Chemical resistance of lime-based grouts for masonry strengthening

Manuk Aghajanyan

Final dissertation report submitted to

Escola Superior de Tecnologia e Gestão

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To obtain the Master Degree in

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Professor Ana Maria Alves Queiroz Silva

Professor Eduarda Cristina Pires Luso

Professor Marine Petrosyan

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Abstract

The stone masonry walls are present in many buildings and historical monuments, with undeniable asset value, but also in old buildings housing both in Portugal and in Europe. Most of these buildings in masonry are in certain cases in a high state of degradation needing urgent intervention. This requires the identification of deficiencies and the application of appropriate intervention techniques. One of the possible techniques for structural consolidation works of stone masonry walls is the injection of fluid mortars currently called grouts. The choice of grouts is very important with regard in particular to their chemical and physical properties. In this study, carried out under the Master of Chemical Engineering, two types of lime-based grouts were used, in order to evaluate and compare their chemical resistance due to the crystallization of soluble salts. One of the grouts is a pre-dosed blend commercially available, *Mape-Antique I* from company *Mapei* (CA), and the second grout is a mixture prepared in the laboratory (LB), comprising metakaolin, cement, hydrated lime, water and superplasticizer. With the purpose of evaluating the action of sulphates on these grouts, a series of samples underwent several wetting-drying cycles using two different temperatures, 20 °C and 50 °C. During the experiment it was determined the change of weight and compressive strength in the analyzed grouts, as well as the sulphate ion concentration and pH of the solution in which the samples were dipped. The commercial grout (CA) apparently has a greater chemical resistance to sulphates. However grout LB showed to have positive results in some parameters.

Keywords: Lime-based grout, chemical resistance, sulphate attack, masonry structure.

Resumo

As paredes de alvenaria de pedra estão presentes em muitos edifícios e monumentos históricos, com valor patrimonial inegável, mas também em edifícios antigos de habitação de construção antigos, tanto em Portugal como na Europa. Grande parte destas edificações em alvenaria encontra-se, em certos casos, num elevado estado de degradação pelo que necessitam de intervenção urgente. Isto requer a identificação das deficiências e a aplicação de técnicas de intervenção apropriadas. Uma das técnicas possíveis para trabalhos de consolidação estrutural das paredes de alvenaria de pedra é a injeção de argamassas fluidas denominadas correntemente por caldas. A escolha destas caldas é muito importante no que respeita, em particular, às suas propriedades químicas e físicas. Neste estudo, realizado no âmbito do Mestrado em Engenharia Química, foram utilizados dois tipos de caldas à base de cal, com a finalidade de comparar e avaliar a sua resistência química face à cristalização de sais solúveis. Uma das caldas é uma mistura pré-doseada comercialmente disponível, a *Mape-Antique I* da empresa *Mapei* (CA) e a segunda calda é uma mistura preparada em laboratório (LB), composta por metacaulino, cimento, cal hidratada, água e um superplastificante. Com o proposto de avaliar a ação dos sulfatos sobre estas caldas, submeteram-se uma série de provetes a ciclos molhagem-secagem usando duas temperaturas diferentes, 20 °C e 50 °C. Durante a experiência determinou-se a variação do peso e da resistência à compressão das caldas analisadas, assim como a concentração de ião sulfato e pH da solução onde foram mergulhadas as amostras. A calda comercial (CA) apresenta aparentemente uma resistência química aos sulfatos superior, no entanto a calda LB mostrou ter, em alguns parâmetros, resultados positivos.

Palavras – chave: caldas à base de cal, resistência química, ataque de ião sulfato, alvenaria de pedra antiga.

Ամփոփում

Ժամանակի ընթացում ցեմենտաքարային կառույցների վրա, արտաքին միջավայրի ազդեցությունից առաջացած վնասվածքները վերականգնելու համար օգտագործվում են ցեմենտային խառնուրդներ: Ցեմենտային խառնուրդների համար մեծ կարևորություն ունեն թե քիմիական, և թե ֆիզիկական հատկությունները: Քիմիական կայունությունը համեմատելու և գնահատելու համար ընտրվեցին երկու տեսակի ցեմենտային խառնուրդներ, նրանցից մեկը շուկայում առկա *Mapei, Mape Antique I* է, իսկ մյուսը՝ լաբորատորական հետազոտությունների արդյունքում ստացված խառնուրդը: Փորձի ընթացքում օգտագործվեց իրար հաջորդող խոնավացման և չորացման ցիկլային մեթոդը: Նմուշների խոնավացման համար ընտրվեց նատրիումի սուլֆատի 5 տոկոսանոց լուծույթ, իսկ չորացման համար մինչև 6-րդ ցիկլը իրականացվեց 20 °C-ում, այնուհետև 6-րդ ցիկլից սկսած նմուշների կեսը չորացվեցին 20 °C ջերմաստիճանում, իսկ մյուս կեսը 50 °C-ում: Փորձի ընթացում հետազոտվեցին նմուշների զանգվածները և սեղմման ամրության սահմանը, իսկ նատրիումի սուլֆատային լուծույթի՝ որը օգտագործվել էր նմուշների խոնավեցման համար, սուլֆատի քանակի և ջրածնային ցուցիչի (pH) փոփոխությունները: Ստացված արդյունքներից հետևում է, որ լաբորատորիայում ստացված ցեմենտային խառնուրդը քիմիապես կայուն չէր ի շնորհիվ ջուր և կապակցող նյութ արժեքի բարձր հարաբերակցության և նրանում առկա ալյումինի օքսիդի բարձր չափաբաժնով:

Առանցքային բառեր: Կրային խառնուրդներ, քիմիական կայունություն, սուլֆատային ազդեցություն, կրա-ցեմենտային շաղախի ամրացում

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Nomenclature

A-Surface area (cm^2)

Abs-Absorbance

AFm- Alumina, ferric oxide, mono-sulphate

CA –Commercially available grout

C_3A- Tricalcium aluminate

C_4AF- Tetracalcium alumina ferrite

CH-Calcium Hydroxide

CL- Calcium Lime

Conc-Concentration

C-S-H-Calcium Silicate Hydrate

C_3S- Tricalcium aluminate

C_2S- Dicalcium silicate

CV- Coefficient of variation

DL- Dolomitic Lime

F- Applied force (kN)

H-Height (mm)

H^+- Hydrogen ion concentration

HL- Hydraulic Lime

HRM- High reactivity metakaolin

L-Length (mm)

LB- Laboratory formulation grout

LOI- Loss on ignition

M-Weight (g)

Max-Maximum

MK-Metakaolin

NH- sodium hydroxide

NHL- Natural Hydraulic Lime

OH^-- Hydroxide ion concentration

s-Standard deviation

SCMs- Supplementary cementitious materials

SP-Superplasticizer

T-Specimen is tested

V-Volume (cm^3)

W-Width (mm)

W/B-Water-binder

W/C-Water-cement ratio

f- Compressive strength (repeat)

ρ -Bulk density (g/cm^3)

$\overline{X}$ -Mean

x- Specimen is absent

% w/w-Mass fraction

↓ - Precipitate

1. Chapter 1 - Introduction

Because of environmental conditions a lot of mechanical and chemical processes befall on buildings during years. To repair ancient masonry structures, the method of grouting is being used. Different techniques for repair and strengthening of stone masonry and brick walls were used in the seventies in Italy after earthquakes. Nowadays, one of the most famous technique is the injection grouting. For grouting it is important to choose durable grout. Based on these attributes the chemical resistance of lime-based grouts may also be affected due to environment factors (including rainwater, temperature, humidity). Within this study two types of grout have been chosen to evaluate their resistance to sulphates (Na_2SO_4) attack and then they are compared to choose the most suitable repair grout. Sodium sulphate is generally regarded as one of the most destructive salts in the weathering of historical objects. In this case water soluble salts can be accumulated in porous buildings materials and cause degradation connected with salt crystallization. The crystallization can either be induced by drying and/or cooling of a salt solution in a porous material [1]. In order to determine the chemical strength of both grouts the wetting-drying weathering process was used. A total of forty-two grout specimens were prepared and all the samples were initially dried to constant mass at 105 °C for 18 hours. The initial weight, dimensions and surface appearance of the specimens were recorded and a compressive test was done. Changes in weights of the specimens were measured every day during the experiment. Because of the two types of grouts, sodium sulphate solution was prepared and it was filled into two different containers. PH and sulphate concentration of both solutions were also measured every day until the 12^{th} cycle, then after started 12^{th} cycle each tree days taking 20 mL from both solutions (CA, LB), totally 40 samples (19 from grout CA and 21 from grout LB). After 13^{th}, 20^{th}, 36^{th} wet/dry cycles, the specimens were tested to determine the compressive strength of the grouts and dimensions changes. In durability test all grout specimens during the first six days were immersed in 5% sodium sulphate solution for 6 hours then were dried at 20 °C. Then the two types of grouts (CA, LB) were divided into two parts for drying at 20 °C and 50 °C

during the remaining 30 days without controlling the pH. It should be noted that it is very important to do everything in time without missing cycles and to make sure that specimens are completely immersed in the sulphate solution.

1.1. Motivations of the thesis

It is known that during ageing process of masonry structure damages occur on it. This phenomenon has been observed on historic as well as on modern buildings. The most important factors influencing degradation and damage to masonry are related to environment, used materials, design of building and its maintenance. To solve this problem, the repairing method is being used. It is possible to repair by using injection technique and grout. The main problem concerning the reparation of buildings with grout is the choice of grout materials which should be compatible with original materials. Grouting is a well-known technique, which allows to preserve rheological, physical, chemical and mechanical properties. All these things and plus the wish to work with cementitious substances were the primary reasons to start this subject and compare two types of grouts in order to decide which one of them is the more chemically resistance.

1.2. Objectives of the thesis

The purpose of this investigation is to evaluate the resistance of lime-based grouts to sodium sulphate attack, using wetting-drying cycles (totally 36 cycles) in order to determine the chemical strength, which is important and it should be known before starting the grouting of buildings. To know the durability of a grout is very important for repairing structures, because grout should be resistant to environment factors. To evaluate the durability of grout materials, information is required about possible damages during ageing process and possible changes in its functional properties. The resistance of grout samples to sulphate attack is being defined by surface area loss, weight loss, dimension changes and compressive strength reduction. In this study only the external sodium sulphate attack to two types of prepared grouts is evaluated. One of them is a commercially available grout from Mapei (*Mape-Antique 1*) and the second

one is a laboratory formulation containing 35% of hydrated lime, 30% of cement and 35% of metakaolin mixed with a plasticizer. The objective is to compare these two grouts using wetting-drying method and to understand which one has the best chemical resistance.

1.3. Synopsis of the thesis

In order to answer the defined objectives, the thesis is organised in five chapters.

In the first chapter, Chapter 1 – introduction, the motivation behind the study and the objectives of this study are briefly presented.

In the second chapter, the materials used in the study as well as a bibliographic review related to this study is presented.

In the third chapter, the research strategy materials, methodology and analysis parameters adopted are described.

In the fourth chapter, shows results elaborates upon the main findings of this study.

In the fifth chapter, the main conclusions of the study are presented.

2. Chapter 2 - State-of-the-Art

2.1. Grouting as a repair and conservation method of ancient masonry structures

Masonry structures are famous since ancient centuries. Masonry walls are composite structures defined as macroscopic combinations of two or more distinct materials having a finite interface between them. Formerly in masonry walls basically were used stones, granites etc. with or without lime based bonding mortars. Nowadays, the more common materials are bricks, blocks and cementitious binders as bonding mortars (Figure 1). During years it befalls lot of mechanical and chemical processes on buildings. To repair of ancient masonry structures, the method of grouting is being used. There are different techniques for the repair and strengthening of stone masonry and brick walls. These techniques have been used yet in the seventies in Italy after quakes. Grouting is a technique which is being used to fill voids and re-establish the continuity of the constructional components of a disintegrated masonry. The main problem of the technique depends on small sizes of voids in masonry or the shortage of communication in case of diffused cracks and the difficulty of the grout to penetrate into thin cracks. The repair and strengthening with grouting gives the best result because it does not change morphology and load bearing system. These are the objectives of grouting technique [2].

- Reconstitute the structural continuity of the masonry;
- Increase the masonry homogeneity, filling voids, if existing;
- Improve the masonry mechanical properties, (increase the masonry strength);
- Fill cracks in wall and other masonry structural elements (vaults, domes, etc…)

Figure 1-Masonry walls constructed with stones and bricks.

The grout is a bulked fluid material that can be injected behind plaster, wall paintings, or mosaics to fill cracks and voids and re-establish adhesion between delaminated layers upon setting. Grout is a construction material used to embed rebars in masonry walls, connect sections of pre-cast concrete, fill voids, and seal joints but this study will focus only on cement and lime-based grouts suitable for preserving the historical nature of the structure. Grout is commonly a mixture of water, cement, sand, often colour tint, and sometimes fine grit. Major requirements of grouts are fluidity, injectability and good connection strength of the grout-stone interface. Besides, the new grouting materials chosen for repair and strengthening should be chemically, physically and mechanically compatible. The selection of the type of grout for a particular type of concrete or masonry repair work should be based on the compatibility of the grout with the original material. The success of this operation depends on several parameters, such as the distance between the injection holes, the injection pressure, the rheological properties of the grout, the water absorption capacity and the general condition of the masonry (number and width of cracks) [3]. The preparation process for injection grouts is also important, because it affects the

final performance characteristics. Both the stirring method and the time of mixing have an essential influence on the stability of the grout mixture. Generally, mixing an injection grout at high speed for a longer time produces a grout with better injectability and penetration and less separation of liquid and solid phases [4].

Figure 2-Grout injection procedure. (a) General overview of the process. (b) Drilling holes in mortar joints. (c) Fixing plastic pipes. (d) Injecting grout

Injection grouting (Figure 3) for the conservation of stone masonry structures involves several steps described below [2]:

- Study and choice of the grout;
- Selection of the injection points, the distance between injectors and their layout, according to the crack diffusion, depth, with and localisation;
- Removal of the damaged plaster and superficial crack filling (to avoid loss of grouts);
- Positioning of the injection injectors and repointing by mortar;
- Preliminary water injection in order to remove dust and disaggregate materials but also to saturate the wall, avoiding the masonry suction. The segregation and shrinkage of the grout due to the high rate of absorption of the material should be prevented;

- Evaluation of the injection pressure;
- Grout injection.

In literature there are four general methods for grouting, whose choice depends on nature and condition of masonry. The methods are [5]

- Hand grouting
- Gravity grouting
- Pumped system
- Vacuum system

The simplest method is the hand grouting. This technique is being used for small isolated voids or fine cracks. Gravity grouting is suitable for ancient masonry structures and for filling large voids and it is also necessary to mention that during this method the pressure in the hose should be 70-80kPa (Figure 3). Pumped system is recommended for ancient masonry in unstable conditions. Here the pressure ranges from 70-280kPa and this method is used in large-scale grouting (tunnels, vaults). The vacuum system for masonry structures, indicative to say that at present time information of this system very limited [5].

