starts when reaction zones around CSA (C₄A₃S) particles intersect and stress is generated [164]. Higher temperatures (45-60°C) accelerate the linear expansion and the degree of reaction. Compared with samples cured at lower temperatures (27 °C), the expansion begins at lower stage of reaction, and the maximum expansion and stage of reaction are normally reached earlier [129].

2.4 Oil shale

2.4.1 Origin and petrography

Oil shale is defined as a fine-texture sedimentary rock that contains indigenous organic matter, more precisely a bituminous substance called kerogene, which is mostly insoluble in ordinary petroleum solvents, and from which substantial amounts of oil (4-50 % of the weight of the rock) can
be extracted by heating. Due to the various mineral and textural features, oil shales are sometimes classified as other types of rock such as siltstone, impure limestone, black shale or impure coal. They range in colour from light shades of brown, green-red, to dark brown gray or black [165]. Nearly all types contain at least small amounts of organic matter, and calculation of the stoichiometric composition, for instance from an oil shale in Northwest Germany (Posidonienschiefer) has given the following result: $C_{46}H_{146}O_{19}$ [166]. This bituminous substance is normally contained in dark bands associated with quartz feldspars, clays, and carbonates. Organically associated sulphur was also identified in some samples [167]. Three general categories of oil shale are normally described:

a) carbonate-rich shale: mainly containing carbonate minerals like calcite, dolomite or siderite, and, if they originate from lacustrine deposition, commonly varved consisting of cyclic layers rich in organic matter, small size grains deposits of clays containing kaolinite, chlorite and sometimes quartz and carbonate-rich grains alternated with layers composed mainly of carbonate-(quartz) coarse grained deposits. The mineralogical compositions of these layers mainly depend on the conditions, oxygen-rich flowing waters (aerobic condition) or very still waters (anaerobic conditions), occurred during their deposition [166].

b) siliceous shale, which have detrital minerals like quartz, feldspar or clays as main constituents and where chert, opal and some forms of diatoms are not uncommon;

c) cannel shale, which predominantly consist of organic matter that completely encloses other mineral grains; such rocks are sometimes classed as impure coal, torbanite or marine coals and are largely composed of algal remains. A large proportion of their organic matter is convertible to oil with normal distillation methods [165].

The principal environments in which oil shales are deposited are:

(1) large lake basins, which normally give rise to the thickest calcareous type deposits known (Green River shale from Colorado);

(2) shallow seas on continental platforms, where the circulation of water near the sea floor is restricted, and the formation of siliceous but also of calcareous assemblages is predominantly:
(3) small lakes and lagoons associated with coal-forming swamps, which give rise to coal-bearing rocks and to the formation of the higher grade cannel type, although lower-grade siliceous and calcareous shale are also found [165].

Despite the mineralogical variations within different types of oil shales, typical phase compositions, are depicted in Tab. 2.6 for two deposits.

<table>
<thead>
<tr>
<th></th>
<th>Posidonia shales</th>
<th>Green River shales</th>
</tr>
</thead>
<tbody>
<tr>
<td>organic matter</td>
<td>11.20%</td>
<td>organic matter</td>
</tr>
<tr>
<td>clay substance</td>
<td>17.40%</td>
<td>illite, musc., mont.</td>
</tr>
<tr>
<td>free silic acid</td>
<td>12.00%</td>
<td>quartz</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>40.50%</td>
<td>CaMg(CO₃)₂</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>2.70%</td>
<td>feldspars</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>9.00%</td>
<td>NaAlSi₂O₆·H₂O</td>
</tr>
<tr>
<td>FeS₂</td>
<td>4.60%</td>
<td>FeS₂</td>
</tr>
</tbody>
</table>

Tab. 2.6: Two typical mineralogical compositions of the oil shales. In the Posidonia shales of West Germany [168] alkalis (1.6%) are contained in oxides or as trace elements in the sulfates. Green River oil shales [165].

2.4.2 Age and distribution

Deposits of the Early Paleozoic age are all marine-platform types and are located in northern Europe, northern Asia, and east-central North America (mostly siliceous black shale). Middle Paleozoic oil shale deposits are marine-platform deposits and situated in the eastern and central United States (mostly black shale). Oil shales were found in rocks of the Late Paleozoic on all the continents; most are associated with coal-bearing rocks and are represented by small cannel shale related deposits. The oldest reported large tectonic lake-basin deposit is the Albert Shale of the Early Carboniferous age in eastern Canada, and the world’s largest oil shale deposits are marine black shales, the Irati Shales of the Late Permian age in southern Brazil. Oil shales of the Mesozoic age are reported in nearly all continents; extensive marine-platform deposits of the black shale-phosphorite-chert assemblages of the Cretaceous age are reported in Israel, Jordan, Syria and the southern part of
the Arabian Peninsula. In Europe, marine-platform deposits, mostly black shales, of Jurassic age are widely distributed. The Posidonia shales of West Germany also belong to an oil shale deposit of the Tertiary age. In North America, large marine-platform deposits are located in Alaska and central Canada. Many of the oil shale deposits of the Tertiary age are of non-marine origin. They mostly accumulate in large lake basins or as smaller deposits associated with coal-bearing strata. The larger deposits mostly of the Early and Middle Tertiary age, include oil shale in the Green River formation [167]. Quaternary deposits include lake, lagoon and marine-basin deposits containing organic debris that can yield oil, although the high water content prevents them from being considered as potential source of shale oil [165].

2.4.3 Ashes manufacturing and composition

In the past, oil shales were burnt with various firing systems with the aim of extracting the bituminous substance (kerogene) and yielding oil. Investigations of residues of burnt oil shales burnt at different temperatures showed the high bonding properties of the latter [169]. Because of the different phase compositions, various burning methods, and burning temperatures (600-1000°C) were investigated in order to improve the oil distillation process and the hydraulic behaviour of the ashes. Burning temperatures between 800 and 850 °C gave rise, for instance, to good hydraulic activity of the ashes, resulting in high maximal strength values [169, 170]. With the Rohrbach-Lurgi Processing a rapid heat transfer in the cyclone is promoted, thus increasing the kinetics of the reaction between the mineral components [168]. The different granular components are burnt for several minutes at the bottom of the cyclone at around 810 °C; at the top of the oven fine shale ashes and sulphur gases are burnt at around 1000°C. At the bottom of the cyclone the main aluminate and silicate phases are normally formed [168, 171]. In pulverised fuel firing systems operating between 1300 and 1400 °C, the solid particles are heated extremely rapidly. The coarser fraction, richer in lime, is deposited in the combustion chamber and the finer fraction is collected as fly ash in the cyclones and in the electrostatic precipitator. In industrial practice, fly ash can be separated as part of the process on the basis of particle size into the fractions "coarse", richer in CaO and poorer in CaSO₄ and used for the production of areated concrete and silicate products, "fine", used for blended cements, and "finest" fraction, suitable for producing oil shale cements [172].
The burnt oil shales mainly consist of calcium silicates (mainly $\beta$-C$_2$S and Wollastonite CS), calcium aluminates (CA), calcium sulfate, free lime, quartz ($\beta$-Quartz, $\beta$-Cristobalite), active silicic acid, and CaCO$_3$ [168, 171]. Additional phases such as Gehlenite (C$_2$AS), $\alpha$-Fe$_2$O$_3$, Anorthite (CAS$_2$), Orthoklas (KAS$_6$) and muscovite were also observed [169]. The glassy component of the ashes, for instance the kukersite ashes, may reach values around 30%, and mainly contains on average 33% SiO$_2$, 23% CaO and 19% Al$_2$O$_3$. CaSO$_4$ formed by the reaction of the SO$_2$ formed during the combustion with the CaO, is sometimes deposited as a thin layer on the free lime particles [172]. A comparison between the chemical composition of a burnt oil shale (Tzefa Efe, Israel) burnt at 800 °C and a OPC is given in Table 2.7.

<table>
<thead>
<tr>
<th>Binder</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
<th>SO$_3$</th>
<th>CO$_2$</th>
<th>O.M.</th>
<th>CaO free</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shale</td>
<td>44.5</td>
<td>19.0</td>
<td>8.3</td>
<td>4.3</td>
<td>0.9</td>
<td>0.7</td>
<td>0.4</td>
<td>2.4</td>
<td>8.5</td>
<td>6.2</td>
<td>0.9</td>
<td>10.3</td>
</tr>
<tr>
<td>OPC</td>
<td>63.5</td>
<td>21.1</td>
<td>5.9</td>
<td>2.9</td>
<td>1.6</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>2.6</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

*Tab. 2.7: Comparison OPC-burnt oil shale. Data in Weight %. O. M. = Organic matter. nd = not determined. LOI: ash 11.3 ; LOI: OPC : 2.04. [171].*

The chemical composition of the ash indicates that the material is in general relatively rich in CaO, moderate in SiO$_2$, and that it contains smaller quantities of Al$_2$O$_3$, Fe$_2$O$_3$, SO$_3$ and CO$_2$ [171].

### 2.4.4 Hydration and hydraulic properties

The hydration of the burnt oil shales proceeds through the reaction of free CaO and CaSO$_4$ with aluminate phases to form ettringite (very small needles [173]) within the first few hours. Despite different opinions about the higher reactivity of $\beta$-C$_2$S burnt at lower temperatures mainly attributed to its imperfect crystallization [174], the reaction of $\beta$-C$_2$S with water to form CSH gel (small round particles) follows at a later stage [175]. In all cases, the CSH gel formation appears to be the main hydration product of the ash system [171, 173], even though phases like monosulfate ($C_4A\bar{S}H_{12}$), $C_4AH_{13}$, $C_3AH_6$ and CH were also detected [169].

The hydraulic activity of burnt oil shales appears to be governed to a great extent by both the glass constituent [172] and the reactive $\beta$-C$_2$S [175].
CaO and CaSO₄ operates as activators for the glass phase and form CSH and ettringite. Because of the high Al₂O₃ content of the glass constituent of the ashes (chapter 2.4.3), it reacts with sulfate, whereas the silica in the glass reacts with the CaO. The slow dissolution of the free lime and the slow ettringite formation can cause moderate swelling of the hardened paste; the fact that the free lime contained in the ash appears to be much more reactive than that in the OPC-clinkers, and that the CaSO₄ is sometimes deposited as a thin film on the surface of the free lime must be taken into account for the kinetics of the hydration. Mortars made with burnt oil shales, showed a strength drop with increasing CaO content of the ashes, whereas an increase in the SiO₂ content of the glass constituent showed a positive correlation with the strength development; the content of C₂S + CA seems not to have a statistically recognizable effect. It appears that the clinker constituent of the ashes only plays a subordinate role in the binder properties, and a sharper burning in order to increase the C₂S + CA content shows a harmful effect; this is mainly due to the raised CaO content of the glass constituent, which reduces the hydraulic effectiveness, and to a greater extent than the gain produced by increasing the proportion of C₂S + CA. The fraction of the burnt oil shales which does not dissolve in 3% hydrochloric acid and normally called insoluble residue appears to have pozzolanic properties as well [172].

2.4.5 Comparison between burnt oil shales and cement pastes

The burnt oil shale appears to hydrate at the same [171] or in some cases generally at a slower rate than the cement, although the reactivity of the β-C₂S of the ash seems to be greater than that of cement [175, 176] but, on complete hydration, both combine with essentially the same amount of water. At the same age and water / binder ratio, however, the ash paste is characterised by higher total and capillary porosities, lower specific surface area and, at earlier ages up to 28 days, by a greater threshold diameter (size of the biggest pores). In the ash paste, the total porosity seems to remain constant with time [175]. In cements the total porosity decreases due to the increase in the volume of the hydration products. This implies that within the ash pastes, low voluminous solid products are present and their greater intrinsic strength offsets the negative effect of the greater general porosity present within the ash-based pastes [176]. In some cases, the strength of both ash and cement pastes reach up to 28 days the same values, irrespective of the above differences, but lower values of the ash pastes and mortars (6 to 20 MPa at 28 days) compared to those of cement pastes and mortars (17 to 90
MPa at 28 days) were also observed and attributed to the higher water requirement and the high fineness (Tzefa Efe oil shale 1200 m²/kg Blaine [171]) of the former [177]. The fact that CO₂ curing of the ash sample does not contribute to a gain in strength beyond the first 30 min seems to indicate that two processes are involved in the strengthening of the ash samples: a rapid one giving high early strength, which is activated by CO₂ and a slower one activated by water and responsible for the strength gain at later stages [178]. Despite the generally lower strength values of the ash pastes, their application is considered possible as cementing material for the production of non- and semi-structural building components such as blocks, bricks, tiles etc. [177].

Regarding the expansion in water, burnt oil shale paste exhibits a much lower linear expansion up to 180 days compared to cement pastes. Despite an appreciable amount of ettringite is formed during the hydration, a lower expansion of the ash paste was observed, implying a better accommodation of the hydration products by the capillary pores, and this can be attributed both on the greater porosity of the ash paste and on a smaller increase in the volume of the solids on hydration [173].
Seite Leer / Blank leaf
3. Experimental

3.1 Investigated materials

3.1.1 Cementitious substances

An ordinary portland cement (CEM I 42.5 - OPC) "Untervaz" from the Bündner Cement Industry, Untervaz Switzerland was used. Its chemical and phase composition is depicted in Tab. 3.1. A normal portland cement clinker with a Blaine value of 3000 cm²/g without the addition of gypsum was also used as binder material and was obtained by the Rohrbach Cement Industry in Dotternhausen, Germany.

A Fesil silica fume consisting of ultra fine, amorphous silica particles was employed as mineral additive and its chemical composition is also shown in Tab. 3.1. It derives from the production of ferro silicon and silicon metal in electric arc-furnaces at the Fesil-group’s plants in Norway.

The used technical calciumsulfoaluminate (Rockfast 450) with its typical composition (Tab. 3.1) was provided by the Blue Circle industry, United Kingdom.

The burnt oil shales used in this study came from the Rohrbach Cement Industry in Dotternhausen, Germany, and indicate a density of 3.00 g/cm³ and a Blaine value of 7000 cm²/g. Their chemical and phase composition are depicted in Tab. 3.1.

The chemical analysis of the binding materials were performed at the Swiss Federal Laboratories for Materials Testing and Research (EMPA) for the OPC Untervaz and the condensed silica fume, in Dotternhausen, Germany by the Rohrbach Cement Industry for the burnt oil shales, and at the Blue Circle, United Kingdom for the Rockfast 450.
3.1 Investigated materials

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>OPC Untervaz</th>
<th>Silica fume</th>
<th>Burnt oil shales</th>
<th>Rockfast 450</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>61.7</td>
<td>0.75</td>
<td>29.71</td>
<td>38</td>
</tr>
<tr>
<td>SiO₂</td>
<td>20.6</td>
<td>90.2</td>
<td>35.73</td>
<td>3.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.9</td>
<td>0.66</td>
<td>11.17</td>
<td>47.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.28</td>
<td>1.03</td>
<td>5.84</td>
<td>1.4</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.70</td>
<td>0.56</td>
<td>10.23</td>
<td>7.5</td>
</tr>
<tr>
<td>MgO</td>
<td>1.90</td>
<td>1.03</td>
<td>1.91</td>
<td>0.3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.23</td>
<td>0.66</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.15</td>
<td>1.77</td>
<td>2.02</td>
<td>0.16</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.24</td>
<td>0.01</td>
<td>-</td>
<td>2.2</td>
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<tr>
<td>P₂O₅</td>
<td>0.22</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.04</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SrO</td>
<td>0.09</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>loss at read heat</td>
<td>4.04</td>
<td>3.23</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>Carbon content</td>
<td>0.79</td>
<td>1.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acid insoluble matter</td>
<td>1.33</td>
<td>71.6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab. 3.1: Chemical and phase composition (% weight) of the investigated binding materials. The determination of the acid insoluble residue was performed with a "wet process". The high value for the silica fume was presumably influenced by the methodological specification.
<table>
<thead>
<tr>
<th>Phases composition</th>
<th>OPC Untervaz</th>
<th>Silica fume</th>
<th>Burnt oil shales</th>
<th>Rockfast 450</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>42.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂S</td>
<td>22.9</td>
<td>-</td>
<td>3.55</td>
<td>-</td>
</tr>
<tr>
<td>C₃A</td>
<td>9.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₄AF</td>
<td>6.9</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Free CaO</td>
<td>0.72</td>
<td>-</td>
<td>5.43</td>
<td>0.3</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>4.58</td>
<td>-</td>
<td>15.65</td>
<td>-</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>6.65</td>
<td>-</td>
<td>9.52</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>1.90</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂ quartz</td>
<td>-</td>
<td>-</td>
<td>17.72</td>
<td>-</td>
</tr>
<tr>
<td>CA₂</td>
<td>-</td>
<td>-</td>
<td>3.18</td>
<td>-</td>
</tr>
<tr>
<td>CA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>C₂AS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>C₁₂A₇</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>CT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>C₄A₃S</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>58</td>
</tr>
<tr>
<td>C₆A₃S₃H₃₂</td>
<td>-</td>
<td>-</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>Na₂Ca(SO₄)₂</td>
<td>-</td>
<td>-</td>
<td>3.24</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>-</td>
<td>-</td>
<td>2.51</td>
<td>-</td>
</tr>
<tr>
<td>FeS₂</td>
<td>-</td>
<td>-</td>
<td>0.94</td>
<td>-</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>-</td>
<td>-</td>
<td>0.62</td>
<td>-</td>
</tr>
<tr>
<td>Amorphous</td>
<td>-</td>
<td>-</td>
<td>37.40</td>
<td>-</td>
</tr>
</tbody>
</table>

*Tab. 3.1: Chemical and phase composition (% weight) of the investigated binding materials. The calculation of the phase composition was done after "Bogue" for the OPC Untervaz and for the silica fume, whereas for the burnt oil shales a Rietveld method with an internal standard (Boehmite) was used.*
3.1.2 Admixtures

The chemical admixtures used in this work were prepared in the laboratories of the SIKA AG, Zurich Switzerland and consisted of a plastizicer and 3 main accelerators.

The plasticizer was composed of a sodium carboxylate polysulfonate aqueous solution.

One alkali-free accelerating admixture consisted of powdery calcium-sulfoaluminate with the addition of powdery Al₂(SO₄)₃·14 H₂O as main components (alkali-free accelerator I AF). The other alkali-free accelerator was mostly composed of a Al₂(SO₄)₃·14H₂O-based polymer-containing viscous solution (alkali-free accelerator II L50) with a water content of 36.058 wt%. The alkali-rich admixture was mainly constituted of a KAl(OH)₄ aqueous solution with a water content of 36.459 wt% (alkali-rich accelerator L20).

3.2 Mixing procedures and curing

3.2.1 CSA / accelerators

Both cement paste and mortar (0-8 mm) specimens were prepared. Mortars (0-8 mm) were obtained by dry mixing the aggregates and the OPC Untervaz for 1 minute. Thereafter, water previously mixed with 1% (% cement weight) of the plasticizer was added and the mixtures mixed for further 3 minutes. The accelerating admixtures were then added (Tab. 3.2) and the mixing procedure was stopped 45 seconds after the addition of the accelerators. The cement pastes were mixed with the same previously described procedure.

In addition, the CSA component (RF) and the powdery Al₂(SO₄)₃·14 H₂O (AS) which were constituents of the alkali-free accelerating admixture I, were separately investigated (RF: 1.6%; AS 3.98%).
Admixture Dosage

<table>
<thead>
<tr>
<th>Admixture</th>
<th>Dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali-free accelerator I (AF)</td>
<td>6%</td>
</tr>
<tr>
<td>Alkali-free accelerator II (L50)</td>
<td>8%</td>
</tr>
<tr>
<td>Alkali-rich accelerator (L20)</td>
<td>4.5%</td>
</tr>
</tbody>
</table>

Tab. 3.2: Accelerating admixtures and dosages (referred to the cement content in weight %).

The W/C ratio was constantly held at 0.46, except when silica fume was added. In this case, the W/C ratio was raised to 0.48, because of the high water requirements of the silica fume. The mixtures in which no plastizicer was added were mixed with a W/C ratio of 0.56. In order to keep a constant W/C ratio, the water content of the liquid accelerators must be considered and the total amount of mixing water required was then calculated according to equation (3.1).

\[ W_1 = C_1 \times \frac{W}{C} - (W_a \times A \times C_1) \]  

(3.1)

\[ W_1: \] water required to maintain the W/C ratio  
\[ C_1: \] cement amount  
\[ W/C: \] water to cement ratio  
\[ W_a: \] water content of the accelerator  
\[ A: \] accelerator dosage

The mixing water temperature was held at 21°C ±1°C, and the laboratory conditions at 21°C ± 1°C and 65% ± 3% relative humidity.

