Sulfate Attack on Cementitious Materials

DIogo DOMINGUES ARAÚJO

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Orientador: Professora Doutora Maria Joana Álvares Ribeiro de Sousa Coutinho, FEUP

Orientador: Prof. Dr. Ing. Wolfgang Brameshuber, RWTH

Mentor Científico: Dipl.-Ing. Johannes Haufe, RWTH

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To Johannes Haufe,
Without whom this work would not be the same.

“You sulfurous and thought-executing fires,
Vaunt-couriers of oak-cleaving thunderbolts,
Singe my white head!”

— William Shakespeare, Hamlet
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ABSTRACT

Sulfate attack was first referred in 1887 by Candlot from observations of the mortars used in fortifications in Paris. These were near the sea and constantly swept by waves and Candlot observed the formation of ettringite due to the high content of sulfates on sea water, as well as in the ground. For many years, and somewhat in use today, ettringite was named candlot’s salt for this reason.

Even though it has been more than 125 years since then, sulfate attack is still today a very mysterious form of concrete attack. Its true mechanisms still elude researchers today albeit several different types of sulfate attack and for a number of causes being known and being one of the most common concrete degradation causes, just after reinforcement corrosion, according to an inquiry carried out by the OCDE in 1989 about degradation causes observed in 800,000 bridges all over the world.

However, in 2013, sulfate attack still has much to reveal.

The scope of the work developed in this work, is to shed some light on the sulfate attack question, but being more focused specifically in the resistance shown by different cementitious materials namely sulphate resistant cement and binders with fly ash addition (Type II A and B cements with different percentages of fly ash and k-values).

All of these were submitted to different sulfate solutions and different concentrations (3.000 ppm and 30.000 ppm). Also, for each of these cases, different temperatures were used (5 ºC, 8 ºC, 12 ºC and 20 ºC). All the specimens were embedded in the solutions for over a year.

Another objective of this work was to evaluate the effectiveness of the concentration values used during the previously referred year of specimen embedment. Both values are, specially the 30.000 ppm, extremely high compared to current legislation. While the 3.000 ppm usually falls in the “severe” or “very severe” category, the 30.000 ppm value surpasses by far the latter, being two or three times its value.

Groundwater immersed samples were used to verify the feasibility of a new accelerated process more in tune to in situ conditions. Temperature of groundwater was set at 5 ºC both to maximize this similarity and to make possible comparing to samples stored in prepared concentration solutions.

Different methods were applied to evaluate and study these objectives, including XRD layer-by-layer analysis, expansion measurements and Dynamic E-Modulus determination and SEM and optic microscopy imagery.

KEYWORDS:
Durability, cement, fly ash, sulfates, groundwater, XRD
RESUMO
Ataque por sulfatos foi primeiramente referido em 1887 por Candlot através da observação das argamassas utilizadas em Paris. Estando estas localizadas à beira mar e sendo constantemente atingidas pela água do mar, Candlot observou o aparecimento de ettringite devido à elevada percentagem de sulfatos existente na água do mar assim como no terreno. Por esta razão, durante muitos anos, ettringite foi denominada “Sal de Candlot” sendo esta terminologia ainda aplicada nos dias que correm.

Mesmo após terem decorrido mais de 125 anos desde a sua descoberta, o ataque por sulfatos é ainda hoje uma forma misteriosa de ataque ao betão. Apesar de serem conhecidos vários tipos de ataque de sulfatos, quais as suas causas e de este ser um dos principais responsáveis pela degradação do betão logo após o problema da corrosão, de acordo com uma investigação levada a cabo pela OCDE em 1989 realizada com o objetivo de avaliar as causas da degradação observadas em 800.000 pontes por todo o mundo, os investigadores apresentam sérias questões quanto aos seus reais mecanismos.

Apesar de todos estes estudos e desenvolvimentos neste campo, o ataque por sulfatos ainda tem muito por explorar e desvendar.

O real objetivo do trabalho aqui desenvolvido, é de certa forma poder clarificar este tema, mas direcionando-o mais especificamente para a avaliação da resistência observada em diferentes matérias cimentícias, nomeadamente cimento resistente a sulfatos e ligantes com adição de cinzas volantes (Cimentos tipo II A e B com diferentes percentagens de cinzas volantes e valores de K).

Todos estes materiais foram submetidos a diferentes soluções de sulfato e concentrações (3.000 ppm e 30.000 ppm). Importa ainda referir que foram utilizadas, para cada um destes casos, diferentes temperaturas (5 º C, 8 º C, 12 º C e 20 º C). Todos os diferentes provetes foram submersos nestas soluções por mais de um ano.

Outro dos objetivos deste trabalho terá sido a avaliação da eficácia dos valores utilizados nas concentrações, para imersão dos provetes durante o referido ano. Ambos os valores são, especialmente o de 30.000 ppm, extremamente elevados comparando-os com a legislação em vigor. Enquanto o de 3.000 ppm se encontra inserido na categoria “grave” ou “muito grave”, o de 30.000 ppm ultrapassa de longe a escala, sendo duas a três vezes o seu valor.

As amostras submersas em água subterrânea foram utilizadas na verificação da viabilidade de um novo processo acelerado mais de acordo com as condições verificadas in situ. A temperatura das águas subterrâneas foi fixada em 5 º C, tanto para maximizar essa semelhança como para possibilitar a comparação com as amostras armazenadas em soluções concentradas previamente preparadas.

Diferentes métodos foram aplicados para avaliação e estudo deste objetivos, incluindo análise camada a camada por XRD, medições de expansão, determinação do módulo de elasticidade dinâmico, SEM e microscopia ótica.

PALAVRAS-CHAVE:
Durabilidade, cimento, cinza volante, sulfatos, água subterrânea, XRD
ZUSAMMENFASSUNG


Ziel der vorliegenden Arbeit ist es einen Beitrag zum Thema des Sulfatangriffs auf Beton zu leisten. Dabei wird besonderes Augenmerk auf die Sulfatbeständigkeit von HS-Zementen und Bindemittelkombinationen mit Flugaschezusatz gelegt.


Stichworte: Dauerhaftigkeit, Zement, Flugasche, Sulfat, Grundwasser, XRD
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SYMBOLS AND ABBREVIATIONS

C₃A – Tricalcium Aluminate;
C₃S – Tricalcium Silicate;
C₂S – Dicalcium Silicate;
CH or Ca(OH)₂ – Calcium Hydroxide;
C-S-H – Calcium Silicate Hydrate;
SO₄²⁻ – Sulfate;
C-A-H – Calcium Aluminate Hydrate;
CO₂ – Carbon Dioxide;
CO₃²⁻ – Carbonate;
AFm phase – Alumina Ferric Monosulfate;
Al₂O₃ – Aluminium Oxide;
Na₂SO₄ – Sodium Sulfate.

SVA – Sachverständiger des Deutschen Instituts für Bautechnik;
ISA – Internal Sulfate Attack;
ESA – External Sulfate Attack;
PC – Portland Cement;
TSA – Thaumasite Sulfate Attack;
w/c – water/cement ratio;
IBAC – Institut für Bauforschung, RWTH;
RWTH – Rheinisch-Westfälische Technische Hochschule Aachen
XRD – X-Ray Diffraction;
CCCP – Crystalized Content in the Cement Paste;
HS – Hoher Sulfatwiderstand, the same as SR – Sulfate Resistant;
FA – Fly Ash
1 INTRODUCTION

1.1. CONSIDERATIONS

Throughout the world, and more specifically in Germany, concern has grown in the matter of sulfate attack and the implications it has in concrete durability. Testing procedures and results concerning this matter are not always easy to perform and, even harder, is the replication of natural exposure to sulfate attacks, which has more variables and different, and possibly, worse effects than those performed in laboratory.

More than 125 years after the first reference to sulfate attack, the matter still generates much debate and discussion and results obtained have only recently started shedding some light on external sulfate attack mechanisms.

Concrete durability is severely diminished when exposed to sulfates, whatever their origin. Sulfate attack is still one of the most common types of attack in concrete structures, second only to steel corrosion. However, it is interesting that there is no record of structural failing due to sulfate attack. What it does is pave the way for other different other types of deleterious effects to take action by diminishing the quality of concrete, most commonly by reducing its strength and by cracking, making new sulfates or any other aggressive component an easier way to penetrate.

Even though many of the mechanisms regarding sulfate attack are still unclear, many factors that help the mitigation of the attack have been developed.

Perhaps the most important of them, and common, is the reduction of C₃A content in the cement clinker. Usually named “Sulfate Resistant” cements, they are considered as such by eliminating one of the most important reactions in sulfate attack, ettringite. Ettringite forms with available aluminum, sulfates and calcium and requires a large amount of water. Given this, its formation is hugely expansive and produces cracking of the concrete. With less or no C₃A, less ettringite is formed and less damage is done.

Other solutions go by reducing the amount of CH in concrete. CH reacts with sulfates to produce gypsum and concrete loses it strength and general mechanical properties. In order to reduce it, pozzolana or blast furnace slags are used as substitutions. Pozzolana consumes CH in the hydration process and production of C-S-H. This leaves then less CH available for gypsum formation and therefore less damaged concrete. Also C-S-H can be leached by the sulfate solution in a process called “acid-type attack”. This is why that sometimes using sulfate-resisting cement alone is not enough.

However, and, perhaps, even more important than that is the property of pozzolana to produce a more impermeable concrete. This allied with good manufacturing, proper mix and correct curing, can make
a much more impermeable concrete and avoid sulfate attack even before it starts by preventing the sulfates ingress into the concrete and making it less exposed to them at later ages.

Even though these processes are more or less understood and accepted, the penetration mechanisms and ingress of sulfates and the following reactions and attack are not fully understood. There is ongoing discussion to what type of attack governs sulfate attack and in what conditions. Given the large variation of exposure conditions possible the mechanism can have a number of variations. Temperature, \( \text{SO}_4^{2-} \) concentration and type of associated cation all have implications on the attack outcome.

Given all this, sulfate attack is still very much diffuse and in need of more study.

1.2. Objectives

The aim of this thesis is to evaluate sulfate attack mechanisms that occurred on samples exposed to artificial sulfate solutions for over a year, not only at different sulfate concentrations but also at different temperatures. Also, tests will be conducted to evaluate the performance of groundwater as a suitable testing solution at low temperatures, simulating more closely natural conditions and bringing laboratory and in situ work closer together.

This is done following what is currently called the “German Method”, derivative from the “Wittekindt Method”, which uses flat prisms as test samples, as recommended by the SVA. These samples have been stored in sodium sulfate solutions of 3,000 ppm and 30,000 at different temperatures, being studied in this case the higher and lower temperatures available.

The binders to be studied are:

- CEM I 42,5 R-HS
- CEM I 52,5 N 40 % Fly Ash
- CEM I 52,5 N 29,4 % Fly Ash k-value=0,12
- CEM I 52,5 N 29,4 % Fly Ash k-value=0,6

Using the measurement values obtained during sulfate exposure, expansion and dynamic elastic modulus will be determined and used to study the severity of the attack on the different binders, tracing comparisons between them and verifying which were the least affected by sulfate reactions regarding their mechanical properties.

X-Ray Powder Diffraction will be applied and 40 mm × 40 mm × 10 mm sections to study how the attack progressed in depth. This will be done until the middle point and in intervals of 0,5 mm. in order to achieve this the referred thickness will be ground, and the obtained powder will be used in the XRD measurements, without any specific treatment, which is not required. From there, it will be possible to quantify the phases of interest and observe the variation of each of them in depth and have a better idea of how the mechanism of sulfate attack is done.

Given the fact that the specimens are cement mortars and therefore have sand as one of the main constituents, quartz mineralogy data obtained from the XRD measurements makes impossible to quantify correctly the important phases. Therefore a method will be developed to eliminate the quartz corresponding data and then quantify correctly the cement hydration phases and sulfate attack resulting phases for each of the combinations referred before.

Combining the information obtained from the three measurement methods, all binders will be compared and their performance evaluated. From here, the different intervenient on sulfate attack will
be correctly appraised regarding the different binders’ properties and the exposure conditions. The objective is to determine which binder or what properties inherent to it most affect sulfate attack progress and possibly suggest solutions for different situations.

Finally, new prisms will be cast in order to study the feasibility of using groundwater as a substitute for artificial sulfate solutions regularly used in laboratory. In order to do so, the samples will be immersed both in groundwater (1,500 ppm of SO$_4^{2-}$) and a sulfate solution (3,000 ppm of SO$_4^{2-}$) at a temperature of 5 ºC. This is done to achieve the close resemblance with natural environment in underground construction. Expansion and dynamic elastic modulus will be determined regularly to compare their behavior and finally verify if groundwater is a suitable substitute.
2
STATE OF THE ART

2.1. CONSIDERATIONS

2.1.1. INTRODUCTION

Sulfate attack on concrete is still today a topic that promotes a lot of discussion. Discussion may cause division with different ways of thinking, problem approaching and solving but it is always fruitful in terms of knowledge.

Starting by its name, “Sulfate Attack”, is not clearly self-explainable. By using this terminology one assumes that any attack containing a supposed amount of sulfate could ultimately be considered “Sulfate Attack”. However, this may not be entirely true. Considering sulfate attack caused by precipitation of the salt on a concrete surface where, by precipitating, produces expansion and “damages” the concrete. Could this be considered “Sulfate Attack”? How is this any different from any other salt weathering and precipitation damage, be it sulfate bearing or not?

It is defended that sulfate attack should only be referred to types of attack, be it from external or internal origin, that induce some sort of chemical response between the sulfate bearing phase and the concrete resulting, at any given length, in damage to the concrete. This final point is extremely important as any attack should only be considered so if the outcome of that action is, in fact, harmful to the concrete. Solid salts by themselves do not attack concrete and pose no immediate danger to the structure they are on. What any salt needs, be it for concrete degradation and any other reaction, and sulfates are no different, is a medium in which they can dissolve in and begin the reaction (Neville, 1995).

It is important then to define the sulfate attack concept referred to, here. Sulfate attack can be described as chemical reactions that occur between the concrete constituents, more specifically the different components in the cement paste, and the sulfate ions in existence both with concrete origin or external origin and that result in observable, measurable or detected damage to the concrete that may pose it at risk of failing (Neves, 2010).

In terms of sulfate attack it is important to pinpoint the following three compounds which play a significant role in the reactions:

- Calcium Sulfate, known as Gypsum – CaSO$_4$.2H$_2$O;
- Calcium Sulfoaluminate, known as Ettringite – 3CaO.Al$_2$O$_3$.CaSO$_4$.32H$_2$O;
- Calcium Silicon Sulfocarbonate, known as Thaumasite – CaSiO$_2$.CaCO$_3$.CaSO$_4$.15H$_2$O.

The first two are the most common and well known products of sulfate attack. They are the most recurring and most studied of the three, being object of many research. Thaumasite could perhaps be
Sulfate Attack on Cementitious Materials

considered the “poor relative” of the three regarding its “research importance”. Nevertheless, it is still a most influential form of sulfate attack and extremely disruptive. All of them can be considered expansive products as in their formation they tend to occupy much more volume than their constituents, mostly due to the large amount of water molecules, mainly in ettringite and thaumasite.

Even here, a simple yet required division must be made regarding sulfate attack and the object of this study, the difference between Internal Sulfate Attack (ISA) and External Sulfate Attack (ESA).

One of the constituents of Portland Cement (PC) is gypsum which is added to the cement in its manufacturing process in order to control concrete setting. Was this not the case, due to the almost immediate reaction with water by $C_3A$, concrete would experience an extremely fast or instantaneous setting. What the gypsum does is begin reacting with the $C_3A$ and effectively protecting it from the water by producing ettringite. This ettringite is still very expansive. However, since the mix is still in its early ages and in a plastic phase, it is not harmful. Circa 24h later, all the gypsum is consumed and ettringite decays to monosulfoaluminate (3$C_3A$SH$_{12}$ or $C_3A$CSH$_{12}$) with the influence of non-consumed $C_3A$ (Coutinho, 2013). As postulated before, this is not an attack. However, when this process happens after the hardening of the mix, it may result in severe damage to the concrete. It is now that the differentiation between ISA and ESA is possible. When ettringite is formed after hardening, referred to as “Secondary Ettringite” as opposed to the “Primary Ettringite” name given to the process described before, the sulfate origin will mandate how the naming of this process will be handled. According to current nomenclature, ISA corresponds to the sulfate attack that occurs when sulfate are originated from within the concrete, either from water used in the mix, from the aggregates or even from cement itself, because of the gypsum or fuel used during manufacturing (Moreira and Teles, 2012). ESA occurs when sulfates originate from an outside source, frequently, but not necessarily, of natural occurrence (Neves, 2010). These sulfates come from groundwater, seawater, sulfate bearing soils or even fertilizers and industrial effluents (Neville, 1995).

What is common to both types of sulfate attack is the requirement of existing water circulation inside the concrete, for whatever initial reason, to allow for dissolution, precipitation, leaching or any other processes that may disrupt the concrete bulk (Neves, 2010).

Thaumasite is a very particular case, frequently treated separately from the other two products of sulfate attack, even giving itself a name to a separate form of sulfate attack, Thaumasite form of Sulfate Attack (TSA). Thaumasite forms, reportedly, in environments with low temperature, usually below 15 ºC. It requires a source of calcium silicate, carbonate ions and sulfate ions. It also needs a high level of humidity to be formed and, as such, is most commonly found in underground works like tunnels or foundations. This form of sulfate attack has the particularity of completely destroying cement paste, turning it into a mush and making it lose all its binding properties (Skaropoulou et al., 2006).

In the present study, the focus will remain on External Sulfate Attack from outside origins, in an attempt to simulate, as possible, the conditions concrete elements may experience from natural occurrences and the damage they suffer throughout their service life.

2.1.2. HISTORY

Sulfate attack, despite its elusiveness, has been recorded as a proper concrete pathology almost since the beginning of the re-use of concrete in modern ages. In this time period, the first recorded use of a cementitious binder was in 1724, by John Smeaton to build a Lighthouse, already looking for a “water-resistant mortar” in that time. However, the first patented of the named “Portland Cement” was
obtained by Joseph Aspdin in 1824, and its production began in 1843, by its son, William Aspdin (Locher, 2006).

Then, as soon as 1856, Louis-Joseph Vicat, himself a celebrated engineer by the invention of artificial cement (later replaced by PC) and the “Vicat needle” test which is still in use today, documented the deleterious influence of seawater in hydraulic components which expanded and formed cracks in the structure. He did not comprehend however the mechanism nor did he know about any of the referred sulfate attack products referred before. Nevertheless, existence of sulfate attack is undeniable (Coutinho, 1988).

However, the first attested scenario of sulfate attack was brought forward by Candlot circa 1880, only 40 years after the invention of PC. While studying the effect of sea water in hydrated cement, he found the correlation between the amount of alumina (Al$_2$O$_3$) and calcium oxide (CaO) that led to expansion effects and cracking. He predicted the existence of what came to be called Candlot’s Salt, whose chemical formula was eventually determined correctly by Deval. This salt eventually was named “Ettringite”, the name for which is known today, because of the finding of the same mineral in Ettringen, Germany by Lehman in 1874. Then, while studying mortars on the Paris fortresses, Candlot correctly identified sulfate attack and the occurring “Ettringite” as a degradation cause, marking the beginning of ESA study (Neves, 2010).

Thaumasite, even though it was identified much more recently (circa 1878 by Nordenskjöld), was only referenced in the second half of the 20$^{th}$ century, much later than both gypsum and ettringite, by Erlin and Stark (Neves, 2010). However, only in the last 30 years has thaumasite phenomena been investigated intermittently and much more recently has it been completely widespread throughout the scientific community (Hartshorn et al., 2002). A few notable examples of this attack are referred to in literature, including a study on Swiss tunnels to access the conditions of this, extremely deleterious type of attack (Romer et al., 2003) and a study in the United Kingdom by the “Thaumasite Expert Group” in a number of bridges throughout its territory (Clark et al., 2002).

In Portugal a notable example is the occurrence of a measured expansion in the mortars used in the joints of the Leixões’ Harbour’s, pier number 1. Here, the cause was found to be the reaction between seawater and the aggregates used in the mortar, which contained reactive alumina from the feldspars. Initially, it was thought the reaction originated from the alumina in the cement, which was eventually proven otherwise (Coutinho, 1988).

In Germany, sulfate attack is regarded as one of the main concerns in concrete durability. Sulfate attack study procedures have been employed, tested and standardized since the use of DIN 1164 in 1958 (Locher, 2006). Work is still ongoing frequently at the present, as is the case of this study, as well as many others, even quite recently and performing a similar process as the one employed in this work (Heinz et al., 2012).