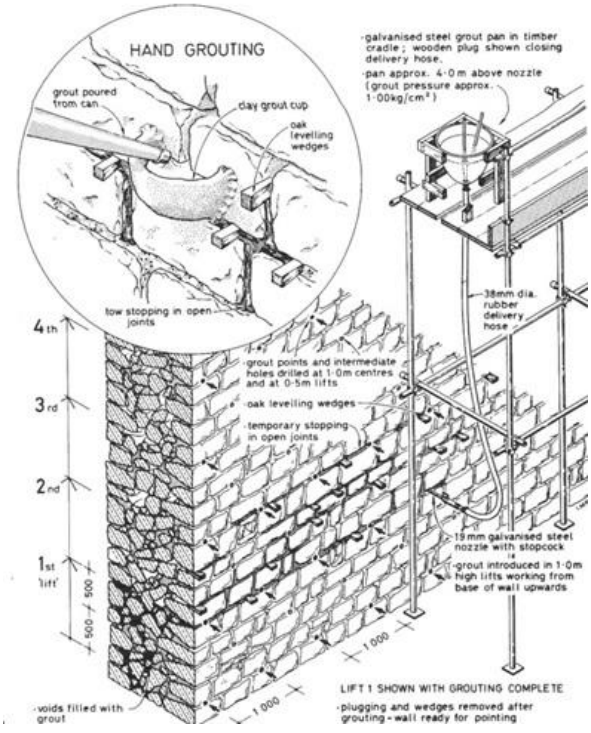

Figure 3-Hand and gravity grouting [5].

2.2. Materials constituents of grouts

2.2.1. Introduction

Injection grouts are composed of one or more binders, aggregates or not, admixtures (typically superplasticizers or plasticizers) and water. To obtain similar and good injectability the use of superplasticizer for some grouts is essential.

The binders are divided into inorganic (aerial or hydraulic binders) and organic binders. Hydraulic binders include cement and hydraulic lime. Whereas, aerial binders include the gypsum and hydrated lime. The combination of different materials gives totally different results with different properties and behaviour, namely injectability, mechanical and durability characteristics. As it is known there are basic types of grout, which are non-sanded (or unsanded) and sanded.

In this study non-sanded grout is used. To prepare specimens cement, hydrated lime, metakaolin and superplastizier were used in this study. These materials are explained below.

2.2.2. Cement

Cement belongs to hydraulic binders. The raw materials are limestone and clay. Cement is made by finely grinding together around 95% cement clinker with 5% gypsum until getting fine powder and it is a hydraulic binder because it gets harden and sets in air and even under water. The quality of cement clinker is directly related to the chemistry of the raw material used. Around 80-90% of raw material for the klin feed is limestone. Clayey raw material accounts for about 10-15%. Upon combining water with cement, Tricalcium Silicate reacts instantaneously to release Calcium Ions and Hydroxide Ions, then Calcium Hydroxide starts to crystallise and formation of Calcium Silicate Hydrate (C-S-H) begins. The chemical reaction is shown in (Eq. 1). Hydration process of Dicalcium Silicate acts in a similar manner to Tricalcium Silicate, with product of Calcium Hydroxide (or Portlandite) and a rigid C-S-H gel which contributes to later age strength. The chemistry of these components must be taken

into account when determining the stability of cement. This is represented in (Eq. 2) [6]

Tricalcium Silicate + Water→ Calcium Silicate Hydrate+ Calcium Hydroxide

$$2\,(CaO)_3(SiO_2) + 7H_2O \rightarrow (CaO)_3{\cdot}(SiO_2)_2{\cdot}4(H_2O) + 3Ca(OH)_2 \qquad \text{(Eq. 1)}$$

Dicalcium Silicate + Water → Calcium Silicate Hydrate + Calcium Hydroxide

$$2(CaO)_2(SiO_2) + 5H_2O \rightarrow (CaO)_3{\cdot}(SiO_2)_2{\cdot}4(H_2O) + Ca(OH)_2 \qquad \text{(Eq. 2)}$$

The other major components of Portland cement, tricalcium aluminate and tetracalcium alumina ferrite also react with water. Their hydration chemistry is more complicated as it involves reactions with the gypsum as well. Because these reactions do not contribute significantly to strength they are not written in the frame of this study. After mixing the acquisition paste it is possible to use within three hours, but it depends on the composition and fineness of the cement, usage of any admixtures, mixture proportions, and temperature conditions. Most of the hydration and strength development takes up to the first month, however, it continues for a long time with proper moisture and temperature. Continuous strength increases exceeding 30 years have been recorded [7] see Figure 4.

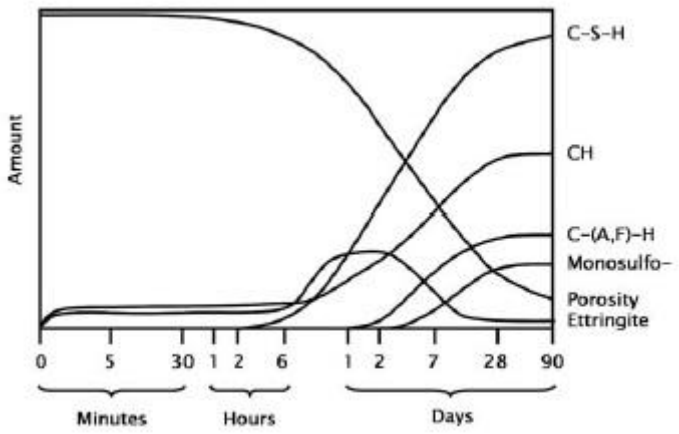

Figure 4-Schematic view of cement hydrates formation.

When water is added, the reactions which occur are mostly exothermic, due to the reactions that generate heat. Cement has many types but the more famous types are five [8] see Table 1. Differences of the cement such as setting time, strength, soundness and heat of hydration setting time, strength, soundness and heat of hydration can be

found by EN 197-1 European standard and the I II, III IV, V are types of cement. In this time the most famous type of cement is Portland cement. Portland cement is made by heating a mixture of limestone and clay in a kiln at about 1450°C, then grinding up to a fine powder with a small addition of gypsum to control flash setting. Initial setting and early strength of Portland cement is due to tricalcium aluminate (C_3A). Tricalcium silicate is a very reactive compound, hydrates quickly and contributes more to the early strength. Basically the early high strength related with increased percentages of C_3S. The contribution of dicalcium silicate (C_2S) takes place after 7 days and may continue for up to 1 year, because it enters slowly to reaction then tricalcium silicate. Tricalcium aluminate hydrates quickly, generates much heat and makes only a small contribution to the strength within the first 24 hours and it has problems with sulphate attack. As is known for obtaining sulphate resistant cement is necessary to reduce C_3A content in clinker because sulphate reacts with aluminate and calcium components to produce disruptive products such as ettringite and gypsum.

Table 1-Types of Cement, within European standard EN 197-1 [8].

Cement type	Designation	Notation	Clinker (wt.-%)	Mineral addition (wt.-%)
CEM I	Portland cement	I	95-100	-
CEM II	Portland slag cement	II/A-S	80-94	6-20
		II/B-S	65-79	21-35
	Portland silica fume cement	II/A-D	90-94	6-10
	Portland pozzolans cement	II/A-P	80-94	6-20
		II/B-P	65-79	21-35
		II/A-Q	80-94	6-20
		II/B-Q	65-79	21-35
	Portland fly ash cement	II/A-V	80-94	6-20
		II/B-V	65-79	21-35
		II/A-W	80-94	6-20
		II/B-W	65-79	21-35
	Portland burnt shale cement	II/A-T	80-94	6-20
		II/B-T	65-79	21-35
	Portland limestone cement	II/A-L	80-94	6-20
		II/B-L	65-79	21-35
		II/A-LL	80-94	6-20
		II/B-LL	65-79	21-35
	Portland composite cement	II/A-M	80-94	6-20
		II/B-M	65-79	21-35
CEM III	Blastfurnace cement	III/A	35-94	35-65
		III/B	20-34	66-80
		III/C	5-19	81-95
CEM IV	Pozzolanic cement	IV/A	65-89	11-36
		IV/B	45-64	36-55
CEM V	Composite cement	V/A	40-64	36-60
		V/B	20-38	61-80

As this has been studied at the U.S. Bureau of Reclamation in the 1960s and 1970s they pointed out that higher amount of the highly reactive alumina is less suitable than small amount for improving the sulphate resistance of concrete which means that with increased Al_2O_3 content can be more susceptive to the formation of ettringite [9]. Gypsum, which is added to cement during final grinding, slows down the initial hydration rate of C_3A. Cements with low percentages of C_3A are especially resistant to soils and waters containing sulphates. Tetracalcium alumino-ferrite is comparatively inactive. It hydrates relatively slowly and contributes very little to strength. C_4AF and its hydrates influence on colour [10] [11].Often supplementary cementitious materials (SCMs) are blended with clinker, including fly ash, ground granulated blast furnace slag, silica fume, calcined clays and natural pozzolans. The practice of using SCMs is increasing, with the world average percent clinker in cement having decreased from 85% in 2003 to 77% in 2010, and it is projected to further decrease to 71% in the future [12]. Basically Portland cement is familiar by grey colour but there is also a white Portland cement and sulphate resisting Portland cement. Clinker consists of various calcium silicates including alite, belite celite and ferrite. The raw materials (clay and limestone) for clinker manufacture consist primarily of materials that supply four primary oxides. Typical clinker contains 67 % CaO, 22 % SiO_2, 5 % Al_2O_3, 3 % Fe_2O_3 and 3 % other components with % w/w and usually four major crystalline phases [13] which are shown in Table 2. Depending on the percentage of clinker and gypsum (calcium sulphates) and possibly additional cementitious (slag, fly ash, natural pozzolanas, etc.) in cement different types of cement are generated.

Table 2-Clinker main minerals (phase composition of cement clinker).

Cement Chemist Notation	Actual Formula	Name	Mineral Phase
C_3S	$3CaO{\cdot}SiO_2$	Tricalcium silicate	Alite
C_2S	$2CaO{\cdot}SiO_2$	Dicalcium silicate	Belite
C_3A	$3CaO{\cdot}Al_2O_3$	Tricalcium aluminate	Aluminate or Celite
C_4AF	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	Tetracalcium alumina ferrite	Ferite

2.2.3. Hydrated Lime

Hydrated lime or air lime are called non-hydraulic lime. Hydrated lime ($Ca(OH)_2$) is also known as calcium hydroxide or slaked lime. This is an alkaline product which has fine powder and pH>12. Calcium carbonate is burned in lime kilns (˜900 °C) and calcium oxide (quicklime) is obtained. This reaction is reversible and calcium oxide can react with carbon dioxide for forming calcium carbonate, see Eq. 3. Slaking is the process of converting quicklime (CaO) to hydrated lime (calcium hydroxide) by adding water, as shown in the (Eq. 4) [14]

$$CaCO_3 \leftrightarrow CaO + CO_2 \quad \text{(Eq. 3)}$$

$$Ca(OH)_2 \rightarrow CaO + H_2O \quad \text{(Eq. 4)}$$

When lime is mixed with water, it forms calcium hydroxide. The reaction of calcium hydroxide with carbon dioxide is faster, producing a mortar that hardens more quickly, see Eq. 5.

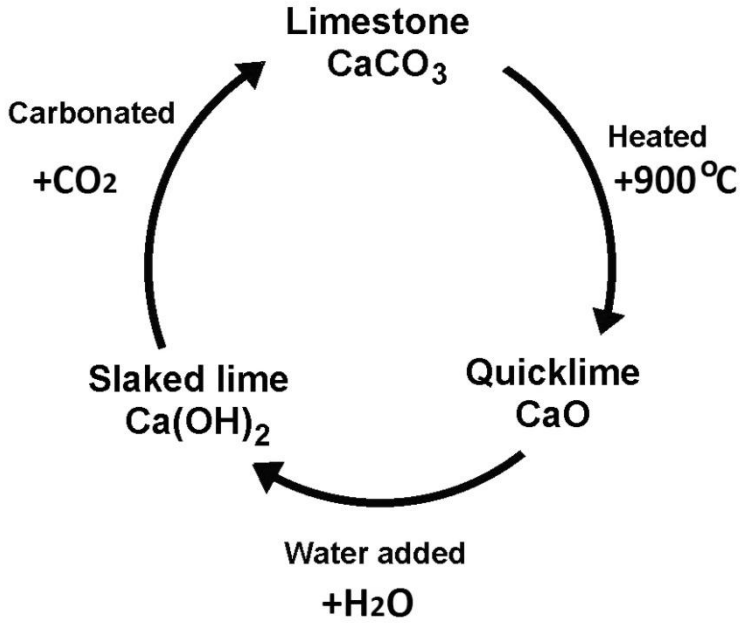

Figure 5-Lime Cycle.

It forms Calcium Carbonate ($CaCO_3$) again and the called lime cycle is closed, see Figure 5.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad \text{(Eq. 5)}$$

Air lime or hydrated lime (calcium lime and dolomitic lime) gets harder in air by reacting with atmospheric carbon dioxide. That is why this is an aerial binder. The hydrated lime is commercially available in two versions: putty lime and hydrated lime. Lime putty can be made from either type of lime, and is made by adding an excess of water to quicklime. Hydrated lime is made by adding the exact amount of water. Within EN 459-1:2001 there are two types of air lime which are classified as following (see Table 3).

Table 3-Types of building lime and classification.

Type of Building Lime	Type Classifications
Calcium Lime	CL90, CL80, CL70
Dolomitic Lime	DL85, DL80

Within EN 459-1:2001 the classes of Calcium Lime and Dolomitic Limeare defined by their percentage of lime content (CaO + MgO) as shown on Table 4.

Table 4-The classes of calcium lime and dolomitic lime.

Type of Building Lime	CaO + MgO	MgO	CO_2	SO_3
CL 90	≥90	≤5	≤5	≤2
CL 80	≥80	≤5	≤7	≤2
CL 70	≥70	≤5	≤12	≤2
DL 85	≥85	≥30	≤7	≤2
DL 80	≥80	≥5	≤7	≤2

2.2.4. Hydraulic Lime

The raw material for hydraulic lime is a limestone ($CaCO_3$) which contains calcium carbonate together with a proportion of clay. Most limestones for hydraulic lime production contain between 15 and 35 percent silica together with alumina - two important constituents of clays. Hydraulic lime capable hardening and setting under

the water. More hydraulic lime gets more strength, but less flexible and breathable. There are two types of hydraulic lime three classes within (EN459-1) see Table 5.

Table 5-Types and classification of hydraulic lime.

Type of Building Lime	Type Classification
Natural Hydraulic Lime	NHL5, NHL3.5, NHL2
Hydraulic Lime	HL5, HL3.5, HL2

It is noteworthy, that natural hydraulic lime and hydraulic lime are measured by their minimum compressive strength in MPa. Moreover, the compressive strength bands for natural hydraulic lime and hydraulic lime are based on 28 day results and have broad tolerances, because of limits on the accuracy of the measurement equipment and testing error. The Table 6 presents classes of hydraulic lime within EN 459-1:2001.