The mixtures were cast depending on the type of measurement and demoulded for the measurements after preassigned hydration times (chapter 3.3). The mortar (0-8mm) specimens were then cured at 20°C and at 95% relative humidity, whereas the cement samples were cured under deionized water at 22°C.
3.2.2 Mixtures subjected to sulfate attack

The same mixing procedure as described previously (chapter 3.2.1) was used for the mixtures subjected to sulfate attack. The accelerators used were two type of alkali-free (I: Sigunit AF-49; II: Sigunit L50-AF) and the alkali-rich one (Sigunit L 20). Two different mixing procedures were used for the alkali-free accelerator I (Sigunit AF-49) added to the cement samples: one in which the accelerator was normally added to the mixture (chapter 3.2.1) ("wet mixing procedure"), and the other one where it was added at an initial stage thus homogeneously dry mixed with the OPC Untervaz for 1 minute. Water was then added and the mixture further mixed for 3 minutes and 45 seconds ("dry mixing procedure").

The mixing water was held at 20 °C and the laboratory conditions were 22°C ±1°C and 55 % ± 4% relative humidity.

The investigated specimens were immersed in deionized water and in 5% Na₂SO₄ (Na₂SO₄ powder 99.5%) solution at 23°C and at 65°C up to 6 months, and prepared for the measurements after preassigned curing times (chapter 3.3). The sulfate solutions were not renewed over time.

3.2.3 CSA / burnt oil shale-based cement

This cement type was obtained by dry mixing the OPC clinker with a Blaine value of 3000 cm²/g, calciumsulfoaluminate, and burnt oil shales as main components. The blend type corresponds to the Sikacem 501 developed by the SIKA AG, Zurich Switzerland [12, 13]. In some investigated blends, CaO was added to the dry components, respectively reducing the burnt oil shales amount. Aggregates (0-8 mm) were then added and dry mixed with the binding components for 1 minute. Afterwards mixing water was added and the mixtures mixed for further 3 minutes. A W/C ratio of 0.46 was used. The cement samples were mixed with the same procedure and conditions as the mortars.

The mixing water was held at 20 °C and the laboratory conditions were 20°C ±1°C and 56 % ± 4% relative humidity.
The mixtures were cast depending on the measurement type. The mortars specimens (0-8 mm) were cured at 20 °C and at 95% relative humidity, whereas the cement pastes under deionized water at 22°C. The specimens were then demoulded after preassigned hydration times (chapter 3.3).

The burnt oil shales were cured at 23°C and at 65% relative humidity under both normal atmospheric conditions and in a saturated CO₂ atmosphere for three months. The curing in a CO₂ saturated atmosphere was performed in a conditioning cabinet where the relative humidity of 65% was held constant by the presence of a saturated aqueous solution of NaNO₂.

3.3 Investigation techniques

3.3.1 Measurement of the mechanical properties

3.3.1.1 Compressive strength

Mortar mixtures (chapter 3.2.1) were cast in 40 x 40 x 160 mm prismatic polyethylene forms, whereas the mortars described in chapter 3.2.3 were cast in 40 x 40 x 160 mm steel forms.

The strength measurements for the mortars described in chapter 3.2.1 were performed after 4 hours, 5 h, 1 day, 7, 28, 56, 91, and 182 days, whereas for the mortars of chapter 3.2.3 after 30 min, 1 hour, 1.5, 2, 3 and 4 hours. The measurements were performed on 40 x 40 x 160 mm mortar specimens (0-8 mm) according to the EN 206-Norm.

3.3.1.2 Fracture mechanic tests

The material used for this study consisted of 6 mixture series (chapter 3.2.1) of 12 cement pastes prisms cast in steel 40 x 40 x 160 mm forms for 1 day. The prisms were then demoulded and sawn in the middle down to 20 mm with a diamond wiresaw (Fig. 3.1).
The notched beams were then measured after 28–29 days of hydration with a three-point bend test according to RILEM TC50-FMC [179], with a Universal 10 kN Zwick testing device at a constant speed of 0.2 μm/s. The arrangement of the notched beams is specified in Fig. 3.1. The fracture mechanical features and the calculation of the adsorbed fracture energy is described in chapter 2.2.3.

![Fig. 3.1: Experimental arrangement of a notched beam by means of the three-point bend test.](image)

3.3.1.3 Length change

Mortars and cement pastes (chapter 3.2.2) were cast in polystyrene 120 x 120 x 120 mm forms, covered with a plastic sheet for 1 day. The cubes were then demoulded and stored for 56 days in deionized water at 23°C. Afterwards each cube was bored in order to obtain three drill cores of 50 mm diameter. The cylindrical specimens were cut to a length of 100 mm. Holes were then drilled at the edges of the cylindrical specimens and bolts were glued with a special rapid adhesive (X-60) from Hottinger Measurement Technik Darmstadt, Germany. The specimens were then vertically placed on a grate at the bottom of a plastic box in order to allows a homogeneous contact of the specimens with the attacking Na$_2$SO$_4$ solution.

The half of the specimens of each mixture type were immersed into deionized water, whereas the other half under the Na$_2$SO$_4$ solution at two different temperatures (chapter 3.2.2). The measurements were performed weekly up to 28 days, afterwards every two weeks up to 6 months. The
values of the linear expansion were obtained through the difference between
the sulfate and the water cured specimens. The measurements of the length
change were performed according to the ASTM C 1012-95 a Norm.

3.3.1.4 Early shrinkage

Mortars (chapter 3.2.3) were cast in triangular prismatic forms with an
eedge length of 80 mm and a total length of 360 mm. The mean free path was
300 mm. At the ends the prisms were penetrated with anchor hulls. The hulls
were screwed with the endplates, which were mobile along the rail (Fig. 3.2).
The measurements with the early shrinkage device system (Fig. 3.2) gave
informations about the shrinkage behavior of the mixtures during the first 24
hours of the hydration. The length changes were detected on a sensing
element throughout the end plates. The change in the tension arising from the
sensor was transmitted to a PC through a voltmeter (Fig. 3.2).

![Fig. 3.2: Early shrinkage measurement device.](image)

3.3.1.5 Setting time

Mortar mixtures 0-4 mm (chapter 3.2.1; chapter 3.2.3) were used for this
investigation.

The setting times were registered with a Proceq Typ R 31 211 penetrometer
where a needle, which penetration force equalized the penetration resistance
of the mortar, slowly penetrated into the sample (Fig. 3.3).
The cementitious sample moved upward with a constant speed of 0.39 cm/h (motor I1) and the needle penetrated into the sample. At a certain point the cement reached a consistency and pushed up the needle. A lever arm (F) closed then an electrical contact (K) and activated a motor (I2). This motor moved a suspension point downward and a spring became under tension (a2). At this time the contact (K) was opened again, the motor (I2) turned off, and the needle reached the initial position overcoming the sample resistance. This process was repeated through the time increasing the tension of the spring (a2) proportional to the consistency increase of the sample. The continuous downwards movement of the suspension point yielded the consistency increase of the sample. A recorder was fixed on the suspension point and the consistency was drawn on a roller which made a rotation within 6 hours.

3.3.2 Microstructural characterization

3.3.2.1 Scanning electron microscopy

Cement pastes (chapter 3.2.1; chapter 3.2.3) were cast in plastic boxes 32 x 26 x 15 mm. The prisms were demoulded, fractured and evacuated at $10^{-2}$ Torr in a desiccator with silica gel at the bottom. The sulfate attacked
samples (chapter 3.2.2) consisted of cement disks with a thickness of 7 mm cut from the cylindrical specimens 100 x 50 mm and were also evacuated at 10^{-2} Torr.

Fractured surfaces (chapter 3.2.1; chapter 3.2.3) and fractured border of the sulfate attacked specimens were glued on sample holders with a conductive carbon cement-based glue (Neubauer Chemicals, Germany), further evacuated for 24 hours at 5.10^{-2} mbar and then coated with gold.

SEM measurements were carried out, depending on the mixture type, after the following times: 4 hours, 1 day, 7, 28, 182 days (chapter 3.2.1), 30 min, 1 hour and 1.5 hour (chapter 3.2.3) and 56 days (chapter 3.2.2). A conventional JEOL JSM 840 (wolfram filament) equipped with a Tracor Microtrace TM Silicon x-ray Spectrometer with Pulsed Optical Feedback Preamplifier 505 and a Tracor software system was used. The accelerating voltage was kept at 20 kV. Qualitative investigations were also performed on uncoated samples with an Electroscan E-3 Environmental Scanning Electron Microscope (LaB_{6} filament) equipped with a Si (Li) crystal detector from the Noran Instrument. The measurement parameters were kept at 20 kV for the accelerating voltage, and at 4.0 Torr for the sample containing vacuum chamber. The evaluation was then performed with a Voyager II x-ray Quantitative Microanalysis System.

3.3.2.2 Confocal microscopy

Fractured surfaces of cement samples (chapter 3.2.1) with a dimensions ranging around 9 x 9 x 4 mm were sticked on a glas plate. A contrast medium consisting of a solution of 50 μl tetramethylisothiocyanate, 250 μl methanol and 200 μl glycerine was set on the fracture surfaces and a thin glas plate was placed on the preparations.

The measurements were performed after 28 days with an imaging system consisting of a Leica inverted microscope DM IRB/E, a Leica true confocal scanner TCS NT and a Silicon Graphics workstation. The images were recorded using a Leica PL APO 20 x /0.60 objective with a step size between 0.3 and 0.5 μm. The system was equipped with an argon/krypton mixed gas laser. Image processing was done on a Silicon Graphics workstation using "Imaris" (Bitplane AG, Zurich, Switzerland), and a 3D multi-channel image processing software specialized for confocal microscopy images [180].
3.3.2.3 Mercury intrusion porosimetry

The cement mixtures (chapter 3.2.1) used for the measurement of the porosity were moulded in plastic boxes and prepared as described in chapter 3.3.2.1.

The mercury intrusion porosimetry measurements are based on a non-wettable liquid ($\theta > 90^\circ$) that enter under pressure the pores of a porous solid. The pores are assumed to be cylindrical, and the pressure ($p$) which force the liquid to enter them is described by the Washbrun equation (3.2) [41.

$$p = -4\gamma \cos \frac{\theta}{d}$$  \hspace{1cm} (3.2)

$\gamma$: surface energy of the liquid (Hg: $\gamma = 0.483$ N/m)
$\theta$: contact angle (Hg: $\theta = 117^\circ-140^\circ$)
d: pore diameter

The fact that the pore structure may change during the intrusion of mercury at high pressure, and that a clear distinction in size between capillary and gel pores remains difficult must be taken into account [4].

The broken cement samples were placed in a glass dilatometer filled to a preassigned level with mercury. The volume of the samples was then determined according to equation (3.3).

$$V_s = \frac{M_1 - M_2}{\delta Hg}$$  \hspace{1cm} (3.3)

$M_1$: mass of mercury
$M_2$: mass of the mercury and the sample
$\delta Hg$: Hg density (13.5438 g/cm$^3$)
The cumulative porosity was calculated according to equation (3.4).

\[ C = \frac{V_i}{V_s} \times M_s \]  

(3.4)

C: cumulative porosity in %  
Vi: intruded mercury volume  
Vs: volume of the sample  
Ms: mass of the sample

The pore size distribution was then calculated through the derivate of the intruded volume curve after the logarithm of the radius according to the Savitzky and Golay filtering [181].

The investigations were carried out after 30 min, 4 hours, 1 day, 7, 28, and 182 days, with an High Pressure Porosimeter 4000 Carlo Erba Instrument.

3.3.3 Laser UBM surface analysis

Fracture surfaces 9 x 9 x 4 mm of cement samples (chapter 3.2.1) prepared as described in chapter 3.3.2.1 were used for the investigation of the surface features.

Samples hydrated for 28 days were investigated with a laser UBM Profilometer which allows a non-contacting measurement of the surface. Autofocus optical sensors featured a measuring range of up to 1 mm and a resolution of up to 10 nm [182]. Four profiles with an average length of 6.7 mm were measured for each sample type, where a spot density of 500 p/mm was established. The extremities of the profile lines (1/7 total gauge length) were cut-off from the evaluation in order to avoid errors caused by the instability of the device during the initial and the final phase of the measurements. The calculation of the roughness parameters represented the mean of the 4 scanned profiles.
3.3.4 Investigation of the phases

3.3.4.1 X-ray diffraction

Cement specimens (chapter 3.2.1; chapter 3.2.3; chapter 3.2.2) were prepared as previously described (chapter 3.3.2.1) and pulverized to pass a 63 µm sieve. The sulfate attacked samples were pulverized along the exposed borders in a constant depth of 4 mm and an internal standard (20% boehmite) was then admixed.

The samples were prepared for the measurements after: 30 min, 4 hours, 1 day, 7, 28, 91, and 182 days (chapter 3.2.1), 30 min, 1 hour, 1.5, 2, and 4 hours (chapter 3.2.3), and 1 day, 7, 14, 21, 28, 56, 91, and 182 days (chapter 3.2.2). The devices consisted of a Seifert OED and a Philipps APD 1900 X-ray diffractometer using CuKα (λ=1.5405 nm) radiation. The mixtures described in chapter 3.2.1 were measured at 30 mA, 40 kV, 0.2° step size, 3.0 s counting time, from 5 to 65° (2θ) and with the rotation of the sample holder in order to avoid crystal orientational effects. The mixtures in chapter 3.2.3 were measured at 30 mA, 40 kV, 0.03° step size, 3.0 s counting time, from 5 to 80° (2θ) and with the rotation of the sample holder, whereas the ones in chapter 3.2.2 were measured with the same latter described parameters but from 5 to 65° (2θ). A semi-quantitative evaluation was done for the samples in chapter 3.2.1 using a Mac diff 3.3.0 software. For the samples described in chapter 3.2.3 and in chapter 3.2.2 a Quantitative Rietveld Analysis [183] was performed using an Autoquan 2.0.0.0 software respectively cernel routine BGMN®. The diffraction spectra were calculated considering the crystallographic data and device parameters and were iteratively adapted to the measured diffraction diagrams throughout a refinement of the phase specific parameters and phase contents [184] with boehmite as internal standard. The calculation of the phases formed during the sulfate attack was obtained as the difference between the sulfate and the water cured specimens.
3.3.4.2 Thermogravimetric and differential thermal analysis

Pulverized cementitious samples (40-160 mg) (chapter 3.2.1; chapter 3.2.3) prepared as described in chapter 3.3.2.1 were investigated.

The thermal analysis methods used for the investigations consisted of thermogravimetric measurements, which indicated weight losses of the samples occurring during dehydration or loss of CO₂ and were determined with a thermobalance. Differential thermal analysis indicated temperature differences relative to a thermally inert material [185, 186]. The DTA curves recorded these temperature differences during reactions within the samples. Accordingly, heat requiring reactions (endothermic) or heat releasing reactions (exothermic) were conventionally classified [185]. The emission gas analysis (EGA) was used as further thermal analysis method for the determination of the volatile gaseous reaction products [186].

The thermal analysis allows the investigation and the clear resolution of the phases in pure cementitious systems [187-189]. On the other hand, phase overlapping problems (30-200°C) took place at later hydration stages within the investigated complex cementitious systems, where this technique evidenced limitations in the phase resolution.

The different mixture types were measured after: 30 min, 4 hours, 1 day, 7, 28, and 182 days (chapter 3.2.1), 30 min, 1 hour, 1.5 and 2 hours (chapter 3.2.3). The pulverized samples were weighed in a platin pot, warmed at 10 K/min in flowing dry air (3 l/h) from 30 up to 1000 °C. Mass losses in the thermobalance were simultaneously drawn with the liberated H₂O and CO₂ gases through the mass spectrometer. These liberated gases were conveyed throughout a narrow capillary to the ionization chamber of the quadrupole mass spectrometer (QMS) and there ionized, separated and detected depending on the mass-charge ratio [190, 191]. The gas detection limit was < 1 %. The measurements were performed with a Mettler TGA/DTA 851e thermobalance coupled with a Balzers Thermostat quadrupole mass spectrometer. The evaluations were made with a STAR© 5.0 Mettler Toledo software.
3.3.5 Other investigations

3.3.5.1 Temperature curves

Mortar mixtures (chapter 3.2.1; chapter 3.2.3) were moulded in plastic sheet-containing cylindrical polystyrene forms. A sensor was then immersed into the mixture and connected to the measurement device.

The variation of the temperature during the hydration was carried out with a Grant 1200 Series 12-Bit Squirrel Meter/Logger with 16 channels. The temperature was measured with a time interval of 3 minutes for 4 hours (chapter 3.2.3), and every 10 minutes for 18 hours (chapter 3.2.1).

3.3.5.2 Ionchromatographic analysis

Cylindrical cement paste specimens (chapter 3.2.2) 100 x 50 mm without bolts were prepared as described in chapter 3.3.1.3 and completely covered with an epoxy resin. They were then cut along the longitudinal side to allow a unidimensional attack of the sulfate solution and stored as described in chapter 3.2.2. After 28 days and 91 days curing time respectively, disks of 200 mm thickness were then sawed from the cylindrical specimens and the exposed surface were pulverized down to 5 mm with a step of 1 mm each. The cementitious powder was then collected in tight plastic containers.

The preparation of the suspensions for the mixtures described in chapter 3.2.2 were then made by mixing 0.50 g powder, 40 ml deionized water and 10 ml hydrochloric acid (0.5 M). The filtered solutions were then measured after 28 and 91 days of sulfate curing of the specimens. The total bound sulfates resulted from the differences between the specimens previous to sulfate immersion and the one after the sulfate curing. The suspensions prepared from the cementitious mixtures described in chapter 3.2.3 were prepared with a W/binder ratio of 10, continuously stirred and filtered after: 30 min, 45, 60, 75, 90, 105, 120, 135, 150, 165, 180, and 240 min.

The measurements were performed with a Metrohm Ion Chromatograph. The working conditions were set at 2000 µl/min at 20 °C and at a pressure of 79 bar. The eluent consisted of a solution of 2mM phthalic acid / 10% acetone / pH 5.0 (NaOH). The dilution was 1:100 and the standard calibration solution had a concentration of 200µM SO₄²⁻. The quantitative method used
was a Custom IC-metrodata for windows Metrohm Ltd. The other ion-chromatograph consisted of a Dionex DX-100 Ion Chromatograph with a eluent flowing rate of 2.0 mL/min at 20°C. The eluent consisted of a solution of 1.8 mM Na₂CO₃ /1.7 mM NaHCO₃. The standard consisted of 208 μM SO₄²⁻ solution. The quantitative analysis were made with a Peaknet 4.30 software system.

### 3.3.5.3 pH measurements

The cement samples (chapter 3.2.2) were prepared as described in chapter 3.3.5.2 without the addition of hydrochloric acid. The suspensions prepared from the cementitious mixtures described in chapter 3.2.3 were prepared with a W/binder ratio of 10, continuously stirred and filtered.

The measurements were performed after 28 and 91 days (chapter 3.2.2) and after 30 min, 45, 60, 75, 90, 105, 120, 135, 150, 165, 180, and 240 min (chapter 3.2.3) with an Orion 960 Autochemistry system consisting of a Orion 960 Module and a EA 940 pH/ISE Meter. The module consisted of a microprocessor, which control the system, an autodispenser, and an electrode tower.

### 3.3.5.4 Determination of the conductivity

The cement samples (chapter 3.2.2) were prepared as described in chapter 3.3.5.2 without the addition of hydrochloric acid.

The measurements were performed after 28 and 91 days with an auto range CDM 83 Conductivity Meter with a pure platinum conductivity cell. The cell consisted of 3 electrodes in the form of platinum bands on a glass tube, and was immersed into the solutions until a constant conductivity value was reached.
Seite Leer / Blank leaf
4. Results and data evaluation

4.1 CSA / accelerators

4.1.1 Introduction

Accelerating admixtures influence the rate of cement hydration, thereby shortening the setting time and, in some cases, increasing the rate of early strength development. Two main subdivisions exist, although some overlap between them may occur [2]:

1) accelerators which mainly affect the tricalcium aluminate phase (C₃A): alkalis which aid the dissolution of silica and alumina and interfere with the C₃A-gypsum reaction.

