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# Characteristics of Portland Cements for Sulfate and Weather Resistant Concrete

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

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# Sulfaadi- ja ilmastikukindla betooni tootmiseks vajalike portlandtsementide iseloomulikud parameetrid

TIINA HAIN

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## Contents

## List of abbreviations:

| | |
|---|---|
| C | CaO (Lime) |
| S | $SiO_2$ (Silica) |
| s | $SO_3$ (Sulfur trioxide) |
| F | $Fe_2O_3$ (Iron Oxide) |
| A | $Al_2O_3$ (Aluminum Oxide) |
| H | $H_2O$ (Water) |
| $C_3A$ | $3CaO\cdot Al_2O_3$ (Tricalcium Aluminate; Aluminate) |
| $C_3S$ | $3CaO\cdot SiO_2$ (Tricalcium Silicate; Alite) |
| $C_2S$ | $2CaO\cdot SiO_2$ (Dicalcium Silicate; Belite) |
| $C_4AF$ | $4CaO\cdot Al_2O_3\cdot Fe_2O_3$<br>Tetra Calcium Alumino Ferrite; Ferrite |
| CH | $Ca(OH)_2$ (Calcium hydroxide, Portlandite) |
| C-S-H ($x CaO\cdot SiO_2\cdot y H_2O$) | (Calcium silicate hydrate) |
| CAH | Calcium aluminate hydrate |
| $C_3ACsH_{12}$; AFm | Monosulfate Hydrate |
| $C_3ACs_3H_{32}$; AFt | Ettringite |
| Cs | $CaSO_4$ (Gypsum anhydrite) |
| $CsH_2$ | $CaSO_4\cdot 2H_2O$ (Gypsum) |

The constituents of cement are abbreviated as follows:

| | |
|---|---|
| C | Clinker |
| $T_T$ | High temperature burnt shale |
| $T_K$ | Low temperature burnt shale |
| S | Slag (Granulated blast furnace slag) |
| L | Fine limestone |

# 1. Introduction

## 1.1 Overview

Deterioration of concrete by external sulfates is a commonly observed durability problem in concrete structures exposed to seawater, soils, industrial and agricultural waste, groundwater containing high concentrations of sulfate ions. This durability problem, also known as sulfate attack, occurs after a series of chemical reactions between sulfate ions, cement paste and moisture. The two manifestations of sulfate attack are expansion caused by formation of ettringite and gypsum and loss of strength and mass caused by the deterioration of the cohesiveness of the cement stone. It is often required to recommend concrete mixes for use in aggressive environments where the progress of desirable service life rather than strength is the main parameter for concrete design.

The thesis addresses the characteristics affecting sulfate resistance of cement in various pastes, mortars and concrete in contact with water containing sulfates. Portland composite cement with mineral constituents is an effective way to improve the strength and durability of concrete. The behavior of Portland cement without and with burnt shale, fine limestone or/and granulated blast furnace slag addition in aggressive solutions was studied. Various parameters, such as cement type, cement constituents and clinker composition, factors affecting concrete failure and several exposure conditions have been studied.

## 1.1 Problem Statement

Despite very long-term and large-scale research neither universally accepted criteria for sulfate resisting cement nor a criterion for failure of concrete exposed to sulfate-rich environment have been established. Although several main constituents can improve many physical and mechanical properties of concrete, their effects on the resistance of concrete to sulfate attack are unstable. When exposed to an aggressive sulfate environment, the resistance of concrete to the sulfate ions is dependent upon the permeability of the concrete and the composition of the cement stone.

The thesis gives insight into the understanding of sulfate resistance and proposes the compositions and constituents available in Estonia for producing durable and sulfate resisting cement and concrete.

## 1.3 Objective of the Study

The objective of this thesis is to understand the effect of different cement compositions on mortar and concrete exposed to sodium sulfate solution. For that concrete a cement must be produced that reacts a little with sulfate solutions due to its composition and that its type of porosity enables us to prevent the ingression of the external environment into the concrete, characterized by the ingress of sulfate ions from the surrounding environment, finally leading to expansion, cracking, spalling and complete disintegration of the material.

To reach the maximum efficiency by use of mineral constituents, first their physical and chemical properties were studied. This characterization eased the proportioning of the composite cement so that for a given clinker, the desired properties were acquired. Afterwards the microstructure of the hydration and corrosion products was examined and compared to that of hydrated Portland cement. The microstructural properties of the paste and the interfacial zone between aggregate and paste determine most of the macrostructural characteristics, durability to different exposure conditions, mechanical behavior, porosity, diffusivity, and permeability.

The research included studies on the effects of sulfate attack on time dependent properties, such as compressive strength and durability issues, by means of microstructural studies using Scanning Electron Microscope (SEM). The microstructure observations were useful as the basis for better understanding of the mechanisms and the reaction products developed during a sulfate attack. The collection of expansion data along with SEM and XRD examination of specimen sections allowed the construction of a more detailed picture of the kinetics of the reaction.

To determine the role of a given type of cement as the main constituent in concrete, research efforts were made to characterize the microstructural and macrostructural properties of materials used for making composite cements and the effect of microstructural changes on the durability of the material.

## 1.4 Scope of the Study

The thesis deals with aspects of sulfate corrosion resistance, using:

- Portland cements CEM I and CEM I/A-L with 5 % limestone;
- Portland burnt shale cements CEM II/A-$T_T$ with 15 % and 20 % burnt shale $T_T$, CEM II/B-$T_T$ with 25 % and 30 % burnt shale $T_T$;
- Portland burnt shale cements CEM II/A-$T_K$ with 15 % and 20 % burnt shale $T_K$, CEM II/B- $_K$ with 25 % burnt shale $T_K$;
- Portland limestone cements CEM II/A-L with 10 % and 15 % limestone;
- Portland slag cements CEM II/A-S and CEM II/B-S with 10 %, 20 % and 30 % slag; slag cements CEM III/A and CEM III/B with 50 %, 60 % and 70 % slag content.
- Multicomponent composite cements with various main constituents.

Since it is known that the use of different main constituents may influence the corrosion resistance of concrete, several mineral constituents, including burnt shale and blastfurnace slag were used in the present study. The good durability of high temperature burnt shale $T_T$ cement has been studied and reported by Raado (1975). Under a modernized combustion regime and hence different properties of burnt shale, the present research revised also the properties of burnt shale $T_T$ cement tested with different methods.

The relationship between sulfate resistance and the chemical, physical, and mineralogical composition of selected cements has been elucidated. The microstructural analysis performed for sulfate attack was performed after an exposure period of the Wittekindt flat prisms method.

## 1.5 Organization of the Thesis

Section 1 contains the introduction, overview, problem statement, objectives and scope of the study.

Section 2 reviews the literature, including a brief introduction to the theory of sulfate resistance, types of sulfate attack, the mechanism of degradation involving sulfate attack, testing and standards for sulfate resisting cements.

Section 3 describes the procedures selected for the experimental work. Also, the characteristics of raw materials are given.

Section 4 describes the physical and mechanical properties of the tested Portland cements.

Section 5 discusses in detail the results and experimental observations of expansion measurements of Portland cements depending on the main constituents in sulfate solutions, and microstructural studies.

Section 6 discusses the test results of concrete durability properties.

Section 7 presents the concluding remarks of the work summarized in this thesis.

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# 2. Literature review

## 2.1 Background to the Research

Portland cement concrete, a construction material designed to stand loads and resist the applied stresses that may be met in service, has a wide and long-term use. As properly composed, placed and cured concrete exhibits a long service life under most natural and industrial environments, early failures of concrete structures around the world have attracted special attention to the performance of concrete in sulfate containing waters and soils.

Experience with concrete as a physical-chemical system subject to damage and deterioration by chemicals arising from exposure to normal service environments is not completely known. Several mechanisms are known to cause the degradation of the quality of concrete with time - aggregate alkali reaction, carbonation, chloride ingress, delayed ettringite formation, pure water attack, microbial attack and internal or external sulfate attack, etc. (Hewlett 1998).

The use of certain second constituents in cement or concrete will improve the properties of concrete, at the same time reducing the quantity of waste disposal. This is mainly because the second constituents are chemically reactive, displaying latent hydraulic properties (blast furnace slag) or pozzolanic properties (burnt shale). Their physical properties, such as particle shape and size distribution, are of great importance regarding to aggregate-paste interface characteristics, fresh concrete workability or packing efficiency.

The concrete structures are designed to perform for 50 to 100 years with minimal maintenance, even under aggressive conditions, such as contact with a sulfate containing environment. The deterioration of concrete caused by sulfates is a relatively rare but complex damage phenomenon. Sulfate related deterioration has resulted in expensive restoration of concrete structures in several countries. Skalny et al. (2002) specify that sulfate attack is the term used to describe chemical reactions between sulfate ions and the components of hardened concrete, principally the cement paste.

Skalny et al. (2002) categorize as follows:

- internal sulfate attack – the source of sulfate is internal to concrete,
- external sulfate attack – is caused by a source external to concrete,
- chemical sulfate attack – the result of chemical reactions involving sulfates,
- physical sulfate attack – sulfate salt or salt hydration distress.

The present thesis focuses on external chemical sulfate attack. The problems related to and caused by internal sulfate attack are not observed.

Concrete elements that may be exposed to attack by sulfates in certain soils and groundwater include footings, foundation walls, retaining walls, piers, piles, culverts, pipes, and surface slabs. Sulfates may be present in groundwater, and are often of natural origin, but can also come from fertilizers and industrial effluents (Neville 1995) or polluted atmospheric air (Figg 1999). Soils differ not only in their concentrations of various chemical species, but also with respect to their plasticity, permeability, pH, etc. Sulfates in soils of either a geological or industrial origin may also vary with respect to the distribution of relevant cations (usually between $Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$), all of which may play a significant role in concrete deterioration (Hewlett 1998). All of these compounds are highly soluble; thus, in the presence of water the soil composition may guarantee a continuous supply into concrete of soluble sulfates. The principal effect of sulfate attack is to reduce the service life of the concrete structures due to degradation.

Concrete structures exposed to sulfate water must be designed for sulfate resistance (Monteiro and Curtis 2003). This is especially important now because the durability of manufactured cementitious products is increasingly becoming a serious economic and ecological issue. Case studies that include the original concrete mixture proportions and construction practices are rare in the literature, and those that have been published are not comprehensive, making prediction of sulfate resistance more difficult. The attack is more commonly associated with cement-based products in which Portland cement has been used, although other types of cement may be attacked. It is more likely to occur in constructions that are persistently wet – hydrotechnical, underground, sea building.

Degradation of cement stone exposed to sulfate salts is the result of sulfate ion transport through the pore system, chemical reaction with the hydration product phases present, generation of stresses due to the creation of the expansive reaction products, and the mechanical response (typically spalling and cracking) of the bulk material due to these stresses (Ferraris et al. 2006).

The chemically aggressive environments can be classified according to aggressive ions and their concentrations in solutions and surroundings. On the other hand, the aggressive environment is usually accompanied by physical corrosion, such as wet, freezing and thawing influences, i.e. weather conditions. Depending on the chemical form of the sulfate and the atmospheric environment to which the concrete is exposed, sulfate attack might show itself in different forms: in the form of loss in strength, expansion, surface spalling, mass loss, and eventually disintegration (Taylor 1997). The severity of the attack depends on concrete quality, chemical nature, concentration of the sulfates and environmental conditions.

According to the European concrete standard EVS-EN 206-1:2007, high sulfate-resisting cements have to be used for possible sulfate attack of the exposure classes $XA_2$ (up to 3000 mg sulfate/l) and $XA_3$ (> 3000 mg sulfate/l). In Table 2.1.1 the different parameters of the exposure class related to the aggressive water are reported: the composition of the aggressive environment and some prescriptions, like the maximum w/c ratio, the minimum strength class and the minimum cement content.

Table 2.1.1 Exposure class XA: chemical attack (EN 206-1)

| Exposition class | Environment description water | | | | | Max w/c | Minimum strength class ($N/mm^2$) | Minimum cement content ($kg/m^3$) |
|---|---|---|---|---|---|---|---|---|
| | $SO_4^{2-}$ (mg/l) | pH | $CO_2$ (mg/l) | $NH_4^+$ (mg/l) | $Mg^{2+}$ (mg/l) | | | |
| XA1 | ≥ 200<br>≤ 600 | ≤ 6.5<br>≥ 5.5 | ≥ 15<br>≤ 40 | ≥ 15<br>≤ 30 | ≥ 300<br>≤ 1000 | 0.55 | C30/37 | 300 |
| XA2 | > 600<br>≤ 3000 | < 5.5<br>≥ 4.5 | > 40<br>≤ 100 | > 30<br>≤ 60 | >1000<br>≤ 3000 | 0.50 | C30/37 | 320 |
| XA3 | > 3000<br>≤ 6000 | < 4.5<br>≥ 4.0 | > 100 | > 60<br>≤ 100 | >3000 | 0.45 | C35/45 | 360 |

EVS-EN 197-1:2011 gives seven sulfate-resisting common cements. The requirements comply with $C_3A$:

- In the case of CEM I: CEM I SR 0 specifies maximum $C_3A$ content of 0 %,
- CEM I SR 3 specifies maximum $C_3A$ content of 3 %,
- CEM I SR 5 specifies maximum $C_3A$ content of 5 %.
- In the case of cement CEM III/B and CEM III/C (sulfate-resisting blastfurnace cement), sulfate resistance with no requirements for $C_3A$ of the clinker is considered.
- Also, cements with pozzolanic additions to cement CEM IV/A, CEM IV/B (sulfate-resisting pozzolanic cement) are included, where maximum $C_3A$ is 9 %.

In recent years, there has been an increasing need to develop new testing methods for monitoring the sulfate attack on concrete structures. Many test methods are available to assess the quality and degradation of concrete structures, but no generally recognized normative of the sulfate resistance of concrete and no methods of testing exist today. Therefore, no universally accepted criteria for failure of concrete exposed to a sulfate containing environment have been established. A number of failure criteria can be found in the literature, each distinctly different from the other. This diversity has resulted from different testing methods used by the researchers. The source of attack, the cation type present, the concentration of the sulfate source, and the specimen sizes and shapes (beams, cubes, cylinders, etc.) vary from test to test. Different properties, such as strength loss, change in the dynamic modulus of elasticity, expansion (length or volume), loss of mass, and visual assessment, have been used to evaluate sulfate induced deterioration. Test specimens have been prepared of paste, mortar, and concrete. A change in any of these factors can have a significant effect on the assessment of sulfate attack. So far sufficiently low scatter of repeatability and reproducibility has not been gained with any of these test methods. A good correlation between accelerated laboratory test results and actual field concrete performances is still missing.

Usually it is assumed that the performance of concrete regarding its resistance to external sulfate attack depends on the composition of the cement used (Ferraris et al. 2006). Therefore, most of the standard tests are based on measuring macroscopic properties of cement pastes or mortars, such as expansion, modulus of elasticity, or compressive strength. Depending on the values obtained, after a test duration of three months to a year, conclusions are drawn regarding the suitability of the cement tested to be used in a high sulfate environment. The result is a test that characterizes how a particular cement or concrete performs under specific conditions. If the field conditions are different, the performance of the concrete can also be different. Usually only the expansion or strength loss or other macroscopic deterioration, is measured over a prescribed period of time. If the deterioration is lower than a pre-set value, the cement is considered sulfate resisting. The seriousness of sulfate attack on concrete depends on (www.concrete.net.au):

- Type of sulfate: $MgSO_4$ and $(NH_4)_2SO_4$ are the most damaging to concrete.
- Concentration of the sulfate: the amount of sulfate present is considered in classifying the severity of the attack.
- Whether the sulfate solution is stagnant or flowing: severity of the attack increases in the case of flowing waters. Thus, the nature of the contact between the sulfate and the concrete is important. More intensive attack takes place on the concrete that is exposed to the cycles of wetting and drying than on the concrete fully and continuously submerged in the solution. Extensive research of Liu et al. (2012) proved that if concrete elements are partially exposed to the sulfate rich environment, the upper part of concrete in contact with air would be deteriorated more severely than the underground part.
- Pressure: severity of the attack increases because pressures tend to force the sulfate solution into the concrete.
- Temperature: as with any chemical reaction, the rate of the reaction increases with temperature.
- Presence of other ions: other ions present in the sulfate solution affect the severity of the attack.

Concrete is a porous material and it is impossible to prevent completely the ingress of potentially harmful agents. Micro-cracks and macro-pores will always exist on the concrete surface, providing a path for the transportation of aggressive ions into the interior of concrete (Aguiar et al. 2008). Cracks often occur parallel to the surface of the concrete, but also at the aggregate/paste interface. They are often filled with gypsum and/or ettringite. These minerals can be identified by optical microscopy or SEM (Thaulow and Jakobsen 1997). The reduction of the transport mechanism of aggressive sulfate ions is the main factor for improving the sulfate resistance of concrete (Mehta 1992). Improved cements, chemical admixtures, mineral constituents, and construction techniques are now available so that low permeability can be accomplished in many ways.

Low porosity, permeability and concrete penetration to moisture and gases are important parameters to protection against several deterioration mechanisms. The durability of concrete depends largely on how hard or easy fluids in liquid or gas form can migrate through the concrete hardened mass. They can move through the concrete in different ways, but all transport depends primarily on the structure of the hydrated paste (Neville 1995). Commonly, reinforcement corrosion is initiated in the environments that contain high chloride levels whereas environments with low pH or high sulfate concentrations are the most likely to lead to a breakdown of the cement matrix.

Porosity increases or decreases due to the chemical reactions and the resulting dissolution and/or precipitation of specific solid phases (Hewlett 1998), including amorphous gels and discrete minerals. As some or all of the pores within the cement are filled with expansive solid phases, strain develops which leads to stress and cracking. This in turn accelerates further diffusion of the ions.

This was proved by Leeman and Loser (2011) who studied the concrete lining of a vertical ventilation shaft exposed to sulfate-bearing groundwater for 45 years and found that a dense concrete with low w/c in a structure of homogeneous quality and few weak spots (cold joints, cracks, poor compaction) offered the best resistance to sulfate attack, independently of the cement and aggregates used. The sulfate resisting cement used for concrete production was not able to prevent the damages in the areas of poor concrete quality or low concrete thickness. In the case of good quality concrete, sulfate ingressed mainly by diffusion. Due to the slowness of the process, sulfate was penetrated only a few centimetres at the outer surface of the concrete lining exposed to the groundwater.

It is generally accepted that in the case of wet and dry cycles with exposure to sulfate solution, the pores are filled slowly with salts that precipitate in the pores during the dry cycle. During the wet cycles, the pores are filled with salt crystals and supersaturated solutions (salt concentration higher than the solubility value). The pore size distribution, the type of salt, and the environmental conditions (relative humidity, temperature, and duration of the cycles) are paramount to the type and extent of the deterioration observed (Ferraris et al. 2006).

Frost damage in concrete can be a consequence of the use of non-frost-resistant aggregates, or the use of non-frost resistant paste, or both. By using properly selected frost-resistant aggregates in the concrete mixture, frost damage is solely related to the ability of the paste fraction to support the internal pressures generated during freezing (ACI 2001). Concrete may be degraded due to the pressure generated by the movement of water or ice through the internal pore system of hardened concrete. As postulated by Powers (1949), upon freezing, the 9 % increase in the volume of freezing water in an initially saturated specimen forces a flow of water away from the regions where ice is forming towards air-filled spaces. While frost damage in the core concrete is associated with the formation of interior cracks, frost damage in the concrete surface is associated with the scaling phenomenon. Scaling is the flaking or peeling-off of the finished concrete surface (Mehta 1986). In connection with de-icing salt or sulfate solutions, the frost attack is considerably stronger. Salt scaling is defined by Valenza and Scherer (2007) as the ”superficial damage caused by freezing a saline solution on the surface of a concrete body”, which can advance into concrete over time and takes place by the removal of ”small flakes or chips" of the paste with the removal of very few small aggregates. Verbeck and Klieger (ACI 2001) showed that scaling of the concrete is greatest when ponded with intermediate concentrations (3 to 4 %) of de-icing solutions. Not only is salt scaling visually unpleasing, but also the surface of a scaled specimen would be more sensitive to the penetration of fluids and detrimental ions (Ahani and Nokken 2012). There is general agreement that cement paste of adequate strength and maturity can be made immune to damage from freezing by means of entrained air, unless unusual exposure conditions result in filling of the air voids (ACI 2001). As Pinto and Hover (2001) point out, an effective air void system in the concrete, both near the surface and in the core of the hardened material, is the most important parameter for frost durability in normal-strength concrete. Concrete with a properly dispersed air void system can withstand a large number of freeze-and-thaw cycles without loss in serviceability. A proper air void system is characterized by a large number of small, well-dispersed air voids in the hardened material. This system is obtained with the utilization of air-entraining admixtures, which stabilize the smaller air voids during mixing. The incorporation of small voids in the cement paste fraction of the hardened material leads to a reduction of the stresses generated upon freezing and the same process may take effect also in the case of sulfate attack.

Schneider et al. (1999) indicated the vulnerability of cement-based materials to stress-corrosion. They investigated the degradation of mechanical properties (compressive and flexural strength) of mortar/concrete under sustained load and chemical attack (ammonium sulfate, sodium sulfate, sodium chloride and ammonium nitrate). It was concluded that stress is an influential factor affecting the rate of degradation of cement-based materials exposed to chemical attack depending on the level of applied stress.

One form of degradation is caused by expansive crystallization of sulfate salts at the surface of the concrete when water evaporates. According to Svennerstedt et al. (1999), very high concentrations of sulfate may build up within concrete structures which are only partially immersed, or are in contact on only one side, with sulfate water or soils. This is due to the continuing evaporation and capillary suction that will occur under such conditions, and crystallization above the ground or water level. Thus, a severe attack may occur even where the sulfate content of the liquid in contact with the concrete is not initially high. This will lead to both chemical attack on the cement paste and corrosion of reinforcing steel (Skalny et al. 2002). Surface layers of concrete are mostly composed of cement paste that tends to be more porous than that of bulk concrete. Since surface layers are often subjected to drying and wetting, some extra microcracks can be induced and the pore size distribution of cement paste may be altered (Glinicki and Zielinski 2009).

Carbonation of the surface of the concrete converts the $Ca(OH)_2$ to relatively stable $CaCO_3$ and can reduce the permeability. Both carbo- and chloro-aluminates can be formed, reducing the degree of sulfate attack in concrete (Newmann and Choo 2003).

## 2.2 External sulfate attack

The purpose of this section is to outline the fundamental chemistry involved in sulfate attack. Durability refers to the ability of concrete to resist deterioration from the environment or service in which it is placed. Sulfate attack is a generic name for a set of complex and overlapping chemical and physical processes caused by reactions of numerous cement components with sulfates originating from external or internal sources (Skalny et al. 2002). Sulfate attack is an external attack and it progresses slowly from the surface to the center of specimens (Irassar et al. 2003).

Cement chemistry is generally denoted in simple stoichiometric shorthand terms for the major constituent oxides. The major oxides in clinker are combined essentially into just four cement or clinker minerals, denoted in shorthand: tricalcium silicate or 'alite' ($C_3S$); dicalcium silicate or 'belite' ($C_2S$); tricalcium aluminate ($C_3A$); and tetracalcium aluminoferrite ($C_4AF$) and the cement phase composition can be determined from Bogue calculations (Hewlett 1998; Taylor 1997). While the compound content determined through Bogue calculations offers approximate values for major cement phases, they do not account for the presence of impurity oxides (Stutzman 1996; Taylor 1997).

The hydration of a Portland cement is a dynamic system, the calcium silicates and calcium aluminates mechanisms are not independent but are subjected to interactions. The hydrate phase most abundant in hardened cement paste is calcium silicate hydrate denoted C–S–H. Stark (2011), emphasizing that it has remained difficult to study this phase due to a variable chemical composition, the lack of a true long range order, a very high surface favoring the absorption of foreign ions, and the sensitivity to vacuum, elevated temperature, and $CO_2$. The C–S–H growing from the cement grains is responsible for setting of the cement and strength development. In addition to C-S-H, different phases in hydrated Portland cement are: $Ca(OH)_2$, AFm, AFt, pores and anhydrous phase (Taylor 1997).

Degradation of the cement matrix due to sulfate attack has been accepted to manifest itself in two forms: expansion of the matrix and the progressive loss of strength and mass (Cohen and Mather 1991). These two forms involve different chemical reactions:

- *Ettringite formation*

Sulfate-induced expansion of the cement paste is generally attributed to the formation of ettringite. This process involves reactions between the $C_3A$ component of Portland cement or its hydration products and sulfate ions (Skalny et al. 2002). Initially, gypsum present in Portland cement in the amount of 2…4 %, combines with $C_3A$ and water to form ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$). If the pore fluid becomes depleted with respect to the sulfate ion before the $C_3A$ and its hydration products are completely sulfated, then the sulfate ion from the ettringite may go into the pore fluid and react with the remaining $C_3A$ and its hydration products to form monosulfoaluminate ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$). Once this compound is brought into contact with a new source of sulfate ions, either through external sulfate attack or delayed solution of sulfate in the system, ettringite is formed again. Continued formation of ettringite within confined solids causes internal pressure, leading to expansion and cracking.

*- Gypsum formation*

The other form of sulfate attack, progressive loss of strength and mass, occurs when concrete is exposed to external sources of highly concentrated sodium sulfate ($\geq 24$ g $SO_4^{2-}$/l) or magnesium sulfate (Gollop and Taylor 1996). In these situations, the sulfate ions that have infiltrated the concrete react with $Ca(OH)_2$ of the cement to form gypsum (Tian and Cohen 2000). The higher the $C_3S$ content in sulfate-resisting Portland cement, the more $Ca(OH)_2$ is formed during hydration and the more vulnerable are these cements to the formation of gypsum (Gonzáles et al. 1997). Metha (1983) and Monteiro and Kurtis (2003) state that cements containing little or no $Ca(OH)_2$ performed much better when exposed to sulfate attack than cements with high $C_3S$ contents. However, in practice the secondary gypsum formation is of lesser importance as higher sulfate concentrations than for ettringite formation are required or else additional magnesium ions must be present (Gollop and Taylor 1995). The transformation of $Ca(OH)_2$ into gypsum:

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O + 2Na^+ + 2OH^- \qquad (2.1)$$

This reaction (2.1) can cause expansion. Mehta (1983) and Irassar et al. (2003) reported that beside the observed expansion, also softening of the near surface regions due to gypsum formation was observed. The softening has been attributed to the decalcification of the C-S-H phase. Consequently, it is assumed that the formation of gypsum is a significant factor during sulfate resistance experiments performed in the laboratory according to the Wittekindt method used in this research because of the use of high sulfate concentrations to accelerate sulfate attack.

Instead of gypsum, other forms of calcium sulfate can be used: hemihydrate $CaSO_4{\cdot}0.5H_2O$ or anhydrite $CaSO_4$. The nature of the sulfate is a key parameter due to its relative dissolution rates (dissolution rate: hemihydrate > gypsum > anhydrite) (Taylor 1997).

The five primary compounds that constitute Portland cement are $C_3S$, $C_2S$, $C_3A$, $C_4AF$ and gypsum. $C_3S$ and $C_2S$ react with water to form calcium silicate hydrate (C-S-H) and $Ca(OH)_2$. $C_3A$ and gypsum combine to form ettringite (Skalny et al. 2002):

$$C_3A + 3CaSO_4{\cdot}2H_2O + 26H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O \qquad (2.2)$$

Ettringite was found to be stable at pH levels between 10.5...13.0 in pure systems and stable up to pH of 14 in cement systems but starting to decompose with decreasing pH ($\leq 10.5$) (Mehta 1983). As hydration progresses, the concentration of sulfate drops as gypsum is consumed. Mehta (1973) has hypothesized that ettringite formed in the presence of $Ca(OH)_2$ is colloidal, and that the formation of colloidal ettringite in hardened concrete can lead to disruptive expansion. The formation of ettringite from its constituent materials involves an increase in volume of 9.37 % (Skalny et al. 2002). In the case where ettringite forms before the cement paste has gained strength, the increase in the volume can be accommodated without producing cracking. If ettringite forms after the paste has gained strength, the crystallization can cause cracking (Wolter 1997). The ettringite becomes unstable with this decrease in sulfate concentration and reacts with the remaining $C_3A$ to form monosulfate:

$$2C_3A + CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 4H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O \quad (2.3)$$

In parallel, the calcium silicates ($C_3S$, $C_2S$) react to form the C-S-H phases and $Ca(OH)_2$:

$$2C_3S + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \quad (2.4)$$

$$2C_2S + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \quad (2.5)$$

The alumino-ferrite phase ($C_4AF$) of the unhydrated cement was found to be less reactive than the $C_3A$ phase in alkaline conditions of cements (Taylor 1997). The critical reaction that defines sulfate attack occurs when the concrete is in hardened state. If hardened concrete is exposed to an external source of soluble sulfate ions, the concentration of sulfates in the concrete pore water may increase. As sulfate ion concentration increases, the monosulfoaluminate becomes unstable and reverts back to ettringite:

$$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O + 2CaSO_4 \cdot 2H_2O + 16H_2O \leftrightarrow CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (2.6)$$

The ettringite phase that is formed occupies twice the volume of the monosulfoaluminate phase (Stephens, Carrasquillo 2000). When the void spaces in the paste cannot accommodate any further expansion, internal tensile strains may cause cracking of the hardened concrete. This leads to the loss of seduction and deterioration that is typical of sulfate attack in concrete (Stephens, Carrasquillo 2000).

In the presence of $Ca(OH)_2$, secondary ettringite would be more likely to form in regions close to the initial aluminium source, causing expansion. In the absence of $Ca(OH)_2$, as in the case of leached samples, ettringite could be more likely to form in the regions of higher porosity, causing less expansion, as suggested by Taylor and Gollop (1992).

A simplified cracking mechanism of mortars exposed to a sodium sulfate solution has been proposed by Santhanam and Cohen (1998), based on microstructural observations. Ettringite forms in the surface layer, which leads to cracking in this layer and to a lower amount of cracking in the subsequent layers into which sulfate ions have not ingressed yet; then, when ettringite is formed in this second layer, it induces cracking in the next non-invaded layer, whereas its own expansion is being restrained by the presence of the third layer.

Monosulfate will normally also be present in composite cements containing blastfurnace slag, fly ash or natural pozzolana but in these cements alumina is also present in phases such as hydrotalcite or hydrogarnet or substituted in C-S-H in which latter forms it does not appear to be available to form an expansive reaction product (Gollop and Taylor 1996).

- *Influence of the cation on sulfate degradation:*

Depending on dissolved compounds, the reactions with the solid phases in hardened cement paste are described by (Taylor 1997; Bhatty and Taylor 2006). Skalny et al. (2002) underline that the cations show different deterioration; the extent of destruction was found to be influenced by the type of cations present, in particular $MgSO_4 > Na_2SO_4 > CaSO_4$.

- *Sodium Sulfate ($Na_2SO_4$)*

$Na_2SO_4$ solution reacts with $Ca(OH)_2$ to form gypsum and NaOH:

$$Na_2SO_4 + Ca(OH)_2 + 2\ H_2O \rightarrow CaSO_4{\cdot}2H_2O + 2\ NaOH \qquad (2.7)$$

$Na_2SO_4$ also reacts with calcium aluminate hydrate (CAH) and results in the formation of ettringite:

$$\begin{gathered} 6\ Na_2SO_4 + 3(4CaO{\cdot}Al_2O_3{\cdot}13H_2O) + 34\ H_2O \rightarrow \\ 2\ (3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O) + 12\ NaOH + 2\ Al(OH)_3 \qquad (2.8) \end{gathered}$$

- *Calcium Sulfate anhydrite ($CaSO_4$)*

In aqueous conditions, $CaSO_4$ reacts with CAH to form ettringite (Bensted 1983):

$$3CaSO_4 + 4CaO{\cdot}Al_2O_3{\cdot}13H_2O + 20\ H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O + Ca(OH)_2 \ (2.9)$$

When the supply of Cs becomes insufficient to form additional ettringite, $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ reacts with ettringite already produced to form monosulfate (Bensted 1983):

$$\begin{gathered} 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O + 2\ (4CaO{\cdot}Al_2O_3{\cdot}13H_2O) \rightarrow \\ 3\ (3CaO{\cdot}Al_2O_3{\cdot}CaSO4{\cdot}12H_2O) + 2\ Ca(OH)_2 + 20\ H_2O \qquad (2.10) \end{gathered}$$

- *Magnesium Sulfate ($MgSO_4$)*

$MgSO_4$ attacks C-S-H and $Ca(OH)_2$ to form gypsum:

$$MgSO_4 + Ca(OH)_2 + 2\ H_2O \rightarrow CaSO_4{\cdot}2H2O + Mg(OH)_2 \quad (2.11)$$

$$3MgSO_4 + 3CaO{\cdot}2SiO_2{\cdot}3H_2O \rightarrow 3CaSO_4{\cdot}2H_2O + 3Mg(OH)_2 + 2SiO_2{\cdot}H_2O \quad (2.12)$$

$MgSO_4$ also reacts with CAH to form ettringite:

$$3\ MgSO_4 + 4CaO{\cdot}Al_2O_3{\cdot}13H_2O + 2\ Ca(OH)_2 + 20\ H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O + 3\ Mg(OH)_2 \quad (2.13)$$

In the case of $MgSO_4$ solution, a layer of brucite ($Mg(OH)_2$) forms on the surface of the mortar specimen (Gollop and Taylor 1995; Bonen and Cohen 1992). The penetration of the sulfate solution then occurs by diffusion across this surface layer. As the attack progresses, the formation of attack products, such as gypsum and ettringite, in the paste under the surface leads to expansion and strength loss. The expansion also causes cracking in the surface brucite layer, and this leaves the mortar susceptible to direct attack by the $MgSO_4$ solution. Conditions favorable for the decalcification of C-S-H are thus created, and the ultimate destruction of the mortar occurs as a result of the conversion of C-S-H to the noncementitious magnesium silicate hydrate (M-S-H) (Santhanam et al. 2003). C-S-H gel is more susceptible to magnesium than to sodium sulfate attack. In the advanced stages of attack, therefore, the Ca ions in the C-S-H can be completely replaced by Mg ions, leading to the decalcification of the C-S-H, and the loss of the cementitious structure (Santhanam et al. 2003). However, the barely soluble brucite can also act as a protective layer, which decreases the ingress of further sufate ions, as mentioned by Santhanam et al. (2003).

- *Ammonium Sulfate* (($NH_4)_2SO_4$)

The reactions that are involved with $(NH_4)_2SO_4$ are:

$$Ca(OH)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4{\cdot}2H_2O + NH_3\uparrow \quad (2.14)$$

Ammonium compounds (sulfate, nitrate, super-phosphate) cause serious deterioration of concrete in a relatively short time (Perkins 1997). The aggressive action of $(NH_4)_2SO_4$ is thought to be connected with the increased solubility of gypsum in $(NH_4)_2SO_4$ solutions (Lea 1970). Another contributory mechanism is likely to be the formation of ammonia gas. Upon formation, ammonia gas will readily diffuse from the concrete enabling the gypsum formation reaction to eventually proceed to completion rather than to establish equilibrium (Collins and Green 1990). Diffusion of ammonia gas from the concrete will also render the concrete more porous and permeable and thus more susceptible to further attack from $(NH_4)_2SO_4$ solution.

The microstructure of cements is affected by the formation of secondary sulfate phases. Changes between the surface and the core of the influenced structures have been studied in many cases and can be directly characterized by the uptake of sulfate and leaching of CaO (Skalny 2002; Bonen and Cohen 1992). The expansion is often attributed to the deposition of secondary sulfate phases but no clear evidence was found linking expansion to, e.g. the amount of secondary ettringite formed as different physical and chemical effects often overlap (Taylor et al. 2001). Different theories exist regarding the mechanisms of expansion, e.g. increase in solid volume (Taylor 1997), topochemical reactions (Brown and Badger 2000), swelling or crystal growth (Diamond 1996) but often field and laboratory observations do not match. Gollop and Taylor (1996) concluded that expansion was not a straight consequence of ettringite formation, but could be a delayed and possibly indirect consequence of it. Recent theories emphasize that crystallization pressure develops in nanometric pores of the cement paste, producing the initial tensile stress and subsequently expansion of the matrix, as suggested by Scherer (2004). It correlates with the macroscopic observations. Santhanam et al. (2003) found that gypsum and ettringite can both contribute to expansion especially in Portland cements with high $C_3S$ contents. Brown and Taylor (1999) concluded that there is no linear relationship between the amount of ettringite formed and the observed expansion.

Physical and chemical changes during leaching have been observed and modeled by various authors (Taylor et al. 2001). Leaching, the dissolution of $Ca(OH)_2$ and decalcification of the C-S-H phase, affects the pore structure and the stability of the major hydrate phases. Haga et al. (2005) found that leaching leads to an increase in porosity, especially capillary porosity of the affected concrete structures.

When the strength of the cement stone is reached, micro-cracks are initiated, leading to changes in the diffusivity and a reduction in the elastic properties of the cement stone. Changes in the diffusivity due to cracking further affect the concentration gradients of sulfates. The stiffness of the cement stone is also degraded, depending on the location of the cracking front (Tixier and Mobasher 2003). Crack formation related to sulfate interaction is often observed to be partly parallel and partly perpendicular to the sample surface. The parallel cracks are often filled with gypsum, whereas the perpendicular cracks are often observed along the aggregates and at greater depth of the affected samples (Brown and Hooton 2002). Gollop and Taylor (1992) found that the regions where crack propagation was observed and expansion took place were described as areas where ettringite has formed. It appeared that expansion was a delayed or possibly an indirect consequence of ettringite formation and that gypsum recrystallized in cracks formed by other mechanisms.

After the formation of the cracks due to sulfate interaction, the microstructure started to break down, the compressive strength decreased and gypsum as well as ettringite were observed by Irassar et al. (2003). According to Monteiro and Kurtis (2003), in the presence of cracks the expansion of the samples was accelerated due to an increase in sulfate uptake.

The $C_3A$ content of Portland cement has long been assumed to be the main contributor to volume change in sulfate attack. Substitution of $C_4AF$ for $C_3A$ has been shown to reduce susceptibility to sulfate attack (Hewlett 1998), although it has also been shown that too much $C_4AF$ can decrease the resistance of low $C_3A$ cement. Emanuelson et al. (1997) point out that ferrite is the major oxide interstitial phase in a sulfate-resisting Portland cement. To achieve this, the $Al_2O_3/Fe_2O_3$ ratio in $C_4AF$ is decreased by the addition of iron, which in turn raises the $C_4AF$ content. $C_4AF$ also produces ettringite, but at a reaction rate much slower than $C_3A$ (Odler 1991), the resulting ettringite crystals contain iron along with aluminum in the lattice and the iron-containing ettringite phases are much less expansive than iron-free phases.

The early hydration of $C_3A$ plays an important role in concrete rheology and is affected considerably by the dissolution rate of calcium sulfate which itself depends on a number of factors, such as presence of organic admixtures, anhydrite/gypsum relation, and size of $C_3A$ particles. Most of these factors have a direct impact on the amounts of AFm and AFt being formed (Stark 2011).

## 2.3 Testing and standards for sulfate resisting cements

The permitted compositions of product specification standards for sulfate resisting cements are based upon long-standing laboratory test results and also on satisfactory performance in the field. National differences reflect different exposure conditions and differences in the nature of the available cement constituents. Harmonization of knowledge and developed testing methods up to present is problematic because the properties of the various cements are not the same in different countries. Moreover, the actual properties of cements vary over time, and the standard requirements for cements are also not immutable.

There are no standard concrete tests for assessing sulfate resistance. The reason is that even in highly concentrated sulfate solutions, the test would take several years to show visual damage, expansion or strength loss. It is widely assumed that the performance of concrete regarding its resistance to external sulfate attack depends on the composition of the cement used. Therefore, most standard tests are based on measuring macroscopic properties of cement pastes or mortars, such as expansion, modulus of elasticity, or compressive strength (Ferraris et al 2006), the experimental conditions varied widely. Few models are based on the analysis of the problem of sulfate attack on a wide database of experimental results. Kurtis et al. (2000) performed a statistical analysis of expansion data collected from a long-term experiment, and they were able to arrive at a predictive model that could suggest the damage in terms of expansion due to sulfate attack based on the chemistry of the cement ($C_3A$ content) and the characteristics of the mixture (w/c). The most important parameter of concrete was considered to be limiting the mix w/c depending on the severity of exposure (to limit sulfate ingress).

In general, research today identifies $C_3A$ as the primary measurable component of Portland cement that influences sulfate resistance in concrete. Portland cement containing less than 5 % $C_3A$ has been classified as sulfate-resisting cement and used as the specification criterion in many codes and standards for cement all over the world. Low $C_3A$ sulfate resisting cements provide a chemical resistance to sulfate attack. The products of reaction with sulfates are not expansive and consequently the cement stone is not disrupted facilitating further attack. The unreactive nature of the hydration products of low $C_3A$ cements is attributed to a low level of monosulfate and/or the formation of an iron-rich form which is slow reacting and produces a 'non-expansive' form of ettringite (Odler 1984).

The sulfate resistance of concrete is dependent upon a number of factors, including mortar permeability and the type and concentration of the sulfate solutions involved. Other aspects, directly related to the cement characteristics, include $Ca(OH)_2$ concentration and the $C_3A$ content:

- In the solutions used in a typical test, as described in the literature (Skalny et al. 2002; Clifton et al. 1999; Moir 1999), specimens are exposed to aqueous solutions with a different type of ions ($Na_2SO_4$ or $MgSO_4$). Hewlett (1998) states that $Na_2SO_4$ solutions have a more pronounced effect on cements with high $C_3A$ contents, while $MgSO_4$ solution has a more pronounced effect on cements of lower $C_3A$ content.

- Various concentration of solutions. According to Biczok (1967), the mechanism of reaction changes when the concentration of the solution changes. Many investigations use high sulfate concentrations to accelerate physical and microstructural changes in the samples within a short time. In the presence of high sulfate concentrations, gypsum is often formed besides ettringite, whereas under field conditions gypsum is rarely observed under field conditions where moderate or low sulfate concentrations are present (Gollop and Taylor 1996; Bellmann et al. 2006). Higher concentration of sulfate leads to quicker deterioration. Al-Dulaijan et al. (2003) studied the performance of Portland and composite cement mortar cubes of 50 mm size exposed to the $Na_2SO_4$ solution of varying concentration (1.0, 1.5, 2.0, 2.5 and 4.0 %) for up to 24 months. The degree of deterioration was evaluated by strength reduction and by visual inspection. Results of the study indicated that the rate of deterioration increased with an increase in sulfate concentration for both Portland and composite cements. High sulfate concentrations, as used in such tests, lead to the precipitation of gypsum, while lower sulfate concentrations, as present under field conditions, lead to no or only very little gypsum precipitation (Schmidt et al. 2009).

- The temperature of exposure. Usually the temperature is controlled. Temperature may affect the rate of chemical attack indirectly, since as temperature rises, the moisture content of affected concrete becomes reduced, making it drier and more permeable to additional fluid due to expansion. The formation of gypsum and ettringite was accelerated by increasing the temperature by Santhanam et al. (2003). As temperature falls, contraction may sometimes cause sufficient shrinkage to create small open cracks, allowing greater penetration of liquid into its interior. Hekal et al. (2002) studied the effect of temperature at exposure by observing sulfate exposure at room temperature, at 60 °C and at 60 °C temperature with the drying-immersion cycle. The increase in temperature of the sulfate solution accelerated the sulfate attack on all types of specimens of mortars. The drying-immersion cyclic process at 60 °C accelerated the sulfate attack considerably and it was considered as an accelerated method to evaluate sulfate resistance.

- The specimen may be exposed to wet/dry cycles, to partial immersion, or to continuous immersion. Cyclic wetting-drying exposure can be more harmful than continuous soaking. The frequency of the exchange of the solutions (Lothenbach et al. 2010) is also a factor influencing the expansion. In their study Lothenbach et al. (2010) conclude that periodic exchange of the $Na_2SO_4$ solutions, as prescribed for most sulfate tests, affects strongly the composition of the solution, as with each renewal the sodium and sulfate concentration increases while the pH decreases. Frequent exchanges lead to a stronger leaching of calcium compared to samples where the solution is not exchanged. Under field conditions, where the sulfate containing solutions can flow continuously, leaching will be even stronger. In addition, the exchange has a non-negligible effect on the mineralogical profiles and might affect expansion (Ferraris et al. 1997). Results of comparative tests between controlled and uncontrolled pH conditions by Brown (1981) showed that keeping the pH constant accelerated the test, both the loss of strength and the expansion rate and the time to reach a certain level of expansion for the uncontrolled pH condition was roughly twice as much as for the controlled pH condition (Brown 1981; Ferraris et al. 1997).
- The size of specimens varies widely. For specimens with increasing cross sections, expansion is reduced and retarded accordingly (Ferraris et al. 1997). Using smaller size specimens allows obtaining the test response in a shorter time which is an important factor in studying the sulfate resistance of newly developed composite cements.

All these conditions influence the results obtained (usually the macroscopic deterioration, such as expansion, strength, and weight loss, is measured over a prescribed period of time), because sulfate attack is an external attack and it progresses slowly from the surface to the center of specimens. The tests carried out in different laboratories show large variations (Moir 2006).

Therefore, it is likely that the material response and service life might not be the same in the laboratory and in the field. If the deterioration is lower than a pre-set value, the cement is considered sulfate resisting. This approach could be misleading if the field conditions are not similar to the conditions of the laboratory experiment (Ferraris et al. 2006).

Stark (2002) evaluated concrete performance in field and laboratory sulfate exposures on the basis of a long-term test program over a period of 16 years. Cyclic crystallization and growth of sodium sulfate salts in concrete appeared to be a predominant mechanism of deterioration in the concrete specimens, regardless of variables in the concrete mixtures. The salt crystallization process was a major cause of concrete distress compared with the traditional hypothesis of chemical reaction of aluminates from cement hydration and sulfates from external sources. W/c ratio was the primary factor affecting the durability and performance of concrete in the sulfate soils exposures, ratios of about 0.40 or less resulted in higher performance. Furthermore, a major mechanism of deterioration in these concrete specimens appeared to be cooling and heating, and wetting and drying. The traditional explanation of expansion of concrete due to chemical reaction of sulfate ion with alumina bearing cement hydration products was of relatively minor significance in these tests.

One problem in determining the resistance of concrete to practical levels of sulfate exposure is that deterioration may not occur within a reasonable period of time. Therefore, to obtain information on the long-term performance of a concrete in a sulfate-rich environment, the rate of sulfate attack must be accelerated in the laboratory. Several short-term methods of testing include: increasing the reactive surface, using highly concentrated solutions, raising the temperature of the aggressive environment, and other methods. Using techniques that deviate from field conditions, however, may have significant effects on the nature of the attack mechanism; an example of which is the possible transition from ettringite to gypsum formation as the concentration of sulfate is increased. As a result, these accelerated methods cannot be easily used to accurately predict the service life of concrete in a sulfate-rich environment. They can, however, be used to assess the relative performances of various concretes exposed to sulfate attack. Just as cement formation involves a series of chemical processes, so does cement deterioration. The chemical nature of concrete deterioration is often unappreciated; this lack of understanding results in the violation of some basic chemical principles that, in turn, lead to concrete deterioration and loss of its service life.

Different test methods have been developed to study the sulfate resistance of cements, from which ASTM C 1012 Test Method for Length Changes of Hydraulic-Cement Mortars Exposed to a Sulfate Solution is considered the most common approach and abundant data is available in the literature based on the results of this test method. ASTM C 1012 measures the amount of expansion on mortar bars upon continuous exposure to sulfate solution and determines the resistance of hydraulic cements. This test is suitable for evaluating the sulfate resistance of composite cements as well as Portland cements. Continuous immersion of the specimens does not necessarily represent the field conditions, as the sulfate concentration and pH of the site generally remain constant. Furthermore, the field specimens are subject to environmental effects, such as wetting–drying and heating–cooling, therefore, some researchers simulated field exposure conditions in the laboratory (Sahmaran, Erdem et al. 2007). Both ASTM C 1012 and ASTM C452 Standard Test Method for Potential Expansion of Portland-Cement Mortars Exposed to Sulfate have been the subject of much criticism. Many researchers, including Brown (1981), Cohen and Mather (1991), Mehta, 1992; and Tumidajski and Turc (1995) have shown that existing accelerated test methods are not adequate to predict field performance. Much of the criticism concentrates on the specimen size, specimen curing, form of sulfate exposure, duration of test, and assessment of sulfate resistance by expansion measurements. Both ASTM methods are too sensitive to specimen size and geometry. ASTM C452 neglects field conditions because addition of sulfate (Tumidajski and Turc 1995) and inadequate curing of cement results in anhydrous cement compounds being exposed to attack (Mehta and Gjorv 1974).

Ouyang (1989) proposed a model for sulfate attack on cement mortars based on the concept of progressive fracturing. An initial damage of the mortar was assumed to be a function of the gel–space ratio. The expansion of the matrix due to sulfate attack was incorporated as additional nucleated voids, which increase the existing initial damage prior to loading of the specimens. This model was able to predict the mechanical properties of cement mortars subjected to compression while undergoing sulfate attack.

In his study of sulfate resistance of composite cements, Irassar (1990) described a new criterion for evaluation of sulfate resistance, which he called the 'crack-time'. Flexural strength development was used as the test parameter to evaluate the different phases of sulfate attack including the following: filling of pores, cracking, strength loss, and deterioration of the structure. With time, the flexural strength of mortar bars in sulfate solution was found to increase up to a maximum, and then decrease rapidly. The crack-time was defined as the time at which the flexural strength of mortar bars was a maximum. Using this parameter, successful predictions could be made for the performance of concrete containing various composite cements in sulfate solutions.

Mehta (1986) based an evaluation on strength loss, a drop of more than 25 % indicating failure. It is now accepted that strength, especially compressive strength, is an inadequate measure of concrete durability or sulfate resistance. Thus, it is inappropriate to relate the probability of sulfate attack directly to a single variable such as the compressive strength at a selected time. Progress of the deterioration must be characterized both by the rate at which, and the degree to which, the sulfate-related reactions have already altered (and continue to alter) the concrete, and that subsequently resulted in the loss of mechanical properties, such as permeability, volumetric stability, and strength. Variables other than permeability to aggressive solutions and cement type are involved. Stark (1990) devised a visual rating scale for evaluation of concrete. Ratings were based on a scale of 1.0...6.0, with the upper limits indicating failure.

Linear expansion is so far the most widely used performance indicator in published papers and reports. PrCEN/TR 15697:2007 underlines that the major weakness of sulfate resistance assessment based on expansion measuring is that it measures the deterioration associated with the formation of ettringite from monosulfate. Investigations in which both expansion and strength have been determined have indicated that composite cements can undergo deterioration while showing relatively low levels of expansion. Thus, whilst expansion may be an appropriate test procedure for CEM I cements, or cements with a relatively high clinker content, it may be less reliable when applied to composite cements. Caution should be exercised in interpreting the expansion results. The test method is inherently of lower precision than other performance tests, e.g. strength or drying shrinkage.

To date there is no uniquely accepted standard to specify the criteria for the determination of the sulfate resistance of cements. The extensive work by the European Committee for Standardization (CEN) organization to improve expansion measurements (Moir 1999) did not result in an accelerated test.

PrCEN/TR 15697/2007 reviews and analyzes several test procedures and reports main features of a possible EN test method for sulfate resistance. The method proposed differs from the Wittekindt method (described in detail in section 3.1) used in the present research:

- Specimen's size is (40x40x160) mm (instead of (10x40x160) mm).
- Curing period is minimum 4 weeks instead of 14 days.
- ph and $SO_4^{2-}$ are automatically controlled.
- Testing temperature 10 ºC or 5 ºC is also suggested to create more relevant conditions (not only 20 ºC).
- Failure criteria to be based on the relative flexural and compressive strength of specimens (Wittekindt test method measures relative expansion).
- Testing time - 1...2 years.

The proposed method implicates that compared to the Wittekindt method, several important dissimilarities exist:

- The size of the specimen is larger. Therefore, testing time is considerably longer.
- Advantages are: Control of solution pH - enables sulfate attack to be accelerated without the use of unrealistically high sulfate concentrations. Testing at low temperature conditions - relates better to field conditions.