### 2.2. External Sulfate Attack Mechanisms

#### 2.2.1. Considerations

As said before, ESA is one of two types of sulfate attack that may occur in concrete. It implies the interaction of sulfates originating from an external source and being able to penetrate into the structure. Also, what is required is a soluble medium in which the sulfate salts can dissolve in and the chemical reactions can occur, otherwise no attack would take place.
However, ESA cannot be so easily simplified. In 2004, Adam Neville gives the title “The Confused World of Sulfate Attack on Concrete” to a review paper he wrote (Neville, 2004), denoting the general uncertainty regarding the very different mechanisms, methods and implications that surround sulfate attack on concrete.

Sulfate attack occurs when concrete is exposed to a sulfate solution of a relative high concentration. This allows the solution to have enough “strength” to attack the concrete as enough $\text{SO}_4^{2-}$ ions are available to allow the reaction with concrete to continue. Regarding this aspect, it is even more important the solution renovation, which is constant in nature but hard to simulate in the laboratory without specialized equipment to do so. Then, different solutions have different constitutions and each of them, or several different combinations will make the attack outcome and the concrete behavior very different, making the analysis even more difficult to be studied and conclusions to be found. Plus, the concrete composition and its exposure to the environment bring even more variables to the equation, where it becomes increasingly difficult to preview the behavior of all of them. Also, quite a few are intrinsically connected and it is impossible to vary one without affecting the other (Neville, 2004).

Some of these variables will be tackled in point 2.3 individually, for better understanding.

2.2.2. MAIN REACTIONS

It is important to begin the explanation of sulfate attack with the occurring reactions that can be observed with the sulfate attack phenomenon.

As referred to before, sulfate attack mainly results in three types of, potentially, deleterious products: gypsum, ettringite and thaumasite.

These may or may not appear at the same time, and their origin has mostly to do with the type of sulfate present, that is, the cation that accompanies $\text{SO}_4^{2-}$.

The most common types of sulfates are sodium, magnesium and calcium sulfates, each of them with different properties and different ways of interacting with concrete. Calcium sulfate is itself important because of its high solubility, implicating that ground waters that contain this type of sulfate can easily contain others, making the attack on concrete much more severe as the other sulfates can react with different compounds other than Ca(OH)$_2$ (Neville, 1995).

The reactions of the various types of sulfates can be resumed as follows (Neville, 1995; Neves, 2010):

- **Sodium sulfate** reacts with Ca(OH)$_2$ available in the cement paste to form gypsum (calcium sulfate). This process can occur indefinitely if the solution can be renovated (as in flowing water) constantly supplying sodium sulfate and removing calcium hydroxide. If NaOH accumulates, equilibrium can be reached; if not, all the calcium hydroxide can eventually be leached and removed;

- **Calcium sulfate** mainly reacts with C$_3$A, available either from the concrete hydration process or from the remains of the reaction of sodium sulfate with calcium hydroxide. These two reagents combine to produce ettringite, already explained in the beginning of this chapter;

- **Magnesium sulfate** reacts with both Ca(OH)$_2$, C-A-H (Calcium Aluminate Hydrate) and C-S-H (Calcium Silicate Hydrates), the main components of cement paste. Mg$^{2+}$ removes calcium from the calcium hydroxide in order to replace it, being magnesium hydroxide less soluble and less alkaline than calcium hydroxide. This in turn leads to a solution with higher amount
of magnesium hydroxide which makes it more acidic, in turn leading to leaching of more calcium hydroxide. This then is replaced by magnesium hydroxide and the process goes on until full transformation. Also, along with that reaction, magnesium sulfate produces brucite. This mineral forms on the surface of the concrete, creating a layer and effectively protecting the concrete from further sulfate attack. This makes the magnesium sulfate attack even more complicated as its occurrence is both deleterious and beneficial to concrete. Magnesium sulfate solution was not used in this study and, as such, the focus will be on sodium sulfate and its reactions;

- Thaumasite is a different kind of reaction, as previously referred. It can form by the reaction between C-S-H, available SO$_4^{2-}$ and a source of carbon, be it CO$_2$ from the atmosphere or CO$_3^{2-}$, available in the solution (commonly available in groundwater). Thaumasite attack differs from gypsum and ettringite attack because, since it directly reacts with C-S-H of the cement paste, a great loss of concrete strength can occur, effectively turning it into a mushy substance with no form at all.

2.2.3. CONCRETE EXPOSURE AND SULFATE PENETRATION

There are mainly three conditions that have to be verified, as explained by Collepardi, 2003, in order for the attack to begin:

- An external source with sufficient concentration of sulfate ions;
- Presence of water in intimate contact with concrete;
- High permeability of concrete.

Of course sulfate attack might occur even if the concrete is not very permeable, but as a good approach these conditions can be valid.

Sulfates penetrate into concrete mainly by two ways, diffusion and absorption. Each of them occurs depending on the concentration of the sulfate solution and the progress of the attack that has occurred so far. Both of them however allow the sulfates to ingress into the cementitious paste of the concrete, making its compounds available for reaction (Ferraris et al., 2006).

2.2.4. ATTACK PROGRESS

It is commonly accepted that sulfate attack results in the uncontrolled expansion of concrete, destroying and cracking it, allowing progress of more sulfate ions into its core, worsening even more the concrete susceptibility to attack.

However, the reasons for this expansion are not fully understood and agreed upon.

Frequently, this expansion is attributed to the formation of ettringite inside the concrete where water is abundant. The mechanism on how it makes concrete expand is also a motive of disagreement.

There is ongoing discussion as to what really makes expansion occur. As discussed, thaumasite is left out of this part of the study since it is a different aspect of sulfate attack. The dispute lies with the expansion being caused by ettringite, gypsum or a combination of both.

It is commonly accepted that gypsum by itself is harmful to concrete, even if only due to the reactions described earlier, in 2.2.2. However, the mechanism of gypsum attack is not fully understood. Consensus has not yet been achieved if gypsum formation leads to expansion which is mainly attributed to ettringite and not gypsum.
Tests were performed to verify if gypsum effectively leads to expansion of concrete (Tian and Cohen, 2000). In this paper, an interesting analysis is done considering literature both supporting and contradicting this view.

Supporting the notion that gypsum does not lead to expansion, Tian and Cohen, 2000 present the arguments by Hansen, 1966 and Mather, 1997, defending that gypsum formed by through solution mechanism cannot form enough volume to occupy voids in existence and the volume left by CH (calcium hydroxide) consumption. Mather, 1997 goes further by saying that the subsequent evaporation and precipitation of gypsum does not cause cracking by stating “You cannot break a bottle full of saturated solution by removing the cork and letting the water evaporate.”.

On the other hand, Bonen and Sarkar, 1993 and Yang et al., 1996 defend the exact opposite, actually referring that gypsum formed by through solution mechanism in the interfacial zone (the boundary of the aggregate and cement paste) can create thick deposits, which crystallization leads to tensile forces and consequent damage. Similarly, another theory regarding crystallization defends that when it occurs, the result is high expansion forces. This occurs when the solid product forms in a confined space and “the activity product of reactants in the pore solution is greater than the solubility product of the solid products under atmospheric pressure”, meaning that the crystallization must be originated from a supersaturated solution which will provide energy for expansion (Ping and Beaudoin, 1992a and Ping and Beaudoin, 1992b).

Finally, on “nonaligned” opinions, Mehta, 1983 claims that the first occurrence is large concrete expansion and cracking followed then by stiffness reduction caused by gypsum formation and sulfate adsorption by C-S-H. A similar exposure is done by Gollop and Taylor, 1995, also stating the occurrence of two layers, but where cracking was limited to the gypsum formation zone. They also attributed the expansion neither to gypsum nor ettringite but to water absorption by the cement gel, however, without forwarding any detail on cement gel type and expansion method. It is interesting to note that, perhaps, both studies hinted on the same phenomenon, but ending in different conclusions.

The paper concludes by suggesting that gypsum formation is indeed expansive. However, it fails to find the correct mechanism and opines that expansion should not be attributed exclusively to ettringite formation because tensile stresses in concrete due to gypsum formation may also have influence in expansion and cracking (Tian and Cohen, 2000).

Years after, Santhanam et al., 2002a propose a new and improved version of these layered models. A model was proposed which explained sodium sulfate attack by phases in which different processes would occur.
Sulfate Attack on Cementitious Materials

Figure 1 - Step by step explanation of the mechanism proposed by Santhanam et al., 2002a

Step 1 demonstrates the beginning of the experimentation. The sample has just been placed in sodium sulfate solution which naturally has a neutral value of pH, around 7. Immediately after the specimen insertion however, the solution’s pH rises to alkaline values, around 11 or 12. In nature this would not occur as the solution would be constantly renovated maintaining the original pH value. However, in laboratory, it is hard to keep this condition and what is usually done is the solution substitution. This helps, but does not mimic natural occurrence. As seen in its previous paper (Santhanam et al., 2002b) a lower pH the time it takes for, what was called, “Stage 1”, a first occurrence in expansion at a small rate, to occur. Nevertheless, he claims that “Stage 2”, the next phase where expansion is more rapid, will progress at the same rate, and is depicted in step 2.

In step 2, the initial formation of gypsum and ettringite is depicted. These form along the lines of what was previously established as the conditions for their development. The surface zone where these two minerals have formed, tends to expand due to those crystals. However, the bulk of the mortar beneath it is still unaltered and tries to restrain this movement, effectively suffering tensile forces, as shown in step 3. Eventually, the cracks and damage depicted in step 4 appear due to the inefficacy of concrete to resist these tensions.

With passing of time, the reaction continues to occur, with the solution eventually penetrating the cracks originated before. Now, with free access, the solution effectively reacts with the hydration products both in the unaltered cement paste and inside the cracks, worsening even more the attack. Gypsum deposits in cracks and voids, the best sites for nucleation. This moves the area of the attack further into the specimen causing new gypsum and ettringite deposition in the cracks, as seen in step 5.

Finally, step 6 shows the occurring different layers in the mortar, the disintegrated surface, the mineral deposition zone and the new cracked but chemically unaltered area further inside the mortar. This process is repeated indefinitely as long as there are enough reagents.
Also, it is alleged that thaumasite can form in the outer and disintegrated layer. This claim is done because here the solution has access to decalcified C-S-H and ettringite which, along with atmospheric CO$_2$, make available all the reagents needed to the formation of thaumasite.

This process is quite similar to the ones described before, with much more detail. The layered behavior is repeated and the formation of both gypsum and ettringite is proved. However, it is not clearly depicted which of the products effectively lead to expansion. Nevertheless, mortar destruction is attributed to both of them.

In a recent paper (Yu et al., 2013), also discusses the expansion mechanism of sulfate attack. The paper begins by presenting four theories which are also discussed, most concerning ettringite, but stating that gypsum was also put forward as the expansion cause:

- One is the hypothesis of ettringite taking more space than the AFm phases (alumina, ferric oxide, monosulfate phase formed from the reaction of C$_3$A with CH) from which it originates when the sulfate solution penetrates. This is dismissed because, as stated, cementitious materials have enough porosity to allow the formation of ettringite without expansion;
- Second, the possibility of ettringite formation by solid state mechanism is discussed and dismissed by saying that ettringite crystal structure is completely different from the phases it originates from;
- Also discussed is a mechanism advanced by Mehta, that ettringite expands when it forms as crystals of colloidal dimensions with the presence of lime. However, this is also dismissed as in some cases, there is no free lime and expansion from ettringite still occurs;
- The final theory, which is supported in the paper, is the crystallization pressure theory. This is the same one advanced before by Ping and Beaudoin, 1992b.

This paper then proceeds to verify this same theory and the driving mechanism of this process is presented.

It is observed that, as sulfate ions ingress in the cementitious materials, they start by reacting with the available monosulfate that exists in pockets increasing the amount of SO$_4^{2-}$ in the pore solution until all the available Al$_2$O$_3$ is consumed. Once the solution is oversaturated, the fine monosulfates available react with C-S-H and begin their transformation to ettringite which, according to the crystallization theory, will occur in the C-S-H small pores and be responsible for the measurable expansion. This is also compared to what happens in the phenomenon of heat induced “Delayed Ettringite Formation”, when concrete curing is done at extremely high temperatures and ettringite forms after the mix has hardened and not while it is still plastic.

Finally, the paper concludes by confirming what has been referred to before, that the attack progresses by layers. Again, as explained by Santhanam et al., 2002a, cracks appear in the process as explained before, and the attack moves inwards, with and the cycle being repeated. However, Yu et al., 2013 defend that once this happens, the sulfate ions can enter the cracks freely and then react with portlandite to produce gypsum, which is formed freely in the cracks and is not a cause for expansion.

As it can be seen, the ESA mechanisms are not yet fully understood. The tendency noted here is that the attack occurs by phases or layers where ettringite forms, in the outer, unscathed area of the concrete causing expansion during its formation and effectively cracking concrete. Then, sulfates ingress and start attacking the cement paste, effectively reacting with CH and CSH and forming, among other compounds, gypsum, which does not contribute to expansion but contributes to general
concrete deterioration by destroying the binding paste. Finally, the cycle repeats itself and the attack progresses inwards.

As a final, but not unimportant note, Thaumasite Sulfate Attack (TSA) should also be taken into consideration.

General belief is that thaumasite can only occur in low temperatures (Neville, 1995). However, recent studies have shown the occurrence of thaumasite in environments that had near ambient temperature of around 20 °C (Romer et al., 2003 and Diamond, 2003), much higher than the supposed upper limit, which shows the general lack of knowledge in this mechanism.

Romer et al., 2003, advance with two likely mechanisms of thaumasite formation, one direct and another indirect.

The direct mechanism consists in the known interaction between sulfates and the C-S-H phase. In this case, in order for thaumasite to form, calcium has to be added along with sulfate and carbonate. With the leaching of C-S-H phase and the transformation of some of the cement paste to thaumasite, this occurs when the cement paste consist of a high amount of C-S-H, usually over 70%.

The indirect mechanism refers to transformation of ettringite to thaumasite, with the exchange of aluminium by silicon, and water and sulfate by carbonate in the crystal structure of already existing ettringite. It is also stated that they can both coexist under different conditions.

2.2.5. CONCLUSION

Concrete can become severely damaged caused by expansion due to sulfate attack. Not only is it the most studied effect of sulfate attack, it can pose large problems to structural integrity when restrained expansion occurs.

All the products derived from sulfate attack accrue from the reaction occurred between sulfates and the hydration products of cement. This leads to the loss of the most important intervening agents in concrete strength, like CH or C-S-H, and probable risk of collapse.

Also, in running solution, that is, solution which can be replaced constantly, the risk of leaching of the cement phases is very high and again leading to the loss of strength in concrete.

Finally, TSA (Thaumasite Sulfate Attack) is a very destructive kind of sulfate attack, and mostly disregarded or not sufficiently looked into. Its ability, under appropriate conditions, to turn concrete into nothing more than a pulp is extremely disruptive. More research should be carried out in this area to confirm causes and consequences.

Another noticeable point, is the fact that most papers deal only with a few different points in sulfate attack. None of them try to generalize and all of them diverge from in situ testing. This concern is defended by Neville, 2004, who states that work carried out in the laboratory is discrepantly more abundant than on construction sites. This leads to conclusions that are biased and do not possess the required overview and understanding of sulfate attack, that is needed in this area.

2.3. INFLUENCE OF THE MAIN INTERVENING AGENTS IN SULFATE ATTACK

In this chapter, an overview is given on the different issues, with influence on sulfate attack, according to the available literature.
2.3.1. Sulfate Solution

Severity of sulfate attack mainly depends on the available sulfate solution. Its characteristics determine the way how, how hard and how fast the attack will progress, depending then on the resistance capabilities of the concrete.

Unfortunately, there is not much variation in this topic. A few different solutions are used, concerning ions and concentration, but most fall in the sodium sulfate category and high concentrations. As Neville, 2004 refers, “it suits Phd students” that a high concentration solution is used, concerning the speed of the attack. However, a more “natural” solution could be investigated and research done closer to conditions observed in situ.

2.3.1.1. \( \text{SO}_4^{2-} \) Concentration

Among all the properties of the solution, sulfate concentration is perhaps the one most regarded, taken into account and also important.

According to standing regulation, and referring here EN 206-1, sulfate concentration is considered at the most higher level of exposure class at a value of \( \text{SO}_4^{2-} \) mg/l between 3,000 and 6,000. Taking into consideration the standard concentration values used in sulfate attack studies, it is plain to see that the used concentrations are indeed very high and only acceptable as accelerated tests. This is not to say that such concentrations cannot be found in nature. However, from what is observed in the different studies, the minimum usual value used in these accelerated tests is a concentration of 3,000 mg/l \( \text{SO}_4^{2-} \), already in the highest exposure class available, if these tests are performed with solutions and not in soil, as some have been done (Kurtis et al., 2000). Neville, 2004 also defends this view comparing the values himself has used before for sulfate concentration (50,000 mg/l) with the “several thousand parts per million encountered in the field”. Nevertheless, the importance of \( \text{SO}_4^{2-} \) concentration is clearly known.

<table>
<thead>
<tr>
<th>Medium</th>
<th>XA1</th>
<th>XA2</th>
<th>XA3</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>≥200 and ≤600</td>
<td>&gt;600 ≤3000</td>
<td>&gt;3000 and ≤6000</td>
<td>( \text{SO}_4^{2-} ) mg/l</td>
</tr>
<tr>
<td>Soils</td>
<td>≥2000 and ≤3000</td>
<td>&gt;3000 ≤12000</td>
<td>&gt;12000 and ≤24000</td>
<td>( \text{SO}_4^{2-} ) mg/kg</td>
</tr>
</tbody>
</table>

Al-Dulaijan et al., 2003 performed sulfate attack tests in different binders, plain cements and with additions at different concentrations during 24 months. The concentrations used varied from 1 % to 4 % of \( \text{SO}_4^{2-} \) solutions and all the binders were exposed to all the solutions (1 % equals 10,000 mg/l of \( \text{SO}_4^{2-} \)). The binders were tested for compressive strength and the loss measured was plotted into graphs to clearly show the results.
It is undeniable that all the binder types generally suffered from the concentration increase, with more or less intensity. The only exception perhaps is the Type-I cement used that maintained its value. However, since even at 1% of $SO_4^{2-}$ present in the solution, it is unreliable to study it in the same way. Nevertheless, an increase in compressive strength loss can be seen.

Santhanam et al., 2002a, also refer an increase in expansion rates given an increase in sulfate concentrations in their work. This is also referred in the paper by El-Hachem et al., 2012, where increasing concentration led to sooner expansion effects.

Neville, 2004 however refers that above 1% concentration, for sodium sulfate, the effect of concentration on the rate of the attack is small. However, this view is not shared among the other researchers, mentioned before.

Again, disagreement is present even in the most basic sulfate solution characteristic. Nevertheless, it is the widely known that the higher the concentration, the more severe the attack is.

2.3.1.2. Solution pH

The pH of the “attacking solution” has been investigated more thoroughly in the past years. It is generally accepted that the lower the pH, the worse the attack is due to a number of reasons.

Regularly, groundwater has a neutral pH, oscillating between 6 and 8. It has been observed constantly that when sulfate attack tests on concrete are made, the pH of the solution immediately rises to values closer to that of the cement paste, 11 or 12 trying to find equilibrium between both of them. However, in natural occurrences, groundwater is constantly renovated and its pH value tends to be kept around 7. The implications of this matter have been discussed (Cao et al., 1997).

In this article, studies are done to verify the behavior of different binders at different pH exposures. It was generally found that the lower the pH, more severe the attack was. The results showed a decrease in specimen expansion from solution pH levels of 12 to 7 and an increase from 7 to 3. It is reported
that, with the lowering of the pH, an acidic type of attack is done and leaching of Ca and C-S-H dominate the attack, leading to erosion and softening of the specimen. This is even more noticeable when compression strength retention tests were done clearly showing that with reduction of pH less compressive strength remained and happened earlier (Cao et al., 1997).

Another report in pH levels is the inability of ettringite to remain stable at low pH. It was reported that when the pH of the pore solution reduced to levels below 11.5, ettringite could not keep stable and decomposed to gypsum. It is yet another implication in tests where pH is not controlled (Santhanam et al., 2001).

Also, concerning TSA, it was found that thaumasite did not remain stable at pH exposures lower than 11. When this happened, thaumasite reacted with the available ions in the test to decompose to calcium phosphate, calcium silicate and calcium carbonate. Then, at values between 11 and 13, the rate and quantity of this reactions was lowered and above 13 thaumasite was entirely stable (Jallad et al., 2003).

In these points it is clearly shown the influence of pH in the effect of the attack. The lack of control on pH leads to fallible results.