2) accelerators which mainly affect the alite (C₃S) phase to promote early strength: acids or their salts which aid the dissolution of lime.

Calciumsulfoaluminate-based, alkali-free (AF, AS, L50) accelerators were developed in order to substitute the alkali-rich (L20) admixtures and to improve the mechanical properties and the working conditions (chapter 2.2.2). These accelerators are used in "wet" shotcrete applications and appear to influence both the C₃S and the C₃A hydration. Consequently, these admixtures greatly affect the setting and the strength of the mixtures in which they are added and their influence was carefully studied.

The alkali-free accelerators (AF, AS, L50), are grouped in a category called "E", when no remarkable qualitative differences are observed. The RF mixture, describes the addition of pure calciumsulfoaluminate (CSA), and does not basically belong in "senso strictu" to the accelerating admixtures, but it is also separately investigated for a comparison, since it represents a component of the CSA-based alkali-free accelerator AF.
4.1.2 Early stage of hydration

4.1.2.1 Effect on the setting times

Setting is a process in which a "fresh" cement paste of freely flowing or plastic consistency is converted into a set material which has lost its unlimited deformability under the effect of a sufficiently great external force [2]. The investigated accelerators strongly shorten both the initial ($S_i$) and the final setting time ($S_f$) (Fig. 4.1 left).

![Graph showing setting times](image)

**Fig. 4.1:** Left: Penetration resistance against time for the reference and the accelerated samples (mortar). Right: Detail of the alkali-free (AF, AS, L50) and the alkali-rich (L20) accelerators.

The reference sample (ST), consisting of pure OPC without accelerators, shows an initial setting at ca. 6 hours and reaches the final setting within 7 hours. The addition of pure CSA (RF) slightly shortens the setting time to ca. 1 h and 40 minutes. The alkali-free admixtures (AF, AS, L50) strongly shorten the initial setting times ($S_i$) to 15 minutes and the final ones ($S_f$) to 40 minutes. The alkali-rich admixture (L20) displays shorter setting times. The different dosages and the form in which the substances are added do not appear to remarkably influence the setting behavior.

4.1.2.2 Phases and temperature development

Within the alkali-free accelerated samples, ettringite is formed in considerable amounts already after 30 minutes. With the addition of the alkali-rich and the calciumsulfoaluminate component (RF) generally less ettringite is formed (Fig. 4.2).
The XRD measurements carried out after 30 minutes show gypsum to be barely present within almost all the specimens. Conversely, DTA indicate that gypsum (peak at 120-140°C) is still present but in a semi-crystalline or amorphous state (Fig. 4.3).
Consistent to XRD measurements, DTA show a great ettringite development between 60 and 120 °C for the alkali-free accelerated samples, whereas for the reference sample (ST) and the CSA-enriched sample the ettringite peak is developed to a smaller extent (Fig. 4.3). The peak at 250 °C represents the formation of hemi-carboaluminates such as $\text{C}_4\text{A}_8\text{CH}_{11}$ and $\text{C}_4\text{A}_6\text{C}_{0.5}\text{H}_{12}$. The high presence of these latter two phases within the accelerated samples is mainly due to the high aluminum content of the admixtures. With the alkali-rich admixture, the ettringite peak appears more "diffuse", and a broad peak around 120 °C is probably the result of a superposition between amorphous gypsum and an amorphous KCASSH-like phase (chapter 4.1.3.3). Furthermore, the peak at ca. 450 °C and attributable to CH is remarkably present compared to the other samples (Fig. 4.3).
The different admixtures used, accelerate the consumption of both the clinker phases C\textsubscript{3}A and C\textsubscript{3}S at early stages (4 hours), and promote the formation of ettringite (Fig. 4.4).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.4.png}
\caption{XRD-Phases development of the mixtures between 30 minutes and 4 hours. ST: unaccelerated sample; AF, AS, L 50: alkali-free accelerated samples; RF: CSA-enriched sample; L 20: alkali-rich accelerated sample.}
\end{figure}

Despite the C\textsubscript{3}A - C\textsubscript{3}S interactions [2], it is possible to notice a relationship between the C\textsubscript{3}A consumption and the ettringite formation. The alkali-free admixtures exert the largest influence on these phases. With the alkali-rich admixture slightly more ettringite is formed compared to the reference, and a good correlation with the C\textsubscript{3}A decrease is also noted. The C\textsubscript{3}S hydration is accelerated for all the admixture-containing specimens.

Up to 4 hours the increase in the amount of ettringite and hemi-carboaluminates can be especially observed for the alkali-free accelerated samples, whereas for the unaccelerated (ST) and the CSA-enriched small gypsum amounts still persist (Fig. 4.5). A further increase in the CH amount for the alkali-rich accelerated sample also occurs (Fig. 4.5).
Fig. 4.5: DTA-$H_2O$ liberation curves. Phases after 4 hours hydration. * Y-axis scale.

The heat liberation of ordinary portland cements during hydration generally indicate a first exothermic peak within a few minutes due to the initial rapid hydration of $C_3S$ and $C_3A$ in the pre-induction period, followed by a dormant period, in which the rate of the hydration is slowed down. A second main exothermic peak, with a maximum after a few hours indicate the hydration of $C_3S$ and the formation of the CSH phase and CH. Thereafter, the heat release decreases [2].
The addition of the accelerators changes this general behavior (Fig. 4.6).

![Graph showing temperature development of mixtures](image)

**Fig. 4.6: Temperature development of the mixtures (mortar) at early stages.**

The alkali-free accelerated samples show a fast temperature increase within the first 30 minutes, thus correlating with the ettringite development (chapter 4.1.3.3). After a "dormant" period follows, at ca. 4 hours, a renewed temperature increase (AS, L50). The alkali-free accelerator AF (RF + AS) does not show a "dormant" period. The presence of the "dormant" period was observed by both mixing the CSA (RF) and the aluminum sulfate (AS) separately, and adding them to the OPC. Different experiments carried out with cement pastes and mortars showed the water available for the hydration (W/C) and the dissolution of the alkali-free accelerator AF to remarkably influence the course of the temperature curves. Despite the fast setting, the alkali-rich admixture shows a slight but continuous temperature increase with no "dormant" period. The addition of pure CSA shows a shift of the main peak to shorter times and to lower temperatures, compared to the reference sample. The final setting of the reference sample and the CSA-enriched sample after 6 hours and 5 hours respectively (Fig. 4.1), well correlate with the initial increase in the temperature (Fig. 4.6).

### 4.1.2.3 Microstructural development

Remarkable differences occur within the microstructure of the mixtures at early hydration stage (4 hours). The development of the microstructure is characterized by the formation of ettringites of different morphology, the precipitation of amorphous hydrates, the development of CSH and the crystallization of CH present in different amounts (Fig. 4.7).
Fig. 4.7: Microstructural development of the mixtures within the first 4 hours. Left: general overview of the structure (magn. 1500). Right: details (magn. 10000). 1: KCASSH; 2 CH. "E": samples accelerated with the alkali-free admixtures (AF, AS, L50).

In the reference sample (ST) the structure is loose, and the clinker grains still generally remain poorly reacted, although between 30 minutes and 4 hours most of the clinker grains indicate an initial hydration. The hydrates formed up to 4 hours have an amorphous or foil-like morphology, typically of CSH gel, as evidenced by the SEM-EDX measurements. Small (few μm) CH plate
particles form close to the clinker surfaces or precipitates from the pore solution. Ettringite needles occasionally arrange radially on the clinker surfaces (Fig. 4.7 ST), but also precipitate from the pore solution. Amorphous and cluster-like ettringites were also detected. With the CSA addition (RF), the structure becomes slightly more compact because of the increased ettringite formation. In this case, the ettringites, mainly crystallize as small prisms (< 1 μm), and contribute in linking the clinker grains (Fig. 4.7 RF).

The alkali-free accelerators ("E") favor the crystallization of many ettringite prisms (2-7 μm) between the clinkers, thus creating a more compact structure (Fig. 4.7 E). SEM-EDX measurements indicate that the ettringites often contain silicon as foreign ion, as also reported by Lukas [148], and Fe³⁺, which can substitute the Al³⁺ ion within the crystal lattice [147] (Fig. 4.8 left).

The alkali-rich accelerated sample (L20) shows poorly reacted clinker grains, and the hydrates formed do not appear to link the grains to a compact structure, although the sample has already set. Thin rod-like ettringites (3 - 4 μm) mainly crystallize from the pore solution, and partially fill the pores between neighbouring clinkers (Fig. 4.7 L20). Furthermore, the precipitation of platy CH (< 2 μm) from the solution often occurs. Amorphous KCASSH-like hydrates (Fig. 4.8 right) precipitate on the clinker surfaces, partially contributing in linking the clinker grains.

![EDX Spectra](image_url)

**Fig. 4.8:** EDX Spectra. Left: typical spectrum of the ettringite prisms crystallized with the addition of alkali-free accelerators. Right: composition of the amorphous precipitate occurring with the addition of the alkali-rich admixture (L20).
Generally, the amount of hydrates formed between 30 minutes and 4 hours remarkably increases.

Because of the rapid setting of the accelerated mixtures, porosity measurements were performed within the first 4 hours of hydration as depicted in Fig. 4.9.

![fig49](image)

*Fig. 4.9: Pore radius distribution with time. Left: 30 minutes; right: 4 hours.*

Up to 4 hours, a general shift towards smaller pore sizes is attained. Furthermore, generally smaller variations in the pore size are observed.

### 4.1.3 Hydration at later stages

#### 4.1.3.1 Compressive strength of the mixtures

Strength is the most known engineering parameter used to characterize cement-based materials. Compared to the unaccelerated mixtures without (N) and with the addition of the plasticizer (ST), all the accelerated mixtures which show a final setting time within the first 40 minutes display a general decrease of the compressive strength up to 6 months. The strength decrease is especially remarkable at low W/C ratio (Fig. 4.10 right). This fact is presumably due to the reduced porosity of the microstructure, in which the accelerators may better exert their influence.
4. Results and data evaluation

4.1.3.2 The hydration of the silicate phases

The investigated chemical admixtures have a great influence on the hydration of the main phases, $C_3S$ and $C_{54}S_{16}AM$. The CH development is also affected, but it cannot be used as a general indirect measure of the CSH.
development (chapter 5.1.2.2). However, the CSH development can be partially followed with the DTA (Fig. 4.12; Fig. 4.13; Fig. 4.14). As highlighted in Fig. 4.11, a faster consumption of the silicate phases takes place for all the accelerated mixtures up to 7 days.

The $C_3S$ hydration is accelerated by both the alkali-free accelerators and by the addition of pure CSA up to more than 7 days, and then decreases almost stopping. A further hydration step is then observed up to 6 months. The alkali-rich sample strongly accelerates the $C_3S$ consumption up to 1 day, afterwards its hydration is slowed down, almost stopping up to 3 months, and continues until 6 months only to a very small extent.
The $C_{54}S_{16}AM$ phase shows a lower reactivity compared to the $C_3S$ phase (curve slopes). Analogously, the addition of CSA and the alkali-free admixtures increase the $C_{54}S_{16}AM$ hydration up to 7 days, thereafter a remarkable slow down is observed. The alkali-rich admixture, also accelerates the $C_{54}S_{16}AM$ hydration, but from 1 day, the further reaction is almost obstructed.

Compared to the reference sample (ST), the CH development up to 6 months appears to be reduced for all the accelerated mixtures. Both XRD and TG evaluations show a similar development of the CH, although a variation for the alkali-rich one can be noted (Fig. 4.11 bottom). Hence, the CH is also present in an amorphous state.

The CSH and the CH development up to 6 months can be partially followed with DTA. Because of the superposition (125-225°C) of the CSH phase with phases such as ettringite and KCA$S$SSH (chapter 4.1.3.3), the evaluation must be, however, carefully considered.

![Typical DTA-$H_2O$ liberation curves of the mixtures after 1 day hydration.](image)

Up to 1 day, the reference sample shows a typical cement pattern [4] with the CSH gel main peak between 120 and 130 °C, and the CH at 475 °C. The CSA-enriched sample shows a sharper CH peak at 460°C. The alkali-free accelerated samples (E) display a smaller CH peak, whereas the alkali-rich accelerated one shows a broad CH peak at 450°C. Up to 28 days the main
hydration takes place, and the curve pattern show a general increase in the bound water and a broadening of the peaks indicating the presence of more amorphous structures (Fig. 4.13).

Fig. 4.13: Typical DTA-H2O liberation curves of the mixtures after 28 days hydration.

At this hydration stage the CSH (150-220°C) and the CH (450-540°C) further develop, with a general shift (20-40°C) of the peaks towards higher decomposition temperatures.

Up to 6 months (Fig. 4.14) the amount of bound water further increases, and the distinction of the phases at T < 300°C (peaks superposition) becomes difficult.

In all cases, broader peaks (100-300°C; 450-560°C) occur for both the unaccelerated and the CSA-enriched sample compared to the accelerated mixtures (Fig. 4.14).
4. Results and data evaluation

4.1.3.3 The hydration of the aluminate phases

A general acceleration of the C₃A and C₄AF is obtained with the addition of the admixtures as depicted in Fig. 4.15.

The main acceleration of the C₃A phase occurs within 1 day for all the accelerated samples. From 1 day the hydration is strongly slowed down for all the mixtures and almost coincides with the reference (ST) up to 6 months (Fig. 4.15).

The C₄AF phase, being less reactive (curve slopes), shows a slow but continuous reaction over time compared to the C₃A. As depicted in Fig. 4.15, the hydration of the ferrite phase is accelerated by all the admixtures, compared to the unaccelerated sample.

Fig. 4.14: Typical DTA-H₂O liberation curves of the mixtures after 6 months hydration.
Ettringite forms mainly within the first 4 hours for all the accelerated samples, whereas for the reference and the CSA-enriched the highest amount is reached after 1 day hydration. Because of the accelerated $C_4AF$ consumption during the first 4 hours, the ferrite phase may also contribute to the formation of Fe-rich ettringite. As observed with the 1 day DTA (Fig. 4.12 E), higher amounts of ettringite crystals are obtained in particular with the addition of the alkali-free accelerators within the first 4 hours, up to 6 months (Fig. 4.15). The alkali-rich accelerated sample indicates a broad peak at 170°C probably due to the superposition of both ettringite and KCA$\tilde{S}$SH, and the presence of $AH_3$ at 350°C (Fig. 4.12 L20). The CSA-enriched sample shows an ettringite peak at 150°C, and the reference only a small peak overlap at ca. 150°C (Fig. 4.12). Up to 6 months, these ettringite peaks become less distinguished and overlap with the CSH peaks (Fig. 4.13, Fig. 4.14). However, the ettringite amounts tend to slightly decrease up to 6 months for all the investigated samples (Fig. 4.15).
Between 4 hours and 1 day, the C\textsubscript{3}A shows a further reaction, and this does not always correlate with a simultaneous ettringite formation, at least not for all the alkali-free accelerated samples. Therefore a formation of phases such as C\textsubscript{4}A\textsubscript{C}\textsubscript{2}H\textsubscript{11} and C\textsubscript{4}A\textsubscript{C}\textsubscript{0.5}H\textsubscript{12} must also be taken into account. It is important to emphasize that monosulfate was generally not detected. This is presumably due to the carbonation with the atmospheric CO\textsubscript{2} which reacts with the aluminates to the former phases, as also reported by Taylor [4], or to the reaction with CaCO\textsubscript{3} added to the cement (chapter 5.1.2.2).

![Graph](image)

**Fig. 4.16:** XRD semi-quantitative evaluation of the AF\textsubscript{m} phases development up to 6 months (time-log scale)

All the accelerated mixtures contain increased amounts of C\textsubscript{4}A\textsubscript{C}\textsubscript{0.5}H\textsubscript{12} (Fig. 4.16), although from 28 days all the curves reach and coincide with the reference up to 6 months. The C\textsubscript{4}A\textsubscript{C}\textsubscript{11} development displays an opposite behavior. Compared to the reference sample, an initial reduced formation of this phase is observed, whereas from 28 days up to 6 months higher amounts are detected.

A phase transformation AF\textsubscript{m}\textsubscript{12} towards AF\textsubscript{m}\textsubscript{11} occurs over time. This can be followed with the DTA (Fig. 4.17; Fig. 4.18; Fig. 4.19).
Up to 1 day all the samples display a CaCO\(_3\) peak at 720 °C, and on its left flank the peak of the C\(_4\)A\(_{0.5}\)H\(_{12}\) phase at 660°C (Fig. 4.17). Furthermore, the presence of C\(_4\)A\(_{11}\)CH\(_{11}\) is observed at 810°C for the alkali-free and the alkali-rich accelerated samples.

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**Fig. 4.17:** Typical DTA-CO\(_2\) liberation curves of the mixtures after 1 day hydration.

**Fig. 4.18:** Typical DTA-CO\(_2\) liberation curves of the mixtures after 28 days hydration.
Up to 6 months, the C₄AbestosCH₁₁ peak at 850°C appears more clearly, although the C₄AvesC₄H₁₂ peak at 660 °C still slightly persists.

4.1.3.4 Microstructures of samples with accelerators

The addition of the accelerators largely influences the microstructural development at early and at later stages. As highlighted in Fig. 4.20, after 1 day, remarkable structural and morphological differences can be observed.

The reference sample (ST) appears in general loose, and still shows big capillary pores (ca. 8 µm). The structure remains relatively inhomogeneous with the massive crystallization of CH bundles occasionally intermixed with fibrous CSH I gel, and CH hexagonal plates precipitated from the pore solution. Ettringite needles precipitated from the pore solution and radially arranged on the clinker surfaces are both present. Nevertheless, these needles are in general not sufficient to fill the pores, linking neighbouring hydrates or clinkers (Fig. 4.20 ST).
Fig. 4.20: Microstructural development of the mixtures after 1 day hydration. Left: general overview of the structure (magn. 1500). Right: details (magn. 10000).
Fibrous CSH I and honeycomb CSH II gel are both present. Tightly packed CSH III grains, prominent for older pastes [4], are rarely present on some clinker surfaces. The presence of the Mg-rich CSH gel indicates the hydration of the C34S phase (Fig. 4.21 left).

![EDX Spectra: Left: hydrated Mg-rich CSH gel. Right: Silicium incorporation in the CH lattice.](image)

The incorporation of Al, S, K, and Fe in the CSH gel occurs (Fig. 4.21 left), and minor traces of Al, S, K, Fe and Si are present in the CH (Fig. 4.21 right), although it remains unclear if these are incorporated in its structure or are present as small inclusions [192]. The microstructure of the CSA-enriched mixture (RF) appears slightly more compact. More short prismatic ettringite crystals (1μm) are homogeneously distributed within the structure and partially fill the pores. Compared to the reference sample, radial arrangements of ettringite often occur. The ettringite prisms are partially intermixed with CH bundles and with CSH fibrous gel (Fig. 4.20 RF).

The addition of the alkali-free accelerators favors the segregation and the enrichment of great amounts of bigger sized (5μm) ettringite prisms and their relative inhomogeneous distribution within the microstructure. These crystals are in some cases interlocked or occasionally closely intermixed with the neighbouring hydrated mass (Fig. 4.20 E), mostly filling up the pores down to 1 μm. CH bundles are less present. Outside the ettringite-enriched zones, the hydration proceeds as for the unaccelerated sample.

The addition of the alkali-rich accelerator indicates a generally high capillary porosity between the hydrated mass. Thin elongated ettringites are homogeneously distributed, and are mainly precipitated from the pore solution. The numerous platy CH crystals precipitated within the pores, are occasionally intermixed with the ettringites and rarely with the CSH II gel and partially close the pores (Fig. 4.20 L20).
Up to 7 days the further growth of the CSH gel is observed, although within the alkali-rich accelerated sample this process appears strongly delayed (Fig. 4.22 L20).

The structure of the reference sample is compact, and the dimensions of the capillary pores are reduced (1-2 μm). The CSH II gel is still present, but a partial development to granular CSH III and to amorphous CSH IV takes place. The ettringites do not generally change their dimensions, but because
of the CSH gel growth, they are now more able to close the pores. CH bundles are present in large amounts. The structure of the CSA-enriched sample is also compact. The more homogeneous distribution and intermixing of the small prismatic ettringites with the CSH II and their higher amount (Fig. 4.22), allows these hydrates to further fill the pores.