Test methods carried out at a room temperature of 20 °C do not cover the lower temperatures which may occur, especially with foundation structures or regions of cold climate. Temperature variations above and below the freezing point can lead to surface weathering or internal destruction of the structure in concrete constructions. In Europe, the frost resistance of concrete is defined by descriptive regulations. Different test methods vary in sample form and sample size, degree of saturation of the test samples, temperature profile of the cycles, maximum and minimum temperature as well as duration and number of the cycles (Boos, Giergiczny 2010). The conditions applied in laboratory test methods rarely correspond to actual conditions in the field. The number of natural freeze-thaw cycles may differ greatly from those in the accelerated tests by fast repetition of freeze-thaw cycles; a different salt may be used or at a different concentration; the age of the concrete when it experiences the first freezing cycle may not be 14 or 28 days old; and the rate of freezing in the field is rarely as high as the one applied in laboratory tests. Therefore, these test methods only indicate potential susceptibility of a concrete to damage by freezing and thawing (Pinto and Hover 2001). Based on a specific type of sulfate attack – the damaging formation of thaumasite – the behavior of concretes and mortars during sulfate attack in conjunction with low temperatures also has attracted special interest in the last years.

Depending on the selected degradation measure, different conclusions can be drawn regarding the performance of concrete under sulfate attack. Most of the analysis of sulfate attack is based on the laboratory studies involving relatively simple chemical systems of pure materials, however, in actual practice the situation is more complicated. In field structures, one of the critical aspects is varying concentrations, as the same concrete element may be attacked in different regions by different concentrations of sulfates, due to the development of drying fronts, wetting fronts and other reasons. The field conditions of concrete exposed to sulfate are numerous and variable. The aggressiveness of the conditions depends, among others, on soil saturation, water movement, ambient temperature and humidity, concentration of sulfate and type of sulfate or combination of sulfates involved.

Long-term studies (Mehta and Williamson 1973) based on the test results of 67-year old massive concrete blocks lying submerged in sea water showed that under certain conditions even good quality cements made with sulfate resisting type Portland cements can be vulnerable to long-time sulfate attack. Based on their long-term testing in Sacramento, California Irassar (1996), Liu et al. (2012) concluded that pozzolanic additions, such as fly ash, blast furnace slag or silica fume, as cement constituents resulted in lower durability than the concrete with Portland cement. The results of Monteiro and Kurtis (2003) showed that the amounts of $C_3A$ (0…8 %) in the cement do not necessarily protect from sulfate deterioration. In contrast, the w/c ratio of the investigated samples had a major impact on the failure time of the samples during 40 years of exposure under real conditions. They concluded that the permeability as porosity of the concrete samples investigated has a major influence on the deterioration of the samples. These observations were confirmed by Khatari and Sirivivatnanon (1997). On the basis of his study, Stark (2002) concluded that a major mechanism of deterioration in the field tests (but absent in the laboratory) is cooling and heating, and wetting and drying by natural variation with cyclic crystallization of sodium sulfate salts. When a permeable concrete is subjected to cyclic wetting with sulfate-bearing solution and subsequent drying, the repetitive crystallization of salt within the pores near the surface of the concrete may cause exfoliation or spalling regardless of whether or not a chemical reaction takes place between the cement paste and the sulfate salts. These damaging phenomena cannot be captured by the continuous immersion exposure used in the current testing methods. Irassar (1996) and Liu et al. (2012) concluded that w/c ratio seemed to be the primary factor affecting the rate and severity of deterioration according to long-term studies. Years ago it was almost impossible to make concrete with lower w/c, less than about 0.40. Nowadays several possibilities exist to make concrete with low w/c and thereby to reduce permeability and to limit penetration of sulfate solution into concrete. In contrast, Ficcadenti (2001) concluded on the basis of 18-year long tests in Denver, Colorado, in the USA that w/c of the concrete had little impact on chemical sulfate attack expansion over time. Marchand et al. (2002) showed that the formation of gypsum is rarely observed under field conditions where moderate or low sulfate concentrations (5…10 g $SO_4^{2-}$/l) are present.

As can be seen from the abovementioned results, the deductions based on the results of different methods are very controversial. Therefore as concrete is so miscellaneous material and the conditions that influence concrete in field are variable it is only possible to approximately predict the behavior of concrete in certain circumstances and to try to minimize detrimental risks by precisely selecting constituents and compositions of concrete.

## 2.4 Second constituents of Portland cement

The development of Portland composite cements is considered to be the state of art on cement production. The initial aim was to reduce the cost. But further objectives added were: to improve performance, to save the energy, to use conventional raw materials or industrial by-products and to achieve the ecological benefits (Voglis et al. 2005, Neville 1995). The use of composite cements has allowed to reduce the $CO_2$ emission per ton of produced cement and made the way for innovations, such as high performance concrete and self compacting concrete (Stark 2011).

The benefits of the use of second constituents are the reduction in concrete permeability and the replacement of the Portland cement clinker. The role of second constituents in improving the sulfate resistance of concrete, as indicated by several investigators, involves lowering the permeability by a decrease of porosity by C-S-H formation that slows the penetration of sulfate ions into hardened concrete (Santhanam et al. 2003) while replacing the Portland cement reduces the presence of compounds such as $C_3A$ that cause ettringite formation. One approach to increase sulfate resistance is to reduce the $Ca(OH)_2$ in the hydrated cement paste by using cements that contain puzzolans and ground granulated blastfurnace slags and thereby can enhance sulfate resistance of concrete. The role of these components is to consume $Ca(OH)_2$ in the pozzolanic reaction and to dilute the $C_3A$ content of the system (Bhatty and Taylor 2006). Hence, all the aluminate-bearing phases will accordingly be reduced. Therefore, the formation of ettringite will be mitigated. The reduced availability of Ca may also result in the formation of ettringite with a morphology and distribution throughout the cement stone, which is not expansive (Brown, Taylor 1999). The formation of secondary C-S-H also results in the densification of the cement stone since it is deposited in the pores thereby making composite cements impermeable and, therefore, sulfate ions cannot easily diffuse through the concrete (Al-Dulaijan et al. 2003). Due to the consumption of $Ca(OH)_2$ by the pozzolanic reaction, the formation of gypsum itself is reduced (Santhanam et al. 2003).

The European Standard EN 197-1 identifies type II cements that may contain various materials as main constituents, in percentages ranging from 6 % to 35 %. Pozzolana, fly ash, ground granulated blastfurnace slag and limestone are the main constituents that are permitted by the EN 197-1. The principal hydration products in composite cements are almost similar to those found in Portland cement but the added constituents may affect the hydration rate of hydration products (Taylor 1997).

### *2.4.1 Burnt oil shale*

Oil shale is the most important natural resource in Estonia. The majority of mined oil shale is utilized in thermal power plants for electricity and heat production. About 20 % is used for retorting shale oil and the rest is mostly used in the cement industry. Despite long-term research of reusability options, a vast majority of ash is still deposited on ash sediment field next to the power plants. Currently, less than 10 % of oil shale is applied in Estonia, a benefit derived for the construction material industry (e.g., making Portland cement, gas-concrete), for the road construction industry (stabilization of roadbeds) and for agriculture, e.g., liming of acid soils. The high Ca-sulfate content in burnt shale could limit its application in the construction material industry and in road construction (Pihu et al. 2012). The amount of ash that remains after burning constitutes 45...50 % of the oil shale mass.

A Pozzolana is defined by the American Society for Testing and Materials (ASTM) as “a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with $Ca(OH)_2$ at ordinary temperature to form compounds possessing cementitious properties.”.

In the renovation process since 2004, the high temperature combustion system (PF) is being replaced with fluidized bed firing (CFBC).

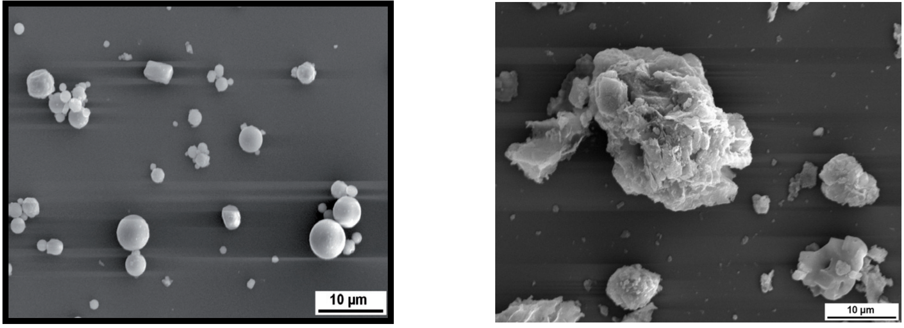
Different combustion conditions in the PF and CFB technologies cause remarkable differences in the phase composition as well as in chemical composition of ash fractions.

#### *2.4.1.1 High temperature combustion burnt shale $T_T$*

High temperature burnt shale $T_T$ has been successfully used in Estonian cement industry as a second constituent for years. As it is a very important constituent in Estonian cement industry and the properties of burnt shale have changed because of the modernization of the manufacturing process, the usage of burnt shale in this research was of special interest.

Pulverized firing uses pulverized oil shale (median size 45…55 µm) that is fed into the combustion chamber by hot air as a transporting medium and mixed there with hot secondary air. During the combustion heat is released and transferred through heat transfer surfaces to water (steam). At the same time various conversion processes with fuel mineral matter occur, and ash is formed. The combustion temperature inside the furnace is about 1350…1450 °C and can reach 1500 °C (Ots 2006).

Besides burnt shale $T_T$, the main constituent that reduces the clinker content of Portland cement, it also gives Portland cement some unique properties. The use of burnt shale $T_T$ as a cement constituent makes the concrete less permeable to harmful ions due to its finer particle size distribution and pozzolanic reactions. This results in an enhanced performance and more durable concrete. The main benefits of the use of burnt shale $T_T$ in cement and concrete are: enhanced workability due to the spherical shape of the ash particle, reduced bleeding and less water demand, increased compressive strength, reduced permeability, lower heat of hydration, and greater resistance to sulfate attack (Kikas 1997).


A. Burnt at ≥ 1300 °C burnt shale $T_T$

B. Burnt at ≥ 800 °C burnt shale $T_K$

Figure 2.4.1 Shape of burnt shale particles (Raado and Nurm 2007).

Burnt shale $T_T$ has spherical particles covered with smooth glassy material. Burnt shale $T_T$ with particle size ≤ 10 µm is presented in Figure 2.4.1.A. Low temperature burnt shale $T_K$ has an indefinite geometric configuration. Figure 2.4.1.B shows burnt shale $T_K$ particles with porous stratified surface. The described surface and the shape formed during various combustion processes show changes in the binding properties of burnt shale from hydraulic $T_T$ to pozzolanic $T_K$, these changes lead to an increasing water demand.

Estonian oil shale consists approximately of 55…65 % of inorganic matter. Burnt shale has been collected by dust collecting systems, the finest fraction by the electric precipitators. Since 1960 burnt at ≥ 1300 °C oil shale has been used as the main constituent of cement in the Kunda cement plant production. Besides clinker minerals $C_2S$ and CA (about 13 %) and active glassy phase ~33 %, the burnt oil shale contains free $CaO_{free}$ ~ 10 % (more than limit value for flyashes), $CaSO_4$ ~17 % and an insoluble residue ~27 % (Kikas et al. 1999). $CaO_{free}$, if present in larger amounts than acceptable, causes an expansion of the hardened cement paste due to its conversion to $Ca(OH)_2$ (Odler 2001). Minerals containing iron and alumina oxides melt in the extremely rapid combustion process at temperature of about 1300 °C. As a result, fine spherical particles are covered with a melt glassy layer. The hydrous transformation of amorphous Al-Si glass phases controls the cementation of the ash mainly by the formation of secondary Ca-rich hydrate phases, including $Ca(OH)_2$, ettringite and gypsum and subsequently by the carbonation of $Ca(OH)_2$ (Pihu et al. 2012).

As a consequence, burnt shale $T_T$ as the main constituent of Portland cement reduces the water requirement of the cement paste. In a fresh mortar, the fine spherical particles of burnt shale $T_T$ covered with a glassy layer have a so-called ball bearing effect: water requirement for the same standard consistency is reduced. Thus, burnt shale $T_T$ has both plasticizing and pozzolanic properties (Raado and Nurm 2006). It also binds free lime chemically in cementitious compounds, rendering it unavailable for sulfate reaction.

The binding capacity of the high temperature burnt shale $T_T$ is controlled by secondary Ca-phases including belite and $CaO_{free}$, and the pozzolanic properties of silicate glass phase (Pihu et al. 2012).

Burnt shale $T_T$ is liquid at 1200...1400 ºC, so it will alter to spherical particles and cohere to each other due to surface tension when cooled, resulting in porous glasses with compact structure. As a result, the active $SiO_2$ and $Al_2O_3$ inside the particles are difficult to dissolve and react with lime. The high-temperature combustion process in the PF boilers ensures major decomposition of carbonate mineral phases (dolomite, calcite) and melting of clay minerals that form a source for reactive silica as well as aluminium, thus controlling the formation of secondary Ca-silicate and Ca-Al-silicate phases (Bityukova 2010).

By EVS 636:2002 burnt shale as a fine product of combustion contains less than 12.5 % of $CaO_{free}$, less than 0.42 % of $Cl^-$ and has a specific surface by Blaine ≥ 350 $m^2/kg$. Ground burnt shale reaching specific surface about 500 $m^2/kg$, tested by EN 196-1, must show a compressive strength higher than 25.0 $N/mm^2$. Estonian standard EVS 636:2002 defines burnt shale for the production of Portland cement as the material consisting of the clinker phase mainly of $C_2S$, monocalcium aluminate; glassy phase with latent binding properties and pozzolanic $SiO_2$. The other components are $CaSO_4$ and fine particles of $CaO_{free}$. Common constituents of burnt shale are CaO, $SiO_2$, $Fe_2O_3$, $Al_2O_3$, MgO, $Na_2O$, $K_2O$, $Cl^-$ and $SO_3$. Common specific surface of $T_T$ used for Portland cement production is about 400 $m^2/kg$ (Raado and Nurm 2007).

#### *2.4.1.2 Low temperature combustion burnt shale $T_K$*

In the renovation process since 2004, the high temperature system is being replaced with fluidized bed firing (CFBC). The CFBC technology is believed to have a considerably smaller impact on the environment, and new CFBC units are more efficient than pulverized firing units. The introduction of the CFBC units ensures almost complete capture of $SO_2$ from the flue gases and $CO_2$ emissions are reduced by 4...8 % compared to $CO_2$ emissions from the older PF units (Pihu et al. 2012).

The flue gas superficial velocity exceeds the gravitational force; particles leave the bed and are transported by rising flue gas to the separator, where most of the particles are captured and returned to the bed, and continuous circulation of the solid phase takes place (Ots 2006). The firing temperature of a flying bed boiler is about 750…900 °C. This leads to a sustainable change in the quality of the resulting ash. Thus, the properties of the resulting burnt shale $T_K$ undergo serious changes. Particles of high temperature combustion are spherical and have a smooth surface. Particles of burnt shale burnt at 800 °C (Figure 2.4.1.B) have no clear geometrical form and no smooth surface was detected (Raado and Nurm 2006). The glassy phase is not formed. At a lower combustion temperature $CaO_{free}$ reacts more readily with $SO_2$ forming a solid $CaSO_4$ (anhydrite) phase.

The considerably lower combustion temperature and the enhanced phase separation in the CFBC units result in significantly different chemical, physical and phase compositions of the ash products compared to the high temperature burned ashes (Pihu et al. 2012).

Burnt shale $T_K$ contains less Ca silicate phases (e.g., belite b-$C_2S$) and is richer in anhydrite. Consequently, the ash hydration processes and secondary phases forming in burnt shale $T_K$ are slightly different than in burnt shale $T_T$ (Liira et al. 2009). The content of potential cementing phases in the burnt shale $T_K$ is considerably lower because the ash products are formed at significantly lower temperatures. First, the content of $CaO_{free}$ in the finest fractions is at least two times lower in the burnt shale $T_K$ compared to the burnt shale $T_T$. This result is mainly due to the effective sulfation and formation of $CaSO_4$ at the expense of $CaO_{free}$ after the decomposition of the carbonate phases (Pihu et al. 2012).

Because the temperature in the CFBC boiler is approximately 800...850 ºC, sandy-clay silicate mineral melting is limited. This is evidenced by the common presence of illite-type clay mineral in the burnt shale $T_K$. As a result, the amount of secondary Ca-silicate phases, as well as amorphous glass phases, is smaller or absent in the ash products; therefore, burnt shales $T_K$ have lower pozzolanic potential (Pihu et al. 2012).

The firing temperature in CFBC boilers allows thermal decomposition of dolomite, but only partial decomposition of calcite. Therefore, $T_K$ burnt shale contains less reactive CaO than $T_T$ burnt shale. Also, the clay mineral phases are preserved, but they lose physically bound (including in interlayer position) water and for most part of the chemically bound hydroxyl groups (Bityukova 2010) and therefore burnt shales $T_K$ contain a higher share of residual mineral phases.

Solid residues from CFBC boilers contain components from three general groups: fuel ash with unburned coal, desulphurization products (almost exclusively anhydrite), and products of ground limestone sorbent decomposition. Therefore, and also because of rather low combustion temperatures, burnt shales $T_K$ distinctly differ in their physical, chemical and phase compositions from burnt shales $T_T$ produced in conventional pulverized coal combustion boilers, which are commonly used as a cement constituent (Glinicki and Zielinski 2007).

Common industrial standards for the use of fly ash as a concrete additive, such as ASTM C 618-05 or EN 450-1, contain no fly ash from fluidized bed combustion. Although burnt shale $T_K$ did not meet the requirements imposed by these standards, especially with respect to $SO_3$ content, free CaO and unburned calcium and magnesia carbonate, some tests (Havlica et al. 1998) revealed the potential of such products as cement or concrete constituent.

Class F fly ashes are described as pozzolanic because they primarily hydrate by reacting with $Ca(OH)_2$ formed from Portland cement's calcium silicates. They improve chemically the sulfate resistance of concrete by consuming $Ca(OH)_2$ and thus reduce the potential for the formation of ettringite (Stephens and Carrasquillo 2000). Literature reveals that puzzolanas with low lime contents mitigate sulfate attack by reducing alumina levels in the mixture. Conversely, a high lime content fly ash may decrease sulfate resistance (Tikalsky and Carrasquillo 1992). Calcium content of fly ashes is a major factor influencing the effect of fly ashes on a concrete sulfate resistance, also silica, alumina, iron oxide and sulfate compounds are considered most critical. Alumina may be present as part of the glassy phases or in several crystalline phases (Stephens and Carrasquillo 2000). In burnt shale $T_K$ alumina takes the crystalline form of mullite, which is stable in sulfate environments. The effectiveness of different burnt shales may vary significantly because of the large variation in these compounds depending on several factors. Liquid phase can hardly occur at 800...950 °C, compact structure cannot be formed.

### *2.4.2 Fine limestone*

Limestone is used for various purposes in cement and concrete: as a raw material of clinker, as aggregate in concrete and a constituent in cement. The production of Portland limestone cements seems to be very challenging, due to the satisfactory properties of the limestone cements as well as the low cost and the high availability of limestone in Estonia.

Since the European Standard for Common Cement first published in 1992 as pre-Standard ENV 197-1, the use of limestone as a main cement constituent has been an increasing trend. It is applied in high performance concrete as well as in normal or low performance concrete. European standard EN 197-1 identifies two types of Portland limestone cements (PLC): Type II/A-L containing 6...20 % and Type II/B-L containing 21...35 %. In addition, the inclusion of 5 % of filler material that can be calcareous is accepted in all cements.

Adding 5 % fine limestone to Portland cement was a subject of discussions in the past. Proponents suggested energy savings during production, without impairing the quality of the cement and concrete properties. Whereas the opponents claimed that fine limestone is merely an adulterant, leading to a reduction in quality. The effect of 5 % fine limestone addition to the fresh and hardened properties of concrete is generally small (Matthews 1994). Regarding the compressive strength, both enhanced strength and reduced strength have been reported upon limestone addition. Certain amount of limestone (up to around 5 %) reacts to give calciumaluminocarbonate phases and monocarbonate is formed as the stable AFm phase instead of monosulfate (Lothenbach 2008). This results in a larger volume of hydrates and more aluminate is initially bound as ettringite, which might chemically increase sulfate resistance. Beside that the higher volume of hydrates physically lowers the porosity. It was found by Tsivilis et al. (2003) that small amounts of fine limestone added to the cement reduced porosity and permeability at a constant w/c ratio. Higher amounts of fine limestone added to the cement resulted in higher permeability of the investigated cements and faster degradation during sulfate attack according to Irassar et al. (2003). Limestone addition also influences the chemistry of the cement stone. The presence of carbonate in the cement leads to the formation of monocarbonate as the stable AFm phase (Lothenbach et al. 2008). Furthermore, the additional calcite was found to act as a source of calcium buffering the cement, e.g. in the case of leaching (Catinaud et al. 2000).

The results of sulfate performance of cement mortars containing fine limestone show different trends. Some authors (Zelic et al. 1999) conclude that fine limestone could increase the sulfate resistance of cement, while other researchers (Gonzalez and Irassar 1998) have found a decrease in sulfate resistance of this cement depending on the replacement level and clinker composition. A benefit of the addition of small amounts of carbonate is a reduction of the expansion observed upon sulfate attack, which is most prominent for cements with high $C_3A$ content (Schmidt et al. 2009; Weerd et al.

2011). Investigation by Gonzalez and Irassar (1998) based on the ASTM C1012 test, reports that the addition of 10 % limestone showed no significant effect on sulfate performance of cements.

The study of Irassar et al. (2003) showed that sulfate attack in mortars containing fine limestone is characterized by an inward movement of the reaction front leading first to the formation of ettringite, later to gypsum deposition, and finally to thaumasite formation when the decalcification of mortar led to the breakdown of C-S-H. The presence of limestone in mortars suppresses or delays the conversion of ettringite to monosulfoaluminate and, instead, the monocarboaluminate is formed (Bonavetti et al. 2001). The contribution part of the aluminates that remains crystallized as ettringite due to the monosulfoaluminate decomposition by carbonate ions appeared not to be significant for the sulfate performance of limestone containing cements.

Portland cements containing fine limestone exposed to the sulfate environment can be damaged due to the formation of ettringite and gypsum and also by the formation of thaumasite because the presence of finely divided limestone could favor the formation of these compounds in cold and very wet environment (Bre 1991). Thaumasite ($CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$) was detected as early as 1965 by Erlin and Stark (1965) in damaged concrete. In contrast to the situation for ettringite (lowering the $C_3A$ content of the cement) and gypsum (reducing the amount of portlandite present in hardened cement paste), no simple chemical concept has been introduced to ensure a protection of hardened cement paste against the formation of thaumasite (Bellmann and Stark 2007). Crammond and Halliwell (1995) report that concretes containing limestone aggregates designed to provide a good sulfate resistance have suffered a particular type of sulfate attack in which thaumasite is formed. Thaumasite formation is identified in the degradation process of masonry mortar, historical building, and concrete in marine environment. Hartshorn et al. (1999) reported that the performance of paste containing 0 %, 5 %, 15 %, and 30 % of fine limestone exposed to cold (5 ºC) solution became worse with increasing limestone addition and increasing concentration of $MgSO_4$ solution. They attributed this behavior to thaumasite formation. Also, Hooton and Thomas (2002) emphasize that field experience with up to 5 % limestone in Portland cement in Canada and Europe for over 20 years has not produced any known cases where this has contributed to thaumasite sulfate attack. Problems may exist concerning much higher levels of limestone (15 to 35 %, or where the carbonate fines originate from the aggregate), where used in cold temperatures combined with wet and aggressive sulfate environments that indicates more susceptibility to the thaumasite form of sulfate attack. The experimental tests and analysis of the present thesis do not cover the problems derived from the possible thaumasite formation.

Bensted (1995) suggests that the fine limestone grains modify the paste microstructure and that the topochemical growth of $Ca(OH)_2$ upon $CaCO_3$ crystals might occur and hence facilitate the access of $SO_4^{2-}$ to form gypsum.

Also, fine limestone increases the hydration rate of Portland cement leading to the precipitation of $Ca(OH)_2$ located around the filler grains and the aggregate surfaces, but it does not have pozzolanic properties. Consequently, fine limestone does not produce C-S-H at later ages that consumes part of the $Ca(OH)_2$, fills the pores, and improves the transition zone as other active constituents (e.g., fly ash, silica fume, natural pozzolan).

The research of Irassar et al. (2003) revealed that moderate $C_3A$ Portland cements containing fine limestone were found more susceptible to sodium sulfate attack and less durable than the corresponding Portland cement mortar, as indicated by their larger expansions, greater surface deterioration, deeper transition zone of attack, greater deposition of gypsum, and higher degree of $Ca(OH)_2$ depletion. Further, the deposition of ettringite and gypsum around the aggregates indicates the vulnerability of the paste–aggregate transition zone in limestone composite cements to chemical attack.

It is expected that the future world production of Portland limestone cement will be continuously increased. The wide use of limestone cement requires a thorough knowledge of the cement and concrete durability properties.

### *2.4.3 Granulated blast furnace slag*

Ground granulated blast furnace slag (GGBFS; hereafter referred as slag) is a byproduct of the steel industry. The American Society of Testing and Materials (ASTM) defines blast furnace slag as “the non-metallic product consisting essentially of calcium silicates and other bases that are developed in a molten condition simultaneously with iron in a blast furnace.” In the production of iron, blast furnaces are loaded with iron ore, fluxing agents, and coke. When the iron ore, which is made up of iron oxides, silica, and alumina, comes together with the fluxing agents, molten slag and iron are produced. The molten slag then goes through a particular process depending on what type of slag it will become. Air-cooled slag has a rough finish and larger surface area when compared to aggregates of that volume which allows it to bind well with Portland cements as well as asphalt mixtures. The granulated slag is produced by quenching the liquid slag with a large amount of water to produce sand-like granulates. The granulates normally contain more than 95 % of glass.

The major oxides in the slag are lime (CaO), silica ($SiO_2$), alumina ($Al_2O_3$), magnesia (MgO) and some other substances ($SO_3$, FeO or $Fe_2O_3$, $TiO_2$, $K_2O$, $Na_2O$, etc.) in minor amounts. Compared to the typical oxide composition of clinker, slag generally contains less lime, more silica, alumina and magnesia than clinker. Slag is glassy in nature and thus reacts with $Ca(OH)_2$ in hydrated cement paste (Bhatty and Taylor 2006). The high glass content of slag and the metastable nature of the glass is an important source of activation energy during its hydration. The presence of small amounts of crystalline minerals does not influence the performance of slag significantly. The presence of large amounts of crystalline minerals reduces the reactivity of slag greatly, which leads to poor performance of the slag.

The slag is known for its latent-hydraulic property, i.e. it is reactive with water, but only at such a slow rate that it is normally mixed with activators, which can accelerate the reaction of slag. The most commonly used activators for slag are sulfates, Portland cement, sodium silicate, and $Ca(OH)_2$. The hydration rate of slag in composite cement is comparable to that of $C_2S$ in Portland cement paste (Taylor 1997). However, it can differ greatly from one slag to another due to the different reactivity of slag. The reactivity of slag depends on some factors like the oxide composition, presence of crystalline minerals, glass structure, pH values of the activation solutions.

The molten slag at a temperature of about 1500 °C is rapidly chilled by quenching in water to form a glassy sandlike granulated material. The granulated material, which is ground to less than 45 microns, has a surface area fineness of about 400 to 600 $m^2/kg$ Blaine. The relative density (specific gravity) for ground granulated blastfurnace slag is in the range of 2850 to 2950 $kg/m^3$. The bulk density varies from 1050 to 1375 $kg/m^3$.

Slag reacts with water and produces C-S-H from its available supply of calcium oxide and silica. A pozzolanic reaction also takes place, which uses the excess $SiO_2$ from the slag source, $Ca(OH)_2$ is formed from the clinker hydration and interacts with the slag hydration to increase the C/S ratio in C-S-H. The amount of $Ca(OH)_2$ entering the slag hydration is related to the blend proportions of the slag in the cement.

The use of slag will decrease the $C_3A$ content of the cementing materials and decrease the permeability and $Ca(OH)_2$ content of the mortar or concrete. Tests have shown that the alumina content of the slag also influences sulfate resistance and that high alumina content can have a detrimental influence at low slag-replacement percentages (ASTM C 989-06). The combinations of slag and Portland cement, in which the slag content was greater than 60 to 65 %, had high sulfate resistance, always better than the Portland cement alone, irrespective of the $Al_2O_3$ content of the slag. The highest sulfate resistance was achieved with higher $C_3A$ contents. The low alumina (11 %) slag tested increased the sulfate resistance independently of the $C_3A$ content of the cement (Locher 1998). To obtain adequate sulfate resistance, higher slag percentages were necessary with higher $C_3A$ cements. Higher levels of cement replacement by slag (over 60 %) appear to be more effective as the consumption of $Ca(OH)_2$ becomes more pronounced. The use of slag in producing sulfate-resisting concrete has been recognized by both ACI and ASTM who reported composite cements with 60 % to 65 % slag as widely used in sulfate- and seawater resisting concretes.

Many methods have been investigated to improve mechanical performances: grinding slag leads to an increase of specific surface area and to the improvement of the hydration rate of slag cement, early-age strength can be improved by thermal curing (at 60 ºC) but at the cost of reduced medium-term strength (Michel et al. 2011). Early and medium-term strength varies according to the gypsum ratio.

In 1971 Gjorv reported the results of a 30-year study on 2500 concrete test blocks stored in sea water near Trondheim Harbor, Norway. Concrete mixtures with 18 different kinds of cements, and water-cement ratios from 0.55 to 0.65 were made. While concretes made with Portland cements were affected; those made with ordinary Portland cements (7…11 % $C_3A$) were severely affected, but the ones made with sulfate resisting Portland cements (0…3 % $C_3A$) were also significantly affected, the concrete made with blast furnace slag Portland cement were found to be unaffected.

Slag is particularly interesting for cement producers, primarily due to its chemical composition very close to that of Portland cement. It has a latent hydraulicity allowing high levels of replacement. Slag as constituent in cement has a great $CO_2$ reduction potential, and is cost-saving regarding clinker production. Mixing of slag with cement is simple due to the close chemistries of both materials. Concrete made from slag cement has also certain engineering advantages, such as low heat release, low permeability and good durability in aggressive environments (Glasser 1991).

# 3. Testing methods and materials

This section describes the strategy of the experimental program, test methods and the materials used in this study.

Majority of the testing was put into practice in the Laboratory of Building Materials, Tallinn University of Technology (TUT).

## 3.1 Wittekindt flat prisms method for the determination of sulfate resistance of cement mortars

To test the sulfate resistance of the cements, the Wittekindt flat prisms method was used (Wittekindt 1960; Locher 1998; Moir 2006).

Cement mortars (cement to sand ratio 1:3 by weight and water to cement ratio of 0.50) were made (by EVS-EN 196-1) using CEN standard sand. With every cement, six so-called Wittekindt flat prisms (10 x 40 x 160) mm were cast.

An important factor due to the effect of size in exposure to chemical solutions where diffusion is predominant is attributed to the surface area to volume ratio of the specimens calculated as 0.38.

After two weeks hardening in the saturated $Ca(OH)_2$ solution, the length of prisms was measured with a special measuring device DIN 52450 “FORM+TEST” (Figure 3.1.1) with an accuracy of 0.001 mm and recorded as initial expansion. Three prisms were exposed into the 4.4 % $Na_2SO_4$ solution (29800 mg sulfate/l) and as reference sample three prisms of the same mortar were stored in the saturated $Ca(OH)_2$ solution at (20 ± 1) °C. The storage solutions were refreshed every four weeks. The saturated $Ca(OH)_2$ solution was used to avoid excessive leaching of $Ca(OH)_2$ from the cement.

Relative expansion due to sulfate attack by the length measurement of prisms was determined after 14, 28, 42, 56 and 91 days of storage in the 4.4 % $Na_2SO_4$ solution and expressed as rate to expansion of prisms stored in the saturated $Ca(OH)_2$ solution.

$$\Delta \varepsilon = (l_{sulf} - l_{ref}) \times 1000 / 160 \tag{3.1}$$

In terms of the used method, cements with relative expansion after 91 days of storage $\Delta \varepsilon \leq 0.50$ mm/m are classified as sulfate resisting cements.

According to the test method, the tests were not conducted with a controlled pH environment. It has been reported that the pH of the solution rises rapidly upon the immersion of mortar bars up to a value similar to that of the cement (11.0…13.0), which decelerates the kinetics of deterioration (Skalny et al. 2002).

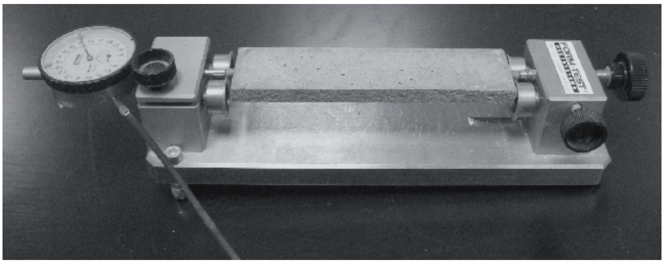


Figure 3.1.1 Test specimen and testing device for the determination of the sulfate resistance of the cement mortar by the Wittekindt method

## 3.2 Compressive strength

### *3.2.1 Compressive strength of cement mortars*

Compressive strength of cement mortars was determined according to EVS-EN 196-1. The method comprises the determination of the compressive, and optionally the flexural strength of prismatic test specimens (40 x 40 x 160) mm in size. These specimens were cast from a batch of plastic mortar containing one part by mass of cement, three parts by mass of CEN standard sand and one half part of water (water/cement ratio 0.50). The specimens were cured in water at (20 ± 1) °C until testing. Compressive strength test was carried out with Tony Technic 1540 cement testing machine on halves of the prism broken on flexural testing.

### *3.2.2 Compressive strength of concrete*

Compressive strength of concrete was determined according to EVS-EN 12390-3. Specimens were cast in the cubical moulds (100 x 100 x 100) mm used for compressive strength testing. Hardening of concrete cubes took place at (95 ± 5) % relative humidity at (20 ± 2) °C. The strength testing of concrete was performed at the ages of 2, 7, 28 and 91 days with constant rate of loading (0.6 ± 2) MPa/s with “Matest” compression machine. Three specimens from each mixture were tested at each testing age.

## 3.3 Freeze-thaw resistance

### *3.3.1 Freeze-thaw resistance of cements*

The specimens (40 x 40 x 160) mm were cast from a batch of plastic mortar by EVS-EN 196-1 containing one part by mass of cement, three parts by mass of CEN standard sand and one half part of water (water/cement ratio 0.50). The specimens were cured in water at (20 ± 1) °C until testing. The freeze-thaw testing started at the age of 28 days. The freezing took place in a freezer in air at -(18 ± 2) °C with duration 2.5...16 hours. Thawing was in water +(18 ± 2) °C for (2.0 ± 0.5) hours.

### *3.3.2 Freeze-thaw resistance of concrete*

After preconditioning, the concrete specimens were freeze-thaw tested in accordance with EVS-814 method that was established following the Swedish standard SS 137244. This method indicates external structural damage and is based on the determination of loss from the surface of concrete (scaling). A water-saturated specimen covered with 3 mm of distilled water or NaCl solution and optionally also with 2.2 % and 4.4 % $Na_2SO_4$ solution was exposed to alternate freezing and thawing.

The principle of the freeze-thaw test is that specimens with one side in contact with a freezing medium are exposed to 24-hour long freeze-thaw cycles, cycling the temperature between about +20 °C and –18 °C. The scaling resistance of the tested concrete is evaluated from the mass of material scaled off from the test surface of the specimen. The scaled-off material resulting from the freeze-thaw exposure, is regularly collected after 7, 14, 28, 42 and 56 freeze-thaw cycles. The scaled material is dried at +105 °C, and the accumulated amount of scaled material is calculated. The results are expressed as scaled material in kg per square meter test surface ($kg/m^2$), as a function of the number of freeze/thaw cycles.

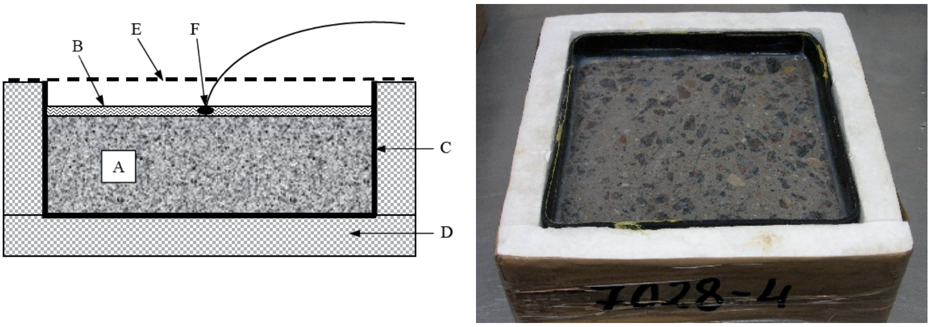


Figure 3.3.1 Concrete test specimen for determination freeze-thaw resistance. A - concrete specimen (150 x 150 x 50) mm, B - freezing medium (3 mm), C - rubber sheet for moisture insulation, D - polystyrene cellular plastic for thermal insulation, E - polyethylene sheet to prevent the freezing medium from evaporating F – temperature measuring device

## 3.4 Water penetration

The depth of penetration of water under pressure was tested by the EVS-EN 12390-8 method. Cubic concrete specimens with dimensions of (150 x 150 x 150) mm at the age of 28 days were placed in apparatus and a water pressure of (500 ± 50) kPa for (72 ± 2) h was applied. The specimens were split in half perpendicularly to the face on which the water pressure was applied and the depth of penetration of the waterfront was measured.

## 3.5 Water absorption

### *3.5.1 Water absorption of concrete test series 1*

Concrete specimens were stored after hardening for 28 days in water (20 ± 2) °C at 23 °C and relative humidity 50 % up to gaining constant mass. The sides of concrete cubes were covered with wax and specimens were laid with open side into the water. Mass changes were recorded for 8 weeks and the water absorption by mass percent was calculated.

### *3.5.2 Water and solution absorption of concrete test series 2*

In addition to the water, the absorption was determined also with 3 % NaCl, 4.4 % $Na_2SO_4$ and 3.6 % $MgSO_4$ solutions. Specimens were dried at a temperature of (70 ± 5) ºC. The dimensions of the faces (100 x 100 x 50) mm to be immersed were measured. The specimens were placed with their faces supported on a supporting device, as shown in Figure 3.5.1 and were immersed in water or salt solution to a depth of (5 ± 1) mm for the duration of the test at (20 ± 2) ºC and relative humidity (65 ± 5) %. After the immersion time, the surface water was wiped off and specimens were weighed.

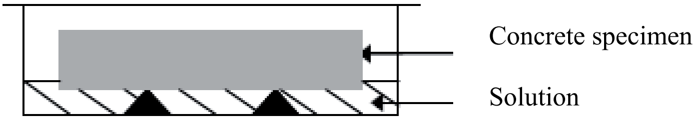


Figure 3.5.1 Experimental set-up for water and solution absorption

The uptake of water or solution by capillary absorption was measured through the weight gain of the concrete surface in contact with water or solution at the set time intervals of 10, 20, 30 min, 1 h…49 days.

## 3.6 Capillary porosity

The capillary porosity is defined here as the volume available also for salt precipitation. The porosity was measured on 28 days in water cured and 91 days in the 4.4 % $Na_2SO_4$ cured mortar samples, the porosity was derived from the difference in mass of the water saturated sample to the dried sample. Thereby, the values for the total porosity were obtained from saturated samples the mass change up to 105 °C.

## 3.7 Dynamic modulus of elasticity

### *3.7.1 Dynamic modulus of elasticity (Ed) of cement mortars*

Resonance frequency measurements were carried out by measuring the fundamental transverse frequency of standard prisms (40 × 40 × 160) mm made according to EVS-EN 196-1, stored in water and sulfate solution to determine the dynamic modulus of elasticity. This device (Figure 3.7.1) gives the frequency of vibration created by a slight shock on the sample. The elastic modulus is calculated from this frequency.

### *3.7.2 Dynamic modulus of elasticity (Ed) of concrete*

Dynamic modulus of elasticity of concrete was determined by measuring the fundamental transverse frequency of the concrete specimen (70 x 70x 210) mm at each test interval. A reduction in the fundamental transverse frequency can be used as an index to the extent of internal micro-cracking of the sample.

Figure 3.7.1 The device for measuring dynamic modulus of elasticity of mortar or concrete

## 3.8 X - ray diffraction analysis (XRD)

The XRD analysis was performed in the Department of Geography, Institute of Ecology and Earth Sciences, the University of Tartu (UT), to explain the sulfate resistance performance behaviors of cement pastes. XRD diffractograms were developed to identify the products formed. The preparations were measured on a Dron-3M diffractometer using Ni-filtered CuKa radiation in 2..45° 2θ region, with a scan step of 0.03° 2θ and a count time of 5 s per step.

In the case of mortars, the large excess of inert material (sand) prevents an efficient application of XRD to detect hydrated compounds: spectra becomes completely dominated by the quartz and to a lesser extent by the feldspar peaks. Therefore, in order to obtain representative samples, for XRD analysis the paste specimens were made and studied. Samples were taken from the surface at 50 mm from top and bottom of the specimen.

### 3.9 Scanning electron microscopy (SEM)

SEM analysis was performed in the Centre for Materials Research, Tallinn University of Technology (TUT). The studies were complemented by scanning electron microscope JEOL JSM840A and ZEISS EVO MA15. The mortar samples were examined by scanning electron microscopy SEM using backscattered electron images. Sample preparation included drying, impregnation with epoxy resin, cutting, polishing, and coating.

### 3.10 Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry was performed in the Laboratory of Inorganic Materials, Tallinn University of Technology (TUT).

The cured cement pastes were oven dried at 40 ºC; the temperature was selected so that no microstructure changes and cracking would occur in order to be examined by means of MIP. Mercury porosimetry data are obtained by recording the volume that penetrates the porous specimen as a function of pressure. The distribution curves are presented in order to estimate and evaluate the pore structure of the hardened cements.

### 3.11 Materials

Laboratory cements based on industrial clinkers were produced to cover the possible cement contents for the commercial products produced and used in Estonia.

All raw materials used for producing Portland cements - Portland cement clinkers, burnt shales, slags, fine limestone and gypsum - were chemically analyzed and their physical and chemical properties were investigated. Chemical analysis was conducted according to EVS-EN 196-2. The chemical compositions of raw materials are given in Table 3.11.1.

Table 3.11.1 Chemical compositions of raw materials – mass percent

| Material | Content, % | | | | | | | | LI |
|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | MgO | $SO_3$ | $K_2O$ | $Na_2O$ | 900° |
| Gypsum G | 7.40 | 0.99 | 4.11 | 44.17 | 3.46 | 34.2 | 0.00 | 0.00 | 6.42 |
| Burnt shale $T_{T1}$ | 30.25 | 3.96 | 8.87 | 36.64 | 3.79 | 9.08 | 4.46 | 0.14 | 3.73 |
| Burnt shale $T_{T2}$ | 33.00 | 4.20 | 9.00 | 34.50 | 3.50 | 8.63 | 5.20 | 0.20 | 2.41 |
| Burnt shale $T_K$ | 36.22 | 4.38 | 9.50 | 29.56 | 4.84 | 5.69 | 4.35 | 0.18 | 4.95 |
| Slag $S_1$ | 32.78 | 3.31 | 17.95 | 36.28 | 5.98 | 1.37 | 0.29 | 0.38 | 0.85 |
| Slag $S_2$ | 36.36 | 2.64 | 15.70 | 37.48 | 4.12 | 0.81 | 0.58 | 0.81 | 0.80 |
| Clinker $C_1$ | 20.22 | 3.32 | 5.35 | 64.38 | 3.46 | 1.39 | 1.44 | 0.12 | 0.40 |
| Limestone L | 8.88 | 1.32 | 2.28 | 44.91 | 2.90 | 0.40 | 1.02 | 0.04 | 38.10 |

The graded standard sand in making the mortars was the EN 196-1 CEN standard sand.

Although the composite cements with several main constituents are widely used, the higher number of constituents has rendered the concrete system more complicated and there is currently a high interest in understanding the interactions between clinker phases and mineral constituents.

To determine the influence of several main constituents for the strength and durability properties the cements were made in laboratory from a raw materials by grinding in a laboratory ball mill so that the specific surface of cements was 350…380 $m^2/kg$ and $SO_3$ content ~3.5 %.

It is well-known that the compressive strength of Portland cement increases with Blaine specific surface area and that cements with a narrow-size distribution have higher strength than those with a wide one. Variation in cement fineness affects hydration rate and cement reactivity. Odler (1991) showed an increase in expansion with fineness when mortar was exposed to the sulfate environment. Based on these considerations, it was decided to eliminate fineness as a variable.

As a reference, Portland cement was prepared. By combining main constituents in cement, several Portland limestone cements, Portland burnt shale cements, Portland slag cements, slag cements, and multicomponent composite cements were made following the allowed compositions and requirements of EVS-EN 197-1. The main structure of testing series of cements is given in Table 3.11.2.

The list presents the structure of main cement compositions that are tested and analyzed throughout the thesis.

Also, the research included numerous additional tests where additional clinkers were used that are not listed in Table 3.11.1. Some tests were reduplicated by variation of the main constituents that is not reflected in Table 3.11.2. All relevant parameters and results of these tests are covered in the sections to follow.

In formulating the test programme, it was decided to use different levels of second constituents, to optimize the use of the material and to work within the framework of cement types covered in EVS-EN 197-1.

Table 3.11.2 Compositions of the main tested Portland cements

| Cement | Composition of cement, % | | | | | |
|---|---|---|---|---|---|---|
| | Clinker | Gypsum | Limestone | Burnt shale | | Slag |
| | | | | Low temp. | High temp. | |
| | $C_l$ | G | L | $T_K$ | $T_T$ | S |
| CEM I | 93.5 | 6.5 | | | | |
| CEM I/A-L (5 % L) | 88.4 | 6.6 | 5.0 | | | |
| CEM II/A-L (10 % L) | 83.2 | 6.8 | 10.0 | | | |
| CEM II/A-L (15 % L) | 78.1 | 6.9 | 15.0 | | | |
| CEM II/A-$T_K$ (15 % $T_K$) | 77.9 | 4.1 | | 18.0 | | |
| CEM II/A-$T_K$ (20 % $T_K$) | 76.2 | 3.8 | | 20.0 | | |
| CEM II/B- $T_K$ (25 % $T_K$) | 71.8 | 3.2 | | 25.0 | | |
| CEM II/A-$T_T$ (15 % $T_T$) | 82.1 | 2.9 | | | 15.0 | |
| CEM II/A-$T_T$ (20 % $T_T$) | 78.2 | 1.8 | | | 20.0 | |
| CEM II/B-$T_T$ (25 % $T_T$) | 74.4 | 0.6 | | | 25.0 | |
| CEM II/B-$T_T$ (30 % $T_T$) | 70.0 | 0.0 | | | 30.0 | |
| CEM II/A-S (10 % S) | 83.5 | 6.5 | | | | 10.0 |
| CEM II/A-S (20 % S) | 73.5 | 6.5 | | | | 20.0 |
| CEM II/B-S (30 % S) | 63.5 | 6.5 | | | | 30.0 |
| CEM III/A (50 % S) | 45.0 | 5.0 | | | | 50.0 |
| CEM III/A (60 % S) | 35.0 | 5.0 | | | | 60.0 |
| CEM III/B (70 % S) | 25.0 | 5.0 | | | | 70.0 |
| CEM II/B-M(20%$T_T$+15%S) | 63.2 | 1.8 | | | 20.0 | 15.0 |
| CEM II/B-M(15%$T_T$+20%S) | 62.1 | 2.9 | | | 15.0 | 20.0 |
| CEM II/B-M(10%$T_K$+15%$T_T$) | 73.4 | 1.6 | | 10.0 | 15.0 | |
| CEM II/B-M(15%$T_K$+10%$T_T$) | 72.9 | 2.1 | | 15.0 | 10.0 | |
| CEM II/B-M(20%$T_K$+10%$T_T$) | 68.5 | 1.5 | | 20.0 | 10.0 | |
| CEM II/B-M(15%$T_T$+10%L) | 71.8 | 3.2 | 10.0 | | 15.0 | |

# 4. Physical and mechanical properties of cement depending on the type of second constituent

## 4.1 Strength properties

The soundness by the Le Chatelier expansion and setting times were determined by EVS-EN 196-3.

The compressive strength was determined according to EVS-EN 196-1. All these tests were carried out with the water-cement ratio 0.50.

The physical, mechanical (Table 4.1.1) and chemical properties (Table 3.11.1) of cements were used as inputs to predict the durability properties and undesirable expansion of cements subjected to sulfate attack. The compositions of cements were chosen based on the permitted constituents (section 2.4) and percentages by the standard EVS-EN 197-1 and on availability and practical application in Estonia.

Table 4.1.1 Physical and mechanical values of the tested Portland cements

| Cement | Paste water demand, % | Soundness, mm | Setting time, min | | Compressive strength, MPa | | |
|---|---|---|---|---|---|---|---|
| | | | Initial | Final | 2 days | 7 days | 28 days |
| CEM I | 27.6 | 2.0 | 170 | 230 | 31.1 | 42.1 | 52.0 |
| CEM I/A-L (5 % L) | 26.0 | 2.5 | 140 | 215 | 31.9 | 41.8 | 51.6 |
| CEM II/A-L (10 % L) | 25.2 | 3.5 | 130 | 200 | 29.0 | 37.4 | 50.1 |
| CEM II/A-L (15 % L) | 25.0 | 4.0 | 150 | 220 | 26.2 | 34.4 | 45.6 |
| CEM II/A-$T_K$ (15 % $T_K$) | 35.5 | 1.5 | 150 | 210 | 33.8 | 42.3 | 52.8 |
| CEM II/A-$T_K$ (20 % $T_K$) | 36.0 | 1.0 | 150 | 205 | 31.9 | 41.8 | 52.5 |
| CEM II/B- $T_K$ (25 % $T_K$) | 36.8 | 1.0 | 155 | 220 | 29.8 | 41.1 | 51.5 |
| CEM II/A-$T_T$ (15 % $T_T$) | 23.8 | 3.5 | 165 | 220 | 32.2 | 46.9 | 54.9 |
| CEM II/A-$T_T$ (20 % $T_T$) | 23.6 | 4.5 | 165 | 230 | 31.6 | 46.7 | 55.2 |
| CEM II/B-$T_T$ (25 % $T_T$) | 22.8 | 4.0 | 155 | 225 | 30.2 | 47.3 | 56.3 |
| CEM II/B-$T_T$ (30 % $T_T$) | 22.3 | 5.0 | 160 | 210 | 31.3 | 47.2 | 56.6 |
| CEM II/A-S (10 % S) | 26.8 | 1.0 | 195 | 255 | 27.2 | 37.7 | 49.7 |
| CEM II/A-S (20 % S) | 26.7 | 1.0 | 220 | 290 | 22.2 | 31.0 | 45.4 |
| CEM II/B-S (30 % S) | 26.9 | 0.5 | 225 | 295 | 17.8 | 26.0 | 43.0 |
| CEM III/A (50 % S) | 26.6 | 0.5 | 260 | 355 | 9.9 | 17.9 | 36.4 |
| CEM III/A (60 % S) | 27.2 | 0.5 | 275 | 360 | 5.3 | 13.3 | 28.6 |
| CEM III/B (70 % S) | 28.0 | 0.5 | 290 | 360 | 3.4 | 11.4 | 25.0 |
| CEM II/B-M (20%$T_T$+15%S) | 26.7 | 1.5 | 195 | 250 | 25.0 | 42.6 | 52.8 |
| CEM II/B-M (15%$T_T$+20%S) | 26.9 | 2.0 | 210 | 260 | 23.4 | 39.5 | 50.6 |
| CEM II/B-M (10%$T_K$+15%$T_T$) | 27.8 | 1.0 | 150 | 210 | 32.5 | 41.6 | 56.1 |
| CEM II/B-M (15%$T_K$+10%$T_T$) | 28.2 | 1.5 | 125 | 205 | 31.2 | 40.2 | 53.9 |
| CEM II/B-M (20%$T_K$+10%$T_T$) | 32.6 | 1.0 | 150 | 225 | 30.6 | 39.4 | 53.0 |
| CEM II/B-M (15%$T_T$+10%L) | 25.5 | 2.5 | 160 | 210 | 23.7 | 41.2 | 50.6 |

The soundness of the cements (expansion according to the Le Chatelier process) was satisfactory. The workability of paste, density of hardened mortar and flexural strength values are presented in the Appendix (Table A2).

