Universidade de Aveiro Departamento de Geociências
2018

FÁBIO ANDRÉ CANCELAS MATOS

MELHORAMENTO DE PROPRIEDADES TÉRMICAS DE UMA ARGAMASSA DE CAL POR ATIVAÇÃO ALCALINA

IMPROVEMENT OF A LIME-BASED MORTAR'S THERMAL PROPERTIES USING ALKALINE ACTIVATION

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Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Geomateriais e Recursos Geológicos, realizada sob a orientação científica do Doutor Fernando Joaquim Fernandes Tavares Rocha, Professor Catedrático do Departamento de Geociências da Universidade de Aveiro e coorientação do Doutor Luís Filipe Mariz de Matos Ferreira, diretor de pesquisa e desenvolvimento de Domínio Do Ligante – Argamassas Tradicionais Pré-doseadas Lda.

o júri

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agradecimentos

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palavras-chave

Ativação alcalina, cimento de portland, aluminosilicato, hidróxido alcalino.

resumo

Esta dissertação foi desenvolvida como proposto pela empresa Domínio Do Ligante – Argamassas Tradicionais Pré-doseadas Lda. em cooperação com o Departamento de Geociências da Universidade de Aveiro, concedendo ao autor a conclusão do segundo ciclo de estudos em Geomateriais e Recursos Geológicos pela instituição supracitada.

O objetivo principal deste estudo é melhorar as propriedades de isolamento térmico, nomeadamente a condutividade térmica, da argamassa de cal ‘DDL.ECM Projeção’ procedendo à ativação alcalina da mesma ao invés da hidratação tradicional. Como objetivo secundário pretende-se avaliar ainda a viabilidade técnica do produto desta experiência no que diz respeito a propriedades mecânicas, absorção por capilaridade e resposta à dissolução ácida.

Para cumprir estes objetivos, quatro ensaios laboratoriais foram levados a cabo. Em cada ensaio, um grupo de controlo e dois grupos de teste foram preparados misturando a argamassa com soluções aquosas de hidróxido de sódio e hidróxido de potássio, respetivamente, a uma concentração de 3 molar, sendo que o grupo de controlo foi apenas hidratado com água. As misturas foram então aplicadas em moldes e deixadas a curar até ao desmolde. Após isto, os espécimes seriam testados de acordo com os parâmetros em causa.

Os quatro ensaios do procedimento experimental não foram capazes de produzir um suficiente número de espécimes viáveis para testar dada a fragilidade ou inconsistência dos mesmos. Estes resultados tornam impossível a medição das propriedades em estudo para resolução da questão problema, sendo o objetivo principal da dissertação inconclusivo.

Cumpre-se, no entanto, o objetivo secundário afirmando a inviabilidade técnica da ativação alcalina da argamassa DDL.ECM Projeção pelos métodos utilizados neste procedimento. Conclui-se que o conteúdo de CaO da argamassa é inadequado para a realização deste tipo de processo quando comparado com o muito inferior conteúdo quer de SiO_2 quer de Al_2O_3; não permitindo a criação de um sistema híbrido estável.

keywords alkali activation, ordinary portland cement, aluminosilicate, alkali hydroxide.

abstract

This dissertation was developed as proposed by company Domínio Do Ligante – Argamassas Tradicionais Pré-doseadas Lda. In cooperation with the Department of Geoscience of University of Aveiro, granting the author the conclusion of the second cycle of studies in Geomaterials and Geological Resources by the aforementioned institution.

The main goal of this study is to improve the thermal insulation properties, mainly thermal conductivity, of lime-based mortar 'DDL.ECM Projeção' through alkali activation instead of traditional hydration. As a secondary objective, the study intends to evaluate the technical viability of the product of the experiment in respect to its mechanical properties, capillary absorption and response to acid dissolution.

To fulfill these goals, four laboratory trials took place. In each trial, a control group and two test groups were prepared by mixing the mortar with aqueous solutions of sodium hydroxide and potassium hydroxide, respectively, at a concentration of 3 molar, with the control group being hydrated with water only. The mixtures are then cast in molds and left to cure until demolding. After this, the specimens are to be teste according to the parameters of the study.

The four experimental procedure trials were incapable of producing a sufficient number of viable specimens for testing given their fragility and inconsistency. These results rend impossible de measuring of the properties at study in order to resolve the problem question, as such, the main goal of the dissertation is inconclusive.

The secondary goal, however, is achieved, affirming the technical unviability of alkali activation of DDL.ECM Projeção by the methods employed in this procedure. It is concluded that the CaO content in the mortar is inadequate for this type of process when compared to the inferior content of either SiO_2 and Al_2O_3; not allowing the formation of a stable hybrid system.

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1 INTRODUCTION

1.1 Scope

The current dissertation stands as the result of a curricular internship born from the cooperation between Universidade de Aveiro and Domínio Do Ligante – Argamassas Tradicionais Pré-doseadas Lda. (DDL Arg). The latter party approached the University to propose a partnership in the development of this project, taking the initiative to offer an internship during which research would be conducted that would benefit both parties.

This internship was carried out in the scope of the curricular unit ‘Dissertação/Projeto’ of the second year of the second cycle of studies in ‘Geomateriais e Recursos Geológicos’ in the Department of Geoscience of Universidade de Aveiro, with the goal of obtaining a master’s degree in said scientific area.

The project upon which this internship was based, and which stands as the focus of this dissertation, was developed at Universidade de Aveiro under the guidance of Prof. Fernando Joaquim Fernandes Tavares Rocha, Full Professor at the Department of Geoscience of Universidade de Aveiro, and Doctor Luís Filipe Mariz de Matos Ferreira, head of Research and Development at DDL Arg.

Throughout the course of this internship, and by planning and executing experimental procedures in search of an answer to the problem question, several qualities and skills were developed and honed such as knowledge of cementitious materials, understanding of laboratory methodologies, experience in bibliographical research, and perhaps the most important aspect of this project, the capacity to approach the subject with a multidisciplinary view.

1.2 DDL Arg

Domínio Do Ligante – Argamassas Tradicionais Pré-doseadas Lda., henceforth referred to as 'DDL Arg', specializes in research and development as well as production of traditional lime mortars for rehabilitation and restoration of ancient and historic buildings as well as modern day construction. DDL Arg offers a wide range of standard and customizable solutions for mortar products based on the structural and decorative characteristics required for each specific application (Figure 1.2-2.1.1-1).

DDL Arg's product line ECM 'Evolution Cork Mortar' distinguishes itself, and the company, from the competition for containing a significant portion of ground cork in its composition. This cork is not only a clean and natural material as it is also reused from cork industry waste, thus establishing DDL Arg's position as an environment friendly company.

Figure 1.2-2.1.1-1: a) DDL Arg company logo. b) Examples of commercial mortar products by DDL Arg. c) Example of a real life application of a DDL Arg mortar on a degraded wall. Retrieved from www.ddlarg.com.

1.3 Background and Objectives

The past decades of rapid industrial advancement in an ever-insatiable society have been paved with trial and error, success through failure and rediscovery. The industry of construction materials is one that evolved considerably since then, but it still has a long way to go before the perfect methods are reached. Problems such as material longevity, environmental damage and workability are among the priorities of modern-day material scientists.

DDL Arg is a company specializing in mortars for various applications and with several different characteristics. Among their innovative Evolution Cork Mortar line is a product by the designation of DDL.ECM Projeção, a hydraulic lime-based mortar with thermal insulating properties. This is the base material for this project's endeavors as DDL Arg presented the following question: How can this mortar's thermal insulating characteristics be improved?

The problem statement here is broad enough to allow a degree of liberty regarding the research method. The idea that geopolymerization has been shown in the past to be effective in the creation of insulating and heat resistant building materials was the starting point for the direction taken with this dissertation. Still, a construction mortar must obey certain rules regarding its mechanical behavior, as such, other parameters would eventually be looked at as well to ensure the viability of the final product. The primary goals of this experiment can then be described in descending order of priority as follows:

- Improvement of subject mortar's thermal insulating properties using alkaline activation methods.
- Investigation of final product's technical viability regarding chemical and mechanical parameters.

1.4 Thesis Layout

Following after the introduction is Chapter 2, State of the Art, which constitutes a succinct review of the most important notions necessary in order to understand the theme of this thesis. It starts with an introduction to traditional cements, then moving on to the focus of the thesis, alkali activated cements, beginning with an overview and a brief history of the subject before moving on to the reaction mechanisms of the different types of systems, finishing with quick notions about the types of components used in the process.

Chapter 3, Materials, Methodologies and Analytical Methods, opens with a presentation of the mortar used in the experimental procedure, including its technical characteristics. A second part of the chapter details the not only the goals of the experiment, broken down into simple objectives, but also explains the parameters that were changed and which degree of impact they're expected to cause. The experimental methodology is explained along with the mix design of the samples and the preparation of reagents used. Lastly, the analytical X-Ray methods used, Fluorescence and Diffraction respectively, are summarized in the final section of this chapter.

Chapter 4, Results and Discussion, presents the information acquired from the experiment and aims to correlate the varying parameters to the results observed to better understand their effects. The chapter ends with a characterization of the mortar used regarding its chemical and mineralogical composition based on the analytical methods' results.

Lastly, Chapter 5 acts as the conclusion to the thesis. This chapter details what was learned throughout the course of the dissertation, what worked successfully, and what could have been done differently to achieve better results. It will also try to answer the problem questions displayed as objectives to fulfill the goal of the thesis.

Following this, Chapter 6 contains the bibliographical references used in this dissertation.

2 STATE OF THE ART

2.1 Traditional Cements and concretes

In EN 197-1:2011, the European Committee of standardization defines cement as a hydraulic binder, i.e. a finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water. The cement adheres to the added aggregate and hardens, becoming a solid, resistant material. ASTM C219-14a describes a natural cement as a hydraulic cement produced by calcining a naturally occurring argillaceous limestone at a temperature below the sintering point and then grinding to a fine powder.

The aggregate used can vary in composition and grain size depending on the needed properties of the resulting product. Fine aggregates such as sand are often used in the making of masonry mortar while coarse gravel is used to make concrete.

Cements used in construction are generally inorganic although organic polymers may be used in the production of certain concrete cements. The most common components of cements are Lime and calcium aluminium silicate but other components can be used such as gypsum or pozzolans. Cements can also be divided into Hydraulic or Non-Hydraulic depending on whether they are able to set in the presence of water or require dry conditions respectively.

In geology, usually when studying sedimentary rocks, the term cement refers to the interstitial material that holds together the rock clasts. This denomination is given to this material due to its purpose's similarity to that of artificial cements. These mineral cements can be made of calcite, silica and iron oxides, among others, and are present in rocks such as sandstones, breccias and conglomerates, etc.

The most common cement is perhaps the Ordinary Portland Cement or OPC, which will be used as reference for comparison with Alkali Activated Cements in the course of this paper.

2.1.1 ORDINARY PORTLAND CEMENT

Portland cement is the most broadly used cement binder in the world, being the primary constituent of all OPC based concretes and mortars.

The discovery of Portland Cement is credited to John Smeaton in Britain, who began experimenting with limestone and other geological materials as early as 1756 for potential application in the construction of a lighthouse (Blezard, 2004). He later discovered that a calcined mix of limestone and clay formed a workable cementitious material that set and hardened quicker than lime. That product was then patented in 1824 by Joseph Aspdin who named it Portland cement (Vickers, Riessen & Rickard, 2015). The name was chosen due to the hydrated cement's color and resistance, which was reminiscent of the high-quality limestone quarried from the isle of Portland off the British Coast (Mehta, Scarborough & Armpriest, 2013). Portland cement quickly rose in popularity, needing only about 30 years to surpass that of the then established Roman cement patented in 1796 by James Parker (Saikia, Bhargab & Madan, 2010; Blezard, 2004). Joseph Aspdin's son, William, moved to Germany and further developed his father's prototype cement by mixing it with hydraulic lime (Rayment, 1986). At the time, this proto-Portland cement exhibited variable properties due the clinker used in its preparation being calcined at relatively low temperatures (Vickers et al., 2015). In 1845, Isaac Johnson first used a glass making kiln to burn the raw materials instead of the then used cooler lime kiln. By heating the mixture up to 1400~1500ºC, today's recommended clinkering temperature, he created a product resembling the modern era Portland cements (Gani, 1997). Over the 200 years that followed its creation, Portland Cement went on to become the world's major construction material (Shi & Mo, 2008).

The name Portland cement nowadays is used as a generic designation for that type of product rather than a specific brand. ASTM international standards describes Portland cement as a hydraulic cement produced by pulverizing portland-cement clinker, and usually containing calcium sulfate (ASTM C219-14a). Several types of Portland cements can be categorized according to specific added components;

European standards group them into five categories based on their composition (EN 197-1:2011):

- CEM I Portland cement
- CEM II Portland-composite cement
- CEM III Blastfurnace cement
- CEM IV Pozzolanic cement
- CEM V Composite cement

Then primary use of OPC is in the form of concrete used in construction. First generation concrete consists simply of OPC mixed with an aggregate while second generation concrete or ‘reinforced concrete’ gains added resistance through the incorporation of iron or steel bars in its application. A third generation of concrete, also called ‘prestressed concrete’, was developed in 1880 to avoid the usual cracking that occurs in standard reinforced concrete. This is achieved by stretching the reinforcing steel in key structural points of the building.

Since the role of OPC concrete as a structural element is mainly to resist compressive forces, its main design index is “Compressive strength at 28 days”, a relatively easy value to measure and one that is related to other properties of the cement. A higher compressive strength is obtained by reducing the water to cement ratio, however the malleability of the material is also reduced which results in the cement being harder to work with. Development of higher resistance concretes is made through the addition of water reducing admixtures that help maintain workability even at the low water-cement ratios that yield the desired compressive strength values. These are further boosted by the use of low particle sized mineral admixtures such as furnace slag, fly ash and silica fume which react with the calcium hydroxides formed in concrete while promoting the formation of a denser matrix (Vickers et al., 2015). Nowadays, concretes come with several chemical and mineral admixtures that effectively separate them from traditional products in terms of composition and final properties; these new generation products are called contemporary concretes (Li, 2011).

The OPC industry starts with the production of the clinker. The European committee for standardization defines Portland cement clinker as being made by sintering a precisely specified mixture of raw materials (raw meal, paste or slurry) containing elements, usually expressed as oxides, CaO, SiO_2, Al_2O_3, Fe_2O_3 and small quantities of other materials (EN 197-1:2011). Furthermore, the raw meal, paste or slurry is finely divided, intimately mixed and therefore homogeneous (EN 197-1:2011).

The process starts at Limestone quarries which provide the raw materials necessary. High-calcium or “pure” limestone contains approximately to 95% calcium carbonate ($CaCO_3$) which occurs mainly as calcite, while dolomitic limestones contain 60 to 80% $CaCO_3$. Either source can be utilized depending on availability to provide the lime that makes up most of the OPC clinker. Lime can refer to “quicklime”, calcium oxide (CaO), but most often refers to hydrated or “slaked” lime, Calcium hydroxide ($Ca(OH)_2$); the latter is the required component for making OPC. Both of these products can be obtained from the same Limestone source by applying different treatments in what is commonly referred to as the Cycle of Lime (Figure 2.1.1-1). The limestone is crushed to approximately 1.6 cm sized particles and mixed with clay or shale and an iron source. The mixture is ground to a fine dust and stored in silos to before moving on the kiln. The kiln is a rotating cylinder where the mixture is exposed to very high temperatures in a process called calcination. The angled structure increases the temperature as the mixture proceeds. The starting sections heat up the mixture to 1000ºC causing CO_2 to be expelled from the limestone, turning it into quicklime (Equation 2.1.1-1); in the later portions of the kiln, temperatures of up to 1500ºC induce partial fusion of the raw materials which form complex calcium compounds in the form of approximately 2.5 cm clinker pellets. These are then mixed with gypsum, which acts as a set retarder, and ground to a fine powder. The final product is a gray cement with particles sizes averaging at from 15 µm (Kosmatka & Panarese, 1988). A representation of the whole process can be seen in (Figure 2.1.1-2).

$$CaCO_3 \xrightarrow{Heat} CaO + CO_2$$

Equation 2.1.1-1: Calcination reaction for CaCO₃.