The microstructure of the alkali-free accelerated samples is also characterized by the development of the CSH gel, and by the almost unchanged morphology of the ettringite prisms (Fig. 4.22 E), although some prismatic cavities, especially present on the CSH IV gel, probably indicate an initial dissolution of the ettringite crystals, as confirmed by XRD measurements (Fig. 4.15). At this stage of the hydration the presence of ettringite-enriched zones becomes clearly visible (Fig. 4.22 E).

The porosity within the alkali-rich accelerated sample remains high, and the CSH II gel is highly present (Fig. 4.22 L20) and rarely develops to CSH IV. In some areas the intermixing between the thin elongated ettringite rods, the CSH II and the CH remains scarce.

Up to 28 days, a general lowered porosity and a crystallization of the CSH II to CSH IV dense gel is observed for all the samples (Fig. 4.23), except for the alkali-rich one, where the development and growth to the CSH IV is generally delayed, and the connection between hydrated mass is therefore barely achieved (Fig. 4.23 L20). Locally, the reference sample shows small elongated ettringite prisms intermixed with CSH II gel which lead to a more dense structure (Fig. 4.23 ST). With the addition of pure CSA the intermixing CSH II-ettringite prisms is promoted (Fig. 4.23 RF), and the structure becomes more compact.

The growth of the CSH gel, allows the ettringite-rich zones of the alkali-free accelerated samples to become distinguishable. Within these high porosity zones CH hexagonal plates are often present (Fig. 4.23 E).
Up to 6 months the CSH gel further hydrates to CSH IV except for the alkali-rich accelerated sample where this development is clearly delayed (Fig. 4.24 L20).
The reference sample shows the CSH IV dense gel which is partially intermixed with the CH massive bundles. Small ettringite prisms are occasionally present in the residual pores and the structure becomes generally very dense and compact (Fig. 4.24 ST). The higher amount of ettringites and their homogeneous distribution within the microstructure of the CSA-enriched sample, allows a frequent tight intermixing between the
ettringite small prisms and the CSH IV dense gel (Fig. 4.24 RF). This leads to a very compact structure.

The ettringite enrichment zones present within the alkali-free accelerated samples occasionally exhibit a variation in the morphologies of the prisms ranging from thin elongated to short big ones.

The alkali-rich accelerated sample indicates the general highest porosity within the whole microstructure. CSH II early stage honeycomb gel is still largely present (Fig. 4.24 L20). Occasionally, CH hexagonal plates and thin elongated ettringites are also present.

4.1.3.5 The development of the porosity

Generally, the cement paste includes pores with radii < 1 μm. Pores with smaller radii, are believed to be an integral part of the hydrated material and are called "gel pores". Pores with greater radii, whose volume increases with increasing W/C ratio and overall porosity are called "capillary pores". Such a differentiation remains, however, rather arbitrary [2]. The investigated porosities range within the former values, and a differentiation between the mixtures up to pore radii smaller than 0.01 μm remains difficult. Compared to the early stages, up to 6 months the pore size distribution curves show a general shift towards smaller radii, and a narrower distribution of the pore sizes (Fig. 4.25).

Compared to the unaccelerated sample (ST) and the one in which CSA is added (RF), the addition of the alkali-free accelerators generally shift the 1 day main peak to smaller pores. On the contrary, the alkali-rich accelerated sample (L20) display a wide range of pores (Fig. 4.25 1d).

Up to 7 days the peaks of the reference and the CSA-enriched sample shift towards smaller pore size, whereas for the alkali-free samples this shift occurs to a smaller extent, and almost coincide with the unaccelerated sample. The addition of CSA generally indicates wider pore radii compared to the reference sample, whereas for the alkali-rich one, a wide range of big pores with radii up to 0.05 μm persists (Fig. 4.25 7d).
Fig. 4.25: Pore radius distribution with time. The sample NQ indicates the addition of silica fume to the mixture (W/C 0.48) and is displayed for comparison (chapter 4.1.5.2). The graph after 1 day hydration displays a pore radius scale up to 1 μm.

Up to 28 days, smaller pore radii are observed for all the samples (Fig. 4.25 28d), whereas up to 6 months a narrowing of the main peaks is observed (Fig. 4.25 182d). The pore radii distributions almost coincide, although the alkali-free accelerated mixtures indicate an increased intruded volume, compared to the unaccelerated sample. The alkali-rich accelerated mixture further displays the widest distribution of big pore radii.
4.1.4 Fracture mechanical characteristics

4.1.4.1 Fracture surfaces

From 7 days up to 6 months hydration, SEM investigations showed constant topographical features in the fracture surface of the mixtures. These morphological aspects already appear after 28 days, and they can also be partially observed by naked eye.

![Fracture surface images](image)

*Fig. 4.26: Typical fracture surface topography of the specimens after 28 days (magn. 50).*

In fact, both the unaccelerated and the CSA-enriched sample show a relatively smooth planar fracture surface (Fig. 4.26 ST; RF), whereas the alkali-free accelerated show an extremely tortuous one. Within these latter samples, many "internal" fracture surfaces are present on the whole surface topography (Fig. 4.26 E). Along these "internal" surfaces, ettringite prisms enriched zones with CH hexagonal plates and CSH II (chapter 4.1.3.4) mainly occur, and many of the cracks systems arise from these zones. The tortuosity of the alkali-rich accelerated sample (Fig. 4.26 L20) is less remarkable compared to the latter samples.

The fractures run along the cleavage of the CH bundles, and occasionally around the clinker grains. Multiple fine cracks also run within isolated areas and throughout the CSH IV dense gel. The intergranular fractures observed at early stages, become transangular as hydration proceeds.
The characterization of the fracture roughness can be achieved with a laser UBM profilometer (Fig. 4.27; Fig. 4.28).

**Fig. 4.27:** Typical roughness profiles of the fracture surfaces of the mixtures after 28 days of hydration.

**Fig. 4.28:** Typical waviness (Wt) of the fracture surfaces after 28 days. Wt: maximum height between peaks and valleys of the low-pass filtered (<1.21mm) profiles.
The high roughness present with the addition of the alkali-free accelerators clearly appears (Fig. 4.27 E), and it is further confirmed by the other roughness parameter, namely the waviness (Fig. 4.28 E).

Moreover, as depicted in Fig. 4.29, the evaluation of the main roughness parameters allows a better quantification of the roughness between the specimens.

![Graph](image)

**Fig. 4.29:** Roughness of the fracture surface of the specimens. Ra: arithmetic average of the absolute value of all points. Rq: root mean square of the value of all points. Rz ISO: maximum individual peak to valley height (arithmetic mean of the 5 highest peaks and the 5 lowest valleys). Wt: maximum height between the peaks and valleys of the low-pass filtered (<1.21 mm) profiles.

Supplementary e.g. three-dimensional topographic informations may also be attained with a confocal microscope. The higher fracture roughness of the alkali-free accelerated samples was also evidenced, although a clear resolution and quantitative differentiation between the samples was partially difficult.

However, the higher roughness of the fracture surfaces of the alkali-free accelerated samples can be definitively stated.
4.1.4.2 Fracture energy vs. fracture surface roughness

The specific fracture energy describes the absorbed energy per unit crack area for the complete separation of the crack surfaces (chapter 2.2.3). These energy values of the investigated samples indicate a general trend, and can be correlated with the roughness of the fracture surfaces as highlighted in Fig. 4.30.

![Fracture Energy vs. Roughness](image)

Fig. 4.30: Correlation between the specific fracture energy (mean std. 0.00086) and the fracture surface roughness (RZ ISO mean std. 12.92 μm) after 28 days.

The alkali-free accelerated samples show the highest fracture roughness and a generally high fracture energy, whereas the unaccelerated and the CSA-enriched sample show lower values. The alkali-rich sample shows low roughness and fracture energy values.

4.1.4.3 Correlations with the compressive strength

A general relationship between the roughness, the fracture energy and the compressive strength can be determined, according to the Fig. 4.31.
A remarkable distinction between the alkali-free accelerated (AF, AS L50) and the other samples (ST, RF, L20) is highlighted in Fig. 4.31. In fact, the higher roughness of the fracture surfaces of the former, coincides with a compressive strength decrease. Despite the low roughness of the fracture surface of the alkali-rich accelerated sample (L20), this shows the lowest strength values. Almost the same remarks can be made for the relation strength-fracture energy, since a good correlation between fracture energy and the fracture surface roughness is observed (Fig. 4.30).

4.1.5 Influence of silica fume addition

The addition of silica fume in shotcrete generally improves the adhesion, cohesion, thickness of the build-up layer of the plastic shotcrete, reduces the rebound and to some extent the amount of accelerator required. Furthermore, the mechanical properties of the hardened shotcrete such as the compressive, the flexural strength, and the durability are generally also increased [7] (Tab. 2.1).
4.1.5.1 Silica fume composition

The investigated silica fume, consists of rounded layered particles (0.005-2 mm) and its structure is depicted in Fig. 4.32. It mainly contains 90.2 % amorphous SiO₂, 1.03 % Fe₂O₃, 1.03 MgO, 1.77 % K₂O and organic carbon (1.35 %).

![Polished sample of silica fume particles intermixed with epoxy resin.](image)

The light inclusions consist of silicium, iron oxides, and partially of organic matter. Si metallic may also be considered as a part of the inclusion.

4.1.5.2 The development of the compressive strength

The addition of silica fume remarkably changes the strength development especially at later ages. Compared to the unaccelerated sample (NQ), the alkali-rich one shows a considerable strength decrease (Fig. 4.33 L20). The strengths of the alkali-free accelerated and the CSA-enriched sample, almost coincide and indicate higher strength values than the reference sample (NQ) up to 6 months (Fig. 4.33).
4.1.5.3 Microstructural interactions with the cement paste

Slightly reduced porosities compared to the samples without silica fume are present over time for the unaccelerated mixtures, as indicated by MIP measurements (Fig. 4.25 NQ, ST). Nevertheless, SEM investigations indicate considerable amounts of homogeneously distributed poorly reacted silica fume grains (10-100 μm). The interface cement paste-silica fume remains, however, the main microstructural feature and indicates remarkable differences between the mixtures (Fig. 4.34).

In the reference sample a high capillary porosity exists between the silica fume grains and the cement paste. The porous zones can extend more than 50 μm away from the silica fume grains. Ettringite needles are often enriched in these zones and arrange radially in contact with the silica fume surface (Fig. 4.34 NQ). Occasionally, CSH IV dense gel and CH platy crystals are also observed. In the CSA-enriched sample the higher amounts of ettringite prisms reduce the capillary porosity (Fig. 4.34 RF).

With the alkali-free accelerated samples the porosity of the interface is enormously reduced due to the intergrowth of the ettringite prisms and their intermixing with the CSH IV dense gel (Fig. 4.34 E). The ettringite prisms along these contact zones do not form enriched high porosity domains but are rather good intermixed with the CSH IV dense gel, thereby reducing the porosity.
The alkali-rich accelerated sample shows a high porosity within the whole microstructure. The sporadic presence of CSH II, CH platy and occasionally enrichments of thin elongated ettringites (Fig. 4.34 L20), cannot be considered as a particular feature along the silica fume grains, because of their presence within the whole structure.

Fig. 4.34: Microstructural development of the interface cement paste-silica fume for the mixtures after 6 months hydration. Left general overview (magn. 1500). Right: details (magn. 10 000). The white lines clarify the cement paste-silica fume boundary.
4.1.5.4 Influence on the hydration

The addition of silica fume does not remarkably change the phases development of the mixtures. However, compared to the samples without silica fume, a slight consumption of the CH through the pozzolanic reaction takes place (Fig. 4.35).

Fig. 4.35: XRD semi-quantitative CH amounts up to 6 months (time-log scale). Left: without silica fume. Right: with silica fume.

4.2 Sulfate attack

4.2.1 Introduction

As previously stated (chapter 2.2.5.1) [17, 81], shotcrete exhibits the same durability features as conventional concrete. Generally, sulfate rich circulating waters which come in contact with the concretes cause extensive damage. Therefore, the durability of concrete, in particular the long-term predictions, is matter of considerable investigations, and becomes nowadays increasingly important for shotcreting in tunnels.

An unaccelerated reference (ST), a CSA-based alkali-free accelerator with an homogeneous distribution of the admixture within the cement paste (AF), an alkali-free accelerated with an inhomogeneous distribution of the admixture (L50) and an alkali-rich accelerated mixture (L20) are investigated. The addition of the CSA-based alkali-free accelerator inhomogeneously distributed (AF2) is displayed for comparison in order to
clarify the influence of the mixing procedure on the expansion behavior (Fig. 4.36). Being the shotcrete in tunnels partially subjected to increased temperatures, the investigations were carried out at 23°C and 65°C, in order to find out the effect on the sulfate resistance.

4.2.2 Dimensional stability

Measurements of the linear expansion at 23°C and 65°C indicate different behaviors of the mixtures up to 6 months (Fig. 4.36).

At 23°C the homogeneous distributed alkali-free accelerator (S/AF) shows the fastest and greatest expansion, which results in the almost complete softening and disintegration of the samples within the first 40 days. The inhomogeneous dissolution of the alkali-free accelerator (S/L50) and the inhomogeneously distributed alkali-free one (S/AF2), cause a delay in the expansion, and both reach 6 months of sulfate curing with a slight cracking and disruption of the samples. The expansion of the alkali-rich accelerated samples (S/L20) takes place within ca. 30 days and show considerable cracking and spalling of the exposed surface layers. The unaccelerated one (S/ST) indicates merely a slight expansion up to 6 months with almost no damage.

At 65°C, variations in the expansion behavior and in the extent of the damage are observed. In fact, compared to the samples at 23°C, the homogeneous alkali-free accelerated samples (ST/AF) show a delayed expansion and reach
after ca. 45 days a slightly reduced disintegration. The inhomogeneously distributed alkali-free accelerated samples (ST/AF2) do not expand and show only slight damage up to 6 months, whereas the inhomogeneous addition of the alkali-free admixture (ST/L50) shows a slightly accelerated expansion and cracking compared to the similar samples at 23°C. The alkali-rich one (ST/L20) indicates a slowdown of the expansion, resulting in lowered cracking and spalling, whereas the reference samples (ST/ST) strongly accelerate their expansion, cracking and disruption.

4.2.3 Development of the main phases

The reactions which occur when sodium sulfate reacts with the CH and the hydrated aluminates mostly lead to the formation of gypsum and ettringite, as already reported [2]. The restrained crystallization of the latter phase is associated with expansion and damage caused by a considerable increase in the solid volume [88]. Consequently, being ettringite and gypsum generally considered the main cause of damage when cementitious specimens are attacked by sulfates [2], the development of these phases was followed up to 6 months (Fig. 4.37).

Generally increased ettringite amounts for the specimens cured at 65°C are observed (< 28 days), although for the homogeneous alkali-free accelerated samples (ST/AF) and for the alkali-rich ones (ST/L20), a reduction in the amounts is observed at later stages (Fig. 4.37).

The gypsum amounts at 23°C fluctuate, and show a general increase for the alkali-free (S/AF; S/L50) and the reference (S/ST) samples up to 6 months. Unlike, the alkali-rich samples (S/L20) indicate a decrease of this phase. At 65°C the gypsum forms within the first 15 days (Fig. 4.37), and tends towards negative values up to 6 months.

Generally, the maximum gypsum variations at 23°C and 65°C (ca. 2.8 %) are much smaller than ettringite (18 %).
4. Results and data evaluation

4.2.4 Ionic diffusion

4.2.4.1 Background

The ion diffusion (I, Cl, Cs⁺) through water saturated cements was mostly investigated in the nuclear industry for the immobilization of radioactive waste [193], or in the point of view of the corrosion of reinforcement (Cl⁻)[2]. Experiments conducted for Cl and alkali ions [194, 195] showed large differences in the diffusivity of these ions, and this is a first indication that the ion migration through a cement paste, may not be a
simple diffusion process. The difference in ionic diffusivity between anion and cation was accounted for by a co-diffusion of Ca$^{2+}$ ions [195-197].

Ionchromatographic, pH and conductivity measurements allowed a clear direct and indirect differentiation of the diffusion and adsorption of the SO$_4^{2-}$ ions between the investigated mixtures. As most of the workers [194, 195, 198], the second law of Fick for porous media was used to analyze the results. Instationary apparent diffusion coefficients were then extrapolated. The calculation of the apparent diffusion coefficients "$D_a$" was done graphically by drawing log c(x) at a certain time against x$^2$ according to equation (4.1).

$$\log C(x) = \text{const} - \frac{0.1086}{D_a t} x^2$$  \hspace{1cm} (4.1)

C: concentration  
t: time of diffusion  
x: distance from the source  
$D_a$: apparent diffusion coefficient

The slope of the straight line is then proportional to the apparent diffusion coefficient "$D_a$". This graphical method was also used for the diffusion of ions through other porous materials [198]. A constant concentration of the curing sulfate solution is assumed, and a linear interpolation was used to calculate the coefficients. Nevertheless, because of the scattering of some values, caused by the irregular adsorption behavior of the mixtures (Fig. 4.38), the calculated average "$D_a$" must be taken as indicative values.

### 4.2.4.2 Apparent diffusion of the SO$_4^{2-}$ ions

Sulfate ions penetrate into the water saturated cementitious specimens in different amount and manner, and undergo chemical reactions with the cement phases. The main interactions appear to lead to the ettringite and the gypsum formation (chapter 4.2.3) and to the CSH gel disintegration (chapter 4.2.5.1). The ionchromatographic measurements indicate a higher sulfate adsorption for all the accelerated specimens at all curing times and temperatures (Fig. 4.38). After 28 days of sulfate curing, a large sulfate adsorption is observed for all the samples within the first 2 mm from the
4. Results and data evaluation

surface. Up to 91 days, the amounts of adsorbed sulfate show a general increase and reach for some of the alkali-free accelerated samples constant high values along the entire profile down to 5 mm (S/AF, ST/AF), as depicted in Fig. 4.38.

![Graph](image)

Fig. 4.38: I onochromatographic measurements: penetration depth vs. total amount of adsorbed sulfate at 23°C and 65°C after 28 days (left) and 91 days (right) of sulfate curing.

After 28 days at 23°C, the reference sample (S/ST) indicates a remarkable penetration of the sulfate ions within the first 2 mm. The inhomogeneous addition of the alkali-free accelerator (S/L50) shows slightly increased amounts, although for the reference samples (S/ST) and the alkali-free accelerated (S/L50) the main sulfate penetration takes place within the first 2 mm. An increased penetration depth is reached with the homogeneously distributed alkali-free accelerator (S/AF). The addition of the alkali-rich one (S/L20) causes a higher adsorption within the first 2 mm. At 65 °C generally increased adsorbed amounts of sulfate are observed. The adsorption is particularly enhanced with the homogeneous addition of the alkali-free (ST/AF) and the alkali-rich admixture (ST/L20).

Up to 91 days, generally higher amounts of adsorbed sulfate and increased sulfate penetration depths are displayed (Fig. 4.38 right). A noteworthy feature is the higher adsorption of sulfate at 23°C for the homogeneous alkali-free accelerated samples (S/AF). This fact is also observed up to 3 mm for the alkali-rich accelerated (S/L20), partially for the inhomogeneous alkali-free accelerated up to 2 mm (S/L50) and for the reference samples up to 2 mm (S/ST) (Fig. 4.38 right).
Diffusivity of sulfate ions through portland cement-based material calculated with different techniques, including radioactive tracer methods, lie in the range $2-30 \times 10^{-14} \text{m}^2\text{s}$. An average $D_a$ of $3.2 \times 10^{-11} \text{m}^2\text{s}$ is calculated for the investigated specimens cured at $23\degree C$ for 1 months. The curing at $65\degree C$ results in an higher average $D_a$, namely $5.18 \times 10^{-11} \text{m}^2\text{s}$. Up to 3 months an average value of $1.02 \times 10^{-10} \text{m}^2\text{s}$ at $23\degree C$ and $1.24 \times 10^{-10} \text{m}^2\text{s}$ at $65\degree C$ are calculated. Up to 3 months, the $D_a$ generally increase and level off for both the $23\degree C$ and the $65\degree C$ cured samples. This levelling is further confirmed by the higher sulfate adsorption of the $23\degree C$ cured samples and is especially remarkable for the homogeneous alkali-free accelerated samples (S/AF-ST/AF), and for the alkali-rich one (S/L20-ST/L20) (Fig. 4.38 right).