Table 6-Classes of hydraulic lime within EN 459-1:2001.

Type of Building Lime	Type Classification	Compressive Strenght (MPa) at 28 day
Natural Hydraulic Lime or Hydraulic Lime	NHL2 or HL2	≤ 2 to ≤ 7
	NHL3,5 or HL3,5	≤ 3.5 to ≤ 5
	NHL5 or HL5	≤ 5 to ≤ 15

2.2.5. Metakaolin

Metakaolin belongs to the pozzolanic additives. Metakaolin (MK) is a alumin-silicate pozzolan, dehydroxylated form of the clay mineral kaolinite at temperatures of from 550 to 650 °C. Metakaolin can be combined with calcium hydroxide to form hydrates and this contributes to improving properties of mortar and concrete, see chemical equation in the Eq. 6. [15].

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O = Al_2O_3 \cdot 2SiO_2 + 2H_2O \quad \text{(Eq. 6)}$$

The major chemical components of metakaolin (Table 7) are oxides as SiO_2, Al_2O_3 and in smaller quantities the oxides Fe_2O_3, TiO_2, Na_2O and K_2O and as it noticed it is similar to Portland cement. If the amount of product consists at least 90% of silica and alumina is called High reactivity metakaolin (HRM) [16].

Table 7-Chemical composition of metakaolin(HRM).

Chemicals	Percentage (%)
SiO_2	62.62
Al_2O_3	28.63
Fe_2O_3	1.07
MgO	0.15
CaO	0.06
Na_2O	1.57
K_2O	3.46
TiO_2	0.36
LOI	2.00

Metakaolin helps to increase following aspects of cement and concrete [17]:

-Flexural and compressive strength

-Density

-Chemical resistance

-Alkali-silica resistance

Metakaolin is available in many different varieties and qualities. Some of them also provide special reactivity. Metakaolin is a valuable admixture for concrete or cement applications because it provides many specific features. When is used as a partial replacement substance for cement in concrete, it reacts with $Ca(OH)_2$ one of the by-products of hydration reaction of cement at ambient temperature and produces in additional C-S-H gel which results in increased strength and lower porosity and permeability (because there is less $Ca(OH)_2$ to be removed by leaching). The chemical reactions are given below Eq. 7, 8 [6] [18] [19].

$$\text{Cement} + \text{Water} = \text{C-S-H gel} + Ca(OH)_2 \quad \text{(Eq. 7)}$$

$$Ca(OH)_2 + \text{Metakaolin} = \text{C-S-H gel} \quad \text{(Eq. 8)}$$

Usually 8% - 20% (by weight) of Portland cement replaced by metakaolin will contribute to increased strength, reduced permeability, greater durability, effective control of efflorescence, and control of degradation caused by alkali-silica reaction. The use of pozzolans will also decrease the amount of CH in the hydrated cement paste of

Portland cements, reducing the quantity of CH in the hydrated cement paste will limit the effects of this form of sulphate attack[17].

Metakaolin combines with the calcium hydroxide to produce additional cementing compounds. Metakaolin is generally whiter than other pozzolans. Whiteness is most important advantage over other pozzolans. Due the white colour it does not let the colour of white concrete made with white Portland cement change. Improving the consistency of mortars and concretes allows to produce high quality dry mixture. In recent years metakaolin has been used much often than ever as a mineral admixture for getting more strength and durable concretes. Sabir (2001) has recently reported a comprehensive review of the studies on the use of the metakaolin as a partial pozzolanic replacement for cement in mortar and concrete [20].

2.2.6. Superplasticizers and Plasticizers

Superplasticizers (SP) are chemical admixtures which are polymers and they are basically used in concrete or mortar processing as a dispersants to avoid aggregation and improve the flow characteristic of concrete such as increase the rheological properties of hardening pastes. The extra water is trapped in the solid structure and increases porosity and reduces strength. This can be compensated by superplasticizers which interfere with the fast hydration reactions of C_3A and C_3S which cause rapid thickening of the cement [19]. Superplastizier increases the workability of normal Portland cement concrete or greatly reduce its water content. Normally the superplasticizer is added to the truck mixer after it arrives at the jobsite and at the last convenient moment before discharge. Within 5 minutes or less the workability of mortar or concrete improve and at that time the user can get the most advantage from the high fluidity of the concrete [21]. When superplastiziers are used in the mix water, it is reducing up to 35-40%, increasing mechanical strength, permeability and durability [22].The superplastisizers are generally referred to as high range water reducing admixtures which dissipate the water in concrete matrix. This attribute is often called as dispersion-fluidification property of concrete admixture.

Admixtures are used to [23]:

- Congested reinforcement;
- Self-leveling consistence;
- For high-strength concretes by decreasing the water/cement ratio as a result of reducing the water content by 15–25%;
- Improved resistance of hardened concrete to the action of freezing and thawing;
- For improved cohesion and handling properties (workability), especially in harsh or lean mixes;
- Increased cohesion reduces segregation and bleeding, especially when a mix lacks fines;

The superplasticizer has a considerable impact on the various properties of concrete both in fresh and hardened forms due to the following facts [16].

- Reduction in interfacial tension.
- Multilayered adsorption of organic molecule.
- Release of water trapped amongst the cement particles.
- Retarding effect of cement hydration.
- Change in morphology of hydrated cement.

To obtain high-performance water reducing additives is being used and the types are shown in Table 8 [24].

Table 8- Types of additives water reducing/ high water reducing

Reducing water	High water reducing/Superplasticizers
-lignosulfonate acids, acid salts of lignosulfonate -hydroxylated polymers, -carboxylic acids, salts of carboxylic acids, -sulfonated melamin or naphthalene formaldehyde condensates, -polyether polycarboxylates.	-sulfonated melamin formaldehyde condensates, -sulfonated naphtalene formaldehyde condensates, -modify lignosulphonates -polyether polycarboxylates.

2.3. Commercially available grouts and laboratory Formulations – Literature Survey

Grouting is one of common mechanism for repair and strengthening of masonry structures, or either in presence of voids or cracks. It is necessary to know the composition of the grout that should improve the behavior of the injected system without impressing its durability. There are different types of commercial grouts and some examples are presented in Table 9. Formulation of the hydraulic grouts to historical buildings was first suggested in 1982 with the use of cement and marble powder. Later opted for the addition of pozzolans and stone powder, with the objective of reducing shrinkage (<4%) and control the mechanical strength (the intention was to obtain compressive strength in the range of 3-8MPa and 0,3-1,2MPa in the diametrical test). Later, new formulations were evaluated using tri-composite grouts with hydrated lime, cement, pozzolan and superplasticizers. The effectiveness of ternary compositions has been proven in experimental studies in one and three leaf walls, even if grout formulations remain, mostly, an empirical process and that due to reduced cement content [25]. However, beyond cements, pozzolans and lime, other compositions were also studied, for example using hydraulic lime, gypsum and also bentonite [26]. Based on Luso and Lourenco (2016) after testing many compositions in laboratory included that mixing 35% of hydrated lime, 30% of cement and 35% of metakaolin, 3.33% of superplasticizer and 60% of water offered good results.

Table 9-Information available in the technical data sheet from the producers[26].

Grout	Description
Mape-Antique I, from Mapei	Super-fluid, salt resistance, fillerized hydraulic binder, based on lime and eco-pozzolan, for making injection slurries for consolidation masonry
Albaria Iniezione from BASF	It is a lime pozzolanic premixed grout without cement with a fine grain (less than 12 μm) high fluidity and excellent workability
Calce per Consolidamento from Cepro	Is a compound for structural consolidation injections on masonry at low pressure
Lime-Injection from Tecnochem	Is a binder ideal for injection consolidation of brick masonry, or stone Its hydraulic setting is fundamentally based on lime-silica microactive reaction and in the presence of hydraulic lime free of harmful soluble salts

2.4. Durability of Construction Materials – Chemical Resistance

Durability is defined as the ability of the material to remain serviceable for an acceptable period without excessive or unexpected maintenance. Durability has important meaning for construction materials. The durability of construction materials is important for exact assessment of buildings or engineering structures and is needed for engineers and designers responsible for quality. The evaluation of the durability of grout materials gives information about possible damages during ageing process of

materials and changes in its functional properties. During ageing process, physical or chemical degradation occurs. Solar radiation, temperature variations, mechanical stresses, water, oxygen, pollutants etc. are examples of degradation agents [27]. For durability of materials important parameters are permeability and porosity, and chemical composition of material. Permeability of the concrete is basically dependent on the water/cement ratio. The relationship between the coefficient of permeability and the water/cement ratio is presented in Figure 6 [6], so if ratio is low that means there is low permeability. If porosity in the materials is high durability decreases.

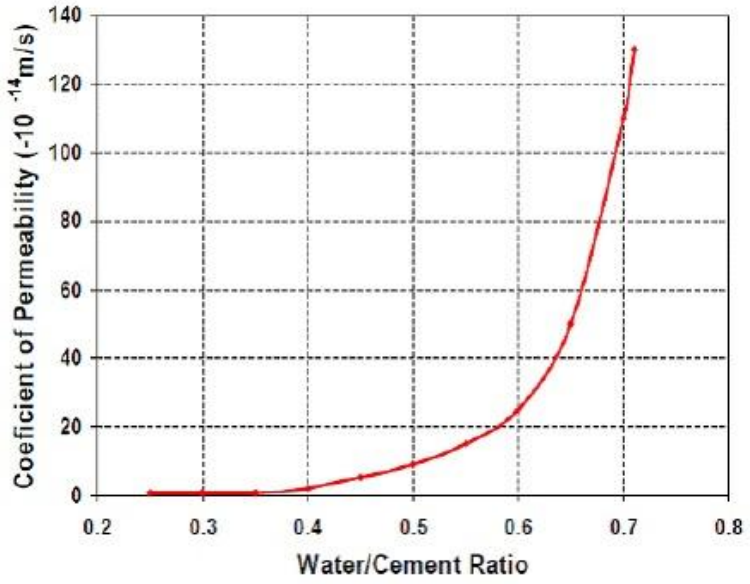

Figure 6-Relationship between permeability and porosity.

Pore size is an important factor: materials with a lot of very small pores are generally less durable than materials with fewer but larger pores [28]. Over time, salts migrate into porous masonry materials and start to clog pore spaces. Where pores become filled with salt, repeated cycles of dissolution/crystallisation and sometimes also hydration/dehydration within pores will lead to the imposition of considerable stress on the surrounding pore walls. As known salts consist of a combination of positively (cation) and negatively (anion) charged ions. Table 10 shows those that make up the salts commonly encountered in walls.

Table 10– Salt types.

Cations (+)	Anions (–)
Sodium (Na^+)	Chloride (Cl^-)
Potassium (K^+)	Sulphate (SO_4^{2-})
Magnesium (Mg^{2+})	Nitrate (NO_3^{2-})
Calcium (Ca^{2+})	Carbonate (CO_3^{2-})

Salt attack problems in walls commonly are being produced by sodium sulphate, calcium sulphate (gypsum) and sodium chloride. Combination of permeable masonry, moisture, soluble salt, and evaporation are an important part of sulphate attack process. The effect of salt attack on masonry material and structures can be present in different forms, i.e., efflorescence, scaling, cracking, crumbling, and softening [29].

2.4.1. Evaluation of Sulphate attack Resistance – Literature Survey

Sulphate attack (salt crystallisation) is a complex process that injures masonry structures (Figure 7). The final result of sulphate attack can be excessive expansion, cracking, loss of strength and deterioration of the material [30]. The crystallization of soluble salts in porous construction materials is an important weathering process contributing to the decay of masonry, cement and mortar in a range of environments. Basically the salt crystallization mechanism is affected by the properties of the salt solution, the climatic conditions and the properties of the substrate. Source of sulphates can be external or internal, and the damage effect can be chemical in nature, due to alteration of hydration of products, or physical in nature, due to phase changes in the penetrating sulphate solution.

Figure 7-Salt attack in bricks causing damage.

Sulphates can enter masonry materials via following sources [28] [29]

- saline soils and groundwater;
- sea-spray;
- air-borne salt;
- air pollutants;
- inorganic garden fertilisers;
- biological-pigeon droppings, micro-organisms, leaking sewers;
- salt naturally occurring in the stone, brick clay, or mortar sand;
- salty water used for puddling brick clay or mixing mortar;
- salts used for de-icing roads in cold climates;
- cleaning compounds that contain (or react to produce) salts in walls.

In groundwater or soil sample commonly mixed sulphates can be found. There are many types of sulphates that begets damages in concrete and in masonry. The main reaction products are gypsum, ettringite, thaumasite, brucite and silica gel. The most common types of sulphates are the sodium, calcium and magnesium of sulphate attack. There is more than one theory proposed to identify the mechanism of cementitious material deterioration due to physical sulphate attack:
(1) Solid volume change, (2) Salt hydration distress, and (3) Crystallization pressure [31]. There are three key chemical reactions between sulphate ions and hardened cement pastes. These reactions are:

- recrystallisation of ettringite;
- formation of gypsum;
- decalcification of the main cementitious phase (C-S-H).

Waters containing sulphates react with hydration products of the tri-calcium aluminate (C_3A) phase of Portland cement, and with calcium hydroxide ($Ca(OH)_2$) to form an expansive crystalline product called ettringite. Ettringite, a typical reaction product of classical sulphate attack on concrete, is a voluminous phase associated with expansion, cracking and spalling of concrete. The idea about primarily damages of cementitous system is related with dissolution of the main phases of hydrated cement

paste and formation of ettringite and gypsum but of course this is being discussed yet. Sodium sulphate (Na_2SO_4) can react with calcium hydroxide ($Ca(OH)_2$) to produce gypsum ($CaSO_4 \cdot 2H_2O$), and sodium hydroxide (NH) according to the following reaction (Eq. 9)[32].

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O + 2NaOH \quad \text{(Eq. 9)}$$

The gypsum forming according to the reaction (9) can react further with aluminate unhydrated tricalcium aluminate to produce ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) according to the following equation (Eq. 10).

$$3CaO \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 26H_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad \text{(Eq. 10)}$$

As it is known the formation of ettringite depends on temperature and pH of solution. From Figure 8 it is possible to point out that gypsum becomes stable at lower sulphate concentrations with increasing temperature, significant change is being noticed started at 50°C degree. Until 50°C dominate the ettringite phase [8].