### *4.1.1 Influence of limestone constituent*

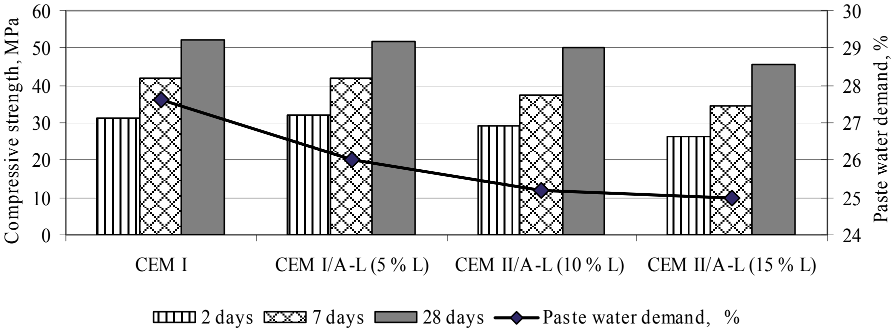


Figure 4.1.1 Compressive strength and paste water demand of Portland limestone cements compared to CEM I

The addition of limestone lowered the standard consistence compared to CEM I (Table 4.1.1 and Figure 4.1.1). In CEM I/A-L(5%L), there was a reduction of water demand from 27.6 % to 26.0 %. The increase of the limestone content to 15 % caused a decrease of the water demand to 25.0 %. This was due to different particle size distribution of limestone cement, as pointed out by Yilmaz and Olgun (2008). Limestone also accelerated setting times compared to CEM I.

The results clearly showed the decreased values of compressive strength with the increased replacement levels of fine limestone. In particular, a significant decrease was observed in the early strength. The reason may lie in the reduction of hydraulically active clinker fraction of cement upon the limestone replacement. This trend is ambiguous. The loss in strength can also be offset of the use of the same water cement ratio 0.50, but the paste water demand decreased with the increased replacement levels of fine limestone. Also, the cements were made with the same fineness. For a given clinker and a given limestone, the more limestone added the higher the clinker fineness should be to produce a cement of the same strength (Sprung and Siebel 1991). Regarding the compressive strength, both enhanced strength and reduced strength have been reported in literature upon limestone addition. Some authors refer to several problems that occur with limestone addition, mostly on lower temperatures (Schmidt et al. 2009; Weerdt et al. 2011).

The results obtained from the strength development of the investigated mortar specimens showed that limestone addition of 5 % slightly increased the compressive strength after two days of curing compared to the CEM I mortar. However, a slightly negative influence of 5 % limestone addition was observed after 28 days of curing. High amounts of limestone addition, for instance 15 %, showed a significant negative effect on the compressive strength after 2, 7 and 28 days of curing. With an increasing content of limestone also flexural strength decreased after 2 and 28 days (Table A2). The density of the hardened mortar was the same for CEM I and for Portland limestone cements.

The compressive strength did not correlate with the determined porosities (Table 4.3.1). Limestone addition of 10 % led to a decrease in porosity, resulting in a decrease of compressive strength compared to the CEM I cement without limestone addition, as limestone is an inert constituent of cement.

### *4.1.2 Influence of burnt shale constituent*

#### *4.1.2.1 High temperature burnt shale $T_T$*

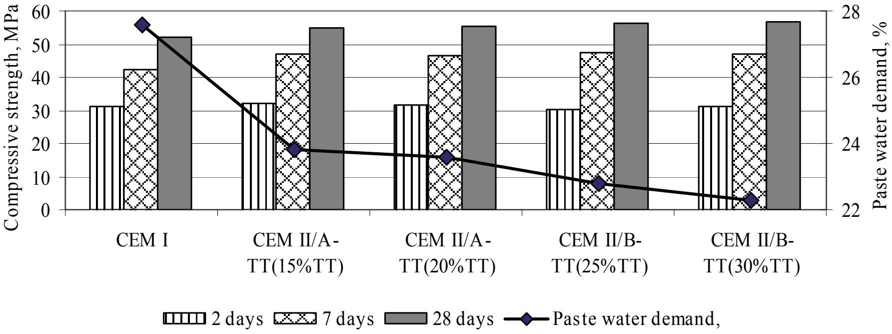


Figure 4.1.2 Compressive strength and paste water demand of Portland burnt shale $T_T$ cements compared to CEM I

Although Portland cements with a high temperature burnt shale $T_T$ content had higher expansion caused by high content of $CaO_{free}$, the values of soundness complied with the EVS-EN 197-1 requirements.

Particle shape of burnt shale $T_T$ plays an important role. Due to its spherical shape, it has a positive impact on the rheological properties of cement applications. The reduction in water requirement was due to the spherical shape and the smooth surface of burnt shale $T_T$, which helped the flow and workability of the mix. The water requirement of the mortar made from CEM II/B-$T_T$ (30 % $T_T$) was the least. The paste water demand was reduced to 22.3 %, which was quite substantial compared to the value of 27.6 % for the CEM I mortar.

The initial setting time accelerated with the increased burnt shale $T_T$ content in the cement compared to CEM I due to $CaO_{free}$. More $CaO_{free}$ accelerated the initial setting time.

The strength of Portland burnt shale $T_T$ cements was significantly improved as compared to that of the CEM I mortar (Table 4.1.1 and Figure 4.1.2). In fact, the strength of CEM II/B-$T_T$ (30 % $T_T$) mortar at the age of 28 days was 56.6 MPa, which was higher than 52.0 MPa of the CEM I mortar at this age. Flexural strength was of equal strength with all compositions of Portland burnt shale cements and CEM I.

Although the compressive strength of Portland burnt shale $T_T$ cements was higher at all ages than the strength of Portland cement, the results were not directly comparable. Mortar prisms were made with an equal water-cement ratio of 0.50. Because burnt shale $T_T$ as the main constituent of Portland cement reduced the water requirement of the cement paste, the water requirement for the same standard consistency was reduced. Too high amount of water by this test method obviously decreased the potential compressive strength because of an accompanying excess of water. The density of the hardened cement mortar increased with the increasing burnt shale $T_T$ content – from 2247 kg/m$^3$ (CEM I) to 2290 kg/m$^3$ (CEM II/B-$T_T$ (30 % $T_T$)). The porosity of Portland burnt shale $T_T$ cement decreased (Table 4.3.1).

### *4.1.2.2 Low temperature burnt shale $T_K$*

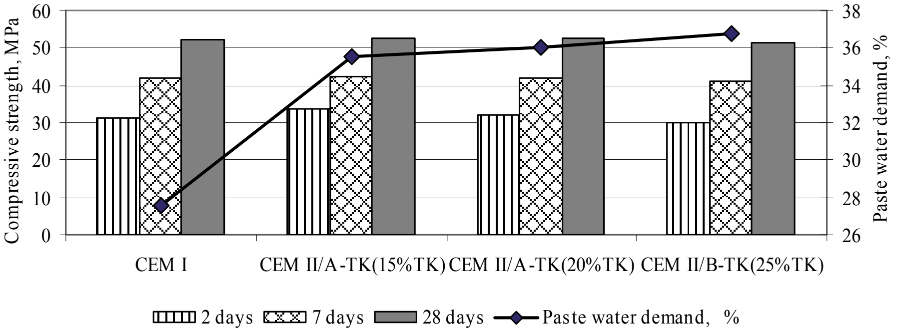


Figure 4.1.3 Compressive strength and paste water demand of Portland burnt shale $T_K$ cements compared to CEM I

Soundness tests results showed no direct impact of low temperature burnt shale $T_K$ in contrast to Portland cement. Expansion showed a slight decreasing effect with an increase of the burnt shale $T_K$ content. Thus, the lower content of $CaO_{free}$ and large specific surface of the low temperature burnt shale $T_K$ compared to burnt shale $T_T$ had a decreasing impact on the expansion value. The Le Chatelier expansion of cements with burnt shale $T_K$ was noticeably lower than that of cements with burnt shale $T_T$.

The standard consistence of cements with burnt shale $T_K$ was substantially higher (Table 4.1.1 and Figure 4.1.3) than the standard consistence of cements with any other constituent. Standard consistence of cement with 20 % $T_T$ (23.6 %) was significantly lower than the standard consistence with 20 % $T_K$ (36.0 %). The rate of the increase of paste water demand in cement depending on burnt shales $T_T$ and $T_K$ content is represented in Figure 4.1.4. The higher water requirement of the burnt shale $T_K$ was due to the irregular shape of larger particles with rougher surface.

The hydration reactions of Portland cements with burnt shale $T_K$ accelerated compared to CEM I, as seen from the initial setting time.

The strength of the Portland burnt shale $T_K$ cement mortar was quite good. In fact, the strength was similar to that of the CEM I mortar despite the fact that the water demand of the CEM II/B-$T_K$ (25%$T_K$) cement was 33 % higher than that of the CEM I. An increase of the burnt shale $T_K$ content caused a decrease of the strength of cements at all ages. The strength values of Portland burnt shale $T_K$ cement were equivalent to Portland cement and lower than those of Portland burnt shale $T_T$ cement. Also, the density of the hardened mortar was of the same value as CEM I.

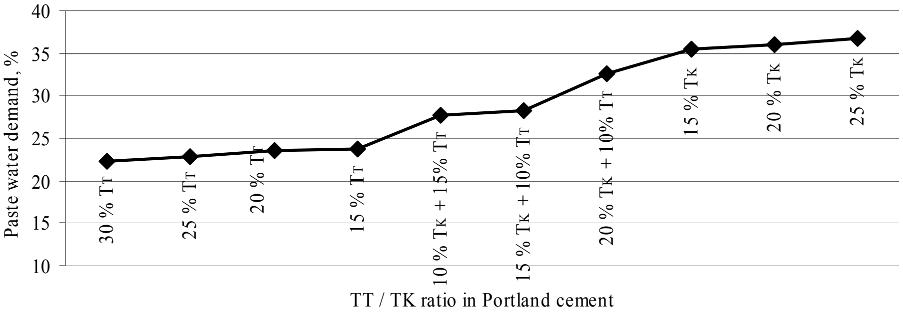


Figure 4.1.4 Increase of paste water demand in cement depending on $T_T$ and $T_K$ proportion

Regarding multicomponent composite cements ($T_T$ + $T_K$), variations in the proportions of burnt shales $T_T$ and $T_K$ in cement did not affect substantially initial and final setting times according to this test series. Paste water demand was observed to depend on $T_T$ and $T_K$ proportions (Figure 4.1.4). Compressive strength of CEM II/B-M cement appeared to depend directly on the proportions of burnt shales $T_T$ and $T_K$ in cement. With an increasing content of burnt shale $T_T$ in cement, the compressive strength increased and with an increasing content of burnt shale $T_K$ the compressive strength of cement decreased.

### 4.1.3 *Influence of slag constituent*

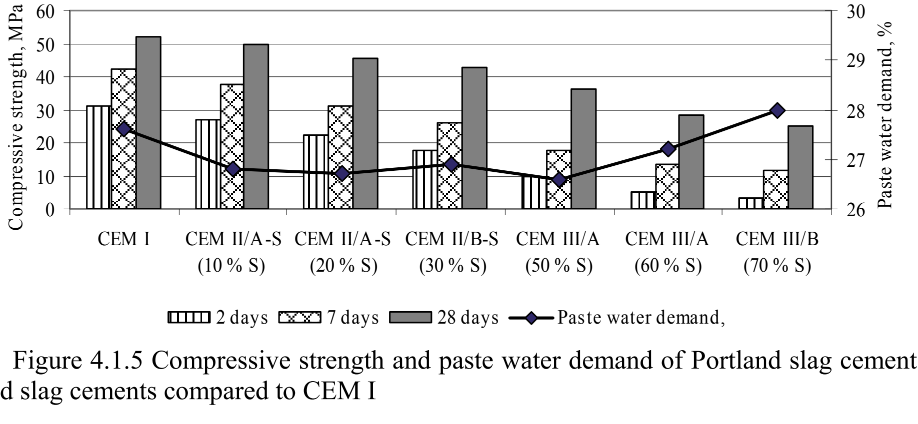


Figure 4.1.5 Compressive strength and paste water demand of Portland slag cements and slag cements compared to CEM I

The addition of slag retarded the setting time of mortar. However, when slag was incorporated with burnt shale $T_T$, the hydration rate of multicomponent composite cement with burnt shale $T_T$ and slag increased at the early age. As the proportions of slag increased in the composite cement, the setting or stiffening time extended. A 30 to 70 % increase in the slag content in cement increased the initial setting time of mortar by approximately 65 minutes.

Test results (Table 4.1.1 and Figure 4.1.5) showed a slight decrease of the early strength for Portland cements made with slag 10...30 % as compared to the same for Portland cement and Portland limestone cement mortar. The low early strength caused also the decline of frost resistance of slag cement mortars and the need for sufficient curing before sulfate storage. The compressive strength and flexural strength fell as the quantity of slag was increased.

With slag cements with higher slag replacement level (50…70 %) the decline of early strength values was particularly large. 2-day compressive strength of CEM III/B (70 % S) was only 3.4 MPa. With time the difference with CEM I diminished, but 28-day compressive strength of CEM III/B (70 % S) was 48 % (25.0 MPa) of CEM I (52.0 MPa).

The density of hardened Portland slag cement mortar (10…30 % S) was lower (2223…2239 $kg/m^3$) than that of any other cement mortar. The densities of slag cement mortars (50…70 % S) were comparable with CEM I and Portland burnt shale $T_K$ cements.

In multicomponent composite cements ($T_T$ + S) the strength results were in correlation with cement composition. The selection of the type of Portland cement and the amount of the other main constituents was accomplished with the purpose to research the effect of the structure of the formed cement stone on corrosion resistance and durability. The test results revealed that the addition of burnt shale $T_T$ increased the compressive strength of the multicomponent composite cement.

## 4.2 Frost resistance of cement mortars

The investigations reported here were aimed at comparing the understanding of sulfate resistance of mortars at normal temperatures and potential behavior of the same cement mortars at low temperatures. According to the dissimilarities in the characteristics and hardening kinetics that became evident in previous section 4.1 in testing cements with various compositions, the frost resistance test was carried out. The durability of water-saturated hardened cement mortar in the situation of alternate freezing and thawing characterizes the formed structure of cement stone. On the other hand, sulfate resistance characterizes the reaction ability of cement and an aggressive environment.

Cement mortar prisms with dimensions (40 x 40 x 160) mm were made according to EVS-EN 196-1. The prisms were hardened in water (20 ± 1) °C. Frost resistance tests were started after 28 days of hardening. The test prisms completely immersed in water, were stressed by repeated freeze-thaw cycles. Freezing took place in a refigerator at (-18 ± 2) °C 2.5...16 hours. Thawing in water at (+18 ± 2) °C with duration (2.0 ± 0.5) hours. The freeze-thaw resistance was evaluated by the determination of the percentage mass loss of the test prisms after every 10 cycles. The cement mortars were tested up to 200 cycles. The evaluation parameter was set - the percentage mass loss not exceeding 10 %. The test results are presented on Figure 4.2.1.

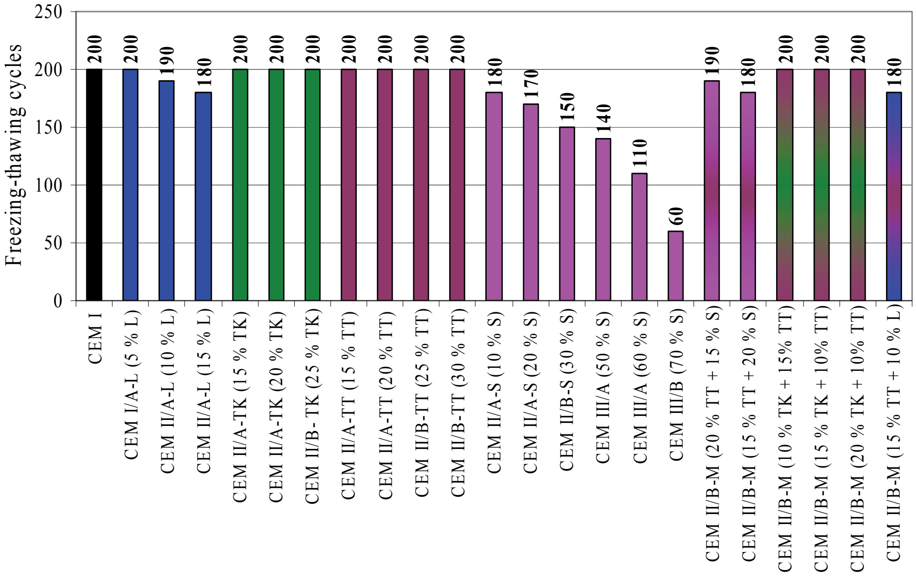


Figure 4.2.1 Frost resistance of cement mortar specimens

CEM I cement complied with the requirement of 200 cycles. One reason to obtain a good result was high $C_3S$ content (Table 5.1.3) of used $C_1$ clinker – 63.7 %. For example, CEM I made with clinker $C_2$ ($C_3S$ – 54.1 %) decomposed already after 140 cycles.

Fine limestone reduced the frost resistance. As 5 % fine limestone content withstood 200 cycles, every added 5 % limestone decreased the frost resistance by 10 cycles.

All Portland burnt shale cements that contained burnt shale $T_T$ or burnt shale $T_K$ and composite cements ($T_T$ + $T_K$) fulfilled the set frost resistance criterion – 200 cycles. The results of frost resistance affirmed the improvement of cement stone structure due to burnt shale addition caused by means of the increased compressive strength which was also a presumption for improved sulfate resistance of cements.

The frost resistance of slag cements was reduced in proportion to the increase of slag content in cement. The frost resistance of CEM II/B-S (30 % S) was 25 % lower than that of CEM I and with CEM III/B (70 % S) only 60 cycles were gained. Substantially on high slag contents, the frost resistance was found to depend on the $SO_3$ content in cement (Table 4.2.1) as well as it influenced sulfate resistance and strength parameters (Figure 5.4.2).

Table 4.2.1 Influence of $SO_3$ level in slag cements for frost resistance properties

| $SO_3$ content in cement, % | Number of freeze-thaw cycles | | |
|---|---|---|---|
| | Slag content in cement, % | | |
| | 50 | 60 | 70 |
| 2 | 150 | 130 | 80 |
| 3 | 140 | 110 | 60 |
| 4 | 90 | 80 | 30 |

In multicomponent composite cements ($T_T$ + S) the frost resistance decreased with the decrease of burnt shale $T_T$ and the increase of slag constituent.

Frost resistance with mortar prisms was also determined with commercial cements for comparison on account that cements ground in the cement plant have major uniformity of particle distribution and better homogeneity of cement. Chemical composition of these cements is given in Table 5.6.1 and the results of frost resistance in Table 4.2.2.

Table 4.2.2 Frost resistance of commercial cement mortars

| Cement | Cycles | Cement | Cycles | Cement | Cycles |
|---|---|---|---|---|---|
| CEM I 42.5 HS | 200 | CEM II/B-T 42.5 R - 1 | 200 | CEM II/B-M 42.5R | 200 |
| CEM I 42.5 SR/LA | 130 | CEM II/B-T 42.5 R - 2 | 190 | CEM I 42.5R - 2 | 200 |
| CEM II A 52.5 R | 200 | CEM I 42.5R - 1 | 200 | CEM II/B-T 42.5 | 200 |
| CEM II A 42.5 R | 160 | CEM II/B-T 42.5R | 200 | CEM I 42.5 | 200 |
| CEM I 42.5 SR | 200 | | | | |

Of the tested cements, three were unsatisfactory: CEM I 42.5 SR/LA, CEM II A 42.5 R and CEM II/B-T 42.5 R - 2. From the notation of CEM I 42.5 SR/LA became evident that it was sulfate resisting Portland limestone cement. Lower frost resistance (130 cycles) compared with other cements may be attributed to the limestone constituent. Estonian CEM II/B-T 42.5 R – 2 satisfied 190 cycles while other cements resisted at least 200 cycles.

The influence of the increase of capillary porosity of cement stone on the decreasing effect of frost resistance is generally acknowledged. The results of comparative porosity of cement stone are presented in section 4.3.

## 4.3 Porosity of cement pastes

The measure of water permeable void volume of a concrete is commonly (Chalmers and Trinder 1999) used as an indication of potential concrete durability. Most of the properties of hardened concrete are related to the quantity and the characteristics of the pores in the concrete (ACI 201, 2001). This study showed that strength, sulfate resistance, permeability, and water diffusion were directly influenced or controlled by the amount and size of pores. The traditional classification of pores in cement stone considers two classes: gel pores (0.5…10 nm), which are associated with the formation of hydration products, and capillary pores (10 nm to 10 µm). The inert, puzzolanic or hydraulic properties of the second constituent cause variations in the behavior of products filling capillary pores in alternate immersion-drying conditions. Therefore, by the fulfilment of capillary pores and the decrease of their radius during the formation of cement stone, their similar behavior in alternate immersion-drying conditions is not guaranteed.

The porosity, as used in the continuum transport equation, is the capillary porosity. The capillary porosity is defined here as the volume available for salt precipitation due to the migration of solutions by capillary absorption. The corresponding value for concrete is the paste porosity multiplied by the volumetric paste content. The capillary porosity is calculated from the mass of water lost from a saturated surface-dry specimen at room temperature upon heating to 105 °C.

Table 4.3.1 Porosities of some cement pastes

| Cement | At 50 °C, % | At 100 °C, % | Total porosity, % | At 50 °C, % | At 100 °C, % | Total pore porosity, % | At 50 °C, % | At 100 °C, % | Total pore porosity, % |
|---|---|---|---|---|---|---|---|---|---|
| | 14 days in saturated $Ca(OH)_2$ solution | | | 91 days in saturated $Ca(OH)_2$ solution | | | 91 days in the 4.4 % $Na_2SO_4$ solution | | |
| CEM I | 12.7 | 4.4 | 17.1 | 12.1 | 3.9 | 16.0 | 12.3 | 4.0 | 16.3 |
| CEM II/A-$T_T$ (20 % $T_T$) | 11.3 | 5.1 | 16.5 | 10.6 | 5.3 | 15.9 | 10.8 | 5.3 | 16.1 |
| CEM II/A-$T_K$ (20% $T_K$) | 15.7 | 5.3 | 21.0 | 15.2 | 4.9 | 20.0 | 15.4 | 4.9 | 20.2 |
| CEM III/A (60 % S) | 12.4 | 4.0 | 16.4 | 12.2 | 4.0 | 16.2 | 11.9 | 4.1 | 16.0 |
| CEM II/A-L (10 % L) | 12.3 | 4.4 | 16.8 | 11.8 | 4.1 | 15.9 | 12.0 | 4.2 | 16.2 |

As shown in Table 4.3.1, 20 % $T_K$ replacement for Portland cement led to the highest proportion of total pores, while the CEM II/A-$T_T$ (20 % $T_T$) with $T_T$ exhibited the much lower number of pores. The overall variation in permeable voids was small but as expected pastes containing slag achieved the lowest values. The cements CEM II/A-$T_T$ (20 % $T_T$) and CEM III/A (60 % S) exhibited finer pore structure. The highest total porosity was shown by CEM II/A-$T_K$ (20% $T_K$).

91-day curing provided lower permeable porosity than 14-day curing. It indicated that relatively larger amount of hydration products was produced and these hydration products filled greater spaces in pores, and thus enhanced obstruction to the flow path and reduced the continuity of pores.

The results showed that the main impact of limestone additions on resistance to sulfate degradation was physical, i.e., addition of 10 % in Portland cement reduced slightly the porosity and might increase the resistance to sulfate.

As the fine pore structure of cement stone is very sensitive to drying procedures, the 105 ºC drying method might result in microstructural damage in cement stone. The microcracking due to drying may also add an apparent increase in the permeable porosity. Therefore, the oven-dry mass was found after getting the saturated surface-dry mass and the buoyant mass of the saturated specimens.

The increase in the total porosity values of hardened cement pastes after the storage of 91 days in 4.4 % $Na_2SO_4$ solution was related to the increase of gypsum and other products that increased the total porosity with the high concentration of $Na_2SO_4$ in the samples. In contrast, the total porosity of slag cement specimens was decreasing in the sulfate solution. That was due to the formation of C-S-H due to the reaction of slag with $Ca(OH)_2$.

### 4.4 Dynamic modulus of elasticity

Dynamic modulus of elasticity ($E_d$) of cement mortars was determined with specimens (40 x 40 x 160) mm in two series. The first series was made under the same conditions as the Wittekindt expansion measurement but with specimens with different sizes (Table A8). Mass change (Table A6) and expansion (Table A7) were also monitored. In the second series cement mortar specimens (40 x 40 x 160) mm were stored in the 4.4 % $Na_2SO_4$ solution and in water up to one year (Table A9). $E_d$ was measured.

Dynamic modulus of elasticity (Tables A8, A9) did not appear as a sensitive indicator of damage during the first stage, as the modulus of attacked specimens remained equal or higher than the modulus of control specimens even if expansion and damage were observed. When the mortars were exposed to sulfate, at very early ages, the crystallization of salts, new formatted ettringite and $CaSO_4$ filled the micro-cracks and pores. This led to an increase in $E_d$. Lee et al. (2005) and Sahmaran, Kasap et al. (2007) have also shown the positive effect of sulfate attack on mechanical properties, before they finally decrease. The decrease of the dynamic modulus of elasticity of CEM I became significant after a one-year curing in the 4.4 % $Na_2SO_4$ solution. The $E_d$ and compressive strength of other tested cements tended to increase continuously after one-year storage both in the 4.4 % $Na_2SO_4$ solution and in the saturated $Ca(OH)_2$ solution. Increases in the strength did not provide much information about sulfate resistance; such results only showed that the cement continued to hydrate in sulfate solution over the test period.

In previous long-term experiments (Raado and Hain 2003), comparative sulfate resistance in the 5 % $Na_2SO_4$ solution of mortar prisms (40 x 40 x 160) mm made with CEM I and CEM II/B-$T_T$ was analyzed. The $E_d$ of mortar prisms exposed into the 5 % $Na_2SO_4$ solution for five years showed a decrease in the case of Portland cements CEM I after 12...18 months. Mortars made with CEM II/B-$T_T$ showed no signs of degradation even after a five-year exposure.

There was certain correlation between the results of the strength measurements and the damage due to sulfate corrosion.

### 4.5 Section summary and conclusions

Portland cement CEM I mortar was made as reference mortar. All properties of composite cements with various constituents and compositions were compared to CEM I. CEM I cement exhibited satisfactory frost resistance – it complied with 200 cycles requirement. The dynamic modulus of elasticity of CEM I started to decrease after one year curing in the 4.4 % $Na_2SO_4$ solution and the compressive strength of CEM I in the 4.4 % $Na_2SO_4$ solution decreased although the $E_d$ and compressive strength of other tested composite cements increased continuously both in the 4.4 % $Na_2SO_4$ solution and in the saturated $Ca(OH)_2$ solution.

The addition of inert constituent limestone of 10 % led to a decrease in porosity, but resulted in a decrease of compressive strength of Portland limestone cements compared to the CEM I cement. With increasing content of limestone in cement compressive and flexural strength decreased. Every added 5 % limestone in cement decreased the frost resistance by 10 cycles. The density of hardened mortar was the same for CEM I and for Portland limestone cements.

The strength of Portland high temperature burnt shale $T_T$ cements was significantly improved as compared to CEM I mortar. Burnt shale $T_T$ reduced the water requirement of the cement paste due to its spherical particle shape (Raado 1975). The density of hardened cement mortar increased with the increasing burnt shale $T_T$ content. Portland burnt shale $T_T$ cement mortars had also best frost resistance.

The standard consistence of Portland cement with low temperature burnt shale $T_K$ was substantially higher than that with any other constituent. The Le Chatelier expansion of cements with burnt shale $T_K$ was noticeably lower than that of cements with burnt shale $T_T$. Burnt shale $T_K$ replacement in Portland cement led to the highest total porosity. The compressive and flexural strengths were similar to those of the CEM I mortar. An increase of the burnt shale $T_K$ content caused a decrease of the strength of cements at all ages. The density of hardened Portland burnt shale $T_K$ cement mortar was of the same value as CEM I. Portland burnt shale $T_K$ cement mortars fulfilled the set frost resistance criterion.

The addition of slag retarded the setting time of the cement mortar. The low early strength caused also the decline of frost resistance of slag cement mortars. The frost resistance of slag cements lowered in proportion the increase of slag content in cement. The compressive strength and flexural strength decreased greatly as the quantity of slag was increased. The densities of slag cement mortars with slag 50…70 % were comparable with CEM I and Portland burnt shale $T_K$ cements. Unlike other constituents, the total porosity of slag cement specimens decreased in sulfate solution.

The types of second constituents are different and not all the test methods are equally suitable for distinguishing the differences. It was found that there was certain correlation between mechanical and physical properties and visible damage on the surfaces of mortar specimens and expansion values of mortar prisms exposed to sulfate solutions.

# 5. Sulfate resistance of Portland cements depending on the main constituents

The sulfate resistance of cements in this thesis is defined mainly by linear expansion determined according to the Wittekindt method. As indicated in many published papers, whilst expansion may be an appropriate test procedure for CEM I cements, or cements with a relatively high clinker content, it may be less reliable when applied to composite cements.

Relative expansion due to the sulfate attack of prisms was measured after 14, 28, 42, 56 and 91 days of storage in the 4.4 % $Na_2SO_4$ solution and expressed as rate to expansion of prisms stored in the saturated $Ca(OH)_2$ solution and the values of relative expansion are given in Table 5.1.1. The measured values of expansion in the 4.4 % $Na_2SO_4$ solution and the saturated $Ca(OH)_2$ solution are given in Appendix, Table A1. Every number represents the average of three tested specimens.

In terms of the Wittekindt method, cements with relative expansion after 91 days of storage less than 0.50 mm/m are classified as sulfate resisting cements.

Table 5.1.1 Relative expansions of main cements

| Cement | Relative expansion $\Delta\varepsilon$, mm/m | | | | |
|---|---|---|---|---|---|
| | 14 d | 28 d | 42 d | 56 d | 91 d |
| CEM I | 0.07 | 0.15 | 0.30 | 0.50 | 0.84 |
| CEM I/A-L (5 % L) | 0.08 | 0.14 | 0.30 | 0.52 | 0.88 |
| CEM II/A-L (10 % L) | 0.08 | 0.13 | 0.33 | 0.54 | 0.96 |
| CEM II/A-L (15 % L) | 0.09 | 0.11 | 0.32 | 0.56 | 0.89 |
| CEM II/A-$T_K$ (15 % $T_K$) | 0.13 | 0.23 | 0.34 | 0.41 | 0.63 |
| CEM II/A-$T_K$ (20 % $T_K$) | 0.12 | 0.19 | 0.31 | 0.41 | 0.55 |
| CEM II/B- $T_K$ (25 % $T_K$) | 0.14 | 0.19 | 0.33 | 0.38 | 0.51 |
| CEM II/A-$T_T$ (15 % $T_T$) | 0.07 | 0.17 | 0.29 | 0.39 | 0.55 |
| CEM II/A-$T_T$ (20 % $T_T$) | 0.12 | 0.22 | 0.33 | 0.44 | 0.54 |
| CEM II/B-$T_T$ (25 % $T_T$) | 0.12 | 0.20 | 0.22 | 0.34 | 0.50 |
| CEM II/B-$T_T$ (30 % $T_T$) | 0.10 | 0.20 | 0.25 | 0.33 | 0.48 |
| CEM II/A-S (10 % S) | 0.12 | 0.28 | 0.39 | 0.56 | 0.87 |
| CEM II/A-S (20 % S) | 0.12 | 0.26 | 0.37 | 0.46 | 0.82 |
| CEM II/B-S (30 % S) | 0.11 | 0.25 | 0.34 | 0.39 | 0.66 |
| CEM III/A (50 % S) | 0.14 | 0.14 | 0.26 | 0.26 | 0.33 |
| CEM III/A (60 % S) | 0.16 | 0.15 | 0.17 | 0.19 | 0.28 |
| CEM III/B (70 % S) | 0.06 | 0.10 | 0.11 | 0.14 | 0.16 |
| CEM II/B-M (20 % $T_T$ + 15 % S) | 0.15 | 0.15 | 0.26 | 0.33 | 0.61 |
| CEM II/B-M (15 % $T_T$ + 20 % S) | 0.17 | 0.18 | 0.31 | 0.38 | 0.55 |
| CEM II/B-M (10 % $T_K$ + 15% $T_T$) | 0.13 | 0.16 | 0.21 | 0.33 | 0.50 |
| CEM II/B-M (15 % $T_K$ + 10% $T_T$) | 0.10 | 0.16 | 0.26 | 0.39 | 0.59 |
| CEM II/B-M (20 % $T_K$ + 10% $T_T$) | 0.12 | 0.17 | 0.24 | 0.31 | 0.46 |
| CEM II/B-M (15 % $T_T$ + 10 % L) | 0.23 | 0.30 | 0.51 | 0.62 | 0.94 |

## 5.1 Portland cement CEM I

As the expansion value characterizing the sulfate resistance of Portland cement CEM I made with clinker $C_1$ was ~1.7 times higher (Table 5.1.1) than the planned failure criteria, comparable tests with Portland cements with various clinkers were implemented.

The cement clinkers were produced with different production regimes to modify mineralogical parameters of the clinkers. Figure 5.1.1 presents the relative expansion values according to the Wittekindt test method for the tested Portland cements with $C_3A$ contents 7.2...9.4 %.

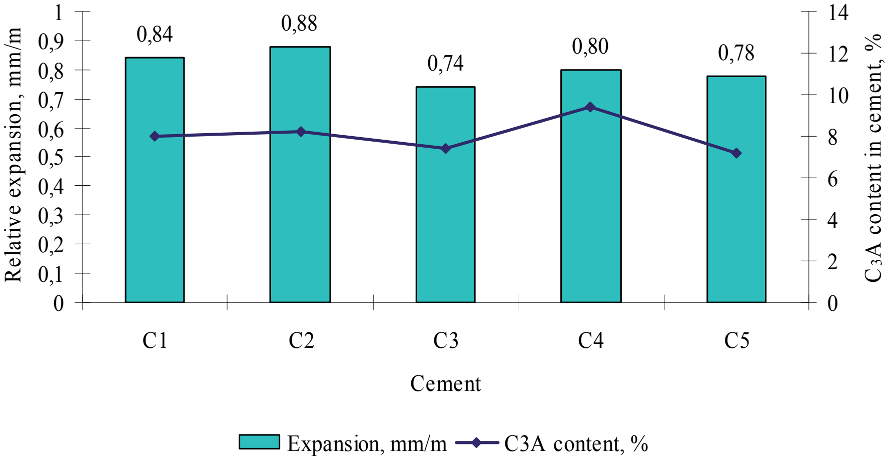


Figure 5.1.1 Relative expansion of Portland cements made with clinkers $C_1$...$C_5$ depending on the $C_3A$ content of cement ($SO_3$ content of all cements is 3.5 %)

Table 5.1.2 Chemical compositions of Portland cement clinkers

| Clinker | Content, % | | | | | | | | LI |
|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | MgO | $SO_3$ | $K_2O$ | $Na_2O$ | 900° |
| $C_1$ | 20.22 | 3.32 | 5.35 | 64.38 | 3.46 | 1.39 | 1.44 | 0.12 | 0.40 |
| $C_2$ | 20.60 | 3.29 | 5.38 | 63.01 | 3.77 | 1.75 | 1.41 | 0.20 | 0.36 |
| $C_3$ | 20.40 | 3.53 | 5.25 | 63.41 | 2.90 | 1.29 | 1.54 | 0.21 | 0.68 |
| $C_4$ | 20.76 | 3.15 | 5.79 | 62.80 | 4.12 | 1.11 | 1.09 | 0.23 | 0.42 |
| $C_5$ | 20.54 | 3.55 | 5.11 | 62.72 | 3.98 | 1.44 | 1.31 | 0.20 | 0.22 |

The potential phase analysis of the Portland cement clinkers is presented in Table 5.1.3. It can be seen that the cement has usual Bogue $C_3A$ content in the clinker of 7.5…10.0 % influencing the sulfate resistance. The ordinary Portland cement, such as the investigated cements, is not resistant to the attack of sulfates because it has a considerable content of $C_3A$ whose hydrates react with sulfate ions, giving expansive compounds.

Table 5.1.3 Calculated phase composition of Portland cement clinkers by formulaes derived by R.H. Bogue (Taylor 1997)

| Clinker | Potential phase composition of Portland cement clinkers, % | | | |
|---|---|---|---|---|
| | $C_3S$ | $C_2S$ | $C_3A$ | $C_4AF$ |
| $C_1$ | 63.8 | 9.9 | 8.6 | 10.1 |
| $C_2$ | 54.1 | 18.2 | 8.7 | 10.0 |
| $C_3$ | 59.1 | 13.9 | 7.9 | 10.7 |
| $C_4$ | 51.3 | 20.8 | 10.0 | 9.6 |
| $C_5$ | 55.7 | 16.9 | 7.5 | 10.8 |

As can be seen from Figure 5.1.1, the test results had no direct relation expected between sulfate resistance determined by the Wittekindt method and $C_3A$ content. This disparity can partly be explained because cement with a higher Bogue $C_3A$ content has a significantly different effect than that with high crystalline $C_3A$ (Tikalsky et al. 2002).

According to the literature, the difference in the $C_3S$ content could be significant also in view of sulfate resistance. An increase in the $C_3S$ content of cement generates a significantly higher amount of $Ca(OH)_2$, as a byproduct of hydration, resulting in a gypsum-oriented sulfate attack characterized by softening of the cement (Al-Dulaijan et al. 2003) and increase in expansion with an increasing $C_3S$ content (Shanahan and Zayed 2007).

The results of Blaine and Arni (Tikalsky 2002) showed that for high $C_3A$ cement, the principal variables in sulfate expansion, other than $C_3A$, were $Fe_2O_3$ and the $CaO/SiO_2$ ratio. A high $Fe_2O_3$ content and/or a high $CaO/SiO_2$ ratio resulted in lower expansion at all durations of the test. Rozière (2009) concluded that the results are influenced by the forces coming from the formation of expansive products, and the resistance (tensile strength) of the material. The diffusivity influences the kinetics.

Although the $SO_3$ content of clinkers was slightly different, no correlation was examined between the $SO_3$ content of the cement and the sulfate attack expansion in this study because all the cements were optimized to ~3.5 % $SO_3$ content.

The highest $C_3A$ content had cement No 4 (9.4 %) made of clinker ($C_4$) with 10 % $C_3A$. Relatively slight expansion may be explained by the smaller amount of CaO and $C_3S$ content. Cements that have higher proportion of CaO and high proportions of $C_3S$ produce more $Ca(OH)_2$ on hydration and leaching of $Ca(OH)_2$ can thus increase the ingress of sulfate ions in the cement. Moreover, reaction with sulfate is likely to produce more gypsum and ettringite, which are responsible for expansion and damage. Slight changes of composition parameters can thus significantly affect the potential expansion or the strength, thus the behavior of mortar in the sulfate containing environment.

CEM I ($C_1$), as the main reference cement in the current research, had $C_3A$ content 8.0 %. The content of $C_3S$ was the highest of the tested CEM I cements. This is one reason for higher expansion values compared to CEM I ($C_3$) and

CEM I ($C_5$) with the comparable $C_3A$ content. This also reflects in strength parameters – both compressive and flexural strength values are higher than those of the other four CEM I cements (Table A5).

Scanning Electron Microscopy (SEM) was used to study the microstructure of the specimens after 14-day curing in the saturated $Ca(OH)_2$ solution (Figure 5.1.2) and after following 91 days of exposure to the sulfate solution. SEM images of Portland cement samples presented in Figures 5.1.3...5.1.5 show the reaction products near or within cracks and air voids due to sulfate attack after 91 days of exposure in the 4.4 % $Na_2SO_4$ solution.

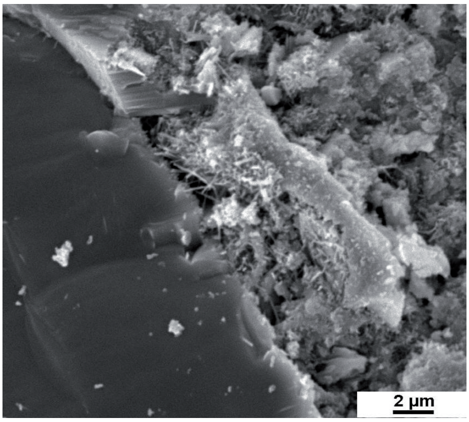


Figure 5.1.2 CEM I mortar cured for 14 days in the saturated $Ca(OH)_2$ solution. Crystals are growing into paste-aggregate interfacial zone.

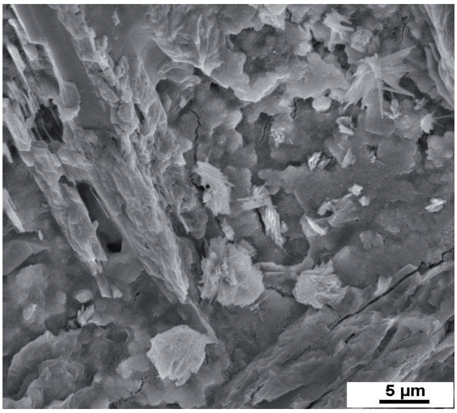


Figure 5.1.3 CEM I mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. Figure shows the bottom of an air void. The hydration products are cotton-shaped CSH gel, plated-shaped $Ca(OH)_2$, gypsum and ettringite. Cracks in the bottom.

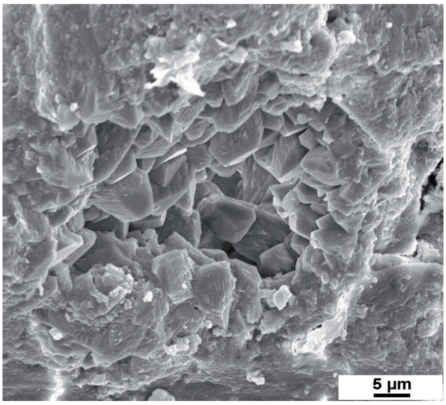


Figure 5.1.4 CEM I mortar after 91 days in the 4.4 % $Na_2SO_4$ solution. Formation of gypsum crystals in an air void in near-surface region.

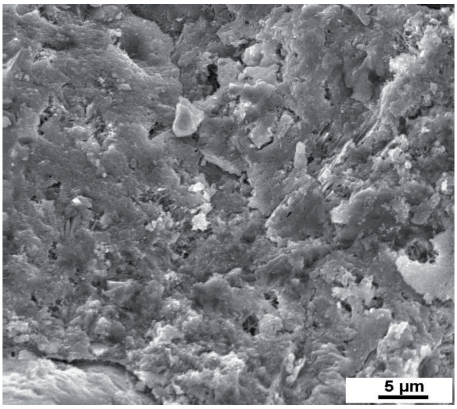


Figure 5.1.5 CEM I mortar 91 days in the 4.4 % $Na_2SO_4$ solution. The cement stone is tight. Pores of cement stone are filled with gypsum and ettringite crystals.

Figure 5.1.4 presents the formation of gypsum crystals within the air void near the outer side of the specimen. Gypsum could actually play an important part in the mechanism of degradation at such high sulfate concentrations.

The precipitation of secondary hydrated minerals can be observed within the empty capillary pores of the cement caused by the reaction of the sulfate ions with $Ca(OH)_2$ and $C_3A$ and thus reduce its porosity. This argument is fully supported by the results of SEM observations.

After 91 days of storage in the 4.4 % $Na_2SO_4$ solution, ettringite crystals were formed near cracks and in the contact zone between the aggregate filling the transition space or the space created by the cracking due to the localized expansion and the cement stone. The presence of gypsum and ettringite explains the results of high expansion measurements.

The results of the SEM observations are in good agreement with Bing and Cohen (2000) who mentioned that sulfate attack on Portland cement is caused by two reactions - the sulfate ions react with $C_3A$ and its hydration products to produce ettringite that results in expansion and subsequent cracking and the sulfate ions react with $Ca(OH)_2$ to produce gypsum. From this study, it can be clearly noted that the pores, which are filled with secondary gypsum minerals, may have damaged the cement stone with their destructive expansive action. However, Metha (1983) emphasizes that the loss of adhesion and strength of the cement, not expansion and cracking, is the primary consequence of sulfate attack.

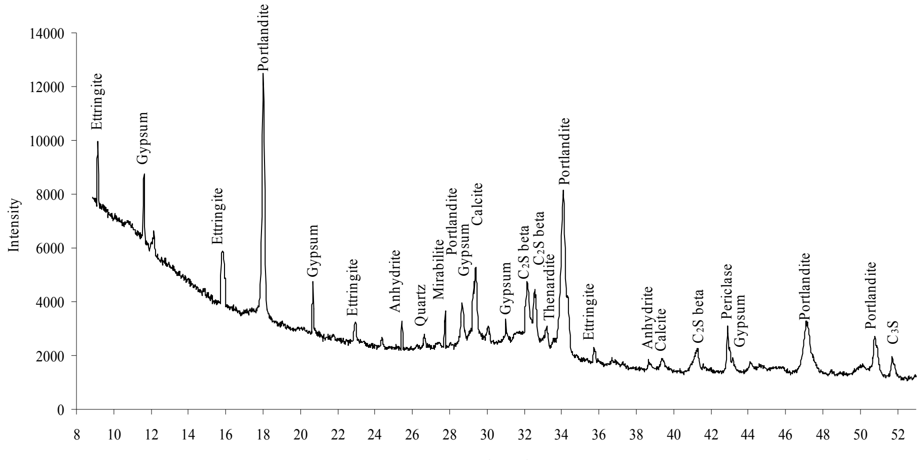


Figure 5.1.6 XRD analysis of CEM I paste after exposure to the 4.4 % $Na_2SO_4$ solution for 91 days

XRD difractograms were made in UT and in the interpretation materials published by Stutzman (1996) were used. The peaks in the diffraction pattern were checked against a database of previously identified phases.

The XRD data of the paste sample showed that after 91-day curing in the 4.4 % $Na_2SO_4$ solution besides some unhydrated clinker, mainly $Ca(OH)_2$, ettringite as well as gypsum and anhydrite were present as the main hydrates.

This result suggests that $SO_4$ ions supplied from the external solution penetrated into the mortar, and by the reaction with $Ca(OH)_2$, monosulfate was transformed to ettringite. The ettringite is confirmed both by XRD and SEM results. Traces of monosulfate were also identified, i.e. some ettringite has already partially reacted with residual aluminate. Also, calcite was detected to be present in the hydrated Portland cement, indicating that only part of the calcite is reacting to form hydrate phases.

Also, formation of a large amount of gypsum crystals, was observed in the XRD analysis (Figure 5.1.6) and SEM images (Figures 5.1.3 and 5.1.4). The formation of gypsum when exposed to the sodium sulfate solution seems to have been associated with considerable expansion and strength loss in the mortar system.

Loss of $Ca(OH)_2$ (from 15.6 % at the age of 14 days cured in $Ca(OH)_2$ solution to 6.4 % at the age of 91 days cured in $Na_2SO_4$ solution) may contribute to a lowered pore solution pH and, as a result, the instability of some products of cement hydration, which ultimately will lead to decreased strength and adhesion. However, the presence of ettringite suggests that the pH remains suitably high for most products of cement hydration.

The pore structure of CEM I paste is graphically demonstrated by the results of Mercury intrusion porosimetry (MIP) test (Figure 5.1.7).

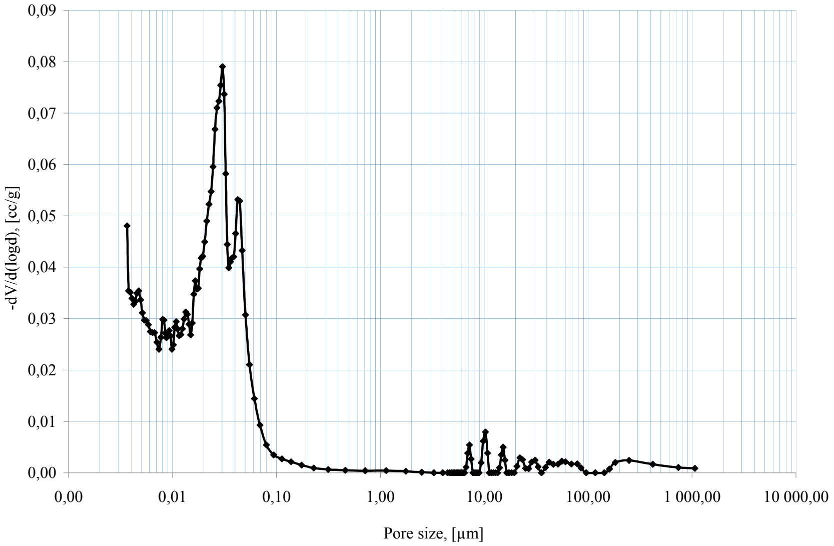


Figure 5.1.7 Pore size distribution of CEM I paste after exposure to the 4.4 % $Na_2SO_4$ solution for 91 days

Portland cement occupies significantly different pore size distributions compared to composite cements. Portland cement paste has a large amount of small capillary pores with sizes ranging from 0.01 to 0.1 μm of which 0.01 to 0.05 μm size pores are easily prone to damage by the sulfate solution. Moreover, Portland cement paste has higher permeability (as proved in Figures 6.4.1 and 6.4.4) than composite cement paste owing to its higher total porosity (Table 4.3.1). Therefore, it can be believed that the pore characteristics of Portland cement mortar influenced the extent of sulfate damage that contributed to the disintegration of specimens by $Na_2SO_4$ attack.

Visually, the damage started at the edges and corner, followed by cracking and spalling of the specimens. Results indicated that deterioration of mortar was manifested after 56 days when small cracks appeared on corners. According to Irassar et al. (2003), that kind of corrosion of edges and corners described by the visual assessment is attributable to the gypsum formation in parallel veins to the sulfate attack front, gypsum was also detected with SEM and XRD. Subsequently, specimens expanded rapidly and they appeared with a large curvature at 91 days. Within one year, specimens were severely damaged presenting surface softening, the mortar was reduced to a soft pulpy mass and could be broken easily with the hand.

With the same test conditions as in the Wittekindt test method, but with the specimens with increased size (40 x 40 x 160) mm, a comparison test was conducted. The results are given in the Appendix Tables A6…A9. Relative expansion of CEM I mortar in the 4.4 % $Na_2SO_4$ mortar was 0.20 mm/m, 3..4 times higher than that of composite cements. Compressive strength and dynamic modulus of elasticity ($E_d$) initially increased, followed by the action of sulfate solution with a steady decrease of both characteristics at the age of one year in the 4.4 % $Na_2SO_4$ (Table A9), while the compressive strength and $E_d$ of mortar specimens stored in water increased continuously at the age of one year.

None of tested Portland cements satisfied the requirements of the Wittekindt test method for the determination of the sulfate resistance of cement. Obviously, Portland cement is not resistant to sulfate attack as all tested Portland cements showed major relative expansion results and their values exceeded substantially the permitted values of the test method. As the clinkers were manufactured in the same plant under different operating conditions to obtain clinkers with several mineralogical compositions in different times, the results are of the same value. The expansion of Portland cements was found to depend partly on the $C_3A$ content of Portland cement clinker. Therefore, the sulfate resistance of the cement could be predicted by the $C_3A$ content of the clinker. The poor resistance of Portland cement to $Na_2SO_4$ attack is due to the presence of large pores and free $Ca(OH)_2$ in the cement paste. The formation of ettringite and gypsum in the 4.4 % $Na_2SO_4$ solution was confirmed both by the XRD and SEM results.

## 5.2 Influence of limestone constituent in Portland cement

Limestone constituent in cement is one of the most contradictious issues in literature. Some authors find that a benefit of the addition of small amounts of fine limestone reduces the expansion observed upon sulfate attack, which is most prominent for cements with high $C_3A$ content (Schmidt et al. 2009; Weerdt et al. 2011). The study of Sezer (2012) revealed that the expansions of mortars with 5 %...35 % limestone were slightly lower than Portland cement mortars and the sulfate resistance increased with the increasing content of limestone in cement. The present research confirmed that despite the decreasing effect of the $C_3A$ content in cement, all the properties of cements and concrete with limestone addition were underachieved. The relative expansion values with Portland limestone cements were higher than those with Portland cements. These results are in accordance with the results of Irassar et al. (2003) of mortars made of cements with high amounts of limestone (up to 20 %) that showed high expansion independent of the type of cement used (high or low $C_3A$ content).

The results indicated a significant increase in the expansion of the mortar specimens with increased replacement levels of the fine limestone. The test specimens under continuous immersion of sulfate solutions showed most detrimental fracture, the mortar bars were curved and with large cracks.

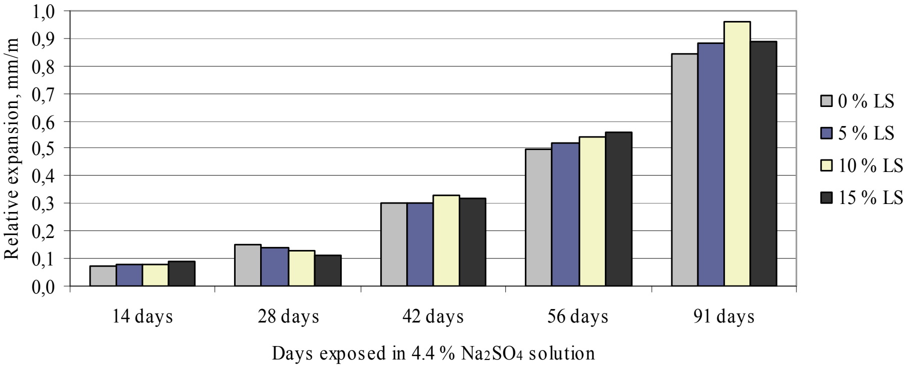


Figure 5.2.1 Relative expansion values of Portland limestone cements with limestone content 5, 10 and 15 % compared to Portland cement CEM I

As can be seen in Figure 5.2.1, the relative expansion of Portland limestone cements is not substantially dependent on the amount of limestone (5... 15 %) in cement. The permitted expansion value of the Wittekindt test method (0.50 mm/m) was exceeded at the age of 56 days.