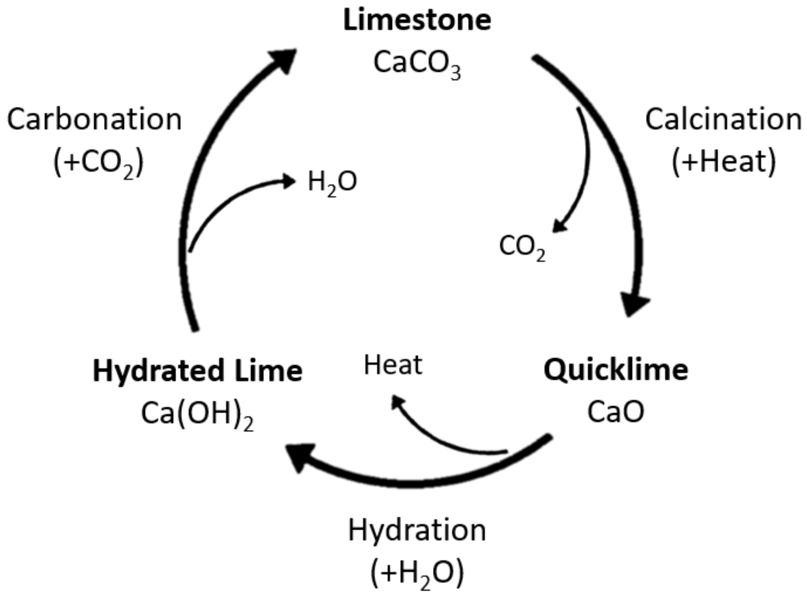


Figure 2.1.1-1: Diagram depicting the Cycle of Lime.

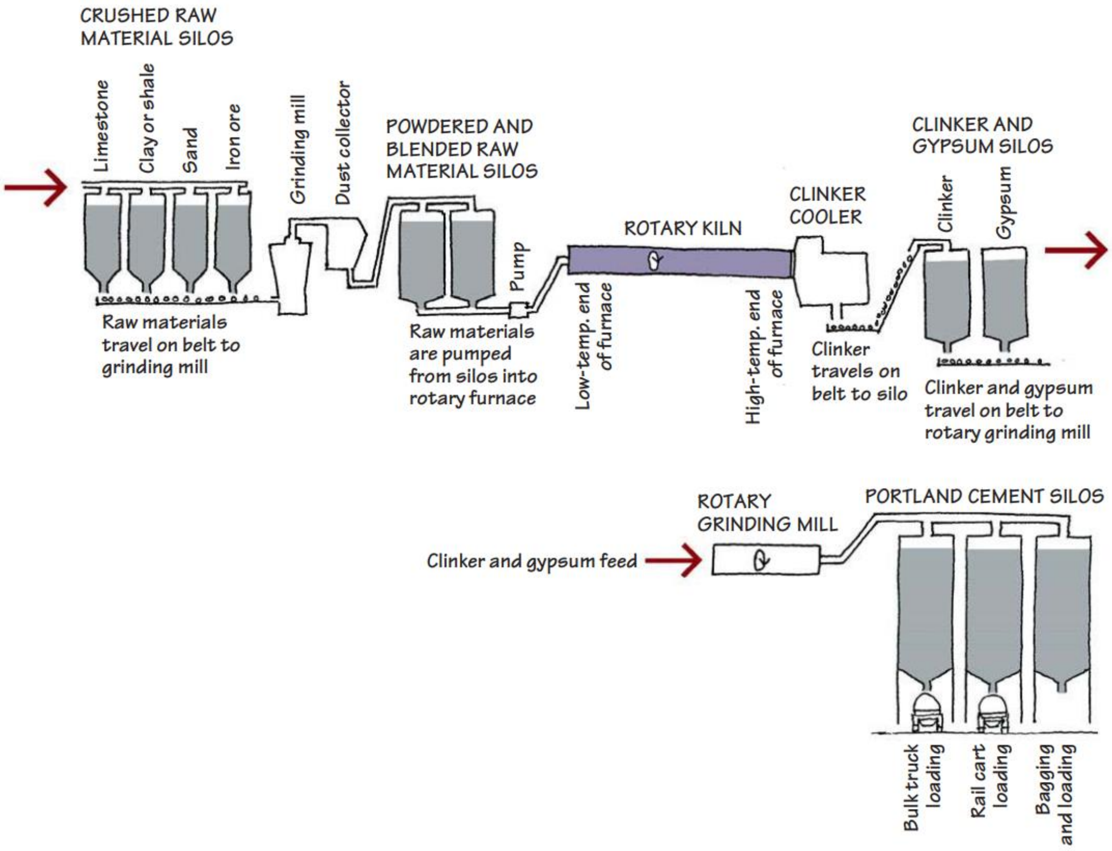


Figure 2.1.1-2: Schematic representation of OPC manufacturing process. Adapted from Mehta et al. (2013).

The composition of Portland cement clinker according to the European Standards is of at least two-thirds by mass of calcium silicates ($3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$), the remainder consisting of aluminium and iron containing clinker phases and other compounds. The ratio by mass (CaO)/(SiO_2) shall be not less than 2,0. The content of magnesium oxide (MgO) shall not exceed 5,0 % by mass (EN 197-1:2011). Most OPC clinkers are composed of several calcium compounds with values as shown in Table 2.1.1-1 and Table 2.1.1-2, as well as other elements. Alite, or tricalcium silicate hydratee and hardens very rapidly (2~6 hours); it contributes to the initial set and early strength of the cement. Belite, or dicalcium silicate hardens more slowly, being responsible for long term strength of the cement. Celite, tricalcium aluminate, contributes to a portion of the initial strength and releases considerable heat when hydrated; this reaction is slowed by the presence of gypsum. The presence of elevated amounts of celite in the cement reduce its sulfate resistance. Tetracalcium aluminoferrite has no real role in the properties of the cement but helps reduce energy consumption during its manufacture by allowing the other raw materials to fuse together at lower temperatures. Gypsum is used to control setting speed so the cement is malleable for enough time to be worked before beginning to harden. The alkali content of the cement is kept below 1% to avoid alkali-silica reaction (alkali activation) between the cement and the aggregate.

Table 2.1.1-1: Compounds present in standard OPC clinker (Mindess & Young, 1981; Vickers et al., 2015).

Cement Compounds	Chemical Notation	CCN	% weight
(Alite) Tricalcium Silicate	$(CaO)_3 \cdot SiO_2$	C_3S	45~70
(Belite) Dicalcium Silicate	$(CaO)_2 \cdot SiO_2$	C_2S	15~25
(Celite) Tricalcium Aluminate	$(CaO)_3 \cdot Al_2O_3$	C_2A	2~12
Tetracalcium Aluminoferrite	$(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	5~15
Gypsum	$CaSO_4 \cdot 2H_2O$	$C\bar{S}H_2$	3~5
Alkali oxides	$Na_2O + K_2O$	N + K	<1

Table 2.1.1-2: Chemical composition of a normal OPC clinker (Mindess & Young, 1981; Vickers et al., 2015).

Oxides	Chemical Notation	CCN	% weight
Calcium Oxide	CaO	C	61~67
Silicon Oxide	SiO_2	S	21~23
Aluminium Oxide	Al_2O_3	A	3~6
Ferric Oxide	Fe_2O_3	F	2~6

The clinker components undergo hydration reactions while setting, resulting in new compounds being formed; this can be seen in Equation 2.1.1-2. Like the clinker components, the amount of hydration products will vary among different products; typical numbers for this type of cement are seen in Table 2.1.1-3. The C-S-H (Calcium Silicate Hydrate) gel is the core element in the concrete and the one responsible for its physical properties. This element also forms dense bonded aggregations with other crystalline phases and unhydrated cement grains as well as the aggregate used, cementing the whole structure together (Copeland & Schulz, 1962). Calcium Hydroxide on the other hand makes no contribution to the strength of the concrete and can cause efflorescence.

$$2\,C_3\mathrm{S} + 6\mathrm{H} \rightarrow C_3S_2H_3 + 3\,\mathrm{Ca(OH)_2}$$

$$2\,\mathrm{C_2S} + 4\mathrm{H} \rightarrow C_3S_2H_3 + \mathrm{Ca(OH)_2}$$

$$C_3A + 6H \rightarrow C_3AH_6$$

Equation 2.1.1-2: Chemical equations for the hydration of Alite, Belite and Celite respectively in Cement Chemist Notation (CCN).

Table 2.1.1-3: Compounds present in hydrated OPC (Mindess & Young, 1981; Vickers et al., 2015).

Hydration Products	Chemical Notation	CCN	% weight
Calcium Silicate Hydrate	$(CaO)_3 \cdot (SiO_2)_2 \cdot (H_2O)_3$	CSH	50~70
Calcium Hydroxide	Ca(OH)2	CH	20~25
Calcium Sulfoaluminate (Ettringite)	$(CaO)_3 \cdot Al_2O_3 \cdot (CaSO_4)_3 \cdot (H_2O)_{30\text{-}32}$	-	10~15

2.2 Alkali Activated Materials

2.2.1 OVERVIEW

Since the popularization of alkaline activation in the 90s, academic interest in the field has grown exponentially and many publications were made all over the world throughout several scientific branches such as ceramics engineering, materials engineering, geochemistry, et cetera. As a result of these factors, many and varied terminologies were created which hinder the work of modern-day researchers who have to try several different keywords when using academic search engines. Terms like "soil silicate cements", "inorganic polymer glasses", "zeocements", "hydroceramics", "alkali-ash materials", "F-concretes", "alkali-bonded ceramics", and several others are all used in bibliography pertaining to the study of what we globally call "Alkali-Activated Materials" (Provis & Jakob, 2014; Provis & van Deventer, 2009).

An alkali-activated material can be broadly described as the solid, inorganic binder resulting from the reaction of an alkali source with a solid silicate powder (Provis & Jakob, 2014; Buchwald, Kaps & Hohmann, 2003; Shi, Krivenko & Roy, 2006). The alkali source usually comes in the form of a solution containing alkali hydroxides, although, other substances can also be used. In sum, any alkali providing source which can also raise the pH of the system can be used to as an activator. The silicate material to undergo this reaction, also called precursor, can be fly ash, blast furnace slag, metakaolin, calcium silicate, silica fume, or natural pozzolan among other options. A diagram depicting the rough composition of Alkali Activated cements can be observed in Figure 2.2.1-1. Alkali-earth compounds can also be used in high calcium environments such lime-pozzolan based systems, although some authors don't consider these to be traditional Alkali Activated techniques.

Within this definition we find a smaller subset of materials by the denomination of 'Geopolymers' (Figure 2.2.1-2). Geopolymers are Alkali-Activated Materials formed from an almost exclusively aluminosilicate-based precursor, typically calcined clays such as Metakaolin, and an alkali hydroxide or silicate (Provis & Jakob, 2014). These solid, highly stable materials form Zeolite-like polymers where the structural units are Alumina and Silica tetrahedra (Xu, 2002; Provis, Lukey & van Deventer, 2005). It's important to note that the term Geopolymer is sometimes incorrectly used when referring to the broad topic of alkali-activated materials. This isn't such a common occurrence in academic studies but can be seen in certain commercial scenarios for marketing reasons (Provis & Jakob, 2014).

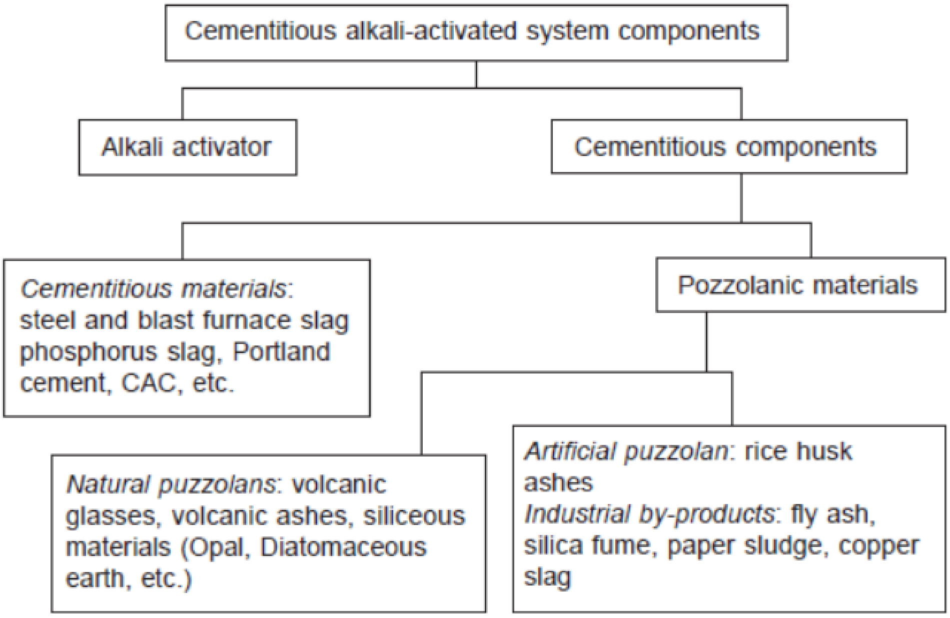


Figure 2.2.1-1: Components of Alkali Activated Systems, adapted from Garcia-Lodeiro, Palomo & Fernández-Jiménez (2015b).

Alkali activated materials distinguish themselves from their commercial competitors such as the widely used Portland Cement due to their high stability and resistance to corrosion. Many authors claim to have achieved varying degrees of physical and chemical properties that often surpass those of regular cements, but such comparisons are still subject of discussion in the academic community.

When it comes to Alkali Activated Cements, we can broadly speak of two major groups. One is based on the activation of silicon and aluminium rich materials, also designated as Low Calcium Binder; while the other aims to activate materials with high Calcium contents in addition to Si and Al, these are the High Calcium Binders. The latter type works in the same way as Portland Cement in that it relies on the creation of a hydrated calcium silicate (C-S-H or C-A-S-H) gel similar to that of OPC. The Low calcium system, on the other hand, forms an alkaline silicoaluminate gel (N-A-S-H) through the polycondensation of the silica and alumina precursors relying on high alkali content to achieve structural strength (van Jaarsveld, van Deventer & Lukey, 2002).