2.3.1.3. Available Cations

Cation influence in sulfate attack has been discussed and explained in point 2.2.2. It is clear that different ions will change the process of sulfate attack and the more ions in existence in the solution, more different reactions will occur.

It is frequent that groundwater has several different kinds of available sulfate types and all of them will react with concrete in their own way. Thus, the attack is usually more severe than would be supposed by testing performed in laboratory where it is usual to use only one or two cations at the same time and even ammonium sulfate which is specially deleterious along with magnesium sulfate (Neville, 1995).

It is not by chance that these cations are limited in quantity in EN 206-1, along with aggressive CO₂, effectively limiting the existence of both those sulfates and the formation of thaumasite, also seen as very dangerous.

Table 2 - Exposition class concentration limits of different sulfate attack reagents, as depicted in NP EN 206-1

<table>
<thead>
<tr>
<th></th>
<th>XA1</th>
<th>XA2</th>
<th>XA3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg²⁺ mg/l</td>
<td>≥300 and ≤1000</td>
<td>&gt;1000 ≤3000</td>
<td>&gt;3000</td>
</tr>
<tr>
<td>NH₄⁺ mg/l</td>
<td>≥15 and ≤30</td>
<td>&gt;30 ≤60</td>
<td>&gt;60 and ≤100</td>
</tr>
<tr>
<td>CO₂ mg/l</td>
<td>≥15 and ≤40</td>
<td>&gt;40 ≤100</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

These are separate conditions than sulfate concentration that define the same class exposure, thus revealing the importance that each of them has in increasing sulfate attack severity.

2.3.1.4. Temperature

Temperature has an enormous influence in sulfate resistance of concrete. It is well known that ettringite formation is much higher at low temperatures, being 40 °C the usual limit for its formation and 0 °C for its highest point. Given this, a lower temperature induces a higher ettringite formation in
concrete causing it to expand more and more rapidly with the deleterious effects known before (Neville, 1995).

Also, low temperatures promote the formation of thaumasite. Even though it was discussed that thaumasite may form at higher temperatures, it is known that the lower the temperature, more deleterious is thaumasite formation, which deteriorates the concrete extremely fast.

With both these actions, the severity of the attack is evident. On the one end there exists a mechanism that cracks concrete, allowing the entry of more attacking agents, and on the other thaumasite forming that causes consumption of C-S-H and weakens concrete by removing the most important phase that contributes to concrete strength.

2.3.2. CEMENT AND MIX

Regarding the properties of the cement used and its mixture, there are some niceties that also need to be addressed when studying sulfate attack.

The type of cement used is of great importance when trying to limit the extent and severity of the damaged cause by sulfates, because of the reactions explained before between sulfates and hydrated phases.

Concerning this, several types of cements have been introduced in the last decades to try and tackle some of the issues present here. Mainly of notice are the called SR (Sulfate Resistant) cements. These cements address the issue of sulfate attack by limiting the C\textsubscript{3}A content and/or introducing additions to limit its value, as well as C\textsubscript{3}S content (Neville, 2004).

2.3.2.1. Cement Content and w/c ratio

These two characteristics are of course hand in hand with each other. It is impossible to speak about w/c ratio without addressing cement content. Of course the first could be changed without the second, just by changing water content, however cement content is extremely important, both in mix calculations and of course economically.

There is ongoing debate to which of these two, or if both, have most effect on sulfate resistance of concrete. Neville, 2004 claims that cement content is not the influential force in sulfate resistance, contradicting a statement made by the Bureau of Reclamation which claimed that the second most important factor in sulfate attack is cement content. It is defended in that paper that what is of true concern is the w/c ratio, which should be low, and the sequential high density of concrete. This would prevent the entry of sulfates inside the concrete. Here, “high density” is meant to be understood as a very low permeability, the opposite of which has been one of the stated requirements of the beginning of sulfate attack.

Of course a good impermeability is not achieved only by making concrete with a low w/c ratio. Before anything else, concrete must be calculated, the mix must be performed, casting and compacting must be done and finally, a good curing process is of utmost importance. This is done frequently under not the best conditions and, unfortunately, by not the best professionals and, as such, concrete may not result as it is “in paper” (Neville, 2004).

Also reported in the influence of w/c ratio is that, if it is too low, it can have a negative influence in sulfate resistance. A low ratio may lead to inexistence of pores in the cement matrix, or at least only very small pores. The outcome may be that, once expansion products appear, there may be not enough
space for the products to expand to, and subsequent tensile forces will appear very soon, given this, sulfate attack may be worsened by this effect. However, it is still required that sulfates enter the paste and, as such, low concrete permeability is a good practice (Baghbra Al-Amoudi, 2002).

### 2.3.2.2. C₃A content

As previously discussed, C₃A content has a strong influence in sulfate attack. In fact, Type V cement was invented to address this situation. By limiting the amount of C₃A that is in the cement, there will be fewer amounts available to react with calcium sulfate and less ettringite can be formed (Neville, 2004). Also, basic Type I cements with low C₃A ratio exist and, regarding sulfate attack, there are standard requirements in existence that limit the C₃A content in cements. These define the upper limits of C₃A in CEM I, CEM II and CEM IV cements when they are to be used as sulfate resisting cements (EN 197-1).

In this case, it is important to refer that this only applies to the ettringite forming part of sulfate attack. It has been proven that, even though low C₃A content cement has been used, or even with 0% C₃A, sulfate attack did occur and concrete was damaged (Tian and Cohen, 2000). This deals however with another ide of sulfate attack, which is the reaction of sulfates with C₃S. When a low C₃A cement is used, usually it has a higher C₃S/C₂S ratio, turning the problem away from ettringite formation (Al-Dulaijan et al., 2003).

### 2.3.2.3. C₃S/C₂S ratio

Given the problem of C₃S/C₂S ratio, it is important to explain the influence of this characteristic. Both C₃S and C₂S have the same influence in concrete: its hydration forms the bases of the cement paste, which are C-S-H and CH, which will provide the required strength prevenient from the cement. However, as depicted before, when sulfates entrain the concrete, they will react with available CH and C-S-H and effectively corrode the cement paste and robbing the concrete of its strength. It may then be followed by expansion and cracking effectively worsening even more the attack rate and consequences and turning the material into a “mush” (Al-Dulaijan et al., 2003).

Ramyar and İnan, 2007 refer that, at high sulfate concentrations (> 8.000 mg/l) in cements containing a high C₃S content, the main attack is due to the formation of gypsum, causing what is called “gypsum corrosion”, that, as referred, reduces cohesion of the paste and general strength of the paste.

### 2.3.3. Fly Ash

Fly ash is one of the most common cement substitutions or, as properly named, supplementary cementing materials. It is retrieved by the burning of pulverized coal from electric power generating power plants. When the coal is burned, several mineral impurities in it fuse and float out along with the gases from burning. As it rises, these minerals cool down and solidify into small spherical particles – Fly Ash (Siddique and Khan, 2011).

Fly ash by itself, being a pozzolana, has little or any cementing value and thus is unable to gain any cementing property with only water addition, as cement. In order to achieve this, fly ash requires calcium oxide, usually available from the cement hydration, and water to produce highly cementitious products. The existent silicates in self-cementing fly ash react with calcium ions and the available water to give origin to C-S-H, contributing to strength resistance along with the cement. The rate or
intensity that this phenomenon will happen is called “Pozzolanic Activity” and is dependent mostly of
the fly ash fineness, calcium content, specific surface, among others (Siddique and Khan, 2011).

When applied in concrete manufacture, fly ash will provide it with a set of benefits that will largely
improve concrete quality. Given that fly ash is used as cement substitution, and it is a by-product of
another process, the first is much cheaper than the latter, effectively reducing concrete costs. Also, for
the same reason, it also is more environmentally friendly by using a product that otherwise would go
to waste and substituting another that is extremely pollutant (one ton of produced clinker releases
approximately one ton of CO\textsubscript{2} to the atmosphere (Coutinho, 2013)). Also, due to its rounded form, fly
ash also gives concrete a better workability when it is being cast, for the same w/c ratios, meaning that
less water can be used in order to achieve the same level of workability. Another important factor is
the reduced heat of hydration when the concrete is curing. Since fly ash takes longer to react than
cement, the total heat energy is spread over more time, effectively reducing hydration heat, which can
be prejudicial, for example in the Delayed Ettringite Formation (DEF) problem. Furthermore, given
the production of additional cementitious materials, the pore interconnectivity is reduced as well as the
existence of capillary pores, effectively reducing the permeability of concrete and providing it with a
long term durability and increased resistance to external factors of deteriorations. These are only some
of the advantages of fly ash substitution (Siddique and Khan, 2011).

Concerning sulfate resistance when fly ash additions are used, they also have large implications in this
matter.

The last point is obviously important. As it was referred in 2.2.3, a requirement for sulfate attack is a
permeable concrete. Given that fly ash ensures, up to a certain point, concrete impermeability, it is
automatically a plus in sulfate attack reduction.

Another important factor is that, since a certain cement quantity is replaced, high levels of reactive
aluminates are also removed from the mix. These aluminates, as explained before, are the main basis
for ettringite formation with the introduction of sulfates in concrete. Reducing these effectively
reduces the quantity of ettringite formed and the deleterious effect of sulfate attack. However, even
though the last sentence is true, fly ash substitution does not guarantee it. If a fly ash has a high
reactive aluminate phases content it will also contribute to expansion products when exposed to
sulfate, reducing the concrete resistance (Siddique and Khan, 2011).

Besides, gypsum type of attack is also diminished with the use of fly ash. As explained, in order to
form gypsum there needs to be available CH to react with sulfates in the solution. However, fly ash
also uses CH in its process to form cementitious materials. The implication of this is that at least some
of the CH has been consumed in the fly ash hydration process, leaving less to react with sulfates and
form gypsum. Furthermore, this process leads to the formation of more C-S-H effectively making a
denser, more compact and resistant cement paste (and concrete) and negating even more the sulfate
penetration and therefore the attack.
3 METHODOLOGY

3.1. INTRODUCTION

In order to evaluate sulfate attack on concrete, a number of different methods have been developed, each of them evaluating a different parameter that may, or may not, indicate the severity of sulfate attack. Currently, the most used ones are expansion measurements, loss/increase of mass, strength loss and elastic modulus variation. Also, visual assertion is always a very important way to determine, not so much the extent of the attack, but more the resistant capability of the material. Of course, this implies that damage has occurred and is visible. While each of them may provide good results in identifying the existence and extent of sulfate attack, none provide the required information to explain the mechanism of development of external sulfate attack (El-Hachem et al., 2012).

As it would be expectable, the use of different types of binders will offer different results in the end. As this work is attached to an investigation required by a private company, not all types of cements were readily available. Also, being the samples already emerged in sulfate solution for over a year at the beginning of this study the choice was limited due to availability and interest of observations, as some of them had already deteriorated.

Not many binders are advisable to resist external sulfate attack. The most commonly used and studied are, of course, sulfate resisting cements with low C₃A content, CEM-I SR 0, CEM-I SR 3, CEM-I SR 5 (with respectively 0 %, less than 3 % and less than 5 % of C₃A content), cement with ground granulated blast furnace slag, CEM-III/B or C, and cement with pozzolanic additions, CEM-IV/A or B. These are indeed, the only cement types referred as Sulfate Resistant (SR) by the current European Standard in use (EN 197-1:2012).

Concerning the origin of sulfate ions, standard procedure is to leave the specimens immersed in sulfate solutions of different concentrations, at different temperatures and also with different cations in the sulfate solution (Ferraris et al., 2005; Skaropoulou et al., 2006 and others). This method allows the observer to study the phenomena expected for each of the mixtures prepared in an accelerated way and with the ability to study the different interactions between the different cations, the sulfate ion and the mixture. This however, poses a tremendous obstacle in defining which constituents interfere in what and makes the final analysis and the gathering of conclusions much more difficult (Neville, 2004).

Although the “Study of Sulfate Attack on Cementitious Materials” is the main aim and reason behind this study, the true field of interest lies within the concrete application borders. It is of the utmost interest to take the lessons from this type of studies and apply it to “real life” phenomena in order to
improve the knowledge and engineering practices on the field. This implies an approximation of laboratory studies to the *in situ* testing conditions (Neville, 2004).

However, in a laboratory, this practice is not always achievable for a different number of reasons. It would not be manageable to produce a complete concrete structure and devise a way to completely submit it to any form of concrete attack on a lab. Even though this has been done for a time range of many years (Kurtis et al., 2000 and Monteiro and Kurtis, 2003), to perform accelerated attack tests it is not manageable. Therefore, it is necessary to find a compromise between time and effort.

Mortar specimens have been used for a different number of studies (Sumer, 2012; El-Hachem et al., 2012 and others). They provide closeness to concrete without the encumbrance it presents while maintaining the ease of handling in a laboratory. There is however, the nonexistence of coarse aggregate, which may, by itself, change the way the attack develops. But, as El-Hachem et al., 2012 defend that, “The behavior of mortar is relevant to evaluate the binder. It takes into account the effect of aggregates without the disadvantage of the study on concrete.” This is, of course, the main concern of the study, the evaluation of the binder resistance to sulfate attack.

### 3.2. Method

Flat prism for studies of sulfate attack on cement has been in use in Germany in compliance with an old German standard, DIN 1164:1958, where a method called the “Wittekindt flat prism method” is presented. This method involves the study of 10 mm x 40 mm x 160 mm mortar flat prisms with defined parts by mass of cement, fine and coarse sand and water/cement ratio. Also, the prisms are exposed to a high concentration of sulfate solution renewed monthly and expansion measurements are done within the same time span. Interestingly, in the same referred standard, another method using the called “Koch-Steinegger small prism method” is also presented. This method is in almost everything analogue to the Wittekindt method but uses 10 mm x 10 mm x 60 mm prisms instead of the flat ones as it was used to measure the bending strength of the prisms after sulfate exposure (Locher, 2006).

From 1957 and during the following years, until 1964, the German Cement Works Association conducted a series of tests in order to evaluate the suitability of these methods to be applied as standard to evaluate the sulfate resistance of cements. Behavior comparison between mortar and concrete samples was evaluated on a first test series. On the second series, the suitability of the referred tests to be applied as standards was studied. Finally, on the third series, comparison studies were made between the two methods, in order to evaluate the scattering of the results obtained in each of them. It was then defined that the precision of the flat prism method was higher than the one obtained from the small prism method. However, large comparability scatter results meant that neither of them could be considered for standardization (Locher, 2006).

Nevertheless, the Wittekindt test is still very much in use nowadays, especially in Germany, but in another number of tests outside it (Frearson, 1986 and Frearson and Higgins, 1992).

The practical reasons for the use of flat prisms are easy to grasp. With these flat prisms, the attack can penetrate in less time to the interior of the specimen and give more reliable results. If thicker specimens were used, the observed expansion measured would be much less and it would only be result of the attack occurred on the surface of the specimens and causing more damage on the surface, than on the inside leading to opposed expansion between layers. Although this might be similar to what can happen in reality, for the purpose of the work, this effect is minimized.

Standards also consider the solution composition. In order to achieve an accelerated test, it seems impossible to apply “natural” concentration values of sulfate ions in the solution. So, in order to allow
for a faster development of the attack, high sulfate concentration solutions are used to imbue the prisms.

In the original Wittekindt method, an accelerated method the solution used for this test had a concentration of 0.15 mol Na₂SO₄ or 14,400 mg/l SO₄²⁻ (Locher, 2006). Comparing this concentration of SO₄²⁻ to the concentration limits provided by current European Standards (EN 206-1:2007), it will fall 2.4 times higher than the upper limit of the XA3 chemical attack exposition class, which is already the most aggressive class. It is implied that these limits are for aqueous solutions and not soils, without the occurrence of freeze-thaw events. If that was the case, the limits would be different.

Another important issue named in the Wittekindt method is the renewal of the solution. This is done in order to maintain a high concentration of SO₄²⁻ so the attack can continue to occur. Also, even though the mentioned standard defines the exposition classes assuming water flowing speeds sufficiently low to simulate a static scenario, usually, in nature, the SO₄²⁻ origin is constantly being renewed, at a higher or lower rate. This provides a fresh supply of sulfate ions.

One test feature not tackled on this study, but that is minored applying the aforementioned practice and that has a high influence on the way sulfate attack develops, is the variation of pH. As referred to before, during the sulfate attack, OH⁻ ions are leached from the cement paste of the specimens raising the pH to values close to 14. This has implications on the progress and outcome of sulfate attack, as already discussed. In recent tests, different methods were applied to minimize the effect of pH change, in order to try and keep the pH in values that are in tune with what is found in nature or at the work site the study relates to (El-Hachem et al., 2012 and Sumer, 2012).

Finally, the last great factor involved in sulfate attack procedures is the temperature at which the specimens are stored during the laboratory work. It is advisable to keep specimens in a reference temperature and study, at least, at the temperature of interest of the working site, for in situ/laboratory comparisons, or in a range of different temperatures to obtain results varying accordingly to temperature. One of the most common objectives tried to achieve with temperature change is the study of thaumasite occurrence in external sulfate attack. Nevertheless important to assess temperature effects at all times, and not only for that particular case (Santhanam et al., 2002a and Romer et al., 2003).

On a final note, even though it is one of the most influential points when studying sulfate attack, in this investigation it was not taken into account the use of different cations in existence in natural sulfate bearing sources.

3.3. INITIAL CONSIDERATIONS

As stated before, the conception of this work has been tightly tied from the beginning with, not only a proposed investigation made by a cement company to evaluate the different sulfate resisting properties of their cements, but also by the conducted studies made thereafter to achieve this purpose. Hence, all the specimens used in this part of the work had already been cast and prepared beforehand, as well as stored in their respective solutions for a little over a year, when this study began. This is a very important notion to maintain because, had the specimens been cast at the beginning of this work, the sulfate attack would not have had time to develop itself in an appropriate way to guarantee the results of the tests described later. However, as explained ahead, some specimens were cast anew to begin the study of the effect of sulfate bearing groundwater, in opposition/comparison to high concentration laboratory sulfate solutions.
The solutions used in this experiment were, for all the combination of binders, Na$_2$SO$_4$ solutions, with an SO$_4^{2-}$ concentration of 3.000 ppm (mg/l) and 30.000 ppm (mg/l) to evaluate the sulfate attack on the different binders.

To obtain the required “realism level” proposed by the objectives of this study, groundwater was collected from a strongly affected region in Germany and used throughout the length of the experiment. This groundwater has a measured SO$_4^{2-}$ concentration of 1.500 ppm (mg/l) which in itself is a much more reasonable value than the previous ones. However, it contains other constituents which may also affect the outcome of the test. 3.000 ppm (mg/l) solutions were also employed in this step in order to have an interesting comparison level and, perhaps, try to connect both parts of this study.

Ca(OH)$_2$ solutions were also used in order to have a criterion, with which to compare the deteriorated specimens due to the influence of sulfate attack.

Finally, all the binder types, at all different solution exposure, were kept at different temperatures. These were at 5 ºC, 8 ºC, 12 ºC and 20 ºC. This is done, as explained before, to evaluate the attack at different temperatures. The groundwater kept specimens were only kept at 5 ºC to verify if collected groundwater at low temperatures can also simulate equally or perhaps better the attack, as any of the other two solutions used.

It is to be noted that not all of the binder/solution/temperature combinations were used in this thesis. Each of the parameters, and the choices that were made, will be explained and dealt with in the subsequent chapter.

From points 3.4 to 3.7, the description deals only with the samples stored in sulfate solutions prepared at IBAC. Only point 3.8 deals with the groundwater samples.

### 3.4. Specimen Selection

#### 3.4.1. Binder Selection

In the beginning of this work, the initial and, perhaps, one of the most important steps to take, was the definition of which, among the large variety of choice, binder possibilities to work with.

This exercise had to be made in order to work with the binders that would offer, within themselves, good and interesting case studies. This means that the choice had to be made taking in consideration not only interesting comparisons between binders, but also the expected results of the final tests performed, with the help of the test values that were already available at date. Also, some of the specimens kept in certain solutions and temperatures (usually high concentration solutions and low temperature) were already destroyed thus rendering impossible their study and comparison to other binders.

In the beginning of this process, there were two major groups of available binder combinations. Even though they resembled each other in terms of available binders, with a few differences, the group chosen was the group in which the specimens were cast more recently (the specimens were about 1 year and 4 months old), as in the older group, many of the individuals had been completely destroyed by the sulfate solutions, due to the long term exposure. Also, it was not recommendable to choose binders from the two groups as the components used in each group were different (even though, for example, the cements used could be of the same class in some cases, etc.).