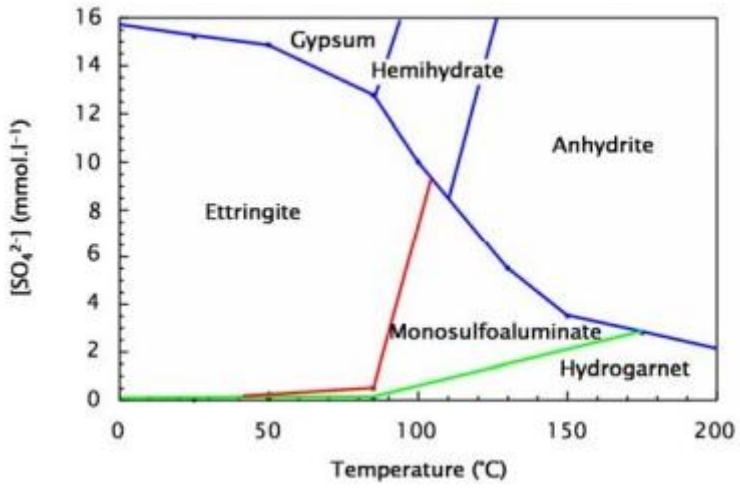

Figure 8-Effect of temperature on sulphate-bearing phases stability [8].

Hampson and Bailey have shown that in pure systems, the pH drops below which buffered by portlandite, ettringite becomes stable (Figure 9) [33].

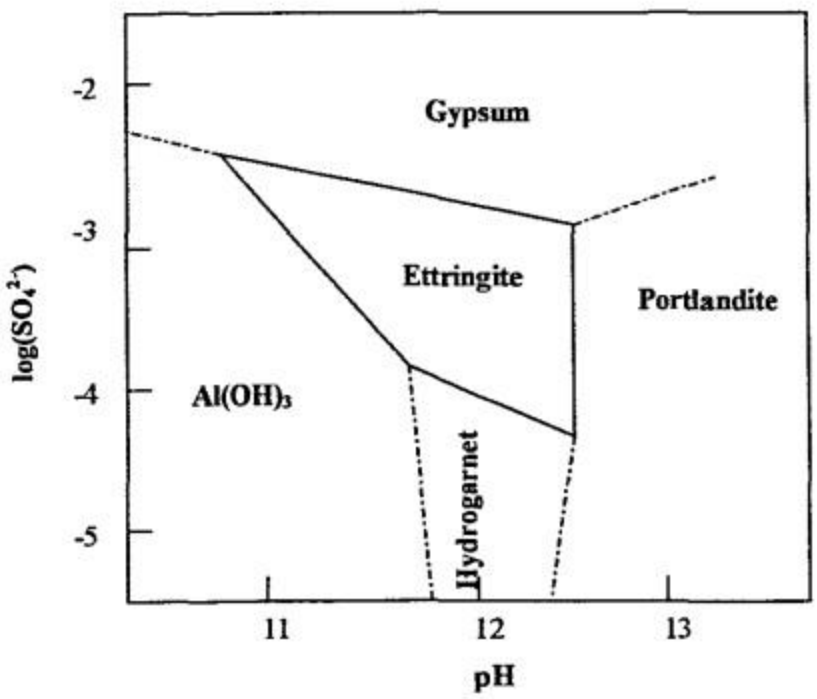

Figure 9-Ettringite stability in alkaline environments as a function of pH and sulphate ion concentration [33].

Between pH values of 12.45 and 12.7, the sulphate concentration slowly increases, whereas it rises dramatically from that level on. In solutions in which sodium ions are the counterpart of the hydroxide ions, the precipitation of gypsum can take place until pH values of approximately 12.9. Beyond that mark, a further increase of the sulphate concentration is unable to lead to the formation of gypsum. Concerning ettringite, ettringite is not stable in an environment with pH value below 11.5-12.0. At this low pH range, ettringite decomposes and forms gypsum [9].

The damaging effects on the C-S-H gel are only due to the action of magnesium sulphates. It is accepted that salt weathering is a major cause of damage in building stones and other porous building materials such as brick and concrete [34]. Several factors affect the resistance of masonry materials to sulphate attack. These factors include the chemistry of the cementitious material, the permeability and porosity, the concentration of external sources of sulphate ions. Thermodynamic studies as well as experimental studies show that damage depends on the quantity of salt in the stone and the characteristics of the porous network, as well as on the environmental conditions (e.g. temperature and relative humidity) [35].

The sodium sulphate phase diagram is shown in Figure 10 [36]. There are three crystalline phases known for sodium sulphate: the anhydrous phase Na_2SO_4, also called thenardite, and two hydrous phases: Mirabilite, $Na_2SO_4 \cdot 10H_2O$, also called decahydrate and heptahydrate, $Na_2SO_4 \cdot 7H_2O$, which is a metastable phase [37].

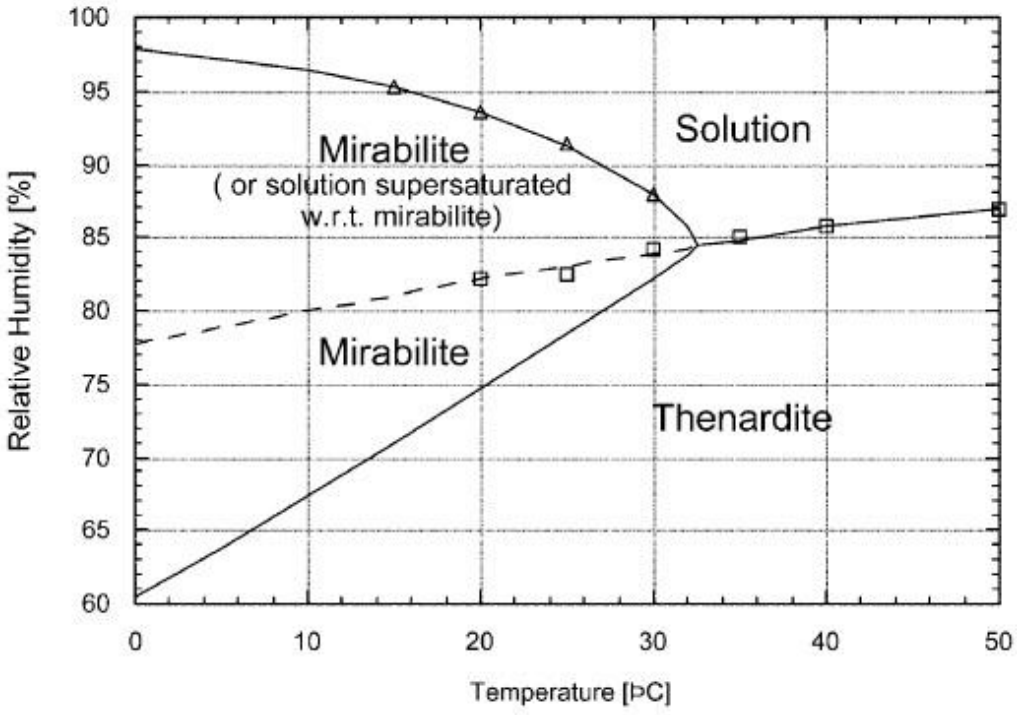

Figure 10-The sodium sulphate phase diagram [36].

About 50 salt types commonly appear on buildings. Characteristically, the salt types have very different physical and chemical properties. Sodium sulphate is known to be a salt that causes the worst crystallization decay on porous materials and has become widely used in accelerated durability testing [9]. Sodium sulphate is known example for appearing as thenardite (Na_2SO_4) when water-free and being able to change to the water-rich salt phase mirabilite ($Na_2SO_4 \cdot 10H_2O$) [38]. Thenardite (Na_2SO_4) is the anhydrous phase and it is reported to sediment instantly from solution at temperatures above 32.4C, below this temperature stable phase is the mirabilite ($Na_2SO_4 \cdot 10H_2O$) that quickly dehydrates and it depends humidity and below 71% (20 °C) to form thenardite. Thernardite will rehydrate to mirabilite if the humidity rises over 71%. Sodium sulphate heptahydrate ($Na_2SO_4 \cdot 7H_2O$) has been described as precipitating at temperatures below the mirabilite - thenardite transition point [39].

2.4.2. Evaluation of chloride attack Resistance – Literature Survey

Chloride ions ingress of the masonry materials may devote initiation. Most popular chloride salt is sodium chloride . Many factors influence chloride induced corrosion. The factors are grout mix properties, exposed environment, cure practices, and importantly water/cement (w/c) ratios. The transport of chlorides is influenced strongly by the exact sequence of wetting and drying. When salts first disrupt masonry they enlarge the pores slightly [40][41][6]. After a cycle of wetting and drying, salts fill the enlarged pores and the new crystal growth further disrupts the masonry and enlarges the pores some more. The main mechanisms for chloride transport in concrete are capillary suction, diffusion, permeation and migration [42].Chloride can penetrate into concrete by the effect of: [6]

- Exposure to seawater spray or direct contact with seawater wetting;
- Application of de-icing to combat the build-up of snow and ice on transport infrastructures;
- Exposure to chemical substance;
- Internal contamination of chlorides in grout mixture.

The rate of chloride penetration into concrete is affected by the chloride binding capacity of the masonry materials. A portion of the chloride ions reacts with the concrete matrix becoming either chemically or physically bound, and this binding reduces the rate of diffusion. The chloride binding capacity is controlled by the cementing materials used in the concrete. The inclusion of supplementary cementing materials affects binding, though the exact influence is unclear. Also, the C_3A content of the cement influences its binding capacity, with increased C_3A content leading to increased binding [43].Chloride binding is a significant factor related to reinforced masonry durability for three reasons:

- reduction of the free chloride concentration in the vicinity of the reinforcing steel will reduce the risk of corrosion;
- chloride binding will delay the chloride penetration;

- formation of calcium chloroaluminate results in a less porous structure and slows down the transport of Cl^- ions) .

The establishment of the chloride threshold level has been one point of increasing interest. However, this parameter is affected by a large number of characteristic factors, such as: [44]

- the interstitial solution chemistry and pH;
- water to cement ratio;
- material composition, namely, cement type use of additives, such as fly ash and other mineral admixtures;
- pore and capillary structure;
- curing period and curing and exposure temperature.

The resistivity of concretes is a function of porosity (inherent, time dependent materials property) the chemical composition (conductivity) of the solution in the pores and the number and distribution of pores filled with solution as a result of the interaction with the environment. Based on these three aspects is possible to get information about corrosion of embedded steel in the initiation and in the propagation period. The electrical resistivity of concrete can be related to two processes involved in corrosion of reinforcement: initiation (chloride penetration) and propagation (corrosion rate) .So if concrete structure will have low resistivity it will let early corrosion to the concrete accelerating chloride penetration and increase corrosion rate [45].For constant moisture content, the resistivity is increased by longer curing (hydration), lower w/c ratio and by addition of reactive materials such as alternative cementing materials: fly ash, blast furnace slag, metakaolin and silica fume [40]

3. Chapter 3 – Experimental Program

3.1. Materials and Preparation of Specimens

The experimental research presented in this thesis involved the preparation and testing of specimens of two kinds of grouts. One is a commercially available grout from Mapei, Mape Antique I (named grout CA).The second grout (named a grout LB) is a laboratory formulation with cement, metakaolin, hydrated lime, water and a superplastizier. All the procedures necessary to the preparation of samples were performed in the Materials Laboratory of Polytechnic Institute of Bragança, Portugal.

For the preparation of first grout (CA) were mixed 10 kg of commercial available grout and 3.5 L of water. It means that ratio of water to binder (w/b) is 0.35. After mixing 10 minutes, the obtained blend was passed through a sieve. After this, the blend was filled into prismatic moulds with dimensions 4×4×16 cm^3, see Figure 11.

Figure 11-Filled blend of commercial grout in the moulds.

After these steps the specimens were kept at room temperature about 48 hours before being available (Figure 12).

Figure 12-Available concretes of grout CA.

3150 gr. of hydrated lime, 3150gr. of metakaolin, 2700 gr. of white cement, 5.4 L of water and 300 mL of plasticizer *SR1* (*Dynamon SR1 from Mapei*)(w/b-0.54) were used

for the preparation of laboratory grouts. The first hydrated lime, metakaolin, white cement were mixed with water then during mixing plasticizer added. Again, it was mixed during 10 minutes, thereafter passing trough sieve and the obtained blend fill same prismatic moulds (4×4×16 cm^3) (Figure 13).Then, they were kept also at room temperature about 48 hours. The total numbers of specimens were 42 (21 from grouts CA and 21 from grouts LB).

Figure 13-Filled blend of LB grout in the moulds.

Then the concretes were put in the humidity chamber where temperature is 20 °C and humidity 90-95 %. Specimens were kept in humidity chamber for 90 days. Before the starting experiment all specimens were dried to constant mass at 105 °C for 18 hours and were measured the dimensions (Length(L), Width(W), Height(H)) using a digital calliper. The weights (M) of the specimens were measured with digital scale and compressive strength tests were done with a compressive testing machine. From dimensions of the samples it was possible to calculate volume of prismatic samples and then was used equation of bulk density whose formula is shown in Eq. 11, where M (g) is the weight and V (cm^3) is the volume of specimen. All these obtained results are shown in Table 11 and Table 12.

$$\rho = \frac{M}{V} \qquad \text{(Eq. 11)}$$

Table 11-Initial information (weight, volume and bulk density and) of the commercial specimens (CA).

Grout	Weight(g.)	V (cm^3)	ρ(g/cm^3)
CA1	415.9	251.92	1.65
CA2	418.2	249.03	1.68
CA3	414.5	249.46	1.66
CA4	420.2	253.95	1.66
CA5	421.1	249.13	1.69
CA6	419.5	248.19	1.69
CA7	433.3	252.28	1.72
CA8	409.6	250.73	1.63
CA9	422.2	245.84	1.72
CA10	419.8	252.28	1.66
CA11	407.8	245.66	1.66
CA12	404.7	246.21	1.64
CA13	418.2	246.39	1.70
CA14	422.9	248.49	1.70
CA15	419.7	248.91	1.69
CA16	409.3	250.35	1.64
CA17	419.2	247.34	1.70
CA18	425.3	252.46	1.69
CA19	427.3	247.25	1.73
CA20	411.2	251.01	1.64
CA21	413.8	244.48	1.69
Averages of values	417.8	249.12	1.67

Table 12-Initial information (weight, dimension, volume and bulk density) of the lab-specimens (LB).

Grout	Weight(g.)	V (cm^3)	ρ(g/cm^3)
LB1	338.90	247.02	1.37
LB2	327.01	237.44	1.38
LB3	330.96	242.83	1.36
LB4	337.08	243.59	1.38
LB5	331.70	246.37	1.35
LB6	348.87	249.78	1.40
LB7	330.54	240.21	1.38
LB8	333.70	244.51	1.36
LB9	333.63	242.51	1.37
LB10	343.24	246.12	1.39
LB11	332.67	243.83	1.36
LB12	352.02	247.75	1.42
LB13	346.32	245.37	1.41
LB14	334.38	240.89	1.39
LB15	347.63	245.02	1.42
LB16	344.52	243.02	1.42
LB17	356.17	249.71	1.43
LB18	353.43	250.59	1.41
LB19	341.84	245.16	1.39
LB20	334.65	245.25	1.36
LB21	348.43	250.76	1.39
Averages of values	340.37	245.13	1.39

During the experiment the compressive strength was measured four times. The first was done at the beginning of the experiment, the second after the 13th cycle the third after the 20th cycle and the fourth, at the end, after the 36th cycle. On Table 13 and Table 14 are shown the initial results obtained at the beginning and stems from here a information about coefficient of variation (CV) calculating the mean ($\overline{X}$) of each sample and the standard deviation (s). Formulas to calculate the coefficient of variation are presented below (Eq. 12, 13, 14).

$$\overline{X} = \frac{\sum x}{n} \quad \text{(Eq. 12)}$$

$$s = \sqrt{\frac{\sum(x - \overline{X})^2}{n-1}} \quad \text{(Eq. 13)}$$

$$CV = \frac{s}{\overline{X}} \quad \text{(Eq. 14)}$$

Table 13-Initial information (compressive strength and coefficient of variation) of commercial samples.