Although the relative expansion at the age of 91 days of CEM II/A-L cements was higher than that of CEM I, it should be noted that the expansion of CEM II/A-L cements in the saturated $Ca(OH)_2$ solution was smaller (0.050…0.065 mm/m) than that of CEM I (0.125 mm/m), Table A1. Therefore, the relative expansion value of CEM II/A-L cements also becomes enlarged.

The SEM image of the CEM II/A-L (10 % L) cement cured for 14 days in the saturated $Ca(OH)_2$ solution is shown in Figure 5.2.2. The structure is uneven, with many voids of different sizes.

Figure 5.2.4 shows that after storage for 91 days in the 4.4 % $Na_2SO_4$ solution there is a great deal of needle-shaped ettringite and plated-shaped $Ca(OH)_2$ in Portland limestone cement mortar, and large pores can also be observed.

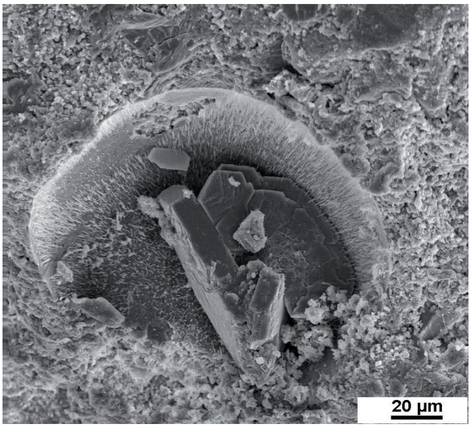


Figure 5.2.2 CEM II/A-L (10% L) mortar cured for 14 days in the saturated $Ca(OH)_2$ solution. Ettringite crystals grow at the surface of the mortar in voids.

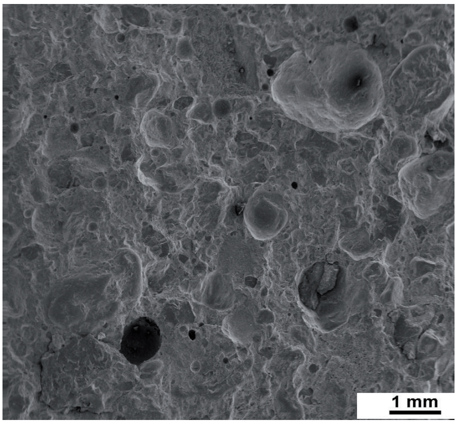


Figure 5.2.3 CEM II/A-L (10% L) mortar cured for 91 days in the saturated $Ca(OH)_2$ solution. Many air voids with different sizes can be seen.

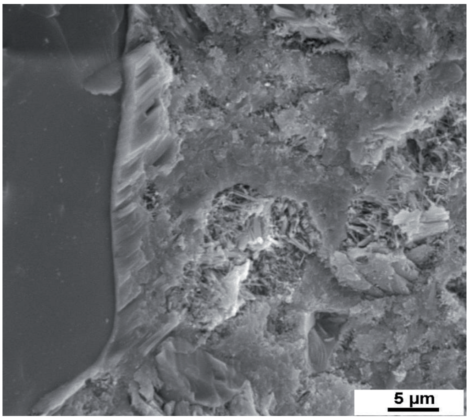


Figure 5.2.4 CEM II/A-L (10% L) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. The main hydration products are C-S-H gel and needle-shaped ettringite in pores and voids.

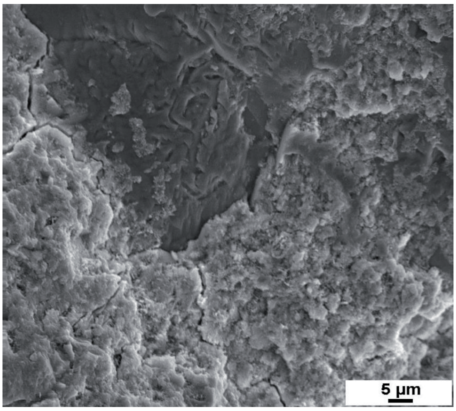


Figure 5.2.5 CEM II/A-L (10% L) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. The structure is fragile with many cracks.

The principal hydration products in Portland limestone cements are essentially similar to those found in Portland cement. Unhydrated clinker, $Ca(OH)_2$ and ettringite were found both in the SEM (Figures 5.2.4 and 5.2.5) and in the XRD (Figure 5.2.6) analysis after 91 days of storage in the 4.4 % $Na_2SO_4$ solution. It was not clear whether these ettringite formations are responsible for high expansions of these cements or just a product of ettringite recrystallization in existing voids.

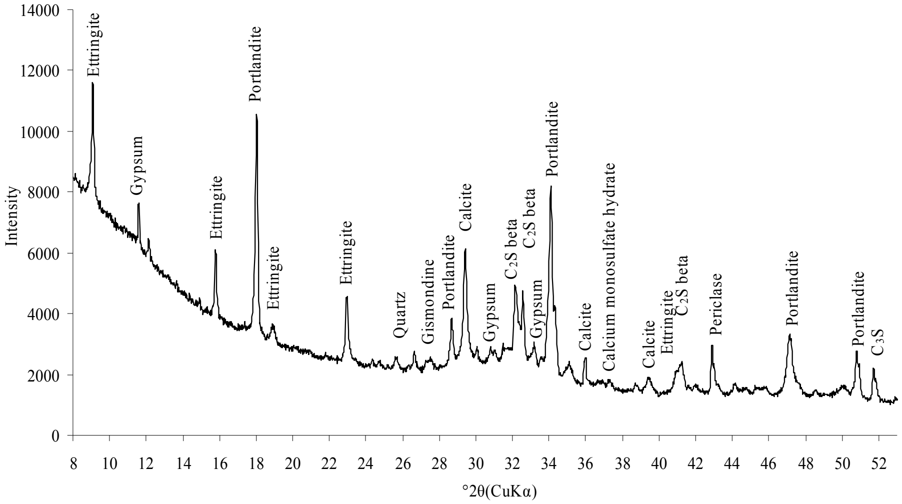


Figure 5.2.6 XRD analysis of Portland limestone cement CEM II/A-L (10% L) paste after exposure to the 4.4 % $Na_2SO_4$ solution for 91 days

In CEM II/A-L (10% L) the formation of monocarbonate led to the formation of slightly more ettringite, which was detected by XRD compared to CEM I, indicating sulfate uptake. This finding agrees with the investigations of Bonavetti et al. (2001) who found more ettringite in the carbonate containing cement systems. In the limestone containing cement a higher percentage of available aluminium in the cement had reacted to form hydrate phases.

The maximum ettringite formation, as detected with SEM, was present in the surface region, partly intermixed with the C-S-H phase filling voids, cracks or space around aggregates. This ettringite might be expansive, as indicated by the small cracks forming in the microstructure. The observed ettringite formation at high sulfate contents might expand already existing cracks and thus accelerate sulfate interaction.

$Ca(OH)_2$ content is lowered compared to CEM I. In limestone cement pastes, carbonate ions incorporated in calcium aluminate hydrates and carboaluminates are formed. The stabilization of monocarbonate rather than monosulfate in the presence of calcite indirectly stabilizes ettringite, as there is proportionately more sulfate to alumina after the formation of the monocarbonate. This observation is in agreement with thermodynamic calculations of Lothenbach et al. (2008). This stabilization of monocarbonate and ettringite in the presence of calcium carbonate leads to an increase in the volume of the hydrated phases at the same degree of hydration of the clinker component, leading to a decrease in the relative porosity of about 0.5% (Lothenbach et al. 2008).

This agrees with the trends in porosity (Table 4.3.1) derived from the 91-day cured experimental results, which decreased slightly from 16.3 % to 16.2 % respectively for CEM I and CEM II/A-L (10%), indicating small differences. The higher replacement of a cement clinker by limestone, however, leads to an increase in porosity: For CEM II/A-L (15%) a capillary porosity of 17.3 % was measured. This increase of porosity with high replacement of limestone has also been noted in literature (Irassar et al. 2003) and corresponds to a decrease in the amount of reactive clinker capable of filling space with hydrates.

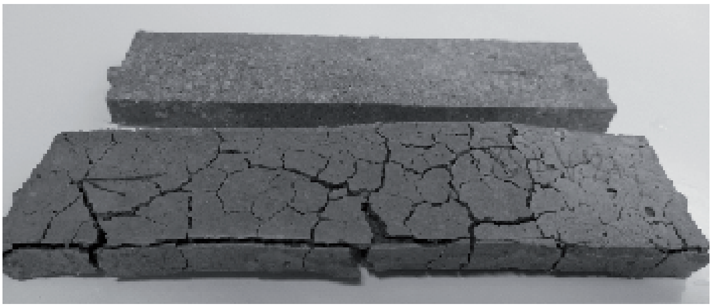


Figure 5.2.7 Examples of specimens after 91 days of exposure of CEM II/A-L (15 % L) in the 4.4 % $Na_2SO_4$ solution and in the saturated $Ca(OH)_2$ solution

It was clearly observed that the degree of surface deterioration was different with the replacement levels of limestone. The extent of surface deterioration after 91 days of exposure had a tendency to increase with the increased replacement level of limestone. In other words, the CEM II/A-L (15 % L) mortar sample displayed many wide cracks, spalling and substantial material loss at the faces as well as at the corners and edges.

As shown in Figures 5.2.5 and 5.2.7, the mode of failure in Portland limestone cement mortar specimens was mainly due to the formation of expansive cracking. This type of failure is typical of the sodium sulfate attack in moderate to high $C_3A$ cements (Al-Dulaijan et al. 2003). Expansive reaction takes place when excessive hydrated aluminate phases present in the cement react with the sulfate ions in the presence of $Ca(OH)_2$. This reaction leads to the formation of ettringite.

In the corroded surface, the complete depletion of $Ca(OH)_2$ caused by gypsum formation was also accompanied with a deposition of calcite crystals, which could cause a decrease in the amount of gypsum due to the decomposition of solid phases containing sulfate. According to Rasheeduzzafar (1992), in this degradation stage, mortar shows a dominant gypsum environment and the C-S-H will be affected by reduced intrinsic strength and stiffness.

The additional C-S-H formed during hydration in the case of limestone addition could also explain the decrease in capillary porosity, as described by Thomas and Jennings (2006), leading to lower permeability of the cement paste.

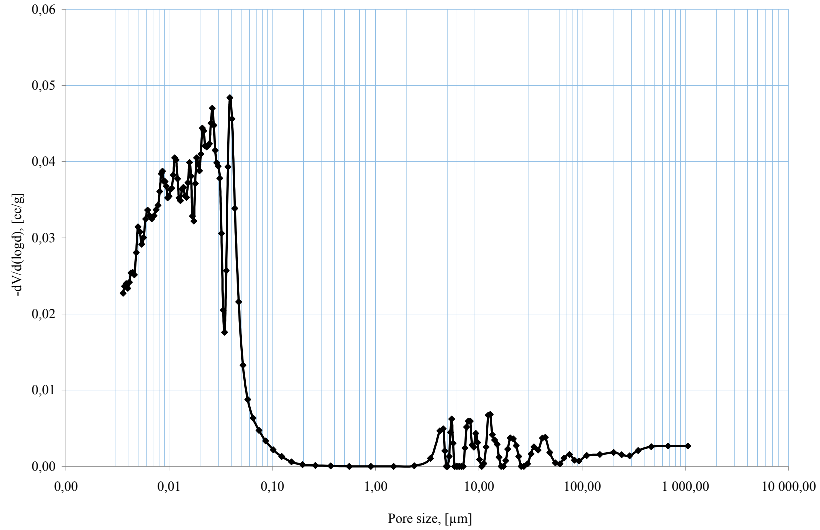


Figure 5.2.8 Pore size distribution of Portland limestone cement CEM II/A-L (10 % L) paste. Specimens were stored in the 4.4 % $Na_2SO_4$ solution for 91 days

The pore size distribution of CEM II/A-L (10% L) paste compared to that of CEM I indicates that by adding limestone 10 %, critical diameter increases (from 30.3 nm to 38.8 nm). This leads to the conclusion that limestone addition in cement produces larger interconnected pores in the cement paste that are of the same magnitude. The addition of limestone created a larger amount of medium capillary pores (0.01 to 0.05 µm) that derive from the reduction of large capillaries due to the filling effect of fine limestone. Also, the amount of small (gel) capillaries was increased probably due to the higher hydration rates (Taylor 1997) that limestone cements present.

As can be seen, the CEM II/A-L (10 % L) cement paste has many pores of the same size due to the filling effect that mineral constituents have. According to Pipilikaki and Beazi-Katsioti (2009) it means that it is more difficult for chemical species to enter the hardened cement, however, they transport easier inside the cement stone because the pores have approximately the same size.

CEM II/A-L (10 % L) cement has more air voids than CEM I paste and therefore should result in a better performance of limestone cements against freeze–thaw and salt decay.

Bensted (1995) suggests that the fine limestone grains modify the paste microstructure and that the topochemical growth of $Ca(OH)_2$ upon $CaCO_3$ crystals might occur and hence facilitate the access of $SO_4^{2-}$ to form gypsum.

Also, fine limestone increases the hydration rate of Portland cement, leading to the precipitation of $Ca(OH)_2$ located around the grains and the aggregate surfaces, but it does not have pozzolanic properties. Consequently, limestone filler does not produce C-S-H at later ages that consumes part of $Ca(OH)_2$, fills the pores, and improves the transition zone as other active constituents.

Dynamic modulus of elasticity ($E_d$) and compressive strength of CEM II/A-L (10 % L) after 28 days and one-year storage in the 4.4 % $Na_2SO_4$ solution and in the water of cement mortar specimens with dimensions (40 x 40 x 160) mm were thereabout the same as those of CEM I, except that unlike CEM I the $E_d$ of CEM II/A-L (10 % L) after one-year storage in the 4.4 % $Na_2SO_4$ solution was still slightly increasing.

The test results demonstrated that mortar and paste samples incorporating 5...15 % replacement levels of fine limestone were more susceptible to sulfate attack than CEM I. The results were similar to findings of Irassar et al. (2003). The disintegration of Portland limestone cement is more severe and rapid, the higher is the limestone content of the cement used. This fact can be attributed to the hydration process, which differs between Portland limestone cements and the Portland cement. Specifically, the incorporation of limestone accelerates the cement hydration process increasing the $Ca(OH)_2$ formation. The reaction between sulfates and $Ca(OH)_2$ in the paste results in an alteration of the predominant mechanism of sulfate attack. Also, the initial capillary porosity is increased, leading to more rapid sulfate induced deterioration.

Currently composite cements are available with up to 35 % of limestone replacing the Portland cement clinker, although the current test results enable to state that Portland limestone cements are not allowed for use in environments where sulfate attack is possible.

## 5.3 Influence of burnt shale constituent in Portland cement

### *5.3.1 High temperature burnt shale $T_T$ cements*

The chemical composition of high temperature burnt shales $T_T$ is dominated by CaO, whose proportion varied from 34.5...36.6 % (Table 3.11.1). MgO (in the current research 3.5...3.8 %) is mostly derived from the thermal decomposition of dolomite. $Al_2O_3$ content was 8.8...9.0 %. The proportion of $Fe_2O_3$ was remarkably high 4.0...4.2 %.

The sulfate resistance of Portland burnt shale $T_T$ cements by the Wittekindt expansion was tested with two different burnt shales $T_T$ and the addition of $T_T$ in cement was 15 %, 20 %, 25 % and 30 %.

The satisfactory resistance of Portland burnt shale $T_T$ cements in $Na_2SO_4$ solution was already proved by Raado (1975). To determine corrosion resistance (40 x 40 x 160) mm specimens were stored in the 5 % $Na_2SO_4$ solution for three years. Mortars were made by methods of GOST 310 with the same flow diameter on the flowing table. No expansion occured in mortars made with the 20...30 % burnt shale cement CEM II/B-T during a three-year storage.

Since then the burnt shale combustion technology has changed and the properties of burnt shale $T_T$ are different. Therefore it is important to study the behavior of present-day burnt shale $T_T$ in sulfate environments as main constituent of cement.

Cement mortars were made with the water-cement ratio 0.50. As the water demand of Portland burnt shale $T_T$ cements is lower than that of Portland cement, these cements are in inferior position. Reducing the water-binder ratio actually improves strength and resistance to the ingress of the sulfate ions by diffusion. It should be pointed out here that the water requirement of CEM II/B-$T_T$ (30 % $T_T$) mortar was the lowest and hence a dense mortar with less porosity would be expected for this mortar. This would increase the resistance to the ingress of the sulfate solution.

Visually all specimens made with Portland burnt shale $T_T$ cement after 91-day storage in the 4.4 % $Na_2SO_4$ solution were not notably damaged.

Reduced expansion of mortars containing cement with 15...30 % burnt shale $T_T$ illustrated improved sulfate resistance afforded by burnt shale $T_T$ use.

The expansion values in the 4.4 % $Na_2SO_4$ solution and in the saturated $Ca(OH)_2$ solution are represented in Figure 5.3.1 and in Table A1. The values of relative expansion are illustrated in Figure 5.3.2.

The initial expansion (Table A1) of Portland burnt shale $T_T$ cements was much higher (0.094…0.144 mm/m) than that of CEM I cement (0.069 mm/m). The initial expansion increased with increasing burnt shale $T_T$ content in cement and was caused mainly by the hydration of $CaO_{free}$ derived from burnt shale $T_T$. The expansion in the early stage of hardening is harmless to the cement stone.

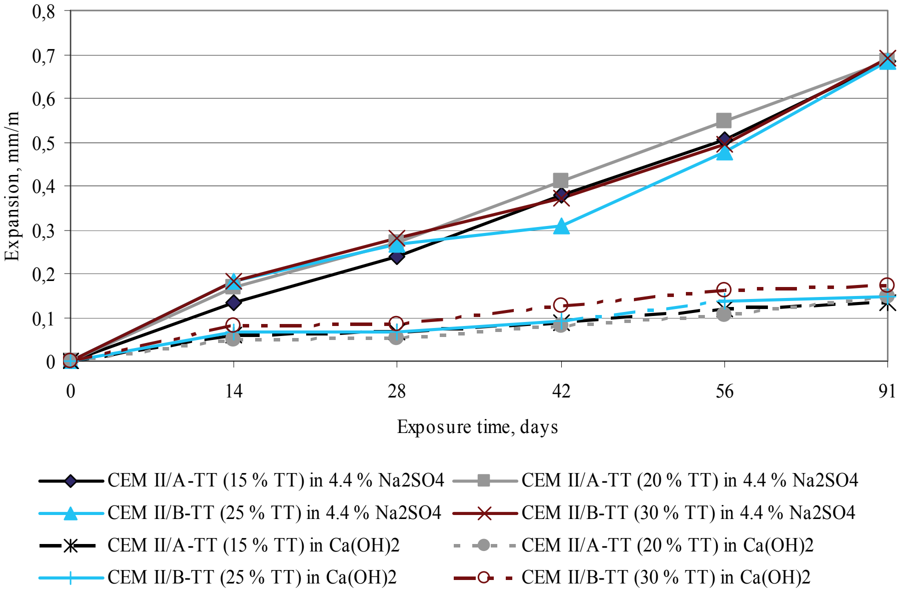


Figure 5.3.1 Expansion of Portland burnt shale cements depending on $T_T$ content in cement in the 4.4 % $Na_2SO_4$ and in the saturated $Ca(OH)_2$ solutions

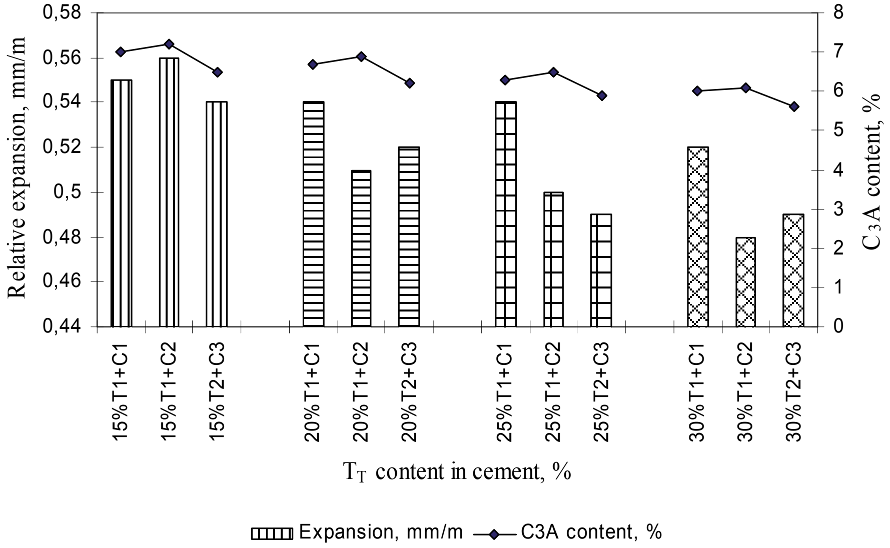


Figure 5.3.2 Relative expansion of Portland burnt shale $T_T$ cements depending on cement $C_3A$ and burnt shale $T_T$ content. Cements are made of various clinkers ($C_1$, $C_2$ and $C_3$) and burnt shales ($T_{T1}$ and $T_{T2}$)

Portland burnt shale $T_T$ cements had high sulfate resistance if they contained at least 20 % by mass of burnt shale $T_T$ (Figure 5.3.2). The content of $C_3A$ of CEM II/B - $T_T$ (30 % $T_T$) cement was 5.6…7.0 %. For sulfate resisting Portland cement it is a relatively high content. Portland burnt shale $T_T$, as a constituent of the Portland burnt shale $T_T$ cement, contributes to the Portland burnt shale cement CEM II/B- $T_T$ properties, increasing the corrosion resistance of concrete. On the one hand, it decreases the $C_3A$ content and diminishes the water demand of cement. On the other hand, the formation of C-S-H gel reduces the diameter of capillaries.

As can be seen in Figure 5.3.2, cements made with various clinkers and burnt shales $T_T$ had variations in expansions, depending on the used clinker and burnt shale $T_T$. More expanded cements were made with burnt shale $T_{T1}$ with higher CaO and $CaO_{free}$ content. The chemical composition of the clinker showed a higher effect. There was no direct correlation between the expansion of cement and $C_3A$ content, but there was appreciable correlation between expansion and $C_3S$ content (phase compositions in Table 5.1.3). Cements made with clinker $C_1$ ($C_3S$ - 63.8 %) had highest expansions and cements made with clinker $C_2$ ($C_3S$ - 54.1 %) had considerably lower expansions in the sulfate solution.

SEM images of Portland burnt shale cement with 20 % $T_T$ are presented in Figures 5.3.3…5.3.6. Analyses revealed the reaction products near or within cracks and air voids due to sulfate attack.

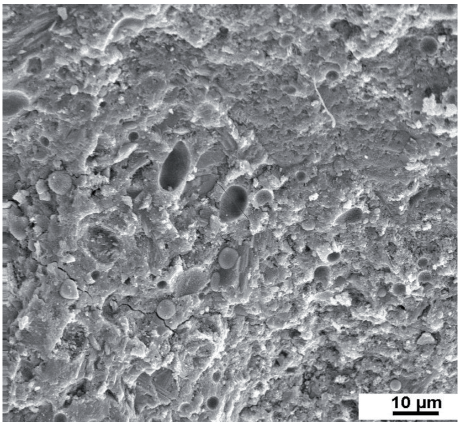


Figure 5.3.3 CEM II/A-$T_T$ (20% $T_T$) mortar cured for 14 days in the saturated $Ca(OH)_2$ solution. The particles of burnt shale $T_T$ are visible.

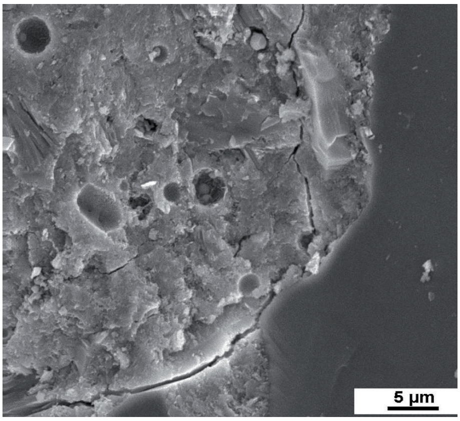


Figure 5.3.4 CEM II/A-$T_T$ (20% $T_T$) mortar cured for 91 days in the saturated $Ca(OH)_2$ solution. The cement stone is fragile, cracks.

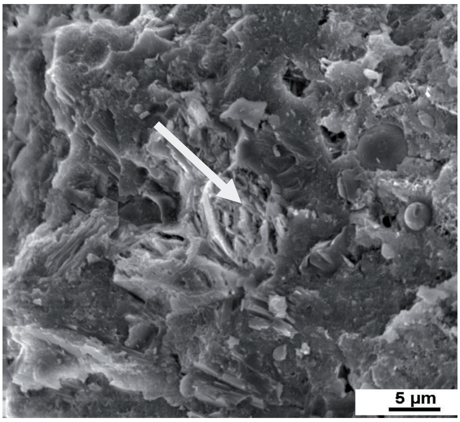


Figure 5.3.5 CEM II/A-$T_T$ (20% $T_T$) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. Air void filled with secondary reaction products.

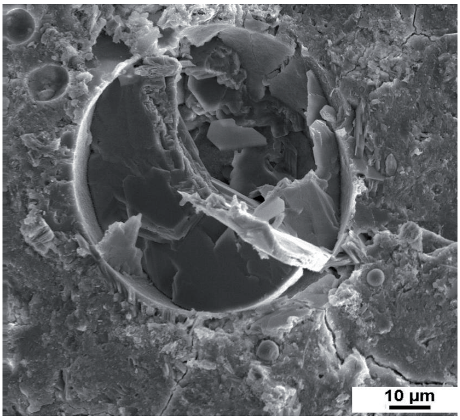


Figure 5.3.6 CEM II/A-$T_T$ (20% $T_T$) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. Air void filled with expanded products and void centered cracks.

SEM images showed a slight formation of gypsum crystals near cracks. Ettringite crystals were formed within the air void near the outer side of the specimen. The structure was dense, most air voids were found to be filled with the reaction products. Gypsum, ettringite and $Ca(OH)_2$ crystals were observed in air voids both near the outer side of the specimen and in the middle section. Additionally, large amounts of the spherical shape of burnt shale $T_T$ were seen everywhere. Gels with high Ca-Si-Al-S composition were also observed to partially fill some air voids. These were mostly observed near the exposed surfaces of the specimens.

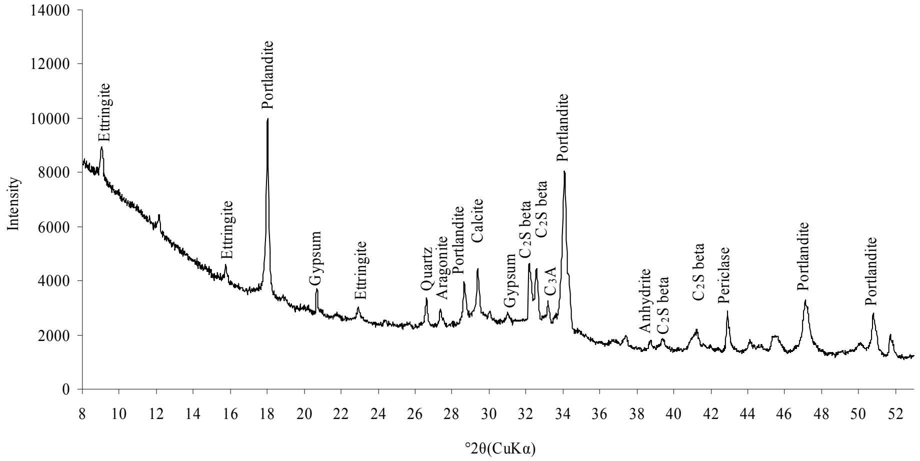


Figure 5.3.7 XRD analysis of Portland burnt shale cement CEM II/A-$T_T$ (20% $T_T$) paste after exposure to the 4.4 % $Na_2SO_4$ solution for 91 days

The cement with burnt shale $T_T$ effectively converted $Ca(OH)_2$ into the secondary C-S-H phase, as confirmed in the XRD diffractogram (Figure 5.3.7).

In contrast to CEM I, there was only slight evidence of the formation of gypsum in the surface of mortar specimens even though they were subjected to attack. This explained why the expansion values of these specimens were relatively smaller than those of the CEM I mortar specimens.

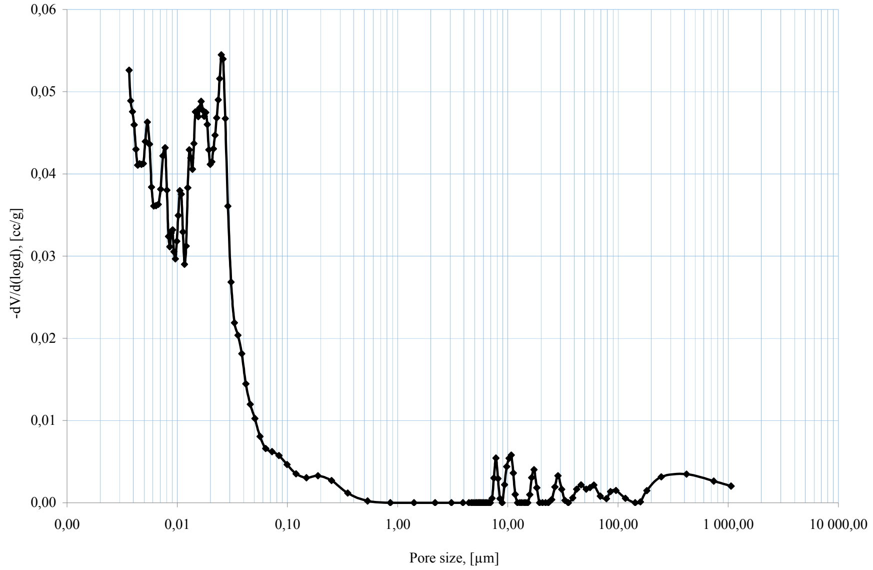


Figure 5.3.8 Pore size distribution of Portland burnt shale cement CEM II/A-$T_T$ (20 % $T_T$) paste. Specimens were stored in the 4.4 % $Na_2SO_4$ solution for 91 days

From Figure 5.3.8 it is obvious that CEM II/A-$T_T$ (20 % $T_T$) paste has a denser microstructure with a finer distribution of the pores than the CEM I paste.

It can be observed that secondary hydrated minerals precipitate in the pores that were inside the cement and thus reduce its porosity. The XRD result presented in Figure 5.3.7 shows that the CEM II/A-$T_T$ (20 % $T_T$) paste still has unreacted $C_2S$ and $C_3S$. This means that the paste was not fully hydrated.

The content of large capillary pores (> 0.05 µm) determines the permeability and migration of the aggressive solution into the material. It means that the sulfate corrosion may occur. As compared to the CEM I mortar, the content of large capillary pores was decreased by adding 20 % of burnt shale $T_T$. Thus, an addition of burnt shale $T_T$ caused the reduction of dangerous migration of aggressive solutions, which causes destruction. Medium capillary pores were finer with CEM II/A-$T_T$ (20 % $T_T$). Content of gel pores (< 0.01 µm) was higher with CEM II/A-$T_T$ (20 % $T_T$) compared to CEM I. This also means higher resistance to sulfate attack. The wider particle size distribution also reduces the water demand, increasing the density and the strength.

Comparison of test results with the specimens of increased sizes (40 x 40 x 160) mm shown in Tables A6…A9 reveals that relative expansions of Portland burnt shale $T_T$ cements with burnt shale 15…30 % in the 4.4 % $Na_2SO_4$ are 0.05…0.13 mm/m. Compressive strength and dynamic modulus of elasticity increased. The values of $E_d$ of CEM II/A-$T_T$ (20 % $T_T$) in the 4.4 % $Na_2SO_4$ solution and in water at the age of one year were the same. But the compressive strength (70.1 MPa) in water exceeded the strength of specimens stored for one year in the 4.4 % $Na_2SO_4$ (65.3 MPa). Burnt shale $T_T$ content in multicomponent composite cements increased both early and one year $E_d$ and compressive strength values in the 4.4 % $Na_2SO_4$ solution. These results confirmed the good performance of Portland burnt shale $T_T$ cement mortars in $Na_2SO_4$ solution.

Portland high temperature burnt shale $T_T$ cements had high sulfate resistance if they contained at least 20 % by mass of burnt shale $T_T$. The initial expansion and expansion in the $Ca(OH)_2$ solution were high in Portland burnt shale $T_T$ cements and increased with increasing burnt shale $T_T$ content in cement and were caused mainly by the hydration of $CaO_{free}$ derived from burnt shale $T_T$. SEM images showed a slight formation of gypsum crystals near cracks, ettringite crystals within the air void near the outer side of the specimen. The structure was dense, most air voids were found to be filled with the reaction products. Compared to the CEM I mortar, the content of large capillary pores was decreased by adding 20 % of burnt shale $T_T$, medium capillary pores were finer and the content of gel pores (< 0.01 μm) was higher, therefore sulfate resistance was higher. The results of $E_d$ and compressive strength after one-year storage in the 4.4 % $Na_2SO_4$ confirmed the good performance of Portland burnt shale $T_T$ cement mortars in $Na_2SO_4$ solution.

### *5.3.2 Low temperature burnt shale $T_K$ cements*

SEM analysis and pore size distribution of initial low temperature burnt shale $T_K$ (Raado and Nurm 2006, 2007) show that the material is composed of 5…20 µm size porous particles and aggregates that are characterized by an irregular shape and a very uneven surface (Figure 2.4.1). Only a few glassy spherical particles were found that can be explained by considerably lower burning temperatures compared to burnt shale $T_T$ that are characterized by glassy spherical particles. Compared to cements with burnt shale $T_T$ (22.3…23.8 %) the water demand of cements with burnt shale $T_K$ was much higher (35.5…36.8 %). 28-day compressive strength of cements with burnt shale $T_K$ was lower (51.5…52.8 MPa) than that of cements with burnt shale $T_T$ (54.9…56.6 MPa). The different chemical, physical and mechanical properties of burnt shales influence the pore structure and permeability and therefore also the sulfate resistance of cements made with burnt shales $T_K$ or $T_T$ as second constituents.

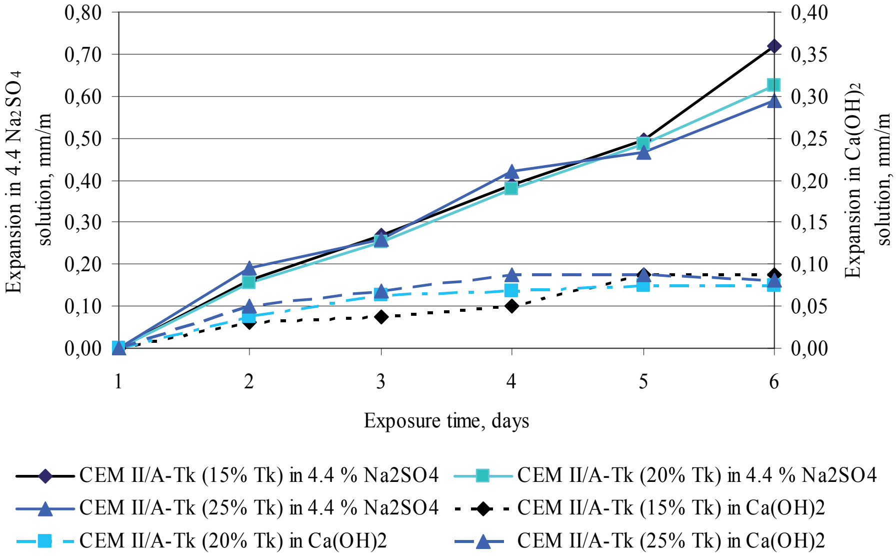


Figure 5.3.9 Expansion behavior of flat mortar prisms of Portland burnt shale $T_K$ cements with 15%, 20% and 25% $T_K$ immersed in the 4.4 % $Na_2SO_4$ solution and in the saturated $Ca(OH)_2$ solution

The initial expansions of Portland burnt shale $T_K$ cements (Table A1) were higher than the expansions of CEM I but lower than the expansions of Portland burnt shale $T_T$ cements because the content of amorphous phase increased in burnt shale $T_K$.

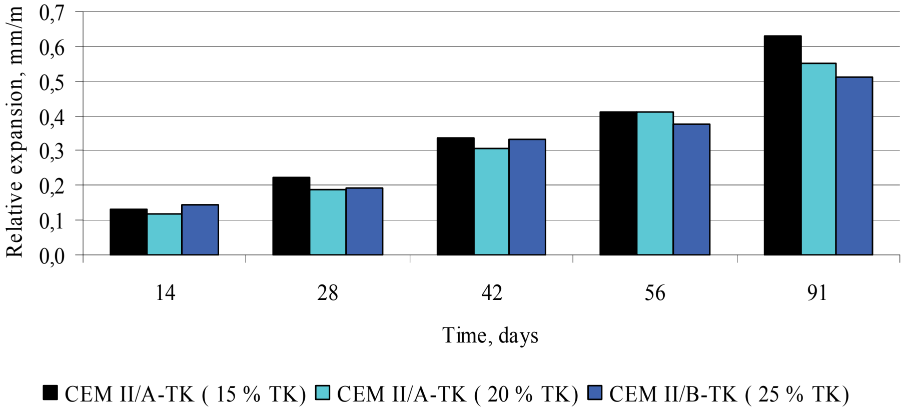


Figure 5.3.10 Sulfate resistance of Portland burnt shale $T_K$ cements expressed as the Wittekindt relative expansion

The relative expansions of Portland cements with burnt shale $T_T$ and burnt shale $T_K$ were of the same value. But the expansions in solutions were not. Burnt shale $T_T$ containing cements expanded more in the saturated $Ca(OH)_2$ solution, as it contained more $CaO_{free}$ and less in the 4.4 % $Na_2SO_4$ solution than the burnt shale $T_K$ cements. After 91-day storage in the 4.4 % $Na_2SO_4$ solution the relative expansion of Portland burnt shale $T_K$ cements exceeded slightly (0.63…0.51 mm/m) the limit value (0.50 mm/m), see Figure 5.3.10. With an increasing content of burnt shale $T_K$, the sulfate related expansion of Portland burnt shale $T_K$ cements decreased.

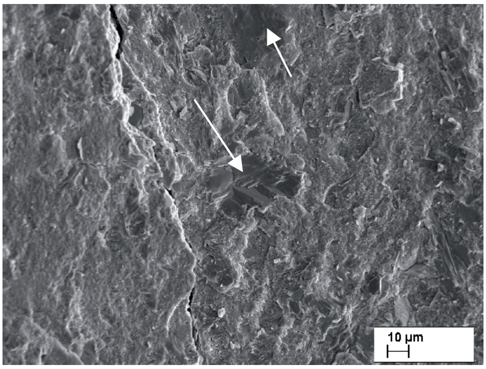


Figure 5.3.11 CEM II/A - $T_K$ (20 % $T_K$) paste cured for 91 days in the 4.4 % $Na_2SO_4$ solution. Ettringite nests.

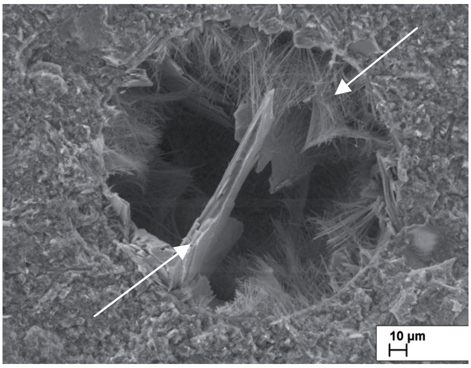


Figure 5.3.12 CEM II/A - $T_K$ (20 % $T_K$) paste stored for 91 days in the 4.4 % $Na_2SO_4$ solution. An air void partly filled with ettringite needles. In the middle is $Ca(OH)_2$ crystal.

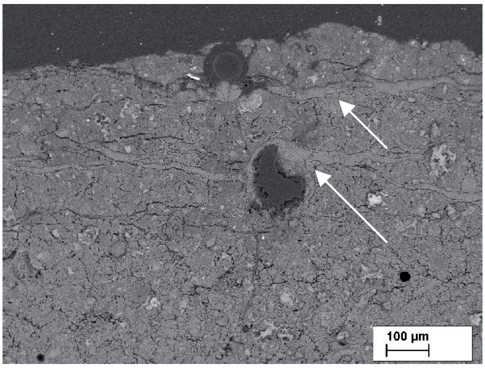


Figure 5.3.13 CEM II/A - $T_K$ (20 % $T_K$) paste stored for 91 days in the 4.4 % $Na_2SO_4$ solution. Near the surface of specimen gypsum was detected up to the depth of 385 µm.

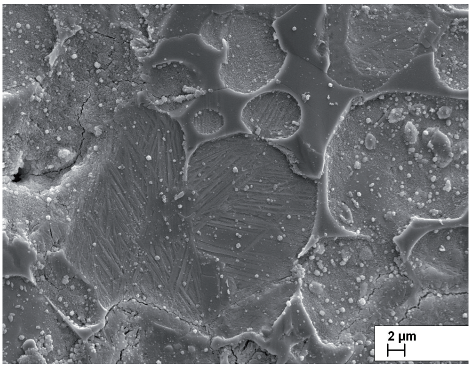


Figure 5.3.14 CEM II/A - $T_K$ (20 % $T_K$) paste stored for 91 days in the 4.4 % $Na_2SO_4$ solution. Voids filled with ettringite.

SEM images (Figures 5.3.11…5.3.14) revealed a very dense structure of CEM II/A-$T_K$ (20 % $T_K$). Near the surface region (up to the depth of 385 µm) a very distinct gypsum area in stripes and filling voids was detected. Deeper the gypsum quota decreased and the proportion of ettringite increased. Large air voids were partly filled with, and smaller voids were filled up with ettringite.

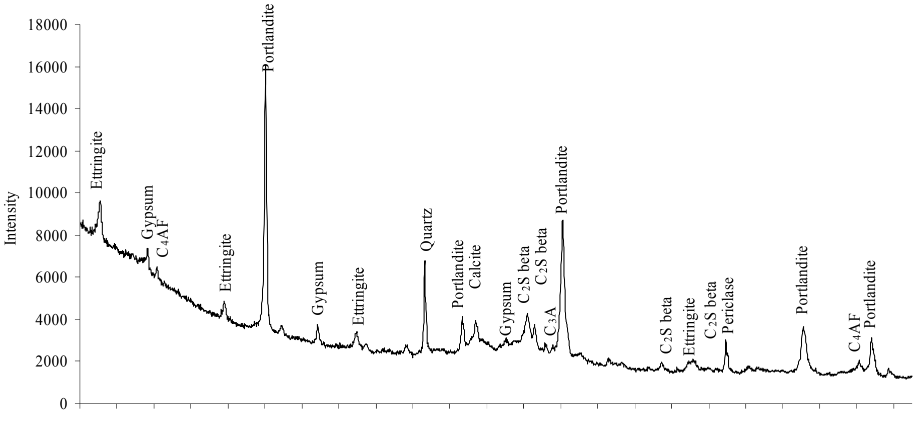


Figure 5.3.15 XRD analysis of Portland burnt shale $T_K$ cement CEM II/A-$T_K$ (20% $T_K$) paste after exposure to the 4.4 % $Na_2SO_4$ solution for 91 days

After 91 days of 4.4 % $Na_2SO_4$ exposure of the experiment, ettringite, gypsum, $Ca(OH)_2$ and monosulfate hydrate were detected as well as some residual $C_4AF$ (Figure 5.3.15). The $Ca(OH)_2$ content in CEM II/A-$T_K$ (20 % $T_K$)

paste decreased from 20.8 % to 5.0 %, ettringite increased up to 2.9 %, the content of gypsum was stable. The content of Ca-silicate (β-$C_2S$) was decreased.

CEM II/A-$T_K$ (20 % $T_K$) paste with low temperature burnt shale $T_K$ obviously had a higher peak of $SiO_2$ than CEM II/A-$T_T$ (20 % $T_T$).

By a reaction between the reactive $SiO_2$ of the second main constituent burnt shale $T_K$ and $Ca(OH)_2$ initiated by the hydration of clinker minerals, the extra amount of C-S-H was generated and that had a decreasing impact on the capillary diameter and reduced the water penetration of the concrete.

CEM II/A-$T_K$ (20 % $T_K$) showed a higher peak of non-decomposed $CaCO_3$ than CEM II/A-$T_T$ (20 % $T_T$). The peaks of $C_2S$ in CEM II/A-$T_K$ (20 % $T_K$) were much lower than in CEM II/A-$T_T$ (20 % $T_T$).

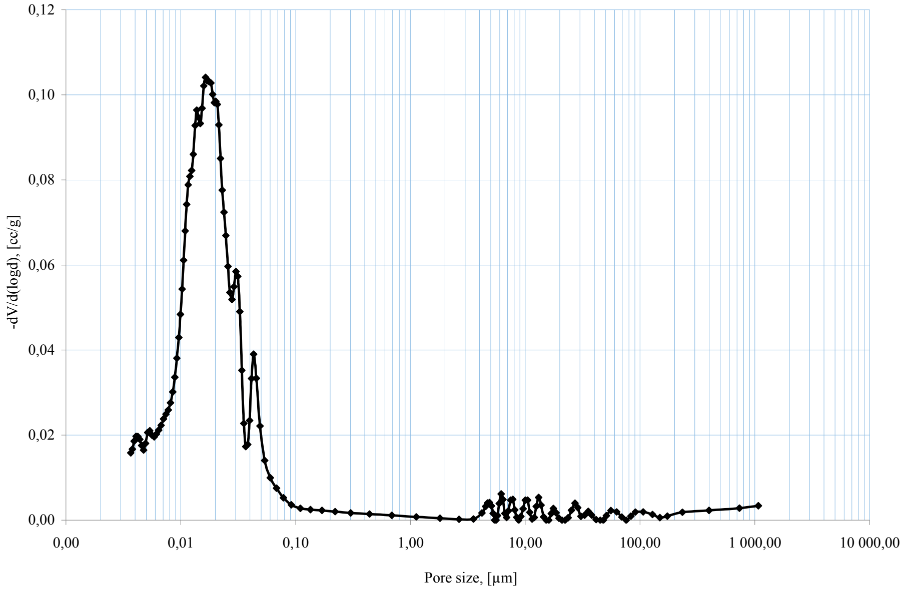


Figure 5.3.16 Pore size distribution of Portland burnt shale $T_K$ cement CEM II/A-$T_K$ (20 % $T_K$) paste. Specimens were stored in the 4.4 % $Na_2SO_4$ solution for 91 days

The lower 28-day compressive strength of CEM II/A-$T_K$ (20 % $T_K$) can be attributed to the higher percentage of macropores (10...0.05 µm). Increasing water demand of burnt shale $T_K$ containing cements increased the amount of capillary pores.

Comparing the pore size distribution of CEM II/A-$T_K$ (20 % $T_K$) (Figure 5.3.16), CEM II/A-$T_T$ (20 % $T_T$) (Figure 5.3.8) and the pore size distribution of burnt shale pastes with $T_K$ and $T_T$ (Figure A1) it was obvious that the pores of burnt shale $T_K$ paste were filled with hydration and corrosion products and hence made the structure of CEM II/A-$T_K$ (20 % $T_K$) paste denser.

Figure A1 presents pore size distributions and XRD results of burnt shale $T_T$ and $T_K$ pastes. Specimens were made with burnt shales on standard consistency and cured in water for 91 days. From the results of pure burnt shales several differences can be observed. Ettringite is presented in burnt shale $T_T$, but is missing in burnt shale $T_K$, for which the Portland burnt shale $T_K$ mortars also developed lower compressive strength. $Ca(OH)_2$ in burnt shale $T_T$ and burnt shale $T_K$ pastes has practically disappeared compared to burnt shale cement pastes. The ratios Si/Ca in the various hydrated Ca-Al silicates detected by XRD in burnt shale $T_K$ were very high. High content of $SiO_2$ in CEM II/A-$T_K$ (20%$T_K$) was derived from burnt shale $T_K$, as was apparent in the diffractogram made with burnt shale $T_K$ paste (Figure A1d).

The water demand of cements with low temperature burnt shale $T_K$ was high compared to CEM I and other composite cements. As strength parameters with Portland burnt shale $T_K$ cements were comparable with CEM I, a considerable effect for sulfate resistance related expansion was noticed. The relative expansions of the Wittekindt method of Portland cements with burnt shale $T_T$ and burnt shale $T_K$ were of the same value. After 91-day storage in the 4.4 % $Na_2SO_4$ solution the relative expansion of Portland burnt shale $T_K$ cements exceeded slightly the limit value. Sulfate resistance was increased with an increasing content of burnt shale $T_K$ in cement. It was observed that for Portland burnt shale $T_K$ cements inwards expansion was due as the proportion of amorphous phase was high and expansion was harmless for crystals. Le Chatelier expansion for Portland burnt shale $T_K$ cements was notably low. SEM images revealed a very dense structure of CEM II/A-$T_K$ (20 % $T_K$). Large air voids were partly filled with, and smaller voids were filled up with ettringite, gypsum and hydration products. Higher percentage of macropores was detected. Increasing water demand of burnt shale $T_K$ containing cements increased the amount of capillary pores.

## 5.4 Influence of slag constituent in Portland slag cements and slag cements

Slag is known as one of the most effective constituents to increase the sulfate resistance of cements. Despite the variable mineralogical compositions of the used slags, the sulfate resistance was considerably improved. But the usage of slags in cements is limited because it reduces the most important durability properties of concrete. The higher the content of slag in cement, the worse are the compressive strength and frost resistance of concrete.

Portland slag cements and slag cements were made with two different slags $S_1$ and $S_2$ but with the same clinker $C_1$. The chemical compositions of slags are given in Table 3.11.1. The results of relative expansion by the Wittekindt method are presented in Figure 5.4.1.

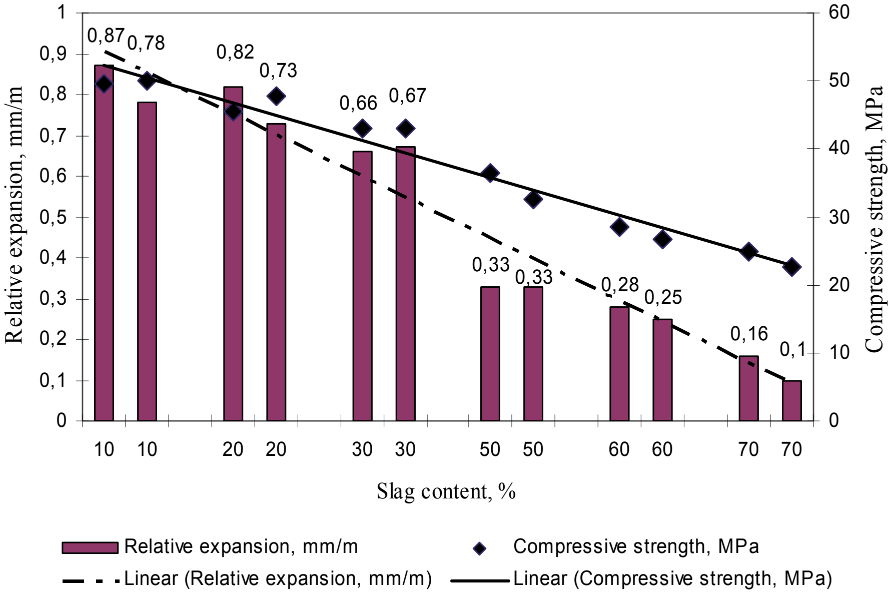


Figure 5.4.1 Sulfate resistance of Portland slag cements and slag cements ($Al_2O_3$ content in slag $S_1$= 17.95 %, $S_2$ = 15.70 %)

Figure 5.4.1 shows the relative effect of $Al_2O_3$ in slag. Cements were made with the same $SO_3$ content 3.5 %. $C_3A$ content in cements with both slags in 10 % replacement level was 7.1 %, with an increasing slag content in cement, the $C_3A$ lowered up to 2.1 % in 70 % replacement level. Cements made with slag with lower $Al_2O_3$ ($S_2$) had reduced sulfate related expansion but also inferior strength properties, especially early strength. The lower content of $SiO_2$ and higher content of MgO of slag $S_1$ increased the strength of cements made with slag $S_1$.