Among the group chosen, there were 7 types of binders available to choose from. These were:
Sulfate Attack on Cementitious Materials

- CEM I 42,5 R-HS (where HS stands for “Hoher Sulfatwiderstand” in German which can be translated as High Sulfate Resistance), or in European Standards referred to as SR;
- CEM I 42,5 R with 40% of fly ash replacement;
- CEM I 52,5 N with 40% of fly ash replacement;
- CEM I 52,5 N with 29,4% of fly ash replacement and \( k\)-value=0,12;
- CEM I 52,5 N with 29,4% of fly ash replacement and \( k\)-value=0,6;
- CEM III/A 52,5 N – Manufacturer 1;
- CEM III/A 52,5 N – Manufacturer 2.

With these different combinations in hand it was decided to focus the study on the cements with fly ash addition. Even though the comparison with these to the cements with blast furnace slag would be very interesting, to ascertain which of them would have a better behavior to sulfate attack, ultimately this was not done.

It was also decided to test only one of the two cements with 40% fly ash substitution.

Removing CEM III/A binders was done for two reasons. The first reason was that all the used binders had cements from Manufacturer 1, except the second CEM III. Then, it did not make sense to compare on the same basis cements from different origins. With this decision made, only one CEM III/A cement would be left, which was ultimately also removed because even though it would have been interesting to compare it to pozzolanic cements, it was decided to focus on the fly ash substitution ones. Then, among the pozzolanic cements, the CEM I 42,5 R with 40% of fly ash replacement was also not studied. This, unfortunately, had more to do with time constraints, as the thesis had an established deadline, than with any other reason.

In the end, the final list of used binders was:

- CEM I 42,5 R-HS (where HS stands for “Hoher Sulfatwiderstand” in German which can be translated as High Sulfate Resistance), or in European Standards referred to as SR;
- CEM I 52,5 N with 40% of fly ash replacement;
- CEM I 52,5 N with 29,4% of fly ash replacement and \( k\)-value=0,12;
- CEM I 52,5 N with 29,4% of fly ash replacement and \( k\)-value=0,6;

with the first one being used as reference for all the others, the second one as a sulfate resisting cement with high pozzolanic content and the last two, with less pozzolanic substitution but with a \( k\)-value associated with each of them.

Thus, the remaining binders were selected for this study.

3.4.2. Sulfate Solution Selection

Following the decision on the types of binders that would be studied along the course of this work, it was necessary to make a selection from which sulfate solutions the referred specimens would be retrieved from.

As stated before, all binders were immersed in sulfate solutions of Na\(_2\)SO\(_4\) with 3.000 ppm and a 30.000 ppm of SO\(_4^{2-}\) solutions.

It was decided that both the 3.000 ppm and 30.000 ppm Na\(_2\)SO\(_4\) solutions would be used for each binder, when available. This was because it would be interesting not only to compare the extent of sulfate attack between each other, but also to try and provide some correlation with both the
concentration of the solution and the temperature to which the specimens had been exposed to, always trying to approach the laboratory work with in situ conditions, having in mind that the 30,000 ppm are hardly realistic.

Also very important, is the connection of this first part of the study, with the second one, which deals with the exposure of the test specimens to natural groundwater instead of artificial sulfate solution. This topic will be evaluated in another point.

3.4.3. EXPOSURE TEMPERATURE SELECTION

The final selection step to be taken in order to make a sensible selection of the specimens to be studied was the temperature at which these were exposed to during the year of sulfate bathing.

As stated, there were four available temperatures levels: 20 ºC, 12 ºC, 8 ºC and 5 ºC. The question posed was at which temperature level the comparison would be more interesting.

Several criteria could be and were applied to solve this. Firstly, for each binder/solution combination, both the specimens in higher and lower temperature available were chosen, presuming extreme case studies with opposite effects. “Available” is used here because, in some cases, the lowest temperature corresponding specimens had completely vanished as a result of the respective sulfate attack conditions. So, although the first idea was to use both the 20 ºC and 5 ºC specimens and in the case that one of them was not available (greater probability of being the low temperature ones), the batch on the next temperature threshold would be chosen as replacement. This idea was intended so as to consider specimens both from ambient temperature and underground temperatures where, as it has been discussed, sulfate attack tends to be more harmful due to the low temperatures in that environment.

3.4.4. FINAL SELECTION

As a result of the previous steps and criteria applied to the universe of available specimens, the final list of the batches that were studied for this work is:
It is possible to see that some of the chosen specimens were already not available (N/A) to be used at the time of the sample collection.

It is important to refer however, that data exists for these specimens, regarding the expansion and Elastic Modulus tests performed at IBAC, while it was still possible to obtain these results. However, since these specimens were not available to be prepared and tested on XRD at the time of this study, they will also not be considered for the expansion and Elastic Modulus analysis.

The name of the samples has an inherent meaning to them. The first set of characters only refers to a name given in the lab to identify the used mixture. The second set is the temperature at which the sample was stored and the third is the respective sulfate solution concentration.

In accordance with information on the table, for all the binder types except one, it can be seen that a low temperature-low concentration and a high temperature-high concentration combinations always exist. This is extremely important as one of the objectives of this study is to try and bring both natural and artificial sulfate attacks closer to each other. So, using these specimens, it will be possible to see if, or if not, using a low concentration solution at lower temperatures, has good quality results without the need to use a higher concentration, higher temperature and “more artificial” solution.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Temperature (ºC)</th>
<th>$\text{SO}_4^{2-}$ (ppm)</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 42,5 R-HS</td>
<td>20</td>
<td>3 000</td>
<td>HS 20 3k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 000</td>
<td>HS 20 30k</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3 000</td>
<td>HS 5 3k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 000 (N/A)</td>
<td>-----</td>
</tr>
<tr>
<td>CEM I 52,5 N 40% FA</td>
<td>20</td>
<td>3 000</td>
<td>FA40 20 3k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 000</td>
<td>FA40 20 30k</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>3 000</td>
<td>FA40 12 3k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 000 (N/A)</td>
<td>-----</td>
</tr>
<tr>
<td>CEM I 52,5 N 29,4% FA</td>
<td>20</td>
<td>3 000</td>
<td>FA k0,12 20 3k</td>
</tr>
<tr>
<td>k-value=0,12</td>
<td></td>
<td>30 000</td>
<td>FA k0,12 20 3k</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3 000</td>
<td>FA k0,12 5 3k</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 000 (N/A)</td>
<td>-----</td>
</tr>
<tr>
<td>CEM I 52,5 N 29,4% FA</td>
<td>20</td>
<td>3 000</td>
<td>FA k0,6 20 3k</td>
</tr>
<tr>
<td>k-value=0,6</td>
<td></td>
<td>30 000</td>
<td>FA k0,6 20 30k</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3 000 (N/A)</td>
<td>-----</td>
</tr>
</tbody>
</table>

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3.5. Specimen Casting and Keeping

As stated earlier the whole experimental procedure described in this section, is in accordance with recommendations from the SVA “Betontecnoologie” which must be followed by all the institutions, including IBAC and research work performed in Germany regarding concrete.

3.5.1. Specimen Casting

All specimens used were produced from mortar according to EN 196-1.

Where procedure, equipment and mortar composition is defined for determination of strength of cement the same composition was applied in the present.

The mixture must contain “one part of cement, three parts of normalized CEN sand and half a part of water (water/cement ratio of 0.5). With an established amount of 1350 g of normalized sand bags, the constituents considering each binder are, for:

- Cement mortars:
  - 450 g of cement;
  - 1350 g of normalized sand;
  - 225 g of water;
  - w/c ratio of 0.5.

- Pozzolanic cement mortars with 40% substitution:
  - 270 g of cement;
  - 180 g of fly ash;
  - 1350 g of sand;
  - 225 g of water;
  - w/ceq ratio 0.73.

The water/cement (or cement equivalent) ratio is obtained according to DIN 1045-2.

For the binders with a k-value associated to them, the composition is not obtained so directly. To access the required amount of water to obtain the expected k-value, one must do as follows.

Given a defined water/binder ratio (in this case 0.5) and supposing the inclusion of a fly ash, as it is the case, the calculation is as showed in (1).

\[
\frac{w}{c_{eq}} = \frac{w}{c+f} = 0.5
\]  

(1)

Where,

- \(w\) is the water content by weight;
- \(c_{eq}\) is the cement equivalent content, by weight;
- \(f\) is the fly ash content, by weight, when applicable;
- \(s\) is the silica fume content, by weight, when applicable.

Then, given the k-value of, for example 0.12, it is implied that only 12 % of the fly ash introduced in the mixture will count to the amount of “available” binder. Therefore, to the fly ash content must be applied a factorization equal to the given k-value.
Also, if the ratio between fly ash content and cement content is over 0,33, then only that percentage of the fly ash (33%), at the most, is taken into account for the calculation of the water/binder ratio (EN 206-1:2007). However, this is only done concerning concrete and, with these mortars, this was not applied.

Afterwards, knowing the values of the water/cement equivalent ratio and the cement and fly ash percentages (70,6% and 29,4%, respectively, of the 450 g of binder content) it is possible to obtain the water content using the formula above.

\[
\frac{w}{c_{eq}} = 0,5 = \frac{w}{c + k \times f} = \frac{w}{317,7 + 0,12 \times 132,3}
\]

And the obtained water content is, for a k-value of 0,12:

\[
w = 166,79 \text{ g}
\]

Thus, the final quantities used for:

- Pozzolanic cement mortars with 29,4% substitution and k-value=0,12:
  - 317,7 g of cement;
  - 132,3 g of fly ash;
  - 1350 g of sand;
  - 166,79 g of water;
  - w/c_{eq} ratio of 0,46.

- Pozzolanic cement mortars with 29,4% substitution and k-value=0,6:
  - 317,7 g of cement;
  - 132,3 g of fly ash;
  - 1350 g of sand;
  - 198,5 g of water;
  - w/c_{eq} ratio of 0,55.

With all the mortar constituents prepared and correctly weighed within the tolerance limits, the mixing process can begin.

All the mortars were prepared according to EN 196-1, except for the molds used to cast flat prisms. These are flat prisms specific molds, with all the required material and dimensions as specified in the standard, with the exception of allowing the molding of six 160 mm × 40 mm × 10 mm flat prisms and the possibility of inserting pins in all of them.

These pins are fixed in each extremities of the mold of three flat prisms in each batch, required for future expansion measurements. All the other holes are covered with plasticine as to not interfere with the prisms, as shown in Figure 3.
Concluding this point, an explanation to why an unusual \textit{k-value} of 0.12 was used. As referred, this work uses specimens and data cast one year before its start. So, all the specimens used were not prepared by the author but by IBAC personnel. In the beginning, the intended \textit{k-value} for this binder as of 0.4. However, due to an error in quantifying the amount of water to be inserted in the mix, the specimens were cast with much less water than it was supposed and it was found, during the course of this investigation, that the real \textit{k-value} was of 0.12.

3.5.2. SPECIMEN STORAGE

When the casting process is over, all the specimens must go through a curing stage to achieve necessary strength and comply with what is required in the European Standard EN 196-1.

As this same standard requires that, immediately after the molding process is finished, the molds are placed inside a humidity cabinet for 24h, with moist air reaching all faces of the mold and no molds being placed on top of each other.

In this work, the process was almost the same, with the exception that the molds were kept in the humidity cabinet for 48h, which is also considered by the standard when required strength is not achieved in the first 24h. This was done because cements containing pozzolanic additions achieve required strength at a slower rate. So, in order to maintain equity between the different mixtures, all molds were left in the humidity cabinet for 48 hours.

Always according to the rules established by the SVA, immediately after de-molding, each batch of prisms was immersed in Ca(OH)$_2$ saturated solutions and stored in a controlled environment room for 28 days. This room has a constant relative humidity of 50\% and a constant temperature of 20$^\circ$C. The objective of this procedure is to keep the hydration processes occurring for that period, in perfect conditions in order to have the specimens properly cured for the beginning of sulfate attack.
All prisms, whether for storage in Calcium Hydroxide solutions or any sulfate solution, are stored in white rectangular boxes, with $200 \times 200$ mm$^2$ dimensions. Inside them, supports were placed in order to maintain prisms separate from each other and the box itself. This was done to make sure that the solution, in which the prisms are immersed in, is at all times, in contact, with the all surfaces of each prism, as it is shown in Figure 4.

Unfortunately, due to the large number of prisms being studied at the time, it was impossible to ensure that all the prisms had both extremities placed in a suitable support. When this was the case, it was ensured that at least one of the extremities was placed in the support, as to maintain the lower face of the prism not in contact with the box, except for the point in the other side of the prism.

Given this period of one month imbued in Calcium Hydroxide solution, the specimens were then ready to be immersed in the respective sulfate solution.

When the date was due, all specimens were removed from their boxes and these were washed using de-ionized water, to clean any vestiges of the previous solution. Then, the sulfate solution intended for each batch was placed in the box covering, with at least 1 cm depth all of the prisms the corresponding solution was 1.8 l, therefore maintaining a ratio of prism volume/solution volume of 1:3-5, which is kept from approximately 1,152 l to 1,920 l of solution.

Then, each batch of prisms, in the corresponding solution, was placed in appropriate refrigerators to be kept at the temperature previously decided for sulfate attack. From then on, testing of expansion and dynamic Elastic Modulus took place.

### 3.6. Expansion and Dynamic E-Modulus Tests

One of the most frequent tests used in assessment of sulfate attack, is measurement of the expansion of prisms.

Another test becoming more and more popular is the measurement of variation of the dynamic elastic modulus in the prisms. With the formation of the referred reaction products and the deterioration of the mortar, for whichever reason it happened (leaching, internal stresses, etc.), the dynamic elastic modulus will change noticeably and this change can be measured with suitable equipment. However, in order to do this, it is required to apply a procedure not usually used with concrete or mortars, but with stones. This will be explained in the following pages.
3.6.1. **Procedure Common to Both Tests**

Since both tests have a common procedure that connects them, it is important to refer to this point before moving along to each of them. This is more related to timing and general practices of the procedure than on the procedure itself.

3.6.2. **Measurement Frequency**

As to achieve the expected results on the tests described later in this chapter, periodic measurements have been made.

These measurements take place at 0 d, 1 d, 14 d, 28 d, 56 d, 91 d, 180 d, 270 d and 365 d. These are the main measurement dates. However, any other measurements can be made in between if it is of any interest, but not any of these can be skipped.

3.6.3. **Solution Replacement Frequency**

Concerning the solution replacement, importance of which has already been exposed several times before in this paper, its frequency is also a target of the impositions made by the SVA and, of course, performed accordingly at IBAC.

These solutions change must take place invariably at every 14 d, counting from the first day the prisms are inserted in the sulfate solution, or 0 d.

After the elapse of 180 d of the procedure, the solution replacement starts occurring every 28 d, instead of the previous 14 d. As the experiment progresses the rate of sulfate consumption by the prisms decays, as well as the leaching of the cement paste. Thus, the need to change the solution frequently, in order to maintain sulfate and pH values in check, decreases and the increase in solution replacement periodicity is explained.

3.6.4. **Expansion Test Performed at IBAC**

At the established measurement dates mentioned before, all the specimens included in the experience were evaluated for their respective expansion, up to that date. It is important that all of them are measured at exactly the same age and suitable steps must have been taken in order to achieve this, such as different casting date.

The first step of this measuring test is the calibration of the instruments used to perform it. This is done before a new batch of prisms is measured and whenever there is any disturbance with the apparatus.

The equipment used to perform the measurement on this test is very basic, in terms of usage. It is composed of:

- One extensometer;
- One support in which to fix both the extensometer and the prism;
- One calibration bar, to be used as standard for the measurements on the prisms.

The process begins with the removal of the specimen container from the storage equipment. Albeit this may not seem an important step, it is necessary to pay attention to what temperature the specimens are kept. This is because, if the specimens are stored at temperatures different from ambient temperature, their measurement must be done quickly as not to allow any heating of the prisms and therefore alter
the significance of the measurements. In order to minimize this effect, it is important to be swift and take the same amount of time, approximately, to measure each batch of prisms. Also, only one box at a time should be out on the measuring area. All the other should be kept at their storage conditions for the same reasons as stated above.

As it is obvious, only the prisms with knobs inserted in them will be handled here. These, after removal from the solution must be dried conveniently with soaking paper to remove the excess of solution from them. After, the knobs must be cleaned to prevent any glued substance in them that might interfere with the measurement.

Then, with the prism in place as seen in Figure 5, it must be rotated on itself to make sure that it is correctly in place, as there will always be some variation in the values when this is done. When the prism is rotated and no variation is visible, then that is the correct value. This value should be written down for future reference and calculations.

The calculation of the expansion is obtained by:

$$\varepsilon_{x_d} = \frac{\Delta l_{x-1}}{l_0} = \frac{v_{x_d} - v_{1d}}{l_0}$$  \hspace{1cm} (2)

Where,

- $\varepsilon_{x_d}$ is the expansion at age $x_d$, in millimeter per meter;
- $\Delta l_{x-1}$ is the length difference between age $x_d$ and age 1d, in millimeters;
- $l_0$ is the initial length of the prism, before insertion in solution, between the knobs, in meters;
- $v_{x_d}$ is the measured value at age $x_d$, in millimeters;
- $v_{1d}$ is the measured value at age 1d, in millimeters.

The measured values are always the difference between the length of the prism and the length of the calibration bar.

An important detail denoted in (2) the information placed before, is the $l_0$ value, which is said to be the distance of “existing” prism between the knobs. This is because, since the knobs are inserted in the
prism, the expansion that is measured is the one the prism suffers within these boundaries. It is known that each knob is buried, approximately, 5 mm into the prism. So, knowing the initial length of the prism, one only has to subtract 10 mm to that value in order to obtain \( l_0 \).

As a reference, the binder is considered resistant to sulfate attack if at 91 d the expansion measured is not above 0.5 mm/m or if at 180 d is not above 0.8 mm/m. However, with this in mind, this cannot be the only evaluation parameter. The combined result, as well as this one, will be the final determination.

3.6.5. Dynamic E-Modulus Test Performed at IBAC

The dynamic E-Modulus determination for each specimen was made by using the method described in EN 14146:2006, the continuous excitation method. Even though this standard is used as a basis for the test, it is only referenced here as a theoretical and guideline basis because the procedure was not fully followed. It is also important to refer that this standard is for natural rocks and not concrete. However, the principle is the same and its application to concrete is possible. All the specimens were measured at the dates established before.

The dynamic Elastic Modulus is obtained in this test by measuring the resonant frequency of each prism. This is done with a proper apparatus, a resometer, for this purpose which is composed by an emitter, a receiver and a support for the prism, all of these in an external vibration free system.

The data values can then be read in dials that show the frequency being applied at the time and the occurring amplitude from it.

The purpose and final value of interest of this test is to obtain the frequency to which the amplitude measured is higher, as it befits the notion of resonant frequency.

The value of the Elastic Modulus is given by equation (3) present on EN 14146:2006, which is:

\[
E_d = 4 \times 10^{-6} \times l^2 \times F^2 \times \rho \quad (3)
\]

Where,

- \( E_d \) is the dynamic E-modulus value, in MPa;
- \( l \) is the length of the prism, in millimeters;
- \( F \) is the measured frequency for the maximum amplitude, in Hertz;
- \( \rho \) is the bulk density of the prism, in kg/m\(^3\).

In order to calculate the bulk density of the prisms, they have to be dried properly and weighed before the frequency measurement. To the volume calculation, the 160 mm × 40 mm × 10 mm dimensions are assumed.

The prism is then placed in the resometer, as shown in Figure 6. The aim is then to measure at which frequency the measured amplitude is maximal. The amplitude dial, the one on the left side of the right picture, must be kept preferably around the value of 50 µA, when the maximum amplitude is reached, in order to obtain more suitable results.
The obtained frequency value, displayed on the right hand side, is then dully noted and applied using equation (3) to obtain the dynamic E-modulus.

3.7. X-RAY POWDER DIFFRACTION STUDY

3.7.1. WORKING PRINCIPLES

X-Ray (Powder) Diffraction (XRD) has been in use for a long time in every field of materials investigation of any kind and has innumerable applications. In cement, it is commonly used to identify the different crystalline phases that are contained in it and, more recently, due to the invention of the Rietveld Method by Hugo Rietveld (Rietveld, 1969), became easier to peek to what is inside the sample, and to see how much of each crystalline phase is in there, since the older methods required an extraordinary amount of time.

As its name suggests, the working principle behind this method is the application of an X-Ray beam to a sample of interest and, by the study of its resulting diffracted beam, sample information can be retrieved.

An XRD machine is essentially composed of 3 main important components: an X-Ray beam emitter, a receiver and a sample stage holder, being the first two movable and the sample stage holder capable of rotation by means of a goniometer as seen in Figure 7.