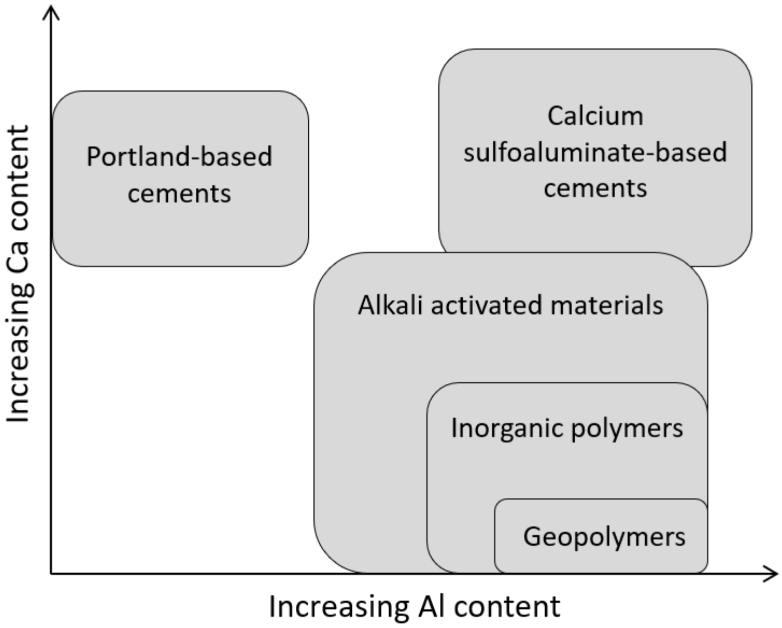


Figure 2.2.1-2: Graph illustrating the common cementitious materials in relation to their Calcium and Aluminium contents respectively. Adapted from Provis & Jakob (2014).

2.2.2 HISTORY

The science of alkali-activated materials is a relatively recent discovery, however, evidence of alkaline activation techniques in construction can be found by examining buildings left over by civilizations of ancient times. Some authors speculate that uses of aluminosilicate cements can go as far back as the year 3600 BC in Sumeria or 2500 BC in Egypt (Bauer, 2007; Demortier, 2004; Davidovits, 2008). The best studied cases of these applications come were left by the ancient Greek and Roman empires such as the Pantheon or the Colosseum. Romans specifically are known to have experimented with all manner of materials ranging from milk to animal fat and even blood in search for more durable building materials (Modena, Lourenço & Roca, 2005). A common method used at the time was the mixing of quicklime with volcanic ash (pozzolana) and clays, and subsequently adding seawater to the mixture. The sea water hydrated the quicklime and reacted with zeolite group minerals (Phillipsite) in the volcanic aggregate used to form concretes with a higher stability and longevity than modern Portland cement-based products (Wayman, 2011; Guarino, 2017.

In 1908, German engineer Hans Kühl (1908) patented his own mixing method for slag cement, a product he claimed to be "fully equal to the best Portland cements". In the same document he describes the mixing process to create a cement from vitreous blast furnace slag using sodium or potassium-based carbonates or sulfates (Kühl, 1908).

In 1930, Kühl studied the setting of ground slag powder when mixed with a caustic potash solution (potassium hydroxide) (Kühl, 1930). This work is considered by some authors as being the first important study in the history of alkali-activated cements despite the existence of his previous patented solution (Shi, Roy & Krivenko, 2003). Later, in 1937, Chassevent measured the reactivity of slags using caustic potash and soda solutions (potassium and sodium hydroxide, respectively) (Chassevent, 1930). This remains an important event in alkali-activated cement history although Chassevent's goal at the time was to better study the behavior of the slag in alkaline conditions and not the creation of new cementitious materials (Provis & Jakob, 2009).

In 1940, Belgian scientist Purdon published a journal article where he tested over 30 different blast furnace slags with various concentrations of sodium hydroxide, up to 10 wt%, where he noted that weight percentages ranging from 5 to 8 yielded the highest compressive strength results in the final product. He also tested the use of calcium hydroxide along with sodium carbonate which react, in the presence of water, to produce sodium hydroxide which then allows the setting of the slag (Vickers et al., 2015.). Purdon then concluded that incorporating Calcium hydroxide and sodium carbonate to the slag meant the mixture then needed only the addition of water to create a rapid hardening binder with strengths comparable to those of Portland cements (Purdon, 1940). He theorized that the alkali worked as a catalyst for the setting and hardening of the slag, which he later confirmed by recovering the added alkali from the mortar produced. He noted that some practical difficulties from using this technology may arise relating to the use of concentrated caustic reagents in the dissolution process. Despite this, Purdon praised the finished material’s properties of tensile and flexural strength compared to similar compressive strength Portland cements.

In the aftermath of the second world war, many infrastructures had to be rebuilt, which caused a high demand for construction materials. Portland based cements and other low-cost materials were widely used in these times, but the end products often had a relatively short life-span. This became the subject of study of Ukrainian scientist Victor Glukhovsky at KICE (Kiev Institute of Civil Engineering, in the USSR). Glukhovsky studied ancient roman binders in an attempt to discover why they were more durable than modern ones. In 1957 he discovered that compounds made with alkali metal showed hydraulic binding capabilities similar to those based on alkali-earth metals such Calcium (Vincenzini, 2010). The common occurrence of aluminosilicate minerals which are highly stable at surface conditions was the catalyst of this discovery. Glukhovsky was also the first to identify solidification products of alkali activated cements as sodium aluminosilicate hydrates (Zeolites) which he thought could benefit the construction industry. In the following years he developed alkali activated binders which he called “soil cements” by mixing aluminosilicate slags with alkali industrial waste (Davidovits & Joseph, 2008; Glukhovsky, 1965).

The first use of alkali activated slag cements in large scale construction goes back to the 1950s when the Concrete Division of the United States Army Waterways Experiment Station, supervised by Herbert K. Cook and Thomas B. Kennedy, made use of the Trief Cements in their trials (Fulton & Crawford, 1974). Developed by Belgian scientist M. Victor Trief, these cements were activated by the addition of 1.5% NaCl and 1.5% NaOH to the remaining 97% ground slag mixture (1955; U.S. Army Engineer Waterways Experiment Station, 1953). In 1960, slag-based cements were already being used in housing, railway sleepers, drainage channels, flooring and precast materials such as slabs and blocks (Krivenko, 2005).

Between the years 1970 and 1973, France suffered a series of fires which caused vast property damage. To prevent further disasters of this nature, French Engineer Professor Joseph Davidovits began researching heat and fire-resistant materials to create non-flammable construction alternatives. Davidovits experimented with the alkaline activation of metakaolin and was the first to coin the term 'Geopolymer' which he used to define a class of solid materials synthesized from the reaction between an alkaline solution and an aluminosilicate powder (Davidovits, 1982, 1991). In 1979, Davidovits founded the Geopolymer Institute, a non-profit organization with sights set upon the technological development of geopolymer science.

From the 1990s onwards, the scientific community began to understand the fundamental principles of Geopolymer technology. We can consider this decade as the starting point of modern day Geopolymer studies. Some authors consider Palomo and Glasser's work in Spain, 1992, as the first detailed scientific study on metakaolin geopolymers (Provis & Jakob, 2009; Palomo & Glasser, 1992).

Following this, works conducted in several countries helped further develop the scientific understanding of the subject: in Belgium (Rahier et al. 1996a, 1996b, 1997) and Australia (Xu and van Deventer 2000; van Jaarsveld and van Deventer 1999) on geopolymerisation mechanisms; in the Unites States (Lyon et al. 1997; Kriven 2008) on fire resistant composite and refractory applications, New Zealand (Nicholson et al. 2005) on geopolymer synthesis; and many others (Vickers et al., 2015; Rahier et al., 1996a, 1996b, 1997; Xu & van Deventer, 2000; van Jaarsveld & van Deventer, 1999; Lyon et al., 1997; Kriven, Bell & Gordon, 2008; Nicholson et al., 2005).

Geopolymer science in the present day is a topic of study and development all around the world and with growing popularity as the industry realizes all the potential applications this technology could revolutionize.

2.2.3 HIGH CALCIUM SYSTEMS: $(NA,K)_2O$-CAO-AL_2O_3-SIO_2-H_2O

The most often used precursor for high-calcium activated systems is ground granulated blast furnace slag (GGBFS or simply BFS), a vitreous sub-product of the steel industry. When smelting iron ore, clays and other siliceous gangue materials release silica and alumina which react with calcium oxide from the limestone used as flux in the process. The rapid cooling afterwards, leads to the rapid consolidation of the resulting products which become the glassy waste known as Blast Furnace Slag.

Chemically, slag is made up of CaO, SiO_2, MgO and Al_2O_3 with minor amounts of Fe_2O_3, S, MnO and K_2O as seen in **Erro! A origem da referência não foi encontrada.** (Provis & van Deventer, 2009). Containing both network forming anions $(SiO_4)^{4-}$, $(AlO_4)^{5-}$ and $(MgO_4)^{6-}$ as well as network altering cations $Ca2^+$, Al^{3+} and Mg^{2+}, blast furnace slag is a suitable precursor for polymerisation. Slag is 90~95% vitreous; a depolymerized calcium silicate, while the remaining portion constitutes crystalline phases of gehlenite (2CaO.Al2O3.SiO2), akermanite (2CaO.MgO.2SiO_2) with melilite family crystals (Fernández-Jiménez, 2000; Shi et al., 2006). It has been stipulated that slag reactivity in alkaline activation is directly related to vitreous phase content for which values of over 90% are recommended (Swamy & Bouikni, 1990). This is important because the lower the degree of polymerisation in the slag, the higher the its hydraulic activity will be. Another important factor is that the (CaO + MgO)/SiO_2 ratio should be >1 to ensure a basic pH as the lime controls the activation of the slag (Fernández-Jiménez, 2000).

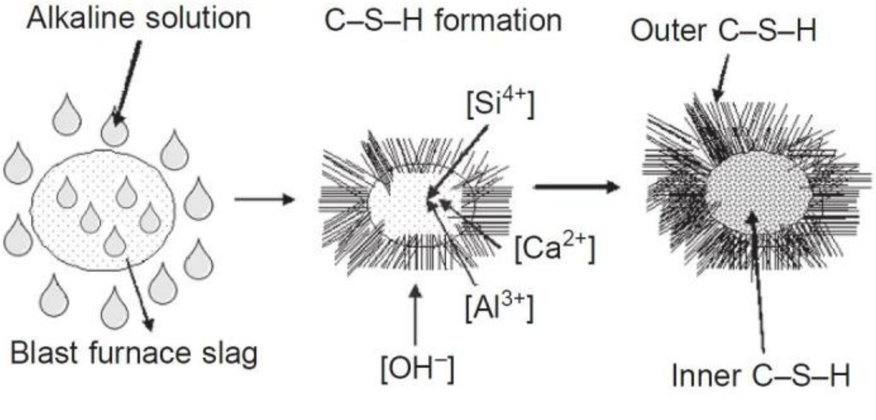


Figure 2.2.3-1: Visual representation of the reaction mechanism in the alkali activation of blast furnace slag, adapted from Garcia-Lodeiro et al. (2015a).

Table 2.2.3-1: Mean chemical composition of blast furnace slag (Garcia-Lodeiro et al., 2015b).

SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	S	Cr_2O_3	Na_2O+K_2O	MnO_2	P_2O_5	TiO_2
27~40%	30~50%	5~33%	2~2.1%	<1%	<3%	<0.01%	1~3%	<2%	<0.1%	<3%

The alkali activation of blast furnace starts outside of the particles and progresses inwards as time passes. This process takes place in several different stages starting with the alkali reagents attacking the BFS particles at a surface level, breaking the outer most layer, until polycondensation of the reaction products occurs. This initial layer of precipitated reaction products then hardens, and a solid-state mechanism takes place where ionic species are slowly diffused into the centermost layers (Chithiraputhiran, 2012). A visual representation of this process is illustrated in Figure 2.2.3-1.

2.2.4 CSH AND C(A)SH GELS

The main reaction product of the alkali activation of BFS is a C-(A)-S-H gel, a Hydrated Calcium Silicate gel with Aluminium in its composition [$(Na,K)_2O-CaO-Al_2O_3-SiO_2-H_2O$] comparable to the product of Portland cement hydration and which is responsible for the mechanical and chemical properties of most cements and concretes on the market (Provis & Jakob, 2014). This remains true to this day, even after decades of studies and research done on possible cement alternatives. This variant however has a lower Calcium/Silica (C/S) ratio than that of OPC (Garcia-Lodeiro et al., 2015a).

After the chemical attack, the alkali cation (M^+) acts as a structure-templating catalyst in the initial phases of hydration where the cations are freely exchanged with Ca^{2+} ions as can be seen in Equation 2.2.4-1 (Torgal et al., 2015). The physical and chemical properties of the resulting product will depend on curing temperature, pH, humidity, alkali availability, etc

$=Si\text{-}O^- + M^+ \rightarrow =Si\text{-}O\text{-}M$

$=Si\text{-}O\text{-}M + OH^- \rightarrow =Si\text{-}O\text{-}M\text{-}OH^-$

$=Si\text{-}O\text{-}M\text{-}OH^- + Ca^{2+} \rightarrow =Si\text{-}O\text{-}Ca\text{-}OH + M^+$

Equation 2.2.4-1: Formation of CSH gels (Garcia-Lodeiro, 2015a).

The occurrence of secondary products varies depending on the precursor composition, activator used as well as concentration, curing conditions, pH, among others. A hydrotalcite phase, a natural oxide mineral, is commonly encountered in BFS activated with sodium-based reagents such as NaOH (Fernández-Jiménez, 2000). Other products of this reaction include C_4AH_{13} phases which manifest as sub-microscopic platelets.

Professor Harold Taylor, a renowned cement chemist from Scotland, proposed in 1986 a structural model for the C-S-H gel formed as a result of the hydration of Ca_3SiO_5. He stated that the $CaO\text{-}SiO_2\text{-}H_2O$ system was comprised of two local structures similar to tobermorite and jennite respectively, each presenting as two silica chains flanking a central Ca-O layer (Taylor, 1992). These silica chains present a 'dreierketten' structure in which two paired tetrahedra share an oxygen atom while a second member of the pair also shares an O atom with a third outer tetrahedron (Provis & Jakob, 2014). This outer tetrahedron also shares one oxygen with the first tetrahedron of the following pair and is also called the 'bridging tetrahedron'. All paired tetrahedra are linked to the inner Ca-O layer via their 2 remaining oxygens, and the interlayer is occupied by H_2O and additional Ca cations (Provis & Jakob, 2014). A schematic representation of this can be seen in Figure 2.2.4-1.

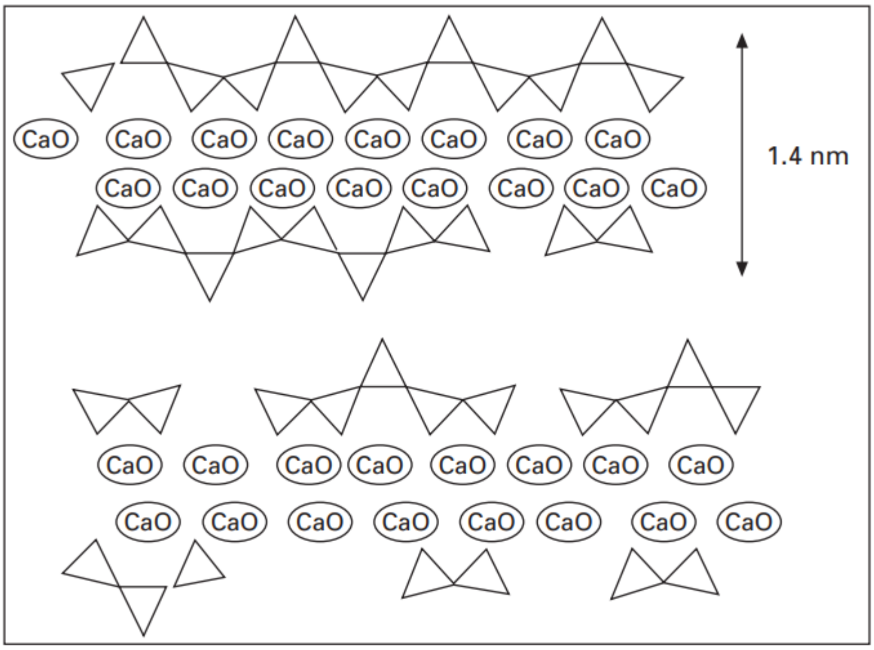


Figure 2.2.4-1: Schematic representation of a CSH gel, adapted from Taylor (1990).