Sample	Strength(MPa)	Coefficient of Variation (%)
CA1	17.54	7.9
CA2	16.44	9.5
CA3	15.47	5.3
CA4	17.57	3.9
CA5	17.40	3.8
CA6	16.84	9.6
	Total average 16.88	Total CV(%) 4.8

Table 14-Initial information (compressive strength and coefficient of variation) of the lab-samples.

Sample	Strength	Coefficient of Variation (%)
LB1	35.97	0.6
LB2	32.80	10.5
LB3	35.49	7
	Total average 34.75	Total CV(%) 4.9

3.2. Reagents

In this study several types of reagents have been used. For wetting-drying process sodium sulphate anhydrous (Na_2SO_4) and sodium sulphate decahydrate ($Na_2SO_4 \cdot 10H_2O$) were used for preparing 5% sodium sulphate. Magnesium chloride ($MgCl_2 \cdot 6H_2O$), sodium acetate ($CH_3COONa \cdot 3H_2O$), potassium nitrate (KNO_3) and acetic acid (CH_3COOH; 99%) were also used to prepare the buffer solution which was used during measurement of sulphates and here sodium sulphate (stock solution) and barium chloride ($BaCl_2$) were used too. Specifications of these reagents are presented on Table 15.

Table 15-Specifications of sodium sulphate hydroxide and decahydrate, barium chloride dihydrate, sodium acetate trihydrate, magnesium chloride 6-hydrate, potassium nitrate and acetic acid.

Chemical Name	Brand	Linear Formula	Molar Mass (g/mol)	Appearance
Sodium sulphate hydroxide	Carlo Erba	Na_2SO_4	142.04	Solid
Sodium sulphate decahydrate	Alfa Aesar	$Na_2SO_4 \cdot 10H_2O$	322.19	Solid
Barium chloride dihydrate	Scharlau	$BaCl_2 \cdot 2H_2O$	244,28	Solid
Sodium acetate trihydrate	Scharlau	$CH_3COONa \cdot 3H_2O$	136,08	Solid
Magnesium Chloride 6-hydrate	PanReac	$MgCl_2 \cdot 6H_2O$	203.30	Solid
Potassium nitrate	Pronalab	KNO_3	101.11	Solid
Acetic acid	Pronalab	CH_3CO_2H	60.05	Liquid

3.3. Equipment

pH meter

A pH meter is a device that measures the pH of a solution by electrode submerged in the solution The pH value is an expression of the ratio of $[H^+]$ (hydrogen ion concentration) to $[OH^-]$ (hydroxide ion concentration). In this study, pH meter from brand HANNA, the model edge with electrode model HI11310 for measuring pH was used of samples.

Figure 14-pH meter.

Below on Table 16 are shown technical specifications of equipment.

Table 16–Technical specifications of used pH meter.

pH	Range	basic mode: -2.00 to 16.00 pH, -2.000 to 16.000 pH; standard mode: ±1000.0 mV for pH
	Electrode Diagnostics	standard mode: probe condition, response time and out of calibration range
	pH Electrode (included)	HI 11310 glass body pH electrode with 1/8"(3.5mm) connector and 1 m (3.3') cable
	Environment	0 to 50°C (32 to 122°F); RH max 95% non-condensing

Stirring machine

During sulphates measuring by spectrophotometry was used a vortex mixer from brand Heidolph, the model Reax Top for stirring samples.

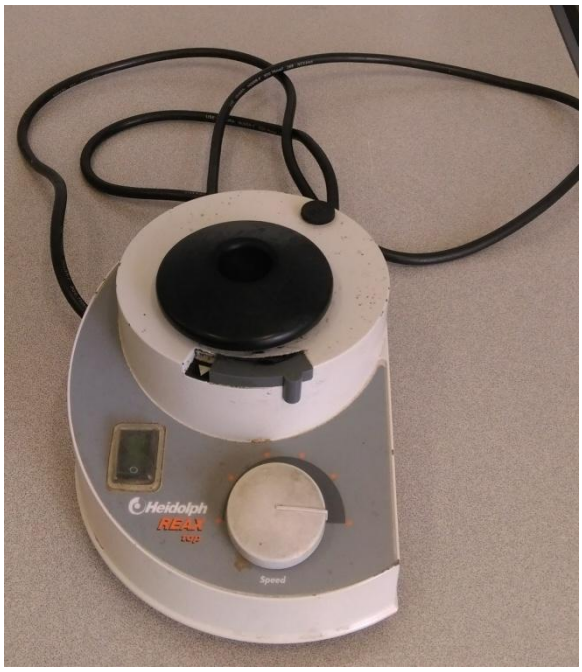

Figure 15-Stirring machine

Technical specifications are shown on Table 17.

Table 17-Specifications of used stirring machine.

Rotation Speed	0 to 2500rpm
Orbit	5mm

Spectrophotometer

UV/Vis technique is being used to determine the absorption or transference of UV/Vis light (180 to 820 nm) by a sample. It can also be used to measure concentrations of absorbing materials based on developed calibration curves of the material. Here is used the spectrophotometer from brand JASCO, the model V-530 which belongs to UV/Visible class. See Figure 16.

Figure 16–Spectrophotometer.

Table 18-Specfications of the spectrophotometer.

Optical system	Double beam, single monochromator with a 1200 grooves/mm concave grating and modified Rowland mount
Spectral bandwidth	2 nm
Wavelength range	190 - 1100 nm
Light sources	Deuterium lamp for UV range (190-350nm), Halogen lamp for VIS range (330-1100nm)

Balance

For weighting small quantity of solids the balance from brand KERN, the model ACS 220-4, has been used.

Figure 17–Balance.

Specifications are listed below on Table 19.

Table 19-Specifications of the balance for weighting reagents

Weighing range (max)	220 g
Stabilization time	3 sec.
Humidity of air	20 ~ 85 % relative
Weighing plate, stainless steel	ø 91mm

Ovens

Wetting-drying process was done using two ovens for drying specimens at 20 °C and 50 °C after 6 hours wetting process. Ovens are from brand Binder and models are FP115 and FP720. Specifications are described on Table 20.

Figure 18-Oven Binder FP115

Figure 19-Oven Binder FP720

Table 20- Specifications of the ovens

Specification	FP115	FP720
Brand	Binder	Binder
Temperature range 5 °C above ambient temperature to [°C]	300	300

Chamber Humidity

Using a chamber humidity, it is possible to set the needed humidity and temperature conditions. Here was used chamber from brand Kide.

Figure 20-Humidity chamber.

Table 21-Specifications of the humidity chamber

Temperature	20±2 °C
Humidity	~90-95%

Compressive test machine

In this study the mechanical property compressive strength was just obtained. For getting information about compressive strength, a compressive test machine from brand Matest with maximum force 3000 KN has been used.

Figure 21–Compressive testing machine.

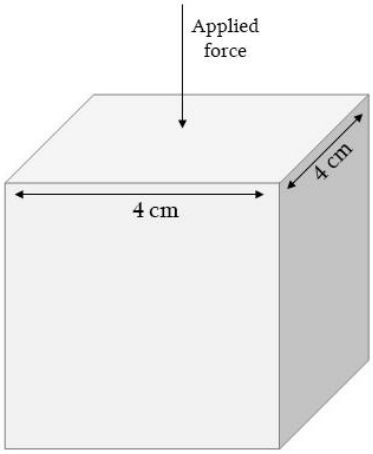

Figure 22- Testing of specimen.

Table 22-Specifications of the compressive machine.

Maximum load capacity(kN)	3000
Platen dimensions(mm)	510×310
Gauges diameter (mm)	300

Digital balance

For weighting specimens a digital balance from brand PJ Precisa, the model Junior 400C-3000D was used.

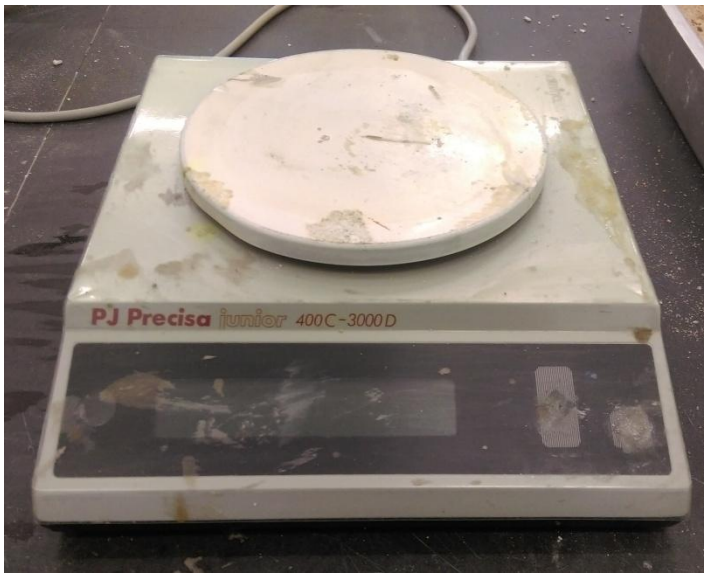

Figure 23-Digital balance.

Digital calliper

The length (L), width (W) and height (H) of prismatic specimens were measured using a digital calliper.

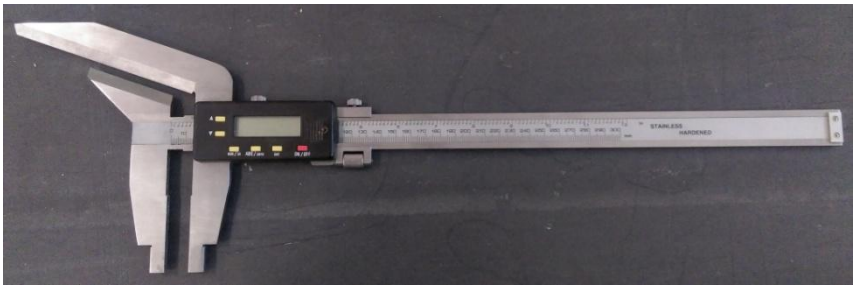

Figure 24-Digital calliper.

3.4. Preparation of sulphate solution

Preparation of sodium sulphate solution 5%

In this study, it was necessary to prepare a sodium sulphate solution with 5% (50 g/L) of solute, to immerse grout samples in it. That means 50 g of sodium sulphate anhydrous (Thenardite, Na_2SO_4) in one litre or 113.4g sodium sulphate decahydrate (Mirabilite, $Na_2SO_4{\cdot}10H_2O$) per litre. First of all, it is needful to weight solid quantity then dissolve it in distilled water and fill up the volumetric flask to 1000 mL. In this study,a total of 23 litres of solution was prepared (Figure 25).

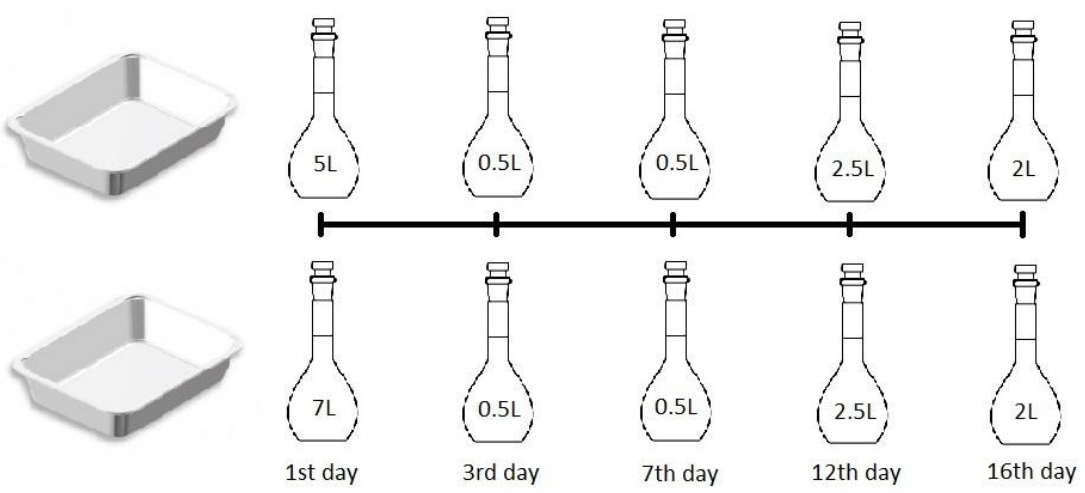

Figure 25-Used sodium sulphate solution during of the experiment.

3.5. Wetting and Drying Cycles

The durability of masonry structures is directly related with environment conditions and considering this, for this study a wetting-drying process was used with total duration of 36 cycles. It is known that, according to Moukwa (1990), cyclic wetting and drying allows for deeper penetration of aggressive ions and according to Yeomans (1994) can lead to corrosion rates 20 times higher than exposure to a continuous salt solution [46]. Before the starting experiment all specimens were dried to constant mass at 105 °C for 18 hours. At the beginning was done 5 cycles using 6 hours for wetting of samples immersed in sodium sulphate solution 5% at room temperature, and 18 hours for drying in the oven of specimens at 20 °C and after each cycle weight measuring was done. At the end of 5th cycle, each group was split into two and then the first half was dried at 20 °C and the second at 50 °C.

3.6. Measurement of Compressive Strength

Compressive strength is the maximum compressive stress that, under a gradually applied load, a given solid material can sustain without shatter. Compressive strength is calculated by dividing the maximum load by the surface area where the force is applied to a specimen. The equation used to calculate the compressive strength is presented below in Eq. 15.

$$f = \frac{F}{A} \quad \text{(Eq. 15)}$$

For the beginning in Eq. 15 is known surface area (A) 4×4cm^2 and after testing by machine applied force (F) measured in kN could be obtained. Compressive test was done four times. The first was done at the beginning of the experiment, the second after the 13th cycle, the third after the 20th cycle and the fourth at the end, after the 36th cycle. Of course every time was indispensable to calculate surface area of sample because after a lot of wetting-drying cycles it loses some quantity of material from surface. At the beginning was planned to carry out test taking 3 samples of each type grout but having a small deviation in test, it went with following numbers of specimens, see on Table 23.

Table 23-Used specimen numbers at each cycle.