The sulfate resisting capabilities of slag have been discussed on many occasions with much of the benefit being attributed to a denser matrix, decreased permeability and a reduction in $Ca(OH)_2$ present in the hydrated system (Al-Dujan et al. 2003). Furthermore, with the formation of a secondary C-S-H phase attributable to the long-term hydration of the slag, much of the alumina in the system becomes 'locked up' in this product and is not available to form ettringite during a sulfate attack (Gollop and Taylor 1996).

The initial expansions of Portland slag cements with 10…30 % slag depending on slag content were similar. With higher slag contents 50…70 % in conjunction with increase of $SO_3$ in cement also the initial expansion values increased greatly. The further expansion in saturated $Ca(OH)_2$ solution with 10…30 % slag was comparable to Portland burnt shale cements with 15…30 % $T_T$.

Slag in amounts of 20…30 % did not considerably affect the sulfate resistance of cement. The relative expansions of Portland slag cements were much higher than those of Portland burnt shale cements both $T_T$ and $T_K$ at the same main constituent replacement level and exceeded far (0.66…0.87 mm/m) the limited value of the Wittekind test method (0.50 mm/m).

The data showed that slag at a replacement level of 50…80 % definitely increased the sulfate resistance of CEM III cements in comparison to the Portland cement, as indicated by much lower expansion despite the low early strength gained. The test specimens were placed in the sulfate solution at the age of 14 days. The compressive strength of slag cement in the time of sulfate deposition was only ca 20 % of CEM I. 28-day compressive strength of cement with 70 % slag was reduced by ca 40…50 %.

It was noted that mortars made with 70 % slag were superior to the sulfate resisting Portland cements (Figure 5.4.1, Table A1) when specimens were compared at the same water-cement ratio. At 50 % slag replacement, the mortars were also better than the commercial sulfate resisting cements (Figure 5.6.1, Table A10). Even 30 % replacement of slag imparted some degree of sulfate resistance, though inferior to that of typical sulfate resisting cements.

The data is in correlation with the test results of Mehta (1973): Cement containing 30 % slag showed significant strength loss and expansion during 28 days of immersion in sulfate solutions, but both the expansion data showed that the cement containing over 70 % slag exhibited excellent resistance to sulfate attack.

One factor often overlooked is that resistance to external sulfates is normally influenced by the level of $SO_3$ in the cement. Using data from several mortars made with slag $S_1$ varying additions of $SO_3$ levels and testing for compressive strength at 2 and 28 days (Figure 5.4.2), it could be noted that $SO_3$ content in slag cement had a major effect on the compressive strength but in present case did not affect substantially the sulfate resistance. The interaction of $SO_3$ with aluminate phases in cement, which resulted in early-age modification of cement paste microstructure, affected expansion, shrinkage, and porosity of the cement mortar. Typically, slag also contains large proportions of alumina that reacts with $SO_3$ to form ettringite and can directly interfere with the sulfate optimization (Bhatty and Taylor 2006). According to Gollop and Taylor (1996), the higher is the level in the range ~1 % to ~4 %, the greater is the resistance. This applies to concrete produced from CEM I cements and also particularly to slag containing concretes. The improved resistance can be attributed to the increased level of sulfated phases, such as ettringite formed during initial hydration, which are stable in the presence of an elevated sulfate level.

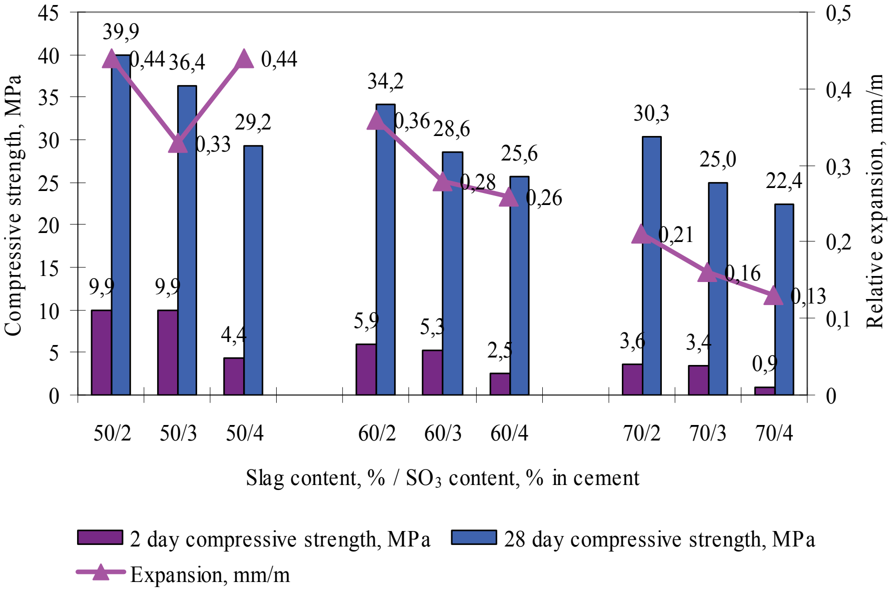


Figure 5.4.2 Influence of $SO_3$ level in slag cements for sulfate resistance and strength properties

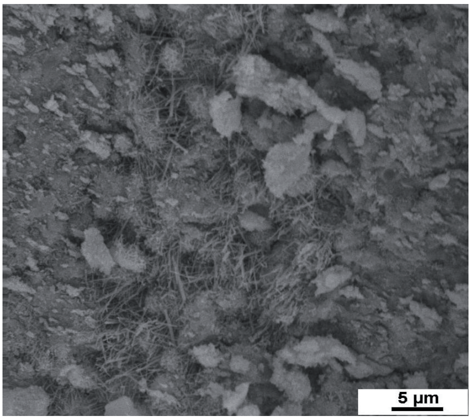


Figure 5.4.3 CEM III/A (60 % S) mortar cured for 14 days in the $Ca(OH)_2$ solution. A great amount of needle-shaped ettringite.

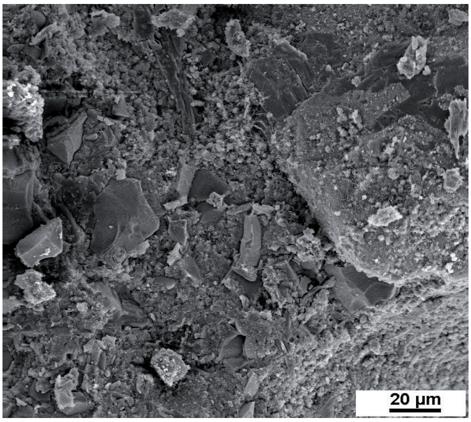


Figure 5.4.4 CEM III/A (60 % S) cured for 14 days in the $Ca(OH)_2$ solution. Cement stone in the middle section of the specimen. Clearly distinguishable slag particles.

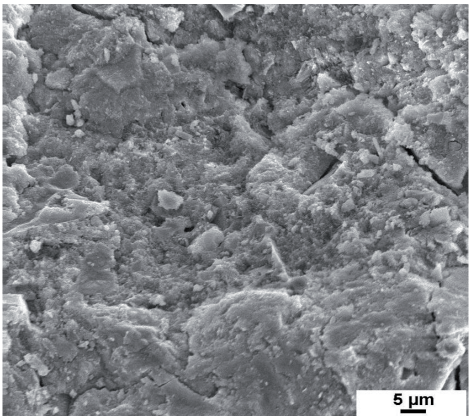


Figure 5.4.5 CEM III/A (60 % S) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. Dense, but uneven micro-structure, and no needle-shaped ettringite nor plated-shaped $Ca(OH)_2$ can be observed.

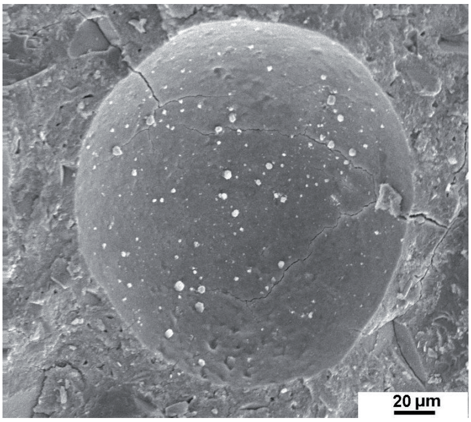


Figure 5.4.6 CEM III/A (60 % S) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. Air voids are empty.

Figures 5.4.3…5.4.6 present the SEM images made with CEM III/A (60 % S) mortar.

The micrograph of CEM III/A (60 % S) showed that there were no significant effects of sulfate. The hydration products of C-S-H did not deteriorate.

The texture was denser than that of CEM I. The preceding observation could be related to the pozzolanic activity and filling properties of slag.

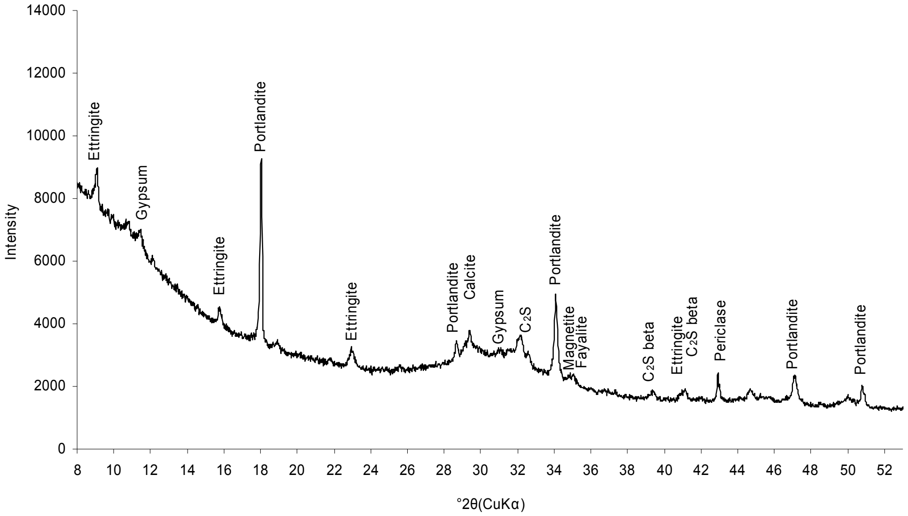


Figure 5.4.7 XRD analysis of slag cement CEM III/A (60 % S) paste after exposure to the 4.4 % $Na_2SO_4$ solution for 91 days

Figure 5.4.7 shows that the 60 % partial replacement of slag in cement resulted in the consumption of $Ca(OH)_2$ due to pozzolanic reaction, and the dilution of the $C_3A$ phase, and thereby reduced the intensity peaks of $Ca(OH)_2$ and ettringite compared to Portland cement. Disappearance of the gypsum peaks in sulfate solution may be explained through poorly crystalline formation of it.

The degree of decalcification may be extensive in cements with high slag contents, in spite of relatively low amounts of ettringite formed, as the amount of formed C-S-H and that of free $Ca(OH)_2$ is also reduced in the hydration of slag cements. For the same reasons, the amount of gypsum in the corrosion zone of slag cement was also low, as shown both by XRD and SEM results. From the chemistry of reactions in the sulfate attack it was obvious that since with the 60 % slag cement, before exposure to the sulfate solution, all the $Ca(OH)_2$ formed by hydration of the 40 % Portland cement present had been consumed by chemical reactions with the slag. This explains why in spite of the availability of a large amount of reactive alumina from the slag, no signs of sulfate attack were observed.

The use of a slag as puzzolana resulted in a denser pore structure in the cement paste, as could be seen in Figure 5.4.8. Also, the chemical reaction of lime crystals to form binders had a direct effect of reduced total porosity and enhanced the sulfate resistance. This presumably was a result of the inability of water containing dissolved sodium sulfate to penetrate to the centre of the specimens under test and was therefore also a reflection of the waterproofing abilities of slag.

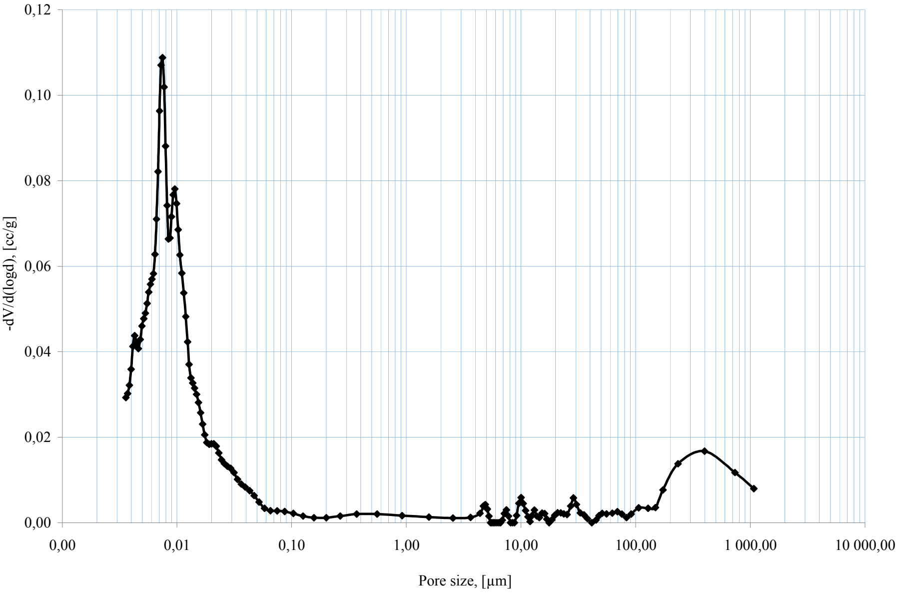


Figure 5.4.8 Pore size distribution of slag cement CEM III/A (60 % S) paste. Specimens were stored in the 4.4 % $Na_2SO_4$ solution for 91 days

The porosity and pore size distribution of the hardened slag cement paste presented in Figure 5.4.8 was totally different from those of Portland cement paste (Figure 5.1.7).

The analysis of pore size distribution supported the idea that slag cement paste with high sulfate resistance and high physical resistance to water penetration had very narrow pores and was thus able to prevent the diffusion of the sulfate ions into the microstructure. Most of the pores were gel pores 0.005…0.01 μm. The increase of pore sizes above 100 μm indicated that the air voids were empty, not filled with reaction products, as also observed with SEM (Figure 5.4.6).

Comparison of test results with the specimens (40 x 40 x 160) mm shown in Tables A6…A9 reveals that a significant suppressing of sulfate attack symptoms can be observed. Instead of a decrease in compressive strength and dynamic modulus of elasticity, a steady increase was observed (Tables A8…A9). As early strength of slag cement was low, the relative $E_d$ and compressive strength values of specimens stored in the 4.4 % $Na_2SO_4$ solution increased considerably with time.

Despite the variable mineralogical compositions of used slags, sulfate resistance of cements was improved. Slag in amounts of 20…30 % did not considerably affect the sulfate resistance of cement. The relative expansions of Portland slag cements were much higher than those of Portland burnt shale cements both $T_T$ and $T_K$ at the same main constituent replacement level and exceeded far (0.66…0.87 mm/m) the limited value of the Wittekind test method (0.50 mm/m). The data showed that slag at a replacement level of 50…80 % definitely increased the sulfate resistance of CEM III cements in comparison to the Portland cement, as indicated by much lower expansion despite the low early strength gained. The microstructure was dense, but uneven, and no ettringite and gypsum could be observed by SEM. The amount of formed C-S-H and $Ca(OH)_2$ was reduced. Slag cement paste with a high sulfate resistance and a high physical resistance to water penetration had very narrow pores and was thus able to prevent the diffusion of the sulfate ions into the microstructure. Most of the pores were gel pores, air voids were empty and not filled with reaction products. The good performance at high slag levels is due largely to the low permeability this provides.

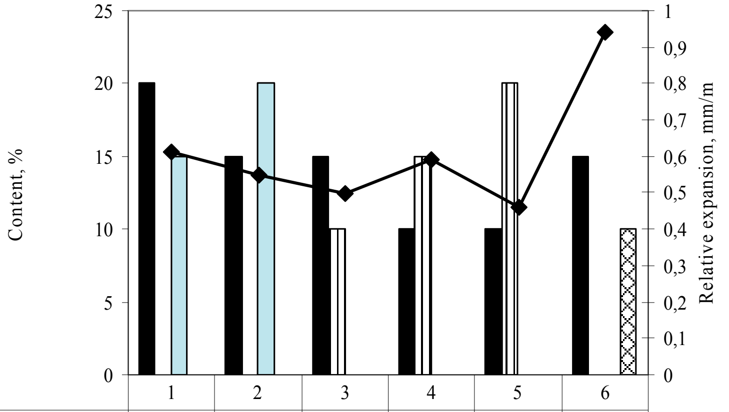
## 5.5 Influence of addition of several main constituents in multi-component Portland composite cements

Traditionally, limestone, slag, burnt shale were used in concrete individually. Today, due to improved access to these materials, cement producers can combine two or more of these constituents to optimize cement and/or concrete properties. Multicomponent Portland composite cements composed of at least three cement constituents, called also ternary cements, are becoming more common.

The purpose is by compositioning different constituents to enlarge the effect of positive characteristics and to compensate negative effects.

The lower relative expansion in composite cements was attributed to the early consumption of $Ca(OH)_2$ through pozzolanic reactions, which thus reduced the potential for the formation of gypsum and ettringite. The secondary C-S-H gel formed as a result of the pozzolanic reactions forms a coating on the alumina-rich and other reactive phases thereby hindered the formation of ettringite. The replacement of part of the cement by mineral constituent also reduced the $C_3A$ quantity. The mineral constituents in composite cements also made the microstructure denser, reduced the permeability and lowered the susceptibility of the paste to a sulfate attack.

Cements containing both burnt shale and blastfurnace slag had better sulfate resistance than cements with slag only, as can be seen from Figure 5.5.1.



| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| ■ Burnt shale Tt | 20 | 15 | 15 | 10 | 10 | 15 |
| ▥ Burnt shale Tk | 0 | 0 | 10 | 15 | 20 | 0 |
| ▭ Slag | 15 | 20 | 0 | 0 | 0 | 0 |
| ▨ Limestone | 0 | 0 | 0 | 0 | 0 | 10 |
| —◆— Relative expansion, mm/m | 0,61 | 0,55 | 0,5 | 0,59 | 0,46 | 0,94 |

Figure 5.5.1 Relative expansion of multicomponent Portland composite cements depending on cement composition

Composite cements containing both burnt shale and slag in various proportions (Σ 35 %) had expansion in the 4.4 % $Na_2SO_4$ solution lower than in the case of slag only. Both slag and burnt shale as constituents of cement have the property of formation geleous hydration products and decreasing pore diameter and thus increasing the sulfate resistance of cement.

The limestone addition for 10 % in the multicomponent composite cement limestone as inert filler deteriorated most of the physical and mechanical properties – sulfate resistance in conjuction with compressive and flexural strength, also frost resistance.

The influence of burnt shales $T_T$ and $T_K$ was found to depend on the proportion and total quantity of burnt shale constituent in cement. As both burnt shales had analogous expansions in the 4.4 % $Na_2SO_4$ solution, the sulfate resistance of CEM II/B-M ($T_K$ +$T_T$) cements improved with an increasing content of burnt shales ($T_K$ + $T_T$) irrespective of the proportion of these constituents. Although it was possible to improve physical-mechanical properties of CEM II/B-M ($T_K$ + $T_T$) cements by adding burnt shale $T_T$ to $T_K$, the high water demand of burnt shale $T_K$ was compensated and also compressive strength of cement mortars was increased.

As slag cement mortars with high slag content (50…70 % S) had very good sulfate resistance, but on the other hand presented very poor physical and mechanical values after sulfate storage, an additional composition of cement was researched to find out if it was possible to increase the physical and mechanical properties of slag cement by adding 20 % burnt shale $T_T$ into slag cement.

Good results were gained with composite cement CEM V/B (20 % $T_T$ + 50 % S), which satisfied the requirements for sulfate resisting cements - the relative expansion by the Wittekindt method was 0.38 mm/m. Also, strength parameters of these cements were much higher than those of CEM III (60 % S) (Table A9). Compressive strength increased steadily with time and it was 57.7 MPa at the age of one year. Unlike other tested composite cements, CEM V/B (20 % T + 50 % S) exhibited better performance in the 4.4 % $Na_2SO_4$ solution than in water. Both $E_d$ and compressive strength values were higher in the 4.4 % $Na_2SO_4$ solution than in water.

The SEM observation of composite cement CEM V/B (50 % S + 20 % $T_T$) in Figures 5.5.2...5.5.5 shows that the microstructure changed remarkably with the incorporation of slag and burnt shale $T_T$ compared to that of CEM III/A (60 % S) (Figures 5.4.5 and 5.4.6) or CEM II/A-$T_T$ (20 % $T_T$) (Figures 5.3.4…5.3.6). The main hydration product was cotton-shaped C-S-H gel.

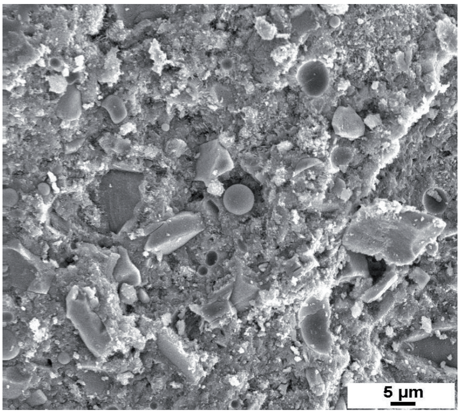


Figure 5.5.2 CEM V/B (50 % S + 20 % $T_T$) mortar cured for 14 days in the $Ca(OH)_2$ solution. The spherical particles of slag and burnt shale $T_T$ are observable.

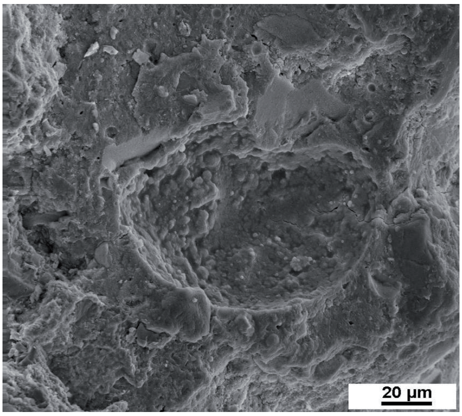


Figure 5.5.3 CEM V/B (50 % S + 20 % $T_T$) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. An air void. The cement stone is very dense.

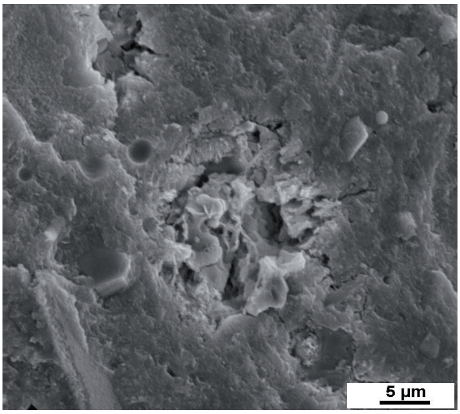


Figure 5.5.4 CEM V/B (50 % S + 20 % $T_T$) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. Air void filled with secondary reaction products.

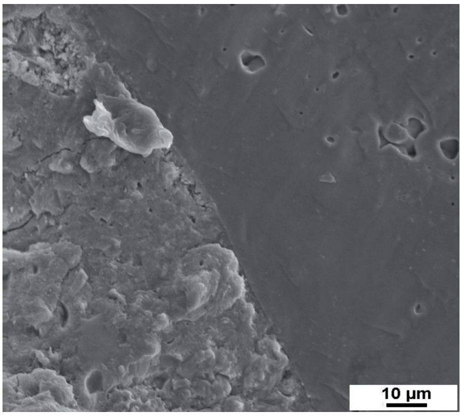


Figure 5.5.5 CEM V/B (50 % S + 20 % $T_T$) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. The paste-aggregate interfacial zone is tight.

Results showed that composite cement CEM V/B (50 % S + 20 % $T_T$) presented an excellent behavior in both short- and long-term compressive strength and in resistance to $Na_2SO_4$ solution (Table A9).

With incorporation of burnt shale $T_T$, slag and limestone, composite cement CEM II/B-M (20 % $T_T$ + 5 % S + 10 % L) was studied.

Multicomponent composite cement CEM II/B-M (20 % $T_T$ + 5% S + 10 % L) presented better behavior in both short- and long-term compressive strength and in resistance to $Na_2SO_4$ attack expressed as change in $E_d$ (Table A9) than CEM I or CEM II/A-L (10% L) and slightly lower values compared to CEM II/A-$T_T$ (20 % $T_T$).

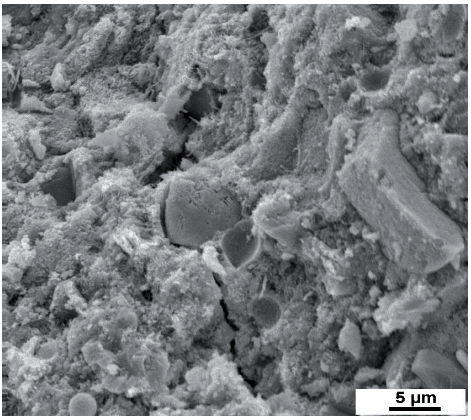


Figure 5.5.6 CEM II/B-M (20%$T_T$ + 5%S + 10%L) mortar cured for 14 days in the saturated $Ca(OH)_2$ solution.

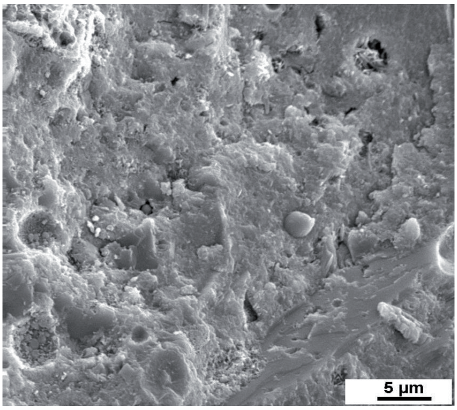


Figure 5.5.7 CEM II/B-M (20%$T_T$ + 5%S+10%L) mortar for 91 days in the saturated $Ca(OH)_2$ solution. Cement stone is coarse in spots. In every void the secondary products are growing.

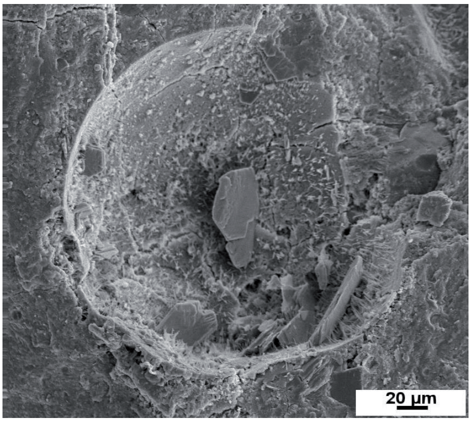


Figure 5.5.8 CEM II/B-M (20%$T_T$+ 5%S + 10%L) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. Near the surface large air voids are visible. Ettringite crystals are growing.

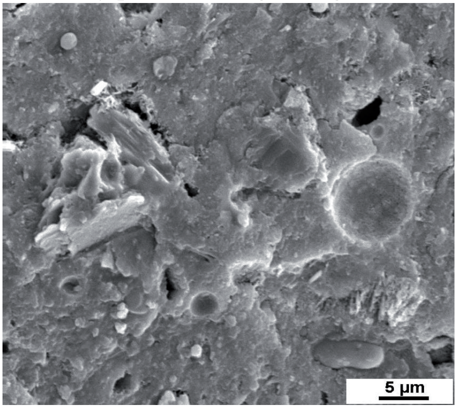


Figure 5.5.9 CEM II/B-M (20%$T_T$+ 5%S+10%L) mortar stored for 91 days in the 4.4 % $Na_2SO_4$ solution. The structure is uneven.

The high activity of slag and burnt shale $T_T$ with the limestone during the hydration mechanism is co-occurring, forming additional amounts of C-S-H. The presence of several constituents in the cement can improve the physical and mechanical properties by simultaneous reduction of the $Ca(OH)_2$ phase, $C_3A$ content in Portland cement and production of the C-S-H phase.

It can be concluded that incorporation of the combination of burnt shale and slag is one of the best ways to achieve a superior sulfate resistance and also to improve physical and mechanical properties of a composite cement.

## 5.6 Control testing with commercial cements

Systematic studies by Thorvaldson (1952) demonstrated that a high content of $C_3A$ can lead to the formation of ettringite and thus to expansion during sulfate attack on the hardened cement paste. The presence of $C_4AF$ in the unhydrated cement was found to be less detrimental due to lower reactivity. These observations led to the introduction of sulfate-resisting Portland cement with a low $C_3A$ content by Ferrari (Hewlett 1998). At present, the use of sulfate-resisting Portland cement is adopted in most guidelines for the production of concrete that is exposed to sulfate attack.

Besides laboratory made cements, 13 commercial cements were also tested to compare the Wittekindt sulfate resistance test results of the described laboratory made cements with acknowledged sulfate resisting cements from Finland, Sweden, Russia and Switzerland and most available commercial cements in Estonian market as industrial separator grinding produces cement with more homogeneous grain size and better homogenization.

Sulfate resisting cements have a low amount of $C_3A$ and $C_4AF$. Therefore, not much $Al_2O_3$ is available in the hardened cement paste produced from these cements and the formation of ettringite can be restricted. In contrast to this, sulfate resisting cements can be prone to the formation of gypsum.

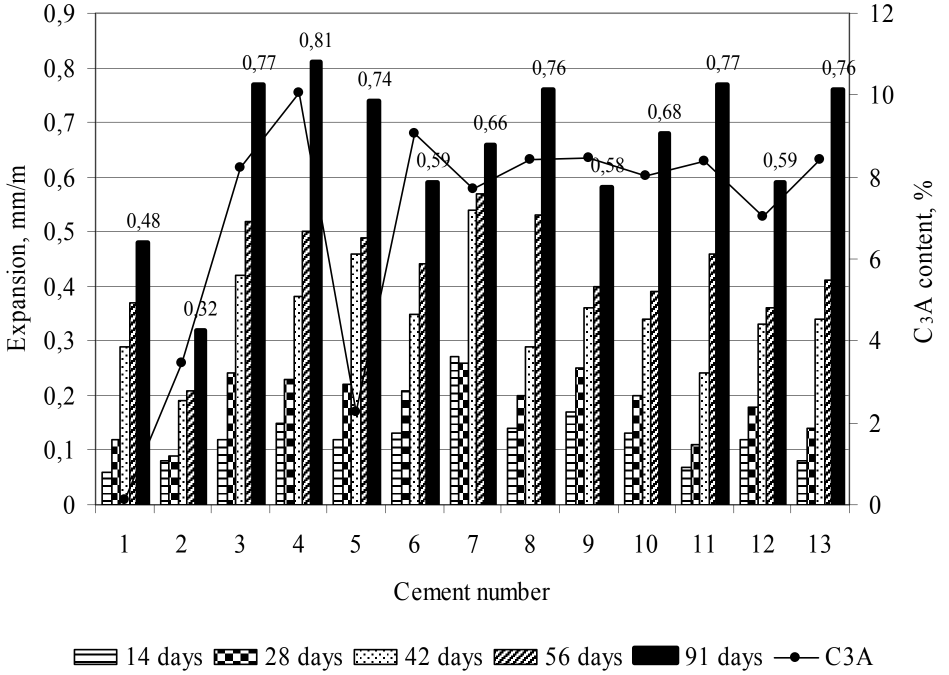
The sulfate attack depends on the availability of $Ca(OH)_2$ and $C_3A$ in the hydrated concrete, hence chemical composition of the cement has an important role in sulfate resistance.

Table 5.6.1 Chemical compositions of commercial cements

| | Cement | Specific surface, $m^2$/kg | Density, $g/cm^3$ | Chemical composition, % | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $SO_3$ | $C_3A$ | $C_4AF$ | $Al_2O_3$ | MgO | CaO |
| | | | | | | | | | |
| Commercial sulfate resisting cements: | | | | | | | | | |
| 1 | CEM I 42.5 HS | 408 | 3.14 | 2.93 | 0.13 | 19.79 | 4.22 | 3.10 | 59.30 |
| 2 | CEM I 42.5 SR/LA | 322 | 3.15 | 2.19 | 3.47 | 13.35 | 4.12 | 2.56 | 61.60 |
| 3 | CEM II A 52.5 R | 568 | 3.15 | 3.56 | 8.22 | 8.97 | 4.99 | 2.15 | 60.70 |
| 4 | CEM II A 42.5 R | 513 | 3.15 | 3.41 | 10.07 | 7.75 | 5.43 | 3.13 | 61.25 |
| 5 | CEM I 42.5 SR | 317 | 3.18 | 2.61 | 2.25 | 16.05 | 4.23 | 0.91 | 62.61 |
| Commercial cements made in Estonia: | | | | | | | | | |
| 6 | CEM II/B-T 42.5 R - 1 | 416 | 3.07 | 3.69 | 9.06 | 7.78 | 7.27 | 3.88 | 54.17 |
| 7 | CEM II/B-T 42.5 R - 2 | 358 | 3.07 | 3.57 | 7.71 | 8.06 | 6.82 | 4.36 | 54.02 |
| 8 | CEM I 42.5R - 1 | 467 | 3.15 | 3.26 | 8.42 | 10.41 | 4.90 | 3.70 | 60.00 |
| 9 | CEM II/B-T 42.5 R - 3 | 405 | 3.06 | 3.89 | 8.46 | 8.81 | 6.30 | 3.60 | 55.00 |
| 10 | CEM II/B-M 42.5R | 514 | 3.05 | 3.77 | 8.01 | 8.41 | 5.80 | 3.80 | 54.00 |
| 11 | CEM I 42.5R - 2 | 420 | 3.15 | 3.31 | 8.40 | 10.24 | 5.40 | 3.68 | 61.50 |
| 12 | CEM II/B-T 42.5 | 375 | 3.07 | 3.72 | 7.05 | 8.02 | 5.20 | 3.28 | 54.85 |
| 13 | CEM I 42.5 | 376 | 3.15 | 3.15 | 8.42 | 10.24 | 5.40 | 3.93 | 62.47 |

Modern cements are made for rapid development of strength, resulting in an increase in the $C_3S$ content in cement. This increase in $C_3S$ results in an increased $Ca(OH)_2$ content in the hardened cement, thereby enhancing the susceptibility to sulfate attack. Rasheeduzzafar (1992) reported that, in addition to the $C_3A$ content, the $C_3S/C_2S$ ratio of cement has a significant effect on the sulfate resistance of cements.

The most important chemical property reported in Table 5.6.1 is the $C_3A$ content of the cements. The requirements of EVS-EN 197-1:2011 are set on $C_3A$. In the case of CEM I, CEM I SR 0 specifies a maximum $C_3A$ content of 0 %, CEM I SR 3 specifies a maximum $C_3A$ content of 3 %, CEM I SR 5 specifies a maximum $C_3A$ content of 5 %. In the case of cement CEM III/B and CEM III/C, no requirements are set for $C_3A$ of the clinker. Also, for cements with pozzolana constituents to cement CEM IV/A, CEM IV/B, maximum $C_3A$ is 9 %. Cement No 4 with its 10.4 % maximum $C_3A$ content is considered unsuitable for sulfate environments.



1. CEM I 42.5 HS
2. CEM I 42.5 SR/LA
3. CEM II A 52.5 R
4. CEM II A 42.5 R
5. CEM I 42.5 SR
6. CEM II/B-T 42.5 R - 1
7. CEM II/B-T 42.5 R - 2
8. CEM I 42.5R - 1
9. CEM II/B-T 42.5R - 3
10. CEM II/B-M 42.5R
11. CEM I 42.5R - 2
12. CEM II/B-T 42.5
13. CEM I 42.5

Figure 5.6.1 Relative expansion values of commercial cements

Cement types that are evaluated are generally considered when choosing a cement for concrete in a sulfate environment. CEM I 42.5R, CEM II/B-T 42.5 R and CEM II A 52.5 R are high early strength cements. CEM I type cements usually have high $C_3A$ contents and are thus not suitable for moderate or severe sulfate environments. CEM II type is considered to be a moderately sulfate resisting cement.

Expansion rates varied significantly for each of the tested cement. The measured expansion values in the 4.4 % $Na_2SO_4$ solution and in the saturated $Ca(OH)_2$ solution are given in Table A10, the relative expansions in Figure 5.6.1. The relative expansions of different sulfate resisting cements $\Delta\varepsilon$ were 0.32...0.74 mm/m. The least expansion was observed with cement No 2 CEM I 42.5 SR/LA (with $C_3A$ content 3.47 %) – 0.32 mm/m and even after half a year storage the test specimens still exhibited no detectable damage. Utmost expansion was shown by cement No 5 CEM I 42.5 SR (with $C_3A$ content 2.25 %) – 0.74 mm/m and it was not able to fulfil the high sulfate resistance criterion of the rapid test method. In contrast to the expansions of the Portland cement mortars, the test specimens made with high sulfate resisting Portland cement expanded only slightly and were undamaged, even after longer storage in the sulfate solution.

As can be seen from the data, the criterion $\Delta\varepsilon \leq 0.50$ mm/m seems to be too strict and therefore in terms of sulfate resistance, based on the results obtained with other acknowledged sulfate resisting cements, the permitted expansion value should be increased or the testing time should be reduced to 56 days.

CEM I cements produced in Estonia had the expansions $\Delta\varepsilon$ of 0.66...0.76 mm/m, the expansions $\Delta\varepsilon$ of CEM II/B-T cements were 0.58...0.76 mm/m on the increase with decreasing specific surface. $\Delta\varepsilon$ of the composite cement CEM II B-M 42.5 R of 0.68 mm/m (main constituents clinker, burnt shale $T_T$ and fine limestone) was remarkably lower than the expansion of laboratory-made CEM II/B-M (15 % $T_T$ + 10 % L) – 0.94 mm/m (Table A1 and Figure 5.5.1). The difference may have resulted from the finer particle size of commercial CEM II B-M cement (514 kg/m$^2$) compared to laboratory CEM II B-M cement specific surface (380 kg/m$^2$).

Figure 5.6.2 presents the expansion values of three cements – CEM I, CEM II/B-T and CEM II/B-M. The difference is in the manufacturing form. The main constituents used – clinker, burnt shale $T_T$ and fine limestone – are the same. Commercial cements are produced in a plant, laboratory cements are ground in a laboratory ball mill. The manufacture on different grinding systems leads to different particle size distribution and fineness of cement and these influence the cement properties. As can be seen from Figure 5.6.2, in addition to chemical composition, the grinding technology influences substantially cement fineness properties, homogeneous particles size distribution, it thereby influences also sulfate resistance values.

From the limited data available on the subject, use of commercial cement (CEM I and CEM II/B-M) showed improved sulfate resistance, primarily attributed to finer and better particle size distribution that enhanced the reactivity and reduced the permeability in mortar.

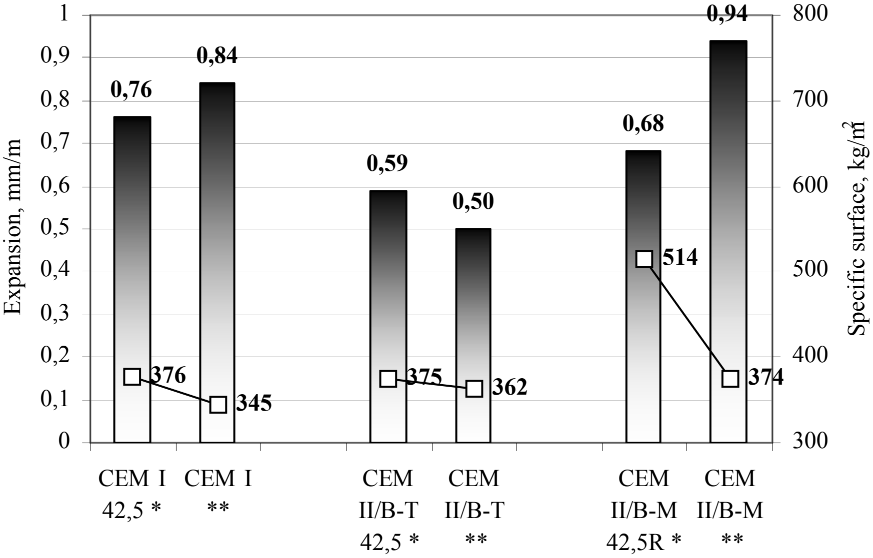


Figure 5.6.2 Comparative values of relative expansion of the Wittekindt test with commercial and laboratory made cements. * - commercial cement, ** - laboratory cement

The results showed lower levels of expansion on mortar prisms, as determined experimentally and an important retardation of the cracking process in the low $C_3A$ concrete specimen as compared to the high $C_3A$ content cement, suggesting a much higher resistance to external sulfate attack in the former case.

Lea (Hewlett 1998) stated that the resistance of Portland cements to attack by sulfate solutions is known to be related in a general way to their calculated $C_3A$ content, but there are many anomalies in this relationship. One reason is that the rate of cooling the clinker influences the morphology of the aluminate: if it is in glass form (amorphous), it is much less susceptible to attack by sodium or magnesium sulfate.

A high $C_3S$ content of cement corresponds to high $Ca(OH)_2$ concentration in the pore solution during hydration. High $Ca(OH)_2$ concentrations lower $C_3A$ solubility, forcing ettringite to form topochemically around the $C_3A$ grains. Thus, there is still some unhydrated $C_3A$ remaining after the paste had hardened. When this cement is placed in a sulfate environment, the interaction of sulfates with unreacted $C_3A$ would result in ettringite formation in the hardened paste.

It should be pointed out that the use of sulfate resisting cement alone will not guarantee the production of sulfate resisting concrete. Other factors are also involved and should be considered as their effect may outweigh the effect of cement on the sulfate resistance of concrete.

## 5.7 Resistance of cement mortars in 1.1 % $(NH_4)_2SO_4$ and 1 % $MgSO_4$ solution

The influence of the associated cation ($(NH)_4^{1+}$ and $Mg^{2+}$) on the mechanisms and manifestations of sulfate attack was examined by measurements of length change. The Wittekindt sulfate resistance testing method was used except instead of the 4.4 % $Na_2SO_4$ solution 1.1 % $(NH_4)_2SO_4$ and 1 % $MgSO_4$ solutions were used to study briefly if the test method is applicable also to testing cements in these sulfate environments. As the limit value of this test method is set only for the 4.4 % $Na_2SO_4$ solution, in $(NH_4)_2SO_4$ and $MgSO_4$ solutions the limit value was ignored.

With the selected cement compositions, the behavior of cements in 1.1 % $(NH_4)_2SO_4$ and 1 % $MgSO_4$ solution was studied. The list of tested cements and the results of measured expansion values are shown in Table A12. Table A13 presents the relative expansion values of cement mortars in 1.1 % $(NH)_4SO_4$ and 1 % $MgSO_4$ solution as the rate to expansion of prisms stored in the saturated $Ca(OH)_2$ solution (Table A1).

### *5.7.1 Resistance of cement mortars in 1 % $MgSO_4$ solution*

The level of deterioration observed in 1 % $MgSO_4$, in terms of the visually observed physical deterioration and the measured expansion, was not as high as in $Na_2SO_4$ or in $(NH_4)_2SO_4$ solutions.

Naik et al. (2006) demonstrated that with $MgSO_4$ the same phases observed under $Na_2SO_4$ exposure were identified, but that an additional thin brucite ($Mg(OH)_2$) layer was observed in the near-surface region. The most noticeable difference between the specimens exposed to $Na_2SO_4$ and $MgSO_4$ solution was the presence of a double layer, consisting of a nearer-surface layer of brucite followed by a gypsum layer at the surface of specimens exposed to $MgSO_4$ solution. The presence of the relatively impermeable surface layer of brucite accounts for the decreased penetration of the sulfate solution into the mortars (Santhanam et al. 2003). In parallel, C-S-H decomposes faster than in $Na_2SO_4$, because of the extremely low water solubility of $Mg(OH)_2$ and the low pH of the solution. Additional amounts of gypsum, brucite and magnesium silicate hydrate are also formed.

Variations in the results of the relative expansion of laboratory made Wittekindt flat prism specimens (as can be seen in Figure 5.7.1 and in Tables A12 and A13) is relatively low – 0.20...0.27 mm/m after 91-day storage in 1 % $MgSO_4$ solution. The cement mortars produced and tested by the Wittekindt test method had no direct correlation between the test results and cement compositions.

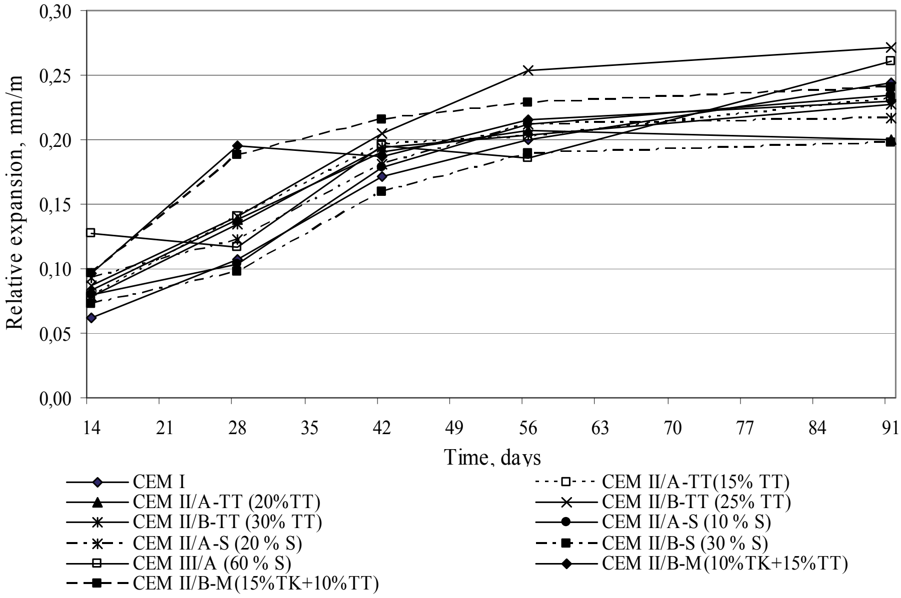


Figure 5.7.1 Relative expansion of cement mortar specimens (10 x 40 x 160) mm in 1 % $MgSO_4$ solution

Figure 5.7.1 shows the expansion behavior of the mortars, i.e., the rate of expansion was highest during the first 42 days of submersion, and then slowly leveled off during the last immersion period. As can be seen, the average expansion rate decreased steadily over time. The steady decrease in the rate of expansion may be explained by continued conversion of the $C_3A$ to ettringite compound and the buildup of sulfate reaction by-products, which typically occupy a greater volume than the compounds they replace, within the pores of the test specimens. The former process can effectively lower the permeability of the pore structures, thus restricting further permeation of the sulfate ions and limiting the potential expansion.

The highest relative expansion was observed with CEM II/B-$T_T$ (25% $T_T$) and CEM III/A (60 % S). It was concluded that burnt shale $T_T$ helps to resist the $Na_2SO_4$ attack, but aggravates the $MgSO_4$ attack. This phenomenon may be largely due to the possible conversion of C–S–H into M–S–H, which is non-cementitious.

The graph of relative expansion of sulfate resisting commercial cements in 1 % $MgSO_4$ is dissimilar to that of laboratory cements (Figure 5.7.2, Tables A12 and A13). Use of low $C_3A$ cements, which is considered to provide resistance to $Na_2SO_4$, can be detrimental when the solution contains $MgSO_4$ or $(NH_4)_2SO_4$.

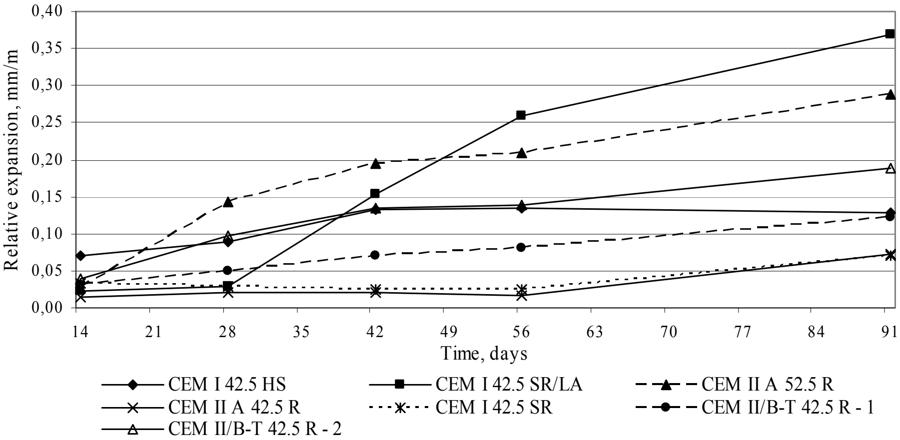


Figure 5.7.2 Relative expansion of commercial cement mortar specimens (10 x 40 x 160) mm in 1 % $MgSO_4$ solution

The highest relative expansion was observed with CEM I 42.5 SR/LA – 0.37 mm/m (with $C_3A$ content 3.47 %). This cement exhibited the best sulfate resisting properties as the least expansion in $Na_2SO_4$ solution, but like in $MgSO_4$ it had insufficient effect also in $(NH_4)_2SO_4$ solution. The lowest relative expansion in 1 % $MgSO_4$ was found in cements CEM II A 42.5 R and CEM I 42.5 SR.

From visual examination, it was clear that mortar specimens stored in a $MgSO_4$ solution behaved very differently from those exposed to a $Na_2SO_4$ solution with respect to the form and degree of deterioration. Mineral constituents are more likely to have a beneficial effect towards $Na_2SO_4$ than towards $MgSO_4$ solutions. Inferior resistance to attack by $MgSO_4$ solution by composite cements, as compared with Portland cement CEM I, may be attributed to the lower content of $Ca(OH)_2$, which through being attacked protects the C-S-H from attack. In a disintegrating weak cement stone due to magnesia corrosion, the expansion is nonexistent.

### *5.7.2 Resistance of cement mortars in 1.1 % $(NH_4)_2SO_4$ solution*

In the case of ammonium sulfate, the behavior of mortar specimens in a sulfate solution was visibly divided into two stages. The first stage, also referred to as the induction period during which $SO_4^{2-}$ ions penetrate into the specimen, was characterized by relatively minor changes in length. At the beginning of the second stage, when the core of the specimens was attacked by sulfate, the expansion increased rapidly and the same rate of expansion was maintained until failure. This was due to the fact that expansion was measured on the center axis of the prisms.

The sulfate reacts with $Ca(OH)_2$ of the paste, resulting in gypsum and the release of gaseous ammonia NH3↑. This reaction takes place until $Ca(OH)_2$ is completely consumed, resulting in a decrease of the existing pH. Concurrently, $(NH_4)_2SO_4$ reacts also with C-S-H, causing initially a decrease of the C/S ratio and a conversion of this phase to amorphous hydrous silica. Due to lowering of the pH, the present AFm and AFt become unstable and convert to gypsum and aluminum sulfate (Skalny et al. 2002).

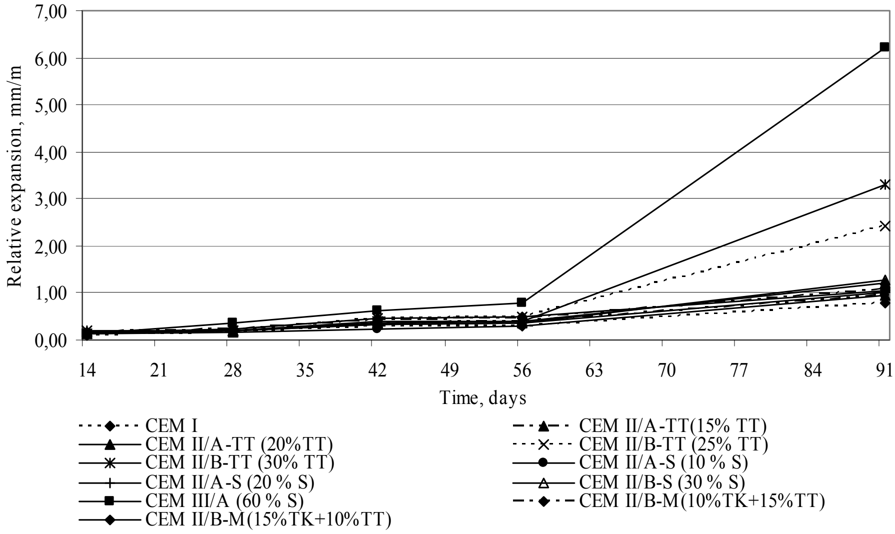


Figure 5.7.3 Relative expansion of cement mortar specimens (10 x 40 x 160) mm in 1.1 % $(NH_4)_2SO_4$ solution

As can be seen from the data of Figure 5.7.3 and Table A13, the degradation of cement stone by $(NH_4)_2SO_4$ is more severe than by $Na_2SO_4$ or by $MgSO_4$.