### 4.2.4.3 Exchange between the $\text{SO}_4^{2-}$ and the $\text{OH}^-$ ions

Based on microstructural features observed during the $\text{MgSO}_4$ attack, a schematic representation of a counter-diffusion pattern of $\text{OH}^-$ ions from the specimens outward and $\text{SO}_4^{2-}$ from the solution inward was reported by Bonen et al. [99]. The same counter-diffusion is assumed to take place also for the $\text{Na}_2\text{SO}_4$ attack, and because of the higher mobility values of the $\text{OH}^-$ ions compared to the $\text{SO}_4^{2-}$ ions, respectively $20.52 \times 10^{-4} \text{(cm}^2\text{s/V})$ and $8.27 \times 10^{-4} \text{(cm}^2\text{s/V})$, pH and conductivity measurements were performed. In fact, the $\text{SO}_4^{2-} \leftrightarrow \text{OH}^-$ exchange can also be taken as a measure of the sulfate penetration. This exchange causes a drop in the conductivity, and in the pH values of the investigated solutions. Moreover, these latter two measurements well correlate one another and with the ionchromatographic measurements (Fig. 4.38), thereby giving a further indication of the sulfate adsorption. A generally higher resolution is obtained with the conductivity measurements compared to the pH (Fig. 4.39). In fact, 28 days pH measurements do not show remarkable differences between the specimens, except for the alkali-rich sample cured at $65\degree C$ (ST/L20), which indicates a pH drop along its profile (Fig. 4.39-28 days).
Fig. 4.39: pH (left side) and conductivity (right side) variations of the solutions added with the pulverized mm layered profiles of the mixtures cured at 23°C and 65°C for 28 days and 91 days.

On the contrary, conductivity measurements display a reduction in the conductivity, within the first 2 mm of the profiles for the reference sample (S/ST) and for the inhomogeneously distributed alkali-free accelerated sample (S/L50). In these latter cases the adsorption is slightly increased at 65°C. The homogeneous distribution of the alkali-free accelerator (S/AF) shows a generally higher sulfate adsorption along the entire profile, and at 65°C this process is accentuated (Fig. 4.39-28 days). The alkali-rich sample indicates a high sulfate adsorption along the profile at 23°C (S/L20), whereas at 65°C (ST/L20) an increased adsorption takes place within the first 3 mm (Fig. 4.39-28 days).

Up to 91 days, a generally increased resolution, lowered pH and conductivity values are observed, and this correlates with the ionchromatographic measurements (Fig. 4.38), thus indicating higher adsorption of sulfates for the accelerated samples. At 23°C pH measurements show a pH drop for the reference sample (< 2 mm), the inhomogeneously distributed alkali-free sample (2-3 mm), and for the homogeneous alkali-free sample which
indicates lowered values along the entire profile down to 4-5 mm. The alkali-rich sample is characterized by a great pH decrease down to 3 mm (Fig. 4.39-91 days). The same observation can also be made for the conductivity measurement (Fig. 4.39-91 days).

Compared to the values at 65°C, generally lower pH and conductivity values are observed at 23°C especially with the homogeneous dissolution of the alkali-free accelerator (S/AF-ST/AF) and partially with the inhomogeneous dissolution of the alkali-free admixture (S/L50-ST/L50). With the addition of the alkali-rich one (S/L20-ST/L 20) the values tend to overlap down to 2-3 mm (Fig. 4.39 91-days). This latter features well correlate with the sulfate adsorption after 91 days (Fig. 4.38).

Conversely, after 28 days the specimens cured at 23°C display generally lower sulfates adsorption (Fig. 4.38) and less decreased pH and conductivity values compared to the samples cured at 65°C (Fig. 4.39-28 days).

4.2.5 Damage types

4.2.5.1 Structural features of the exposed layers at 23°C

In order to clarify the main mechanisms involved during the Na₂SO₄ attack and to characterize the resulting damage, SEM investigations of the exposed layers were performed.

After 56 days of curing at 23°C, the unaccelerated sample (S/ST) show no damage of the exposed surface layer, which well correlates with the high presence of the CSH amorphous dense gel (Fig. 4.40 center side). Small amounts of ettringite prisms (5 μm) are occasionally precipitated within the pores (Fig. 4.40 right side).
The specimens with the alkali-free accelerator homogeneously distributed (S/AF) indicate a complete softening and disintegration. A great disintegration of the CSH gel, which reacts to form ettringite (Fig. 4.40 right side), and a general increase in the porosity takes place. Ettringite is largely present, although some gypsum crystals occasionally occur. The XRD measurements also confirm the higher gypsum amounts of this sample especially after 91 days (Fig. 4.37). On the other hand, a bad homogenization of the alkali-free accelerator (S/L50) results in a very slight disruption and cracking (Fig. 4.40 left side). The dense CSH gel is largely present and reacts to form ettringite prisms only in localized zones (Fig. 4.40 right side), within the cement paste. These zones apparently correlate with the presence of
white efflorescences in the specimen (Fig. 4.40 left side). The addition of the alkali-rich accelerator (S/L20) causes a spalling and cracking of the exposed surface layers (Fig. 4.40 left side). A sharp external zone consisting of tightly packed bundles of ettringite elongated prisms is observed (Fig. 4.40 center-left side).

4.2.5.2 Structural rearrangements at 65°C

The curing of the specimens at 65°C causes considerable microstructural rearrangements and result in a variation in the extent of the damage (Fig. 4.41). Generally, short amorphous-like ettringite prisms are present within all the specimens. The CSH gel still appears to be partially present within the attacked surface layers.

The unaccelerated sample (ST/ST) shows a slight disruption of the surface. Ettringites mostly fill the capillary pores (Fig. 4.41 right side). The addition of the alkali-free homogeneously distributed accelerator (ST/AF) indicates a moderate softening and disintegration of the specimen. The CSH gel is slightly present and ettringite prisms precipitate in large amounts. Small stocky partially amorphous-like ettringite prisms are generally present within the whole microstructure (Fig. 4.41 right side). The inhomogeneous distribution of the alkali-free accelerator (ST/L50), indicates an initial cracking of the exposed surface layer (Fig. 4.41 left side), a high presence of ettringite prisms, the presence of small partial amorphous-like ettringites and the sporadical reaction of the CSH gel to ettringite. The addition of the alkali-rich accelerator (ST/L20) indicates an initial spalling and cracking of the surface layers (Fig. 4.41 left side), the presence of a sharp zone of ettringite prisms and the partial presence of the CSH gel (Fig. 4.41 center side). A considerable high porosity between the ettringite big prisms must also be taken into account (Fig. 4.41 right side).
Fig. 4.41: Comparison between the damage (left side) and the microstructural features of the exposed layers (center side magn. 2500-right side magn. 10 000) of the specimens cured for 56 days at 65°C.
4.3 CSA / burnt oil shale-based cement

4.3.1 Introduction

Compared to the previously alkali-free, calciumsulfoaluminate-based accelerated systems (chapter 4.1), used in shotcreting, the calcium-sulfoaluminate is used here in a burnt oil shale-based cementitious system as a component of the blend and activates the hydration of the burnt oil shale. This new composite cement, mainly used for repair works, attains a very high early strength, and belongs to the very rapid hardening cements.

Greatly improved early strength development is usually achieved by mixing the main phases $\beta$-$C_2S$, $C_4A_3S$, $C_S$ and $C_4AF$ [199] in a calcium-sulfoaluminate-based cement. The high early strength appears to be mainly supported by the formation of the ettringite [131, 140, 144, 174, 199], which also takes place for a $C_4A_3S$-CA-bearing calciumsulfoaluminate cement type activated with gypsum and hydrated lime [138].

A special calciumsulfoaluminate-based cement having burnt oil shales as a main component and CSA ($C_4A_3S$) as activating agent, also results in an accelerated high early strength development [12, 13]. Nevertheless, the different storage time of the burnt oil shales, mostly influences their CaO content, which appears to be the main factor affecting the strength development of the blends at early stages. In this context, the addition of the CaO-rich burnt oil shales results in lower early strength values of the blends.

Thus, the phase variations during the atmospheric storage of the burnt oil shales as well as the hydration behavior, the microstructure and the mechanical features such as strength and dimensional stability of the blends are investigated. In this rapid hardening system, the first 4 hours of the hydration became decisive.
4.3.2 Burnt oil shale: atmospheric storage

As most of the cements [200], burnt oil shales react and form considerable amounts of hydrated products during their storage (Fig. 4.42).

Among the main phases, the CaO and the CaCO₃ display the greatest variations (4%), followed by the amorphous fraction (3%), the β-C₂S, the SiO₂ (ca. 2%), the CaSO₄ and the CH (ca. 1%). Among the secondary phases, remarkable variations are detected only for the glauberite (0.7%), and for the ettringite (0.4%). As depicted in Fig. 4.43, the AH₃, AFm₁₁ and the AFm₁₂ are also subjected to a variation during the atmospheric storage.

Compared to the 1 day stored burnt oil shales (OSF), the 3 months stored burnt oil shales (OSA) indicate higher amount of bound water (peak 0-200°C). CH is also slightly more present (390-550°C), as confirmed by the XRD measurements (Fig. 4.42 left). The AH₃ is slightly present for the 1 day
stored burnt oil shales, but it disappears after 3 months of storage (Fig. 4.43 left). The $\text{SO}_2$ liberation OSA curve indicates weakly bound sulfates (100-300°C), and the shift in the current increase towards lower temperatures indicates the presence of bound sulfates such as ettringite, hydrated glauberite both superposed by anhydrite (Fig. 4.43 center). The CO$_2$ curve shows the CaCO$_3$ at 760°C and the crystallization of C4A$\overline{3}$C$_{0.5}$H$_{12}$ to C$_4$AH$_{11}$, evidenced by the AFm$_{12}$ peak disappearance and the corresponding increase of the AFm$_{11}$ one for the 3 months stored burnt oil shales (Fig. 4.43 right).

4.3.3 Setting behavior

The addition of the two differently stored burnt oil shales (OSF, OSA) as main component of a CSA / burnt oil shale-based cement changes only to a few extent the setting of these latter cementitious systems (SC OSF, SC OSA), as depicted in Fig. 4.44.

4.3.4 Early strength, dimensional stability and CaO

The compressive strength and the shrinkage of the blends highlight different behaviors within the first 4 hours of the hydration (Fig. 4.45).

The blend containing burnt oil shales stored for 3 months at 23 °C and 65% relative humidity (SC OSA) reaches the highest strength values over the entire time intervals up to 4 hours. Unlike, the blend containing the 1 day stored burnt oil shales (SC OSF), shows a remarkable delay in the strength
4. Results and data evaluation

development and greatly lowered strength values, especially within the first 2 hours (Fig. 4.45 left).

![Fig. 4.45: Strength development (mean std. 0.69-left) and shrinkage behavior (mean std. 0.01-right) of the blends (mortar) within the first 4 hours.](image)

The storage of the burnt oil shales in a saturated CO₂ atmosphere lowers the strength values of the blend (SC OSA CO₂) only to a small extent compared to the normal atmospheric storage of the burnt oil shales (SC OSA). The addition of CaO and CH (5.5%) to the SC OSA blend, partially hinders the strength development, although the values remain slightly higher than the SC OSF blend (Fig. 4.45 left).

An important correlation exists between the strength development and the shrinkage behavior. In fact, the blend with the 1 day stored burnt oil shales as a component indicates an expansion between 50 and 80 minutes, thus correlating with the greatest delay in the strength development. On the other hand, the long-term atmospheric storage of the burnt oil shales and the storage in a CO₂ saturated one, results in a progressive shrinkage of the blends in which they are contained. The addition of CH and CaO to the SC OSA blend, lowers the strength values and indicate a slight expansion of these blends between 50 and 100 minutes. Compared to the SC OSF blend, the CH-, CaO-enriched SC OSA blends expand to a smaller extent (Fig. 4.45 right). The addition of AH₃ (present in the 1 day stored burnt oil shales Fig. 4.43 left OSF) to the SC OSA blend gives no remarkable reductions in the strength.
4.3.5 Hydration behavior

4.3.5.1 Phases development

As already noted, the strength differences are apparently caused by the different storage of the burnt oil shales. The two hydrated blends consisting of the 1 day (SC OSF) and the 3 months (SC OSA) stored burnt oil shales as components are constituted of various phases.

The ettringite, the $C_A\bar{S}$, the CH and the $\beta-C_2S$ are the only phases which display distinct developments within the first 4 hours of the hydration (Fig. 4.46) and are consistent with the DTA and the SEM measurements.

Fig. 4.46: XRD-Phases development within the first 4 hours. SC OSF: compound containing the 1 day stored burnt oil shales. SC OSA: compound containing the 3 months stored burnt oil shales. Average $R_{wp}$: 8.88%.
The slower consumption of the $\beta$-C$_2$S phase, and the constant higher values of the CH for the SC OSF blend compared to the SC OSA are evidenced. Furthermore, the former blend also indicates higher amounts of ettringite ($< 80$ minutes), as confirmed by the higher consumption of the C$_4$A$_3$S phase. DTA further show the development of the ettringite and the CSH gel as highlighted in Fig. 4.47.

*Fig. 4.47: DTA-H$_2$O liberation curves. Phases development of the blends (SC OSF; SC OSA) up to 2 hours.*
Up to 30 minutes, the SC OSF blend indicates a high water adsorption caused by the crystallization of the ettringite (140°C). Up to 1 hour, lower amounts of adsorbed water are detected which generally slightly increase again up to 2 hours. The CH (450°C) is constantly present up to 2 hours. Compared to the SC OSF blend, the SC OSA displays a generally higher amount of CSH gel and carbonate-bearing AFm phases (peaks overlap at ca. 220°C). From 1 hour increased ettringite amounts (140°C) for SC OSA is observed and confirmed by the XRD (Fig. 4.46), whereas the CH is not present.

4.3.5.2 Microstructural features

The SC OSF and the SC OSA blends show remarkable differences in their microstructural development up to 30 minutes (Fig. 4.48).

![Fig. 4.48: Microstructural development of the two blends after 30 minutes. Left: general overview (magn. 1500). Right: details (magn. 10000).](image)

The SC OSF blend indicates a loose and barely compact structure, with poorly reacted clinkers grains. Up to this stage amorphous-short prism-like ettringites are crystallized (≤ 1µm), and grow in close contact with the clinker surfaces barely connecting the clinker grains (Fig. 4.48 SC OSF). Unlike, the SC OSA blend shows a more compact structure, with the presence of an amorphous dense CSH gel, and the crystallization of thin elongated prism-like ettringites (5µm) within the pores. These two latter
phases are well interlocked and reduce the porosity, thereby connecting the clinker grains (Fig. 4.48 SC OSA).

Fig. 4.49: Microstructural development of the two blends after 1 hour (4 pictures above), and after 1.5 hour (4 pictures below) of the hydration. Left: general overview (magn. 1500). Right: details (magn. 10000).
After 1 hour, the short-prism amorphous-like ettringites become generally longer (1 µm) and the porosity is generally slowly reduced. CH crystals are largely precipitated and are partially interlocked with the ettringites, although a relative high capillary porosity still persists (Fig. 4.49 SC OSF). The scarce presence of a dense CSH gel, causes the structure to be relatively not compact. On the other hand, the SC OSA blend indicates a strong development of an amorphous dense CSH gel, which is well interlocked with the ettringite prisms, forming a more compact mass. Consequently, the general porosity is remarkably reduced (Fig. 4.49 SC OSA). In this latter blend CH crystals are barely present.

Up to 1.5 hour, the CSH gel generally further develops and the microstructure becomes more compact, especially for the SC OSA blend (Fig. 4.49).

4.3.5.3 Pore solutions

Suspensions were made in order to simulate the composition of the pore solution of the two type of blends. The measured pH and the $SO_4^{2-}$ concentrations indicate important differences between the two blends (Fig. 4.50).

![Graphs showing pH and sulfate concentration over time](image)

Fig. 4.50: pH (left) and $SO_4^{2-}$ (right) development for the solutions of the SC OSF and the SC OSA blends up to 4 hours. The horizontal line in the pH diagram indicates the pH of a saturated CH solution at 25 °C and at 1 bar.

The SC OSF blend indicates constant higher values up to 4 hours, and reaches sporadically the pH value of a CH saturated solution (Fig. 4.50 left).
The ionchromatographic measurements show generally higher $\text{SO}_4^{2-}$ concentrations for the SC OSF blend and a delayed concentration decrease over time. The $\text{SO}_4^{2-}$ concentrations for the SC OSA blend, remain constantly at lower values, and become zero already after 1 hour. After 2 hours, the $\text{SO}_4^{2-}$ ions disappear from the solutions of both the blends, and any renewed presence is observed up to 4 hours (Fig. 4.50 right).
5. Discussion

5.1 CSA / accelerators

5.1.1 Setting behavior of the samples

The setting of the unaccelerated reference sample (ST), mainly follows the general fixed pattern of hydration stages suggested by Taylor and Lea [2, 4]. Its setting is completed within 6 to 7 hours and coincides with the initial increase in the hydration temperature. Up to this stage, the microstructural investigations show an initial CSH crystallization (foil-like, amorphous), and the formation of CH crystals (2-3 μm). Despite their low presence, these two hydrates contribute to the setting of the unaccelerated OPC sample (ST), as also reported by other authors for OPC [2, 4, 22, 23]. The small amounts of hydrates present in the contact point of neighbouring clinker grains appear to be sufficient to bind them together. In addition, since the setting of cement paste is a mechanical process, it does not directly follow the phase development at early stages, as also reported by Guo [24]. The fact that ettringite mainly occurs as precipitate from the solution, but sometimes also arranges radially on the clinker surfaces, indicates that the concentration of the solution with respect to CH changes locally. Min et al. [157] reported a clear relationship between CH concentration in the solution and the mechanism of ettringite formation especially in calciumsulfoaluminate cements. This difference in the mechanism of ettringite formation also occurs within the unaccelerated sample, but to a smaller extent. In all cases, it appears that only the ettringites, which are radially arranged on the clinker surfaces partially linking them, contribute to a small extent to the setting of the reference sample. The low presence and the small dimensions of the precipitated ettringite needles within the solution do not appear to either partially fill the pores, or to link the clinker grains to one another. On the contrary, a recrystallization of the ettringite [19] and its formation with a stubby rod morphology was considered to be the main cause for the setting of OPC [20, 21].
The addition of CSA to the cement causes the $\text{C}_4\text{A}_3\text{S}$ phase to react (eq. (5.1)), with the formation of small prisms of ettringite on the clinker surfaces. As a consequence more coalescence points form between the clinker grains, thus linking the structure. The setting time is therefore shortened by ca. 100 minutes.

The addition of the alkali-free accelerating admixtures strongly accelerates the setting and changes the course of the reactions especially in the early stages. This great acceleration of the setting time was already reported [2, 24]. The calciumsulfoaluminate and the aluminum sulfate components of the investigated accelerators favor the crystallization of ettringite prisms on the clinker surfaces (zones of high local ion concentration) at a very early stage. Within 4 hours these crystals grow and almost fill the capillary pores between the clinker grains, thus reducing the porosity and giving rise to strengths as high as 2-3 MPa. The accelerated consumption of both $\text{C}_3\text{A}$ and $\text{C}_3\text{S}$ phases appears consistent with the very early strength values measured, and is in agreement with investigations already reported [2]. In all cases, the formation of ettringite prisms within the first 30 minutes is largely sufficient to set the samples. The alkali-free accelerators contain high amounts of sulfates and this could be a premise for a false set [4]. Nevertheless, no gypsum is found, because the high aluminum content of these admixtures supports the ettringite formation rather than the gypsum one.