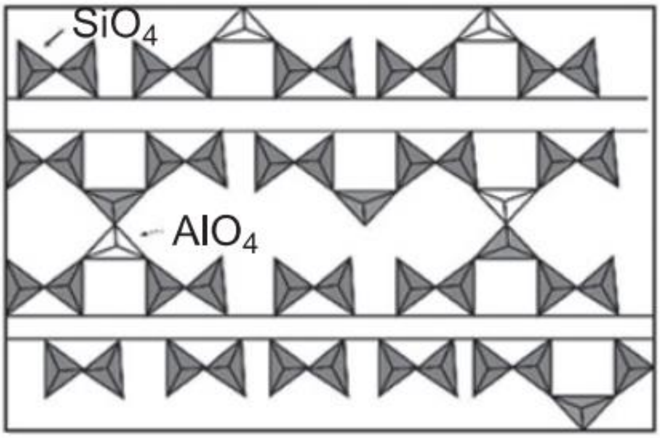


Figure 2.2.4-2: Schematic representation of a CASH gel, adapted from Fernández-Jiménez (2000).

The Jennite like structure is very similar to the Tobermorite one, with the main difference being the replacement of some Silica tetrahedra in the dreierketten chain with OH groups which causes undulation in the Ca-O layer (Provis & Jakob, 2014). A later model by Richardson et al. in 1993 proposed that aluminium atoms could replace silicon in the tetrahedra, with the charge imbalance being corrected by Ca^{2+} ions or alkali cations in the interlayer region (Richardson et al., 1993). This uptake of Aluminium into the system, caused by a higher availability of the element compared to that in OPC systems, allows for gels with longer chains and sporadic inter-chain SiO-O-Al bonds creating cross linked structures (Provis & Jakob, 2014). This main differentiating factor between traditional C-S-H and C-A-S-H gels can be observed in Figure 2.2.4-2.

2.2.5 LOW CALCIUM SYSTEMS: $(NA,K)_2O$-AL_2O_3-SIO_2-H_2O

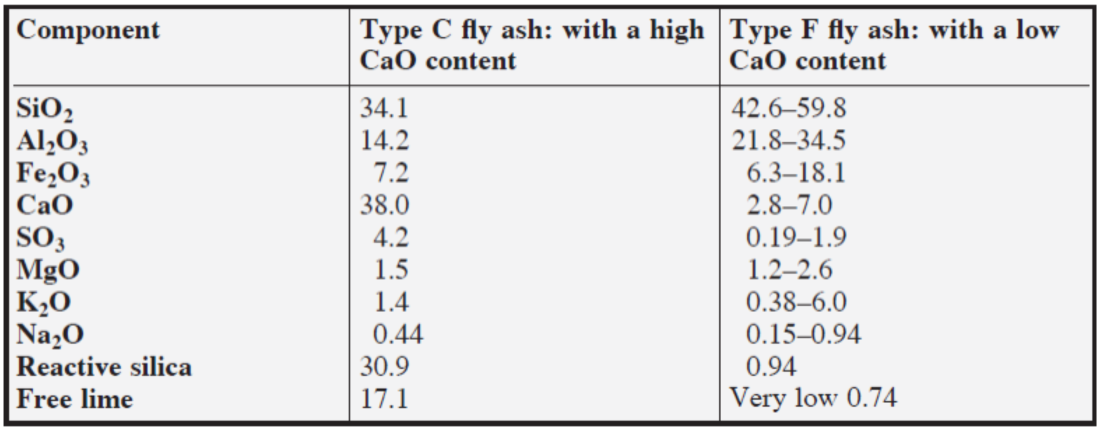
The Low-Calcium Alkaline binders can be considered the true Geopolymers by definition. Unlike their calcium rich counterpart, these make use of precursors whose compositions are almost exclusively aluminosilicate based. The most common materials used in Low Calcium Alkali Activation are metakaolin (or similar calcined clay materials) and fly ash. Experiments with the latter are more common for environmental reasons as well as economical since Metakaolin is generally more expensive.

Fly ash is the designation of the finer, particulate material that results from the combustion of coal in thermo-electric powerplants. These may use Anthracite or bituminous coal as fuel which, when burned, produce large amounts of waste derived from impurities such as clays or lime materials acquired naturally during the coal formation. The heavier ash, called Bottom Ash, deposits at the base of the combustion chamber while the finer particles, fly ash, elevate until they are captured by electrostatic precipitators in the chimney filters.

The composition of fly ash is naturally acidic, containing oxides such as SiO_2, Al_2O_3, and Fe_2O_3, making it suitable for alkali activation (Petermann, Saeed & Hammons, 2010). Two categories of fly ash can be distinguished based on chemical composition, Class C and Class F, the latter being the most abundant and also the most prized for alkaline activation. Class C fly ash is obtained from the combustion of younger coals and carries a higher percentage of CaO (>20%). Class F on the other hand typically contains <10% CaO and presents high values of both SiO_2 (40~60%) and

Al_2O_3 (20~35%) which combined with Fe_2O_3 often amount to ~90% of total content. These values can be seen in Table 2.2.5-1. In terms of Morphology, fly ash consists of hollow spheres as a vitreous phase which can be accompanied by some minor crystalline phases of quartz, mullite and magnetite.

Table 2.2.5-1: Average chemical composition of high and low calcium fly ash (values in weight %), adapted from Garcia-Lodeiro et al. (2015b).



Component	Type C fly ash: with a high CaO content	Type F fly ash: with a low CaO content
SiO_2	34.1	42.6–59.8
Al_2O_3	14.2	21.8–34.5
Fe_2O_3	7.2	6.3–18.1
CaO	38.0	2.8–7.0
SO_3	4.2	0.19–1.9
MgO	1.5	1.2–2.6
K_2O	1.4	0.38–6.0
Na_2O	0.44	0.15–0.94
Reactive silica	30.9	0.94
Free lime	17.1	Very low 0.74

The second most used precursor in Low Calcium alkaline activation is metakaolin. This consists of a pozzolanic material created via calcination of kaolinite Figure 2.2.5-1 clays at temperatures ranging from 650º to 850ºC depending on the purity and crystallinity of the material (Granizo et al., 2002). The reaction is expressed below in Equation 2.2.5-1.

$$XSiO_2 \cdot YAl_2O_3 \cdot ZH_2O \rightarrow \ XSiO_2 \cdot YAl_2O_3 + z\ H_2O$$

Equation 2.2.5-1: Calcination of Kaolinite.

The structure of metakaolin consists of a series of alternating layers of silicates and aluminates in which the silicon has a coordination number of 4, a tetrahedral coordination, 5 or 6 (Torgal et al., 2015). In order to improve the efficiency of the alkaline activation, the metakaolin particles should measure under 5 µm with an intrinsic clay grain size of 20 nm (Li, Sun & Li, 2010).

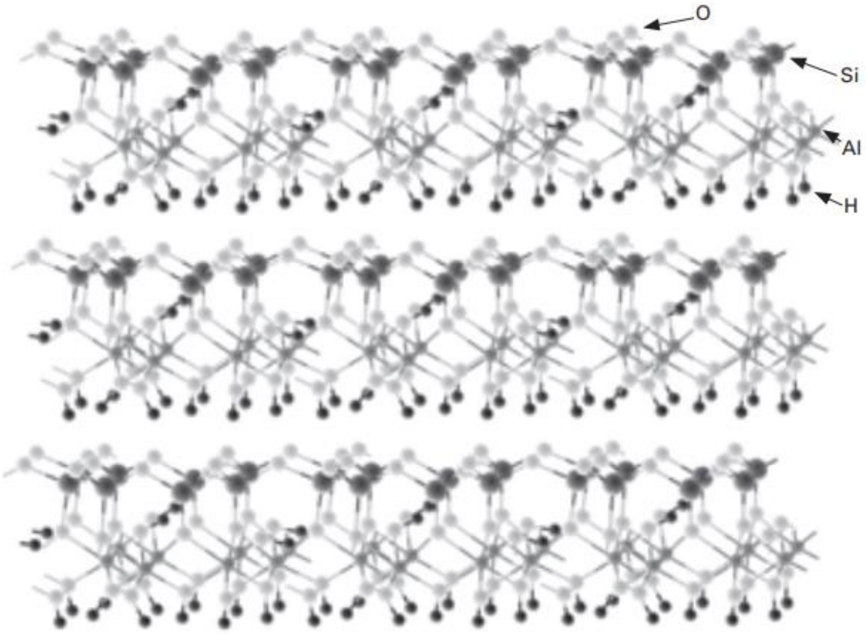


Figure 2.2.5-1: Layered structure of Kaolinite, adapted from Provis & van Deventer (2009).

The alkali activation of fly ash begins with the dissolution of the vitreous phase, an exothermic reaction which allows the covalent bonds of Si-O-Si and Al-O-Al to pass through the solution. These free species accumulate over an "induction period" with little heat liberation. Once enough reactive ions are gathered, a second highly exothermic reaction occurs with condensation of the mixture into a cementitious material. This alkali aluminosilicate gel has high mechanical strength and is semi-amorphous with a structure resembling that of zeolitic precursors. Figure 2.2.5-2 depicts the whole process in different stages. The chemical attack starts occurring on the surface of the fly ash particles and spreading from there. Reaction products start forming as the particles, both hollow and containing other materials, are breached and exposed to the chemical attack from the outside and inside out. The reaction continues until the glassy spheres are completely consumed, at which point other particles will have condensed in the same way with reaction products filling their hollow shells, forming a dense matrix of cementitious material.

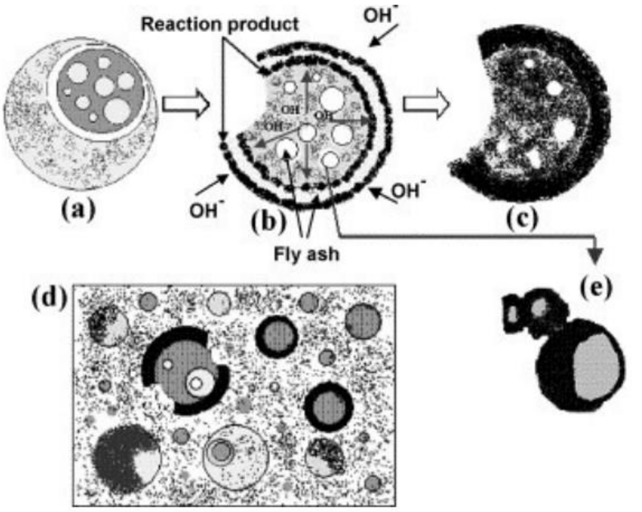


Figure 2.2.5-2: Schematic model of the alkaline activation of fly ash, adapted from Fernández-Jiménez, Palomo & Criado (2005a).

Regarding the geopolymerization of metakaolin, the process is relatively similar to that of the fly ash. The process starts in a similar manner to fly ash geopolymerization, with an alkali chemical attack on the precursor. The dissolution of the metakaolin structure releases silica and aluminate species into the solution with 5 and 6 coordinated aluminium atoms converting into a 4 coordination (tetrahedron) (Duxson, Lukey, Separovic & van Deventer, 2005). It is thought that the release of Al may occur faster than Si due to the additional lattice strain in Al layers in metakaolin (Weng & Sagoe-Crenstil, 2007). The silicon and aluminium species then begin forming aluminosilicate oligomers. The dissolution continues until the concentration of Al is enough to destabilize de silicate solution, at which point the dissolved species precipitate and form a gel (Provis & van Deventer, 2009). This process can be affected by mechanical disruption such as shearing or ultrasonication, as well as by providing nucleation sites via addition of aggregates for example. The geopolymer gel keeps growing until it starts to solidify; the timing of this event varies depending on curing conditions and the existence of contaminants. Depending on mix design and curing environment, setting can take place almost instantaneously or go on for days, and some reaction processes remain active beyond that point (Provis & van Deventer, 2009). If the geopolymer gel is kept sealed in a warm environment it will start crystalizing in the form of simple zeolite frameworks such as sodalite, faujasite, gismondine and Linde type A (Provis & van Deventer, 2009). This occurs preferentially in systems with lower Si/Al ratios.

2.2.6 NASH GELS

Geopolymerization, the process of alkali activating an aluminosilicate-based material, is more complex than the activation of High Calcium systems. This method relies on the formation of N-A-S-H gels containing silicon and aluminium tetrahedra arranged to form a tridimensional structure Figure 2.2.6-1. The final product is a semi-amorphous alkali aluminosilicate material with properties similar to those of zeolite precursors.

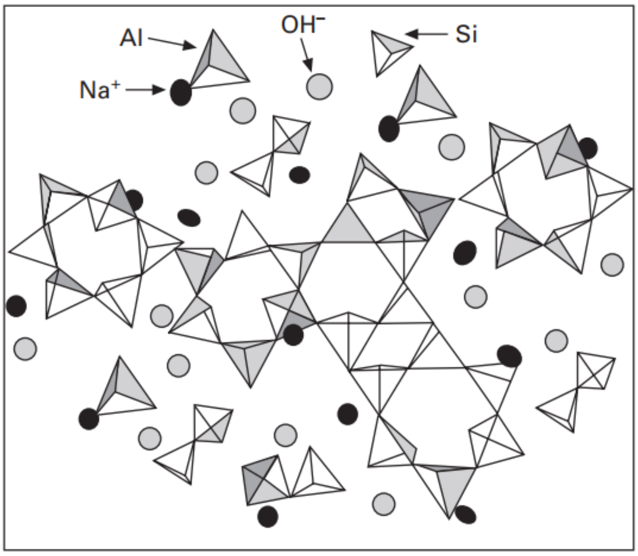


Figure 2.2.6-1: Illustration of the structure of s NASH gel, adapted from Criado (2007).

With the goal of studying the molecular silico-aluminate structures of low calcium activated materials, the term ‘Polysialate’ was coined, which is an abbreviation for silicon-oxo-aluminate. The network is comprised of SiO_4 and AlO_4 tetrahedra linked alternately by oxygen bridges, as seen in Figure 2.2.6-2, in a structure that can be compared to that of sodalite (Davidovits, 1999). The Al^{3+} in IV-fold coordination causes negative charge imbalance which is compensated for by the presence of positive alkali ions in the network cavities such as Na^+ or K^+. This is the primary reason for the use of alkali activators in the making of aluminosilicate binders. The polysialate empirical formula is shown in Equation 2.2.6-1:

$$M_n\,\{-(SiO_2)z - AlO_2\}_n \cdot wH_2O$$

Equation 2.2.6-1: Polysialate formula.

Where 'M' is an alkali metal cation (Na^+, K^+) with an 'n' degree of polycondensation and 'z' is 1, 2 or 3 for polysialate, polysialate-siloxo and polysialate-disiloxo respectively (Xu, 2002).