Figure 7 - Main instruments of an XRD apparatus. *From left to right: Emitter, sample holder and receiver*
3.7.1.1. Crystallography of the sample

Since the sample is the subject of main importance here it should be important to outline its specificities. An XRD measurement can only be applied to crystalline materials. Only with these can the X-Ray beam be diffracted and the sample studied. If there is any non-crystalline (or amorphous) matter in the sample it will simply not be detected and not taken into account to neither phase detection nor quantification.

In order for some material to be crystalline, it has to obey to two very important properties: first it has to be solid and, more importantly, it must have a long range order. This means that any crystal, to be defined as such, has a certain periodic, defined and (almost, due to impurities that might occur) uninterrupted repetition of their atoms or molecules in space. Considering the theoretic part of this, one could say that this repetition is infinite, and this is an important assumption in how XRD works. However, long range order extends from about $10^3$ to $10^{20}$ atomic or molecular dimensions and, of course any crystal must end at some point (Pecharsky and Zavalij, 2009).

Then, crystals are organized in a given order and in a given dimension. This can be in three, two or even one dimensions. Whichever one might be the case, it is assumed that the crystal has perfect periodicity and that this periodicity is repeated by what is called unit cells and lattices. The unit cell is each single molecule that will be repeated along the lattice. So, a unit cell represents the molecular structure that will be repeated along the crystal, and the lattice represents the planes (as many as they are) where that repetition will occur, as seen in Figure 8 (Pecharsky and Zavalij, 2009).

![Figure 8 - Illustration of a two-dimensional lattice with one unit cell hatched vertically (Pecharsky and Zavalij, 2009)](image)

The organization of the unit cell will determine how this repetition develops. Each unit cell, to be studied three dimensionally, must be described using three vectors, named $a$, $b$ and $c$, which will form the three dimensional space of that unit cell. As an example, using the picture above which is 2D, there are only two vectors represented, $a$ and $b$, which are repeated in all the other unit cells, creating a lattice. The origin point can be anywhere, taking into account that the lattice is infinite and the vectors can have positive or negative values, defining then the full lattice (Pecharsky and Zavalij, 2009).
However, these three parameters are not enough. Defined the intensity of the vectors, one must define the direction of each one. This is done by using three other parameters that represent the angles in existence between each vector. Then with \( a, b \) and \( c \), (unit cell parameters) which are the “sides” of each unit cell, and can be multiplied by any integer number in order to get to another unit cell, and \( \alpha, \beta \) and \( \gamma \) which are the angles formed between \( b \) and \( c \), \( a \) and \( c \) and \( a \) and \( b \), respectively. The unit cell parameters are usually measured in Ångström, Å (1 Å = 10\(^{-10}\) m), and the angles in degrees (°) (Pecharsky and Zavalij, 2009).

3.7.1.2. Diffraction and Diffractogram collection

What the XRD equipment does then, is to send an X-Ray beam towards the crystals present in the sample and measure their respective diffraction patterns.

When a X-ray beam travels through a substance, say only one crystal as an example, there are three occurrences that matter for diffraction process, as explained by Pecharsky and Zavalij, 2009:

- Coherent scattering, which is the production of a beam with the same wavelength, read photon energy, as the incident beam;
- Incoherent scattering, where the wavelength of the beam changes due to energy loss by the photons due to the electron collisions that take place, and;
- Absorption of the X-Rays, as some photons are dispersed in random directions and other lose electrons.

The last two are not taken into account for diffraction studies, as their influence can be neglected. Only the coherent scattering is of matter.

When this happens, this scattering occurs in every direction around the affected unit cells. Given the physical properties of the lattice and its randomness and theoretical infinity, and that coherent scattering produces beams with the same wavelength, from all electrons and in all directions, what will happen is a cancelling of the diffracted beams in all directions, but one. This direction is what defines the whole process of X-Ray diffraction (Pecharsky and Zavalij, 2009).

Among each lattice, several beams with different maximum intensities are produced. Each of them, not only has a different intensity associated to them, given by the “amount” of beams concentrated at that given point, but they are also “seen” at certain specific angles of diffraction. This is still talking for a single type of crystal.

These angles of diffraction are explained by what is known as the Braggs’ Law, formulated by father and son (Bragg, 1969).
What Figure 9 demonstrates is the functioning principle of the Bragg's Law, which is given by the following equation:

\[ n\lambda = 2d \sin \theta \]  

(4)

Where,
- \( n \) is an integer;
- \( \lambda \) is the wavelength;
- \( d \) is the spacing between planes in the lattice;
- \( \theta \) is the angle between the incident beam and the planes.

Looking at the picture “2dsinθ” represents the extra path that the beam below must make. When this equals an integer multiple of the wavelength (taken as 1 in all calculations), satisfying Bragg's Law, a constructive interference is obtained and the so called Bragg's Peaks are formed (in the final diffractogram), representing the intensity of the constructed diffracted beam (Pecharsky and Zavalij, 2009).

What happens in the XRD equipment is then a variation of both the incident beam angle \( \theta \) (emitter position) and the resulting diffractioned beam angle \( 2\theta \) (receiver position), as can be seen in Figure 10.

![Figure 10 - XRD measurement explicative diagram (KSAnalyticalSystems, 2010)](image)

With this variation, each crystal present in the sample will “emit” intensity peaks to the receiver at certain \( 2\theta \) values, which are clearly defined for each crystal in existence. What may change is the relative peak intensity, which translates in the same mineral but in different physical states (like a crystal created under great pressures and the same crystal created at atmospheric pressure).

What is obtained in the end is what is called a “Diffractogram”, or more currently “pattern” which relates the \( 2\theta \) variation, as the independent variable, and the intensity count as the non-independent variable, as seen in Figure 11.
Sulfate Attack on Cementitious Materials

Finally, using existing databases of mineral Powder Diffraction Files (PDF), it is possible to run the obtained diffractogram in suitable software (in this case HighScore Plus) and identify the existing phases, in the studied sample. The databases used in this study were from the ICDD (International Centre for Diffraction Data) and from the ICSD (Inorganic Crystal Structure Database). This process is usually referred to as Qualitative Analysis, being it more or less difficult depending on the goodness of the existing database, the complexity of the analyzed pattern and mostly by the experience of the user that is examining it.

3.7.1.3. Rietveld analysis

Rietveld analysis, one of many Quantitative Analysis methods, is the process after the completion of Qualitative Analysis, in which the user intends to obtain the relative concentration of each phase determined in the previous step. This stage represents the bulk of this study regarding objectives completion, data gathering and result analysis. In itself, it is even more delicate and hard to perform than the previous analysis as it requires very much fine tuning and several requirements to be met in order to obtain satisfying results (Pecharsky and Zavalij, 2009).

What this method assumes is that the $2\theta$ peaks retrieved from the exercise before belong to only one unit cell of each phase. The calculations it performs then are used in order to normalize the values of those unit cells in order to fit them to the obtained pattern before, by employing a Scale Factor to each phase (Pecharsky and Zavalij, 2009).

What this means then is that each of these Scale Factor values represents the number of unit cells in existence in the studied sample or, in other words, how much of a phase exists in it. With this information, and the phase identification performed, it is then possible to infer the relative quantity of a particular phase or all of them, as long as they have been identified (Pecharsky and Zavalij, 2009).

This is done by applying equation (5).

$$w' = K \times ZMV$$  \hspace{1cm} (5)
Where,

- \( w' \) is the weight fraction of a particular phase;
- \( K \) is the retrieved Scale Factor from this exercise;
- \( Z \) is the number of formula units in the unit cell;
- \( M \) is the molecular mass of the formula unit, and;
- \( V \) is the volume of the unit cell.

All of the previous values are known from the databases referred before, except for the scale factor that must be calculated from the Rietveld analysis.

This was the method applied to all the used samples in this study in order to identify and quantify the existing reaction products in each layer of the sulfate attacked prisms. It was then possible to obtain the relative quantities of each phase as to see what happened with the attack and, most importantly, how this developed along the depth of the prism.

3.7.2. SAMPLE PREPARATION

3.7.2.1. Considerations

Knowing the geometry of the testing subjects at hand, it was very important to define how the study of sulfate attack development had to be done. This means that it was needed to be taken in consideration the geometry of the prisms and the direction of the attack in order to choose a representative area of the prism and not one that had been both too much or too less attacked.

As it was explained before, specimen storage allowed for an equal attack on all the exposed faces of the prism. Even though this may sound good, on a more attentive glance it is safe to say that the cross sections at the extremities of the prism will suffer a more severe attack. This is due to their excessive exposure when compared to, say, the mid-span cross section. The first are more attacked because they suffer the influence zone of themselves and also from the top and lateral faces of the prism.

![Figure 12 - Flat prism and the defined “excessive attack areas”](image-url)
For this reason, it was declared that the two top 4 cm of every prism (lengthwise) would never be used in the study, as seen in Figure 12. Therefore, 8 cm remained, of which, it was tested to check if 4 cm of prism length were enough to produce the required amount of powder.

It is also here implied, in a way, in which direction this grinding would occur. As to attest the development of the attack in depth, the grinding area would need to be the remaining 4 cm × 4 cm remaining square, after the required cuts.

3.7.2.2. Sample Grinding

In order to comply with the proposed objective, of studying the development of the sulfate attack in depth of the prism, and not only on the surface, a new method procedure had to be developed as no similar study could be found on previous literature. The required procedure had to comply with three requirements:

- Preparation of the prism to be suitable for Powder XRD procedure, both in terms of quantity and powder fineness;
- Employment of a method that allowed the collection of dust from very thin layers of the specimen (up to 1 mm of maximum thickness);
- Prevent the destruction of the reaction products be it mechanically or by heating.

All of these points are intimately related. However the first two are defined by the type of machinery that is employed and that allows the obtainment of matter with those specific qualities. The method found was the simple grinding of the prisms in a prototype machine that is available at IBAC capable of grinding any type of specimen in steps of 0,1 mm, more than suitable for the requirements at hand. The prism grinding thickness, and therefore study, was then defined as steps of 0,5 mm, to obtain suitable and reliable data, as represented in Figure 13.

Since the attack occurred in all the sides of the prism, the grinding would also only be done until the middle point of the prisms as the other half should be symmetrical in terms of attack severity, thus providing the same results.

Figure 13 - Representation of final prism and the grinding steps
Mock prisms were cast to ascertain the compliance of the grinding methodology to the necessities of the study. Being these prisms exactly alike the original specimens, geometry and mix wise, a perfect correlation can be made.

In the same test it was checked if a 0.1 mm step made by the machine would translate itself in a “true” grinding of 0.1 mm in the sample by performing continuous grinding of 0.1 mm steps until a depth of 5 mm was reached. Also, at every 1 mm of grinding the temperature was checked to verify if it did not go higher than 40 °C. This limit was imposed because it is below the assumed temperature point at which ettringite might start decomposing, 50 °C (Pourchez et al., 2006).

<table>
<thead>
<tr>
<th>Trial</th>
<th>Nr grindings</th>
<th>$T_{final}$ (°C)</th>
<th>$t_1$ (mm)</th>
<th>Diff$_{t1}$ (mm)</th>
<th>$t_2$ (mm)</th>
<th>Diff$_{t2}$ (mm)</th>
<th>$t_3$ (mm)</th>
<th>Diff$_{t3}$ (mm)</th>
<th>Avg. Diff. (mm)</th>
<th>Steps/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.64</td>
<td>-</td>
<td>9.28</td>
<td>-</td>
<td>9.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>31.00</td>
<td>8.27</td>
<td>0.37</td>
<td>8.21</td>
<td>1.07</td>
<td>8.41</td>
<td>0.59</td>
<td>0.68</td>
<td>14.78</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>32.40</td>
<td>7.23</td>
<td>1.04</td>
<td>7.22</td>
<td>0.99</td>
<td>7.19</td>
<td>1.22</td>
<td>1.08</td>
<td>9.23</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>31.80</td>
<td>6.26</td>
<td>0.97</td>
<td>6.18</td>
<td>1.04</td>
<td>6.28</td>
<td>0.91</td>
<td>0.97</td>
<td>10.27</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>32.00</td>
<td>5.37</td>
<td>0.89</td>
<td>5.50</td>
<td>0.68</td>
<td>5.34</td>
<td>0.94</td>
<td>0.84</td>
<td>11.95</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>31.50</td>
<td>4.17</td>
<td>1.20</td>
<td>4.08</td>
<td>1.42</td>
<td>4.10</td>
<td>1.24</td>
<td>1.29</td>
<td>8.55</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>30.40</td>
<td>FAIL</td>
<td>FAIL</td>
<td>3.16</td>
<td>0.92</td>
<td>3.14</td>
<td>0.96</td>
<td>0.94</td>
<td>10.64</td>
</tr>
<tr>
<td>Average</td>
<td>31.62</td>
<td>-</td>
<td>1.03</td>
<td>-</td>
<td>1.01</td>
<td>-</td>
<td>1.05</td>
<td>-</td>
<td>1.02</td>
<td>10.13</td>
</tr>
</tbody>
</table>

The columns $t_1$, $t_2$ and $t_3$ represent the measured thickness in each of the corners of the prism. The fourth corner could not be measured as it was unreachable.

The first trial was not correctly done because the specimen had to be repositioned since it had already been grinded, as suggested by the initial testing values, which are lower than 10 mm.

As can be seen in Table 4, the temperature never rose above 32.40 °C, even with constant grinding until 1 mm of depth. Also, the final result showed that to achieve this same depth, an average of approximately 10 steps was required meaning the steps made by the machine were accurate and grinded the specimen conveniently.

The obtained amount of powder was also more than enough to allow measurements of 0.5 mm steps with the final square prism referred before.

Every specimen was tested to verify that no debris from the grinder contaminated the sample powder.

An image of the grinding system is provided in Figure 14.
At the end of any 0.5 mm grinding process, all the pieces in contact with the specimen and/or dust were cleaned properly using an air pressure gun. This includes the blade, the powder holder and the brush used to collect the powder. This is done so that no particles from one sample contaminate the next one.

3.7.2.3. Hydration Stopping Process

So as to stop the hydration process of the specimens and to maintain the interesting phases intact, a suitable process had to be applied.

From previous experience at IBAC, it was known that the application of Isopropanol or Acetone to achieve this was appropriate. Using these two compounds, tests were conducted to ascertain which proved more suitable.

To do this, mock prisms were immersed in isopropanol and acetone for two and four hours in each one, as represented in Figure 15. After the elapsed time, they were inserted in an oven at 40 °C and 105 °C and left there to dry for 24h. Weight measurements were made before immersion, before oven insertion and after oven removal. This allowed seeing how much time the solutions needed to penetrate the samples and then how much time was required for the solution to evaporate completely (all of this information obtained with the mass differences between each step).
The obtained results indicated that between both solutions impregnation, the results were approximate but favoring acetone and the 4h immersion. Concerning time to evaporate, both solutions evaporated satisfyingly within the 24 h in the 40 °C oven.

The chosen solution was to use isopropanol with 4 h immersion and 24 h in oven drying. Isopropanol was chosen because, since it had similar results but is much less aggressive, it would serve the purpose well without causing risk to the samples.

After this process, if any prism was not immediately used, it would be kept in an exicator with grains of silica gel (SiO$_2$) to prevent any water absorption and the restart of the hydration process, also in Figure 15.

3.7.3. XRD MEASUREMENTS
3.7.3.1. Calibration

Before any measurements were conducted for the purpose of this study, the equipment was used to measure ten times the same sample to verify if it was correctly calibrated. Rutile (TiO$_2$) samples were used to run the tests due to its high purity level, being the resulting pattern very well defined. The obtained patterns were all overlaying each other, confirming that the machine was in good conditions.

3.7.3.2. Sample Preparation

The powder obtained from the grinding process had to be suitable prepared to be measured in the XRD. As explained, the sample holder consists of goniometer, and thus a specific powder holder is required.

Also, the sample has to be prepared in a certain way as to eliminate errors concerning sample preparation and handling. The process is shown in Figure 16.

Firstly, the sample is poured into the mold, already in the sample holder with a little surplus. After, the powder must be compacted using an appropriate object with a very smooth surface. If required, some
more dust can be poured to achieve a smooth and even surface with the mold, but never over pressing the powder. This is extremely important because the sample has to be compact, in order to not dislodge itself from the holder but not too much as not to alter its properties.

Then, using a straight and thin object, excess powder must be removed, making sure the surface is even, and the mold cleaned.

Finally, the piece that holds the sample in the XRD is fixed to the mold and the whole group removed from the sample holder, inverting it and dislodging the mold.

For the rutile samples it was always used a Teflon pellicle to prevent the powder from sticking to the sample holder.

All the instruments are cleaned after any preparation is done, using deionized water and/or isopropanol and a clean piece of soaking paper, as to avoid contamination from one sample to the other.

3.7.3.3. Measurement

All the measurements took place in the same machine.

The measurement program used was always the same and was specially configured to these specimens and taking account the total measurement time and required diffractogram definition in order to have suitable results in the end. The program had the following characteristics:

- $2\theta_i$: 5.00835563°
- $2\theta_f$: 69.99848069°
- Step size: 0.00167113 °/2
- Scan speed: 0.034815 °/s
- Time per step: 60,960 s
- Total time: 00:32:11

The measurement is totally automatic and the user only has influence in the sample preparation and sample changing. Afterwards the machine operates on its own until the end of the measurement.

The measurement takes place in a clean environment, but not sterilized. This is required so that the samples are not contaminated by dust or any other type of material that can change the outcome of the measurement.

3.7.4. Qualitative Analysis

Quantitative analysis was performed using the HighScore Plus Software from Panalytical. This type of software allows the user to prepare the diffractogram obtained from the previous step and study it in order to find what phases are inside the sample in cause and afterwards perform the required Rietveld analysis.

To perform the quantitative analysis, one must first configure the software so it performs the “reading” correctly and identifies the peaks with an appropriate background and a peak search process, which implies a significance value.

The “background” is a determined line defined manually by the user or with the aid of the software. It draws a line that will be considered as the baseline for the whole diffractogram and it is to this line the program will determine the “peak intensity values” and find the Braggs’ Peaks referred before. It is
completely artificial and software related. However, it should follow what could be considered the “base” of the diffractogram and not be above or below it, but in the average value.

The “significance” is then a factor which defines the relative peak intensity required for a certain peak to be considered in the qualitative analysis. This means that, with a higher significance value only the biggest peaks (like the quartz peaks in Figure 11, in page 39) will be taken into account. A lower significance will find even the flatter peaks. So, in conclusion, the significance is the factor that determines what intensity difference between the peaks and the background is required for that peak to be considered to the analysis.

This is very important because if the significance is too low, the software might include peaks that do not really exist but are just background “noise”. If it is too high, the software might not consider important peaks to the analysis. A weighted value must be assigned and the result must always be checked by the user.

In this study, the parameters used were:

- **Background**
  - Granularity: 20
  - Bending Factor: 2

- **Peak search**
  - Minimum Significance: 1
  - Minimum tip width ($^\circ$2$\theta$): 0.01
  - Maximum tip width ($^\circ$2$\theta$): 1
  - Peak base width ($^\circ$2$\theta$): 2
  - Method: 2$^{nd}$ Derivative

This layout was applied to all of the studied samples in order to maintain equity among them. It was always verified if the peaks were correctly identified however.

Afterwards, doing what is called a “Search & Match” procedure, the program applies the mechanism explained in 3.7.1.2 (page 37) in order to identify the existing phases. It then retrieves a list of the most appropriate candidates, their respective name, chemical formula and a Score Number, which helps the user choose the most appropriate candidate. The user must also check if the “to be” candidate has its defined peaks in accordance to the peaks shown in the diffractogram because sometimes, even though the score is high, the candidate is does not suit the diffractogram or simply its chemical composition is impossible to exist in the sample.

Therefore, and as it was referred before, the user has a very important role in defining this procedure’s outcome.

### 3.7.5. SAND/QUARTZ PEAKS REMOVAL

#### 3.7.5.1. Overview

During the few first phase searches it became clear that the obtained peaks had a very large disparity in terms of counts values and, therefore, the phase search was being strongly affected by the very large peaks.

What happened in this phase was that, due to the high intensity measured in some peaks, the shallower ones were not correctly being detected, and were considered as background by the software, and their respective phases were not being found.
This was found simply by doing a standard “Search & Match” procedure as described above. What the software returned was that all the main peaks belonged to quartz grains which themselves came from the normalized sand used in the sample casting.