Cycle	Specimen A		Specimen B	
0	CA1,CA2,CA3,CA4,CA5,CA6		B1,B2,B3	
13	CA7,CA8 (20 °C)	CA14,CA15(50 °C)	LB4,LB5,LB6(20 °C)	x
20	CA9,CA10 (20 °C)	CA16,CA17(50 °C)	LB7,LB8,LB9(20 °C)	x
36	CA11,CA12,CA13(20 °C)	x	x	x

Each time specimens were divided into two pieces and was done compressive test obtaining two results from one specimen for making average of compressive strength in MPa and to calculate the coefficients of variation (CV) in % (see Table 24 , 25).

3.7. Measurement of pH

Measuring pH is necessary to know the degree of acidity or basicity of a solution. During this study, a sodium sulphate (5%) solution was used for which it was necessary to control the pH. Before using in the wetting experiments obtained solution of sodium sulphate was subjected to pH measuring by HANNA pH meter with glass electrode and the obtained pH was 6.8. Then the same action was done every day with taken samples, which have been taken each day until the 12th cycle. After 12th cycle started each tree days a sample of 20 mL was collected from both solutions (CA, LB), a total of 40 samples, 19 from CA and 21 from LB. Taken samples were kept in a fridge but before

measuring pH the temperature of solution was allowed to be close to room temperature (approximately 20 °C).

3.8. Measurement of sulphate concentration

Having samples was necessary to determine quantity of sulphate (SO_4^{2-}).The sulphate quantity was determined using a spectrophotometer. First of all, a calibration curve was made following the turbidimetric method. Knowing that the sulphate from experiment have concentration higher than 10mg/L it was prepared a buffer solution by dissolving 15 g magnesium chloride ($MgCl_2 \cdot 6H_2O$), 2.5 g sodium acetate ($CH_3COONa \cdot 3H_2O$), 0.5 g potassium nitrate (KNO_3), and 10 mL acetic acid (CH_3COOH; 99%) in 250 mL distilled water and making up to 500 mL, thereafter a stock solution of anhydrous sodium sulphate (Na_2SO_4) was prepared dissolving 0.1479 g in 750 mL distilled water and diluted up to 1000 mL which means that in this solution is contained 100 mg sulphate per litter (1 mL=100µg SO_4^{2-}).For this measurement is known that sodium sulphate reacts with barium chloride and forms barium sulphate that precipitates, see Eq. 16.

$$Na_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2NaCl \qquad \text{(Eq. 16)}$$

The absorbance of the barium sulphates formed has been measured by a spectrophotometer at 420 nm wavelength and the sulphates ion concentration has been determined by comparison of the read of absorbance value each sample with a standard curve. Calibration curve was obtained by preparing series of standards 10, 20, 30, 40, 50 and 100 mg/L (Figure 26).

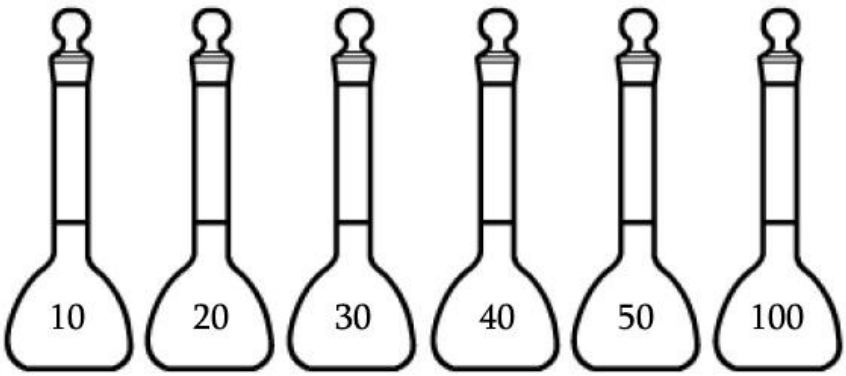

Figure 26-Series of sulphate standard with concentrations from 10mg/L to 100mg/L

These standards prepared as follows: 10mL of standard sulphate solution was filled to the first volumetric flask, 20 mL to the second, 30 mL to the third, 40 mL to the fourth, 50 mL to the fifth and 100 mL to the sixth. All five flasks were topped up to 100 mL mark with distilled water. Starting the measuring procedure for sulphates concentration determination with spectrophotometer first was done auto zero afterwards blank. Auto zero was done with empty chamber of equipment and then for blank were used two glass cuvettes (washed with distilled water) filled with distilled water and both situated to the chamber. After these two steps was measured the absorbance of sulphate standards doing next steps. Mix 10ml of distilled water with 2 mL of buffer solution and a small spoon of $BaCl_2$ and stirring on the stirring machine 60 seconds. All these all steps were done for measuring sulphate concentration of samples too. But in this study the concentration of sulphate in the sample solution was quite concentrated compared with stock solution, therefore it was diluted 2500 times in order to be in the range of calibration curve. It was taken 4 μL of sample and mixed with 10 mL distilled water and then again 2 mL of buffer solution and a small spoon of $BaCl_2$ and stirring on the stirring machine 60 seconds. Then from calibration curve was taken slope value and then concentration of samples were calculated.

3.9. Measurement weight and dimensions of prism grouts.

During wetting-drying process, it is possible to have some changes in dimensions and weight of specimens therefore research was done on how the weight and sizes change in time of it. Weight loss and change in compressive strength can be a good indicator of the degree of the aggravation of sulphate attack [47]. Measurement of the weight was done every day, started from the beginning until the end but the dimensions were measured the first time at the beginning, the second after 13^{th} cycle, the third after 20^{th} cycle and the fourth at the end after 36^{th} cycles like it was done for compressive strength test during the same cycles.

4. Chapter 4 – Results

4.1. Compressive Strength

Results of compressive test of specimens are shown in Figure 27 and Figure 28 and in more detail the compressive test and coefficient of variation (CV, %) are shown in Table 24 and 25. The samples have been dried at 20 °C until 6th cycle then one half continued at 20 °C and the second half at 50 °C.

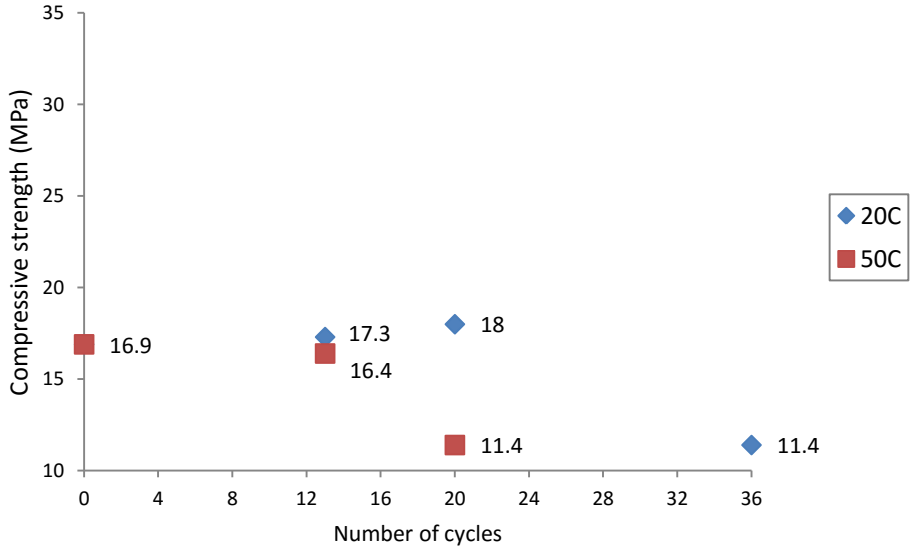

Figure 27- Compressive test results of commercial specimens.

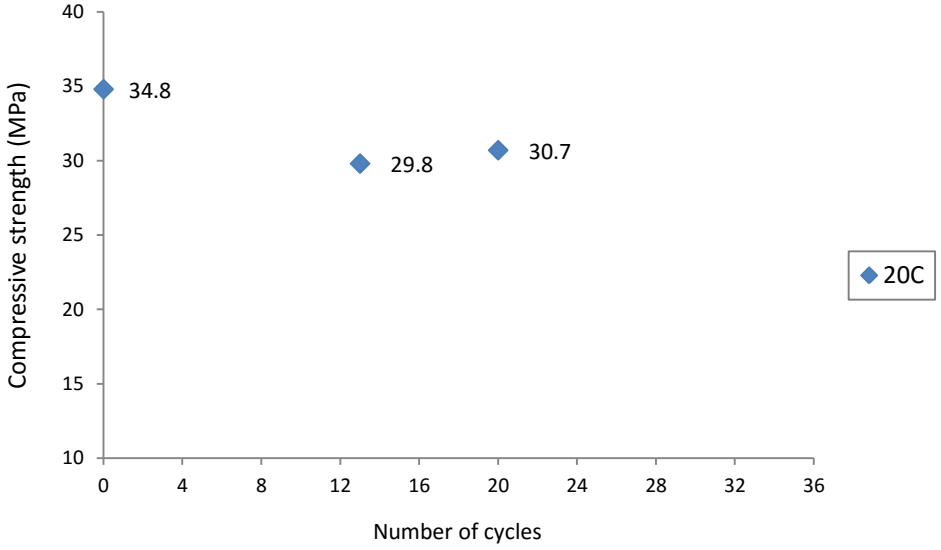

Figure 28-Compressive test results of lab-specimens.

The results of commercial specimens of compressive test done are represented in Figure 27. The first point is the result of the initial strength of specimens then after 5th cycle the specimens (CA, LB) were split into two parts, one part of them started to dry at 20

°C (blue points) and other part at 50 °C (red points) . Up to 13th cycle the results of strength of specimens at 20 °C and 50 °C are comparable and they were close together. After 20th cycle the specimens dried at 50 °C lost their strength instead at 20 °C which shows a bit increase of strength. But after this cycle specimens at 50 °C started breaking-down not resisting until the end of the experiment. But at 20 °C they persisted until the end and could carry out a test after 36th cycle. As shown, the result has decreased compared with a result of 20th cycle obtained. Figure 28 shows information about the strength of lab-specimens. The first point is the initial strength. At 13th cycle point for 20 °C shows that strength is increased but the 20th cycle point shows a bit more increased strength compared with 13th cycle strength. And about 50 °C it could not carry out compressive test for LB specimens even after 13th cycle because during experiment B grout was not resistant to sulphate attack compared with CA grout and they started to brake-down earlier (after 11th cycle) than commercial grout specimens. That is why there is no information on Figure 28 about 50 °C degree.

Table 24-Compressive test results of commercial specimens.

Time and temperature	Specimen	Strength(MPa) and coefficient of variation (CV, %) of each specimen	Total average(MPa) and (CV, %) of the specimens
Initial	CA1 CA2 CA3 CA4 CA5 CA6	17.54(7.9) 16.44(9.5) 15.48(5.3) 17.58(3.9) 17.40(3.8) 16.84(9.6)	Average 16.88 CV 4.8
13th cycle (20 °C)	CA7 CA8	18.72(9) 15.89(12.3)	Average 17.30 CV 11.5
13th cycle (50 °C)	CA14 CA15	16.38(2.3) 16.40(12.1)	Average 16.39 CV 0.1
20th cycle (20 °C)	CA9 CA10	16.75(13.8) 19.21(6.4)	Average 17.97 CV 9.6
20th cycle (50 °C)	CA16 CA17	10.75(24.4) 12.05(21.1)	Average 11.4 CV 8
36th cycle (20 °C)	CA11 CA12 CA13	10.87(33.1) 11.96(6) 11.25(22.2)	Average 11.35 CV 4.8

Table 25-Compressive test results of lab-specimens.

Time and temperature	Specimen	Strength(MPa) and coefficient of variation (CV, %) of each specimen	Total average(MPa) and (CV, %) of the specimens
Initial	LB1 LB2 LB3	35.98(0.6) 32.81(10.5) 35.49(7)	Average 34.75 CV 4.9
13th cycle (20 °C	LB4 LB5 LB6	30.67(7.7) 26.26 (4.4) 29.79(2.7)	Average 28.9 CV 8
20th cycle (20 °C)	LB7 LB8 LB9	31.58(12.5) 31.16(3.4) 29.44(2.9)	Average 30.72 CV 3.6

There is information about coefficient of variation (CV, %) from Table 24 and Table 25, which show that the values are more constant for LB grout specimens then for CA grout.

4.2. pH

The pH value states the relative quantity of hydrogen ions (H^+) contained in a solution. Below Figure 29 and Figure 30 show the pH results of commercial specimens in solution (CA) and for lab-specimens (LB) solution approximately.

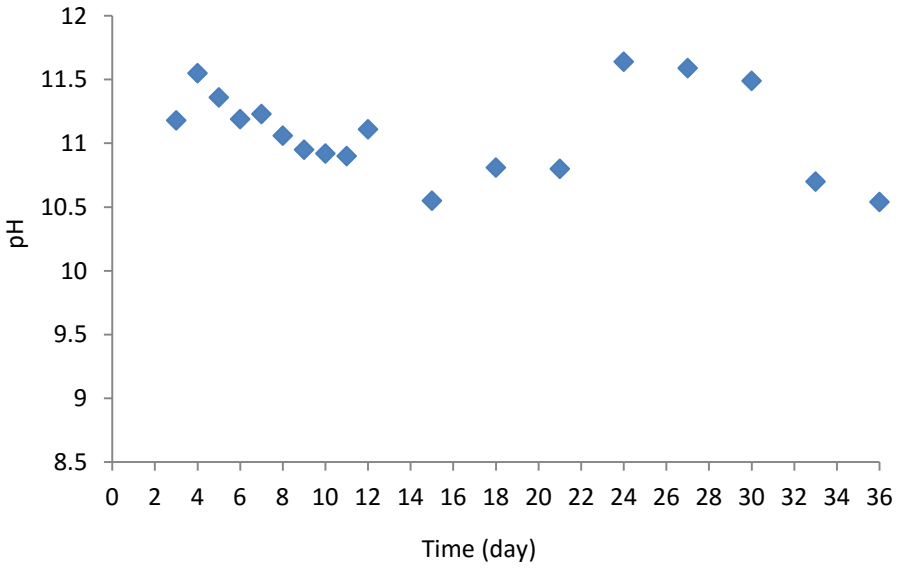

Figure 29-pH of commercial specimens solution.

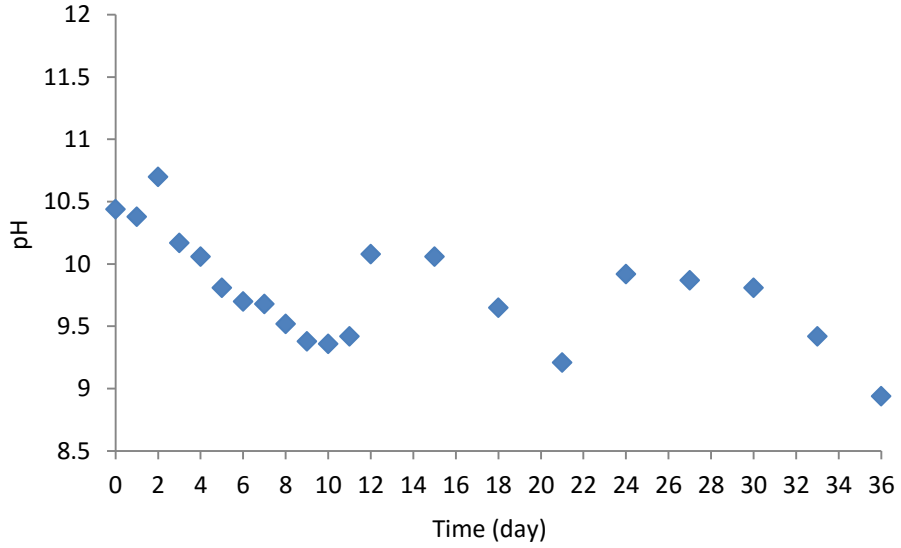

Figure 30-pH of lab-specimens solution.