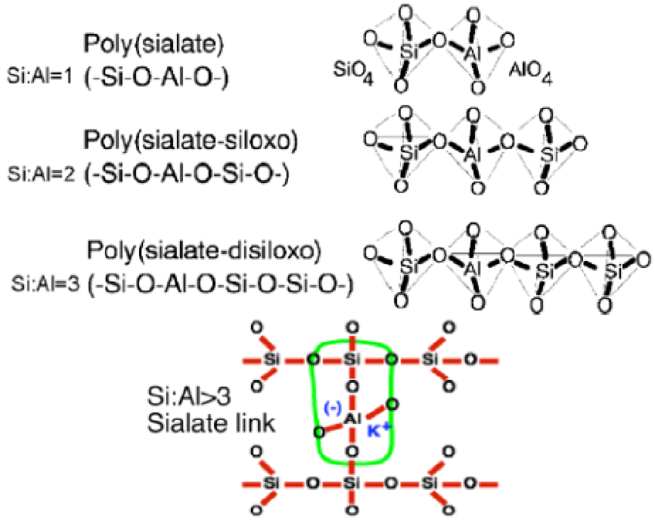
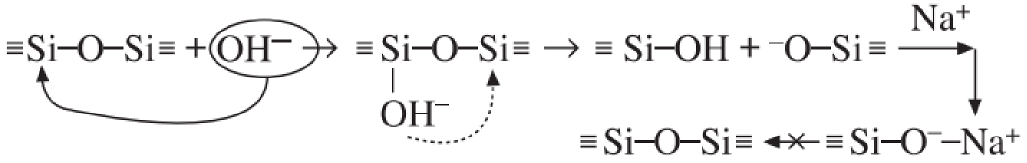


Figure 2.2.6-2: Structure and nomenclature of Sialate type compounds, adapted from Davidovits (2005).

Glukhovsly's model for the alkali activation of aluminosilicate materials describes the process as occurring in three steps: Destruction-Coagulation, Coagulation-Condensation and Condensation-Crystallization (Glukhovsky, 1994).

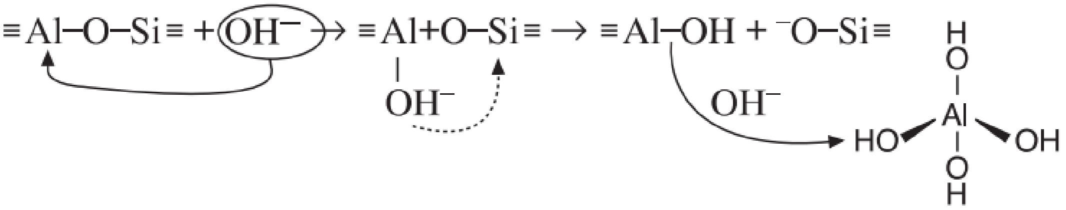
The first stage, Destruction-Condensation, begins with the chemical attack of the alkali activator, where the OH^- ions present in it break the aluminosilicate bonds (Si-O-Si, Al-O-Al, Si-O-Al) in the precursor. Severing these covalent bonds is only possible in a high pH medium which is achievable by using activators such as alkali hydroxides. The ions weaken the Si-O-Si bonds by redistributing their electronic density around the silicon atom, leading to the formation of silanol (-Si-OH) and Sialate(-Si-O$^-$) species as seen in Equation 2.2.6-2. The alkali cation is crucial at this stage, acting as a catalyst, and neutralizing the negative charge imbalance in the resulting products. At this point, the resulting species tend to revert back to siloxane Equation 2.2.6-2, a reaction that is impeded by the formation of stable Si-O$^-$-Na$^+$ complexes by the alkali cation (in this case, sodium).



$$\equiv SiOH + HOSi\equiv \Rightarrow SiOSi\equiv + H_2O$$

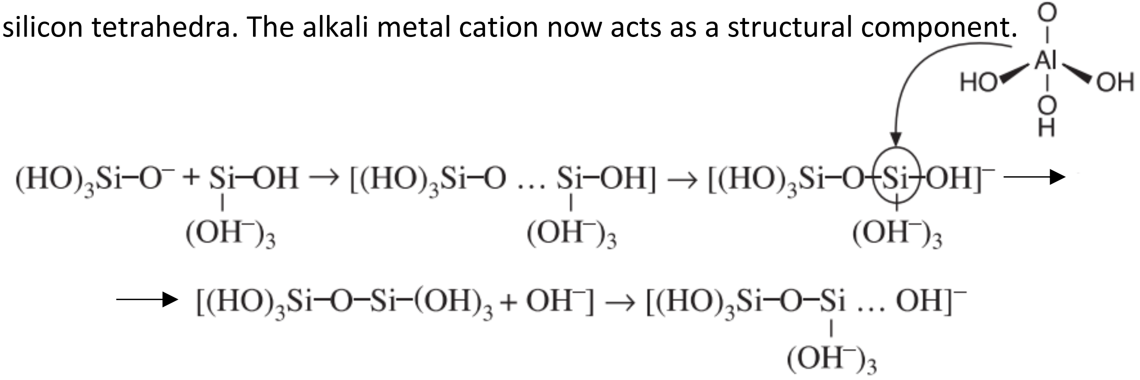
Equation 2.2.6-2: NASH gel formation I, adapted from Torgal et al. (2015).

The chemical attack on Al-O-Si bonds works in the same way Equation 2.2.6-3, yielding complex aluminium species, mainly Al(OH)4$^-$.



Equation 2.2.6-3: NASH gel formation II, adapted from Torgal et al. (2015).

The second stage of the process, Coagulation-Condensation, the now abundant ionic species enhance contact between the disaggregated products; these begin coagulating and polycondensation begins. At high pH values, silicic acid is in molecular state and has higher condensability, originating hydroxilated complexes (Provis & Jakob, 2014). The silica monomers inter-react to form dimers, which in turn react with other monomers to build polymers (Equation 2.2.6-4) (Torgal et al., 2015). This reaction os catalysed by the OH$^-$ anions. The clusters formed as a result of silicic acid polymerisation begin to grow in all directions generating colloids (Torgal et al., 2015). The aluminate species participate in this reaction, substituting isomorphously for silicon tetrahedra. The alkali metal cation now acts as a structural component.



$$(HO)_3Si{-}O^- + \underset{(OH^-)_3}{Si{-}OH} \rightarrow [(HO)_3Si{-}O \ldots \underset{(OH^-)_3}{Si}{-}OH] \rightarrow [(HO)_3Si{-}O{-}\underset{(OH^-)_3}{Si}{-}OH]^- \longrightarrow$$

$$\longrightarrow [(HO)_3Si{-}O{-}Si{-}(OH)_3 + OH^-] \rightarrow [(HO)_3Si{-}O{-}\underset{(OH^-)_3}{Si} \ldots OH]^-$$

Equation 2.2.6-4: NASH gel formation part III, adapted from Torgal et al. (2015).

The third stage of the process is called Condensation-Crystallization. Particles from the condensed structures, as well as particles existing in the initial material, prompt the precipitation of reaction products of varying composition depending on the precursor used, one the alkali activator or even hardening conditions.

Different models have been created to explain the reaction mechanisms of fly ash activation. One such model is based on zeolite synthesis, proposed by Palomo et al. (2005) and consists of two stages. The first is a nucleation stage with the dissolution of the aluminosilicate material and posterior polymerization of complex ionic species in a process that is highly dependent on kinetic and thermodynamic parameters. This englobes the two initial stages proposed by Glukhovsky. The second stage is the growth stage when the nuclei reach critical size and crystals begin to develop. The final product of the alkali activation of aluminosilicate materials is an amorphous matrix of aluminosilicate gel with cementitious properties, a N-A-S-H gel that can be described as a zeolite precursor.

This model has since been revised by several authors. According to recent theorization, N-A-S-H gel formation integrates a series of four stages as illustrated in Figure 2.2.6-3. The alkali activator dissolves the aluminosilicate precursor into several species, mainly, silica and alumina monomers. These react to form dimers, which in turn react with other monomers to form oligomers of escalating degrees. Once saturation is reached, an aluminosilicate gel, N-A-S-H gel, precipitates. Initially, this gel is rich in Al (Gel 1) due to aluminium bonds being weaker which causes faster dissolution and subsequent abundance of that element in the early stages of the reaction. With the evolution of the reaction, more Si species are released into the mixture and the concentration of silicon in the N-A-S-H Gel increases (Gel 2). This structural reorganization process determines the final composition of the polymer as well as its microstructures and consequentially, it's physical properties (Fernández-Jiménez, Palomo & López-Hombrados, 2006c; Sof, van Deventer, Mendis & Lukey, 2007).

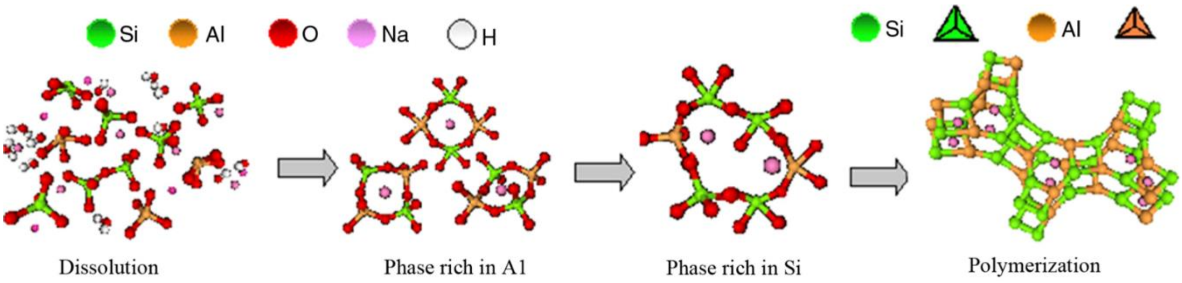


Figure 2.2.6-3: Simplified illustration of NASH gel formation, adapted from Fernández-Jiménez, Palomo & Alonso (2005b) and Shi, Fernández-Jiménez & Palomo (2011).

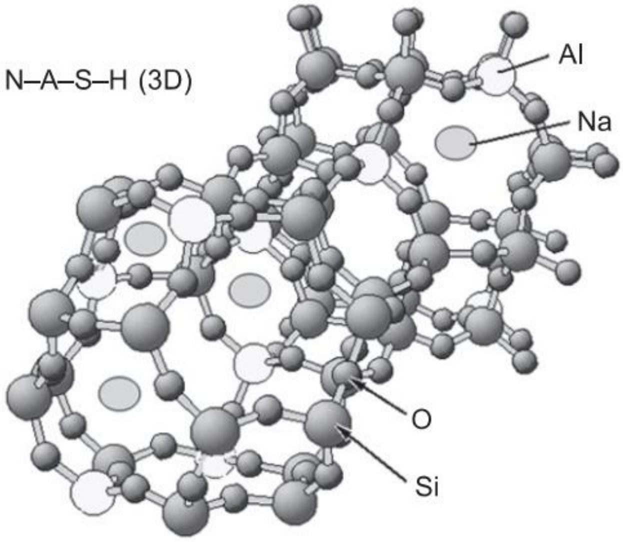


Figure 2.2.6-4: Three-dimensional representation of NASH gel structure, adapted from Torgal et al. (2015).

The final products of this process is an amorphous alkalie aluminosilicate hydrate (M_n-(SiO_2)-(AlO_2)$_n$·wH_2O) cementitious material known as N-A-S-H gel (Palomo, Fernández-Jiménez & Kovalchuk, 2005). Some authors prefer to reserve the N-A-S-H terminology for materials created using sodium-based activators, preferring the term K-A-S-H for the common alternative which is potassium although this sometimes creates confusion due to the similarity to C-S-H gel in OPC. The silicon and aluminium tetrahedra in N-A-S-H gel are randomly distributed, forming a tridimentional skeleton as seen in Figure 2.2.6-4 (Provis & van Deventer, 2009; Fernández-Jiménez, Palomo & Sanz, 2006).

This gel contains large amounts of zeolite-like nanocrystals, having fully crystallyzed zeolites been observed in some instances. These secondary reaction products can include Na-chabazite, analcime, hydroxisodalite, zeolite P/Y, faujasite, among others (Palomo et al., 2004; Provis & van Deventer, 2009; Fernández-Jiménez et al., 2009; Duxson et al., 2007).

It is known that the type of activator used as well as curing temperature affect the reaction kinetics, with the degree of reaction rising with the latter (Palomo et al., 2005; Bahkarev, 2005; Criado et al., 2005). The nature of the reaction products is also susceptible to different curing conditions. A known useful property is that longer curing times increase the formation of cilica rich products which increases the mechanical strength of the material. An important factor to take into account is that silicon may me added to the mix by using an alkali silicate as an activator, which will directly contribute to the formation of the N-A-S-H gel. This addition affects the intermediate products but not the final ones. This is true because the Si/Al ratio of the N-A-S-H gel does not rise indefinitely, rather, studies found that the system tends towards an optimal ratio of 2 regardless of initial conditions, possibly to preserve thermodynamic stability (Criado, 2007).

2.2.7 BLENDED SYSTEMS

Initially, Alkali Activated cements were studied according to either one of the previously mentioned systems, high-calcium or low-calcium. Continued investigation into the topic later revealed that it was possible to create binders from the activation of mixed materials; these are called hybrid or blended binders.

Blended binders consist of alkali activated cements created using different proportions of both high and low calcium precursors in the initial mixture. The properties of the final product are highly dependent on the reaction conditions such as pH, temperature, activator, and, even more so than with standard AAMs, the composition of the precursor mixture. The most frequent blends are the following:

- Portland cement + blast furnace slag;
- Portland cement + phosphorous slag;
- Portland cement + fly ash;
- Portland cement + steel mill and blast furnace slag;
- Portland cement + fly ash + blast furnace slag;
- Multi-constituents.

Blended alkaline cements require a precursor containing CaO, SiO_2 and Al_2O_3 contents of over 20% (Garcia-Lodeiro, Maltseva, Palomo & Fernández-Jiménez, 2012). The products of this reaction are intricated mixtures of cementitious gels. The two gels can co-precipitate under the right conditions, although studies have found them to interact with one another while doing so, undergoing structural and compositional changes, rather than precipitating as two separate products (Garcia-Lodeiro, Palomo, Fernández-Jiménez & Macaphee, 2011).

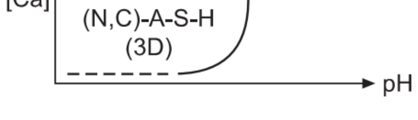


Figure 2.2.7-1: Model of (NC)ASH gel stability depending on pH and Ca concentration, adapted from Torgal et al. (2015).

Several studies conducted by Garcia-Lodeiro *et al*. (2009, 2010a, 2010b, 2011) brought new information regarding the behavior of the reaction products in blended systems with addition of Al and Na to C-S-H gels or Ca to N-A-S-H gels under different pH environments. These same studies found that at high pH values, the presence of Aluminium species in aqueous phase affects the C-S-H gel, as the element gets incorporated in the structure of the gel. Another finding was that dissolved calcium partially replaced sodium in N-A-S-H gel structures, leading to the formation of (N,C)-A-S-H type blends. It was found that at high pH values (>12), the precipitation of C-A-S-H gel is favored over N-A-S-H gel formation so long as there is enough available calcium in the system Figure 2.2.7-1.

Later, a study was conducted by Palomo et al. (2007) investigated the mechanical behavior of blended cements made with 30% OPC clinker and 70% fly ash content. The result values for cementitious materials activated with different reagents at room temperature displayed high variability. Samples activated with sodium hydroxide showed similar values at 28 days (24~28 MPa) while sodium hydroxide activated samples reached values of 37 MPa.