It is important to define here and for the reader to bear in mind that, the stated “main peaks” are peaks with an intensity value above 1,000 counts as seen in the diffractogram. This value was defined because the smallest quartz peak is around 1,300 counts high. Also, the main quartz peak, or the one with higher intensity value, has a value of more than 35,000 counts. What this means is that any other phase in existence in the sample had, as a fair assumption but not always, 35,000 times less counts than the main quartz peak.

Expected phases occurring from the sulfate attack like ettringite, gypsum or thaumasite, that at least one of them was surely inside the sample were, if not detectable at all, barely seen.

Performing a quick and simple Rietveld Analysis, returned values of 92% Quartz content, and the rest 8% divided by some other four or five phases, including microcline and albite, which are also phases belonging to the sand. Most of these phases had a relative content of less than 1%. When performing Rietveld Refinement values below 1% are usually considered as “existing but not correctly measurable”, this means that there should be only traces of those phases. Compared to the amount of quartz, those are, in fact, only traces. However, to this work, the amount of the cement paste phases in existence had to be correctly measured and, for that, the quartz peaks had to be disregarded.

3.7.5.2. Method

For the problem referred before to be solved, first it had to be verified if it was in fact the sand that was causing these problems. Even though the main peaks belonged to the quartz, this verification had to be done. Also, it was important to identify correctly which peaks belonged to the sand, and which didn’t and even more importantly, if there were peaks “hidden” beneath the sand peaks.

The solution to test this was simply to test sand samples retrieved from a normalized sand bag in XRD and then compare the diffractograms obtained from the sand and the mortar.

So as to perform this, the sand had to be prepared beforehand to achieve the required fineness suitable for XRD measurements. Of course the sand could not be grounded in the same way the samples had been so instead it was milled with a mechanic miller, as shown in Figure 17.

Figure 17 - Mechanic miller. *This miller worked by inserting the sand inside and then applying intensive vibration. The rings press on each other and mill the sand*
Before, however, a representative sample had to be retrieved. To do this the “quartering” method was used. Beginning with a normalized CEN sand bag of 1.350 g, the whole content was dispersed on a flat table randomly and then quartered. One of the obtained quarters was again randomly mixed and divided in four once again.

With each of these quarters the objective was to grind each one up to different fineness levels to see which would offer the best results. This is because the fineness levels and grinding times have influence in the XRD measurements as they change the crystal structure features if ground too much by creating excessive surface and, perchance, promoting agglomeration of the particles. If too less, the sample will not have the “required infinity”, so to speak, as there will be not enough particles so its number can be considered infinite, a required property for XRD measurements (Pecharsky and Zavalij, 2009). As a starting point, it was considered that the particle size had to be at least 0.063 µm in diameter so the XRD equipment could measure correctly.

First, the whole quarter was ground until all the grains could pass a sieve of the said opening. With the purpose of grinding the sand to this size, 90 seconds of milling were required. Afterwards, each of the other three quarters were ground more 30 s, 60 s and 90 s to obtain even more fine powder.

For each of the sand samples, five different XRD measurements were made, all of them prepared individually. The purpose of this was to see among which batch the difference in measurement would be lower as that would be the batch with the better grain quality for XRD process. What was compared was the total peak height of the two highest obtained peaks of all the five samples in each batch. Then, statistical treatment was done (average, standard deviation and variance) to access which batch had the least dispersion. This would be the one chosen. As seen in Table 5, the one that offered the best results was the sand milled for an extra 60 seconds.

<table>
<thead>
<tr>
<th></th>
<th>90+0 s</th>
<th>90+30 s</th>
<th>90+60 s</th>
<th>90+90 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>52198</td>
<td>51602</td>
<td>48354</td>
<td>55624</td>
</tr>
<tr>
<td></td>
<td>52144</td>
<td>51720</td>
<td>53661</td>
<td>54341</td>
</tr>
<tr>
<td></td>
<td>52241</td>
<td>53649</td>
<td>52236</td>
<td>53266</td>
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<td></td>
<td>49878</td>
<td>51559</td>
<td>56054</td>
<td>46599</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>52086</td>
<td>53107</td>
<td>52422</td>
<td>50690</td>
</tr>
<tr>
<td>St. Dev.</td>
<td>2599</td>
<td>1118</td>
<td>1139</td>
<td>3489</td>
</tr>
<tr>
<td>Var.</td>
<td>4,989</td>
<td>2,105</td>
<td>2,173</td>
<td>6,883</td>
</tr>
<tr>
<td>Peak 2</td>
<td>26536</td>
<td>259568</td>
<td>258815</td>
<td>266697</td>
</tr>
<tr>
<td></td>
<td>245628</td>
<td>254452</td>
<td>250608</td>
<td>239054</td>
</tr>
<tr>
<td></td>
<td>249365</td>
<td>246230</td>
<td>245111</td>
<td>237853</td>
</tr>
<tr>
<td></td>
<td>233236</td>
<td>237311</td>
<td>227754</td>
<td>234956</td>
</tr>
<tr>
<td>Average</td>
<td>263424</td>
<td>249092</td>
<td>243560</td>
<td>234373</td>
</tr>
<tr>
<td>St. Dev.</td>
<td>3913</td>
<td>6851</td>
<td>4860</td>
<td>4242</td>
</tr>
<tr>
<td>Var.</td>
<td>1,485</td>
<td>2,750</td>
<td>1,995</td>
<td>1,810</td>
</tr>
</tbody>
</table>

Even though this batch does not have the lowest variance values in neither peak study, in the communion of both it is the best, as seen in Table 6.
Table 6 - Variation Average of the four batches

<table>
<thead>
<tr>
<th>Variation Average</th>
<th>90+0 s</th>
<th>90+30 s</th>
<th>90+60 s</th>
<th>90+90 s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3,237</td>
<td>2,427</td>
<td>2,084</td>
<td>4,346</td>
</tr>
</tbody>
</table>

With the correct batch defined, a 50 h measurement on XRD was performed on both a this sand sample and a FA40 20 30k sample (In the figure legend the sample is named “Temp1” as that was the name given at IBAC). The obtained overlapping diffractogram is seen below.

Figure 18 - Overlapping diffractograms from sand and mortar samples. The 3 quartz mains peaks are cut but visible (circa 21 °2θ, 26 °2θ and 50,5 °2θ)

As it is perfectly seen here, the highest peaks all are obtained from sand phase of the mortar. Also very important is that after 52 °2θ, all the peaks belong to the quartz phase. This shows that from that point on the analysis is not necessary as only sand related phases will be in there. Had this procedure been done before, the “°2θ” window could have been lower and, for the same amount of time, the definition could be better.

Afterwards, with all this information in hand, it was necessary to remove the sand peaks. This had to be done with the assurance that no other peaks were underlying these sand peaks because eliminating one might implicate eliminating the others. Again, testing was conducted to verify this.

Every diffractogram inherent properties and values can be accessed using a simple source code editor or a text editor. Inside, all the intensity values can be seen and changed effectively altering the resulting diffractogram. After obtaining this information, all the sand peaks were conveniently identified and their respective °2θ window defined. Then, an Excel sheet was created that allowed the user to combine both the diffractograms and subtract the sand peaks from the original mortar sample diffractogram. If a peak was underlying the sand peak, then it would show on the difference pattern.

This was done by comparing the maximum value of all the sand peaks individually of both diffractograms and scaling the sand ones to the value of their equivalents from the mortar diffractogram. Afterwards, the obtained values in the defined °2θ interval would just be subtracted from the mortar diffractogram and, in theory, the peak would disappear.
The result was satisfactory, but not extremely correct. Even though the objective of underlying peak search was accomplished, which was the important part, the obtained diffractogram would frequently not come perfect due to small $\theta^2$ shifts that occur when the measurement is done. These are predicted errors that always occur and do not affect the quantitative or qualitative analysis as the software predicts them. However in this case, as seen in Figure 19, these caused some trouble when this method was applied. What resulted was that when the subtraction was done, due to these shifts the computation would not subtract the equivalent values in each diffractogram, but a little bit to the side. Therefore, the obtained graphs could not be used for other purposes, such as the Rietveld refinement as the errors would be identified as peaks and the resulting qualitative and/or quantitative analysis would be severely affected in the end.

Figure 19 - Assembly graph from sand peaks removal

The image shows both the sand diffractogram (red) and the FA40 diffractogram (blue). The green line is the assembled diffractogram after calculation and substitution. As can be seen, it wobbles up and down in the “peak window” defined confirming what was explained before. This demonstrates when the sand diffractogram values are higher than the mortar ones (peaks) and the opposite of that (valleys).

The green diffractogram is not at the shown count value. It was raised to that position so guarantee an ease of perception.

Since the previous approach worked for its purpose, but not to eliminate the sand peaks, a new way had to be devised.

As no underlying peaks were found, the solution applied was simply to eliminate the peaks altogether. Using the Excel sheet created before, and the same $\theta^2$ intervals defined, the approach was to create a straight line from the first and last value if the interval. The ten values around the referred two values
were used to create an average so that the used value would bear less error, as it could have been a background relative maximum or minimum.

The obtained graph was extremely different from the one before. Without the existence of the huge sand peaks that were removed, the diffractogram was much more “ridged” and the low definition of the measurement became apparent. However, now the “hidden” peaks were clearly defined and new peaks were found were before none could be seen.

It must also be said, nevertheless, that the approach also had negative aspects, also due to definition. When the $\theta$ was defined, the values were chosen, supposedly, far enough from the peak so that they belonged in the background. This was done manually by the user, without any software help. What happened then was that, in some cases, the initial interval margin was defined already in the peak or the final one still in the peak, leading to a hill in the final diffractogram. Even though this in itself is a substantial error, it was found afterwards that it did not influence the results gravely.

The diffractogram above shows the final FA40 20 30k diffractogram after all the referred changes. Even though it may not seem the same graph, all the values are exactly the same, except for the corrected ones. The corrected intervals can be perfectly seen, represented by the straight and “unnatural” lines at different angles. Also, noticeably, is the $\theta$ value where the graph ends. Since no cement paste phases were defined in values above 52 $\theta$, from that value up to 70 $\theta$ the diffractogram was completely disregarded at never taken into account.

For the reader information and understanding, the peak seen at around 9 $\theta$ is the main ettringite peak perhaps, or even surely, the most important peak to be viewed throughout this study. If the reader compares it with the peak seen in Figure 11 (page 39), the peak definition and relative height are completely different. In the former it is clearly visible and in the latter barely.

When Rietveld Refinement was done to test this diffractogram, a number of other phases not seen before were present such as thaumasite, gypsum, calcite, etc. The final phases studied will be explained in the next chapter.
3.7.6. Rietveld Analysis

As referred, the Rietveld Analysis was performed using the HighScore Plus Software from Panalytical. This type of software allows the user to prepare the diffractogram obtained from the previous step and study it in order to compute the relative quantity of each existing phase altering a number of different values intrinsic to the crystal in cause, in order to approximate the obtained diagram to the diffractogram obtained through measurement. Then, using the areas beneath the each phase diagram, the software computes the relative quantities.

Usually, to perform the Rietveld analysis, the user must first define a series of parameters as explained before and perform a correct “Search & Match”. In this study this was not done in its true sense. All the Rietveld refinements used the same layout of pre-chosen phases. This allowed a better equity among all the analysis. However, there were some cases when the used pattern did not fit perfectly and had to be replaced by another one of its kind (say one ettringite pattern by another with a slightly different structure data). Also, it happened that the samples retrieved showed some Preferred Orientation problems. This can be seen when the main peak is not the one expected to be or not the same as the reference pattern used. In this case, the preferred planes used values were changed to better suit the diffractogram.

The main identified phases in the samples were:

- **Sand:**
  - Quartz;
  - Microcline;
  - Albite;
  - Muscovite.

- **Cement paste:**
  - C\textsubscript{3}S;
  - C\textsubscript{2}S;
  - C\textsubscript{4}AF;
  - Portlandite;
  - Calcite.

- **Sulfate related phases:**
  - Ettringite;
  - Thaumasite;
  - Gypsum.

Even though these were the identified phases, not all of them were used. The sand phases, except for muscovite, were not inserted in the Rietveld refinement. This was done since the sand phases would inhibit the proper detection of the cement paste phases and possibly hinder the final results. However, it was also decided that the muscovite phase should be left in the Rietveld Refinement but the only parameter that would be defined in it would be the scale factor. In the end, the muscovite phase would be left out of the total quantification. This was done because the main ettringite peak is right next to the muscovite peak and if this was not done, during the refinement the ettringite calculation would “leak” to the peak belonging to the muscovite. The proximity of the muscovite, ettringite and thaumasite peaks is shown in Figure 21, which shows the exact same peak but with the three different phases’ main peaks underlined.
With all the phases correctly defined, the approached procedure to the Rietveld refinement was very similar among all the phases. All the scale factors of all the phases were refined in every step. Then, the unit cell parameters (a, b, c and the correspondent angles between them) would be refined in case the peak from the base structure was not correctly lined with the correspondent peak from the diffractogram. Finally, in case it was required, preferred orientation was also refined, usually for gypsum, ettringite, thaumasite and portlandite. Finally, all the peak shape parameters, that would change how the refined peak would be, were almost never touched. This is because they are extremely hard to refine and if not done correctly will give the user “very” incorrect values. The only parameter refined in this group was “W” parameter (full width at half maximum of the peak) for the gypsum peaks, and only when extremely necessary. Finally, the muscovite phase was disregarded, and the relative quantities calculated without it.

It is very important to refer that the quantities presented in the final results are all referring only to what has been coined has “Crystalized Content of the Cement Paste (CCCP)”. What this means is that, since the XRD equipment does not detect anything that is not crystalized, the quantities hereby shown only refer to crystalized content. And since the sand is completely disregarded, it is only from the Cement Paste.

3.8. GROUNDWATER IMMERSED SAMPLES

3.8.1. CONSIDERATIONS

The previous chapters were all of them referring to samples that were stored in laboratory prepared sulfate solutions. This chapter however dwells in one of the most important aspects of this continued study, which is to bridge the gap between in situ testing and laboratory testing.

In order to do so, 130 l of groundwater were collected from a location in Germany in which a large number of very important constructions is taking place. Unfortunately, this location is also susceptible to sulfate attack and thereby this study began, both to verify the length to which this groundwater may damage concrete and to see if the results gathered from this experiment can be compared to the ones obtained using laboratory sulfate solutions.

Unfortunately, the test methods applied to these samples are, so far, very reduced. This is because the casting was only done at the beginning of this study and the samples cannot yet be removed from the respective solutions to perform XRD measurements, and at the same time obtain results with the same quality as the ones from the ongoing project at IBAC.
3.8.2. Binders Used

So as to study the behavior of the specimens to groundwater exposure, the procedure applied was very similar. For that reason, only two binder types were used to make the required comparisons. These were both remnants of the study referred in the previous points, even though not exactly the same mixtures used in them.

In this second part of the study, the available binders used were:

- CEM I 52,5 N – HS
- CEM I 42,5 N + 40% Fly Ash addition

As it can be seen by the mixes presented above, none of them were the exact ones used in the first part of the study. Unfortunately this was not possible due to the limitations in the available components and to the choice made in what specimens would be used in the previous tests. Nevertheless, this does not bring any drawbacks to the work purpose. The mixes are similar enough and, even more interesting, is the comparison made with the groundwater immersed samples and the ones in 3,000 ppm of $\text{SO}_4^{2-}$ immersed ones, using the two aforementioned binders.

3.8.3. Exposure Temperature

As referred before in this work, these specimens were stored only at 5 ºC environment. This is done to better replicate the ambient conditions felt in underground circumstances and also to make a comparison with the lowest temperature samples used in the previous points. This is intended to see what results the general comparison with different solutions and temperatures used will provide.

3.8.4. Specimen Casting and Keeping

All the conditions are exactly the same as referred in point 3.5, with the temperature and solutions mentioned in the previous points.

3.8.5. Expansion and Dynamic E-Modulus Tests

Both the tests referred here were performed in the exact same conditions as the ones referred in 3.6. Again, the only changes were the temperature and solutions mentioned in the previous points.

3.8.6. Composition Validation Tests and Results

3.8.6.1. Considerations

Concerning the purpose of this study, it was necessary to evaluate the mechanical and physical properties of the cements in hand. These were done as safe-proofing tests, in order to assure the quality of the constituents being used and to guarantee that these properties were not lost during storage time.

The chemical tests, being more specific in nature and requiring a more narrow line of work, were considered to be in conformity with the EN 197-1, as they are commercial cements and, as such, previously certified. In this standard, the maximum values for different properties of the cement, regarding chemical requirements are available.
3.8.6.2. Flexural Strength Test According to EN 196-1:2003

Flexural strength test, performed according to NP EN 196-1:2006 with 3 prisms of 40 mm x 40 mm x 160 mm, to measure the strengths R7, R28 and R91.

The obtained results were:

![Figure 22 - Flexural Strength Test Results According to NP EN 196-1](image)

All the obtained results can be viewed more thoroughly in the available appendix.

3.8.6.3. Compressive Strength Test According to EN 196-1:2003

Compressive strength, according to NP EN 196-1:2006, using the two halves of the ruptured prisms used in flexural strength, 6 half-prisms to measure the strengths R7, R28 and R91.

The obtained results were:

![Figure 23 - Compressive Strength Results According to NP EN 196-1](image)
Taking into account the requirements prescribed in EN 197-1:2012, both the mixes comply to their own reference strength, with their 28 d value over the required strength threshold.

It is important to refer however that at 91 d, one compressive test subject did not yield the required performance and did not comply with what is required in the standard EN 196-1. However, after its elimination the mix was still validated, applying the procedure as the standard refers.

All the obtained results can be viewed more thoroughly in the available appendix.

3.8.6.4. Setting Time Test According to EN 196-3:2006

Setting time test performed according to EN 196-3:2006 to both mixes.

The obtained results were:

<table>
<thead>
<tr>
<th>Setting time test</th>
<th>Difference to $T_0$ (min)</th>
<th>Required (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$</td>
<td>14:16</td>
<td>-</td>
</tr>
<tr>
<td>$V_1$</td>
<td>16:42</td>
<td>146</td>
</tr>
<tr>
<td>$V_2$</td>
<td>17:56</td>
<td>184</td>
</tr>
</tbody>
</table>

Both mixtures achieved the required setting times in conformity to what is required in EN 197-1:2012.

3.8.6.5. Mortar Flow Test According to EN 1015-3:1999

Mortar flow test performed according to EN 1015-3:1999. In this case, no conformity values are given. However, the values obtained cannot deviate more than 10% of their average, as prescribed in the referred standard.