The setting of the alkali-rich accelerated sample is due to a combined action of hydrates such as amorphous KCASSH, CH and ettringite thin rods precipitated from the pore solution. Contrarily, an ettringite formation was proposed as main hydrate accelerating the setting of aluminate accelerated samples [25]. The shorter setting time compared to the alkali-free accelerators, is presumably due to the amorphous KCASSH phase and the CH crystallization, rather than the formation of ettringite rods. In fact, since at early stages (seconds to minutes) the concentration of the pore solution is high with respect to $\text{SO}_4^{2-}$ ions, silicate ions, and saturated in $\text{Ca}^{2+}$ ions [2], the addition of this alkali-rich admixture favors the very fast formation of KCASSH and CH directly from the pore solution. The sulfate necessary for the formation of ettringite rod-crystals is not introduced in the system directly with the admixture, like it is for the alkali-free accelerators, but it derives from the gypsum dissolution, thus requiring a little longer time for the sulfate to be available.
5.1.2 General strength correlation factors

5.1.2.1 Introduction

It is clear from other investigations [2] that the hydrated material is mainly responsible for the attained strength of cement paste, although non-hydrated residual cement grains act as a filler and also exhibit the capacity to resist external stresses. Hydrates formed during the hydration of different clinker minerals show an increase in the intrinsic strength at later ages in the order $C_3A < C_4AF < C_3S < C_2S$. It is also clear that the main contribution on the strength is given by the hydration of the $C_3S$ and the $C_2S$ (especially at later stages), and that the contributions of $C_3A$ and $C_4AF$ are relatively small and complex. The effect of alkalis is generally not uniform. A general correlation with the $SO_3$ content always exists: on increasing the content, higher strength values are obtained, whereas $SO_3$ contents above 4 % cause a decrease in the strength [2].

Generally, all the investigated accelerated mixtures indicate lower final strength values compared to the unaccelerated reference as stated by other authors in other investigations [2, 4-8, 14].

Unoriented CH bundles, present within the microstructure of all the investigated samples, may act as crack arrester, and this appears to be the main way in which CH might support the strength, although large CH crystals may act as crack flaws allowing the cracks to pass trough the CH cleavage planes [76].

Strength measurements performed on mortars and on cement pastes after 28 days and 6 months hydration indicate a similar general relationship between the strength values of all the investigated types of mixtures. However, cement pastes display slightly lower values (Fig. 5.1).

This fact, indicates that the microstructural features of the investigated cement pastes overshadow the role of the interfacial zone (cement paste-aggregate) concerning the strength development. In fact, although having a measurable effect, the degree to which the interfacial zone affects the strength of concrete was already questioned [2].
5.1.2.2 Phases development and porosity

The addition of alkali-free and alkali-rich accelerators influences the development of the previously described phases and thereby the strength. In fact, the high content of CSA (C₄A₃S) and aluminum sulfate in the former, and the high content of alkali aluminate hydroxide in the latter, causes the formation of considerable amounts of ettringite already in the early hydration stages, as described in equation (5.1) [139, 140] for the CSA (C₄A₃S) component and in equation (5.2) [4] for the alkali hydroxides aluminates and aluminum sulfate components.

\[
C₄A₃S + xCS + yC + zH \rightarrow jC₆A₃S₃H₃₂ + kAH₃ \quad (5.1)
\]

\[
6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O \rightarrow Ca₆Al₂O₆( SO₄ )₃ · 32H_2O \quad (5.2)
\]
The dissolution of the aluminum sulfate component, present within the alkali-free accelerators, leads, in alkaline environments, to the formation of $\text{Al(OH)}_4^-$ and $\text{SO}_4^{2-}$, thus promoting the ettringite formation. On the other hand, the addition of the alkali-rich accelerator supplies $\text{Al(OH)}_4^-$ ions, and also promotes the ettringite formation, but to a smaller extent (no sulfate is added).

The faster dissolution of the silicate phases up to 4 hours, appears to be forced by the ettringite formation. In fact, the $\text{Ca}^{2+}$ ions entering the liquid phase are promptly used for the crystallization of the ettringites. Nevertheless, SEM investigations did not allow the detection of an increased amount of CSH gel due to the faster C$_3$S dissolution. Thus, the 4-5 h strengths are mainly due to the ettringite precipitation from the pore solution, thereby linking the clinker grains. For the alkali-rich sample, the 4-5 hours strengths are caused by a combined crystallization of CH plates, amorphous KCASSH and ettringite thin elongated rods.

Up to 1 day hydration, all the mixtures show the presence of CSH gel as a general strength supporting factor. The slightly higher strength values of the accelerated samples are mainly due to the presence of the hydrates previously described. In fact, the porosity of the reference sample remains high, whereas the hydrates formed with the addition of the accelerating admixtures favor a remarkable reduction of the capillary porosity.

The phase development up to 6 months indicates the slight constant C$_{54}$S$_{16}$AM hydration which mainly contributes to the long-term strength values, whereas the development of the C$_3$S appears to support the strength especially at earlier hydration stages, as already stated [2]. The CH development displays a generally positive correlation with the strength, although for the alkali-rich sample the CH crystallization is partially promoted by the accelerating admixture, and it is not the result of the hydration of the silicate phases. On the other hand, the alkali-free accelerators consume part of the CH to form ettringite, and this explains the lower CH values with time. The porosity indicates a general correlation with the strength, namely smaller pore radii or less intruded volume coincide with higher strength values.
The contribution of the aluminate phases to the long-term strength development is mainly supported by the $C_4AF$ hydration, whereas the $C_3A$ hydration contributes to the ettringite formation, and therefore mainly to the 1-day strengths. From 1 day the slight decrease of the ettringite amounts for all the investigated samples indicates that this latter phase does not contribute to the long-term strength. Moreover, the ettringite instability appears to adversely affect the porosity (chapter 4.1.3.5) and negatively affects the strength.

In the presence of $CaCO_3$ in the cement hemi-carboluminates are formed, although the atmospheric carbonation of the aluminate phases may not be excluded. The stable phase under atmospheric conditions is $C_4A\bar{C}H_{11}$, which forms according to equation (5.3) as observed by Carlson et al. [153].

$$C_3A + CaCO_3 + 11H_2O \rightarrow C_4A\bar{C}H_{11} \quad (5.3)$$

However, the addition of CSA ($C_4A_3S$) allows other calcium aluminates, such as $C_{12}A_7$ or CA, to react under the further formation of crystalline or gel phases of carboaluminate [201]. The $C_4A\bar{C}H_{11}$ formation has a general positive effect on the strength of all the mixtures, thus preventing the strength loss caused by the conversion of the aluminate hydrates to $C_3AH_6$ and the subsequent decrease in the solid volume [4]. The additional formation of $C_4A\bar{C}0.5H_{12}$ is also detected. Because of the constant exposure of the samples to the atmospheric $CO_2$ during the measurements, and the negligible exposure to $CO_2$ during the water curing of the samples, the decrease of this latter phase and the correspondent increase of the $C_4A\bar{C}H_{11}$ phase, indicates a reaction between the $C_4A\bar{C}0.5H_{12}$ and the carbonate present within the cement (5.4). A dehydration reaction of the $C_4A\bar{C}0.5H_{12}$ to $C_4A\bar{C}H_{11}$ was suggested by Schwarz [202].

$$xC_4A\bar{C}0.5H_{12} + yCO_3^{2-} \rightarrow zC_4A\bar{C}H_{11} + jH_2O \quad (5.4)$$

Nevertheless, as it will be demonstrated later, the decrease of the $C_4A\bar{C}0.5H_{12}$ phase and the increase of the $C_4A\bar{C}H_{11}$ over time contributes to the strength decrease of the accelerated samples only to a negligible extent.
5.1.2.3 The effect of the silica fume addition

The addition of silica fume, required a slightly higher W/C ratio (0.48) in order to allow the necessary workability of the mixtures. Thus, compared with the samples without silica fume, a remarkable strength decrease for the reference (NQ: 12 MPa) and the CSA- enriched sample (RF: 7 MPa) is observed up to 6 months. Despite the slightly higher values for the alkali-free accelerated sample L 50 (4 MPa), the other two alkali-free accelerated samples (AF, AS) and the alkali-rich (L 20), display almost the same strength values up to 6 months.

The modified strength developments, in particular for the reference sample, is likely to be explained from the relatively high porosity of the contact zone between the silica fume grains and the cement paste. A higher porosity gradient is detected as the distance from the interface decrease, although in some cases, presumably depending on the silica fume reactivity a denser contact is formed [2]. The relatively small formation of CSH from the pozzolanic reaction (chapter 4.1.5.3) along the interfaces silica fume-cement paste, is not sufficient to remarkably reduce the porosity. Furthermore, the enrichment of different ions such as Al(OH)₄⁻, CaOH⁺ and SO₄²⁻ and the subsequent precipitation of ettringite needles, are apparently not sufficient to create an interlocking with the CSH gel and to reduce the capillary porosity.

On the contrary, the increased enrichment and precipitation of ettringite prisms and the good interlocking of the latter with the CSH (pozzolanic reaction), obtained with the addition of the alkali-free accelerators allows the formation of a tight contact zone between the silica fume grains and the cement paste (Fig. 4.34 E). Hence, a general reduction of the capillary porosity within these contact zones allows to maintain the same strength values as for the similar samples without silica fume addition.

The strength values of the alkali-rich accelerated sample are independent of the silica fume addition. In fact, the lack of a microstructural recognizable clear contact zone towards the silica fume grains indicates that the main strength determining factor remains the high porosity within the whole microstructure.
5.1.3 Microstructural evidences of the strength decrease

5.1.3.1 Homogenization of the alkali-free accelerating admixtures

The remarkable feature of the samples accelerated with the alkali-free admixtures is the presence of white-brown efflorescences, which mainly consist of ettringite prisms. The precipitation of well crystallized CH within these zones presumably takes place because of the availability of pores created by the formation of the highly voluminous ettringite crystals. The sporadic precipitation of CSH II within these zones also implies the presence of pores and is probably due to the supplementary enrichment of Si\(^{4+}\) ions carried from the circulating pore waters within the microstructure.

The formation of the ettringite enriched zones is generally attributable to the inhomogeneous distribution of the accelerating admixtures within the cement paste. In fact, their solubility in water appears difficult, in particular for the CSA-based alkali-free accelerator. The homogenization of the admixtures also partially depends on the mixing procedure, but as it will be shown later, the efflorescences occur in both the laboratory and the shotcrete specimens (Fig. 5.3). The presence of these ettringite enriched zones indicates that the main accelerating components of these admixtures, namely the ettringite triggering components tend to be inhomogenously distributed within the samples and when they come into contact with water they react to ettringite, thus causing an increase in the solid volume. This also explains the high porosity within the ettringite enriched zones. Despite the relatively high content of aluminum sulfate, within some of these admixtures, the precipitation of aluminum sulfate crystals is hindered because of the high availability of Ca\(^{2+}\) ions within the cement pore solution in the first few hours. In fact, a high concentration of these ions at early hydration stages within unaccelerated cement systems was reported [2, 4].

The presence of these ettringite enriched zones within the microstructure are responsible for the strength loss of the samples. In fact, the higher inhomogeneity of the whole structure appears to contribute decisively to the strength decrease, more than does the porosity. Babkov et al. [77] found that structure-mechanical inhomogeneities decrease the theoretical strength by a factor 50-100, whilst the capillary porosity decreases the strength by 3-10 times. Blümel et al. [18] also evidenced the relationship between the strength and the textural features caused by different shotcrete application techniques.
Furthermore, a general final strength decrease was found in particular when powdery admixtures were inhomogeneously mixed with the concrete [15]. The higher inhomogeneity of the structure is further confirmed by the higher fracture energy and the higher roughness of the fracture surface of the specimens. These two latter parameters appear to correlate well with the lowered strengths of the samples. In fact, when cracks change their path, more energy is needed as observed by Vervuurt et al. [75]. In this case, the cracks presumably need energy to change their paths, overcoming the highly porous ettringite - rich zones, dissipating energy, thus increasing the fracture energy and causing a higher roughness of the fracture surfaces. This is also consistent with the importance of the porosity in the propagation of cracks [4]. The high porosity of the ettringite enriched zones, is a further indication of the structure-mechanical weakness of these domains. In fact, SEM investigation showed the presence of ettringite enrichments within the "internal" fracture zones of the fracture surfaces. It must also be noted that in some of the cases water can presumably come in contact with the domains of unhydrated accelerating components not at early stages (4h), as in most of the cases, but only after the main formation of the CSH gel (1-7 days). In this case, the hydration to ettringite and the subsequent volume increase causes an expansion and the formation of cracks, which in turn spread out into the neighbouring hydrated mass (Fig. 5.3).

Ettringite needles formed within the pores throughout the hydration of the reference sample, are slightly interlocked or rarely intermixed with the CSH gel, but they do not appear to remarkably support the strength. On the contrary, big ettringite prisms formed by the addition of the alkali-free admixtures, contribute to the strength only when they are homogeneously distributed within the whole cement structure, interlocking with the CSH gel as depicted in Fig. 5.2.

The homogeneous distribution of the accelerators causes in fact a very remarkable strength increase, since the homogeneous distribution and interlocking of the ettringite crystals with the hydrate mass acts presumably as crack arrester (Fig. 5.2 AF). Furthermore, the addition of these admixtures favors a general growth in width, rather than in length, of the ettringites. The higher capability of these crystals to be accommodated within the pores and their higher intrinsic resistance as crack arresters, act as an additional strength supporting factor.
This is in turn why even at low dosages (1.6 %) the good homogeneization and dissolution achieved with the addition of the CSA (C₄A₃S) component separately added causes high strength values.

Outside the high porosity domains created by the inhomogeneous distribution of these accelerators, the microstructure shows the similar features as for the reference sample, although in some cases big sized ettringite prisms are sporadically well interlocked with the CSH gel. This positive effect, however, is overshadowed by the negative ones previously described.

It may further be stated that the CSA-based accelerator (AF), since it is the most insoluble in water, clearly shows the importance of a homogeneous distribution within the cement mass. In fact, a good homogenization yields remarkably higher strengths compared to an inhomogeneous distribution, where ettringite enriched high porosity zones are present within the structure (Fig. 5.2 AF2).

5.1.3.2 The influence of the alkali-rich accelerator on the hydration

Contrary to the previously described accelerator group, the addition of the more soluble liquid alkali-rich admixture to the cement, results in a homogeneous distribution within the cement paste and generally influences the microstructure as a whole. In fact, the presence of a remarkable capillary porosity, the general presence of the CSH II gel, and the relative absence of
CSH IV dense gel up to 6 months, explains the generally lowest strength values, although liquid accelerators appear to improve the homogeneization, thus having a positive effect on the final strength [15]. Hubert et al. and Mai [32, 34] also stated the adverse effect on the shotcrete performance of the alkali-rich accelerators compared to the alkali-free. As it will be demonstrated later, the low final strength appears not to be due to the fast crystallization of hydrate products and introduction of alkali-ions into the mixture [15].

The strength is therefore less influenced by local microstructural features as for the previous accelerator group, but is the result of a more general process influencing the whole microstructure. This implies a general delay in the CSH gel development. This fact is also confirmed by the increased consumption of the C₃S and the C₅₄S₁₆AM up to 1 day hydration (Fig. 4.11) and the subsequent rate decrease of further reactions. SEM investigations (chapter 4.1.3.4) showed the constant high presence of CH crystals indicating a Ca²⁺ and OH⁻ supersaturation of the solution. The high supply of OH⁻ ions to the pore solution caused by the addition of the alkali-rich admixture, decreases the rate to which OH⁻ ions are released from the C₃S, and hence increase the rate to which saturation is reached with respect to Ca²⁺ and OH⁻ ions into the solution. The retarding effect on the C₃S hydration obtained with the addition of CH in aqueous suspensions of C₃S was reported by Wu [31]. However, it appears that the concentration of OH⁻ ions within the solution of the accelerated sample remains high throughout time. In fact, the large precipitation of CH crystals within the first hours does not appear sufficient to act as a sink for Ca²⁺ ions, enabling a renewed CSH formation as already postulated [2]. It may also be observed that the incorporation of CH into the CSH may slow down its normal development to CSH IV gel, thus remaining mainly a CSH II gel over time.

Moreover, the CSH II crystallization itself is not sufficient to completely link the clinker to a compact mass, even up to 6 months hydration. Therefore, this latter CSH gel type supports the strength only to a small extent. The CH interlocked with ettringite thin elongated rods and the KCA₅S₉H contributes to the reduction of the big capillary porosity, thus partially supporting the 1 day strength values (chapter 5.1.2.2). Nevertheless, the big capillary porosity between these interlocked crystals does not substantially contribute in supporting the long-term compressive strength. Despite the homogeneous distribution of the elongated thin rods of ettringite precipitated from the
solution, they generally poorly interlock with the CSH II gel, and this is a further negative effect. Furthermore, the interlocking of the elongated thin ettringite crystals appears to generate a residual porosity between them and therefore scarcely contributes in reducing the porosity at later stages. In spite of the crystallization of higher amount of ettringites compared to the reference sample, a negligible strength support is observed.

5.1.4 Alkali-free accelerators: cement paste vs. shotcrete

White-brown efflorescences also appear in shotcrete specimens, although to a lesser extent compared to plain cement pastes. This is probably attributable to the better mechanical mixing procedure attained during the shotcrete applications ("wet" process). Furthermore, the presence of aggregates in the shotcrete mass may also contribute to a slightly better mechanical homogeneization of the accelerator presumably caused by the mutual rubbing of the particles. However, a lack in homogenization of the accelerating admixtures within the microstructure of shotcrete samples also takes place, as highlighted in Fig. 5.3.

The white efflorescences present and previously described within the cement paste (chapter 5.1.3.1), are also present within the shotcrete microstructure and also represent ettringite enriched high porosity zones. Due to the stronger mechanical compactness of the whole structure during the shooting process, these ettringites appear with a more amorphous or short prism-like morphology (Fig. 5.3 AF SC). The hydration of the inhomogeneously distributed ettringite triggering components of the accelerator, after the formation of the CSH gel, leads to the formation of cracks (Fig. 5.3 AF SC).
5.1.5 Summary and outlook

The alkali-free accelerators indicated improved strength development compared to the alkali-rich admixture. Nevertheless, the addition of both the admixtures resulted in strength decrease at later stages. In the case of the alkali-free admixtures this was due to the low dissolution and inhomogeneous distribution of the accelerator within the cement mass. This resulted in the formation of high voluminous ettringite enriched zones that caused a general inhomogeneity of the structure. An improved dissolution and homogeneization of the alkali-free accelerators promoted the homogeneous distribution of the ettringite prisms which acted as crack arrester and enhanced the strength. The calciumsulfoaluminate component separately added supported this mechanical feature. In the case of the alkali-
rich admixture, the lowest strength values were caused by a delay in the CSH gel hydration, which resulted in a general high porosity.

However, the enhanced crystallization of ettringites promoted by the alkali-free accelerators may be a negative premise. In fact, the slight long-term instability of the ettringite crystals appeared to adversely affect the porosity, resulting in a negative strength factor.

Thus it appears that either the development of admixtures with high solubility and reduced aluminum and sulfate content or the improvement of the mixing and homogenization techniques may be at the centre of future investigations in shotcrete technology. Furthermore, the addition of polymer solutions to the accelerating admixtures present nowadays to improve for example the pumpability, the rebound etc. should not adversely affect their solubility within the cement mass.

With regards to the strength development, a general correlation exists between the laboratory mixtures and the shotcrete on site. However, the preparation of mortars, although correlating with the shotcrete strengths, is evidence of difficulty in casting and in moulding of the mixtures which set very rapidly and may result in a distorted strength behavior. On the other hand, the preparation of cement pastes more clearly discloses the dissolution capability of the accelerators within the cement mass and also correlate with the shotcrete strength behavior. In this context, research to improve the dissolution of the alkali-free admixtures within the cementitious mass and a comparison with the shotcrete strength development on site would more easily contribute to an enhancement of the performance. Consequently, the admixture type (powder or liquid) and the shotcreting technique employed would be less decisive.
5.2 Sulfate attack

5.2.1 Ettringite, gypsum and linear expansion at 23°C

A correlation appears to exist between the expansion and the ettringite amounts for the samples in which the alkali-free accelerators were homogeneously and inhomogeneously distributed, and for the unaccelerated sample. On the contrary, a less marked relationship is observed for the fast expansion of the alkali-rich sample, at least at early ages, up to 28 days (Fig. 4.36 left; Fig. 4.37).

This is, a first indication that there is not always a direct relationship between the amount of ettringite formed and the expansion behavior of the specimens as also reported by others authors [4, 93, 104, 105]. In fact, as SEM investigations show (chapter 4.2.5), the ettringite morphology, their arrangements within the attacked exposed layers, and other reaction mechanisms (chapter 5.2.2) also contribute to the expansion. Despite the unclear contribution of gypsum to the expansion [2], the investigated samples do not indicate any correlation between the expansion and the amounts of gypsum formed (Fig. 4.36 left; Fig. 4.37).