The results of these studies confirm that alkaline anions (OH^-) and soluble silica in the activating solution affect the hydration of Portland cement. Furthermore, fly ash activation seems to accelerate in blended systems as opposed to pure alkaline activation. This can be explained by the heat release from the hydration of OPC which favors the dissolution reactions of fly ash as well as the setting and hardening of the gel created (Torgal et al., 2015).

The co-precipitation of C-A-S-H and N-A-S-H gels in blended activated systems can be observed at early ages (up to 28 days) forming complex mixes. Recent studies using 70% fly ash and 30% OPC over longer reaction periods (1 year) showed that (N,C)-A-S-H gels ultimately evolve to compositions with higher calcium and lower aluminium content over time (Garcia-Lodeiro, Fernández-Jiménez & Palomo, 2013b). These results show that C-A-S-H gel formation is favored over N-A-S-H gel in systems that age for longer periods in equilibrium conditions (Garcia-Lodeiro et al., 2011).

Based on both literature study and practical compatibility analyzis between the two synthetic gels, Garcia-Lodeiro et al. (Garcia-Lodeiro et al., 2013a) proposed a conceptual model for the activation process of blended systems containing high silica and alumina with low calcium (Appendix A) .As happens with the low calcium system, the process begins with a chemical attack on the aluminosilicate material, which in this model is fly ash, where the Si-O-Si and Al-O-Al bonds are broken. At the same time, Si-O and Ca-O bonds are also being broken in the calcium rich OPC used in the precursor; this generates a wide variety of dissolved species in the solution (Stage A). When saturation is reached alkali elements react with silicon to precipitate a N-A-S-H gel; meanwhile the same thing happens with Ca^{2+} ions forming a C-S-H gel (Stage B). With the evolution of the reaction, more Si-O groups dissolve from both the OPC and fly ash materials, raising the silicon concentration in the solution and consequently, the Si uptake in both gels.

The N-A-S-H gel changes from type 1 (Si/Al ratio ≈ 1) to type 2 (Si/Al ratio ≈ 2) as a result (Fernández-Jiménez et al, 2006) while in the C-S-H gel, chains incorporate more silica tetrahedra (Stage C). Some dissolved Ca ions interact with N-A-S-H gel to form a (N,C)-A-S-H type gel. This occurs because calcium has a similar ionic radius, as well as electronegative potential, to that of sodium, and is therefore able to replace it in the N-A-S-H gel via ion exchange without changing its structure (Engelhardt & Michel, 1987). At the same time, the C-S-H gel is incorporating aluminium in its structure becoming a C-A-S-H gel (Stage D). Over the progress of the reaction, Ca^{2+} ions keep diffusing through the matrix and interacting with the (N,C)-A-S-H gel where they weaken the Si-O-Al bonds until they break, in favor of the creation of Si-O-Ca bonds instead. As the N-A-S-H gel loses aluminium, less polymerized structures are formed which are analogous to the existing C-A-S-H gel, still taking up Si and AL in its composition. This is stage E, which is reached after 1 year of reaction time. Given enough time and conditions, such as suitable pH or calcium concentrations, the system would evolve towards the most thermodynamically stable composition which is a C-A-S-H type gel (Garcia-Lodeiro et al., 2011).

2.3 Alkali Activators

As was mentioned previously, the activator is a fundamental component in the creation of any alkali activated material, being responsible for the activation process. The activator consists of an aqueous solution that, when added to the solid precursor, will act as catalyst for the dissolution, setting and crystallization of the aluminosilicate species. This is the portion of the mixture that carries the alkali-metal elements that give the AAM their designation; usually sodium or potassium although in rarer cases Lithium, cesium or rubidium can also be used. Because the solution's pH has to be high enough to break the precursor's aluminosilicate bonds, the activator is a highly basic and therefore very corrosive reagent that must be handled with care. Although hydroxides are perhaps most widely used for this effect, several other reagents can be used in the making of the activator depending on the desired results or equipment availability.

2.3.1 ALKALI HYDROXIDES

Sodium and Potassium hydroxides (NaOH and KOH respectively) are widely used chemical substances and are perhaps the most common reagents used in the preparation of alkali activators. cesium and rubidium are rarely used in to this effect due to their limited availability; Lithium on the other hand is hard to work with due to its poor solubility which doesn't exceed 5.4 mol/Kg H_2O at 25ºC when compared to sodium or potassium who remain soluble beyond concentrations of 20 Mol/Kg H2O at 25ºC (Pickering, 1893; Kurt & Bittner, 2006).

NaOH and KOH are industrially produced through the chlor-alkali process (Figure 2.3.1-1) which consists in the electrolysis of NaCl and KCl solutions respectively. Aside from being highly corrosive, the main characteristic of concentrated hydroxides is their viscosity which is very similar to that of water thus making the process of dilution simple and easy. It should be noted that the dissolution of solid alkali hydroxide components is an exothermic reaction and the preparation of such solutions should be handled with care.

Potassium cations (K^+) are more basic than sodium cations (Na^+), thus, KOH promotes a higher degree of dissolution of the precursor, leading to a denser matrix being formed. Despite this, some studies conclude that high concentrations of KOH lower the resulting cement's compressive strength (Khale & Chaudhary, 2007). While not offering the same degree of dissolution, NaOH promotes better liberation of silicate and aluminate monomers. This happens because Na^+ has a smaller ionic radius, being able to move more freely through the gel network and promoting better zeolitization (Rangan, 2008).

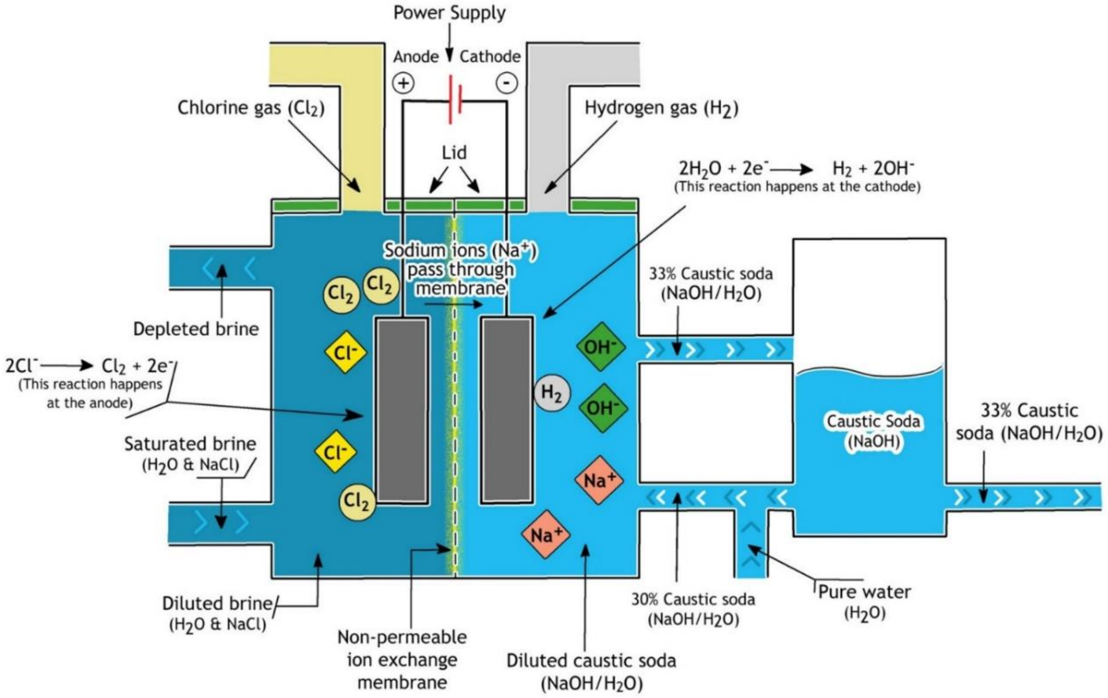


Figure 2.3.1-1: Diagram depicting the Chlor-alkali process of manufacturing Sodium hydroxide (NaOH) also known as "Caustic Soda". Adapted from www.lipmann.co.uk.

A known downside from using alkali hydroxides as activators for AAMs is the occurrence of efflorescence or staining. Although this effect can be mitigated by properly measuring the necessary amount of hydroxide activator in the overall system, it still occurs from time to time. The efflorescence effect occurs when excess alkali reacts with atmospheric CO_2 to create undesirable carbonates or bicarbonates (Provis

& Jakob, 20014). Aside from being visually unaesthetic, these soluble crystals also expand upon precipitation and sometimes negatively impact the properties of the resulting cement. This is more prominent when using sodium as the present alkali metal in the activator but can also happen with other alkali elements.

2.3.2 ALKALI SILICATES

Alkali silicates are rarely used as the sole reagent in alkali activation procedures, although they are often used in tandem with alkali hydroxides to achieve better results. As occurs with hydroxides, the more frequently used alkali silicates are those of sodium ($Na_2O{\cdot}nSiO_2$) and potassium ($K_2O{\cdot}nSiO_2$); with the remaining alkali metals not being used for the same reasons described previously.

Industrially, alkali silicates are produced by fusing sand with an alkali carbonate through the process of calcination (Figure 2.3.2-1). Different methods of producing alkali silicates exist which use alkali hydroxides or sulfates in the main reaction, however, these hold little relevance in industrial mass production. The sand provides silica (SiO_2) while a sodium or potassium carbonate (Na_2CO_3 or K_2CO_3 respectively) provides the desired alkali metal component as described in (Equation 2.3.2-1). After the calcination process, which occurs at temperatures ranging from 1100ºC to 1500ºC, the resulting product called “cullet” can be dissolved with high pressure steam to create a viscous fluid (McDonald & Thompson).

$$x\,Na_2CO_3 + SiO_2 \rightarrow (Na_2O)_x \cdot SiO_2 + CO_2$$

Equation 2.3.2-1: Reaction between sand and Sodium Carbonate to produce Sodium Silicate (Greenwood & Earnshaw, 1997).

Sodium silicates are harder to work with than other reagents, mainly due to the solution’s high viscosity and the silicates’ propensity to precipitate as hydrated metasilicates (Provis & Jakob, 2014). This makes long term storage of sodium silicate products risky and generally, inadvisable. Potassium silicate on the other hand presents a higher stability window when in aqueous solution, and its precipitation products less likely to occur.

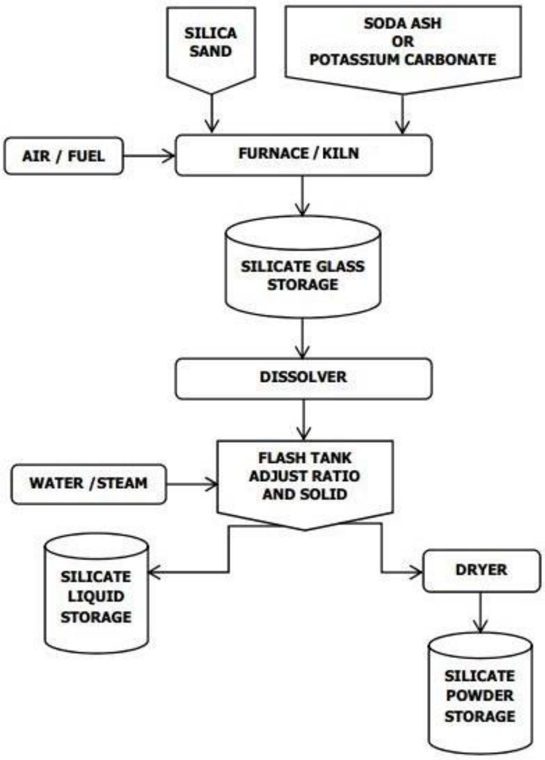


Figure 2.3.2-1: Diagram depicting a production line for sodium silicate or potassium silicate, respectively, depending on the starting material. Note that "Soda ash" refers to the common designation of sodium carbonate (Na2CO3). Retrieved from www.captainindustries.com.

The ratio of alkali silicate to hydroxide is of great importance as too much soluble silica is known to retard the setting and structure formation of the binder by delaying the release of water and hindering polycondensation (Khale & Chaudhary, 2007). On the other hand, increasing the alkali content in the system leads to binders with higher compressive strength values.

2.3.3 ALKALI CARBONATES

It is possible to create alkali activated binders using alkali carbonates instead of the previously mention reagents. Despite not being the more popular activator agent, sodium carbonate has been used in several experiments in the past. Carbonates of potassium and other alkali metals are rarely used in comparison.

Alkali carbonates can be mined directly from carbonate salt deposits or industrially produced through the Solvay Process (Figure 2.3.3-1).

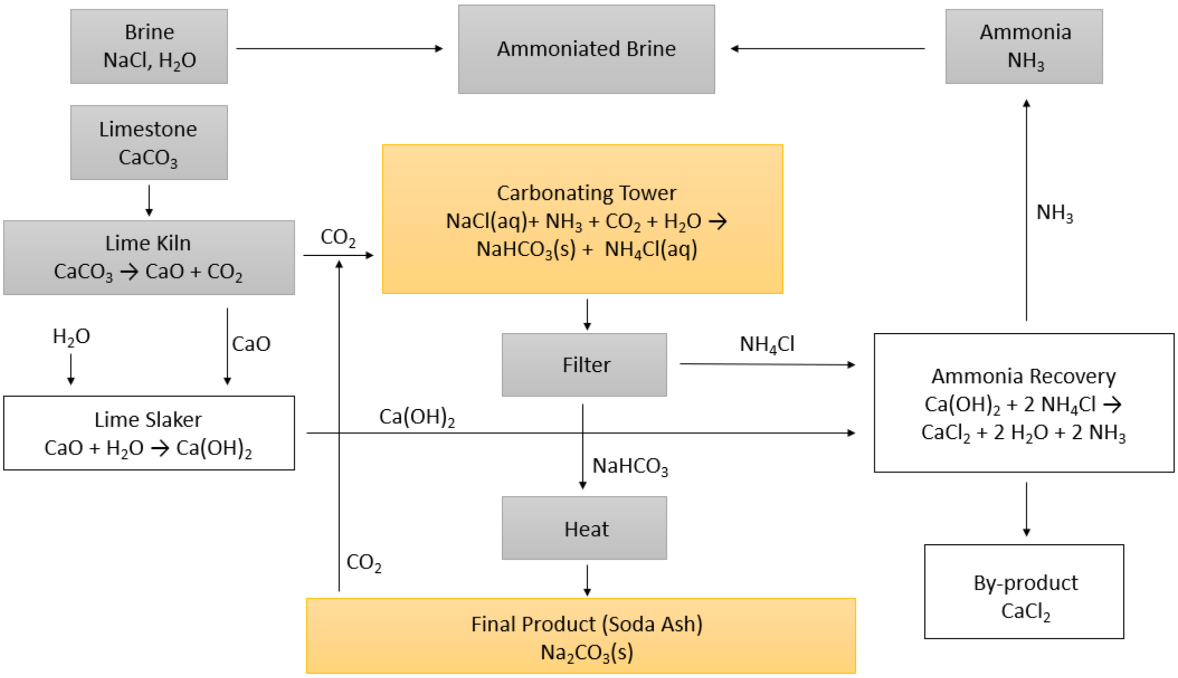


Figure 2.3.3-1: Diagram depicting the Solvay Process for the production of Sodium Carbonate (Na2CO3). Adapted from www.mogckchem.weebly.com.