The lowest expansion (0.78 mm/m) in 1.1 % $(NH_4)_2SO_4$ was observed with CEM I cement, so the results are entirely opposite to those gained in the 4.4 % $Na_2SO_4$ solution.

The specimens of cements CEM II/B-$T_T$ (25% $T_T$), CEM II/B-$T_T$ (30% $T_T$) and CEM III/A (60 % S) started to decompose rapidly after 56 days of storage in $(NH_4)_2SO_4$ solution. The specimens were cracked, expanded massively and curved.

The addition of slag in cement for 60 % had a detrimental effect on the performance during exposure, as measured by length change. This result was unexpected, as the pozzolanic effect of the slag was expected to make the mortar more resistant to sulfate attack by reducing the amount of free $Ca(OH)_2$ available for reaction with the sulfate ions. The poor performance of the slag cements could be attributed to the longer curing time required to achieve full hydration, or to the chemical composition of the slag itself and also the decrease of the existing pH release of gaseous ammonia $NH_3$.

Similarly to slag, burnt shale $T_T$ expanded detrimentally. The expansion increased substantially when more than 20 % $T_T$ was added to cement.

Burnt shale $T_K$ had much lower expansion compared to other constituents. The total quantity of burnt shale ($T_K + T_T$) in both tested CEM II/B-M cements was 25 %. While the relative expansion of CEM II/B-$T_T$ (25 % $T_T$) after 91 days of storage in 1.1 % $(NH_4)_2SO_4$ was 2.43 mm/m, the expansion values of CEM II/B-M (10 % $T_K$ + 15 % $T_T$) and CEM II/B-M (15 % $T_K$ + 10 % $T_T$) were 1.07 mm/m and 1.04 mm/m, respectively.

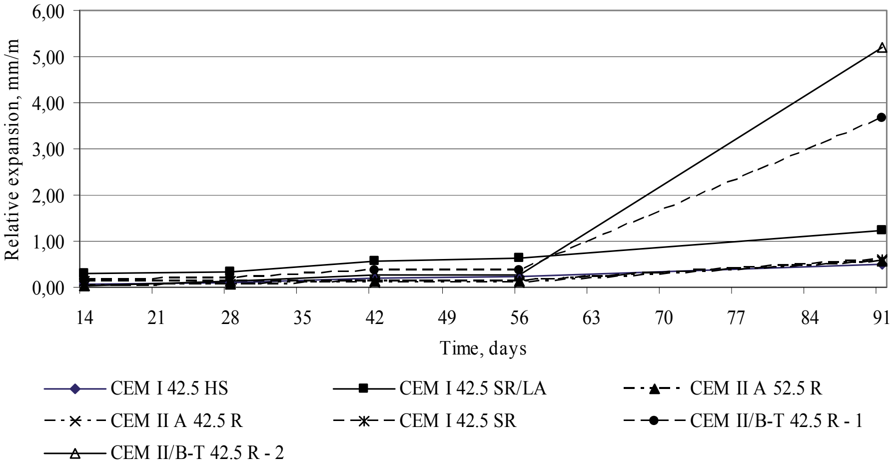


Figure 5.7.4 Relative expansion of commercial cement mortar specimens (10 x 40 x 160) mm in 1.1 % $(NH_4)_2SO_4$ solution

Figure 5.7.4 displays the relative expansion behavior of the mortar flat prisms of commercial cements. Cements CEM II/B-T 42.5R-1 and CEM II/B-T 42.5R-2 had the shortest induction period of approximately 56 days. After that they started to expand and finally decomposed. As both of them were composite cements with burnt shale $T_T$ as second constituents, the behavior of these cements was comparable with laboratory made CEM II/B-$T_T$. Higher expansion developed also sulfate resisting CEM I 42.5 SR/LA cement, which contains fine limestone and had 91-day relative expansion of 1.23 mm/m. The other four sulfate resisting cements behaved similarly and the 91 days relative expansions were 0.49…0.59 mm/m.

The Wittekind test method is not suitable for testing cements for assessing their resistance in $MgSO_4$ or in $(NH_4)_2SO_4$ solution. As revealed from the results, decent outcome was obtained only with some sulfate resisting cements. The results were relatively satisfactory also with Portland cement CEM I. But all composite cements that contained mineral constituents failed the test. The higher the slag, burnt shale $T_T$ or limestone content in the cement, the larger was the destruction of specimens. Also, the results were completely opposite to common knowledge and practice in terms of sulfate resistance of cements.

## 5.8 Section summary and conclusions

The relative performance of different cements was assessed by laboratory investigations of sulfate resistance by the Wittekindt method. The measurement of length gain can be related to the bulk expansion of the samples, as distinct from weight loss, which is more associated with surface effects.

The maximum deterioration was noted in the Portland cement CEM I mortar specimens made with Portland cement clinker with a 8.6 % of $C_3A$ content. The visual examination of the specimens during the exposure also revealed considerable deterioration in the form of cracking. Slight changes in clinkers and composition parameters of cements significantly affected the potential expansion and the strength, thus the behavior of the mortar. The capability of higher absorption of sulfate ions into Portland cement mortar specimens compared to that of composite cement mortar specimens may explain the severe deterioration of CEM I. Expansion, spalling and mass loss were characterized as the degradation process of CEM I mortars by sodium sulfate attack. The poor resistance of CEM I to $Na_2SO_4$ attack was due to the presence of large pores and free $Ca(OH)_2$ in the cement paste. The formation of ettringite and gypsum in the 4.4 % $Na_2SO_4$ solution was confirmed both by XRD and SEM results. Portland cement occupied significantly different pore size distribution compared to composite cements. CEM I paste had a large amount of small capillary pores with sizes ranging from 0.01 to 0.1 μm of which 0.01 to 0.05 μm size pores were easily prone to damage by sulfate solution.

Lower expansion in composite cements was attributed to the early consumption of $Ca(OH)_2$ through pozzolanic reactions, which thus reduced the potential for the formation of gypsum and ettringite. The secondary C-S-H gel formed as a result of the reactions formed a coating on the alumina-rich and other reactive phases, thereby hindering the formation of ettringite. The mineral constituents in composite cements made the microstructure denser, reduced the permeability and lowered the susceptibility of the paste to sulfate attack.

The test results obtained in this study, emphasized the negative effect of 10…30 % fine limestone replacement of CEM I cement on the resistance of mortar specimens when they were subject to sodium and magnesium sulfate attack at ambient temperature. It was especially clearly observed from the visual inspection that the mortar specimens with higher replacement levels of fine limestone suffered more pronounced deterioration in both sulfate solutions, as compared to other composite cements. Limestone addition propagated the rate of sulfate deterioration possibly due to relatively lower strength and increased capillary water absorption properties. For this reason, it can be advised that the limestone replacement ratio of cements should be restricted to 5 % by weight for concrete exposed to sulfate environments. Portland limestone cements were found more susceptible to sulfate attack and less durable than the corresponding

Portland cement, as indicated by their larger expansions, greater surface deterioration, greater deposition of gypsum, and higher degree of $Ca(OH)_2$ depletion.

Portland high temperature burnt shale $T_T$ cements had high sulfate resistance if they contained at least 20 % by mass of burnt shale $T_T$. The initial expansion and expansion in $Ca(OH)_2$ solution were high in Portland burnt shale $T_T$ cements and increased with increasing burnt shale $T_T$ content in cement, caused mainly by hydration of $CaO_{free}$ derived from burnt shale $T_T$. SEM images showed a slight formation of gypsum crystals near cracks, ettringite crystals within the air void near the outer side of the specimen. The structure was dense, most air voids were found to be filled with the reaction products. Compared to the CEM I mortar, the content of large capillary pores was decreased by adding 20 % of burnt shale $T_T$, medium capillary pores were finer and the content of gel pores was higher, therefore sulfate resistance was higher. The results of $E_d$ and compressive strength after one-year storage in 4.4 % $Na_2SO_4$ confirmed the good performance of Portland burnt shale $T_T$ cement mortars in $Na_2SO_4$ solution.

The low temperature burnt shale $T_K$ is a relatively new by-product and its influence on the concrete durability is not yet known. Tests with mortars where burnt shale $T_K$ was used as a constituent of Portland composite cement revealed promising properties of such cement. Burnt shale $T_K$ improved sulfate resistance considerably. After 91-day storage in the 4.4 % $Na_2SO_4$ solution the relative expansion of Portland burnt shale $T_K$ cements exceeded slightly the limit value. Sulfate resistance was increased with an increasing content of burnt shale $T_K$ in cement. SEM images revealed a very dense structure of Portland burnt shale $T_K$ cement. Large air voids were partly filled with, and smaller voids were filled up with ettringite, gypsum and hydration products. Higher percentage of macropores was detected. Increasing water demand of Portland burnt shale $T_K$ cements increased the amount of capillary pores.

Despite the variable mineralogical compositions of used slags, sulfate resistance of cements was improved. Slag in amounts of 20…30 % did not considerably affect the sulfate resistance of cement. The relative expansions of Portland slag cements exceeded the limited value of the Wittekindt test method. Slag at a replacement level of 50…80 % definitely increased the sulfate resistance of CEM III cements in comparison to the CEM I, as indicated by considerably lower expansion. The microstructure was dense, but uneven, and no ettringite and a small portion of gypsum could be observed by SEM. The amount of formed C-S-H and of $Ca(OH)_2$ was reduced. Slag cement paste had very narrow pores. Most of the pores were gel pores, air voids were empty and not filled with reaction products. The good performance at high slag levels is due largely to the low permeability.

Multicomponent Portland composite cements with different constituents enabled the effect of positive characteristics to be enlarged and negative effects of cement constituents to be compensated, hence the durability of the mortar and the concrete was improved. Cements containing both burnt shale and blastfurnace slag had better sulfate resistance than cements with slag only, as both have the property of forming geleous hydration products and decreasing pore diameter and thus increasing the sulfate resistance of cement and also improving physical and mechanical properties. By combining burnt shales in CEM II/B-M ($T_K + T_T$) cements it was possible to improve sulfate resistance and physical-mechanical properties of these cement mortars.

The Wittekindt flat prisms method could be used for assessing sulfate resistance of different commercial cements. Test specimens made with high sulfate resisting Portland cement expanded only slightly and were undamaged, even after longer storage in the sulfate solution. The resistance of cements to sulfate attack was higher with the lower content of $C_3A$ in Portland cement. The results of sulfate resistance testing of commercial Portland cements and Portland composite cements were comparable with the results of sulfate resistance of laboratory made cements.

Test results affirmed that the Wittekind test method is not suitable for testing cements for assessing their resistance in $MgSO_4$ or in $(NH_4)_2SO_4$ solution, as was also reported by Locher (1998). As revealed from the results, decent outcome was obtained only with some sulfate resisting cements. The results with Portland cement CEM I were also relatively satisfactory. But all the composite cements that contained mineral constituents failed the test. The higher the slag, burnt shale $T_T$ or limestone content in cements, the greater was the destruction of specimens. Also, the results were completely opposite to common knowledge and practice in terms of the sulfate resistance of cements.

In the present study at high sulfate solutions, gypsum was detected to be present in all samples. The Wittekindt test conditions used here do not represent real situations of sulfate exposure under field conditions where lower sulfate concentrations are present. At low sulfate concentration, gypsum is rarely observed.

XRD data showed that with the content of high volumes of burnt shales $T_K$ and $T_T$ or slag, the peak intensity of $Ca(OH)_2$ was retarded and free $SiO_2$ peaks appeared in the cement paste containing $T_K$ denoting a certain amount of free $SiO_2$ in $T_K$. This was more pronounced at later age (91 days after storage in the 4.4% $Na_2SO_4$ solution). CEM II/A-$T_T$ (20% $T_T$) and CEM III/A (60 % S) showed the highest consumption of $Ca(OH)_2$. The reduced intensity of $Ca(OH)_2$ is due to the loss of clinker content and the additional hydration products.

According to the above results, the extent of sulfate attack is considerably influenced by the cement chemistry, the sulfate cation type, the solution exposure period, and the pore size distribution of the materials.

# 6. Testing of hardened concrete

In real field exposure, the damage of concrete structures often occurs due to a multitude of mechanisms (chemical, physical and structural). Thus, there is a need to test multiple damage mechanisms to improve the understanding of their combined effects on concretes. Much research has been conducted on the deterioration of cement-based materials under external sulfate attack. However, little research has been done on the combined effects of external sulfate attack with other damage mechanisms.

Most concrete structures are under the complex stress state. The damage-coupled failure criterion can indicate the influence of damage evolution on the failure surface of concrete. Concrete exposed to sulfate solutions can be attacked and may suffer deterioration to an extent dependent on the concrete constituents, the quality of the concrete in place and the type and concentration of the sulfate.

In the previous section, the behavior of cements with different compositions by means of properties of cement stone and mortar was studied. Testing concrete for sulfate resistance is a very long-term process – valid results are expected in more than ten years. Therefore, in the current study sulfate resistance is analyzed on the basis of testing of mortars. On the other hand, it is worth examining the properties of concrete made with tested cements, as sulfate resistance is substantially related to strength parameters, water and frost resistance of concrete. In this section an overall picture of durability properties of concrete is examined.

Table 6.1.1 Properties of aggregates used for making concrete

| Sieve aperture, size mm | Sand | | Granite crushed stone | | | |
|---|---|---|---|---|---|---|
| | 0/4 | | 2/8 | | 8/16 | |
| | Bulk density, Mg/m$^3$ | | | | | |
| | 1.58 | | 1.39 | | 1.38 | |
| | Particle size distribution | | | | | |
| | Retained material, % | Cumulative material passed, % | Retained material, % | Cumulative material passed, % | Retained material, % | Cumulative material passed, % |
| 31.5 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 |
| 16 | 0.0 | 100.0 | 0.0 | 100.0 | 15.0 | 85.0 |
| 8 | 0.0 | 100.0 | 6.7 | 93.3 | 74.4 | 10.6 |
| 4 | 4.3 | 95.7 | 51.3 | 42.1 | 9.6 | 1.0 |
| 2 | 13.0 | 82.7 | 30.8 | 11.3 | 0.8 | 0.2 |
| 1 | 21.6 | 61.0 | 6.4 | 4.9 | 0.0 | 0.2 |
| 0.5 | 27.3 | 33.8 | 1.5 | 3.3 | 0.0 | 0.2 |
| 0.25 | 21.6 | 12.1 | 0.9 | 2.4 | 0.0 | 0.2 |
| 0.125 | 10.8 | 1.3 | 0.8 | 1.7 | 0.0 | 0.2 |

Fresh concretes with the same workability were made with cement content 320 kg/m$^3$ and 450 kg/m$^3$ using granite #2/8, #8/16 as a coarse aggregate. The fine aggregate was natural sand. The properties of aggregates are given in Table 6.1.1.

Concrete mix proportions were established on the basis of small trial batches to verify target slump of 50 to 80 mm. Target slumps were maintained with water-cement ratios allowed to vary. The amount of water added during concrete production has a serious impact on its workability. Later on, much of the mixing water is consumed in chemical reactions with the cement; the remainder still being in the liquid state is enclosed in the microstructure. The remaining water is directly responsible for the porosity of the hardened cement paste affecting mechanical and transport properties of concrete (Stark 2011).

In addition to cement stone properties, durability factors of various concrete compositions depend on the properties of the coarse aggregate. Granite has low water absorption up to 0.5 % while limestone has water absorption of about 2 % and more. High water absorption of limestone aggregate causes an obvious decrease in the frost resistance, despite the cement used. Based on the test results with limestone containing cements it may be asserted that an analogical situation occurs in the case of an inert second main constituent, i.e. limestone, as a constituent of Portland cement. Therefore, this thesis discusses the results of concretes made with granite as coarse aggregate to emphasize the comparable behavior of cements and eliminate the faults caused by aggregate damage.

Concretes were made with air entraining admixture REBAlit LP so that the air content was 5.5…6.5 %. Based on the analysis of their test data, Santhanam et al. (2003) assumed that air entrainment did not affect considerably the concrete properties except the freeze-thaw resistance. Their research indicated that the disintegration of air-entrained concrete was delayed compared to the nonair-entrained Portland cement concrete, although in terms of the physical properties and chemical analyses (amount of attack products forming), the two concretes were not much different. The entrained air voids provide sites for nucleation for the attack products, which leads to a reduced distress in the paste. Air voids can also help in arresting the growth of cracks due to their spherical shape.

Specific data for the mix designs and properties of the fresh concretes are given in Table 6.1.2.

Table 6.1.2 Properties of fresh concrete with various Portland cements

| Cement | Cement content 320 kg/m$^3$ | | | | Cement content 450 kg/m$^3$ | | | |
|---|---|---|---|---|---|---|---|---|
| | W/C ratio | Density, kg/m$^3$ | Slump, cm | Air content, % | W/C ratio | Density, kg/m$^3$ | Slump, cm | Air content, % |
| CEM I | 0.58 | 2360 | 5.0 | 5.7 | 0.49 | 2360 | 8.0 | 5.4 |
| CEM II/A - 10 L | 0.57 | 2410 | 5.0 | 5.5 | 0.46 | 2420 | 5.0 | 5.8 |
| CEM II/A - 15 $T_K$ | 0.61 | 2370 | 6.5 | 5.7 | 0.51 | 2370 | 7.5 | 6.4 |
| CEM II/B - 25 $T_K$ | 0.63 | 2360 | 6.0 | 6.1 | 0.53 | 2350 | 8.0 | 6.5 |
| CEM II/B - 25 $T_T$ | 0.51 | 2410 | 5.0 | 6.2 | 0.41 | 2440 | 6.5 | 6.0 |
| CEM I+10$T_K$+15$T_T$ | 0.54 | 2400 | 6.0 | 5.5 | 0.44 | 2420 | 6.5 | 5.8 |
| CEM I+15$T_K$+10$T_T$ | 0.56 | 2420 | 5.5 | 5.5 | 0.46 | 2420 | 7.0 | 5.6 |
| CEM I+20$T_K$+10$T_T$ | 0.57 | 2410 | 6.0 | 5.5 | 0.47 | 2410 | 8.0 | 5.7 |
| CEM III - 70 S | 0.59 | 2390 | 6.0 | 6.3 | 0.49 | 2390 | 8.0 | 5.5 |

All concrete mixtures were mixed in a concrete mixer, following the procedures recommended by EVS-EN 480-1. Specimens were cast in the cubical moulds (150 x 150 x 150) mm and (100 x 100 x 100) mm used for compressive strength testing. The fresh mixes were consolidated by vibration (5…7 s on a vibrating table). The surface of the concrete was then smoothed and covered until the specimens were demoulded after 24 h in moulds at relative humidity > (95 ± 5) % and at the temperature (20 ± 2) °C. Hardening of concrete cubes took place at RH (95 ± 5) % at (20 ± 2) °C. The air contents were measured using the pressure method according to EVS-EN 12350-7. The strength measurements of concrete were performed at the ages of 2, 7, 28 and 91 days. Three specimens from each mixture were tested at each testing age.

To obtain equal slump, the w/c was varied. The increase in amount of cement in concrete from 320 kg/m$^3$ to 450 kg/m$^3$ decreased the water demand for gaining the same workability. Limestone content reduced the water demand. Burnt shale $T_T$ reduced considerably the water demand. Slag and burnt shale $T_K$ in cement increased the water demand of concrete. The reduction in w/c ratios may contribute to the increased strength and enhanced durability of the concrete structures.

## 6.1 Compressive strength of concrete

Compressive strength tests were performed to confirm the concrete strength. Strength indicates how well stress can be dissipated within the microstructure before macrocracks begin to form.

The results of compressive strength tests at the age of 2, 7, 28 and 91 days are given in Table A14. Figures 6.1.1 and 6.1.2 represent relative compressive strength values of composite cements compared to CEM I.

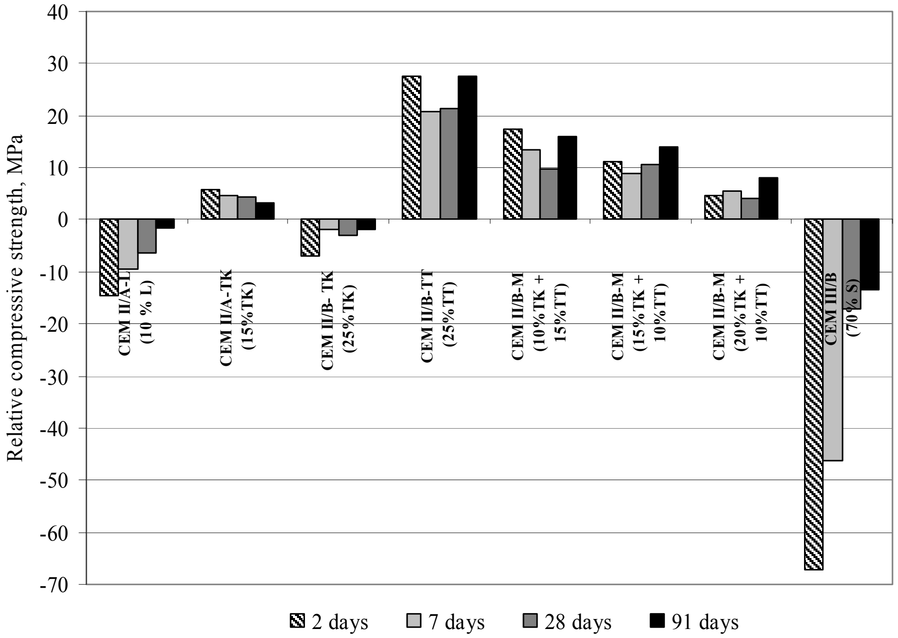


Figure 6.1.1 Relative compressive strength of concrete compared to CEM I (Cement content in concrete 320 kg/m$^3$)

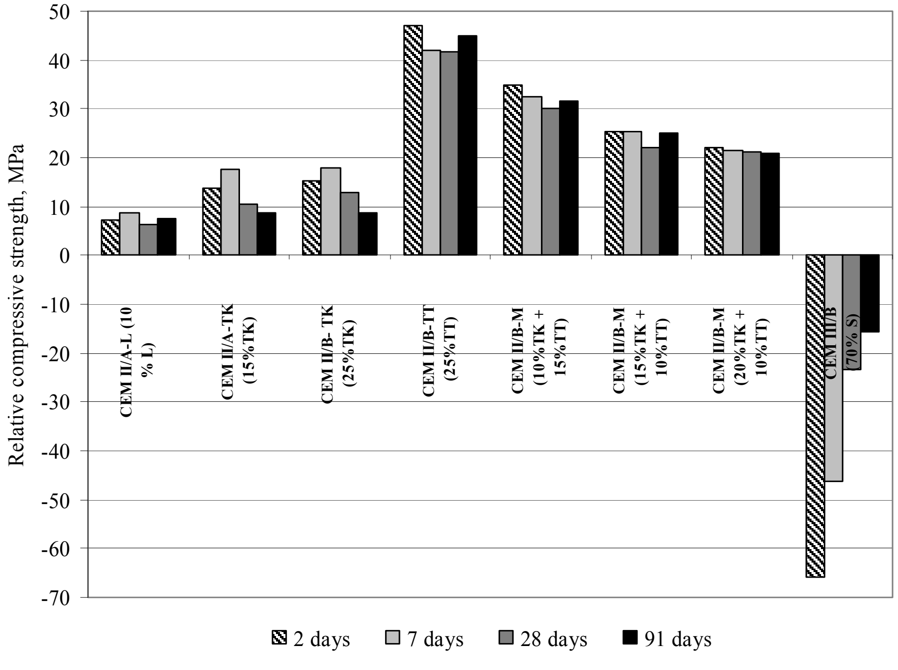


Figure 6.1.2 Relative compressive strength of concrete compared to CEM I (Cement content in concrete 450 kg/m$^3$)

Limestone addition of 10 % reduced the compressive strength of concrete if the cement content in concrete was 320 kg/m$^3$ at all ages. CEM II/A-L (10 % L) had relatively lower strength at an early age – 2 days: compressive strength (22.3 MPa) was 15 % lower than CEM I (26.1 MPa). With time the difference with CEM I diminished but the 91-day strength was still lower than that of CEM I by 2 % (46.9 MPa). In contrast, the strength of concrete with CEM II/A-L (10 % L) with a higher cement content (450 kg/m$^3$) was higher than the CEM I at all ages, even at the age of two days, constituting 7 % (32.1 MPa). The ratio to CEM I remained the same at all ages. 91-day strength was 58.2 N/mm$^2$ (7 % higher than CEM I – 54.2 MPa). This dissimilarity can be explained by different rheology of Portland limestone cement and decreased water demand compared to CEM I.

The addition of low temperature burnt shale $T_K$ for 15 % and 25 % revealed that compressive strength of concrete with burnt shale $T_K$ was in general the same as CEM I. With lower cement content (320 kg/m$^3$), increasing the content of burnt shale $T_K$ 15...25 % in cement the strength of the concrete was reduced, especially at 2 days by 3.3 MPa. With higher cement content (450 kg/m$^3$), concrete increasing the content of burnt shale $T_K$ 15...25 % in cement, no influence on the strength of concrete was observed. The relative strength of concretes with burnt shale $T_K$ cements was higher at early ages and it diminished with time. The results are in correlation with cement strengths (Table 4.1.1). As paste water demand of burnt shale $T_K$ cements was notably higher (35.5... 36.8 %) than with any other constituent, it had also an effect on the concrete and concrete made with CEM II/A-$T_K$ (15 % $T_K$) and CEM II/A-$T_K$ (25 % $T_K$) had higher w/c, the higher water content decreased the strength of concrete.

The concrete mixes containing high temperature burnt shale $T_T$ developed strength faster than the mixes containing burnt shale $T_K$ or Portland cement concrete. The higher strength of Portland burnt shale $T_T$ cement concrete may partly derive from the water reducing effect of burnt shale $T_T$. With lower cement content (320 kg/m$^3$), concrete CEM II/B - $T_T$ (25 % $T_T$) had 2 day compressive strength 27 % (33.3 MPa) and 91-day strength 38 % (65.8 MPa) higher than CEM I. With higher cement content (450 kg/m$^3$) concrete, the differences were even enlarged – 2-day strength - 48 % (44.0 MPa) and 91-day strength - 45 % (78.5 MPa) higher than CEM I.

Concrete with slag cement CEM III/B (70 % S) showed an enormous decrease in the early strength. Compared to CEM I it had only 32 % of CEM I concrete strength. The low early strength caused also the decline of frost resistance of slag cements. With time the slag concrete gained more sufficient strength and 91-day compressive strength was only 13…15 % lower than the compressive strength of CEM I.

Concretes with multicomponent composite cements with burnt shales ($T_T$ + $T_K$) exhibited satisfactory strength results. Compressive strength decreased linearly depending on burnt shale $T_K$ content in cement. With increasing content of burnt shale $T_T$ the compressive strength increased.

## 6.2 Frost resistance of concrete

In many parts of the world, the air temperature multiple or alternate passes through 0 °C and stays at freezing temperatures for long periods. In many regions with freezing temperatures, de-icing agents are used on road surfaces and pavements for safety reasons. However, by using de-icing agents on or near concrete surfaces, a special type of frost action is created. This frost action may lead to salt-frost damage or what is known as scaling of the concrete surface. However, the most serious effect of scaling is that it also opens up a path for other degradation mechanisms, such as reinforcement corrosion. Micro-cracks in the surface layer lead to more rapid ingress of water, salt and sulfates, as well as to higher rates of carbonation.

The degradation of concrete is usually the result of combined action of several deterioration mechanisms. Therefore, the behavior of the concrete subjected to the combined action of two deterioration mechanisms – frost and sulfate - was also studied.

In order to study the influence of damage evolution on the failure surface of concrete, frost resistance to alternate freezing and thawing was tested in distilled water and 3 % NaCl solution. Frost durability was assessed as a surface property. The scaling resistance is related to the quality of the concrete on the surface. The scaling can be enhanced when NaCl is used due to an expansion resulting from precipitation of Friedel's salt; the crystallization pressure from the growth of these crystals causes significant expansion of the paste, and results in high stresses on a local scale near the ice/paste boundary (Glinicki and Zielinski 2009).

A laboratory-testing program was conducted with mixtures with w/c varying from 0.41 to 0.59 at air content levels of 5.4…6.5 %. These tests were intended to determine the effects of variations in the properties of concrete on the freeze-thaw resistance, and were useful in making comparisons of the behavior of several cements. The results are presented in Table A15 and after 56 cycles in Figure 6.2.1.

The salt frost scaling of concrete depends to a great degree on the air void system created in the concrete. More or less the same air-void content was observed in concretes, but the frost resistance differed much depending on cement composition.

Scaling resistance decreases, i.e. frost resistance increases as the amount of certain second constituents in cement increases.

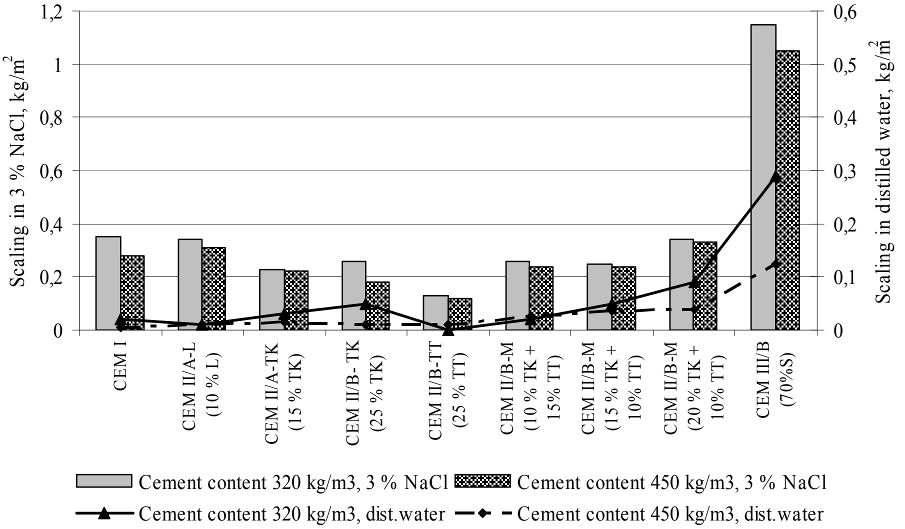


Figure 6.2.1 Scaling of concrete in 3 % NaCl and in distilled water after 56 cycles

Salt frost scaling increased with time for all tested concretes.

It was investigated how the tested CEM II and CEM III concretes approved in different countries perform during the test method according to EVS 814 as compared to the corresponding Portland cement (CEM I) concrete. The EVS 814 correlates the scaling potential with the collected mass loss per unit area. It is suggested that scaling of less than 1.0 kg/m$^2$ after 56 freeze-thaw cycles in the presence of deicer salts indicates that the concrete has an acceptable scaling resistance.

CEM III/B – (70 % S) showed scaling on the surface even after the first 7 cycles. Salt frost scaling increased with large amounts of slag compared with the corresponding scaling of Portland cement concrete. The result corresponds with the outcomes of Boubitsas and Paulou (2000) research. This can probably be explained by the relatively slow hydration process for these concrete qualities indicated in this investigation by the slow development of compressive strength. Also, Afrani and Rogers (1994) addressed two potential reasons for the increased amount of scaling residue in slag concretes; the early finishing before the bleeding has stopped due to the late set of slag concrete which may form a weak layer with a high w/c ratio so close to the surface, and not enough curing duration due to a lower hydration of slag concrete at normal temperature.

Concretes with burnt shales $T_T$ and $T_K$ showed less scaling on their surface than the CEM I. Frost resistance of concretes made with burnt shale $T_K$ was lower than that of burnt shale $T_T$. The burnt shale $T_T$ used in the same proportions (25 %) caused substantially lower material loss (Fig. 6.2.1). Burnt shale $T_K$ content higher than 15 % caused a decrease in the frost resistance of concrete as scaling in distilled water increased. The hydraulic type of the second main constituent burnt shale $T_T$ had an increasing influence on the frost resistance in contrast to the pozzolanic burnt shale $T_K$ or inert limestone constituent.

The results of concrete with limestone containing cement CEM II/A-L (10 % L) were consistent with those reported in the literature at lower limestone levels (Sprung and Siebel 1991). With an increasing content of Portland limestone cement in concrete the frost resistance decreased.

The deterioration due to freezing and thawing was also substantially related to the permeable porosity of concrete, as cements with total porosity lower and pore size distribution more beneficial demonstrated better frost resistance of concrete except the concrete with slag cement. Frost resistance was also strongly influenced by the strength of concrete.

The simultaneous influence of sulfate attack and frost resistance on concrete was investigated. Preparation of specimens and testing was accomplished according to EVS 814 except the $Na_2SO_4$ solution was used as a freezing solution. Test specimens subjected to freeze–thaw cycles in 2.2 % and 4.4 % $Na_2SO_4$ solutions were investigated. The results are given in Table 6.2.1.

Table 6.2.1 Frost resistance of concrete in $Na_2SO_4$ solutions

| Cement content 320 kg/m$^3$ | Scaling (kg/m$^2$), after cycles | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 4.4 % $Na_2SO_4$ | | | | | 2.2 % $Na_2SO_4$ | | | | |
| | 7 | 14 | 28 | 42 | 56 | 7 | 14 | 28 | 42 | 56 |
| CEM I | 0.02 | 0.03 | 0.04 | 0.04 | 0.06 | 0.02 | 0.02 | 0.02 | 0.03 | 0.05 |
| CEM II/A - L (10% L) | 0.03 | 0.03 | 0.03 | 0.05 | 0.06 | 0.02 | 0.03 | 0.03 | 0.05 | 0.06 |
| CEM II/B -$T_K$ (25%$T_K$) | 0.01 | 0.02 | 0.02 | 0.03 | 0.04 | 0.01 | 0.01 | 0.01 | 0.02 | 0.03 |
| CEM II/B -$T_T$ (25%$T_T$) | 0.01 | 0.02 | 0.02 | 0.03 | 0.04 | 0.00 | 0.01 | 0.01 | 0.01 | 0.02 |
| CEM II/B-M (10%$T_K$+ 15%$T_T$) | 0.02 | 0.04 | 0.04 | 0.05 | 0.07 | 0.01 | 0.02 | 0.03 | 0.03 | 0.04 |
| CEM III/B - (70 % S) | 0.02 | 0.04 | 0.06 | 0.16 | 0.31 | 0.02 | 0.03 | 0.07 | 0.15 | 0.25 |

Cements that affect reduction in the water-cement ratio and/or increased sulfate resistance can enhance the frost resistance of concrete in a sulfate-rich environment.

All tested specimens exhibited similar developing trends of the scaling whether freezing and thawing in sulfate solution or in distilled water or in 3 % NaCl. The difference in the scaling extent depending on the freezing substance may be related to the differences in the physical properties of frozen water and solution, such as freezing point, deformability or plasticity.

During the freeze-thaw testing, $Na_2SO_4$ permeated into the pores and the concentration of pore solution increased, which led to the freezing point of pore solution drop, resulting in a more moderate degradation than that of in 3 % NaCl solution. The lower temperature slowed down the diffusion of the sulfate ion and led to a slower sulfate attack. Higher $Na_2SO_4$ concentration and the associated precipitation of gypsum reduced the available pore space.

For CEM II/B - $T_K$ (25 % $T_K$) and CEM II/B - $T_T$ (25 % $T_T$), partly due to the much lower w/c for CEM II/B - $T_T$ (25 % $T_T$) cement, lower total porosity and narrower pore size distribution, the frost resistance in $Na_2SO_4$ improved significantly compared to CEM I.

The results of the investigation showed that CEM II/B - $T_K$ (25 % $T_K$) and CEM II/B - $T_T$ (25 % $T_T$) cements with better sulfate resistance exhibited the property of better sulfate resistance not only at 20 °C but also at low temperature. Such higher sulfate resisting cements are therefore suitable for structures which are exposed to possible sulfate attack (exposure classes $XA_1$ to $XA_3$ as defined in EVS-EN 206-1), regardless of the expected ambient temperature. As an exception, slag cements exhibited significantly reduced sulfate resistance at low temperature when compared to tests at 20 °C.

## 6.3 Water permeability

Waterproof Portland cement concrete is not a real possibility. Instead, the goal in design and formulation of durable concrete is to slow and minimize the potential and rate of moisture ingress and movement. Dense, impermeable concrete is vital where sulfates are present. The increase of the water permeability correlates with higher w/c ratios.

Water permeability of concrete was evaluated by EVS-EN 12390-8 as the depth of penetration of water under pressure. With every concrete mix four cubes with dimensions of (150 x 150 x 150) mm were prepared. After testing the specimens were split and the depth of penetration of the waterfront was measured. During the testing the presence of water on the surfaces not exposed to the water pressure of any specimen was not observed. Test results are presented in Table A17 and Figure 6.3.1.

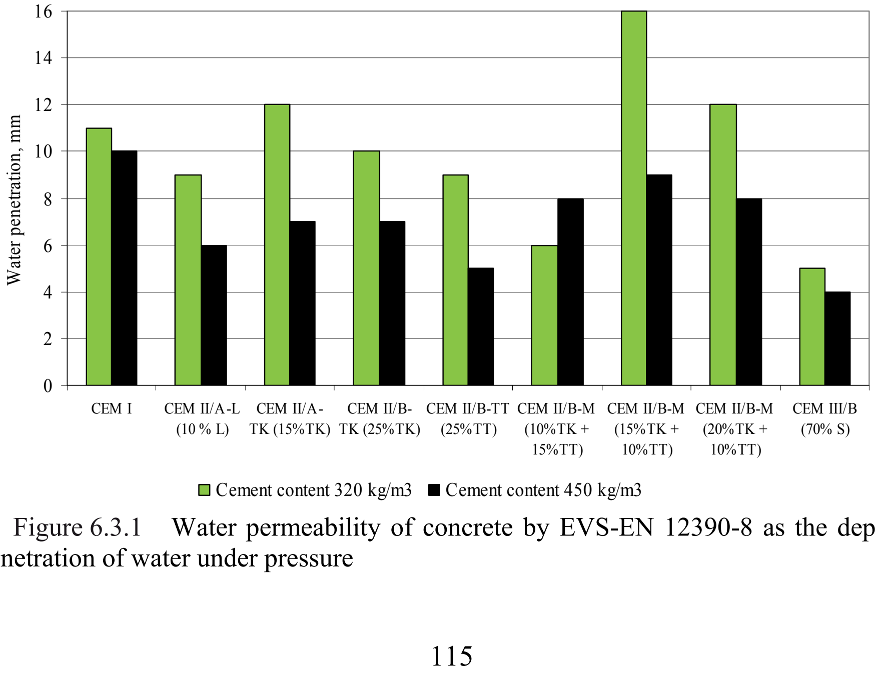


Figure 6.3.1 Water permeability of concrete by EVS-EN 12390-8 as the depth of penetration of water under pressure

The results showed that all tested concrete mixes qualified by high water resistance. Cement content of concrete significantly affected its water permeability, regardless of the composition of the cement, as was evident from Table A17. The data presented represented a range of Portland and composite cements. The rate of deterioration decreased with an increase in the cement content, even in concretes made of CEM I cement. All concrete mixtures with the cement amount of 450 kg/m$^3$ had lower water permeability and hence higher waterproofness than concrete mixtures with cement content 320 kg/m$^3$, irrespective of the cement used.

- Limestone 10 % content in CEM II/A-L (10 % L) cement improved impermeability to water compared to CEM I.
- The most waterproof of the tested concretes was made with slag cement CEM III/B – (70 % S). This confirmed the dense structure of slag cement stone and was one reason for high sulfate resistance of slag cements.
- When the content of burnt shale $T_T$ was increased to 25 %, the penetration decreased. Such a decrease in penetration may be attributed to the decreased pore structure within the mix due to the ettringite crystal formation.
- The increase of burnt shale $T_K$ content (15..25 %) in CEM II/B - $T_K$ did not affect water penetration concrete with the cement amount of 450 kg/m$^3$ whereas with cement the amount of 320 kg/m$^3$ with an increasing content of burnt shale $T_K$, waterproofness of concrete was raised. All concretes with CEM II/A-$T_K$ (15% $T_K$) and CEM II/B - $T_K$ (25 % $T_K$) cements improved impermeability to water compared to CEM I. Concretes with CEM II/B - $T_K$ cement had considerably higher content of nondecomposed limestone and free fine silica content.
- The effect of burnt shale $T_K$ and burnt shale $T_T$ constituents in composite cements ($T_K$ + $T_T$) was ambiguous. Clearly burnt shale $T_T$ increased waterproofness and with increasing content of cement in concrete, also increased the corrective influence of burnt shale $T_T$ constituent in concrete. The water penetration with mixed constituents burnt shales ($T_K$ + $T_T$) was higher than with either of these constituents.

Water permeability of concrete was directly correlated with the sulfate resistance of cement used. Low permeability of concrete is a significant factor influencing its resistance to sulfate attack. Given quality materials, satisfactory proportioning and good concrete practice, the permeability of concrete is a direct function of its water-cement ratio and the curing time.  Through water permeability absorption and diffusion of sulfate can be presumed.

## 6.4 Water absorption

Water ingress into a unsaturated concrete structure is due to sorption, driven by capillary forces, capillary rise (water at the bottom of the specimen). This indicates how much salt solution can enter the microstructure during normal service life or by sulfate attack, the volume of water that can be absorbed, hence the volume of ice that can be created by frost attack. The sulfate will then diffuse through the structure and react with the cement paste hydration products. The absorption of water or salt solutions by a concrete specimen depends heavily on its degree of saturation. A fully-saturated specimen will not absorb water or solution, while a fully-dried specimen will absorb substantially.

Water absorption in connection with sulfates is a considerable parameter, as groundwater tends to dissolve sulfates and carry them into the concrete. In such situations, the bottom of the footing or foundation often becomes completely saturated with sulfate loaded groundwater while the upper section is relatively dry. This moisture gradient creates a transport mechanism for the sulfate water, as it is drawn into the concrete, permeates upward through the footing to the drier regions, and then evaporates upon reaching the surface, as described by Boyd and Mindess (2004). The result is an acceleration in the sulfate attack mechanism induced by larger amounts of sulfates becoming readily available. In severe cases of prolonged exposure, this type of chemical attack becomes visually evident as a line or band of sulfate crystals and surface scaling just above the grade line.

Although the appearance of such scaling implies that significant damage is occurring at that location, the internal damage caused by sulfate attack can be much more severe. As the sulfate loaded water permeates upward through the concrete, the sulfates chemically attack the hydrated cement paste, inducing microcracking and eventually resulting in the degradation of the concrete’s mechanical properties and permeability characteristics (Boyd and Mindess 2004).

*Test series 1 – water absorption of concrete*

Concrete specimens were stored after hardening at 23 °C and relative humidity 50 % up to gaining a constant mass. The sides of concrete cubes were covered with wax and specimens were laid with open side into the water. Mass changes were recorded for 8 weeks and the water absorption by mass percent was calculated. The results are presented in Figure 6.4.1.

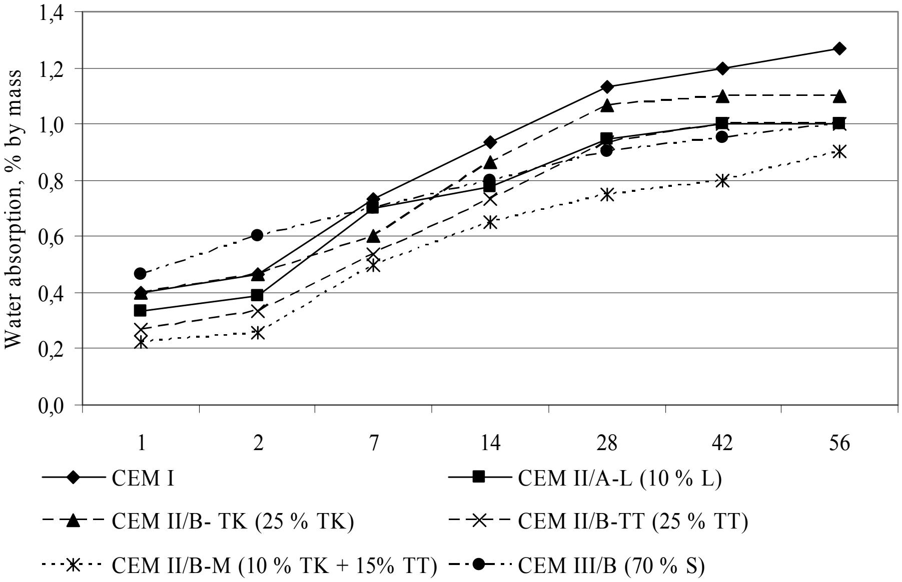


Figure 6.4.1 Water absorption of concretes

Portland cement CEM I with a maximum water absorption of 1.3 % had a peak water absorption.

Slag cement concrete CEM III/B (70 % S) had the highest water absorption at an early age. The absorption level remained relatively constant as in the later age the absorption of CEM III/B (70 % S) concrete decreased as the structure of cement stone grew denser.

Tsivilis et al. (2003) showed that a Portland limestone cement exhibited lower water permeability than ordinary Portland cement. This was in direct contrast with the findings of Pipilikaki et al. (2009) who discovered increased permeability associated with the use of limestone cements. The present research confirmed that the absorption of Portland limestone cement concrete was decreased compared to Portland cement and was the same as the absorption of slag cement. Also, the total porosities of these two cements were the same.

The absorption was the lowest at all ages with concrete made with CEM II/B - $T_T$ (25 % $T_T$).

- *Test series 2 - continuous partial immersion*

The absorption test results of concrete were obtained using (100 x 100 x 50) mm oven dried (after 28 days curing) specimens. Exposure specimens were subjected to four different environments. They were placed in containers, into which a solution was added to a depth of 5 mm. Thus, they were only partially immersed, leaving their upper half exposed to laboratory conditions and creating a similar moisture transport mechanism to concrete footings in sulfate loaded soils. Additional solution was poured to the containers when necessary to maintain the 5 mm depth and account for absorption and evaporation. The exposure specimens were stored under these conditions through testing.

With the 4.4 % $Na_2SO_4$ solution each of the exposure specimens quickly developed a border of sulfate crystals around its perimeter approximately 10...15 mm above the immersion line. This was due to the migration and subsequent evaporation of the sulfate solution, which had been drawn up into the specimens. The sulfate crystals precipitated as this water evaporated. As time passed, more and more crystals were deposited in this way, with the thickness of the crystal layer increasing, a significant difference in the amount of crystal buildup was noted depending on the cement used.

The results are presented in Table A18 and in Figure 6.4.4.


in 3.6 % $MgSO_4$ solution in 4.4 % $Na_2SO_4$ solution in 3 % NaCl solution in water

Figue 6.4.2 Concrete specimens made with CEM I cement. Absorption time 7 days


Figure 6.4.3 Concrete specimen made with CEM III/A (70 % S) cement. Absorption time 49 days in 4.4 % $Na_2SO_4$

It is usually admitted that the uptake of water per unit area of concrete surface follows a linear relationship with the square root of time for the suction period.

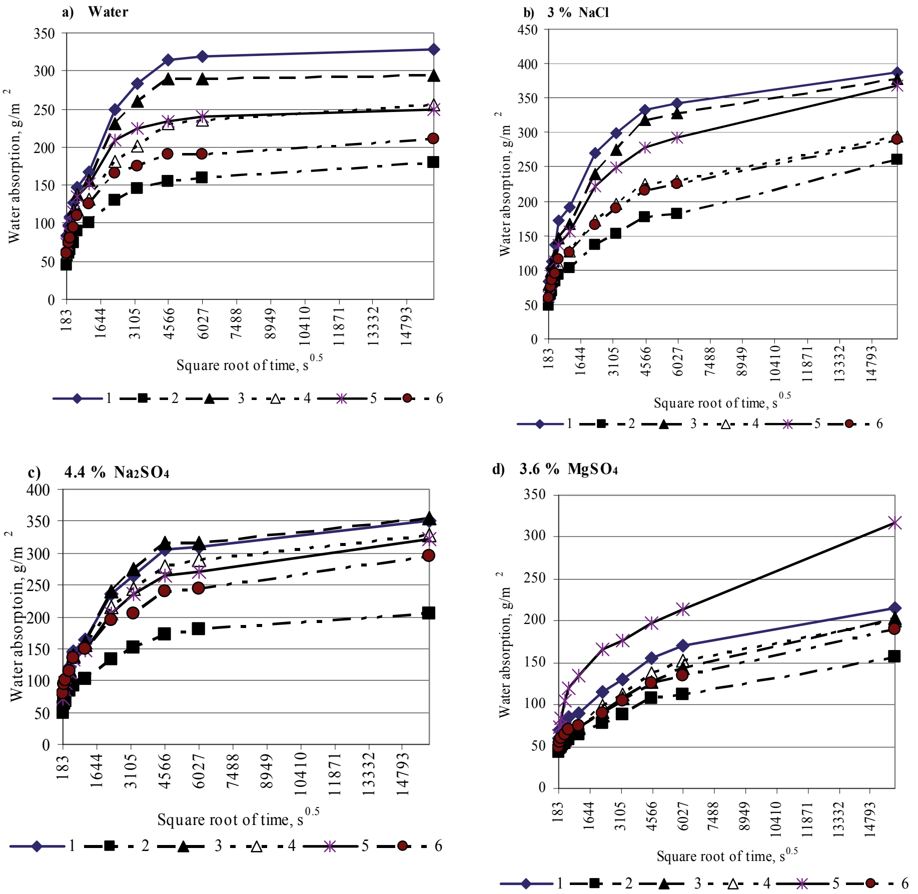


Figure 6.4.4. Water and salt absorption as a graph of $(m_{so,s} - m_{dry,s}) / A_s$ against the square root of the time immersed, in seconds for concretes made with several cements. a) in water, b) in 3 % NaCl solution, c) in 4.4 % $Na_2SO_4$ solution, d) in 3.6 % $MgSO_4$ solution
1. CEM I, 2. CEM II/A-$T_T$ (25% $T_T$), 3. CEM II/A-L (10% L), 4. CEM II/A-$T_K$(25%$T_K$), 5. CEM III/A (70 % S), 6. CEM II/B-M (15 % $T_T$ + 10 % $T_K$)

As shown in Figure 6.4.4, the capillary absorption is divided into two different regimes, both linear with time. The later age sorption coefficient is usually attributed to phenomena, such as filling of larger pores and air voids. The nick-point shows the time at which a filtered path of water or solution forms in the specimen. With water after 24 hour testing the masses of test specimens remained constant and the lines in graph horizontal. But with salt solutions the mass increased continually - during the initial stage with rapid water uptake, the absorption was found to increase almost linearly with the square root of time. During the second stage, with slower water uptake, the absorption also increased almost linearly with the square root of time.

The initial surface absorption test results of concrete at 10 min indicated slight improvements in initial surface absorption for all composite cement concretes compared to that of Portland cement concrete. This is likely to be due to the refinement of the concrete microstructure and filler effect of second constituents. The addition of mineral constituents in Portland cement led to a decrease in water, NaCl or sulfate uptake due to the lower initial capillary porosity of Portland composite cement concretes.

The rate of NaCl solution diffusion was higher compared to that of the $Na_2SO_4$ solution. This led to a faster penetration of chlorides into concrete, allowing them to react first with the $C_3A$ hydrated phases. The result was that chloroaluminate phases, such as Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) might be produced. Greater diffusion rate of NaCl solution was in accordance with the frost resistance test results as scaling with NaCl solution was enlarged compared to scaling in $Na_2SO_4$ solution.

The height of capillary suction for concretes containing second constituents increased with time. However, water absorption was lower than for CEM I concrete. The higher capillary suction of concretes with mineral constituents is due to the process of pore size refinement that results from the addition of mineral constituents. As Irassar et al. (1996) mentioned, this process is beneficial for concretes immersed in sulfate solution because the diffusion rate of ions decreases.

After 49 days of exposure, the salt efflorescence was removed and the damage in concrete specimens was inspected. No significant damage was observed in any types of concretes in any solutions as the testing time was too short for visible concrete degradation. The degradation of concrete expected in this zone is attributed mainly to the physical attack of sulfate. This mechanism has been described by Reading (1980): the sulfate solution rises into the dryer portion of the specimens by capillary action, where the water evaporates easily. Thus, when the concentration of solute exceeds the saturation concentration, salt crystallization takes place and produces internal stresses in concrete pores, which are large enough to cause concrete cracking (Mehta 1986).

By selecting constituents of cement, attention should be paid to producing lower porosity mortar, which results in a lower absorption of concrete and hence increased sulfate resistance.

The results of the absorption test indicated that the initial porosity (permeability) of the cement system influenced sulfate interaction and sulfate resistance.