The obtained results were:

<table>
<thead>
<tr>
<th></th>
<th>$D1$ (mm)</th>
<th>$D2$ (mm)</th>
<th>Average (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 52,5 N - HS</td>
<td>215</td>
<td>214</td>
<td>214,5</td>
</tr>
<tr>
<td>CEM I 42,5 N + 40% Fly Ash</td>
<td>205</td>
<td>208</td>
<td>206,5</td>
</tr>
</tbody>
</table>

All the measured values are within the required intervals, complying with the standard requirements.
### 3.9. MATERIALS AND EQUIPMENT USED

#### 3.9.1. MATERIALS

**3.9.1.1. CEM I 42,5 R-HS**

**Table 9 - CEM I 42,5 R-HS constitution**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Unit</th>
<th>Dried</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss on Ignition, air</td>
<td></td>
<td>2.52</td>
</tr>
<tr>
<td>Loss on Ignition, Argon</td>
<td></td>
<td>n. b.</td>
</tr>
<tr>
<td>Complete amount of Sulfur, as SO$_3$</td>
<td></td>
<td>2.96</td>
</tr>
<tr>
<td>Sulfur as SO$_3$, gravimetric</td>
<td></td>
<td>n. b.</td>
</tr>
<tr>
<td>Complete amount of Carbon, as CO$_2$</td>
<td></td>
<td>1.51</td>
</tr>
<tr>
<td>Complete amount of Carbon, as C</td>
<td></td>
<td>0.41</td>
</tr>
<tr>
<td>CO$_2$ by acid hydrolysis</td>
<td></td>
<td>n. b.</td>
</tr>
<tr>
<td>Chloride</td>
<td></td>
<td>0.012</td>
</tr>
<tr>
<td>Insoluble Constituents, HCl, Soda</td>
<td></td>
<td>n. b.</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>M.-%</td>
<td>0.09</td>
</tr>
<tr>
<td>K$_2$O</td>
<td></td>
<td>1.03</td>
</tr>
<tr>
<td>Na$_2$O Equivalent</td>
<td></td>
<td>0.94</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>2.05</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td></td>
<td>3.91</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td></td>
<td>18.65</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td>18.65</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>Fe$_3$O$_3$</td>
<td></td>
<td>6.91</td>
</tr>
<tr>
<td>Chromate</td>
<td>mg/kg</td>
<td>n. b.</td>
</tr>
</tbody>
</table>
### 3.9.1.2. CEM I 52,5 N-HS

#### Table 10 - CEM I 52,5 N-HS constitution

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Unit</th>
<th>Content based on</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dried</td>
</tr>
<tr>
<td>Loss on Ignition, air</td>
<td></td>
<td>0,98</td>
</tr>
<tr>
<td>Loss on Ignition, Argon</td>
<td></td>
<td>n. b.</td>
</tr>
<tr>
<td>Complete amount of Sulfur, as SO₃</td>
<td></td>
<td>4,12</td>
</tr>
<tr>
<td>Sulfur as SO₃, gravimetric</td>
<td></td>
<td>n. b.</td>
</tr>
<tr>
<td>Complete amount of Carbon, as CO₂</td>
<td></td>
<td>0,76</td>
</tr>
<tr>
<td>Complete amount of Carbon, as C</td>
<td></td>
<td>0,21</td>
</tr>
<tr>
<td>CO₂ by acid hydrolysis</td>
<td></td>
<td>n. b.</td>
</tr>
<tr>
<td>Chloride</td>
<td></td>
<td>0,014</td>
</tr>
<tr>
<td>Insoluble Constituents, HCl, Soda</td>
<td></td>
<td>n. b.</td>
</tr>
<tr>
<td>Na₂O</td>
<td>M.-%</td>
<td>0,21</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td>1,10</td>
</tr>
<tr>
<td>Na₂O Equivalent</td>
<td></td>
<td>0,94</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>2,18</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td>3,96</td>
</tr>
<tr>
<td>SiO₂</td>
<td></td>
<td>19,05</td>
</tr>
<tr>
<td>P₂O₅</td>
<td></td>
<td>0,08</td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td>61,39</td>
</tr>
<tr>
<td>TiO₂</td>
<td></td>
<td>0,17</td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td>0,05</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
<td>6,75</td>
</tr>
<tr>
<td>Chromate</td>
<td>mg/kg</td>
<td>n. b.</td>
</tr>
</tbody>
</table>

#### Table 11 - CEM I 52,5 N-HS phases

<table>
<thead>
<tr>
<th>Phases by Bogue</th>
<th>M.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂S</td>
<td>3</td>
</tr>
<tr>
<td>C₃S</td>
<td>68</td>
</tr>
<tr>
<td>C₂F</td>
<td>1</td>
</tr>
<tr>
<td>C₄AF</td>
<td>19</td>
</tr>
</tbody>
</table>
3.9.1.3. CEM I 52,5 N

Table 12 - CEM I 52,5 N constitution

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Unit</th>
<th>Content based on</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dried</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calcined</td>
</tr>
<tr>
<td>Loss on Ignition, air</td>
<td>n. b.</td>
<td>2,00</td>
</tr>
<tr>
<td>Loss on Ignition, Argon</td>
<td>n. b.</td>
<td>---</td>
</tr>
<tr>
<td>Complete amount of Sulfur, as SO₃</td>
<td>n. b.</td>
<td>3,97</td>
</tr>
<tr>
<td>Sulfur as SO₃, gravimetric</td>
<td>n. b.</td>
<td>4,05</td>
</tr>
<tr>
<td>Complete amount of Carbon, as CO₂</td>
<td>n. b.</td>
<td>1,19</td>
</tr>
<tr>
<td>Complete amount of Carbon, as C</td>
<td>n. b.</td>
<td>0,32</td>
</tr>
<tr>
<td>CO₂ by acid hydrolysis</td>
<td>n. b.</td>
<td>---</td>
</tr>
<tr>
<td>Chloride</td>
<td>n. b.</td>
<td>0,022</td>
</tr>
<tr>
<td>Insoluble Constituents, HCl, Soda</td>
<td>n. b.</td>
<td>0,22</td>
</tr>
<tr>
<td>Na₂O</td>
<td>M.-%</td>
<td>0,22</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td>0,73</td>
</tr>
<tr>
<td>Na₂O Equivalent</td>
<td></td>
<td>0,70</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>1,72</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td>5,03</td>
</tr>
<tr>
<td>SiO₂</td>
<td></td>
<td>21,10</td>
</tr>
<tr>
<td>P₂O₅</td>
<td></td>
<td>0,08</td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td>62,56</td>
</tr>
<tr>
<td>TiO₂</td>
<td></td>
<td>0,26</td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td>0,07</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
<td>2,53</td>
</tr>
<tr>
<td>Chromate</td>
<td></td>
<td>mg/kg</td>
</tr>
</tbody>
</table>

Table 13 - CEM I 52,5 N phases

<table>
<thead>
<tr>
<th>Phases by Bouge</th>
<th>M.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂S</td>
<td>18</td>
</tr>
<tr>
<td>C₃S</td>
<td>57</td>
</tr>
<tr>
<td>C₃A</td>
<td>9</td>
</tr>
<tr>
<td>C₃AF</td>
<td>8</td>
</tr>
</tbody>
</table>
### Table 14 - CEM I 42,5 N constitution

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Unit</th>
<th>Content based on</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dried</td>
</tr>
<tr>
<td>Loss on Ignition, air</td>
<td>1,67</td>
<td>---</td>
</tr>
<tr>
<td>Loss on Ignition, Argon</td>
<td>n. b.</td>
<td>---</td>
</tr>
<tr>
<td>Complete amount of Sulfur, as SO3</td>
<td>2,87</td>
<td>2,92</td>
</tr>
<tr>
<td>Sulfur as SO3, gravimetric</td>
<td>n. b.</td>
<td>n. b.</td>
</tr>
<tr>
<td>Complete amount of Carbon, as CO2</td>
<td>1,45</td>
<td>---</td>
</tr>
<tr>
<td>Complete amount of Carbon, as C</td>
<td>0,40</td>
<td>---</td>
</tr>
<tr>
<td>CO2 by acid hydrolysis</td>
<td>n. b.</td>
<td>---</td>
</tr>
<tr>
<td>Chloride</td>
<td>0,033</td>
<td>0,034</td>
</tr>
<tr>
<td>Insoluble Constituents, HCl, Soda</td>
<td>n. b.</td>
<td>n. b.</td>
</tr>
<tr>
<td>Na2O</td>
<td>0,08</td>
<td>0,08</td>
</tr>
<tr>
<td>K2O</td>
<td>0,71</td>
<td>0,73</td>
</tr>
<tr>
<td>Na2O Equivalent</td>
<td>0,55</td>
<td>0,56</td>
</tr>
<tr>
<td>MgO</td>
<td>1,88</td>
<td>1,92</td>
</tr>
<tr>
<td>Al2O3</td>
<td>5,55</td>
<td>5,64</td>
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<td>SiO2</td>
<td>23,05</td>
<td>23,44</td>
</tr>
<tr>
<td>P2O5</td>
<td>0,09</td>
<td>0,09</td>
</tr>
<tr>
<td>CaO</td>
<td>62,08</td>
<td>63,14</td>
</tr>
<tr>
<td>TiO2</td>
<td>0,29</td>
<td>0,29</td>
</tr>
<tr>
<td>MnO</td>
<td>0,08</td>
<td>0,08</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>2,40</td>
<td>2,44</td>
</tr>
<tr>
<td>Chromate</td>
<td>mg/kg</td>
<td>n. b.</td>
</tr>
</tbody>
</table>

### Table 15 - CEM I 42,5 N phases

<table>
<thead>
<tr>
<th>Phases by Bogue</th>
<th>M.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>37,52</td>
</tr>
<tr>
<td>C₃S</td>
<td>38,92</td>
</tr>
<tr>
<td>C₃A</td>
<td>10,82</td>
</tr>
<tr>
<td>C₄AF</td>
<td>7,43</td>
</tr>
</tbody>
</table>
3.9.1.5. Fly Ash

Table 16 - Fly Ash constituents

<table>
<thead>
<tr>
<th>Constituent</th>
<th>unit</th>
<th>Content based on</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dried</td>
</tr>
<tr>
<td>Loss on Ignition, air</td>
<td>2,75</td>
<td>---</td>
</tr>
<tr>
<td>Complete amount of Sulfur, as SO₃</td>
<td>0,65</td>
<td>0,67</td>
</tr>
<tr>
<td>Complete amount of Carbon, as CO₂</td>
<td>6,87</td>
<td>---</td>
</tr>
<tr>
<td>Complete amount of Carbon, as C</td>
<td>1,87</td>
<td>---</td>
</tr>
<tr>
<td>Free lime, as CaO</td>
<td>0,16</td>
<td>0,16</td>
</tr>
<tr>
<td>Chloride</td>
<td>0,009</td>
<td>0,009</td>
</tr>
<tr>
<td>Insoluble Constituents, HCl, one level</td>
<td>n. b.</td>
<td>n. b.</td>
</tr>
<tr>
<td>Insoluble, HCl/KOH</td>
<td>n. b.</td>
<td>n. b.</td>
</tr>
<tr>
<td>Reactive CaO</td>
<td>2,49</td>
<td>2,56</td>
</tr>
<tr>
<td>Reactive SiO₂</td>
<td>n. b.</td>
<td>n. b.</td>
</tr>
<tr>
<td>SiO₂ + Al₂O₃ + Fe₂O₃</td>
<td>87,25</td>
<td>89,71</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1,22</td>
<td>1,26</td>
</tr>
<tr>
<td>K₂O</td>
<td>1,95</td>
<td>2,01</td>
</tr>
<tr>
<td>Na₂O Equivalent</td>
<td>2,51</td>
<td>2,58</td>
</tr>
<tr>
<td>MgO</td>
<td>1,46</td>
<td>1,51</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>18,58</td>
<td>19,10</td>
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<tr>
<td>SiO₂</td>
<td>59,10</td>
<td>60,77</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0,17</td>
<td>0,17</td>
</tr>
<tr>
<td>CaO</td>
<td>2,49</td>
<td>2,56</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0,94</td>
<td>0,97</td>
</tr>
<tr>
<td>MnO</td>
<td>0,06</td>
<td>0,06</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9,57</td>
<td>9,84</td>
</tr>
<tr>
<td>Total</td>
<td>98,95</td>
<td>98,91</td>
</tr>
</tbody>
</table>

3.9.1.6. Groundwater

Table 17 - Carbon contents of groundwater

<table>
<thead>
<tr>
<th></th>
<th>[ mmol/l ]</th>
<th>[ mg/l ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>c(CO₂)</td>
<td>0,0696</td>
<td>3,06</td>
</tr>
<tr>
<td>c(HCO₃⁻)</td>
<td>2,59</td>
<td>158</td>
</tr>
<tr>
<td>c(CO₃²⁻)</td>
<td>0,0168</td>
<td>1,01</td>
</tr>
</tbody>
</table>
3.9.2. EQUIPMENT

- Expansion Test
  - Extensometer Militast BiMi MT0 0113

- Dynamic E-Modulus Test
  - Resometer

- Grinding
  - Prototype grinding apparatus developed at IBAC

- X-Ray Powder Diffraction
  - PANalytical X’Pert Powder
    - X’Celerator detector
    - Copper K-alpha
    - Nickel filter
  - X’Pert HighScore Plus v3.0.5
4

RESULT PRESENTATION

4.1. CONSIDERATIONS

In this chapter only the results obtained from the test procedures referred in chapter 3 will be presented. Their own discussion will be left to the upcoming chapter because it can have very different points of view and different approaches. Therefore, it felt best to separate both topics for ease of understanding.

The results will be presented to what was obtained for each mix, temperature and solution concentration, with this logical level attribution. In each of them, all the obtained results will be presented, for all the tests and no discussion will be made. Only certain notes of importance might be given, if suitable.

The XRD result graphs show in their horizontal axis the values obtained for dust collected in a certain interval. Therefore, the values are in the middle value of that respective interval.

For the samples studied to verify the behaviour when exposed to groundwater, the measurements only took place until 91 d yet. At the delivery date of this work this was the last measurement threshold available. Further measurements will take place until 365 d, as it was done with the other samples.
4.2. CEM I 42,5 R-HS

4.2.1. EXPANSION TEST RESULTS

Figure 24 - Expansion Test Results for CEM I 42,5 R-HS, difference to Ca(OH)$_2$

4.2.2. DYNAMIC E-MODULUS RESULTS

Figure 25 - Dynamic E-Modulus Test Results for CEM I 42,5 R-HS
4.2.3. X-RAY POWDER DIFFRACTION RESULTS

4.2.3.1. Storage Temperature of 20 °C

- Sulfate Solution of 3.000 mg/l

![Graph](image1)

Figure 26 - XRD Results for CEM I 42,5 R-HS; 20 °C; 3.000 ppm

- Sulfate Solution of 30.000 mg/l

![Graph](image2)

Figure 27 - XRD Results for CEM I 42,5 R-HS; 20 °C; 30.000 ppm
4.2.3.2. Storage Temperature of 5 ºC

- Sulfate Solution of 3.000 mg/l

![XRD results for CEM I 42,5 R-HS; 5 ºC; 3.000 ppm](image)

**Figure 28 - XRD results for CEM I 42,5 R-HS; 5 ºC; 3.000 ppm**

4.3. CEM I 52,5 N 40% Fly Ash

4.3.1. Expansion Test Results

![Expansion Test Results for CEM I 52,5 N 40% Fly Ash](image)

**Figure 29 - Expansion Test Results for CEM I 52,5 N 40% Fly Ash**

The values of the specimens kept at 12 ºC were not available from the 180d age.
4.3.2. **Dynamic E-Modulus Results**

![Dynamic E-Modulus Test Results](image)

Figure 30 - Dynamic E-Modulus Test Results for CEM I 52.5 N 40% Fly Ash

The values of the specimens kept at 12 ºC were not available from the 270d age.

4.3.3. **X-Ray Powder Diffraction Results**

4.3.3.1. Storage Temperature of 20 ºC

- Sulfate Solution of 3.000 mg/l

![XRD Results for CEM I 52.5 N 40% Fly Ash](image)

Figure 31 - XRD Results for CEM I 52.5 N 40% Fly Ash; 20 ºC; 3.000 ppm
• Sulfate Solution of 30.000 mg/l

![Figure 32 - XRD Results for CEM I 52.5 N 40% Fly Ash; 20 °C; 30.000 ppm](image)

4.3.3.2. Storage Temperature of 12 °C

• Sulfate Solution of 3.000 mg/l

![Figure 33 - XRD Results for CEM I 52.5 N 40% Fly Ash; 12 °C; 3.000 ppm](image)
4.4. CEM I 52,5 N 29,4% Fly Ash and K-VALUE=0,12

4.4.1. Expansion Test Results

![Figure 34 - Expansion Test Results for CEM I 52,5 N 29,4% Fly Ash K-VALUE=0,12, difference to Ca(OH)₂](image)

4.4.2. Dynamic E-Modulus Results

![Figure 35 - Dynamic E-Modulus Test Results for CEM I 52,5 N 29,4% Fly Ash K-VALUE=0,12](image)
### 4.4.3. X-Ray Powder Diffraction Results

#### 4.4.3.1. Storage Temperature of 20 °C

- Sulfate Solution of 3.000 mg/l

![Figure 36 - XRD Results for CEM I 52,5 N 29,4% Fly Ash K-VALUE=0,12; 20 °C; 3.000 ppm](image1)

- Sulfate Solution of 30.000 mg/l

![Figure 37 - XRD Results for CEM I 52,5 N 29,4% Fly Ash K-VALUE=0,12; 20 °C; 30.000 ppm](image2)
4.4.3.2. Storage Temperature of 5 °C

- Sulfate Solution of 3.000 mg/l

Figure 38 - XRD Results for CEM I 52,5 N 29,4% Fly Ash K-VALUE=0,12; 5 °C; 3.000 ppm

4.5. CEM I 52,5 N 29,4% Fly Ash and K-VALUE=0,6

4.5.1. Expansion Test Results

Figure 39 - Expansion Test Results for CEM I 52,5 N 29,4% Fly Ash K-VALUE=0,6
4.5.2. **DYNAMIC E-MODULUS RESULTS**

![Dynamic E-Modulus Test Results](image)

Figure 40 - Dynamic E-Modulus Test Results for CEM I 52,5 N 29,4% Fly Ash K-VALUE=0,6

4.5.3. **X-RAY POWDER DIFFRACTION RESULTS**

4.5.3.1. Storage Temperature of 20 °C

- Sulfate Solution of 3.000 mg/l

![X-Ray Powder Diffraction Results](image)

Figure 41 - CEM I 52.5 N 29.4% Fly Ash K-VALUE=0.6; 20 °C; 3.000 ppm
• Sulfate Solution of 30,000 mg/l

Figure 42 - XRD Results for CEM I 52,5 N 29,4% Fly Ash K-VALUE=0,6; 20 °C; 30,000 ppm

4.6. CEM I 52,5 N-HS GROUNDWATER TEST

4.6.1. EXPANSION TEST RESULTS

Figure 43 - Expansion Test Results for CEM I 52,5 N-HS; Groundwater Test
4.6.2. **Dynamic E-Modulus Results**

![Dynamic E-Modulus Test Results for CEM I 52.5 N-HS: Groundwater Test](image)

Figure 44 - Dynamic E-Modulus Test Results for CEM I 52.5 N-HS; Groundwater Test

4.7. **CEM I 42,5 N + 40% Fly Ash Groundwater Test**

4.7.1. **Expansion Test Results**

![Expansion Test Results for CEM I 42,5 N 40% Fly Ash; Groundwater Test](image)

Figure 45 - Expansion Test Results for CEM I 42,5 N 40% Fly Ash; Groundwater Test
4.7.2. Dynamic E-Modulus Results

Figure 46 - Dynamic E-Modulus Test Results CEM I 42.5 N 40% Fly Ash; Groundwater Test
5 RESULT ANALYSIS AND DISCUSSION

5.1. XRD IN DEPTH QUANTIFICATION

With the XRD results obtained before the analysis possibilities are enormous, providing a unique opportunity to study sulfate attack in depth and observe its mechanism in action.

Different ways to perform the analysis are possible. It is interesting to see the influence of the different agents in the different exposure situations and then make the comparison to their performance in the expansion and dynamic Elastic Modulus tests, being this the reason why XRD results analysis is done first.

5.1.1. HS BINDERS EXPOSED TO DIFFERENT CONCENTRATION

FIGURE 47 - COMPARISON OF XRD RESULTS BETWEEN HS 20 3K AND HS 20 30K

Using the results obtained from the HS composition, both at 20 °C exposure but at different concentrations (3.000 and 30.000 ppm) it is possible to see some interesting results, mainly portraying gypsum formation, among others.

As it can be seen, it is clearly visible in Figure 47 that at a lower concentration exposure (left) gypsum formation is much lower than on the right. The difference is of more than 10 % of CCCP. Also, in both cases, gypsum forms mostly in the outer layers especially in the high concentration graph. In the higher concentration graph, it is clearly visible that ettringite content reduces noticeably with the increase in gypsum content, with the inverse occurring afterwards.
Ettringite content, albeit some variation, remains somewhat constant throughout the depth of the prism, with a higher content in the outer layer and small and slow decrease to the inside.

Also, it is interesting to verify that portlandite (CH) exists and rises in quantity when gypsum quantity decreases and the further away from the outer layer, the higher portlandite quantity is observed.

Beginning with the ettringite formation analysis, it is important to remember that both binders are done with HS cement, meaning a low C₃A content. It is therefore expected that in both of them the ettringite formation is reduced.

However, with the gypsum type of attack there are other influences. As referred, gypsum forms by the reaction between sulfates and CH in the cement paste. This can clearly be seen in the previous graphs where, as said, gypsum exists where no, or little, portlandite can be found, revealing the veracity of the previous assumption. The CH in the outer layers has been replaced by gypsum. This has severe consequences in the mortar resistance, as seen in the dynamic elastic modulus results, where HS binders lower the resistance severely when exposed to high concentration of sulfates. This reveals that, at high concentrations the attack is governed by gypsum formation and not ettringite formation.

This can be said because another aspect is the constant quantity of ettringite. One might suppose it would reduce with depth or have a lower value. Taking into account the expansion values it can be said that HS cements have a reduced expansion when compared to fly ash, as seen in Figure 48, this proves true, since most of the expansion should be caused by ettringite. However, ettringite is neither low nor reduces.