5.2.2 Mechanism of attack and physical consequences

5.2.2.1 Alkali-free accelerators

Despite the difference in the chemical composition between the CSA-based accelerator (AF) and the aluminum sulfate-based (L50), the different resistance to sulfates appears to be mainly due to their different homogeneization within the cement paste. In fact, a good homogeneization and dissolution of the CSA-based accelerator, causes a very great expansion and disintegration of the specimens, whereas its bad homogeneization and dissolution results in a reduced and delayed expansion (Fig. 4.36 left S/AF2). The addition and a good homogeneization of this CSA-based admixture promotes a homogeneous high presence of aluminates within the microstructure. The aluminates generally react with the $\text{SO}_4^{2-}$ ions to form ettringite (Fig. 4.37) [2]. The addition of these types of admixtures to cement paste causes the consumption of CH which is needed for the initial ettringite
formation during the normal hydration (Fig. 4.11 bottom right), therefore, a general depletion of CH is present in these kind of accelerated samples.

Consequently, the ettringite formation process requires Ca\(^{2+}\) ions which are normally supplied by CH \([2]\). Because of the general lack of CH part of the Ca\(^{2+}\) ions must be supplied by either the CH present as interlayer material into the CSH gel \([203]\) or directly by the decalcification of the CSH gel. This decalcification process causes the disintegration of the gel, which, because of the general high aluminate content caused by the addition of the accelerators, partially reacts to ettringite (Fig. 4.40 S/AF-S/L50). As a consequence, a softening and a loss of cohesion of the whole structure occurs. Despite the fact that the CSH gel decalcification process appears to take place mainly in MgSO\(_4\) solutions \([93, 96, 98, 106, 107]\), an initial decalcification step in Na\(_2\)SO\(_4\) solutions was already reported by Crumbie et al. \([94]\). Moreover, it can generally be assumed that a penetration of sulfate ions into the pores causes a partial pH decrease. In order to re-establish the high pH required for the stability of the CSH gel (13-13.5) in locally depleted CH pore solutions, lime is liberated from this gel. Even though this process does not proceed to completion, as it does for the MgSO\(_4\) solutions \([2, 97]\), a partial attack of the CSH gel takes place within these types of accelerated samples when stored in Na\(_2\)SO\(_4\) solutions.

The disintegration of the CSH gel causes a general change in the pore structure, resulting in an increase in the porosity of the specimens. This risen porosity promotes the further penetration of SO\(_4^{2-}\) ions which can deeply enter and be adsorbed within the exposed surface as confirmed by ionchromatography (Fig. 4.38 S/AF), pH and conductivity (Fig. 4.39 S/AF) measurements of the samples in which the CSA-based alkali-free accelerator was homogeneously mixed. It is also important to note that the ionchromatography measurements of the sulfate adsorption imply that the adsorption process does not take place as a simple diffusion of sulfate ions, but rather as a penetration of sulfates, which trigger reactions with cementitious phases. Consequently, it can be assumed that higher adsorbed sulfate amounts correspond to increased interactions with the cementitious phases and depending on the conditions, to an increased possibility of deleterious effects. Thus, the further penetration of sulfate solution into the specimens caused by the enhanced porosity of the microstructure, directly contributes to the expansion of the specimens, and this presumably also
explains the lack of a constant direct relationship between the amount of ettringite formed and the expansion, as previously reported [4, 93, 104, 105].

The formation of gypsum appears to occur only after the softening and disintegration of the samples (chapter 4.2.3). This proves that gypsum contributes to these latter damage types only to a very small extent and in this case only at later times (Fig. 4.37). Nevertheless, softening and disintegration was also attributed to gypsum formation especially in the case of MgSO₄ attack [108]. Despite the assumption that high sulfate concentration appears to attack calcium silicate paste, resulting in the formation of gypsum [83], the high presence of aluminates, caused by the addition of the accelerating CSA and aluminum sulfate-based admixtures, appears to be decisive in promoting the disintegration of the CSH gel. The latter process mainly occurs via the formation of ettringite rather than gypsum (Fig. 4.40 S/AF right side).

In addition, a homogeneous distribution of the aluminates achieved via a homogeneous dissolution of the accelerator within the cement paste, appears to have greater deleterious effects than an inhomogeneous one. As a consequence, reduced ettringite amounts (Fig. 4.37 S/L50) and a generally reduced attack of the CSH gel, which takes place only in isolated areas corresponding to aluminate enrichments within the microstructure are observed (Fig. 4.40 S/L50). Under these specific conditions, the time required for SO₄²⁻ ions to reach the aluminate-rich sites on the CSH gel, causing its attack and disintegration, is delayed and this promotes a reduced increase in the porosity and a reduction in the SO₄²⁻ ions adsorption within the specimen (Fig. 4.38 S/L50; Fig. 4.39 S/L50). This results in a delayed expansion and damage of the sample, which mainly tends to disrupt rather than to disintegrate, due to the remaining high presence of a CSH gel framework which supports the cohesion of the sample (Fig. 4.40 S/L50).

Thus, it appears that because of the high aluminate content within the specimens caused by the addition of these admixtures, the extent with which the decalcification of the silicates gel (ettringite formation) takes place, directly contributes to the damage type of the samples. Hence, softening and disintegration occur with the homogeneous dissolution of the admixture (Fig. 4.40 S/AF), whereas a very slight cracking and disruption occur with the inhomogeneous dissolution of the accelerator (Fig. 4.40 S/L50). Although ettringites normally contribute to the expansion and to the
formation of cracks [96], Gollop et al. [93, 100] also found a variable
dependence between the initial $\text{Al}_2\text{O}_3$ content of the cement, the reaction
mechanisms simultaneously involved and the damage type. Despite the
relative dependence of the reaction mechanisms on the type of the attacking
solution [93, 100], it appears that the aluminum additionally introduced via
the admixtures greatly influences the mechanisms of attack, which in this
case appears to be relatively independent of the type of the attacking
solution. In fact, the curing of these samples under $\text{Na}_2\text{SO}_4$ solutions, shows
damaging mechanisms typical for curing under $\text{MgSO}_4$ solutions.

5.2.2.2 Alkali-rich accelerator

Despite the general homogeneous distribution of the aluminates in the
cement paste obtained through the addition of the alkali-rich admixture,
substantial different reasons can be accounted for the expansion and the
damaging mechanisms of the specimens compared to the alkali-free
accelerated.

In fact, CH is largely crystallized within the alkali-rich accelerated
specimens during the normal hydration (Fig. 4.11 bottom right, Fig. 4.20-
Fig. 4.24). In this manner, enough $\text{Ca(OH)}^+$ is available within the pore
solution. Thus, CH acts as $\text{Ca}^{2+}$ supplier as opposed to the CSH gel, the
disintegration and reaction to ettringite of which is avoided. The high
availability of CH, aluminates, and penetrating $\text{SO}_4^{2-}$ ions causes the very
rapid formation of thin surface layers consisting of tightly packed bundles of
ettringite elongated prisms which cause a spalling of the surface layers
(Fig. 4.40 S/L20) and the great expansion of the samples (Fig. 4.36 S/L20).
Compared to the homogeneously distributed alkali-free accelerator, a great
penetration of sulfate ions appears to occur especially within the first surface
layers and not along the entire profile down to 5 mm (Fig. 4.39). As a
consequence, a spalling of the surface layers takes place, and a complete
disintegration of the specimens is avoided.
5.2.3 Influence of the temperature on the sulfate resistance

The sulfate solutions were not renewed during the curing time up to 6 months. Nevertheless, the slight long-term variations in the \( \text{SO}_4^{2-} \) concentration, which may occur by the curing at two different temperatures does not influence the general course of the sulfate attack. In fact, the main attacking mechanisms and damage proceed almost to completion in very shortened times (< 60 days).

An increase in the temperature up to 65 °C appears to accelerate the reactions as also reported by Mangat et al. for temperatures < 40°C [113] and to increase the ettringite amounts at least within the first 28 days for all the samples (Fig. 4.37).

At early ages (< 28 days), a general growth in the size of the ettringite prisms (Fig. 4.41), and an increased \( \text{SO}_4^{2-} \) adsorption (Fig. 4.38 left-Fig. 4.39 28 days) takes place and contributes in reducing the capillary porosity available and to increase the extent of the damage in particular in the samples with no specific aluminate enrichments (ST/ST), or in the samples with an inhomogeneous distribution of the aluminates (ST/L50). In these cases, the CSH gel is almost intact or very poorly attacked, and the restrained growth of the ettringite crystals can exert the pressure to a maximum extent, thus increasing the damage, which in this case consist of cracking and disruption (Fig. 4.41).

At later ages (> 28 days) the high temperature causes a general instability of the big sized ettringite crystals which recrystallize to a small stocky partially amorphous-like morphology. This fact is confirmed by the SEM investigations (Fig. 4.41). This recrystallization process, present within all the investigated samples, greatly affects those with the higher amount of ettringites, namely the one with the homogeneous distribution of the aluminates. XRD measurements also show a general decrease of crystalline ettringite within these samples (Fig. 4.37 ST/AF). The physical consequence of this recrystallization is the delayed expansion of the specimens (Fig. 4.36 ST/AF), and its slightly reduced disintegration (Fig. 4.41 STAF) compared to the curing at 23°C (Fig. 4.40 S/AF). Furthermore it appears that the CSH gel is generally less prone to attack. In fact, more \( \text{SO}_4^{2-} \) and \( \text{Al}({\text{OH}})_4^{-} \) ions can be adsorbed on the CSH gel surface, as also reported by Divet et. al.
[125]. Therefore, a reduced decomposition of the gel to form ettringite and a lowered disintegration of the samples occur.

It must be noted that the decomposition of the CSH gel to form ettringite is different from the delayed ettringite formation process which assumes a decrease in the temperature and a release into the pore solution of $SO_4^{2-}$ and $Al(OH)_4^-$ ions adsorbed on the surface of the CSH gel, which then crystallize to form ettringites [2, 90, 91, 126].

In spite of the reduced diffusion rate of sulfate ions at temperatures $> 40^\circ$C reported by Fevziye et. al. [117], it appears that the higher adsorption capacity of the CSH gel with respect to $SO_4^{2-}$ and $Al(OH)_4^-$, and the subsequent reduced disintegration, results in a lowered $SO_4^{2-}$ penetration and adsorption by the samples (Fig. 4.38 91 days-Fig. 4.39 91 days). Thus, a general slight decrease in the extent of the damage is observed (Fig. 4.41 ST/AF).

The ettringite thermal instability and the variation in the adsorption of the CSH gel with respect to $SO_4^{2-}$ and $Al(OH)_4^-$ ions and the extent of its disintegration both contributes to the lowered damage of the specimens in which the alkali-free accelerator was homogeneously distributed (ST/AF). The shift in the crystallization of small amounts of gypsum to earlier stages (Fig. 4.37) does not accelerate the disintegration. This fact is generally observed and is therefore a further indication of the scarce contribution of this latter phase to the disintegration of the samples.

Some of the aforementioned features also characterize the alkali-rich accelerated samples, although the main cause of the delayed expansion (Fig. 4.36 ST/L20) and the reduced extent of the damage must be related to the microstructural rearrangement and accommodation of the ettringite crystals. In fact, the increased dimensions of the ettringite prisms force them to be accommodated with big pores between the crystals (Fig. 4.41-ST/L20) rather than with tightly packed bundles, as for the similar samples stored at 23°C (Fig. 4.40-S/L20). The high presence of CSH gel further confirms its increased ion adsorption capacity, which result in a reduced deleterious recrystallization to ettringite, in spite of the homogeneously distributed high amounts of aluminates added with the accelerator. On the contrary, the homogeneous distribution of the aluminum exercise its adverse effect mainly at 23°C, especially for the alkali-free accelerated samples (chapter 5.2.2.1).
The Ca$^{2+}$ ions necessary to form the high initial amounts of ettringite (Fig. 4.37 ST/L20) appear to be supplied by the dissolution of the CH crystals, in spite of their lowered solubility at high temperatures as reported by Ping et al. [101]. Hence, the probability for the CSH gel to act as calcium supplier is further reduced, thus preventing it from disintegrating.

Even though compared to the similar samples stored at 23°C, a slight long-term decrease in the ettringite amount takes place for both the alkali-rich and the homogeneously alkali-free accelerated specimens (Fig. 4.37 S/L20; S/AF), it appears that the alkali-rich one does not show particular increased decomposition of the ettringite crystals. This indicates that although increased amounts of alkalis reduce the thermal stability of ettringite [125, 130], it appears that within this particular accelerated cementitious system, the alkalis added with the admixture play a subordinate role in the thermal stability and decomposition of the ettringite crystals.

5.2.4 Short-term prediction: laboratory vs. site

The need for a short-term prediction test providing informations on the sulfate resistance of concrete structures is a matter of considerable concern. Thus, a comparison between different specimen types (cement, mortar and shotcrete) was made in order to investigate possible relationships between the short-term sulfate adsorption on cement samples and the long-term linear expansion of different types of specimen. Attention was payed on the slightly different mixing conditions (chapter 3.2.2) (Fig. 5.4 (1), (2),(3)) and on the accelerator dosages (Fig. 5.4) which influence the resistance to sulfate and consequently the linear expansion. Nevertheless, correlations between the measurements performed were found.

A general correlation exists between the long-term linear expansion of the shotcrete specimens and the sulfate adsorption of the cement samples after 28 days. In fact, the addition of the CSA-based alkali-free admixture corresponds to a higher sulfate adsorption (Fig. 5.4 S/AFH (2)-IC 1 month) and to a simultaneous increase in the linear expansion for the shotcrete sample (Fig. 5.4 S/AF (1) shotcrete).
5.2 Sulfate attack

Fig. 5.4: Comparison between the linear expansion of the specimen types (cement: mean std. 1.38; mortar: mean std. 0.07; shotcrete: mean std. 0.118) and the ion chromatographic measurements of the sulfate adsorption on cement samples after 1 month (IC-1 month). All the samples were cured at ca. 23°C in 5% Na₂SO₄ solutions. Dosages of the admixtures for mortar and cement: AF-6%; L50-8%; L20-4.5%; W/C 0.46. Dosages of the admixtures for shotcrete: AF-6.10% (W/C 0.47); L 50 A-5.20% (W/C 0.48); L 50 B-6% (W/C 0.49); L 20-6.30% (W/C 0.47).

The linear expansion between the shotcrete specimens and the cement samples also show a relationship and indicate an increased expansion for the samples accelerated with the CSA-based alkali-free accelerator (Fig. 5.4 S/AF (1); S/AF H (2)) followed by the both the specimens accelerated with the alkali-free admixture L50 (Fig. 5.4 S/L50 A,B (1); S/L50 (2)) and the alkali-rich (Fig. 5.4 S/L20 (1); S/L20 (2)).
A relationship exists for the homogeneous distribution of the alkali-free CSA-based admixture in the cement paste between the high sulfate adsorption and the big linear expansion of the samples (Fig. 5.4 S/AFH (2)). In fact, higher amounts of adsorbed sulfates imply increased reactions with the cementitious phases and increased deleterious physical consequences (chapter 5.2.2.1).

On the other hand, a very poor correlation exists between the linear expansion of the mortar specimens and both the linear expansion of the shotcrete specimens and the sulfate adsorption of the cement samples (Fig. 5.4 mortar-shotcrete-IC 1 month).

Consequently, the investigation of the reactivity of the cementitious material with respect to sulfate ions (IC, pH, conductivity measurements) appears to give a good qualitative short-term prediction of the sulfate resistance. In spite of the general relationship between the W/C and the porosity concerning the sulfate resistance [4, 87], the performed qualitative measurements on cement samples show the aluminate content and distribution to be far more important than the structural features regarding the sulfate resistance of the specimens. In fact, both the values of the compressive strength (chapter 5.1.3.1) and the porosity (chapter 4.1.3.5) do not necessarily correlate with the resistance to sulfate. The large influence on the rate of attack caused by the strength of the solution and the composition of the cement was already reported [2], whereas Hughes reported that not only the permeability but also the access to susceptible minerals play a decisive role in the sulfate resistance [204].

A lacking correlation in the expansion behavior between shotcrete and mortar is presumably attributable to their different mixing procedures (Fig. 5.4). This fact gives rise to a doubtful reproducibility of the resistance to sulfates between laboratory mortars and shotcrete, which greatly depends on the mixing procedures and on the attained microstructural features of the samples, which within these mixture types play a decisive role.
5.2.5 Summary and outlook

The high aluminum and sulfate content of the admixtures revealed its adverse effects on the sulfate resistance, by promoting the formation of expansive ettringite crystals. The $\text{SO}_4^{2-}$ and $\text{Al}^{3+}$ distribution and the $\text{CaOH}^+$ availability controlled the extent of the disintegration of the calciumsilicate-hydrate gel and consequently the damage type. In this context a low $\text{CaOH}^+$ availability and an homogeneous aluminum distribution disclosed the worst effect. An increase in the temperature affected the extent of the damage by both an homogeneous and inhomogeneous distribution of the admixture. Aluminate distribution, ettringite thermal instability and rearrangements as well as the free calciumhydroxide availability mostly influenced the resistance behavior.

The development of alkali-free accelerators with lower aluminum and sulfate contents would be especially useful in the sulfate durability. Moreover, because of the fast change of the materials and working parameters on site, general accelerated performance sulfate tests are required as an on-time response to the changing conditions. In this context, the investigation of the sulfate susceptibility of the cementing material indicated a qualitative trustworthy and reproducible short-term prediction of the sulfate resistance. This may represent a future research topic.

5.3 CSA / burnt oil shale-based cement

5.3.1 Strength and atmospheric storage of the burnt oil shales

The CaO and the CaCO$_3$ show the largest phase change during atmospheric curing of the burnt oil shales, indicating a carbonation reaction. The CO$_2$ and the H$_2$O adsorption of the CaO and its subsequent reaction to CaCO$_3$ mainly depends on both the partial pressure of the CO$_2$ and the H$_2$O and on the heat treatment of the CaO [205]. The remaining crystalline phases and the amorphous fraction are subject to smaller variations ($< 3\%$) during their exposition.

In order to find out which phases of the burnt oil shales have the greatest influence on the strength development of the CSA / burnt oil shale blends, a heat treatment was performed. Burnt oil shales (3 months stored) were heated
for 24 hours at about 400°C in order to eliminate most of the hydrates formed. The CaO, CH, and the CaCO₃ content of the burnt oil shales was supposed to remain constant before and after the heat treatment. The burnt oil shales with and without heat treatment were then stored at 23°C under vacuum for 1 day and then added as components in two different blends.

Thus, the heat treatment of the burnt oil shales allows important considerations as highlighted in Fig. 5.5.

![Fig. 5.5: DTA- Phases development of the burnt oil shales after the heat treatment and the resulting compressive strength (right) of the mixtures in which they were added as a component.](image)

It is clear that the only hydrate remaining after the heat treatment is CH (420°C). The widening of its peak after the treatment is presumably attributable to a slight conversion towards a more amorphous state, although a starting dehydration reaction may also partially take place. The carbonate is almost constantly present.

Despite the general slight higher strength values for the blend in which the heat-treated burnt oil shales were added, the two type of blends show almost the similar strength values, with a maximum range of 3 MPa. Thus, the most influencing factor concerning the strength appears to be the decrease of the CaO amount and its conversion to CaCO₃ during the storage of the burnt oil shales. The formation of the hydrates during the storage, which are barely involved in the consumption of the CaO, exert only a secondary role in the strength development of the blends.
5.3.2 Strength, expansion and lime saturation

A general relationship exists between the strength development and the shrinkage of the CaO-rich SC OSF and the CaO-poor SC OSA blends. In fact, the latter one, does not show any expansion up to 4 hours of hydration, and this coincides with a fast strength development. On the contrary, the former one contains higher amounts of CaO, and shows a remarkable expansion (at ca.70 minutes), which causes a delayed strength development. Likewise, the addition of CaO or CH to the CaO-poor SC OSA blend, causes a slight expansion (at ca. 60-80 minutes) and a delayed strength development (chapter 4.3.4). The slight variations in the strength and in the expansion behavior between the CaO-rich SC OSF blend and the SC OSA one, in which CaO or CH was added, are attributable to the different CaO burning conditions and consequently to the different reactivity. In fact, it was found that the higher the burning temperature, the slower the CaO reactivity [205]. This well explains the more accentuated expansion and the more delayed strength development for the SC OSF blend, which more reactive CaO was burnt at ca. 800°C. Conversely, the CaO added to the SC OSA blend was burnt at ca. 1100°C. The different reactivity of the CaO, thus differently influences their mechanism of reaction and dissolution.