For Figure 29 it is necessary to mention that information for the first and second days is missing because samples have not been collected. It can be observed that after immersion of samples into the sodium sulphate solution, the pH of both solutions are increased until second day (initial pH of solution is 6.8). It started to increase because of the amount of alkali (Na, K) being in pore solution inside of the specimens and they increased pH value permeating to the solution. In commercial specimen's case, pH has increased until 12 but for solution of lab-specimens it has increased to 10.7, which means that LB grout is less alkaline. Due to concrete carbonation, the pH value of pore solution in the concrete will decrease. Carbonation is the result of the dissolution of CO_2 in the concrete pore fluid and this reacts with calcium from calcium hydroxide and calcium silicate hydrate to form calcite ($CaCO_3$)[48]. When all unreacted $Ca(OH)_2$ has been removed, the Ca/Si ratio will decrease again [44]. Then for 3rd day was added more solution into containers which made change for CA solution which is a bit increased but for LB solution nothing changed. They began to diminish until 11th day then again there is a gain for both solution because of additional solution. But here is needful to point out that the gain for LB solution is higher than CA solution. From 12th day specimens from LB started broke-down what could help to amplify the value of pH. And the same thing for 24th day, but here there is not factor of additional solution,

here just there are broken specimens during that days (Table 26). In general LB grout could provide less value of pH of solution compared with CA grout.

4.3. Sulphate concentration

As it was mentioned above prepared sodium sulphate solution has been divided into two parts: one for commercial specimens (CA) and the other one for lab-specimens (LB) and turbidimetric method has been used to find out what is happening with concentration of solution after immersion of specimens into the solution. At first calibration curve for six standards from prepared stock solution was drawn (Figure 31).

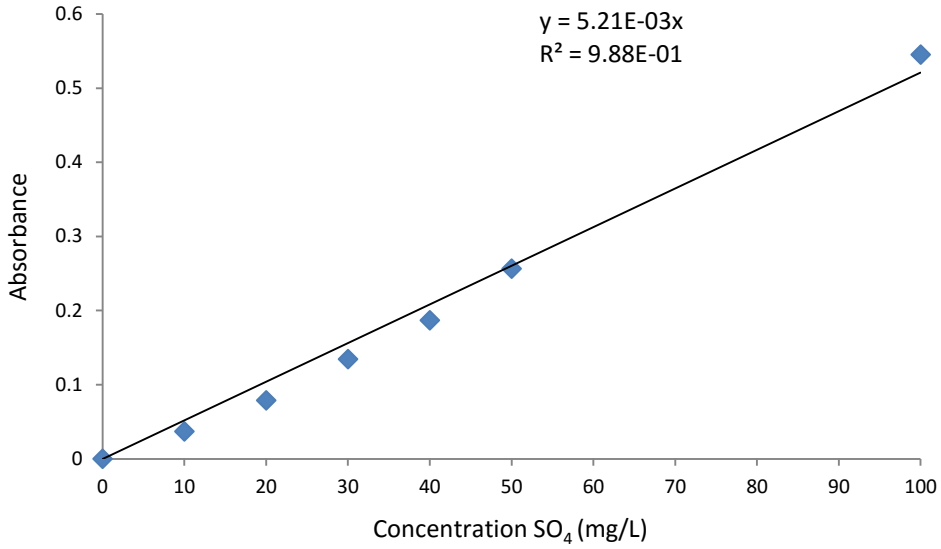

Figure 31-Calibration curve of sulphates using turbidimetric method.

It is noteworthy that the correlation value should be close to 1. It can be observed that the correlation value is 0.988 (Figure 31). Afterwards, information about the concentration of sulphates was obtained from the samples which were taken each day until the 12th cycle then after 12th cycle each tree days (Figure 32 and Figure 33).

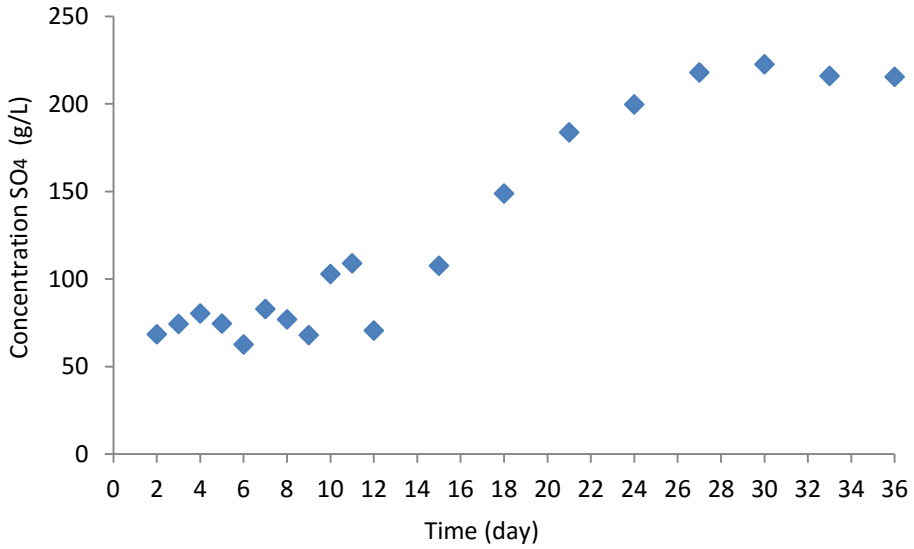

Figure 32-Sulphate concentration changes in solution of commercial specimens during the time.

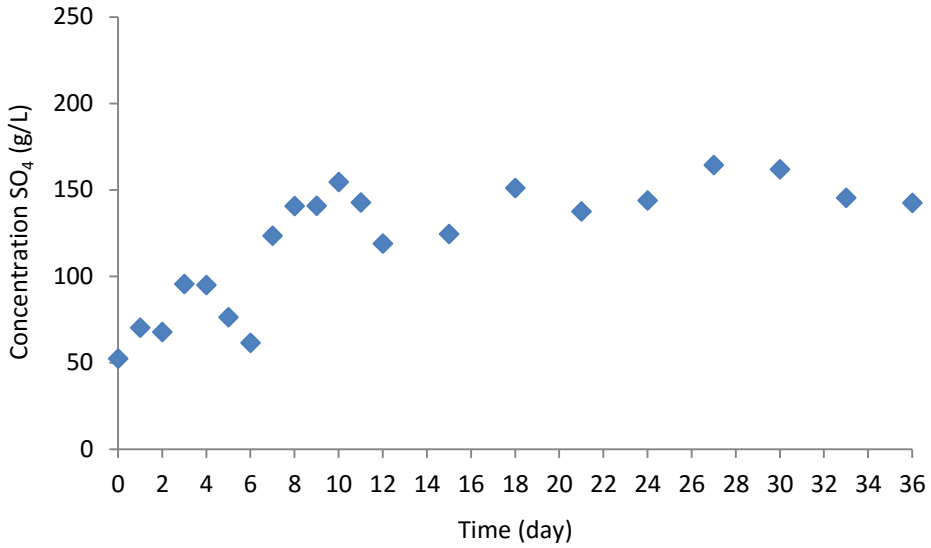

Figure 33-Sulphate concentration changes in solution of lab-specimens during the time.

Figures of sulphate concentration show that sulphate concentration increases from the first day until the end. During these days it managed to grow so that the added solution was decreasing its value during 3rd, 7th, 12th and 16th days. It can be observed that from the beginning the sulphate concentration of LB solution increased earlier than sulphate concentration of CA solution. As it has been mentioned in [49], ingress sulphate ions react with AFm phases, generally calcium alumino monosulphate, making sulphate concentration increased in the solution. This means that lab-specimens are penetrable and react with sodium sulphate more quickly than commercial specimens and it helped to increase sulphate concentration faster.

4.4. Weight

In this study was used wetting-drying cyclic process. It is known that during this cyclic process the specimens lose their weight due to weathering phenomenon. In order to evaluate this phenomena the weight of each grout samples were measured every day and the total average weight of all specimens was calculated for each day (Figure 34 and Figure 35).

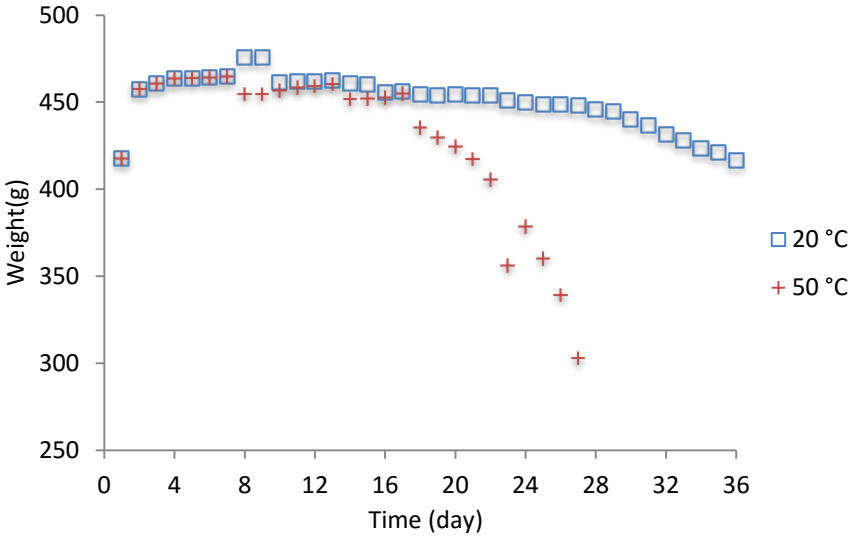

Figure 34-Weight changes of commercial specimen at 20 °C and 50 °C.

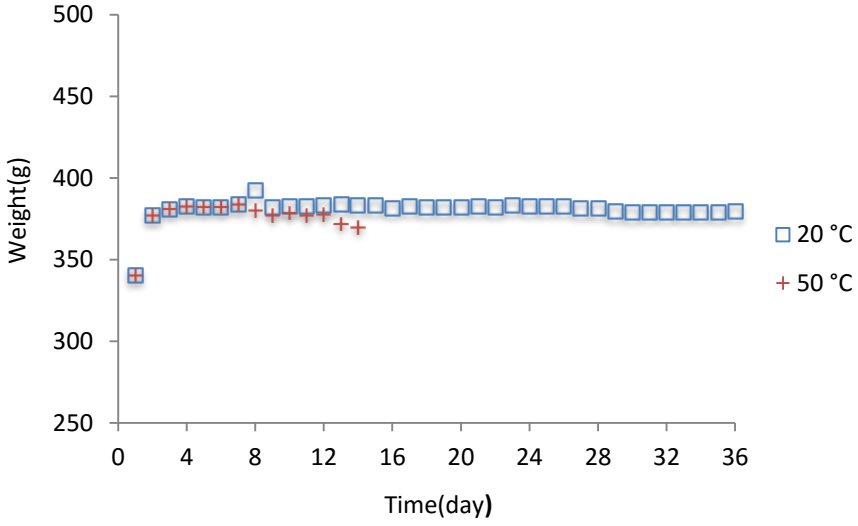

Figure 35-Weight changes of lab-specimen at 20 °C and 50 °C.

Results are calculated based on obtained weights information and their average for each day. About phenomena of degradation in the surface (loss of material) of samples during the test is accepted already a long time. Degradation generally happens when sodium sulphate (Na_2SO_4) reacts with calcium hydroxide ($Ca(OH)_2$) to produce gypsum

($CaSO_4 \cdot 2H_2O$). Gypsum in its turn reacts with aluminate unhydrated tricalcium aluminate (C_3A) to produce ettringite which makes pressure inside of pores. Ettringite is stable in this study used both at 20 °C degree and 50 °C. For the degradation phenomena two types of grouts have been compared which were prepared beforehand. Based on the obtained figures of weight changes of specimens it can be summarized that first points are initial weight of specimens which have increased significantly for all specimens after one day and until the 6th and 7th days the weights have increased due to salt supply from solution then they start to decrease because of degradation. It should be noted that at the 7th day there are gains of weights at 20 °C because of problem which happened in the oven. The required temperature was 20 °C but the temperature in the oven was 15 °C for that day. CA specimens dried at 20 °C degree have relatively constant weight until 23th whereupon they started to lose more material from surface resulting in more lost weight. The LB grout at 20 °C degree shows excellent stability throughout all the experiment. For 50 °C degree case was the worst because the CA specimens were stable until 17th day and then started to decay losing sufficient material from surface (Figure 36) to the solution which made it muddy (Figure 37) and the final specimen was broken at 26th day. But LB specimens even starting from the 7th day had a bit damage on the corners but not as in the case of CA. However, they broke 12 days earlier than CA specimens because of not being enough resistant to sulphate attack.

4.5. Damage

Below in Figure 36 the evolution of damages for two types (CA and LB) of grout at 20 °C and 50 °C degree is shown. As mentioned above specimens lose weight due to degradation during experiments and as a result having lost of materials which penetrate to the solution making it more turbid day after day. For solution of CA grout the turbidity is more than for LB grout solution, see Figure 37.