## 6.5 Dynamic modulus of elasticity, compressive strength and flexural strength of concrete specimens

Measuring the change of dynamic modulus of elasticity of a material, it is possible to detect structural alterations at an early stage. Monitoring of strength reduction is another measure of damage detection. Dynamic modulus of elasticity was determined by measuring the fundamental transverse frequency of the sample at each test interval. A reduction in the fundamental transverse frequency can be used as an index to the extent of internal micro-cracking of the sample.

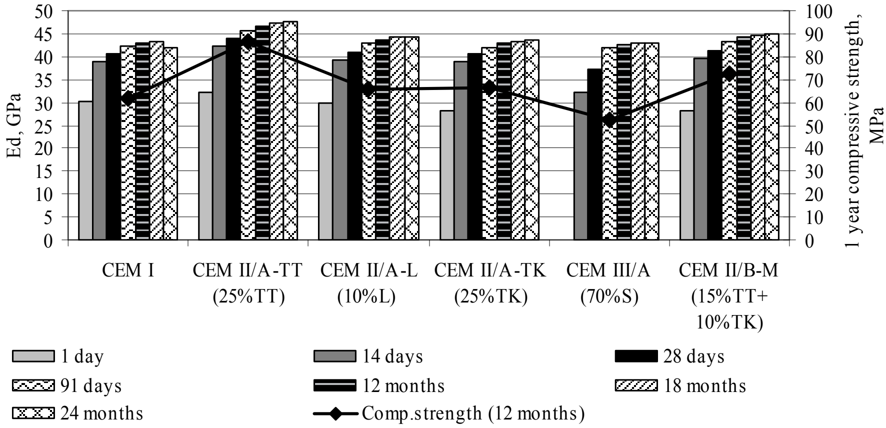


Figure 6.5.1 Dynamic modulus of elasticity up to two years and compressive strength after one year of storage in the 4.4 % $Na_2SO_4$ solution of concrete specimens with dimensions 70 x 70 x 210 mm

Table A19 lists the results of change in the dynamic modulus of elasticity ($E_d$) and Table A20 shows mass change for the concrete specimens immersed in the sodium sulfate solution up to 24 months of exposure and the values of compressive and flexural strengths at the age of one year (table A19).

$E_d$ of most concrete specimens showed a consistent increase with time except Portland cement CEM I, the $E_d$ of which started to decrease after 18 months of sulfate storage. The increase in $E_d$ was accompanied by the increase in the mass of specimens. Even after 24 months in a sulfate environment, a general increase in the mechanical properties was observed due to continuous hydration of the cement and filling of voids with reaction products.

Since all tested concrete specimens with composite cements had comparably improved performance under the full-immersion exposure, it can be presumed that the physical resistance (i.e. low permeability) was as important as the chemical resistance of its cement stone in mitigating the kinetics of deterioration due to external sulfate attack.

In agreement with the expansion results of specimens, $E_d$ results suggested that specimens from composite cement concretes generally performed better and survived longer under the sulfate exposure than the corresponding specimens from Portland cement CEM I.

Average results of the compressive and flexural strength at the age of 12 and 24 months of sulfate exposure are listed in Table A19 and compressive strength values in Figure 6.5.1. Contrary to the $E_d$ increase in a full-immersion exposure, there was an evidence of slight flexural strength loss. Generally, flexural strength results (with a few discrepancies) agreed well with the observed trend of $E_d$ results, confirming the beginning of internal deterioration of specimens.

Two-year exposure is too short for concrete specimens to gain appropriate information for sulfate resistance of concrete with several second constituents and therefore the testing time should be extended and the test continued. However, based on preliminary results, it is demonstrated through physical-mechanical results on specimens subjected to the exposure of sulfate solution that specimens from concrete with composite cements performed notably better than similar specimens from the Portland cement concrete. The results were comparative to the results of the Wittekind flat prisms tests. It can be concluded that as sulfate resistance testing in concrete is inappropriate because of the very long testing time, the Wittekind flat prisms method is reliable to assess the sulfate resistance of cements, as the results were comparable with the results of other tests.

## 6.6 Section summary and conclusions

Concrete may be considered as a two phase composite in the sulfate attack problem, in which the main physical and chemical processes occur within the cement paste, while aggregates remain generally unaltered. As was revealed in the test results, concrete durability in the sulfate containing environment cannot be described only as the sulfate resistance of the cement used. Sulfate attack is actually a complex process, involving different chemical reactions, whose character and mechanisms depend on a variety of parameters, including cement composition, nature of the aggregates and environmental factors. It is also a function of the type and content of various capillary pores of the cement stone and concrete. Most properties of concrete depend much on the quality of the hardened cement paste and the interface between hardened cement paste and aggregate. The hardened cement paste produced by the interaction of cement with water is composed of anhydrous phases, hydrate phases modified by sulfate ions incorporation and adsorption (C-S-H, ettringite, portlandite, AFm), pore solution, and pores.

Concretes with the same workability were made with the cement content 320 kg/m$^3$ and 450 kg/m$^3$ using granite as a coarse aggregate. Target slump was 50 to 80 mm. Concretes were made with an air entraining admixture REBAlit LP so that the air content was 5.5…6.5 %.

Limestone addition in cement reduced the compressive strength of concrete. The compressive strength of concrete with low temperature burnt shale $T_K$ was in general the same as CEM I. The relative strength of concretes with burnt shale $T_K$ cements was higher at early ages and diminished with time. The concretes containing high temperature burnt shale $T_T$ had the highest strength. Concrete with slag cement CEM III/B (70 % S) showed an enormous decrease of the early strength of concrete. With time the slag concrete gained more sufficient strength and 91-day compressive strength was only 13…15 % lower than the compressive strength of CEM I.

The concrete deterioration process most commonly occurring in Estonia is the physical deterioration of concrete by freezing and thawing. The deterioration due to freezing and thawing was found to be related to the permeable porosity of concrete, as cements with low total porosity and more beneficial pore size distribution demonstrated better frost resistance of concrete except the concrete with slag cement. Frost resistance was also strongly influenced by the strength of concrete. Sulfate attack was also linked to the permeable porosity of concrete, as it depended upon the ingress of moisture into the concrete. Furthermore, the permeable porosity of concrete had a significant effect on its strength and other mechanical properties. The hydraulic type of the second main constituent burnt shale $T_T$ had an increasing influence on the frost resistance in contrast to the pozzolanic burnt shale $T_K$ or inert limestone constituent. Concretes with burnt shale $T_T$ and $T_K$ cements showed less scaling on their surfaces than the CEM I. Frost resistance of concretes made with burnt shale $T_K$ was lower than that of burnt shale $T_T$. With increasing content of Portland limestone cement in concrete, the frost resistance decreased. Frost scaling increased enormously with large amounts of slag compared with the corresponding scaling of Portland cement concrete.

The simultaneous influence of sulfate attack and frost resistance on the concrete was investigated. It was found that cements that were subjected to reduction in the water-cement ratio and/or increased sulfate resistance could enhance the frost resistance of concrete in the sulfaterich environment except for slag cement. All tested specimens exhibited similar developing trends of the scaling whether freezing and thawing in 2.2 % and 4.4 % $Na_2SO_4$ solution or in distilled water or in 3 % NaCl. The results of the investigation showed that concretes with Portland burnt shale cements with $T_K$ and $T_T$ as cements with better sulfate resistance exhibited better sulfate resistance not only at 20 °C but also at lower temperature. Such higher sulfate resisting cements are therefore suitable for structures which are exposed to possible sulfate attack, regardless of the expected temperature.

Water permeability of concrete was directly correlated with sulfate resistance of cement. Cement content of concrete significantly affected the water permeability of concrete, regardless of the composition of the cement. The rate of deterioration decreased with an increase in cement content. All concretes with cement amount of 450 kg/m$^3$ had lower water permeability and hence higher waterproofness irrespective of the cement used than concrete mixtures with cement content 320 kg/m$^3$. The most waterproof of the tested concretes was made with slag cement. The water penetration with mixed burnt shale constituents ($T_K$ + $T_T$) was higher than with either of these constituents.

Portland cement CEM I had the highest water absorption. Based on the preliminary performance of the composite cement concretes in the full immersion exposure, they can qualify for use in severe exposure to sulfates. The absorption was the lowest at all ages with concrete made with CEM II/B-$T_T$ (25% $T_T$). The results proved that sulfate resistance is directly dependent on the water absorption of concrete.

The addition of mineral constituents in Portland cement led to a decrease in water, NaCl or $Na_2SO_4$ absorption due to the lower initial capillary porosity of Portland composite cement concretes. The processes of penetration of aggressive ions and deterioration of concrete specimens were most active in the following cases: 3 % NaCl and 4.4 % $Na_2SO_4$ solution. The resistance of concrete partially submerged in sulfate solutions decreased when high amounts of slag in cement especially with $MgSO_4$ solution. Crystallization pressure caused more severe deterioration in these cases. Otherwise, the results of the absorption test indicated that the initial porosity as permeability of the cement system influenced sulfate interaction and sulfate resistance.

## 7. Conclusions

The purpose of the research was to find out the possibilities for increasing the durability of concrete made with various types of cement listed in EN 197-1 using traditional and contemporary research methods. Another aim was to clarify which testing methods suit best for the determination of structural and chemical-mineralogical parameters.

Research reported is fragmentary, not all of the research methods addressing the influence of the sulfate corrosion of concrete are covered. Most of the studies focuse on cement research whereas the present thesis attempts to generalize the influence of various cement types on concrete.

The thesis covers the durability of cement concrete depending on the factors affecting the durability, primarily sulfate resistance of cement in various pastes, mortars and concrete. The applicability of different testing methods to determine sulfate resistance parameters and their influence on concrete durability was examined. Test results showed that tests based only on expansion measurements could not represent the degradation process, but combined with other significant characteristics, such as mass change, XRD, structural and compressive strength, capillary porosity of mortars, could provide valuable characteristics.

The experiments were performed using various types of Portland cements containing inert, puzzolanic or hydraulic second constituents. On a comparative basis, Portland cement CEM I was tested. The influence of the hydration, setting and hardening process on the type of hydration products and the structure of the formed cement stone is covered. Chemical analysis, MIP, XRD and SEM analysis were used.

- Maximum deterioration was found in mortar and concrete specimens made with the Portland cement CEM I. All tested mechanical characteristics – compressive and flexural strength and $E_d$, started to worsen in the sulfate environment much faster than in the case of mortars and concretes made with composite cements. CEM I mortar and concrete had the highest water absorption, in addition, total porosity of CEM I paste was high and it had many 0.01 to 0.05 μm size pores that are easily prone to damage by sulfate solution. CEM I concrete showed higher permeability than concrete with composite cement pastes owing to its higher total porosity. Therefore, the pore characteristics of CEM I mortar influenced the extent of sulfate damage that contributed to the disintegration of specimens by $Na_2SO_4$ attack.
- The addition of limestone as an inert constituent up to 15 % in Portland limestone cements and also in the multicomponent composite cement for 10 %, aggravated most of the physical and mechanical properties – sulfate resistance in conjunction with compressive and flexural strength, frost resistance of concrete, high water and sulfate solution absoption, deterioration in the form of spalling greater surface deterioration, greater deposition of gypsum, and higher degree of $Ca(OH)_2$ depletion.

- Addition of 20 % and 30 % high temperature burnt shale $T_T$ to Portland cement as a replacement for clinker improved the durability of Portland cement to a considerable degree. No deterioration of any sort was noted for Portland burnt shale $T_T$ cement after exposure to 4.4 % $Na_2SO_4$ solution. SEM images showed a slight formation of gypsum crystals near cracks, ettringite crystals within the air void near the outer side of the specimen. The structure was dense, most air voids were found to be filled with the reaction products. Compared to the CEM I mortar, the content of large capillary pores was decreased, medium capillary pores were finer and the content of gel pores was higher, therefore the sulfate resistance was higher. The results of $E_d$ and compressive strength after one-year storage in 4.4 % $Na_2SO_4$ confirmed the good performance of Portland burnt shale $T_T$ cement mortars in $Na_2SO_4$ solution.
- Different mineralogical compositions, high content of decomposed $CaCO_3$ and $SiO_2$, particle shape and surface formation in the combustion process had direct impact on the hydraulic properties of low temperature burnt shale $T_K$ and caused a decrease in the hydraulic properties and an increase in the water demand. Sensitivity of the Portland burnt shale $T_K$ cement concrete to sulfate resistance was revealed in increased water adsorption, decreased compressive strength and lower frost resistance compared to the Portland burnt shale $T_T$ cement concrete. A considerable effect on sulfate resistance related expansion was observed. Sulfate resistance was increased with an increasing content of burnt shale $T_K$ in cement. The structure of cement stone was dense, voids were filled with corrosion and hydration products. A higher percentage of macropores was detected. Increasing water demand of Portland burnt shale $T_K$ cements increased the amount of capillary pores.
- Slag is generally acknowledged as a sulfate increasing constituent of cement and that was affirmed by the current research. Slag in amounts of 20…30 % had no considerable effect on the sulfate resistance of cement. Slag at a replacement level of 50…70 % definitely increased the sulfate resistance of CEM III cements in $Na_2SO_4$ solution in comparison to the CEM I, as indicated by much lower expansion. The microstructure was dense, but uneven, and no ettringite nor gypsum could be observed by SEM. The amount of formed C-S-H and of $Ca(OH)_2$ was reduced. Most of the pores were gel pores, air voids were empty and not filled with reaction products. The good performance at high slag levels is due largely to the low permeability. The results of frost resistance of slag cements and concrete made with slag cement lowered radically on high slag contents. The good sulfate resistance is not a guarantee for high durability.
- Using multicomponent composite cements with both burnt shale and granulated blastfurnace slag as main constituents enabled to produce cements with better sulfate resistance at the same time not worsening strength and frost resistance parameters. These constituents reduced the potential for the formation of ettringite due to the reduction in the quantity of $Ca(OH)_2$ and $C_3A$, and thus improved the resistance of mortars to sulfate attack. Multicomponent Portland composite cements with different constituents enabled to enlarge the effect of

positive characteristics and to compensate negative effects of cement constituents and hence to improve the durability of mortar and concrete. The addition of mineral constituents led to the thinning of the pore size of cement paste, compaction of the hydration production phase and reduction of the unfavorable crystal phase. All of those resulted in the increase of resistance to ion diffusion. But no increasing effect of universal sulfate resistance was detected.

The impact of second constituents of cement on the degradation of concrete in sulfate solutions was dominated by their impact on the cement paste porosity and on the rate of sulfate ingress. Density and capillary pore structure of concrete made with various Portland composite cements varied in a wide range, resulting in differences in water absorption, sulfate resistance and frost resistance. From the results, it was concluded that sulfate resistance and other durability parameters depend directly on the ability of the formed structure to absorb water and salt solutions. Sulfate resistance, in particular, also depends on the type of hydration products in cement stone and reaction activity of these products.

- The results of concrete absorption tests showed that at the beginning of sulfate attack the uptake of sulfate results mainly in the filling of pores and voids and the increase in mass and length were almost linear. Later, during sulfate attack, when the whole available space was filled by the formation of sulfate phases, expansion became more pronounced whereas the mass gain was slowed down. There was a moderate difference in the total water taken up for the different samples. Lower porosity mortars resulted in a lower absorption.
- Cement content of concrete significantly affected its durability properties, such as compressive strength, frost resistance as well as sulfate resistance, regardless of the composition of the cement. Concretes with higher cement contents contained a smaller void structure and were thus more effective in restricting the absorption of the sulfate solution.
- Sulfate resistance and frost resistance are durability properties which depend on the entrance and migration of aggressive liquid medium in cement stone. The lower temperature during freezing slowed down the diffusion of sulfate ion and moderated the sulfate attack. It was found that cements that affected reduction in the water-cement ratio and/or increased sulfate resistance could enhance the frost resistance of concrete in the sulfate-rich environment, except for slag cement. The results of the investigation showed that concrete with Portland composite cement with burnt shales $T_K$ and $T_T$ as cements with better sulfate resistance exhibited better sulfate resistance not only at 20 °C but also at low temperature. Such higher sulfate resisting cements are therefore suitable for structures which are exposed to possible sulfate attack, regardless of the expected temperature.

The methods for testing various aspects of durability - sulfate resistance, water and salt absorption or frost resistance – are not similarly applicable to characterizing all cement types, as the types of second constituents are different and all test methods are not equally suitable for distinguishing the differences.

- The Wittekindt flat prisms method was used to assess sulfate resistance of different cements. Experimental results from a long-term study of concrete on expansion, dynamic modulus of elasticity ($E_d$) and water absorption showed the data from the Wittekindt test to be reliable for assessing the cements in a relatively short time. The Wittekindt flat prisms test is applicable to the comparison of the relative performances of different cements in the sodium sulfate environment. Tests on mortar could be used to qualify cements for a given w/c and volume of paste. Conditions of exposure are not totally controlled and high sulfate concentration could be responsible for a decreasing potential durability of sulfate-resisting Portland cements because of gypsum formation. The test is sensitive enough to show different behaviors of the studied cements. Experimental results from the long-term study of concrete on expansion, $E_d$ and water absorption showed the data from the Wittekindt test to be reliable in assessing the cements in a relatively short time.

- In the present study at high sulfate solutions gypsum was detected to be present in all samples. The hydration products formed in the systems studied were as expected, although they differed in magnitude. $Ca(OH)_2$ was formed initially in all systems, but the amount of $Ca(OH)_2$ formed in the composite cement paste was less than that formed in the Portland cement and Portland limestone cement.

- The analysis of the pore size distribution indicated that cement pastes with a high physical resistance to sulfates had finer pores and were thus able to prevent the diffusion of the sulfate ions into the microstructure. The permeable porosity of cement stone diminished with increased curing age, resulting in a greater amount of hydration products. The porosity of paste specimens after exposure in sulfate solution depended on the type of cement. As the type and content of medium and large capillary pores have a decisive influence on water absorption and conclusively on sulfate resistance of concrete, the behavior of concrete in service must be considered despite the $C_3A$ content, also by the content of capillary pores.

- According to the dissimilarities in the characteristics and hardening kinetics that became evident in testing cements with various compositions, the frost resistance test was carried out. The durability of water-saturated hardened cement mortar in situations of alternate freezing and thawing characterizes the formed structure of cement stone. On the other hand, sulfate resistance characterizes the reaction ability of cement and an aggressive environment.

- Dynamic modulus of elasticity showed that during the first crystallization stage the structure was compacted into cement stone due to the formation of reaction products. Compressive strength measurements monitored for mortar specimens up to a year and concrete specimens up to two years were not reliable for identifying the harmful effects of sulfate attack. Instead, expansion measurements were found to be more effective in identifying the cement against sulfate attack. Under the same test conditions as in the Wittekindt test method but with the specimens with increased size (40 x 40 x 160) mm, test results were compared. Comparable results with specimens with dimensions (10 x 40 x 160) mm were deduced and expansion values were accordingly reduced. The behavior of CEM I and composite cements was similar with both specimens sizes. Compressive strength and $E_d$ increase both in $Na_2SO_4$ and in $Ca(OH)_2$ solution in the case of composite cement mortars, and the decrease of both characteristics in the case of CEM I at the age of one year in 4.4 % $Na_2SO_4$ support the conclusions obtained with MIP, XRD and SEM. Therefore using smaller size specimens allows obtaining the test response in a shorter time, which is an important factor in the analysis of the sulfate resistance of newly developed composite cements.

The thesis was aimed at the examination of the influence of various types of Portland cements. As a result, it can be confirmed that the hardening type of the second constituent affects directly the structure of the formed cement stone and its sensitiveness to the environment of reaction products. To establish a theoretical basis to the aspects of durability of cements with second constituents, the methods for the determination of phase composition should be examined and improved in the future.

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## Appendix

Table A1 Expansions of (10 x 40 x 160) mm specimens in the saturated $Ca(OH)_2$ and in the 4.4% $Na_2SO_4$ solution by Wittekindt method. Cements are made with clinker $C_1$

| Cement | Initial expansion, mm/m | Expansion, mm/m | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Saturated $Ca(OH)_2$ | | | | | 4.4 % $Na_2SO_4$ | | | | |
| | | 14 d. | 28 d. | 42 d. | 56 d. | 91 d. | 14 d. | 28 d. | 42 d. | 56 d. | 91 p. |
| CEM I | 0.069 | 0.046 | 0.058 | 0.070 | 0.096 | 0.125 | 0.117 | 0.208 | 0.369 | 0.594 | 0.967 |
| CEM I/A-L (5 % L) | 0.065 | 0.013 | 0.023 | 0.029 | 0.048 | 0.065 | 0.093 | 0.165 | 0.328 | 0.570 | 0.945 |
| CEM II/A-L (10 % L) | 0.067 | 0.011 | 0.019 | 0.025 | 0.040 | 0.050 | 0.091 | 0.148 | 0.355 | 0.582 | 1.010 |
| CEM II/A-L (15 % L) | 0.064 | 0.011 | 0.019 | 0.019 | 0.046 | 0.058 | 0.100 | 0.130 | 0.338 | 0.605 | 0.948 |
| CEM II/A-$T_K$ (15 % $T_K$) | 0.082 | 0.031 | 0.038 | 0.050 | 0.088 | 0.088 | 0.162 | 0.268 | 0.390 | 0.496 | 0.719 |
| CEM II/A-$T_K$ (20 % $T_K$) | 0.111 | 0.038 | 0.063 | 0.069 | 0.075 | 0.075 | 0.156 | 0.253 | 0.380 | 0.486 | 0.625 |
| CEM II/B- $T_K$ (25 % $T_K$) | 0.100 | 0.050 | 0.069 | 0.088 | 0.088 | 0.081 | 0.190 | 0.260 | 0.420 | 0.468 | 0.590 |
| CEM II/A-$T_T$ (15 % $T_T$) | 0.094 | 0.060 | 0.067 | 0.086 | 0.121 | 0.133 | 0.133 | 0.238 | 0.379 | 0.506 | 0.683 |
| CEM II/A-$T_T$ (20 % $T_T$) | 0.113 | 0.050 | 0.052 | 0.081 | 0.106 | 0.148 | 0.167 | 0.269 | 0.410 | 0.546 | 0.685 |
| CEM II/B-$T_T$ (25 % $T_T$) | 0.138 | 0.065 | 0.067 | 0.091 | 0.138 | 0.148 | 0.181 | 0.265 | 0.310 | 0.477 | 0.685 |
| CEM II/B-$T_T$ (30 % $T_T$) | 0.144 | 0.081 | 0.083 | 0.125 | 0.160 | 0.173 | 0.183 | 0.280 | 0.373 | 0.494 | 0.692 |
| CEM II/A-S (10 % S) | 0.031 | 0.062 | 0.067 | 0.090 | 0.094 | 0.130 | 0.177 | 0.348 | 0.475 | 0.650 | 0.998 |
| CEM II/A-S (20 % S) | 0.038 | 0.065 | 0.075 | 0.090 | 0.096 | 0.135 | 0.185 | 0.333 | 0.456 | 0.554 | 0.959 |
| CEM II/B-S (30 % S) | 0.038 | 0.079 | 0.092 | 0.110 | 0.117 | 0.158 | 0.190 | 0.340 | 0.454 | 0.504 | 0.819 |
| CEM III/A (50 % S) | 0.075 | 0.054 | 0.056 | 0.067 | 0.071 | 0.104 | 0.190 | 0.194 | 0.327 | 0.327 | 0.438 |
| CEM III/A (60 % S) | 0.100 | 0.034 | 0.077 | 0.089 | 0.098 | 0.106 | 0.196 | 0.231 | 0.262 | 0.283 | 0.383 |
| CEM III/B (70 % S) | 0.088 | 0.069 | 0.078 | 0.088 | 0.088 | 0.090 | 0.128 | 0.182 | 0.200 | 0.225 | 0.253 |
| CEM II/B-M(20%$T_T$+15%S) | 0.113 | 0.033 | 0.081 | 0.127 | 0.129 | 0.133 | 0.185 | 0.227 | 0.388 | 0.460 | 0.742 |
| CEM II/B-M(15%$T_T$+20%S) | 0.106 | 0.033 | 0.079 | 0.125 | 0.137 | 0.137 | 0.202 | 0.261 | 0.435 | 0.517 | 0.683 |
| CEM II/B-M(10%$T_K$+15%$T_T$) | 0.125 | 0.050 | 0.063 | 0.100 | 0.075 | 0.125 | 0.180 | 0.222 | 0.311 | 0.406 | 0.625 |
| CEM II/B-M(15%$T_K$+10%$T_T$) | 0.106 | 0.056 | 0.056 | 0.081 | 0.075 | 0.138 | 0.156 | 0.215 | 0.341 | 0.465 | 0.729 |
| CEM II/B-M(20%$T_K$+10%$T_T$) | 0.100 | 0.044 | 0.031 | 0.056 | 0.056 | 0.125 | 0.165 | 0.201 | 0.297 | 0.366 | 0.586 |
| CEM II/B-M(15%$T_T$+10%L) | 0.119 | 0.052 | 0.077 | 0.081 | 0.103 | 0.148 | 0.277 | 0.375 | 0.588 | 0.727 | 1.088 |

Table A2 Physical and mechanical values of the Portland cements

| Cement | Workability, mm | Density, kg/m$^3$ | Compressive strength, MPa | | Flexural strength, MPa | |
|---|---|---|---|---|---|---|
| | | | 2 days | 28 days | 2 days | 28 days |
| CEM I | 141 | 2247 | 31.1 | 52.0 | 6.9 | 9.9 |
| CEM I/A-L (5 % L) | 143 | 2245 | 31.9 | 51.6 | 6.6 | 9.8 |
| CEM II/A-L (10 % L) | 146 | 2240 | 29.0 | 50.1 | 5.8 | 9.6 |
| CEM II/A-L (15 % L) | 148 | 2242 | 26.2 | 45.6 | 5.4 | 9.0 |
| CEM II/A-$T_K$ (15 % $T_K$) | 134 | 2245 | 33.8 | 52.8 | 6.6 | 9.6 |
| CEM II/A-$T_K$ (20 % $T_K$) | 134 | 2250 | 31.9 | 52.5 | 6.5 | 9.5 |
| CEM II/B- $T_K$ (25 % $T_K$) | 132 | 2253 | 29.8 | 51.5 | 6.6 | 9.5 |
| CEM II/A-$T_T$ (15 % $T_T$) | 167 | 2272 | 32.2 | 54.9 | 6.7 | 9.8 |
| CEM II/A-$T_T$ (20 % $T_T$) | 173 | 2280 | 31.6 | 55.2 | 6.9 | 9.6 |
| CEM II/B-$T_T$ (25 % $T_T$) | 176 | 2290 | 30.2 | 56.3 | 6.7 | 9.8 |
| CEM II/B-$T_T$ (30 % $T_T$) | 181 | 2290 | 31.3 | 56.6 | 6.4 | 9.4 |
| CEM II/A-S (10 % S) | 146 | 2223 | 27.2 | 49.7 | 6.3 | 9.3 |
| CEM II/A-S (20 % S) | 148 | 2239 | 22.2 | 45.4 | 5.4 | 8.8 |
| CEM II/B-S (30 % S) | 148 | 2239 | 17.8 | 43.1 | 4.5 | 8.8 |
| CEM III/A (50 % S) | 146 | 2251 | 9.9 | 36.4 | 2.8 | 7.8 |
| CEM III/A (60 % S) | 141 | 2249 | 5.3 | 28.6 | 2.0 | 7.7 |
| CEM III/B (70 % S) | 134 | 2248 | 3.4 | 25.0 | 1.2 | 7.0 |
| CEM II/B-M (20 % $T_T$ + 15 % S) | 167 | 2288 | 25.0 | 52.8 | 6.2 | 9.1 |
| CEM II/B-M (15 % $T_T$ + 20 % S) | 163 | 2267 | 23.4 | 50.6 | 5.4 | 8.6 |
| CEM II/B-M (10 % $T_K$ + 15% $T_T$) | 160 | 2248 | 32.5 | 56.1 | 6.3 | 9.0 |
| CEM II/B-M (15 % $T_K$ + 10% $T_T$) | 158 | 2250 | 31.2 | 53.9 | 6.5 | 9.2 |
| CEM II/B-M (20 % $T_K$ + 10% $T_T$) | 140 | 2255 | 30.6 | 53.0 | 6.1 | 9.3 |
| CEM II/B-M (15 % $T_T$ + 10 % L) | 180 | 2252 | 23.7 | 50.6 | 5.4 | 8.8 |

Table A3 Expansion values of additional tests with CEM I, CEM II/A-$T_T$ and CEM II/B-$T_T$ with (10 x 40 x 160) mm specimens in the saturated $Ca(OH)_2$ and in the 4.4% $Na_2SO_4$ solution by Wittekindt method

| Cement | Initial expansion, mm/m | Expansion, mm/m | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Saturated $Ca(OH)_2$ | | | | | 4.4 % $Na_2SO_4$ | | | | |
| | | 14 d. | 28 d. | 42 d. | 56 d. | 91 d. | 14 d. | 28 d. | 42 d. | 56 d. | 91 p. |
| CEM I ($C_2$) | 0.075 | 0.027 | 0.048 | 0.091 | 0.097 | 0.099 | 0.127 | 0.228 | 0.371 | 0.627 | 0.979 |
| CEM I ($C_3$) | 0.044 | 0.024 | 0.057 | 0.075 | 0.092 | 0.123 | 0.114 | 0.187 | 0.335 | 0.542 | 0.863 |
| CEM I ($C_4$) | 0.062 | 0.059 | 0.062 | 0.128 | 0.133 | 0.153 | 0.119 | 0.222 | 0.398 | 0.613 | 0.953 |
| CEM I ($C_5$) | 0.058 | 0.041 | 0.084 | 0.099 | 0.102 | 0.106 | 0.121 | 0.214 | 0.339 | 0.562 | 0.886 |
| CEM II A ($C_1$)/-$T_T$ (15%$T_{T1}$) | 0.094 | 0.060 | 0.067 | 0.086 | 0.121 | 0.133 | 0.133 | 0.238 | 0.379 | 0.506 | 0.683 |
| CEM II A ($C_2$)/-$T_T$ (15%$T_{T1}$) | 0.088 | 0.069 | 0.073 | 0.108 | 0.148 | 0.165 | 0.246 | 0.375 | 0.473 | 0.556 | 0.721 |
| CEM II A ($C_3$)/-$T_T$ (15%$T_{T2}$) | 0.113 | 0.058 | 0.064 | 0.077 | 0.108 | 0.136 | 0.161 | 0.192 | 0.371 | 0.460 | 0.672 |
| CEM II A ($C_1$)/-$T_T$ (20%$T_{T1}$) | 0.113 | 0.050 | 0.052 | 0.081 | 0.106 | 0.148 | 0.167 | 0.269 | 0.410 | 0.546 | 0.685 |
| CEM II A ($C_2$)/-$T_T$ (20%$T_{T1}$) | 0.106 | 0.075 | 0.088 | 0.098 | 0.137 | 0.170 | 0.238 | 0.331 | 0.404 | 0.471 | 0.677 |
| CEM II A ($C_3$)/-$T_T$ (20%$T_{T2}$) | 0.125 | 0.065 | 0.077 | 0.097 | 0.128 | 0.159 | 0.167 | 0.202 | 0.377 | 0.487 | 0.678 |
| CEM II B ($C_1$)/-$T_T$ (25%$T_{T1}$) | 0.138 | 0.065 | 0.067 | 0.091 | 0.138 | 0.148 | 0.181 | 0.265 | 0.310 | 0.477 | 0.685 |
| CEM II B ($C_2$)/-$T_T$ (25%$T_{T1}$) | 0.125 | 0.085 | 0.087 | 0.106 | 0.135 | 0.181 | 0.258 | 0.358 | 0.427 | 0.475 | 0.680 |
| CEM II B ($C_3$)/-$T_T$ (25%$T_{T2}$) | 0.138 | 0.069 | 0.084 | 0.113 | 0.153 | 0.163 | 0.185 | 0.215 | 0.406 | 0.500 | 0.652 |
| CEM II B ($C_1$)/-$T_T$ (30%$T_{T1}$) | 0.144 | 0.081 | 0.083 | 0.125 | 0.160 | 0.173 | 0.183 | 0.280 | 0.373 | 0.494 | 0.692 |
| CEM II B ($C_2$)/-$T_T$ (30%$T_{T1}$) | 0.125 | 0.085 | 0.123 | 0.135 | 0.135 | 0.187 | 0.277 | 0.402 | 0.498 | 0.515 | 0.667 |
| CEM II B ($C_3$)/-$T_T$ (30%$T_{T2}$) | 0.156 | 0.071 | 0.106 | 0.135 | 0.149 | 0.171 | 0.196 | 0.233 | 0.421 | 0.509 | 0.661 |

Table A4 Expansion values of additional tests with Portland slag cements and slag cements specimens (10 x 40 x 160) mm in the saturated $Ca(OH)_2$ and in the 4.4% $Na_2SO_4$ solution by Wittekindt method

| Cement | Initial expansion, mm/m | Expansion, mm/m | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Saturated $Ca(OH)_2$ | | | | | 4.4 % $Na_2SO_4$ | | | | |
| | | 14 d. | 28 d. | 42 d. | 56 d. | 91 d. | 14 d. | 28 d. | 42 d. | 56 d. | 91 p. |
| CEM II/A-S (10 % $S_1$) | 0.031 | 0.062 | 0.067 | 0.090 | 0.094 | 0.130 | 0.177 | 0.348 | 0.475 | 0.650 | 0.998 |
| CEM II/A-S (10 % $S_2$) | 0.031 | 0.081 | 0.092 | 0.110 | 0.117 | 0.156 | 0.173 | 0.323 | 0.454 | 0.504 | 0.933 |
| CEM II/A-S (20 % $S_1$) | 0.038 | 0.065 | 0.075 | 0.090 | 0.096 | 0.135 | 0.185 | 0.333 | 0.456 | 0.554 | 0.959 |
| CEM II/A-S (20 % $S_2$) | 0.031 | 0.073 | 0.077 | 0.098 | 0.113 | 0.152 | 0.144 | 0.260 | 0.379 | 0.496 | 0.885 |
| CEM II/B-S (30 % $S_1$) | 0.038 | 0.079 | 0.092 | 0.110 | 0.117 | 0.158 | 0.190 | 0.340 | 0.454 | 0.504 | 0.819 |
| CEM II/B-S (30 % $S_2$) | 0.038 | 0.081 | 0.085 | 0.090 | 0.102 | 0.142 | 0.142 | 0.290 | 0.413 | 0.460 | 0.810 |
| CEM III/A (50 % $S_1$) (2% $SO_3$) | 0.081 | 0.042 | 0.051 | 0.065 | 0.073 | 0.108 | 0.202 | 0.240 | 0.379 | 0.431 | 0.548 |
| CEM III/A (50 % $S_1$) (3% $SO_3$) | 0.075 | 0.054 | 0.056 | 0.067 | 0.071 | 0.104 | 0.190 | 0.194 | 0.327 | 0.327 | 0.438 |
| CEM III/A (50 % $S_1$) (4% $SO_3$) | 0.113 | 0.050 | 0.053 | 0.058 | 0.063 | 0.094 | 0.240 | 0.252 | 0.367 | 0.398 | 0.531 |
| CEM III/A (50 % $S_2$) (3% $SO_3$) | 0.075 | 0.063 | 0.066 | 0.069 | 0.062 | 0.110 | 0.173 | 0.196 | 0.275 | 0.308 | 0.440 |
| CEM III/A (60 % $S_1$) (2% $SO_3$) | 0.094 | 0.046 | 0.100 | 0.113 | 0.119 | 0.131 | 0.192 | 0.271 | 0.369 | 0.373 | 0.487 |
| CEM III/A (60 % $S_1$) (3% $SO_3$) | 0.100 | 0.034 | 0.077 | 0.089 | 0.098 | 0.106 | 0.196 | 0.231 | 0.262 | 0.283 | 0.383 |
| CEM III/A (60 % $S_1$) (4% $SO_3$) | 0.188 | 0.061 | 0.081 | 0.081 | 0.083 | 0.096 | 0.167 | 0.225 | 0.263 | 0.277 | 0.358 |
| CEM III/A (60 % $S_2$) (3% $SO_3$) | 0.088 | 0.073 | 0.113 | 0.112 | 0.112 | 0.112 | 0.175 | 0.240 | 0.258 | 0.277 | 0.358 |
| CEM III/B (70 % $S_1$) (2% $SO_3$) | 0.094 | 0.069 | 0.073 | 0.102 | 0.104 | 0.115 | 0.159 | 0.199 | 0.230 | 0.275 | 0.325 |
| CEM III/B (70 % $S_1$) (3% $SO_3$) | 0.088 | 0.069 | 0.078 | 0.088 | 0.088 | 0.090 | 0.128 | 0.182 | 0.200 | 0.225 | 0.253 |
| CEM III/B (70 % $S_1$) (4% $SO_3$) | 0.269 | 0.054 | 0.065 | 0.073 | 0.086 | 0.094 | 0.106 | 0.138 | 0.158 | 0.188 | 0.221 |
| CEM III/B (70 % $S_2$) (3% $SO_3$) | 0.113 | 0.091 | 0.098 | 0.104 | 0.109 | 0.116 | 0.122 | 0.151 | 0.169 | 0.200 | 0.219 |

Table A5 Physical and mechanical values of the additional tests of Portland cements

| Cement | Workability, mm | Density kg/m$^3$ | Compressive strength, MPa | | Flexural strength, MPa | |
|---|---|---|---|---|---|---|
| | | | 2 days | 28 days | 2 days | 28 days |
| CEM I ($C_2$) | 140 | 2246 | 27.2 | 46.1 | 6.8 | 8.9 |
| CEM I ($C_3$) | 135 | 2257 | 29.6 | 51.4 | 6.2 | 9.4 |
| CEM I ($C_4$) | 141 | 2251 | 29.2 | 50.0 | 6.7 | 9.0 |
| CEM I ($C_5$) | 141 | 2254 | 27.8 | 50.9 | 6.6 | 9.1 |
| CEM II A ($C_1$)/-$T_T$ (15%$T_{T1}$) | 167 | 2272 | 32.2 | 54.9 | 6.7 | 9.8 |
| CEM II A ($C_2$)/-$T_T$ (15%$T_{T1}$) | 163 | 2263 | 29.6 | 49.2 | 6.7 | 9.3 |
| CEM II A ($C_3$)/-$T_T$ (15%$T_{T2}$) | 159 | 2269 | 30.5 | 53.1 | 7.3 | 8.9 |
| CEM II A ($C_1$)/-$T_T$ (20%$T_{T1}$) | 173 | 2280 | 31.6 | 55.2 | 6.9 | 9.6 |
| CEM II A ($C_2$)/-$T_T$ (20%$T_{T1}$) | 170 | 2263 | 28.8 | 49.8 | 6.0 | 9.4 |
| CEM II A ($C_3$)/-$T_T$ (20%$T_{T2}$) | 169 | 2269 | 27.8 | 53.5 | 6.8 | 9.3 |
| CEM II B ($C_1$)/-$T_T$ (25%$T_{T1}$) | 176 | 2290 | 30.2 | 56.3 | 6.7 | 9.8 |
| CEM II B ($C_2$)/-$T_T$ (25%$T_{T1}$) | 172 | 2261 | 28.8 | 51.0 | 6.4 | 8.6 |
| CEM II B ($C_3$)/-$T_T$ (25%$T_{T2}$) | 170 | 2276 | 28.4 | 54.2 | 6.5 | 8.9 |
| CEM II B ($C_1$)/-$T_T$ (30%$T_{T1}$) | 181 | 2290 | 31.3 | 56.6 | 6.4 | 9.4 |
| CEM II B ($C_2$)/-$T_T$ (30%$T_{T1}$) | 178 | 2272 | 28.1 | 54.3 | 6.4 | 8.6 |
| CEM II B ($C_3$)/-$T_T$ (30%$T_{T2}$) | 174 | 2290 | 27.2 | 54.3 | 6.5 | 9.4 |
| CEM II/A-S (10 % $S_1$) | 146 | 2223 | 27.2 | 49.7 | 6.3 | 9.3 |
| CEM II/A-S (10 % $S_2$) | 147 | 2227 | 26.3 | 50.0 | 6.3 | 11.3 |
| CEM II/A-S (20 % $S_1$) | 148 | 2239 | 22.2 | 45.4 | 5.4 | 8.8 |
| CEM II/A-S (20 % $S_2$) | 151 | 2238 | 21.0 | 47.7 | 5.4 | 8.8 |
| CEM II/B-S (30 % $S_1$) | 148 | 2239 | 17.8 | 43.1 | 4.5 | 8.8 |
| CEM II/B-S (30 % $S_2$) | 155 | 2242 | 16.0 | 43.0 | 4.1 | 8.7 |
| CEM III/A (50 % $S_1$) (2% $SO_3$) | 159 | 2255 | 9.9 | 39.9 | 2.8 | 8.2 |
| CEM III/A (50 % $S_1$) (3% $SO_3$) | 146 | 2251 | 9.9 | 36.4 | 2.8 | 7.8 |
| CEM III/A (50 % $S_1$) (4% $SO_3$) | 140 | 2232 | 4.4 | 29.2 | 1.4 | 7.1 |
| CEM III/A (50 % $S_2$) (3% $SO_3$) | 142 | 2247 | 8.0 | 32.6 | 2.1 | 7.8 |
| CEM III/A (60 % $S_1$) (2% $SO_3$) | 154 | 2255 | 5.9 | 34.2 | 2.0 | 6.9 |
| CEM III/A (60 % $S_1$) (3% $SO_3$) | 141 | 2249 | 5.3 | 28.6 | 2.0 | 7.7 |
| CEM III/A (60 % $S_1$) (4% $SO_3$) | 131 | 2239 | 2.5 | 25.6 | 0.9 | 7.3 |
| CEM III/A (60 % $S_2$) (3% $SO_3$) | 137 | 2248 | 4.4 | 26.8 | 1.5 | 7.1 |
| CEM III/B (70 % $S_1$) (2% $SO_3$) | 150 | 2264 | 3.6 | 30.3 | 1.4 | 7.4 |
| CEM III/B (70 % $S_1$) (3% $SO_3$) | 134 | 2248 | 3.4 | 25.0 | 1.2 | 7.0 |
| CEM III/B (70 % $S_1$) (4% $SO_3$) | 117 | 2225 | 0.9 | 22.4 | 0.4 | 7.3 |
| CEM III/B (70 % $S_2$) (3% $SO_3$) | 134 | 2246 | 1.6 | 22.7 | 0.6 | 7.0 |

Table A6 Mass change of specimens of (40x40x160) mm in the saturated $Ca(OH)_2$ and in the 4.4% $Na_2SO_4$ solution

| Cement | 14/0 | Mass change, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Ca(OH)_2$ | | | | | 4.4 % $Na_2SO_4$ | | | | |
| | | 28/14 | 42/28 | 56/42 | 70/56 | 105/91 | 28/14 | 42/28 | 56/42 | 70/56 | 105/91 |
| CEM I | 0.89 | 1.16 | 1.29 | 1.41 | 1.48 | 1.59 | 0.88 | 0.89 | 0.93 | 0.96 | 1.03 |
| CEM II/A-$T_T$(15% $T_T$) | 0.96 | 1.20 | 1.31 | 1.41 | 1.49 | 1.60 | 0.90 | 0.93 | 0.97 | 1.00 | 1.09 |
| CEM II/A-$T_T$ (20%$T_T$) | 0.89 | 1.00 | 1.13 | 1.22 | 1.27 | 1.37 | 0.93 | 0.97 | 1.02 | 1.05 | 1.12 |
| CEM II/B-$T_T$ (25% $T_T$) | 0.87 | 0.98 | 1.09 | 1.16 | 1.22 | 1.30 | 0.93 | 0.94 | 0.98 | 1.03 | 1.09 |
| CEM II/B-$T_T$ (30% $T_T$) | 0.94 | 1.10 | 1.20 | 1.27 | 1.32 | 1.42 | 0.97 | 0.98 | 1.02 | 1.07 | 1.14 |
| CEM II/A-S (10 % S) | 1.02 | 1.20 | 1.34 | 1.50 | 1.59 | 1.73 | 1.02 | 1.03 | 1.06 | 1.09 | 1.11 |
| CEM II/A-S (20 % S) | 0.91 | 1.08 | 1.22 | 1.39 | 1.49 | 1.66 | 0.98 | 1.00 | 1.05 | 1.05 | 1.06 |
| CEM II/B-S (30 % S) | 0.99 | 1.09 | 1.24 | 1.39 | 1.47 | 1.62 | 1.11 | 1.12 | 1.16 | 1.14 | 1.14 |
| CEM II/BM(10%$T_K$+15%$T_T$) | 0.75 | 0.90 | 0.99 | 1.04 | 1.10 | 1.20 | 0.86 | 0.84 | 0.85 | 0.88 | 0.97 |
| CEM II/B-M(15%$T_K$+10%$T_T$) | 0.85 | 1.07 | 1.20 | 1.27 | 1.33 | 1.44 | 0.89 | 0.89 | 0.91 | 0.92 | 0.97 |

Table A7 Expansion of specimens of (40 x 40 x 160) mm in the saturated $Ca(OH)_2$ and in the 4.4% $Na_2SO_4$ solution

| Cement | 14/0 | Expansion, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Ca(OH)_2$ | | | | | 4.4 % $Na_2SO_4$ | | | | |
| | | 28/14 | 42/28 | 56/42 | 70/56 | 105/91 | 28/14 | 42/28 | 56/42 | 70/56 | 105/91 |
| CEM I | 0.17 | 0.17 | 0.17 | 0.17 | 0.18 | 0.19 | 0.30 | 0.33 | 0.33 | 0.36 | 0.39 |
| CEM II/A-$T_T$(15% $T_T$) | 0.16 | 0.23 | 0.27 | 0.28 | 0.28 | 0.28 | 0.22 | 0.28 | 0.28 | 0.30 | 0.33 |
| CEM II/A-$T_T$ (20%$T_T$) | 0.21 | 0.28 | 0.28 | 0.28 | 0.31 | 0.31 | 0.28 | 0.33 | 0.33 | 0.36 | 0.39 |
| CEM II/B-$T_T$ (25% $T_T$) | 0.28 | 0.31 | 0.33 | 0.34 | 0.38 | 0.38 | 0.36 | 0.38 | 0.42 | 0.46 | 0.48 |
| CEM II/B-$T_T$ (30% $T_T$) | 0.31 | 0.33 | 0.36 | 0.37 | 0.39 | 0.39 | 0.42 | 0.47 | 0.47 | 0.52 | 0.52 |
| CEM II/A-S (10 % S) | 0.36 | 0.38 | 0.39 | 0.41 | 0.42 | 0.42 | 0.44 | 0.47 | 0.50 | 0.53 | 0.56 |
| CEM II/A-S (20 % S) | 0.31 | 0.34 | 0.35 | 0.39 | 0.41 | 0.41 | 0.47 | 0.48 | 0.54 | 0.57 | 0.58 |
| CEM II/B-S (30 % S) | 0.28 | 0.31 | 0.31 | 0.38 | 0.42 | 0.42 | 0.52 | 0.53 | 0.56 | 0.58 | 0.59 |
| CEM II/B-M(10%$T_K$+15%$T_T$) | 0.20 | 0.20 | 0.20 | 0.24 | 0.24 | 0.24 | 0.22 | 0.26 | 0.28 | 0.30 | 0.33 |
| CEM II/B-M(15%$T_K$+10%$T_T$) | 0.17 | 0.18 | 0.18 | 0.18 | 0.18 | 0.19 | 0.20 | 0.24 | 0.26 | 0.27 | 0.27 |

Table A8 Change of dynamic modulus of elasticity ($E_d$) of specimens of (40 x 40 x 160) mm in the saturated $Ca(OH)_2$ and in the 4.4% $Na_2SO_4$ solution

| Cement | 14/0 days | $E_d$ compared to 7 days result, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Ca(OH)_2$ | | | | | 4.4 % $Na_2SO_4$ | | | | |
| | | 28/ 14 | 42/ 28 | 56/ 42 | 70/ 56 | 105/ 91 | 28/ 14 | 42/ 28 | 56/ 42 | 70/ 56 | 105/ 91 |
| | | | | | | | | | | | |
| CEM I | 101 | 104 | 108 | 110 | 112 | 112 | 105 | 112 | 113 | 114 | 116 |
| CEM II/A-$T_T$(15% $T_T$) | 102 | 108 | 110 | 110 | 111 | 111 | 108 | 110 | 111 | 111 | 114 |
| CEM II/A-$T_T$ (20%$T_T$) | 102 | 107 | 108 | 111 | 112 | 113 | 109 | 114 | 115 | 116 | 117 |
| CEM II/B-$T_T$ (25% $T_T$) | 100 | 104 | 111 | 112 | 114 | 114 | 106 | 111 | 114 | 117 | 117 |
| CEM II/B-$T_T$ (30% $T_T$) | 100 | 104 | 110 | 111 | 111 | 113 | 105 | 110 | 111 | 111 | 114 |
| CEM II/A-S (10 % S) | 104 | 111 | 111 | 112 | 113 | 114 | 114 | 115 | 115 | 116 | 116 |
| CEM II/A-S (20 % S) | 106 | 112 | 116 | 117 | 120 | 121 | 118 | 120 | 121 | 121 | 123 |
| CEM II/B-S (30 % S) | 108 | 114 | 115 | 126 | 126 | 127 | 121 | 125 | 127 | 128 | 131 |
| CEM II/B-M(10%$T_K$+15%$T_T$) | 100 | 111 | 113 | 114 | 115 | 117 | 115 | 115 | 118 | 120 | 122 |
| CEM II/B-M(15%$T_K$+10%$T_T$) | 103 | 110 | 112 | 114 | 115 | 115 | 113 | 114 | 117 | 118 | 120 |

Table A9 Dynamic modulus of elasticity ($E_d$) after 28-days and 1-year storage in the 4.4 % $Na_2SO_4$ solution and in the water and the relative change of $E_d$. Compressive strength after one year. Cement mortar specimens with dimensions (40 x 40 x 160) mm

| Cement | $E_d$ in 4.4 % $Na_2SO_4$ | | | | | $R_s$, MPa | $E_d$ in water | | | | | $R_s$, MPa |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $E_d$, GPa | | | $E_d$ change, % | | | $E_d$, GPa | | | $E_d$ change, % | | |
| | Initial | 28 d | 1 year | $\Delta E_d$, 28 d | $\Delta E_d$, 1year | 1 year | Initial | 28 d | 1 year | $\Delta E_d$, 28 d | $\Delta E_d$, 1year | 1 year |
| CEM I | 35.9 | 41.3 | 36.0 | *15.0* | *0.3* | 49.4 | 35.8 | 40.2 | 41.6 | *12.3* | *16.2* | 60.4 |
| CEM II/A-$T_T$ (20 % $T_T$) | 34.8 | 41.2 | 42.9 | *18.5* | *23.4* | 65.3 | 35.3 | 40.5 | 42.8 | *14.7* | *21.1* | 70.1 |
| CEM II/A-S (20 % S) | 34.1 | 40.4 | 41.5 | *18.5* | *21.8* | 63.9 | 34.4 | 39.6 | 41.3 | *15.3* | *20.1* | 66.6 |
| CEM II/B-M (15 % $T_T$ + 20 % S) | 33.5 | 40.2 | 42.5 | *20.0* | *26.9* | 68.9 | 33.9 | 39.5 | 42.3 | *16.8* | *25.0* | 72.6 |
| CEM III/A (60 % S) | 23.7 | 26.8 | 29.9 | *13.1* | *26.2* | 51.8 | 23.3 | 26.6 | 31.1 | *14.2* | *33.5* | 53.2 |
| CEM II/A-L (10 % L) | 38.3 | 40.0 | 41.2 | *4.4* | *7.5* | 58.7 | 34.8 | 38.8 | 40.2 | *11.3* | *15.3* | 62.9 |
| CEM V (50% S + 20% $T_T$) | 28.8 | 35.8 | 38.0 | *24.4* | *31.9* | 57.5 | 29.1 | 34.5 | 38.4 | *18.3* | *31.8* | 55.3 |
| CEM II/B-M (20 % $T_T$ + 5 % S + 10 % L) | 34.6 | 41.2 | 42.3 | *19.1* | *22.2* | 63.8 | 33.9 | 39.7 | 41.9 | *17.0* | *23.5* | 73.1 |