Alkali carbonates present lower alkalinity than other activating agents and cannot be used in conjunction with all kinds of precursors due to this. Na_2CO_3 also has the disadvantage of being relatively hard to dissolve at lower temperatures (Provis & Jakob, 2014). Likewise, cooling such a solution will cause the sodium carbonate to precipitate while heating it may cause the formation of hydrous carbonate phases. Contact with CO_2 may also lead to the carbonation of the solution and precipitation $NaHCO_3$. On the other hand, the viscosity of Na_2CO_3 and $NaHCO_3$ solutions is similar to that of water which makes these substances easy to work with.

2.3.4 ALKALI SULFATES

Alkali sulfates can also be used in alkali activation of certain aluminosilicate precursors. Sodium sulfate can be used to this effect, while potassium and other alkali metal sulfates are not commonly used.

Sodium sulfate is an easily obtainable reagent and is also relatively inexpensive since it can either be mined directly or obtained as a byproduct of other chemical processes at an industrial level. These processes are mainly associated with the production of Hydrochloric acid (HCl), the Mannheim process and the Hargreaves process respectively (Equation 2.3.4-1) (Butts, 1997; Hargreaves, 1873). It is estimated that two thirds of the world sodium sulfate production come from mining while the remaining one third comes from industrial production.

$$2\,NaCl + H_2SO_4 \rightarrow 2\,HCl + Na_2SO_4$$

$$4\,NaCl + 2\,SO_2 + \;O_2 + 2\,H_2O \rightarrow 4\,HCl + 2\,Na_2SO_4$$

Equation 2.3.4-1: Mannheim process (above) and Hargreaves process (below) respectvely.

A downside of using sodium sulfate is the possible formation of sodium salts during the activation process of hydraulic binders. The products formed depending on temperature conditions are the anhydrous salt, Thenardite, the decahydrate, Mirabilite (Glauber's Salt) or a heptahydrate sodium sulfate phase (Steiger & asmussen, 2008).

3 MATERIALS, METHODOLOGIES AND ANALYTICAL METHODS

3.1 Materials

3.1.1 DDL.ECM PROJEÇÃO OVERVIEW

The mortar used in this experiment is the ‘DDL.ECM Projeção’, a dry, premixed lime-based mortar created and distributed by DDL Arg. It classifies as an industrial, light, thermal insulating mortar meant to be used for both indoor and outdoor applications such as columns, walls and ceilings.

From the technical information data sheet in Appendix D (DDL Arg., 2017a), DDL.ECM ‘Evolution Cork Mortar’ Projeção (Projection), uses both slaked and natural hydraulic lime as well as natural cement binding materials along with properly calibrated aggregates. The core aggregate giving this product its commercial name is granulated cork. This natural element is responsible for the mortar’s light weight and high thermal resistance without compromising mechanical properties; additionally, it reduces the product’s environmental impact.

This product was designed for use as a thermal insulating mortar to be applied in rehabilitation and restoration projects dealing with stone, brick and earth masonry as well as modern construction.

As for technical performance data, DDL.ECM Projeção displays a compressive strength at 28 days between 0.4~2.5 N/mm2 as well as a flexural strength of 0.37 N/m2. The capillary water absorption for this mortar is in the range of under 0.40Kg/m2 at 0.5 minutes and, being a thermal insulation mortar, the value for thermal conductivity is as low as 0.77 W/mK. All of these details can be explored in the official DDL.ECM projeção Datasheet provided in APPENDIX D.

3.2 Planification

3.2.1 GOALS AND APPROACH

As was mentioned in the introduction, the objective of this experiment is to ascertain whether alkali activation methods can improve the physical properties of the studied mortar. While this study prioritizes the development of the mortar's thermal properties, especially thermal conductivity, mechanical behavior of the final product is to be tested as well. Thus, the main course of the experiment can be split into several sub-objectives:

- Understanding how Thermal conductivity evolves for the different preparations over time;
- Understanding how Compressive strength evolves for the different preparations over time;
- Understanding how Capillary water absorption evolves for the different preparations over time;
- Understanding how Acid dissolution response evolves for the different preparations over time.

The main experimental process went through four different iterations which will be called Trials one through four in the continuation of this chapter. Each trial follows the same methodic structure as the others, differing from the previous only by changing a parameter in an attempt to reach a solution to the problem question. A simplified, schematic representation of the method detailed throughout this chapter can be observed in Figure 3.2.1-1.

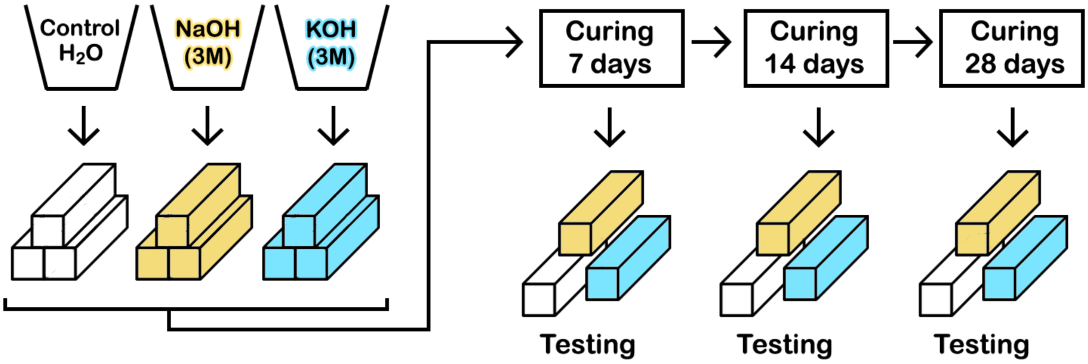


Figure 3.2.1-1: Simplified diagram depicting the methodology of the experiment.

3.2.2 EXPERIMENTAL PARAMETERS

This study is highly experimental in the sense that no alkali activation tests were ever performed on the mortar used. That being the case, the main parameters of the experiment will be *Activators Used* and *Time*. Additionally, and while not expected from the onset, a third parameter *Curing Conditions* can be added due to the changes made to ambient humidity in later trials.

The parameter *Activators Used* is probably the most important focus point of this experiment. Aside from a control specimen hydrated with only water, two alkali activators were used as described in the materials chapter: Sodium Hydroxide (NaOH) and Potassium Hydroxide (KOH). The expectation was that specimens activated with different activators would present different behaviors when testing both mechanical properties and thermal conductivity. The possibility that efflorescence might occur was also a topic of interest and which might be related to the use of a specific kind of alkali.

The parameter *Time* is naturally of high interest as many sub-objective related properties will evolve over the curing period and even afterward. In order to get a good indication of properties such as compressive strength, for example, readings must be taken at several different ages. For this reason, it was decided that specimens of each group would be tested at the ages of seven days, fourteen days and twenty-eight days. This incremental window of time was chosen as it both starts at an early age when testing is already possible (7 days) and ends at an age that allows for the measurement of a standard international metric for material strength (28 days) while keeping a constant doubling rule for time spent until testing.

The parameter *Curing Conditions*, while not initially a part of the study, can be of high relevance depending on the degree of variation within the curing environment. In this case the most prominent property under evaluation in this parameter will be ambient humidity since the only other influencing factor in play, temperature, remained unchanged throughout the different trials. As it is, curing humidity is likely to influence the final properties of an alkali cement, hence why it was added to the parameters.

3.3 Methodologies

3.3.1 ACTIVATOR PREPARATION

Two different alkali activators were used in experimental procedures: sodium hydroxide (NaOH) and potassium hydroxide (KOH). Both of these components were prepared in laboratory conditions using the respective chemical reagent in the form of beads, NaOH and KOH. Specific amounts of hydroxide beads were weighed based on each reagent's molar mass so the addition of a pre-determined volume of water (1L) would result in aqueous solutions with known concentrations (Cowles, 1908). In this experiment, the molar concentrations of the activators used are 3 M (mol/L).

The reagents were placed in labeled goblets and stirred with the addition of deionized water until complete dissolution occurred. This process was carried out in a fume hood and the proper safety equipment was used at all times. The dissolution of both NaOH and KOH is an exothermic reaction, releasing a lot of energy in the form of heat (Provis & van Deventer 2009). For this reason, the newly produced alkali activators were left to cool down for two hours before being transferred to properly labeled volumetric flasks (Figure 3.3.1-1).

Figure 3.3.1-1: Sodium and Potassium hydroxide activators (respectively) in volumetric flasks.

3.3.2 MIXING PROCEDURE

The preparation of the specimens was carried out sequentially for each trial, beginning with the control sample (DDL-H_2O), then the specimen activated with NaOH (DDL-NaOH) and finishing with the KOH (DDL-KOH) sample. The methodology employed was the same for each trial with certain parameters changing to obtain different results.

The process starts with the mortar being scooped from its bag and into a plastic cup on a digital scale in order to weigh the necessary amount of precursor. During the first trial 1.5Kg of mortar were weighed and used in the procedure, an amount that proved more than sufficient and which was subsequently reduced to 400g in the following trials to minimize waste.

As per the preparation instructions for the DDL.ECM Projeção mortar (DDL Arg., 2017b), the product should be mixed with water at a rate of approximately 96% weight of the mortar used. This precursor/activator ratio was used for all specimens across all trials. The control specimen was prepared by mixing the mortar with water only, while the two alkali activated samples were prepared using NaOH and KOH solutions respectively with a concentration of 3M (mol/L) as detailed in the previous topic.

Both the precursor and activator were placed in a 5L bucket and stirred manually for approximately a minute to minimize dust resuspension when mixing. A different container was used in the first trial only, consisting of a 20L bucket, due to the significantly larger amount of material used then. Due to the difference in container size, different mixing utensils were used as well. In the first trial, an industrial grade power drill with a mud beater attachment was used to stir the mixture at roughly 1000rpm for 5 minutes. In trials two and tree, due to constraints regarding the amount of precursor available, a laboratory grade mortar mixer (Figure 3.3.2-1) was used to stir the mixture at 140 rpm for 5 minutes. The same mixer was used in trial four for the same duration, but his time with a mixing speed of 285rpm.

The homogeneous mixture was then cast using two different types of molds (Figure 3.3.2-2). For Trials one and two, standard 3 slot (40 x 40 x 160 mm) cast iron molds were used; these were then replaced with 9 slot (40 x 40 x 160 mm) wooden molds for trials three and four. All molds were coated with a thin layer of protective oil prior to the procedure. The mixture was carefully applied onto the slots with a metal spatula and softly compressed with a wooden prism to help fill any vacuums that might exist. This stage ends with the molds being filled and the mixture spreading out evenly.

Figure 3.3.2-1: Mortar mixer (left) and digital scale (right) used in the mixing procedure.

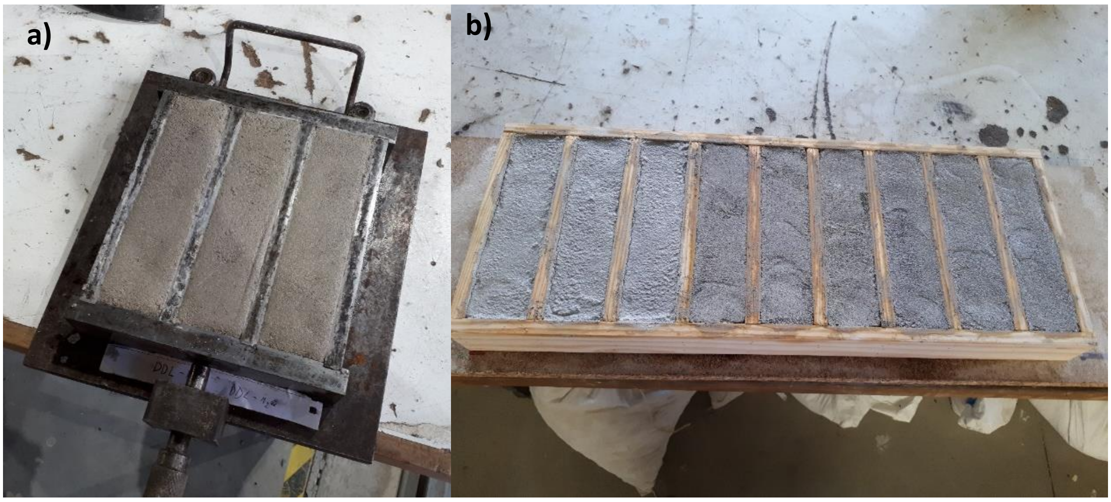


Figure 3.3.2-2: a) DDL-H2O mixture from Trial one in an iron mold. b) DDL-H2O, DDL-NaOH and DDL-KOH, respectively, from Trial four in a wooden mold.

3.3.3 CURING CONDITIONS

Once the mix was cast in the molds it needs time to allow the hydration and geopolymerization reactions occur. The preparations were left to set and cure in slightly different conditions depending on the trial.

As was described in the Planification sub chapter, the plan was to let the mixtures set for 7, 14 and 28 days before testing them (Figure 3.2.1-1). After being cast in their respective molds, the mixtures would cure for 5 days in a climate chamber with a relative humidity of 95% at a temperature of 20º C, before being taken out of the mold (Figure 3.3.3-1). The specimens would then cure for 2 more days in a different climate chamber at 65% relative humidity and 20ºC, totaling 7 days of curing, after which, a specimen from each group (control, NaOH and KOH) would be tested. The remaining two specimens from each group would remain in curing (65% relative humidity) after demolding until the ages of 14 and 28 days respectively before undergoing the tests. This was the method used in Trials one and two. In Trial three, the mixture cured at 95% relative humidity for 7 days before demolding. In Trial four the mixture would spend 3 days curing at 95% relative humidity and then transition to the 65% humidity chamber where it would cure for another 4 days, totaling 7 days of age, before some specimens were demolded, leaving the remaining ones curing until the age of 14 days at which point the same procedure is employed.

Figure 3.3.3-1: Mixtures DDL-H2O (top left), DDL-NaOH (top right) and DDL-KOH (bottom) from Trial one undergoing curing in a climate chamber at 95% relative humidity.

3.4 Analytical Methods

3.4.1 X-RAY FLUORESCENCE (XRF)

Several analytical procedures involving X-Ray methods were employed in the making of this thesis.

The method of X-Ray Fluorescence (XRF) was used to characterize the DDL.ECM Projeção mortar as seen previously. This method involves irradiating a sample with X-Rays and then measuring the emission of fluorescent radiation from the excited particles in the sample (Thermo Fisher Scientific). Each element produces a characteristic pattern of X-ray fluorescence, thus, XRF is a reliable, non-destructive way of getting a detailed chemical analysis of the chosen material.

To start the process, 1g of mortar was weighed and taken for calcination at approximately 1000ºC to determine loss on ignition (LOI). Another 10g of mortar were weighed in a different container and inserted into a hydraulic press (Figure 3.4.1-1 a). The resulting disk is then used in an X-Ray Fluorescence analyzer (Figure 3.4.1-1 b) and the results downloaded into a computer.

Figure 3.4.1-1: a) Hidraulic press used to create sample disks. b) X-Ray Fluorescence analyzer with several sample disks visible.

3.4.2 X-RAY POWDER DIFFRACTION (XRD)

The method of X-Ray Powder Diffraction (XRD) was also used to characterize the mortar, additionally, it was used to analyze material from Trial four samples activated with NaOH and KOH respectively.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample (Moecher, 2004; Hollecher). Incident rays diffracted by the sample material can then be counted and analyzed to determine the mineral phases existent in the sample.