![Figure 48 - Expansion comparison between the different binders. FA k0,6 is unavailable and FA40 was submitted to 12 ºC storage and not 5 ºC as the others](image)

Relating both facts, an explanation might be put forward. The HS cement particularity is only that it has a low C₃A content, so it will still have a high C₅S content, producing high amounts of CH and C-S-H in hydration. When it is exposed to sulfates in high concentration, the governing process is gypsum formation, leading to loss of strength and general mechanical properties. In turn, this leads to excessive cracking of the mortar by the formation of the ettringite. This can clearly be seen in Figure 49, where the mortar exposed to higher concentration cracked immensely. This provides the perfect “highway” for sulfate penetration, allowing them to enter the mortar through these cracked areas and form ettringite in a constant fashion further inside with the available C₃A, which is low, so it will run out sooner than the available sulfates, which are less the further the depth.
With SEM imagery, the gypsum content is also very noticeable along with its decrease and the ettringite being more in depth.

In the outer layer, gypsum is clearly seen in the cracks and formed along the borders of the visible pore. The cracks themselves are hugely important, validating what was previously said. On the right picture however, which is even more magnified, no gypsum can be identified. However, large spots of ettringite exist.

5.1.2. COMPARISON BETWEEN FA AND HS BINDERS

As discussed previously, ettringite is seen to form, in a HS binder, with the same intensity along all the depth of the sample, with the C\textsubscript{3}A availability as an important factor. It is important to observe now what impact does a FA substitution have with this factor.
Looking now to Figure 51, the first thing that stands out is the discrepancy in the ettringite amount of both samples. The FA40 binder, at its peak, counts at 45% of the crystalline content of the cement paste as being ettringite whereas the HS only goes to around 27%.

Interesting is also the small increase in gypsum quantity when the decrease in ettringite occurs and the general low gypsum quantity observed throughout the sample when compared to the HS binder. In this case however, portlandite quantity rises along with gypsum but with the decrease in ettringite.

Taking into account what was said before and comparing now both binders it is possible to put forward explanations for this.

Even though FA40 has a fly ash substitution of 40%, its C₃A content is still high enough to originate high amounts of ettringite when exposed to sulfates. The HS cement however, and as explained before, has reduced C₃A and therefore less ettringite. The result is clearly seen in the expansion results of Figure 48 where FA has much higher rate and final value of expansion, clearly relating the ettringite content and the experienced expansion by the binder.

Concerning the gypsum formation being higher in the HS binder, it is known that even though fly ash substitution also produces C-S-H, it requires CH to produce it, which will react with the silicates from the fly ash to originate C-S-H, as explained in 2.3.3. Then, since it consumes CH, there will be less CH available to originate gypsum when the sulfate ions enter in contact with the mortar, the result being less gypsum formation along all the depth of the sample. Instead, in the HS binder, CH is produced in the cement hydration and none of it is consumed or lost until sulfate ions penetrate. When they do, especially in high amounts, gypsum is formed extensively, until the conditions explained before, in 2.2.2, are met.
As it can be seen in Figure 52, ettringite is clearly present whereas in the HS cement sample seen before almost no ettringite existed. Now the ettringite needles are seen even in the pore as well as in the cement paste in high quantity.

It is interesting to know that, even though much more ettringite is formed and more expansion measured, the FA40 prisms were not nearly as damaged as the HS ones, as seen in Figure 53.

Even though there are some pores, especially in FA40 20 30k, no cracking can be seen as a result of expansion.

This is because since fly ash consumes CH to produce C-S-H, the prisms are able to maintain more of their respective mechanical properties when submitted to sulfate attack since less CH is consumed and more C-S-H is maintained. Also, C-S-H is the main contributor to the resistance with CH being second. So, more of the main cementitious phase is produced and less of the secondary one is consumed in sulfate attack. Therefore, the prisms can maintain better their mechanical resistance.
5.1.3. COMPARISON BETWEEN THE FA BINDERS

Studying the information in Figure 54, it shows the variation of both ettringite and portlandite with the three fly ash binders used and with depth.

Looking first at the portlandite variation, it is clearly seen that the behavior among the three binders is similar in trend, however they vary in portlandite maximum quantity, at the depth where the first percentage of portlandite is measured and the rate of percentage increase, being FA k0,12 the highest one, followed by FA k0,60 and finally FA40.

On the right graph, the ettringite variation in depth is shown. This time the trend of both FA k0,12 and FA k0,60 is similar but FA40 follows a different line. FA40 is also the binder with most ettringite along all its depth, followed by FA k0,60 and finally FA k0,12. Of interest is also the decline in all of them in ettringite content as the attack progresses further inside the prism.

In this case, the influence of the different w/c ratios is clearly seen, which is expressed itself in the concrete’s density after its curing. This will allow for a more impermeable concrete, challenging one of the necessary conditions put forward by Collepardi, 2003 for successful sulfate attack.

The portlandite clearly is kept until shallower depths in the prism with lower w/c ratio, being followed by the second lower w/c ratio and then the third. Not only that but also the percentage increase and maximum quantity follow this trend. This clearly represents until what depth sulfates are able to reach in high concentration and where the attack penetrated into.

Figure 55 - EDX analysis on the cement paste of FA k0,12 in the inner layers
Looking at Figure 55, the picture shows a very close and uniform paste in the inner layers of the specimen, revealing its integrity and that sulfates have not damaged it severely. Also, in the quantification, it is possible to see the high amounts of both Ca and Si and almost no S, also supporting the idea that portlandite has not been leached or transformed and sulfates have no yet entered that area in suitable quantities.

Regarding the ettringite graph, the information is also the same. The lower the w/c ratio, the less ettringite was formed in the prism. Again representing how far the attack penetrated and how intensely.

It is very interesting to see that all of the FA show a decrease in ettringite content, as opposed to the HS binders, albeit higher quantities. The higher quantities have been explained previously, as the available C\textsubscript{3}A is higher in FA binders than in HS. However, the decrease shows the ability of FA to create a denser concrete and contradict sulfate penetration, along with the w/c ratio. Were this not the case, C\textsubscript{3}A content would be constant through the sample, as in HS, and with higher quantities than this one.

### 5.1.4. Thaumasite Formation

![Thaumasite formation in depth for HS, FA40 and FA k0,12, at the higher and lower temperature available for 3.000 ppm solution](image)

Looking at Figure 56, it is possible to see the thaumasite quantity for the referred binders. It is usually thought of that thaumasite only forms, or mostly forms, at lower temperatures. However, it is clearly seen here that thaumasite exists for all the samples and at high and low temperatures. Also, it is fairly constant throughout the depth of all the prisms. The ones with the higher values of thaumasite, in the inner layer are FA40 20 and FA40 12, whereas samples at lower temperatures have less thaumasite.
Again, it is interesting to notice that the binder with higher w/c ratio is the most affected. Also, it is the higher fly ash substitution, perhaps indicating a more content of C-S-H available to form thaumasite, by the hydration of both cement and fly ash.

Nevertheless, the difference is not very large and all of the samples present a fair amount of thaumasite formed.

5.2. Expansion

Expansion measurement is one of the most used indicators for sulfate attack and this work was no different.

As postulated before, the used binders could be considered sulfate resistant, concerning expansion, if:

- At 91 d the expansion measured is not above 0.5 mm/m or;
- If at 180 d is not above 0.8 mm/m.

For high temperature and low concentration, all the binders in the study verified these two conditions, as seen in Figure 57.

All the binders showed similar final expansion values, even though not similar rates. It is interesting to see that the rate of expansion is lower it the w/c ratio inherent to each one, denoting lower sulfate attack with lower w/c ratio.
As put forward before, the FA samples have larger expansions and at higher rates than the HS samples. This shows the effect of the C3A content in the control of expansion. The only case when this is not true is when the sulfate concentration is very high, at 30,000 ppm, clearly revealing the importance of w/c ratio in maintaining the sulfates outside the sample. Otherwise, with the higher availability of C3A, the more ettringite is formed and higher expansions are predicted.

It is also clearly shown that higher concentrations and lower temperatures have a deleterious effect in sulfate attack. These will create the worst conditions for concrete. It is possible to see that a high temperature/low concentration combination posed no problems for the binders to handle – all of them stayed inside the predetermined limits.

On the other two however, only FA k0,12 managed to maintain expansion inside the required limits in both cases. HS binder did it only for the case of lower concentrations. Once again it is shown the importance of the w/c ratio or a dense and impermeable concrete.

5.3. DYNAMIC ELASTIC MODULUS

Figure 59 - Expansion for all binders exposed to 3.000 ppm solution at 5 ºC, except FA40 which is at 12 ºC

Figure 60 - Dynamic Elastic Modulus evolution for exposures of 5 ºC and 3.000 ppm and 20 ºC and 30.000 ppm
For the high temperature and low concentration exposure, none of the binders showed any problem regarding dynamic elastic modulus variation, with their respective values increasing throughout the length of the experiment.

Concerning the other two exposure regimes, it is possible to see that the dynamic elastic modulus has decreased constantly for all the specimens.

The figure above compares different temperatures and different concentrations. However, even though the left graph is at lower temperature, it is the higher concentration that poses more problems regarding the loss of dynamic elastic modulus. This immediately exposes that the governing factor is gypsum formation and its consumption of CH, reducing the specimen’s mechanic properties. As referred before, the higher the concentration the more severe is the attack by gypsum formation.

This is supported also by comparing the behavior of dynamic elastic modulus of the binders in each case. In the lower concentration one, the HS binder has a better behavior than the FA40, even though it is exposed to a much lower temperature. On the other case these positions inverse themselves. Here it can be deduced that, since at higher concentrations the gypsum attack is more important, it will be the binder with the least available CH that will have a better performance. This is the case, even though FA40 has a higher w/c ratio.

Concerning w/c, again it is noticeable that the best performing mix is the denser one. Nevertheless, it is interesting to notice that FA k0.6 performed worse than FA40, despite the fact that it has a lower w/c ratio. This represents that, at some point, it is more important to have enough fly ash substitution, to consume CH before sulfate attack, than a lower w/c ratio or, in other words, for the same w/c ratio, a higher fly ash substitution is advisable. Obviously, with extremely low w/c ratios, the concrete has a low permeability and it suitably defended.

### 5.4. Expansion for Groundwater Exposure

![Figure 61 - Groundwater and sulfate solution exposure expansion results at 5 ºC, for HS GW and FA GW](image)

Concerning the tests performed in groundwater, in this case the expansion results in Figure 61, it is possible to see that for the HS GW binder there was barely any noticeable difference between the solutions. Inclusively, groundwater exposure generated more expansion than the higher sulphate concentration solution.

On the other hand, for the FA GW binder, the sulphate solution originated extremely high expansions, already surpassing the 0.5 mm/m limit at 91 d imposed for sulfate resistance labeling. For the
groundwater exposure, the expansion was more contained but still higher than the one observed in the HS GW binder.

The reasons for the variation in expansion remain the same as before, concerning C₃A content and available sulfates.

The performance between both is comparable with groundwater immersed samples showing variation in their behavior, such as the sulfate immersed ones.

5.5. Dynamic Elastic Modulus for Groundwater Exposure

![Figure 62 - Groundwater and sulfate solution exposure Dynamic Elastic Modulus results at 5 ºC, for HS GW and FA GW](image)

Regarding dynamic elastic modulus, until 91 d of age not much variation has been observed.

For the HS GW binder, in both cases the behavior is the same, as well as its values.

For the FA GW, at 91 d of age a discrepancy can be seen with groundwater exposure samples maintaining their elastic modulus whereas sulfate solution ones already experience a decrease. Again, the influence of concentration can mainly be felt in loss of mechanical properties.
CONCLUSIONS

6.1. CONSIDERATIONS

By the end of this work, it is clear that sulfate attack by itself can be extremely deleterious. Even with a solution with a moderate concentration of 3.000 ppm of \( \text{SO}_4^{2-} \), the exposed binders quickly showed some level of attack and deterioration. Potentially, if there were any other types of attack involved, most of them would be completely ruined.

The attack mechanism of the studied samples seems to follow the one proposed by Santhanam et al., 2002a. In this scenario, given the conditions for sulfate attack to occur, the sulfates start by penetrating the concrete and the reactions to form ettringite begin. At the same time, already some gypsum formation occurs. With enough time, ettringite forms and expands and, if there is not enough space for it, pressure in concrete increases and expansion phenomenon start. Afterwards, since the bulk of the concrete is unaffected, impeded expansion phenomenon occurs leading to the formation of cracks, which will promote sulfate attack further inside. With this, ettringite can form now closer to the center while behind new available hydration products react with sulfates to form gypsum, weakening even more the concrete. This process repeats itself further in, creating the “layered” pattern visible in XRD results.

However, many variations can occur.

Concerning ettringite formation, it is clear that the important factor is the availability of reactive alumina. When this is removed, the formation of ettringite is reduced, leading to less expansion of the samples. Apparently, given enough alumina to react, sulfates will form ettringite preferably than gypsum. This makes ettringite the central point of sulfate attack, as it was before. However, it surely cannot be considered the only one. From the results, the advisable way to diminish this effect is only by making sure that the amount of alumina available is reduced in order to avoid ettringite formation and subsequent expansion. This is currently done with sulfate-resistant cements and, concerning ettringite and expansion, the method seems to work well enough.

It appears that at high concentrations, gypsum type of attack governs ESA. That is not to mean that no ettringite is formed but that the damage is worse due to the loss of strength than expansion. Then again, if there is great loss of strength and then expansion, this will mean wider and deeper cracks, worsening the attack. Sulfate attack does not even need other types of attack to worsen itself. However, gypsum is formed also at lower concentrations and has a noticeable effect in concrete mechanical properties loss in that case. Using the given examples, it is clear that any fly ash substitution improves the resistance to this type of attack. The CH consumption in hydration helps to lessen the gypsum formation and all the inherent strength losses to CH depletion. This fact allied to
expansion by ettringite, even though less than fly ash binders, can explain why the HS cements had worse performance in sulfate attack at high concentrations, and similar at lower concentrations.

Thaumasite formation was not very representative in this study. All of the binders showed similar trends and values, indicating that the optimal conditions were not achieved. This might be explained to the low availability of Carbon, since the other two conditions for thaumasite formation, sulfates and low temperature were available. Nevertheless, it is interesting to notice that thaumasite formed, at the same extent, in high and low temperatures. Here it is where there should be noticed the difference. However, as advanced before, perhaps if there was enough carbon, lower temperatures would promote thaumasite formation and perhaps the attack would have been different. Nevertheless, the formation and high temperatures cannot be dismissed.

It also became clear that higher concentrations and lower temperatures worsen the effect of sulfate attack, both in expansion and loss of elastic modulus. The rate and severity of the attack were noticeable in both cases.

What stands out in this work is the effect of concrete impermeability in the success of the attack. This position is greatly defended by Neville, 2004 and its effect can clearly be seen throughout the experiment. The binder with less w/c<sub>eq</sub> ratio was constantly the best performing one and, generally speaking, the higher the w/c<sub>eq</sub> ratio the worse the attack became. However, a rule cannot be made out of this because, at some point, other factors can come into play.

Finally, it can be said that, until the date of the occurring experiment, groundwater seemed to be a successful medium to study sulfate attack, in the conditions referred. Even though it was being tried along a sulfate solution of twice the concentration, groundwater already showed noticeable effects and attack at some rate. It is important to refer that 91 d is still an early age to draw conclusions and that more time is needed for the experiment to run.

So, to finalize, it can be said that ettringite controls the expansion of concrete. In order to reduce it, HS cements seem to work, but they only solve this problem, suffering less expansion, but deteriorating greatly due to gypsum formation. Inevitably they crack and break. When a fly ash substitution is used, there is less availability of CH and less gypsum is formed, leading to minor loss of strength. However, more expansion occurs, but the samples do not deteriorate as much and crack less. This, along with the natural denser concrete obtained with pozzolana, allows for a better defense, in the beginning and throughout its life. The path of denser, closed, compacted and well performed concrete, here translated as w/c ratios, seems the right one to take. This can be achieved in a number of ways and considering it is the first step taken in any concrete work, if it is not done properly than many problems will arise, and not only concerning sulfate attack.

As Neville, 1995 refers: “… competently used, concrete is a very successful construction material but, in the literal sense of the word, concrete is not foolproof.”.

6.2. FUTURE AND RECOMMENDATIONS

With all the obtained information along this work, in literature as well as experimental, it can be seen that sulfate attack begins to take shape and possibly is going in the right direction to be better understood.

Nevertheless, much work can still be done. It is of utmost importance to start and keep working towards bridging the gap between laboratory and in situ studies. It is apparent that using a solution of 30,000 ppm does not bring any real advantages for the study of the attack besides accelerating it. More
moderate solutions, like the 3.000 ppm one can be used in conjunction with different temperature exposures.

Also, the further study of groundwater as a suitable solution should be looked into. This gives innumerous opportunities to study ESA in another dimension not used before by removing reducing artificality and increasing reality of the study. In this case, groundwater must be properly handled and kept in order to not lose its properties. The future results provided by the experiment that began with this work will perhaps allow the drawing of better conclusions and afterwards better steps can be taken.

The use of flat prisms seems suitable for sulfate attack and perhaps other external origin attacks. They provide good and reliable data which, along with ease of handling and reduced testing time, make them very suitable for experiments. It should be considered the possibility of covering the tops, to improve even more the reliability.

Concerning XRD, the results were satisfactory, providing very reliable data. Nevertheless, the sand inside proved to be very difficult to handle. Perhaps, while dealing with cementitious materials themselves, cement paste should be used in detriment of mortars. This way, only hydration and sulfate attack phases would be “visible” in the data, and a more reliable quantification could be done.

As for the method devised in the work before, perhaps it could be applied more frequently into future works to allow the observance of the phenomena inside the prisms to better understand the mechanism of attack and not only observe the physical effects. Even though these are the result and what matters concerning engineering, the causes behind it should be brought to light to better understand it and increase concrete durability.
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STANDARDS

EN 196-1:2006 - Methods of testing cement, Part 1: Determination of strength
EN 196-3:2006 - Methods of testing cement, Part 3: Determination of setting times and soundness
EN 197-1:2012 - Cement, Part 1: Compositions, specifications and conformity criteria for common cements
EN 1015-3:1999 - Methods of test for mortar for masonry, Part 3: Determination of consistence of fresh mortar (by flow table)
EN 14146:2006 - Natural Stone Test Methods - Determination of the dynamic modulus of elasticity (by measuring the fundamental resonance frequency)
Sulfate Attack on Cementitious Materials
Sulfate Attack on Cementitious Materials

![X-ray diffraction patterns for different sulfate attack stages](image)

- **Stage 1**: Low intensity peaks indicating early stages of sulfate attack.
- **Stage 2**: Increased intensity and sharp peaks showing progress in the attack.
- **Stage 3**: Further enhancement in peak intensity and sharpness, indicating severe attack.

2\(\theta\) (°) vs. Intensity (counts) for each stage.
Sulfate Attack on Cementitious Materials

![Graph 1]

![Graph 2]

![Graph 3]

![Graph 4]
Sulfate Attack on Cementitious Materials

Intensity (counts)

2Theta (°)

Intensity (counts)

2Theta (°)

Intensity (counts)

2Theta (°)

Intensity (counts)

2Theta (°)
Sulfate Attack on Cementitious Materials

The figure shows X-ray diffraction (XRD) patterns for different samples. The XRD patterns are characterized by peaks at specific 2θ (degree) values, which correspond to the crystallographic structures present in the materials. The intensity of the peaks is measured in counts, indicating the strength of the diffraction signal.

The top pattern shows a sample with a significant peak at 2θ = 25°, indicating the presence of a specific crystalline phase. The middle pattern displays a more complex set of peaks, suggesting a mixture of phases. The bottom pattern exhibits a simpler pattern with fewer distinct peaks, possibly indicating a less crystalline or more amorphous material.

These patterns are crucial for identifying the mineralogy and phase composition of cementitious materials, which is essential in understanding their long-term stability and durability in sulfate attack conditions.
Sulfate Attack on Cementitious Materials

Intensity (counts)

2Θ (°)

Intensity (counts)

2Θ (°)

Intensity (counts)

2Θ (°)
Sulfate Attack on Cementitious Materials

![Graph 1](image1)

![Graph 2](image2)
Sulfate Attack on Cementitious Materials

![Graph 1: Intensity (counts) vs. 2Theta (°).](image1)

![Graph 2: Intensity (counts) vs. 2Theta (°).](image2)

![Graph 3: Intensity (counts) vs. 2Theta (°).](image3)

![Graph 4: Intensity (counts) vs. 2Theta (°).](image4)
Sulfate Attack on Cementitious Materials

Intensity (counts)

2Theta (°)

Intensity (counts)

2Theta (°)

Intensity (counts)

2Theta (°)

Intensity (counts)

2Theta (°)
Sulfate Attack on Cementitious Materials

![X-ray diffraction patterns](image)

*Note: Images depict X-ray diffraction patterns with intensity on the y-axis and 2θ on the x-axis. The patterns show distinct peaks indicating the presence of specific crystalline structures.*