Table A10 Expansion of commercial cements. Specimens of (10 x 40 x 160) mm in the saturated $Ca(OH)_2$ and in the 4.4% $Na_2SO_4$ solution by Wittekindt method

| Cement | Initial expansion, mm/m | Expansion, mm/m | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Saturated $Ca(OH)_2$ | | | | | 4.4 % $Na_2SO_4$ | | | | |
| | | 14 d. | 28 d. | 42 d. | 56 d. | 91 d. | 14 d. | 28 d. | 42 d. | 56 d. | 91 p. |
| CEM I 42.5 HS | 0.063 | 0.027 | 0.036 | 0.044 | 0.083 | 0.113 | 0.090 | 0.156 | 0.329 | 0.450 | 0.691 |
| CEM I 42.5 SR/LA | 0.144 | 0.050 | 0.100 | 0.106 | 0.112 | 0.110 | 0.126 | 0.185 | 0.300 | 0.325 | 0.532 |
| CEM II A 52.5 R | 0.119 | 0.042 | 0.065 | 0.085 | 0.097 | 0.110 | 0.158 | 0.304 | 0.502 | 0.612 | 0.906 |
| CEM II A 42.5 R | 0.100 | 0.029 | 0.067 | 0.113 | 0.113 | 0.117 | 0.183 | 0.300 | 0.488 | 0.609 | 0.929 |
| CEM I 42.5 SR | 0.088 | 0.017 | 0.036 | 0.090 | 0.092 | 0.094 | 0.138 | 0.258 | 0.550 | 0.586 | 1.035 |
| CEM II/B-T 42.5 R - 1 | 0.188 | 0.046 | 0.086 | 0.135 | 0.137 | 0.158 | 0.175 | 0.300 | 0.488 | 0.579 | 0.750 |
| CEM II/B-T 42.5 R - 2 | 0.175 | 0.046 | 0.092 | 0.095 | 0.106 | 0.123 | 0.314 | 0.350 | 0.631 | 0.679 | 0.887 |
| CEM I 42.5R - 1 | 0.063 | 0.008 | 0.017 | 0.042 | 0.063 | 0.088 | 0.148 | 0.215 | 0.329 | 0.395 | 0.748 |
| CEM II/B-T 42.5 R - 3 | 0.188 | 0.015 | 0.027 | 0.073 | 0.085 | 0.133 | 0.187 | 0.281 | 0.429 | 0.488 | 0.708 |
| CEM II/B-M 42.5R | 0.156 | 0.008 | 0.015 | 0.048 | 0.067 | 0.084 | 0.140 | 0.217 | 0.388 | 0.456 | 0.765 |
| CEM I 42.5R - 2 | 0.050 | 0.017 | 0.023 | 0.046 | 0.077 | 0.102 | 0.083 | 0.135 | 0.285 | 0.532 | 0.772 |
| CEM II/B-T 42.5 | 0.144 | 0.038 | 0.049 | 0.071 | 0.107 | 0.129 | 0.159 | 0.231 | 0.396 | 0.465 | 0.723 |
| CEM I 42.5 | 0.044 | 0.013 | 0.019 | 0.046 | 0.071 | 0.088 | 0.089 | 0.156 | 0.385 | 0.483 | 0.752 |

Table A11 Physical and mechanical values of the commercial cements

| Cement | Workability, mm | Density, kg/m$^3$ | Specific surface, m$^2$/kg | Compressive strength, MPa | | Flexural strength, MPa | |
|---|---|---|---|---|---|---|---|
| | | | | 2 days | 28 days | 2 days | 28 days |
| CEM I 42.5 HS | 178 | 2272 | 408 | 26.8 | 46.9 | 6.6 | 10.2 |
| CEM I 42.5 SR/LA | 161 | 2308 | 322 | 32.6 | 54.2 | 6.0 | 11.0 |
| CEM II A 52.5 R | 156 | 2270 | 568 | 45.1 | 63.9 | 9.6 | 11.2 |
| CEM II A 42.5 R | 158 | 2270 | 513 | 39.3 | 57.8 | 8.9 | 10.9 |
| CEM I 42.5 SR | 139 | 2277 | 317 | 14.8 | 56.6 | 4.2 | 9.6 |
| CEM II/B-T 42.5 R - 1 | 190 | 2293 | 416 | 34.7 | 59.4 | 8.0 | 9.8 |
| CEM II/B-T 42.5 R - 2 | 193 | 2307 | 358 | 21.7 | 47.9 | 5.6 | 8.5 |
| CEM I 42.5R - 1 | 156 | 2268 | 467 | 34.5 | 56.9 | 7.9 | 9.5 |
| CEM II/B-T 42.5 R - 3 | 204 | 2284 | 405 | 28.7 | 55.5 | 7.1 | 9.3 |
| CEM II/B-M 42.5R | 197 | 2277 | 514 | 30.3 | 54.9 | 7.1 | 9.5 |
| CEM I 42.5R - 2 | 152 | 2258 | 420 | 32.2 | 55.9 | 7.3 | 9.7 |
| CEM II/B-T 42.5 | 194 | 2283 | 375 | 22.6 | 48.7 | 5.9 | 8.6 |
| CEM I 42.5 | 156 | 2253 | 376 | 26.9 | 48.6 | 6.6 | 9.0 |

Table A12 Expansions of (10 x 40 x 160) mm mortar specimens in the 1% $MgSO_4$ and in the 1.1% $(NH_4)_2SO_4$ solution by Wittekindt method

| Cement | Expansion, mm/m | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1% $MgSO_4$ | | | | | 1.1% $(NH_4)_2SO_4$ | | | | |
| | 14 d. | 28 d. | 42 d. | 56 d. | 91 d. | 14 d. | 28 d. | 42 d. | 56 d. | 91 d. |
| | | | | | | | | | | |
| CEM I | 0.108 | 0.165 | 0.242 | 0.296 | 0.369 | 0.158 | 0.208 | 0.363 | 0.394 | 0.908 |
| CEM II/A-$T_T$(15% $T_T$) | 0.138 | 0.208 | 0.283 | 0.323 | 0.365 | 0.179 | 0.238 | 0.454 | 0.500 | 1.079 |
| CEM II/A-$T_T$ (20%$T_T$) | 0.133 | 0.190 | 0.271 | 0.313 | 0.348 | 0.202 | 0.244 | 0.446 | 0.488 | 1.360 |
| CEM II/B-$T_T$ (25% $T_T$) | 0.152 | 0.208 | 0.296 | 0.392 | 0.419 | 0.210 | 0.279 | 0.556 | 0.627 | 2.575 |
| CEM II/B-$T_T$ (30% $T_T$) | 0.160 | 0.217 | 0.319 | 0.363 | 0.400 | 0.269 | 0.287 | 0.504 | 0.544 | 3.488 |
| CEM II/A-S (10 % S) | 0.142 | 0.171 | 0.269 | 0.306 | 0.365 | 0.184 | 0.233 | 0.323 | 0.404 | 1.092 |
| CEM II/A-S (20 % S) | 0.158 | 0.198 | 0.271 | 0.308 | 0.352 | 0.198 | 0.277 | 0.404 | 0.469 | 1.165 |
| CEM II/B-S (30 % S) | 0.152 | 0.190 | 0.269 | 0.306 | 0.356 | 0.227 | 0.304 | 0.425 | 0.477 | 1.425 |
| CEM III/A (60 % S) | 0.161 | 0.194 | 0.284 | 0.284 | 0.367 | 0.173 | 0.425 | 0.696 | 0.890 | 6.333 |
| CEM II/B-M(10%$T_K$+15%$T_T$) | 0.146 | 0.258 | 0.287 | 0.290 | 0.354 | 0.224 | 0.300 | 0.518 | 0.544 | 1.194 |
| CEM II/B-M(15%$T_K$+10%$T_T$) | 0.152 | 0.244 | 0.296 | 0.304 | 0.380 | 0.225 | 0.292 | 0.525 | 0.567 | 1.177 |
| | | | | | | | | | | |
| CEM I 42.5 HS | 0.098 | 0.125 | 0.177 | 0.217 | 0.241 | 0.108 | 0.144 | 0.244 | 0.308 | 0.602 |
| CEM I 42.5 SR/LA | 0.072 | 0.129 | 0.259 | 0.371 | 0.479 | 0.350 | 0.425 | 0.671 | 0.752 | 1.335 |
| CEM II A 52.5 R | 0.069 | 0.209 | 0.279 | 0.307 | 0.398 | 0.073 | 0.144 | 0.206 | 0.235 | 0.683 |
| CEM II A 42.5 R | 0.044 | 0.088 | 0.133 | 0.129 | 0.190 | 0.052 | 0.125 | 0.213 | 0.215 | 0.694 |
| CEM I 42.5 SR | 0.050 | 0.066 | 0.115 | 0.117 | 0.165 | 0.160 | 0.154 | 0.240 | 0.238 | 0.681 |
| CEM II/B-T 42.5 R - 1 | 0.077 | 0.135 | 0.206 | 0.217 | 0.281 | 0.221 | 0.294 | 0.492 | 0.502 | 3.838 |
| CEM II/B-T 42.5 R - 2 | 0.085 | 0.190 | 0.229 | 0.244 | 0.312 | 0.094 | 0.221 | 0.354 | 0.369 | 5.335 |

Table A13 Relative expansions of (10 x 40 x 160) mm mortar specimens in the 1% $MgSO_4$ and in the 1.1% $(NH_4)_2SO_4$ solution by Wittekindt method

| Cement | Relative expansion, mm/m | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1% $MgSO_4$ | | | | | 1.1% $(NH_4)_2SO_4$ | | | | |
| | 14 p. | 28 p. | 42 p. | 56 p. | 91 p. | 14 p. | 28 p. | 42 p. | 56 p. | 91 p. |
| | | | | | | | | | | |
| CEM I | 0.06 | 0.11 | 0.17 | 0.20 | 0.24 | 0.11 | 0.15 | 0.29 | 0.30 | 0.78 |
| CEM II/A-$T_T$(15% $T_T$) | 0.08 | 0.14 | 0.20 | 0.20 | 0.23 | 0.12 | 0.17 | 0.37 | 0.38 | 0.95 |
| CEM II/A-$T_T$ (20%$T_T$) | 0.08 | 0.14 | 0.19 | 0.21 | 0.20 | 0.15 | 0.19 | 0.37 | 0.38 | 1.21 |
| CEM II/B-$T_T$ (25% $T_T$) | 0.09 | 0.14 | 0.21 | 0.25 | 0.27 | 0.15 | 0.21 | 0.47 | 0.49 | 2.43 |
| CEM II/B-$T_T$ (30% $T_T$) | 0.08 | 0.13 | 0.19 | 0.20 | 0.23 | 0.19 | 0.20 | 0.38 | 0.38 | 3.32 |
| CEM II/A-S (10 % S) | 0.08 | 0.10 | 0.18 | 0.21 | 0.24 | 0.12 | 0.17 | 0.23 | 0.31 | 0.96 |
| CEM II/A-S (20 % S) | 0.09 | 0.12 | 0.18 | 0.21 | 0.22 | 0.13 | 0.20 | 0.31 | 0.37 | 1.03 |
| CEM II/B-S (30 % S) | 0.07 | 0.10 | 0.16 | 0.19 | 0.20 | 0.15 | 0.21 | 0.32 | 0.36 | 1.27 |
| CEM III/A (60 % S) | 0.13 | 0.12 | 0.20 | 0.19 | 0.26 | 0.14 | 0.35 | 0.61 | 0.79 | 6.23 |
| CEM II/B-M(10%$T_K$+15%$T_T$) | 0.10 | 0.20 | 0.19 | 0.22 | 0.23 | 0.17 | 0.24 | 0.42 | 0.47 | 1.07 |
| CEM II/B-M(15%$T_K$+10%$T_T$) | 0.10 | 0.19 | 0.22 | 0.23 | 0.24 | 0.17 | 0.24 | 0.44 | 0.49 | 1.04 |
| | | | | | | | | | | |
| CEM I 42.5 HS | 0.07 | 0.09 | 0.13 | 0.13 | 0.13 | 0.08 | 0.11 | 0.20 | 0.23 | 0.49 |
| CEM I 42.5 SR/LA | 0.02 | 0.03 | 0.15 | 0.26 | 0.37 | 0.30 | 0.33 | 0.57 | 0.64 | 1.23 |
| CEM II A 52.5 R | 0.03 | 0.14 | 0.19 | 0.21 | 0.29 | 0.03 | 0.08 | 0.12 | 0.14 | 0.57 |
| CEM II A 42.5 R | 0.02 | 0.02 | 0.02 | 0.02 | 0.07 | 0.02 | 0.06 | 0.10 | 0.10 | 0.58 |
| CEM I 42.5 SR | 0.03 | 0.03 | 0.03 | 0.03 | 0.07 | 0.14 | 0.12 | 0.15 | 0.15 | 0.59 |
| CEM II/B-T 42.5 R - 1 | 0.03 | 0.05 | 0.07 | 0.08 | 0.12 | 0.18 | 0.21 | 0.36 | 0.37 | 3.68 |
| CEM II/B-T 42.5 R - 2 | 0.04 | 0.10 | 0.13 | 0.14 | 0.19 | 0.05 | 0.13 | 0.26 | 0.26 | 5.21 |

Table A14 Compressive strength of the concrete with various Portland cements. The values are expressed as the average of three specimens

| Cement | Compressive strength, MPa | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Cement content 320 kg/m$^3$ | | | | Cement content 450 kg/m$^3$ | | | |
| | 2 d. | 7 d. | 28 d. | 91 d. | 2 d. | 7 d. | 28 d. | 91 d. |
| CEM I | 26.1 | 37.2 | 44.9 | 47.7 | 29.9 | 39.9 | 51.0 | 54.2 |
| CEM II/A-L (10 % L) | 22.3 | 33.7 | 42.0 | 46.9 | 32.1 | 43.4 | 54.2 | 58.2 |
| CEM II/A-$T_K$ (15 % $T_K$) | 27.6 | 38.9 | 46.9 | 49.3 | 34.0 | 46.9 | 56.3 | 58.9 |
| CEM II/B- $T_K$ (25 % $T_K$) | 24.3 | 36.5 | 43.5 | 46.8 | 34.5 | 47.1 | 57.5 | 58.9 |
| CEM II/B-$T_T$ (25 % $T_T$) | 33.3 | 44.9 | 54.5 | 60.8 | 44.0 | 56.7 | 72.3 | 78.5 |
| CEM II/B-M(10%$T_K$+15%$T_T$) | 30.6 | 42.2 | 49.3 | 55.3 | 40.3 | 52.8 | 66.3 | 71.3 |
| CEM II/B-M(15%$T_K$+10%$T_T$) | 29.0 | 40.5 | 49.6 | 54.4 | 37.5 | 50.0 | 62.3 | 67.8 |
| CEM II/B-M(20%$T_K$+10%$T_T$) | 27.3 | 39.2 | 46.7 | 51.6 | 36.5 | 48.5 | 61.8 | 65.6 |
| CEM III/B (70 % S) | 8.6 | 20.0 | 37.2 | 41.3 | 10.2 | 21.4 | 39.1 | 45.7 |

Table A15 Frost resistance of concrete in the distilled water and in the 3 % NaCl solution according to EVS 814:2003

| Cement content 320 kg/m$^3$ | Scaling (kg/m$^2$), after cycles | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 3 % NaCl | | | | | Distilled water | | | | |
| | 7 | 14 | 28 | 42 | 56 | 7 | 14 | 28 | 42 | 56 |
| CEM I | 0.04 | 0.09 | 0.19 | 0.26 | 0.35 | 0.00 | 0.01 | 0.01 | 0.02 | 0.02 |
| CEM II/A-L (10 % L) | 0.07 | 0.14 | 0.22 | 0.28 | 0.34 | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 |
| CEM II/A-T$_K$ (15 % T$_K$) | 0.05 | 0.10 | 0.16 | 0.20 | 0.23 | 0.00 | 0.01 | 0.01 | 0.02 | 0.03 |
| CEM II/B- T$_K$ (25 % T$_K$) | 0.07 | 0.11 | 0.17 | 0.21 | 0.26 | 0.02 | 0.03 | 0.05 | 0.05 | 0.05 |
| CEM II/B-T$_T$ (25 % T$_T$) | 0.03 | 0.06 | 0.09 | 0.11 | 0.13 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CEM II/B-M (10% T$_K$ + 15% T$_T$) | 0.06 | 0.11 | 0.16 | 0.21 | 0.26 | 0.00 | 0.01 | 0.02 | 0.02 | 0.02 |
| CEM II/B-M (15% T$_K$ + 10% T$_T$) | 0.07 | 0.11 | 0.15 | 0.20 | 0.25 | 0.01 | 0.01 | 0.02 | 0.04 | 0.05 |
| CEM II/B-M (20% T$_K$ + 10% T$_T$) | 0.07 | 0.13 | 0.18 | 0.24 | 0.34 | 0.01 | 0.02 | 0.03 | 0.06 | 0.09 |
| CEM III/B (70 % S) | 0.60 | 0.76 | 0.92 | 1.04 | 1.15 | 0.04 | 0.07 | 0.13 | 0.20 | 0.29 |

| Cement content 450 kg/m$^3$ | Scaling (kg/m$^2$), after cycles | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 3 % NaCl | | | | | Distilled water | | | | |
| | 7 | 14 | 28 | 42 | 56 | 7 | 14 | 28 | 42 | 56 |
| CEM I | 0.03 | 0.08 | 0.16 | 0.23 | 0.28 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 |
| CEM II/A-L (10 % L) | 0.06 | 0.12 | 0.20 | 0.25 | 0.31 | 0.00 | 0.01 | 0.01 | 0.02 | 0.02 |
| CEM II/A-T$_K$ (15 % T$_K$) | 0.04 | 0.09 | 0.14 | 0.19 | 0.22 | 0.00 | 0.00 | 0.00 | 0.01 | 0.03 |
| CEM II/B- T$_K$ (25 % T$_K$) | 0.04 | 0.07 | 0.11 | 0.14 | 0.18 | 0.00 | 0.01 | 0.01 | 0.02 | 0.02 |
| CEM II/B-T$_T$ (25 % T$_T$) | 0.01 | 0.03 | 0.06 | 0.09 | 0.12 | 0.00 | 0.00 | 0.00 | 0.01 | 0.02 |
| CEM II/B-M (10% T$_K$ + 15% T$_T$) | 0.03 | 0.06 | 0.11 | 0.18 | 0.24 | 0.01 | 0.01 | 0.02 | 0.04 | 0.05 |
| CEM II/B-M (15% T$_K$ + 10% T$_T$) | 0.04 | 0.07 | 0.12 | 0.20 | 0.24 | 0.01 | 0.01 | 0.03 | 0.05 | 0.07 |
| CEM II/B-M (20% T$_K$ + 10% T$_T$) | 0.06 | 0.08 | 0.14 | 0.24 | 0.33 | 0.01 | 0.01 | 0.04 | 0.06 | 0.08 |
| CEM III/B (70 % S) | 0.55 | 0.70 | 0.84 | 0.95 | 1.05 | 0.03 | 0.06 | 0.11 | 0.17 | 0.25 |

Table A16 Frost resistance of the concrete in the $Na_2SO_4$ solution

| Cement content<br>320 kg/m$^3$ | Scaling (kg/m$^2$), after cycles | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 4.4 % $Na_2SO_4$ | | | | | 2.2 % $Na_2SO_4$ | | | | |
| | 7 | 14 | 28 | 42 | 56 | 7 | 14 | 28 | 42 | 56 |
| CEM I | 0.02 | 0.03 | 0.04 | 0.04 | 0.06 | 0.02 | 0.02 | 0.02 | 0.03 | 0.05 |
| CEM II/A-L (10 % L) | 0.03 | 0.03 | 0.03 | 0.05 | 0.06 | 0.02 | 0.03 | 0.03 | 0.05 | 0.06 |
| CEM II/B- $T_K$ (25% $T_K$) | 0.01 | 0.02 | 0.02 | 0.03 | 0.04 | 0.01 | 0.01 | 0.01 | 0.02 | 0.03 |
| CEM II/B-$T_T$ (25 % $T_T$) | 0.01 | 0.02 | 0.02 | 0.03 | 0.04 | 0.00 | 0.01 | 0.01 | 0.01 | 0.02 |
| CEM II/B-M (10% $T_K$+15% $T_T$) | 0.02 | 0.04 | 0.04 | 0.05 | 0.07 | 0.01 | 0.02 | 0.03 | 0.03 | 0.04 |
| CEM III/B (70 % S) | 0.02 | 0.04 | 0.06 | 0.16 | 0.31 | 0.02 | 0.03 | 0.07 | 0.15 | 0.25 |

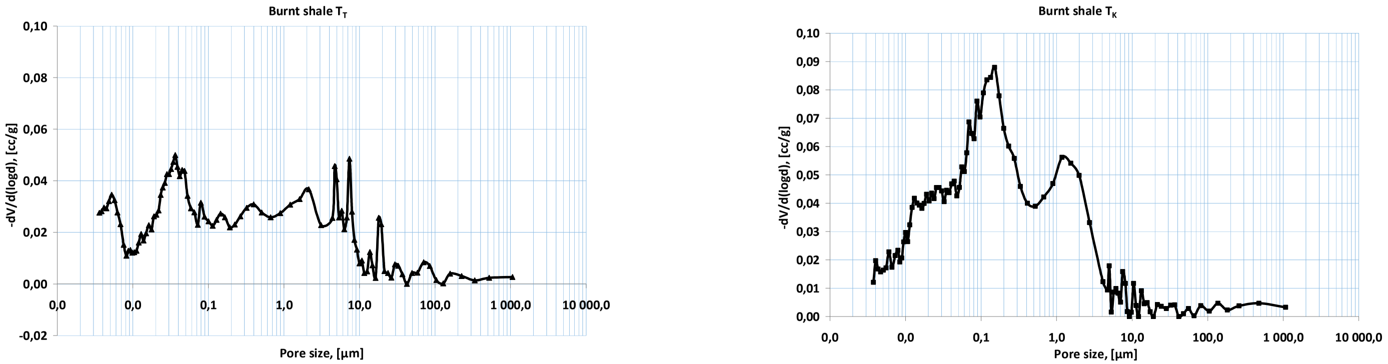
Table A17 Water permeability of concrete by EVS-EN 12390-8 as the depth of penetration of water under pressure

| Cement | Water penetration, mm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cement content 320 kg/m$^3$ | | | | | Cement content 450 kg/m$^3$ | | | | |
| | 1 | 2 | 3 | 4 | max | 1 | 2 | 3 | 4 | max |
| CEM I | 11 | 9 | 10 | 11 | **11** | 6 | 5 | 9 | 10 | **10** |
| CEM II/A-L (10 % L) | 9 | 8 | 9 | 8 | **9** | 5 | 6 | 5 | 5 | **6** |
| CEM II/A-$T_K$ (15 % $T_K$) | 8 | 9 | 11 | 12 | **12** | 6 | 6 | 7 | 6 | **7** |
| CEM II/B- $T_K$ (25 % $T_K$) | 9 | 10 | 9 | 9 | **10** | 7 | 6 | 7 | 7 | **7** |
| CEM II/B-$T_T$ (25 % $T_T$) | 9 | 8 | 9 | 8 | **9** | 5 | 4 | 4 | 5 | **5** |
| CEM II/B-M (10% $T_K$+15% $T_T$) | 4 | 5 | 4 | 6 | **6** | 6 | 5 | 6 | 8 | **8** |
| CEM II/B-M (15% $T_K$+10% $T_T$) | 14 | 16 | 12 | 13 | **16** | 9 | 8 | 9 | 8 | **9** |
| CEM II/B-M (20% $T_K$+10% $T_T$) | 12 | 11 | 12 | 11 | **12** | 7 | 8 | 8 | 8 | **8** |
| CEM III/B (70 % S) | 5 | 4 | 5 | 5 | **5** | 4 | 3 | 3 | 4 | **4** |

Table A18 Water absorption of the concrete specimens as a function of time

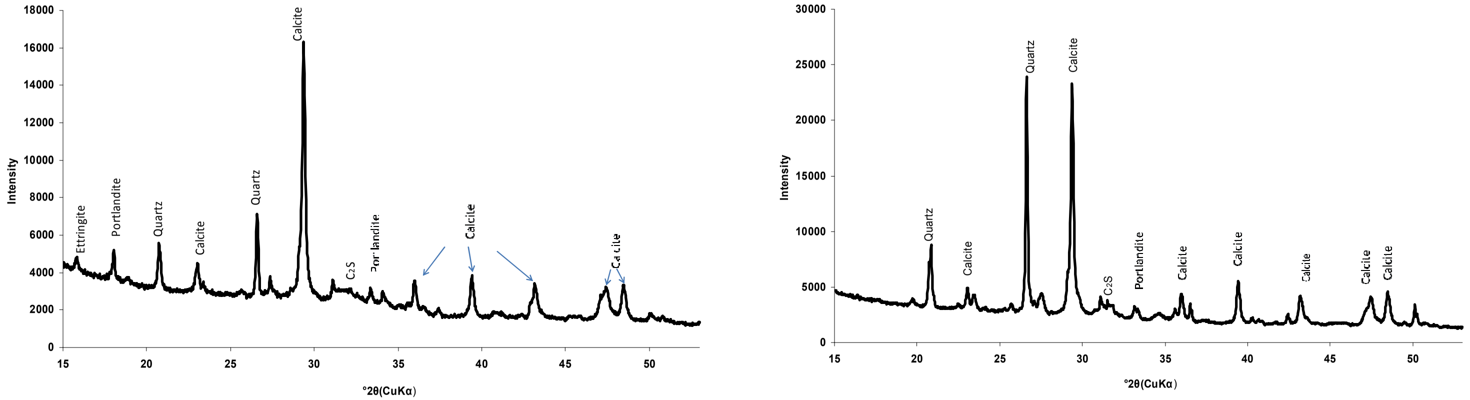
| Cement | Dimensions | | Mass of specimens in g, at testing time | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | a, mm | b, mm | Initial | 10 min | 20 min | 30 min | 1 h | 2 h | 6 h | 24 h | 48 h | 96 h | 168 h | 1176 h |
| **a) Water** | | | | | | | | | | | | | | |
| CEM I | 101 | 100 | 1114.0 | 1122.5 | 1124.0 | 1125.0 | 1127.0 | 1129.0 | 1131.0 | 1139.5 | 1142.9 | 1146.0 | 1146.5 | 1147.5 |
| CEM II/B - 25 $T_T$ | 100 | 100 | 1149.0 | 1153.5 | 1155.0 | 1155.5 | 1156.5 | 1158.0 | 1159.0 | 1162.0 | 1163.5 | 1164.5 | 1165.0 | 1167.0 |
| CEM II/A - 10 L | 100 | 101 | 1133.5 | 1140.5 | 1142.5 | 1143.5 | 1145.5 | 1147.5 | 1149.5 | 1157.0 | 1160.0 | 1163.0 | 1163.0 | 1163.5 |
| CEM II/B - 25 $T_K$ | 101 | 100 | 1123.5 | 1129.5 | 1131.5 | 1132.0 | 1133.5 | 1135.5 | 1137.0 | 1142.0 | 1144.0 | 1147.0 | 1147.5 | 1149.5 |
| CEM III/A - 70 S | 101 | 97 | 1061.0 | 1068.0 | 1069.5 | 1070.5 | 1072.0 | 1074.0 | 1075.5 | 1081.0 | 1082.5 | 1083.5 | 1084.0 | 1085.0 |
| CEM II -15$T_T$+10$T_K$ | 100 | 100 | 1135.5 | 1141.5 | 1143.0 | 1143.5 | 1145.0 | 1146.5 | 1148.0 | 1152.0 | 1153.0 | 1154.5 | 1154.5 | 1156.5 |
| **b) 3 % NaCl** | | | | | | | | | | | | | | |
| CEM I | 101 | 100 | 1108.5 | 1117.0 | 1119.0 | 1120.0 | 1122.5 | 1126.0 | 1128.0 | 1136.0 | 1139.0 | 1142.5 | 1143.5 | 1148.0 |
| CEM II/B - 25 $T_T$ | 100 | 101 | 1172.0 | 1177.0 | 1178.5 | 1179.0 | 1180.5 | 1181.5 | 1182.5 | 1186.0 | 1187.5 | 1190.0 | 1190.5 | 1198.5 |
| CEM II/A - 10 L | 101 | 100 | 1121.5 | 1129.5 | 1131.5 | 1132.5 | 1134.0 | 1136.5 | 1138.5 | 1146.0 | 1149.5 | 1154.0 | 1155.0 | 1160.0 |
| CEM II/B - 25 $T_K$ | 101 | 100 | 1134.0 | 1140.5 | 1141.5 | 1142.5 | 1144.0 | 1145.0 | 1147.0 | 1151.5 | 1154.0 | 1157.0 | 1157.5 | 1164.0 |
| CEM III/A - 70 S | 100 | 103 | 1148.5 | 1155.0 | 1157.0 | 1158.0 | 1160.5 | 1163.0 | 1165.0 | 1172.0 | 1175.0 | 1178.0 | 1179.5 | 1187.5 |
| CEM II -15$T_T$+10$T_K$ | 100 | 100 | 1115.5 | 1121.5 | 1123.0 | 1124.0 | 1125.0 | 1127.0 | 1128.0 | 1132.0 | 1134.5 | 1137.0 | 1138.0 | 1144.5 |
| **c) 4.4 % $Na_2SO_4$** | | | | | | | | | | | | | | |
| CEM I | 99 | 101 | 1112.5 | 1120.5 | 1122.0 | 1123.0 | 1124.5 | 1127.0 | 1129.0 | 1136.0 | 1139.0 | 1143.0 | 1143.5 | 1147.5 |
| CEM II/B - 25 $T_T$ | 100 | 101 | 1129.0 | 1134.0 | 1135.5 | 1136.0 | 1137.5 | 1138.5 | 1139.5 | 1142.5 | 1144.5 | 1146.5 | 1147.5 | 1150.0 |
| CEM II/A - 10 L | 101 | 99 | 1119.5 | 1127.0 | 1128.5 | 1129.5 | 1131.0 | 1133.5 | 1135.5 | 1143.5 | 1147.0 | 1151.0 | 1151.0 | 1155.0 |
| CEM II/B - 25 $T_K$ | 100 | 101 | 1117.5 | 1125.0 | 1126.5 | 1127.5 | 1129.5 | 1131.5 | 1133.5 | 1139.5 | 1142.5 | 1146.0 | 1147.0 | 1151.0 |
| CEM III/A - 70 S | 97 | 102 | 1102.0 | 1109.0 | 1110.5 | 1111.5 | 1113.0 | 1115.0 | 1116.5 | 1122.0 | 1125.0 | 1128.0 | 1128.5 | 1133.5 |
| CEM II -15$T_T$+10$T_K$ | 100 | 100 | 1158.5 | 1166.5 | 1168.0 | 1168.5 | 1170.0 | 1172.0 | 1173.5 | 1178.0 | 1179.0 | 1182.5 | 1183.0 | 1188.0 |
| **d) 3.6 % $MgSO_4$** | | | | | | | | | | | | | | |
| CEM I | 99 | 101 | 1096.0 | 1102.0 | 1103.0 | 1103.0 | 1104.0 | 1104.5 | 1105.0 | 1107.5 | 1109.0 | 1111.5 | 1113.0 | 1117.5 |
| CEM II/B - 25 $T_T$ | 101 | 100 | 1155.5 | 1160.0 | 1160.5 | 1160.5 | 1161.0 | 1161.5 | 1162.0 | 1163.5 | 1164.5 | 1166.5 | 1167.0 | 1171.5 |
| CEM II/A - 10 L | 100 | 99 | 1100.0 | 1105.0 | 1105.5 | 1105.5 | 1106.0 | 1106.5 | 1107.0 | 1109.0 | 1110.5 | 1112.5 | 1114.0 | 1120.0 |
| CEM II/B - 25 $T_K$ | 100 | 101 | 1131.0 | 1136.0 | 1136.5 | 1136.5 | 1137.0 | 1138.0 | 1138.5 | 1141.0 | 1142.5 | 1145.0 | 1146.5 | 1151.5 |
| CEM III/A - 70 S | 100 | 98 | 1060.0 | 1066.0 | 1067.0 | 1068.0 | 1070.0 | 1071.5 | 1073.0 | 1076.0 | 1077.0 | 1079.0 | 1080.5 | 1090.5 |
| CEM II -15$T_T$+10$T_K$ | 100 | 100 | 1073.5 | 1078.5 | 1079.0 | 1079.5 | 1080.0 | 1080.5 | 1081.0 | 1082.5 | 1084.0 | 1086.0 | 1087.0 | 1092.5 |

Figure A1 Results of XRD and MIP analysis. Paste specimens were made with burnt shales $T_T$ and $T_K$ and stored in water for 91 days



a) The pore size distribution of burnt shale $T_T$ paste

b) The pore size distribution of burnt shale $T_K$ paste



c) XRD analysis of burnt shale $T_T$ paste

d) XRD analysis of burnt shale $T_K$ paste

Table A19 Dynamic modulus of elasticity ($E_d$) up to 2-year storage in the 4.4 % $Na_2SO_4$ solution. Compressive and flexural strength after one and two years. Concrete specimens with dimensions (70 x 70 x 210) mm.

| Cement | Dynamic modulus of elasticity ($E_d$), GPa | | | | | | | Compressive strength, MPa | | Flexural strength, MPa | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 day | 14 days | 28 days | 91 days | 12 months | 18 months | 24 months | 1 year | 2 years | 1 year | 2 years |
| CEM I | 30.1 | 39.0 | 40.7 | 42.2 | 42.8 | 43.2 | 41.8 | 61.6 | 60.8 | 7.5 | 6.8 |
| CEM II/A-$T_T$ (25%$T_T$) | 32.2 | 42.2 | 43.9 | 45.7 | 46.8 | 47.3 | 47.6 | 86.5 | 87.2 | 9.0 | 9.1 |
| CEM II/A-L (10%L) | 29.8 | 39.4 | 41.0 | 42.9 | 43.6 | 44.2 | 44.3 | 65.8 | 65.9 | 7.7 | 7.4 |
| CEM II/A-$T_K$ (25%$T_K$) | 28.4 | 39.1 | 40.5 | 42.1 | 42.9 | 43.4 | 43.7 | 66.2 | 66.5 | 6.9 | 6.7 |
| CEM III/A (70%S) | - | 32.3 | 37.2 | 41.9 | 42.5 | 42.8 | 43.0 | 52.4 | 52.7 | 8.0 | 7.7 |
| CEM II/B-M (15%$T_T$+10%$T_K$) | 28.3 | 39.5 | 41.4 | 43.4 | 44.2 | 44.5 | 44.8 | 72.3 | 72.8 | 6.3 | 6.2 |

Table A20 Mass change of the concrete specimens with dimensions (70 x 70 x 210) mm.

| Cement | Mass of specimens, g | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 day | 14 days | 28 days | 91 days | 12 months | 18 months | 24 months |
| CEM I | 2529 | 2535 | 2542 | 2545 | 2547 | 2545 | 2546 |
| CEM II/A-$T_T$ (25%$T_T$) | 2556 | 2560 | 2568 | 2571 | 2573 | 2577 | 2578 |
| CEM II/A-L (10%L) | 2555 | 2560 | 2567 | 2569 | 2570 | 2572 | 2573 |
| CEM II/A-$T_K$ (25%$T_K$) | 2551 | 2556 | 2562 | 2565 | 2567 | 2568 | 2568 |
| CEM III/A (70%S) | 2521 | 2526 | 2532 | 2537 | 2542 | 2546 | 2550 |
| CEM II/B-M (15%$T_T$+10%$T_K$) | 2506 | 2512 | 2518 | 2521 | 2524 | 2527 | 2529 |

## Publications

Raado L.-M., Tuisk T., Rosenberg M., Hain T. (2011). Durability Behavior of Portland Burnt Oil Shale Cement Concrete. Oil Shale, 28(4), pp. 507 - 515.

Raado L.-M., Hain T. (2004). Effect of Portland Cement Composition on Sulphate Resistance, 1st Baltic Conference on Silicate Materials; Kampars,V; Kalninš et al. Material Science and Applied Chemistry Riga: Riga Technical University, pp.75-78.

Raado L.-M., Hain T. (2003). Sulphate Resistance of Various Portland Cements, 15th Internationale Baustofftagung, Weimar, Tagungsbericht, Band 2, pp.2-0975-0981

Raado L.-M., Hain T. (2003). Corrosion of Cement and Concrete - Methods of Testing and Evaluation, Management of Durability in the Building Process, Milan, Proceedings, CDROM, pp.1-7.

# Abstract

The doctoral thesis covers the durability of cement concrete depending on factors affecting the sulfate resistance of cement in various pastes, mortars and concrete. The applicability of different testing methods for determination sulfate resistance parameters and their influence on concrete durability was examined.

Portland composite cement with inert, puzzolanic or hydraulic second constituents is an effective way to improve the strength and durability of concrete. The behavior of Portland cement without and with burnt shales, fine limestone or/and granulated blast furnace slag addition in aggressive sulfate solutions was studied. Various parameters, such as cement type, cement constituents and clinker composition, factors affecting concrete failure and several exposure conditions were studied.

The characterization of physical and chemical properties of second constituents eased the proportioning of the composite cement so that for a given clinker, the desired properties were possessed. Afterwards the microstructure of the hydration and corrosion products was examined by SEM and XRD analysis. By microstructural properties of the hardened paste most of the macrostructural characteristics, durability to different exposure conditions, mechanical behavior, porosity, diffusivity and permeability were explained.

The use of CEM I cement in conjunction with a suitably characterized second constituent of cement enhanced the durability of concrete by increasing its resistance to sulfate attack. The impact of second constituents was dominated by their impact on the cement paste porosity and on the rate of sulfate ingress. Densities and capillary pore structures of concretes made with various Portland composite cements varied in a wide range, resulting in differences in water absorption, sulfate resistance and frost resistance. According to the dissimilarities in characteristics and hardening kinetics that became evident in testing cements with various compositions, the frost resistance test was carried out. The durability of water-saturated hardened cement mortar in situation of alternate freezing and thawing characterizes the formed structure of cement stone. On the other hand sulfate resistance characterizes the reaction ability of cement and aggressive environment.

Test results showed that tests based only on expansion measurement couldn’t represent the degradation process, but combined with other significant characteristics such as mass change, XRD, structural and compressive strength, capillary porosity of mortars, could represent valuable characteristics.

Wittekindt flat prisms method was used for assessing sulfate resistance of different Portland cements with various clinkers and Portland cements with two and more main constituents. Experimental results from long-term study on concrete on expansion, dynamic modulus of elasticity ($E_d$) and water absorption showed the data from the Wittekindt test to be reliable in assessing the cements in relatively short time. The methods for testing various aspects of durability - sulfate resistance, water and salt absorption or frost resistance – are not similarly applicable for characterizing all cement types.

# Kokkuvõte

Uurimistöö eesmärgiks oli püsivate betoonide saamiseks kasutatavate sulfaadikindlate tsementide määratlemiseks vajalike meetodite ja parameetrite uurimine. Sulfaatsetes keskkondades vastupidava betooni koostise väljatöötamiseks pöörati põhitähelepanu tsemendi, kui kõige tundlikuma koostiskomponendi omadustele. Käsitleti erinevate portlandtsemendi koostiskomponentide – varieeruva trikaltsiumaluminaadi sisaldusega klinkrite, põletatud põlevkivide, granuleeritud kõrgahjuräbude ja jahvatatud lubjakivi - mõju tsemendi sulfaadikindlusele.

Betooni sulfaadikindlust võib käsitleda kui tsemendi reaktsioonivõimelisust sulfaatsetes lahustes või/ja sulfaate sisaldava lahuse difusiooni kiirust tsemendikivi sisemusse ja seejärel reageerimist. Senini tsemendi sulfaadikindluse määramiseks kasutatud meetodid ei suuda ühendada mõlemat mõju. Tsementide korrosioonikindluse parameetriks valiti katsekehade paisumise hindamine kiirmeetodil sulfaatses lahuses säilitamisel Wittekindti lameprismade (10 x 40 x 160) mm meetodil EVS-EN 196 kohase tsementmördist katsekehadega vesitsementteguriga 0,50.

Betooni sulfaadikindluse parameetrite määratlemiseks erinevate katsemeetodite kasutatavuse ja mõju uurimise tulemina ilmnes, et katsemeetodid, mis baseeruvad vaid paisumise mõõtmisel, ei väljenda üheselt korrosiooniprotsessi olemust. Kuid kombineeritult massimuutuse, röntgenstruktuuranalüüsi, tugevusnäitajate ja dünaamilise elastsusmooduli muutuse ning mörtide kapillaarpoorsusega saab iseloomustada tsemendi ja betooni käitumist agressiivses keskkonnas.

Uuritud tsementide klinkrisisaldus muutus 25…94 % piires, kõrgel temperatuuril põletatud (tolmkütte elektrifiltri) põlevkivi sisaldus oli 15, 20, 25 ja 30 %, madalal temperatuuril põletatud (keevkihikatla) põlevkivi sisaldus oli 15, 20 ja 25 %, räbu sisaldus oli 10, 20, 30, 50, 60 ja 70 %, lubjakivi lisati 5, 10 ja 15 %. Tsemendid valmistati laboratoorselt lähtudes standardis EVS-EN 197-1 lubatud tsemendi koostiskomponentidest ja nende hulkadest tsemendis. Kõiki erinevate inertsete, putsolaansete või hüdrauliliste koostiskomponentidega komposiittsementide omadusi vaadeldi võrdlevalt lähtudes portlandtsemendi vastavatest omadustest.

Tsemendi sulfaadikindluse seisukohast oluliste tsemendimineraalide käitumist ja moodustuvaid hüdratatsiooniprodukte uuriti elektronmikroskoopia ja difraktomeetrilise analüüsi abil, vaadeldi korrodeerunud tsementmördist katsekehadest prepareeritud katseobjektidel aine tihedust, poorsuse laadi, moodustunud korrosiooniprodukte. Katsetulemustest nähtus oluline erinevus tekkinud korrosiooniproduktides ja katsekeha tihedustes sõltuvalt kivistamise kestusest, kivistamiskeskkonnast ja tsemendi liigist.

Peale korrosioonist tingitud mahumuutuste võeti vaatlusele ka peeneteralise betooni külmutuskindluse muutus ja selle seostamine korrosiooniilmingutega. Külmakindluse määramise aluseks on veega küllastatud betooni allutamine vahelduvale külmumisele-sulamisele. Seega kajastab betooni ja tsemendikivi immutamine just väliskeskkonna difusioonikiirust tsemendikivi sisse.

Portlandtsemendiga valmistatud mördi paisumine 4,4 % $Na_2SO_4$ lahuses 91 päeva kestel ületas sulfaadikindlale tsemendile lubatud paisumise diferentsi piirväärtuse oluliselt. Portlandtsementmört ja -betoon omasid katsetulemustest nähtuvalt suurimat poorsust, veeimavust, veeläbivust, mis tingisid ka sulfaatsete lahuste migratsiooniprotsesside kiirenemise.

Inertse jahvatatud lubjakivi lisand tsemendis halvendas mörtide ja betoonide füüsikalisi ja mehaanilisi omadusi – vähenesid sulfaadikindlus, tugevusnäitajad, külmakindlus. Korrosiooniproduktina kipsi osatähtsus suurenes ja $Ca(OH)_2$ vähenes, seetõttu paisumise suurenemine $Na_2SO_4$ lahuses viis katsekehade purunemiseni.

Tolmpõletusel saadud ehk temperatuuridel 1300...1400 ºC põletatud põlevkivi $T_T$ lisamisega portlandtsemendile paranes tsemendi korrosioonikindlus 4,4 % $Na_2SO_4$ lahuses võrdeliselt lisatava põletatud põlevkivi $T_T$ hulgaga. Moodustuv portland-põlevkivitsemendi CEM II/B-$T_T$ tsemendikivi struktuur oli tihe, enamik pooridest täitunud korrosiooniproduktidega. Portland-põlevkivitsemendi veevajadus vähenes oluliselt võrreldes portlandtsemendiga; poorsus vähenes, kapillaarpooride suurus vähenes ja geelipooride hulk suurenes, mistõttu suurenes ka sulfaadikindlus.

Keevkihikatlas põletatud põlevkivi $T_K$ põletamine, mis toimub madalamal temperatuuril (800 ºC), põhjustab olulisi muutusi põletatud põlevkivi $T_K$ osakeste omadustes ja seeläbi ka põletatud põlevkiviga $T_K$ valmistatud portland-põlevkivitsemendi CEM II/B-$T_K$ omadustes võrreldes põletatud põlevkiviga $T_T$ tsemendiga. Kuna antud katelagregaate on kasutatud suhteliselt lühiajaliselt põlevkivi põletamiseks, siis muutunud mineraloogilise koostisega põletatud põlevkivi $T_K$ tsementide ja betoonide püsivusomadusi ja vastupanu korrosioonile senini oluliselt uuritud ei ole. Erinev mineraloogiline koostis, suurem $SiO_2$ ja $CaCO_3$ sisaldus, ebaühtlane terakuju avaldasid otsest mõju hüdrauliliste omaduste vähenemisele ja putsolaansuse suurenemisele. Portland-põlevkivitsemendi CEM II/B-$T_K$ veevajadus suurenes oluliselt, mistõttu suurenes ka kapillaarpooride hulk. Sulfaadikindlus, tugevusomadused ja külmakindlus vähenesid ning veeimavus suurenes võrreldes põletatud põlevkiviga $T_T$ tsemendiga.

Granuleeritud kõrgahjuräbu manusel 20…30 % tsemendi massist paisumine vähenes portlandtsemendiga võrreldes, kuid paisumise väärtused jäid kõrgemaks lubatud etteantud piirväärtusest. Granuleeritud kõrgahjuräbu osahulga suurenemisega 50…70 % suurenes tsementide korrosioonikindlus märkimisväärselt. Räbutsemendi tsemendikivi mikrostruktuur oli tihe, korrosiooniproduktidest ei nähtunud SEM-iga ei ettringiiti ega kipsi. Räbutsementbetoonidele oli iseloomulik väike varajane tugevus ja väga madal külmakindlus.

Laboratooriumis valmistatud tsementidest sulfaadikindluse seisukohalt kõige perspektiivsemaks osutusid kolmekomponendilised tsemendid. Kasutades tsemendis nii põletatud põlevkivi $T_T$ kui räbu, komposiittsemendi 28 päevased survetugevuse ja külmakindluse näitajad võrreldes portlandtsemendiga oluliselt ei halvenenud, kuid komposiittsemendi sulfaadikindlus tõusis võrreldes portlandtsemendiga. Komposiittsemendi sulfaadikindlus tõus oli MIP, XRD ja SEM analüüsi tulemustest johtuvalt seotud $Ca(OH)_2$ ja $C_3A$ sisalduse vähenemisega, vähenes poorsus, pooride struktuur peenem ja kitsam, vähenes ohtlike korrosiooniproduktide hulk ja seeläbi ka sulfaatsete lahuste difusioon tsemendikivis.

Võrdluseks katsetati ka Euroopas toodetavaid sulfaadikindlaid ja Eestis toodetavaid tööstuslikke tsemente. Tööstuslik jahvatusprotsess võimaldab toota homogeensema terasuurusega ja parema terastiku koostisega tsemente, mis avaldavad tsementide sulfaadikindlusele jm. püsivusnäitajatele otsest mõju ning kajastusid ka laboratoorsete ja tööstuslike tsementide katsetulemuste võrdluses.

Nii paisumise kui ka tugevuskatsete katsetulemustest lähtuvalt võib väita, et 4,4 % $Na_2SO_4$ lahuses annab antud katsemeetod üsna tõeseid ja korratavaid katsetulemusi, mida tõestasid erinevatel aegadel samade tsementidega teostatud korduskatsete ja teiste meetodite alusel teostatud lisakatsete tulemused.

Valitud tsementidega uuriti põhjalikumalt tsementide käitumist betooni püsivusnäitajate mõjutajatena. Betooni koostise valikul lähtuti EN 206 toodud nõuetest sulfaatses keskkonnas töötavale betoonile. Uuriti seoseid tsementide ja betoonide sulfaadikindluse ja teiste betooni püsivusnäitajate vahel. Lisaks tsementide omaduste määramisele uuriti ka nende omaduste määramiste meetodeid, mis tagavad samaaegselt uuritava tsemendiga valmistatud betooni püsivuse agressiivses keskkonnas kui ka kõrge külmakindluse. Erinevat tüüpi tsementidega valmistatud betoonide tihedused ja kapillaarpooride struktuurid varieerusid olulisel määral, mistõttu erinevat tüüpi tsementbetoonide veeimavused, sulfaadikindlused, tugevusnäitajad ja külmakindlused ka erinesid oluliselt. Tulemustest järeldus, et sulfaadikindlus sõltub otseselt moodustunud struktuuri võimest imada vett ja sulfaatseid lahuseid, ning hüdratatsiooni- ja korrosiooniproduktide tüübist ja nende reaktsioonivõimelisusest. Külmumise võimalikkus suurendab agressiivse keskkonna mõju betoonile.

Katsetulemuste põhjal toodi välja erinevad komposiittsementide koostised piiritledes tsementide optimaalsed koostiskomponendid ja hulgad, arvestades kõiki teostatud füüsikalisi, mehaanilisi ja keemilisi katseid. Tsementide ja betoonide paisumise ja külmakindluse katsetulemused seostati korrosioonikindluse määramistega 4,4 % $Na_2SO_4$ lahuses.

Töö tulemused näitasid, et tsemendi koostiskomponentide kivinemistüüp mõjutab otseselt moodustuva tsemendikivi vastupanuvõimet sulfaatsele korrosioonile. Töö tulemused peaksid võimaldama suhteliselt lühiajaliste katsetuste tulemusena ennustada betooni püsivusnäitajaid merelises, keemiliselt agressiivses ja vahelduvas külmumisele ja sulamisele alluvas keskkonnas.

Saadud tulemuste baasil betooni püsivuse teoreetiliste aluste väljatöötamiseks sõltuvalt tsemendi koostiskomponentidest, tuleks arendada ja uurida katsemeetodeid tsemendikivi vedelfaasi koostise määramiseks.

## *Curriculum Vitae*

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Burnt oil shale of fluidized bed combustion as constituent of new type of Portland cement.
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Teadustöö põhisuunad / Teised uurimisprojektid:

Põlevkivi põletamisega kaasnevate tahkjäätmete uute kasutusalade alused.
Põlevkivi kaevandamis- ja töötlemisjääkide kasutamine betoonina tagasitäiteks kaevandatud aladel.

# DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *CIVIL ENGINEERING*

1. **Heino Mölder**. Cycle of Investigations to Improve the Efficiency and Reliability of Activated Sludge Process in Sewage Treatment Plants. 1992.

2. **Stellian Grabko**. Structure and Properties of Oil-Shale Portland Cement Concrete. 1993.

3. **Kent Arvidsson**. Analysis of Interacting Systems of Shear Walls, Coupled Shear Walls and Frames in Multi-Storey Buildings. 1996.

4. **Andrus Aavik**. Methodical Basis for the Evaluation of Pavement Structural Strength in Estonian Pavement Management System (EPMS). 2003.

5. **Priit Vilba**. Unstiffened Welded Thin-Walled Metal Girder under Uniform Loading. 2003.

6. **Irene Lill.** Evaluation of Labour Management Strategies in Construction. 2004.

7. **Juhan Idnurm**. Discrete Analysis of Cable-Supported Bridges. 2004.

8. **Arvo Iital**. Monitoring of Surface Water Quality in Small Agricultural Watersheds. Methodology and Optimization of monitoring Network. 2005.

9. **Liis Sipelgas**. Application of Satellite Data for Monitoring the Marine Environment. 2006.

10. **Ott Koppel**. Infrastruktuuri arvestus vertikaalselt integreeritud raudtee-ettevõtja korral: hinnakujunduse aspekt (Eesti peamise raudtee-ettevõtja näitel). 2006.

11. **Targo Kalamees**. Hygrothermal Criteria for Design and Simulation of Buildings. 2006.

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13. **Sergei Zub**. Combined Treatment of Sulfate-Rich Molasses Wastewater from Yeast Industry. Technology Optimization. 2007.

14. **Alvina Reihan**. Analysis of Long-Term River Runoff Trends and Climate Change Impact on Water Resources in Estonia. 2008.

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19. **Andres Tolli**. Hiina konteinerveod läbi Eesti Venemaale ja Hiinasse tagasisaadetavate tühjade konteinerite arvu vähendamise võimalused. 2008.

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25. **Egon Kivi**. Structural Behavior of Cable-Stayed Suspension Bridge Structure. 2009.

26. **Madis Ratassepp**. Wave Scattering at Discontinuities in Plates and Pipes. 2010.

27. **Tiia Pedusaar**. Management of Lake Ülemiste, a Drinking Water Reservoir. 2010.

28. **Karin Pachel**. Water Resources, Sustainable Use and Integrated Management in Estonia. 2010.

29. **Andrus Räämet**. Spatio-Temporal Variability of the Baltic Sea Wave Fields. 2010.

30. **Alar Just**. Structural Fire Design of Timber Frame Assemblies Insulated by Glass Wool and Covered by Gypsum Plasterboards. 2010.

31. **Toomas Liiv**. Experimental Analysis of Boundary Layer Dynamics in Plunging Breaking Wave. 2011.

32. **Martti Kiisa**. Discrete Analysis of Single-Pylon Suspension Bridges. 2011.

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