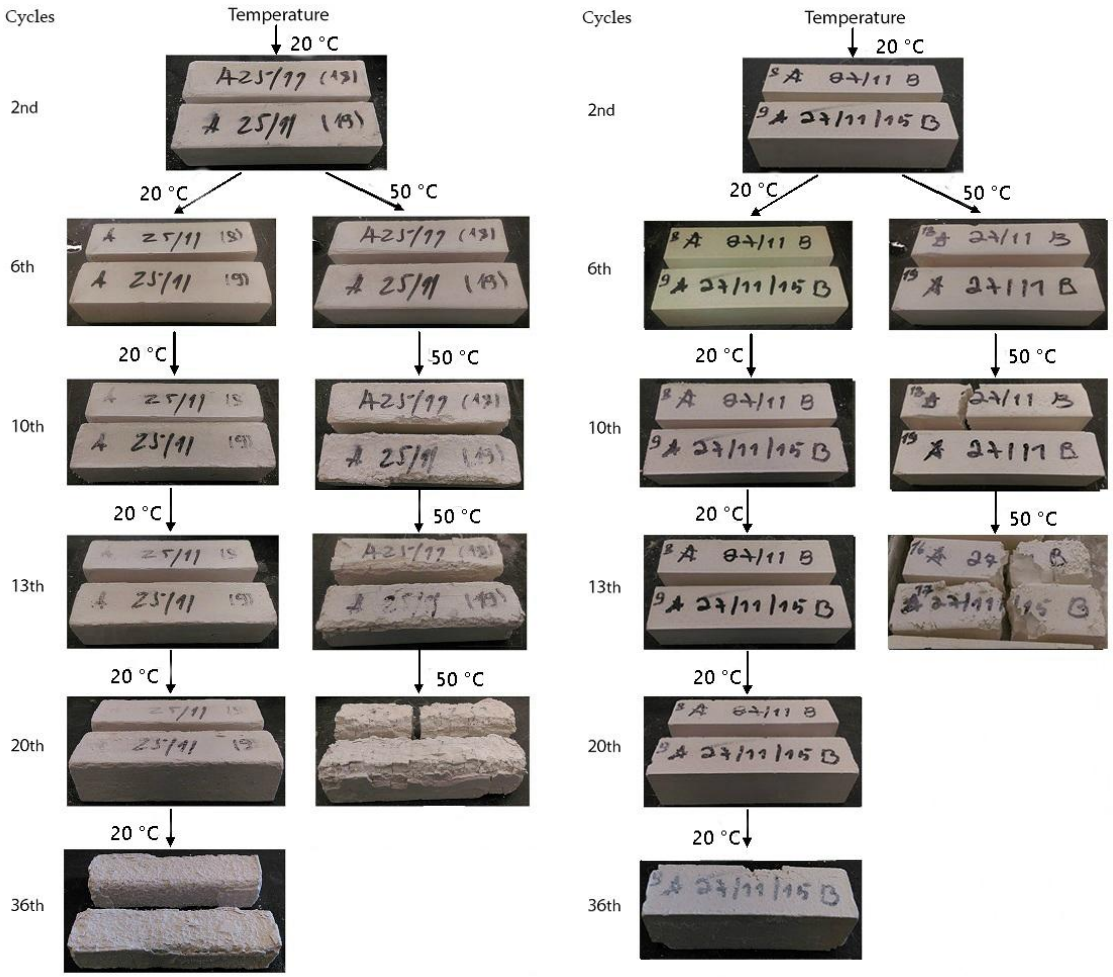

Figure 36-Evolution and damages of commercial specimens CA (left) and lab-specimens LB (right) subjected wetting-drying cycles.

According to Figure 36 at 20 °C it should be noted that the CA grout's surface has suffered destruction but the LB grout is not the same because it just has little damage on some points of the corners. The same can be observed at 50 °C that the LB grout specimens do not have much losses on the corners instead CA grout specimens but because of not being resistant to the break-down earlier at these two temperatures (20 °C and 50 °C) .

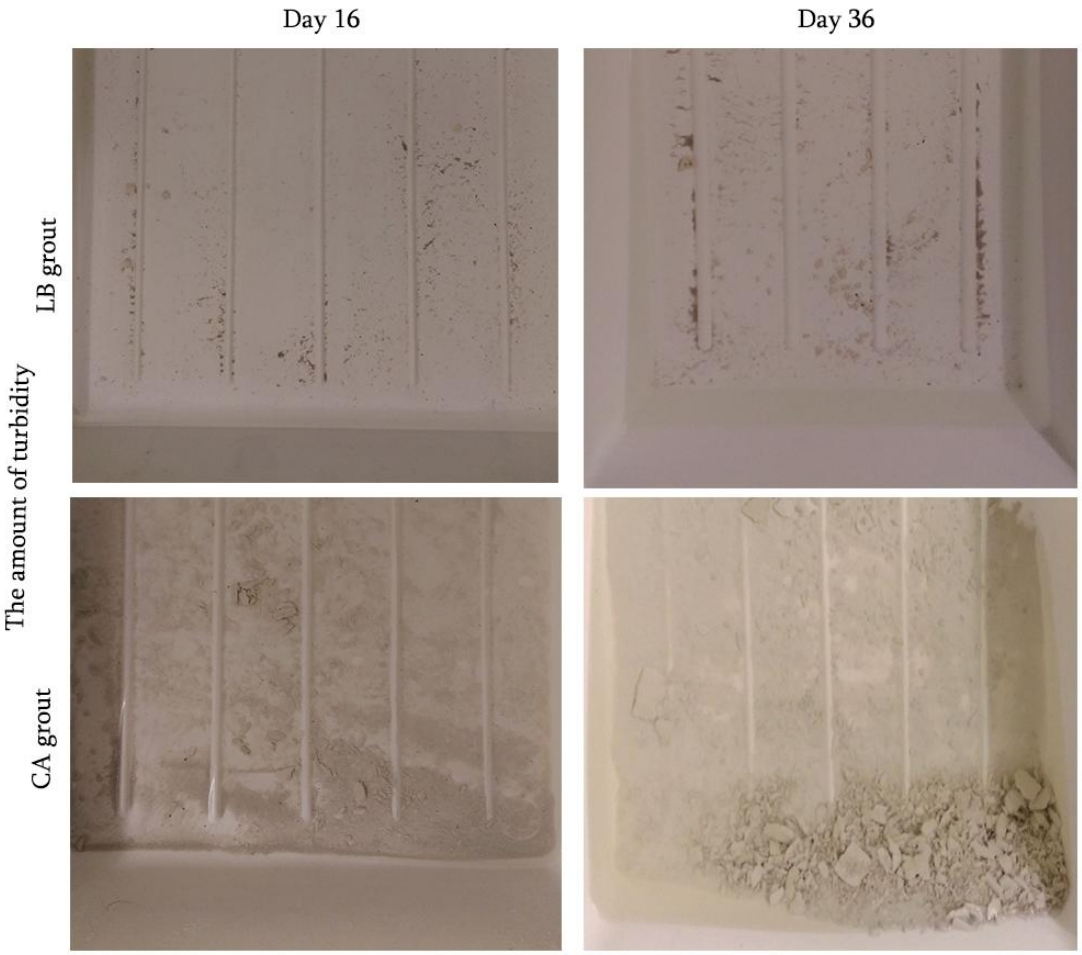

Figure 37-Solution in a containers and the amount of turbidity during the experiment

5. Chapter 5 - Conclusions

5.1. Conclusions

Influences of environment cause damage to masonry structures and in order to repair them lime-based grouts with grouting techniques can be used. This research was based on wetting-drying process with sodium sulphate solution. Two types of lime-based grouts were prepared (CA and LB) in order to evaluate their chemical resistance. Sulphate ions in soil, ground water and sea water may cause deterioration of masonry structures due to factors such as type of cement, sulphate concentration and the period of exposure. Thus, based on the all results it can be summarized that the commercial available grout was more chemically resistant. However, laboratory formulated grout (LB) has its advantages. It has two times more compressive strength (34.75 MPa instead 16.88 MPa) and provides less pH value of the solution(max. 10.44 instead of 12.02) after immersing specimens into solution. As mentioned above the main problem of sulphate attacks is the permeability which is closely related to w/b ratio. If w/b ratio is higher the material has probably more porous (voids) and it is less compact. Hence, the LB grout having higher ratio of w/b (0.54 instead of 0.35) could not to achieve sufficiently low porosity even using admixtures. Sulphate solution could permeate faster into LB grout than the CA grout and produce ettringite or gypsum providing faster breakdown. For the preparation of LF grout metakaolin has been used which contains a hefty portion of aluminium oxide (Al_2O_3). On the one hand it could increase compressive strength of the LB grout. but on other hand improving amount of aluminium oxide helped to form ettringite. And about values of sulphate concentrations of both solutions should be pointed out that for LB solution it increased faster than CA solution. According to the third day's concentration values for LB solution it was 95.4g/L but for CA solution it was 74.4 g/L. It can be assumed again that LB specimens had much porosity and it reacted faster with sulphate solution. Here it is important to mention a factor of error, because for measurement the sulphates samples were diluted 2500 time which is too much.

5.2. Limitation and Future works

During this study evaluation of chloride attack resistance should be performed, but it was not possible to carry because of less number of specimens and also short time. For future investigation it will be good to carry out the experiment of chloride attack and to do microscopic examination which will help for more precise conclusion.

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Appendix

Daily weight(g) changes of specimens are shown below on Table 26.

Days / Number	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
A1	416	T																																			
A2	418	T																																			
A3	415	T																																			
A4	420	T																																			
A5	421	T																																			
A6	420	T																																			
A7	433	463	470.8	472	473	473	474	486.2	476	474	474	475.1	476	473.9	474	T																						
A8	410	460	467.8	469	470	470	471	486.1	472	470	471	471.5	473	463.5	463	T																						
A9	422	451	451.7	454	454	456	455	470.3	456	456	456	456.8	458	456.8	457	456	456	454.8	455	455.5	454.5	454.5	T														
A10	420	453	455.3	456	458	458	461	472.4	459	459	459	459.8	460	459	458	459	459	458	458	457.9	457.6	457.6	T														
A11	408	443	450.2	455	452	463	453	466.4	456	454	454	454.3	455	454.6	455	455	455	453.7	453	454.1	453.8	453.1	453	452	451	452	451	450.3	449	438.8	431	421.41	418.1	417	412	410
A12	405	449	451.3	453	453	454	454	468.6	456	455	455	455.8	456	455.7	456	455	455	454.3	454	454.6	454.2	453.8	453	452	452	450.5	450	448.2	447	442.1	438	434	431.2	428	421	415
A13	418	458	458.7	461	465	463	466	481.2	461	463	462	461.1	460	455.3	454	454	455	450.3	450	449.9	449.4	449.1	447	446	444	444	443	431.8	437	428.1	426	422	420.7	419	416	403
A14	423	462	461.9	464	466	466	467	456.3	456	457	458	458.9	461	451.6	450	T																					
A15	420	453	453.3	460	461	463	462	453.3	454	454	456	456.7	457	449.3	451	T																					
A16	409	455	457.6	461	465	468	468	457.6	459	460	463	464.7	467	460	460	459	462	451.5	446	443.4	439	428	T														
A17	419	457	464.8	463	468	465	468	452.9	452	455	457	456.4	456	448	450	451	453	432.3	426	413.3	406.9	395.3	T														
A18	425	460	468.1	467	472	469	472	457.9	458	460	461	463.5	464	453.9	454	454	458	441.7	438	436.4	423.3	x															
A19	427	465	468	467	469	469	469	456.6	457	459	462	461.8	463	458.5	458	457	458	438.9	433	425.8	418.7	405.4	x														
A20	411	461	468.1	467	472	470	473	454.7	455	458	460	462.3	464	452.6	455	456	459	428.6	425	423.8	416.3	410.3	323	x													
A21	414	455	455	457	459	459	461	447.3	446	446	449	449.7	452	439.6	440	439	441	416.5	411	403.5	399.4	389	x	379	360	339.2	303	x									
B1	339	T																																			
B2	327	T																																			
B3	331	T																																			
B4	337	374	376.3	377	377	378	378	387.6	379	379	378	379	382	380.3	380	T																					
B5	332	377	381.5	381	381	382	383	395.3	383	382	383	382.8	386	384.1	384	T																					
B6	343	389	392.6	394	393	395	394	405.1	394	394	395	395.2	396	397.3	396	T																					
B7	331	363	366.8	366	367	368	368	379.3	368	369	369	370.9	369	363.4	363	370	371	369.3	369	369.9	369.7	369.5	T														
B8	334	375	377.6	381	383	381	383	382.8	380	381	382	380.9	381	381.4	381	381	383	382.1	382	382.1	381.9	381.8	T														
B9	334	373	379.4	383	384	383	385	385.4	383	383	384	384.2	385	384	384	384	385	385.2	384	384.7	385.1	384.7	T														
B10	343	373	379.2	380	381	381	382	391.3	383	383	383	384.3	383	382.6	383	383	384	382.9	383	383.9	383.9	383.5	383	x													
B11	333	372	377.5	380	381	381	382	391.3	382	381	383	380.7	382	381.9	381	382	383	381.8	382	382.1	382.4	381.7	382	381	381	381.2	381	381.2	379	378.9	379	379	379	379	379	379
B12	352	382	384.7	386	387	387	388	396.8	383	388	389	388.1	390	388.7	383	383	391	390.3	390	390.4	390.4	390	384	384	384	383.4	x										
B13	346	387	388.6	390	390	390	391	382.4	383	383	382	382.2	381	x																							
B14	334	376	376.5	378	377	379	379	370.2	371	381	371	370.7	370	370.3																							
B15	348	377	379.5	381	381	382	382	394.5	374	374	374	376	373	369.3																							
B16	345	370	374.3	376	376	377	377	396.7	370	370	370	372.2	360	x																							
B17	356	384	383.5	391	382	382	382	384.2	385	385	385	385.2	384	x																							
B18	353	385	390.7	393	394	383	393	384.6	385	386	386	385.1	x																								
B19	342	370	373.9	378	376	377	377	363.7	369	369	368	369	360	x																							
B20	335	377	382.2	384	384	384	384	376.4	377	377	376	376.5	374	x																							
B21	348	382	386.6	387	387	388	388	379.7	380	380	380	379.4	x																								

Table 27 and Table 28 are shown bulk density (g/cm^3) information obtained during the whole experiment. Calculation was done using Eq. 11.

Table 27-Bulk density of commercial specimens.

Specimen	initial	13th cycle	20th cycle	36th cycle
CA1	1.65	T	x	x
CA2	1.68	T	x	x
CA3	1.66	T	x	x
CA4	1.65	T	x	x
CA5	1.69	T	x	x
CA6	1.69	T	x	x
CA7	1.72	1.88	x	x
CA8	1.63	1.87	x	x
CA9	1.72	1.87	1.88	T
CA10	1.66	1.84	1.86	T
CA11	1.66	1.86	1.86	1.78
CA12	1.64	1.86	1.87	1.75
CA13	1.70	1.86	1.86	1.72
CA14	1.70	1.79	T	x
CA15	1.69	1.81	T	x
CA16	1.63	1.82	1.75	x
CA17	1.69	1.81	1.70	x
CA18	1.68	1.79	X	x
CA19	1.73	1.85	X	x
CA20	1.64	1.80	1.80	x
CA21	1.69	1.75	1.71	x

Table 28-Bulk density of lab-specimens.

Specimen	Initial	13th cycle	20th cycle	36th cycle
LB1	1.37	T	x	x
LB2	1.38	T	x	x
LB3	1.36	T	x	x
LB4	1.38	1.55	T	x
LB5	1.35	1.56	T	x
LB6	1.40	1.58	T	X
LB7	1.38	1.50	1.50	T
LB8	1.36	1.56	1.55	T
LB9	1.38	1.56	1.58	T
LB10	1.39	1.55	1.55	x
LB11	1.36	1.55	1.54	1.53
LB12	1.42	1.54	1.54	x
LB13	1.41	x	x	x
LB14	1.39	x	x	x
LB15	1.42	x	x	x
LB16	1.42	x	x	x
LB17	1.43	x	x	x
LB18	1.41	x	x	x
LB19	1.39	x	x	x
LB20	1.64	x	x	x
LB21	1.69	x	x	x