Nevertheless, the CaO itself and its volume increase during the hydration (1.8 times) does not directly contribute to the expansion of the structure. In fact, the pore solution of CaO-rich SC OSF blend is immediately saturated on Ca(OH)+ ions, and the CH precipitates at early stages where no remarkable amounts of CSH gel are present. Therefore the conversion of CaO to CH may not exert any pressure. This fact is confirmed by the predominant presence of platy idiomorphic CH crystals rather than of massive CH depositions which might eventually contribute to an expansion.

Compared to the CaO-poor SC OSA blend, the CaO-rich SC OSF displays a higher pH in solution resulting in the precipitation of CH crystals. As a consequence, the rate at which the SO_{4}^{2-} ions are used to form ettringite is slowed down for SC OSF (chapter 4.3.5.3). In fact, SEM investigations of the CaO-rich SC OSF sample, show the crystallization of small granular-short-prismatic ettringites (5.5) [139] close to the clinker surfaces, which presumably exert mutual pressure against similarly hydrated neighbouring clinkers, thereby causing expansion.
\[ C_4A_3\bar{S} + 8C\bar{S} + 6C + 96H \rightarrow 3(C_6A\bar{S}_3H_{32}) \]  

(5.5)

The early expansion (<1h) of this blend generally correlates to the advanced stadium of the topochemical ettringite growth, as reported by other authors for calciumsulfoaluminate cements [160-162, 164]. Ogawa et al. [164] reported the mutual stress generated when reaction zones around CSA (C_4A_3\bar{S}) particles intersect, although SEM investigations of the CaO-rich SC OSF blend indicate that ettringites must not be necessarily radially arranged to cause an expansion. Furthermore, the large amount of water adsorbed by these ettringites within the first 30 minutes of the hydration, as shown by DTA measurements (chapter 4.3.5.1), indicate the typical amorphous-colloidal state. These ettrinsites are able to attract large amounts of water thus causing interparticle repulsion and expansion [160-162].

On the contrary, the ettringites crystallized within the CaO-poor SC OSA blend are long thin-prismatic and mainly precipitate within the pore solution by a through-solution mechanism, as according to the equation (5.6) [140].

\[ C_4A_3\bar{S} + 2C\bar{S} + 38H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \]  

(5.6)

Therefore, in agreement with Sherman’s et al. reports for calcium sulfoaluminate cements [140] any contributions to the expansion is given. The absence of an expansion for this blend is not due to a faster CSH gel development and its subsequent strengthening of the structure (chapter 5.3.3) which might impede the expansion, but simply to the absence of a topochemical growth of the ettringites.

Furthermore, within the zones of the microstructure of both the blends in which CH platy crystals are precipitated, the neighbouring ettringites show a well developed elongated prismatic form. This fact indicates that a reduction of the Ca(OH)^+ concentration within the pore solution allows the crystallization of the ettringite by a through-solution mechanism, promoted by the higher dissolution of the aluminates and the lowered pH as also stated by Sahu et al. [146].
The formation mechanism of the ettringite appears also greatly influenced by the lime saturation of the solution as reported by Sahu et al. and Min et al. [146, 157], and although Kurdowski et al. [206] found a greater influence on the rate of the ettringite formation rather than the size of its crystals, the investigated blends show a remarkable influence on the crystal size and the morphology.

However, the ettringite formation process is not the only strength correlation factor. In fact, compared to the CaO-poor SC OSA blend, a delayed β-C₂S hydration caused by the CH saturation of the solution was proved by XRD and SEM investigations for the CaO-rich SC OSF blend which show a general delayed formation of the CSH within the first 2 hours.

### 5.3.3 β-C₂S - C₄A₃S hydration: CH system regulator

It is also clear that the hydration and the strength development at early stages of these CSA / burnt oil shales-based cements are mainly reigned by two main reactions: the non-expansive ettringite formation from C₄A₃S (CSA component) depicted in equation (5.7) [140]

\[
C₄A₃S + 2CS + 38H \rightarrow C₆A₃S₃H₃₂ + 2AH₃ \quad (5.7)
\]

and the formation of CSH gel from the β-C₂S (burnt oil shales component) according to the general equation (5.8).

\[
β-C₂S + 2H \rightarrow CSH + CH \quad (5.8)
\]

The final CSH product may also be identical to tobermorite (C₅S₆H₅₋₇) as reported by Shebl et al. for the hydration of β-C₂S [207].

The interaction between these two reactions and their kinetics is greatly controlled by the Ca(OH)⁺ availability within the pore solution. In fact, in the SC OSA blend, the total lower lime content of the solution, consisting of the lower initial lime of its burnt oil shales and the lime liberated during the
5. Discussion

hydration, presumably maintains the appropriate level of concentration. This results in the formation of thin-prismatic ettringites by a through-solution reaction, yielding a non-expansive ettringite [140], and in the simultaneous acceleration of the β-C₂S hydration. The transitory depletion of CH in the solution caused by the ettringite formation, promotes the hydration of the β-C₂S, which may liberate additional CH for the further triggering of the ettringite reaction.

The initial CH amount necessary to trigger the system appears to be furnished by the OPC and the burnt oil shales [12], even though Khedaywi et al. postulated the higher lime amount liberated by the OPC hydration compared to the amount liberated during the hydration of the burnt oil shales. Furthermore, a reaction between the lime generated and the burnt oil shales may also take place [208]. This might correspond to the activation of the glass phase from the free lime which may react with the silicate contained in the glass phase to form CSH gel as suggested by Kikas [172].

Nevertheless, when the accelerating component C₄A₃S is present, the free lime appears to exert its main influence in regulating the ettringite forming reaction and the simultaneous activation of the β-C₂S component rather than the glass phase. These two latter hydration processes are presumably regulated to maintain a reciprocal steady-state in order to maximize their development. This is, in turn, the reason for the fast and high strength development of the SC OSA blend in which the concomitant crystallization of CSH dense gel intermixed with the thin-elongated ettringite prisms takes place, thereby reducing the porosity and forming a very compact structure.

Hence, the CSA (C₄A₃S) acts as activator for the burnt oil shale component, thus enabling an accelerated ettringite formation and the accelerated proceeding of the β-C₂S hydration to form CSH dense gel. Because of the optimal availability of CH, both the CSH amorphous dense gel and the ettringites develop and contribute in supporting the early strength of this system. The importance of an appropriate CH availability within these rapid hardening systems was also proved by Matkovic et al. [209], who reported that in order to reach reasonable strengths within CaO depleted mixes composed of CSA (C₄A₃S), gypsum and low amounts of β-C₂S or less reactive γ-C₂S, the conditions must be modified in order to substitute the decreased development of CSH gel. This is attained by promoting the
formation of ettringite from the CSA (C₄A₃S) component, namely with the addition of lime (chapter 5.3.4).

Thus, these CSA / burnt oil shale-based blends combine the ettringite formation (strength supporting factor of the calciumsulfoaluminate cement [142, 144]), and the accelerated formation of the CSH gel (reactive β-C₂S of the burnt oil shale) promoted throughout the CH consumption of the ettringite forming reaction (C₄A₃S activator), as the two main hydrates supporting the high early strength. It must also be noted that the glass constituent of the burnt oil shales may also contribute to the early hydraulic properties of the blends, but a quantitative difference in the development of this phase between the blend SC OSF and the SC OSA could not be detected.

Without the C₄A₃S activating component, the development of CSH gel from the β-C₂S phase during the hydration of the pure burnt oil shales, usually occurs only at later stages as stated by Baum et al. [175]. It also appears that the clinker constituents of the burnt oil shales have a subordinate role in their binder properties as reported by Kikas [172]. Moreover, the presence of the CSA (C₄A₃S) component during the hydration of the calciumsulfoaluminate clinker pastes not always accelerates the hydration of the β-C₂S component, which appears to contribute to the strength only at later stages, as reported by Taylor [4]. This fact is presumably due to the different burning procedures between the burnt oil shales and the calciumsulfoaluminate clinkers, which influences the crystallinity and the subsequent reactivity of the β-C₂S. The influence of the burning degree on the β-C₂S reactivity was also observed by Stark [174]. A remarkably accelerated hydration of this latter phase within blends containing CSA (C₄A₃S) as activator may thereby be reached with a more amorphous and reactive state of the β-C₂S, obtained by the lowest allowable burning temperatures.

For the aforementioned reasons, the lime production-consumption of the previously described two main reactions, links them together in an interaction. A higher initial lime content "artificially" added to the solution (CaO-rich SC OSF blend), causes dramatic delays to the course of the hydration, to the strength development, and to a smaller extent to the setting times. In fact, the SC OSF blend, containing higher amounts of CaO compared to the SC OSA, causes the solution to be saturated in lime and this favors the topochemical growth of the ettringites with a short-prismatic granular form, thus reducing their rate of formation. Under these conditions
the CH concentration of the solution remains high (Fig. 4.50 left) and the β-
C₂S hydration is delayed as well (Fig. 4.46). Only when the lime
concentration of the solution is lowered enough, due to the progressive
precipitation of CH crystals, the ettringite crystallize as thin elongated prisms
with a through-solution mechanism (Fig. 4.49 OSF 1 hour), and the main
hydration of the β-C₂S to dense CSH amorphous gel takes place. In addition,
a harmful effect of raised CaO content within the glass constituent of the
burnt oil shales, obtained by the burning at high temperatures, may also
reduce their hydraulic properties as observed by Kikas [172], and further
possible negative interactions between the glass constituent and the CaO
present in the solution within the investigated SC OSF system cannot be
excluded.

Furthermore, the presence of FeS₂ within the systems does not have any
adverse effect during its oxidation and reaction with the cementitious phases
as on the contrary observed for some concretes with pyrite-bearing
aggregates [210].

To further demonstrate the deleterious effects of a too high CaO presence
within the CSA / burnt oil shale systems, a comparison with a simplified
CSA / anhydride system added to various CaO amounts was studied and the
results are discussed in the following section.

**5.3.4 CSA / anhydride- burnt oil shale systems: CaO effect**

The direct influence of the CaO on the hydration of the CSA (C₄A₃S) component and the consequences for the ettringite forming mechanism may
be observed throughout the addition of this oxide to a CSA / anhydride
system. The main hydration taking place within this system is depicted in
equation (5.9) [139, 140].

\[
xC₄A₃S + yCS + zC + jH → wC₆A₃S₃Hₙ₂ + uAH₃
\]  

Maintaining constant all the parameters except the CaO content (z), the
ettringite formation mechanism and amount can be varied as highlighted in
Fig. 5.6.
Fig. 5.6: Microstructural ettringite development caused by the progressive addition of CaO to a CSA/anhydride system (magn. 6000). a: $z = 0$. b: $z = 1$. c: $z = 6$.

If $z = 0$ (no CaO is added), a little amount of small ettringite prisms are formed within the pore solution by a through-solution mechanism (Fig. 5.6 a). If $z = 1$, more ettringite thin-elongated prisms are formed and their formation occurs again by a through-solution mechanism (Fig. 5.6 b). When CaO is added in larger amounts ($z = 6$), short-prismatic granular amorphous-like ettringites starts to form indicating zones with enriched Ca(OH)$^+$ in the solution (Fig. 5.6 c). These type of ettringites, also observed within the CaO-rich SC OSF blend, own their formation to a topochemical mechanism.

Furthermore, a comparison between the CSA/anhydride system and the two types of blends (SC OSF-SC OSA) with regards to the ettringite amounts formed within 30 minutes, indicates an initially higher amount for both the CaO-enriched CSA/anhydride system (Fig. 5.6 c) and the CaO-rich SC OSF blend (Fig. 5.7).

Fig. 5.7: XRD- ettringite amounts for the CSA/anhydride (RF/AB) system and the two blends (SC OSF-SC OSA) within the first 30 minutes of the hydration.
Therefore, it may be concluded that an excessively high initial amount of CaO within the SC OSF blend is responsible for the topochemical growth of the ettringites and their delayed hydration kinetics. The total amount of ettringites does not influence the strength development at early stages as much as their formation mechanism and morphology. Nevertheless, as previously argumented (chapter 5.3.3), the ettringite formation is not the only parameter to be considered during the high early strength development within the CSA / burnt oil shale-based cement systems.

5.3.5 Summary and outlook

The formation of calciumsilicatehydrate gel from the $\beta$-C$_2$S (burnt oil shales) and ettringite from the C$_4$A$_3$S were responsible for the early strength development of the burnt oil shale-based cementitious blends. The kinetics of this two-phase rapid-hardening system was controlled by the lime content of the solution. The differences in the early strength development of the blends achieved with the use of burnt oil shales stored for different times in atmospheric conditions was due to their different CaO content. A high initial CaO content delayed the hydration of the two-phase system and resulted in the formation of expansive ettringite crystals.

The acceleration of the hydration reactions within the CaO-enriched system appears, however, quite difficult. In fact, each admixture which trigger a reaction with the CaO, might positively favor the $\beta$-C$_2$S hydration, but adversely affect the C$_4$A$_3$S hydration. Moreover, the rapid formation of crystals from the reaction of CaO with the admixture may have a deleterious effect on the microstructure.

Thus, it appears that modifying the burning conditions (e.g. temperature and gas atmosphere) of the oil shales may be an attempt to reduce the CaO content of their burnt ashes. An increase in the burning temperature alone might promote a CaO grain coarsening and a reduction of its active surface, which result in a reduced solubility [211]. This appears convenient to avoid the saturation of the pore solution with respect to Ca(OH)$_2$ ions, but a probable increase in the $\beta$-C$_2$S crystallinity might reduce its reactivity. Conversely, an appropriate adjustment of both the temperature and the gas atmosphere in order to allow a better sulfation of the free calcium oxide in the ashes [212] during the burning process may disclose a positive effect.
6. General conclusions

Rapid set and rapid hardening systems were investigated. Within these accelerated systems, the composition, the homogenization and the dosages of the different substances mixed, greatly affected the early hydration behavior, the development of the mechanical properties and the durability.

The alkali-free admixtures used in shocrete significantly shortened the setting times and generally positively affected the mechanical properties of the cementitious blends at early stages. At later stages, however, a decrease in the strength could be detected for all the admixture types (alkali-free and alkali-rich).

The alkali-free admixtures promoted the crystallization of ettringite crystals which were responsible for the setting and for the reduction of the porosity, thus yielding high early 1 day strengths. These admixtures did not affect the hydration of the CSH gel so that their dissolution became decisive for the structure mechanical features of the cementitious matrix. In this context, the accelerating components ($C_4A_3\bar{S}$ and $Al_2(SO_4)\cdot 14 H_2O$), inhomogeneously distributed within the mass, caused the formation of high voluminous ettringite enrichments, which weakened the whole structure and resulted in lowered strength values. A comparison with an alkali-free accelerated shotcrete mixture, showed the similar microstructural features as observed in the laboratory specimens, although the ettringites present within the shotcrete had a more amorphous state. This difference in the ettringite morphology was caused by the compactness attained during the shotcreting procedure. On the contrary, a good dissolution of the admixture promoted the homogeneous distribution of the ettringite prisms within the cementitious mass, thus acting as crack arrester and improving the strength. The contribution to the strength caused by the addition of the calcium-sulfoaluminate was mainly due to its good dissolution within the cementitious mass. Nevertheless, the long-term general instability of the ettringite crystals was at the same time a negative premise for the strength at later stages.
The alkali-rich admixture accelerated the setting times through the formation of CH plates, amorphous KCA$\text{SH}$ and ettringite elongated rods, but greatly delayed the hydration of the calciumsilicatehydrate gel. The generally high porosity of the structure that resulted was responsible for the lowest strength values measured.

The addition of silica fume remarkably affected the strength relationship between the mixtures and the microstructural investigations indicated the interface silica fume-cement matrix to be responsible. Nevertheless, ettringite prism enrichments rather than the pozzolanic reaction caused the variations in the strength values.

The investigation approaches on the sulfate resistance indicated the great importance of using different experimental techniques, which allowed to explain the mechanisms of attack occurring within the specimens. The generally high aluminum and sulfate content of the admixtures disclosed its adverse effect on the resistance. In fact, the formation of high voluminous ettringite was promoted.

The resulting types of damage were greatly controlled by the extent of the calciumsilicatehydrate gel disintegration, which were softening and disintegration for the specimens in which the aluminum and the sulfate were homogeneously distributed. In this case the calciumsilicatehydrate gel strongly reacted to ettringite and disintegrated. This disintegration resulted in an increase in the porosity, that, in turn, promoted the further penetration of the sulfate solution, thus partially contributing to the expansion of the specimens. This was the reason for the partially absent relationship between ettringite formation and expansion. The disintegration of the calciumsilicatehydrate gel was caused by the insufficient free CH availability within the pore solution, so that the gel acted as Ca$^{2+}$ ions supplier thus disintegrating. The reduced amount of free CH within these alkali-free accelerated specimens was caused by the initial ettringite forming reaction, which required considerable amounts of CH.

An inhomogeneous distribution of the Al$^{3+}$ and SO$_4^{2-}$ caused the decalcification of the calciumsilicatehydrate gel only within the aluminate-rich sites, and this resulted in a lower disintegration of the gel. In spite of the localized disintegration, the calciumsilicatehydrate gel present still acted as
a supporting framework so that the specimens failed throughout cracking and disruption.

A homogeneous dissolution of the aluminum and the high availability of CH obtained through the addition of the alkali-rich admixture partially protected the calciumsilicatehydrate gel from the disintegration and resulted in the formation of thick surface ettringite-rich layers. As a consequence, the specimens showed a great expansion and failed through spalling and cracking of this surface layer.

The increase in the temperature had a slight favorable influence on the resistance. In fact, crystal rearrangements and thermal instability of the ettringites which started to decompose, resulted in a reduced extent of the damage. Moreover the calciumsilicatehydrate gel increased its capability to adsorb Al(OH)$_4^-$ and SO$_4^{2-}$ ions, thus reducing its disintegration.

A comparison between the laboratory investigations and the conventional measurements of the linear expansion on shotcrete specimens indicated a positive relationship with the short-term total amount of adsorbed sulfate within the cement specimens. On the other hand, the mortars, showed no correlation between their linear expansions and those of the shotcrete specimens. Thus, the discontinuous correlation between the porosity of the specimens and their sulfate resistance, depending on the particular conditions [113, 213], suggested that a qualitative investigation of the sulfate susceptibility of the binding material might result in a more trustworthy evaluation of the sulfate resistance independently of the casual structural interactions and arrangements which might be caused by the addition of different sized aggregates.

It must be generally stated that a homogeneous distribution of the alkali-free admixtures within the cement pastes promoted the strength development, but conversely resulted in a reduced sulfate resistance. Thus, it appears that the accelerator to be used and the shotcrete mixing technique must be dictated from the technical requirements on site (e.g. strength, sulfate resistance etc.).
The investigation of the new rapid hardening burnt oil shale-based cement revealed the C$_4$A$_3$$\bar{S}$ (from the calciumsulfoaluminate) and the $\beta$-C$_2$S (from the burnt oil shales), which hydrated to form ettringite and amorphous dense calciumsilicatehydrate gel respectively to be the two main phases responsible for the early strength of this system. The pronounced sensitivity of this cementitious system with respect to the lime content of the solution, which resulted in a great variation in the kinetics of the hydration and in the consequent development of the early strengths was demonstrated as well. In fact, the high CaO values of the short-time atmospheric stored burnt oil shales influenced the ettringite crystallization mechanisms, delayed the $\beta$-C$_2$S and C$_4$A$_3$$\bar{S}$ hydration, and consequently the strength development of this burnt oil shale-based cementitious system. With regards to the ettringite crystallization mechanism, a simplified calciumsulfoaluminate / anhydride system demonstrated the deleterious effect of a too high CaO presence. In fact, the formation of the ettringites as also observed within the CaO-enriched burnt oil shales, took place in an expansive form.
7. References


7. References


7. References