For each of the three specimens, 6g of material were collected and ground to fine dust using an agate mill. The dust was then taken for analysis using an X-Ray Powder Diffraction instrument (Figure 3.4.2-1).

Figure 3.4.2-1: X-Ray Powder Diffraction Analyzer.

4 RESULTS AND DISCUSSION

4.1 Results

4.1.1 TRIAL ONE

The samples in Trial one were retrieved from the climate chamber after 5 days according to the established protocol to proceed with demolding. Upon close inspection, the alkali activated samples, still in the iron mold, appeared damp and varying in physical appearance. While DDL-NaOH appeared to have a solid consistency, DDL-KOH was malleable to the touch.

Attempting to demold the samples at this stage produced mixed results. Control samples (DDL-H2O) hydrated with just water detached from the mold with little effort and maintained a solid consistency for the most part. Two out of the three samples from the control group came out intact and were taken to the 65% humidity climate chamber while the third showed damage along the edges and was discarded.

DDL-NaOH and DDL-KOH, the alkali activated samples, all stuck to the mold when demolding. DDL-NaOH revealed to only have a solid consistent layer at the top where air interaction occurred. This layer was 2~3mm thick and covered a spongy and damp core that resembled wet soil. All three specimens also left a significant portion of the material stuck to the mold and crumbled when demolded which resulted in them being discarded.

DDL-KOH yielded similar results to DDL-NaOH. When demolding the samples, significant amounts of material remained stuck to the mold. Unlike with the previous group, DDL-KOH samples did not show any particular layering and instead seemed uniformly damp and inconsistent, also crumbling when demolded. All three samples were discarded. It should be noted that the KOH samples showed slight discoloration when compared to the darker NaOH group.

Unfortunately, due to the lack of viable specimens in each group no further tests could be run to determine thermal nor mechanical properties. It was decided that a second trial could possibly yield better results by changing some parameters.

4.1.2 TRIAL TWO

Again, the samples in Trial two were retrieved from the climate chamber after 5 days for demolding. Preliminary observation didn’t show significant changes when compared to the previous attempt.

The control group, DDL-H_2O, was perhaps the most affected by the parameter changes. This time, the samples looked spongy or porous in consistency. Prodding the samples with a finger easily left noticeable dents and squeezing them in one hand revealed their brittle behavior. All three samples showed damage around the edges after demolding as some material stuck to the mold, being ultimately discarded.

DDL-NaOH behaved similarly to the last trial. All three samples showed solidity in a top layer that covered a damp and crumbly section that stuck to the mold. The samples could not be properly demolded due to their damp soil consistency once again and were discarded.

DDL-KOH also displayed the same behavior. All three inconsistent samples crumbled when demolding as material remained stuck to the mold. All three were discarded. Again, the KOH group shows a lighter color when compared to the NaOH group.

No tests could be conducted from this trial due to the lack of viable samples from each group. A third trial then took place.

4.1.3 TRIAL THREE

Observation of the samples still in the wooden mold left some doubts as to their physical consistency. For this reason, the samples were left to cure for two extra days before demolding.

Control group DDL-H_2O (Figure 4.1.3-1) exhibited similar behavior to the last trial. The samples were spongy and porous, breaking easily under pressure. They also stuck moderately to the mold, which made it impossible to demold the samples without some of them sustaining damage. Two of the three samples cracked in several location while the third specimen suffered material loss on its underside due to what appears to be poor aggregation. Overall, the samples proved brittle and defective, and were promptly discarded.

DDL-NaOH samples (Figure 4.1.3-1) behaved better in this trial. The samples showed a dark color and appeared dry on the surface but maintained some moisture in the core, although not nearly as much as observed in earlier trials. They showed uniform consistency without any observable layering and didn’t leave significant amounts of material stuck to the mold. All three samples were, however, very brittle and cracked under pressure. All samples also lost material around the edges just from being handled. All three samples were discarded.

DDL-KOH samples (Figure 4.1.3-1) behaved like NaOH did in earlier trials. It stuck to the mold when demolding and crumbled if not handled with care. The samples were not consistent, displaying only a top layer with some resemblance of solidity while the damp core fell apart while handling. This time, however, the samples appear darker than those of NaOH in the same trial, probably due to higher amount of moisture observed in DDL-KOH. Two samples were discarded, while one was kept in the 95% relative humidity chamber for over 48 days. When demolded the sample was very moist and crumbled like a pile of watery dirt when demolded, having to be discarded as well.

Without any viable samples to undergo testing, a fourth trial was run.

Figure 4.1.3-1: Results of Trial three experimental procedure; three DDL-H2O specimens, three DDL-NaOH specimens and one DDL-KOH specimen, respectively, from left to right.

4.1.4 TRIAL FOUR

As explained in the Chapter 3.3.4., samples from this trial underwent different curing conditions; 3 days at 95% relative humidity plus 4 days at 65% relative humidity. It's also worth noting that after the first three days the molds were turned on the side so the samples were in contact with air on two surfaces instead of the usual method in which only the top side was open to air.

DDL-H_2O (Figure 4.1.4-1; Figure 4.1.4-2 a)) showed little improvement since the last trial. All three samples displayed the same porous and spongy nature that was observed before. They were also still relatively brittle, breaking around the edges and even along the center if enough pressure was applied. Some of the material remained stuck to the molds when demolding just like before. Again, the three samples were discarded due to damage suffered.

DDL-NaOH (Figure 4.1.4-1; Figure 4.1.4-2 b)) showed appeared very dry and displayed a stained pattern on its surface that was not observed in any other group or trial. The samples were in fact very dry, even in the core which up until now remained damp to moist. As a result, when the samples were demolded, all three of them promptly crumbled into piles of dry soil-like material. The samples were extremely crumbly and did not retain any feasible consistency. All 3 samples were discarded.

DDL-KOH (Figure 4.1.4-1; Figure 4.1.4-2 c)) was uniformly colored brown, aside from that, it behaved similarly to samples from the NaOH group. All three samples broke down into piles of dry, sandy soil when demolding. All three samples were discarded.

Figure 4.1.4-1:Trial four specimens after the curing period; three DDL-H2O specimens, three DDL-NaOH specimens and three DDL-KOH specimens, respectively, from left to right

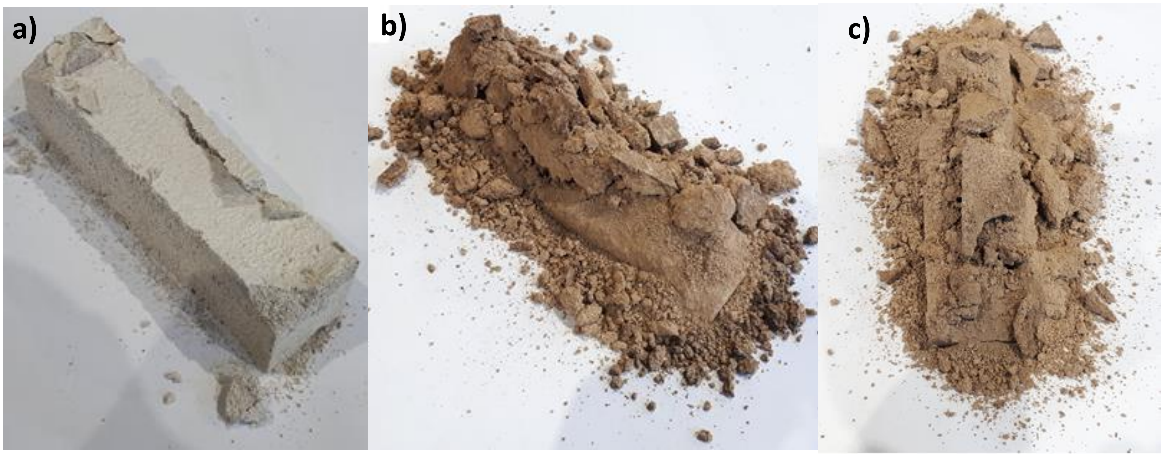


Figure 4.1.4-2: Results of the Trial four experimental procedure. a) DDL-H2O. b) DDL-NaOH. c) DDL-KOH.

4.2 Discussion

From the results of the experimental procedure, the first thing that can be noticed is that across four different trials, attempts to make solid, consistent bricks out of the alkali activated mortar proved unsuccessful. Table 4.1.4-1 resumes the results of the 4 trials in terms of specimen consolidation. Because of this, no viable activated specimens were created at any point which could be used to test for mechanical resistance parameters or thermal properties.

Trial	DDL-H2O	DDL-NaOH	DDL-KOH
Trial One	2 intact, 1 damaged	3 crumbled	3 crumbled
Trial Two	3 damaged	3 crumbled	3 crumbled
Trial Three	3 damaged	3 damaged	3 crumbled
Trial Four	3 damaged	3 crumbled	3 crumbled

Table 4.1.4-1: Specimen integrity upon demolding in each trial.

Table 4.1.4-2: Parameter attributes in each trial.

Trial	Mixing speed (rpm)	Curing humidity	Molds used
Trial One	1000	95% (5 days)	Iron
Trial Two	140	95% (5 days)	Iron
Trial Three	140	95% (7 days)	Wood
Trial Four	285	95%+65% (3+4 days)	Wood

4.2.1 CONTROL GROUP, DDL-H2O

The control group (DDL-H2O) was by far the most successful when it comes to specimen consistency. It was the only group to ever produce viable specimens for testing as seen in Table 4.1.4-1. These results occurred in Trial One and all subsequent Trials produced lower quality samples which broke easily when handled as detailed in the previous sub-chapter (Figure 4.2.1-1). Analyzing Table 4.1.4-2, it is easy to conclude that this change was due to the Mixing speed being altered as all other parameters remained the same between Trials One and Two. Recalling the instructions for the correct application of DDL.ECM Projeção mortar, it is stated that high mixing speeds in the order of 1500rpm should be used. In Trial One, the mix was stirred at 1000rpm while subsequent trials used speeds of 140 and 185rpm respectively, values much lower than advised. The faulty specimens produced by Trials Two through Four can be explained by this parameter as it is possible that the low mixing speeds were not enough to ensure a thorough homogenization and hydration of the mortar constituents. The fragility of the specimens can, therefore, be attributed to incomplete hydration reactions.

Figure 4.2.1-1: a) comparison between Trial one (below) and Trial three (above) DDL-H2O specimens. b) Trial three DDL-H2O specimens. c) close up of Trial four DDL-H2O specimen.

4.2.2 SODIUM ACTIVATED GROUP, DDL-NAOH

The first alkali activated group, DDL-NaOH, activated with Sodium Hydroxide, was uncapable of producing viable specimens across the four trials. As can be observed in Table 4.1.4-1, three of the four trials produced specimens that stuck to the mold and crumbled when demolding while only Trial Three yielded solid 1-piece samples. Analyzing Table 4.1.4-2, allows some interpretation of what the causes of this occurrence might be. Trials One and Two produced similarly crumbly specimens despite the clear change in mixing speed; this parameter does not seem to impact the solidity of DDL-NaOH group specimens.

Samples from these two trials were also damp in their interior which might be attributed to the cast iron mold's poor aeration properties since only the top side of the mixture was exposed to air. This topside produced the hard layer described in the results which covered the damp and unconsolidated core. This is, however, a troubling theory as, theoretically, both C-A-S-H gel hydration and N-A-S-H gel polymerization reactions require high moisture environments to evolve.

Trial Three managed to produce solid, yet, fragile samples (Figure 4.2.2-1 a)) after two parameter changes: curing time and mold material. It can be speculated that the wooden molds allow the mixture to "breathe" a little more effectively since the wood is naturally porous and might facilitate air exchanges in zones that are not exposed to the atmosphere. This could have been the cause of the uniform consolidation in the whole surface of Trial Three's DDL-NaOH specimens whereas previous trials only produced samples with solid top layers. The increase in curing time is likely to have had a positive impact on specimen consistency as well since it allows the polymerization reactions to occur for longer.

In Trial Four makes it clear that alkali activated mixtures require humidity to cure. A slight change in mixing speed (140rpm->285rpm) should not have caused a noticeable impact since it was previously observed that bigger changes in that parameter (1000rpm->140rpm) produced no visible difference. The curing conditions, therefore, explain why the samples all crumbled into piles of material with a consistency reminiscent of dry soil (Figure 4.2.2-1 b)). The three days spent by the mixture in 95% relative humidity conditions were insufficient for the complex inorganic networks to form and the abrupt change to a drier climate chamber at only 65% relative humidity for the remaining 4 days of curing shut down the reactions by drastically reducing the moisture in the system. This resulted in a surface layer of brittle material that easily broke to reveal a dry, unconsolidated core.

The difractogram (Appendix C – DDL-NaOH) from X-Ray Powder Diffraction analysis done on Trial four specimens shows some results worthy of note.

Mineralogical composition is dominated by calcite and alite, both being already predominant in the original mortar; however, the relative amount of alite decreased as well as the relative proportions of the phyllosilicates (mainly micas-illites and kaolinites). This can be interpreted as a result of the sodium hydroxide chemical attack on the mixture which successfully dissolved the aluminosilicate bonds, thus breaking down those minerals.

A more concerning find is that several peaks attributed to Calcite appear on the difractogram, meaning that the dissolution of the calcium phases was mostly incomplete. This could mean the activator used carried a larger than necessary concentration of alkali elements and not enough water to complete the hydration of the OPC phase in the precursor.

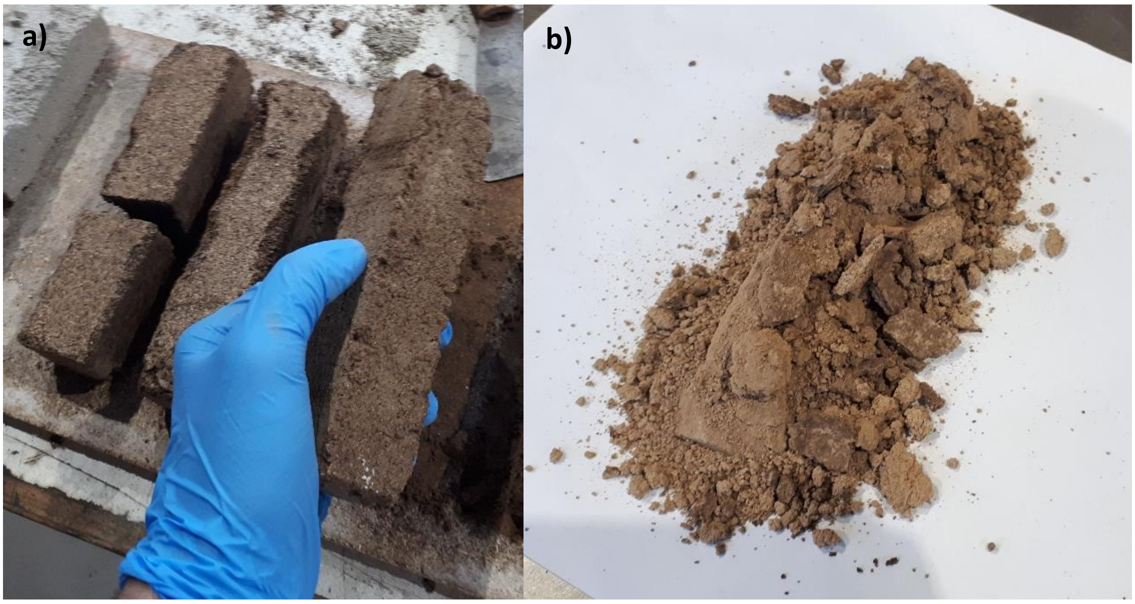


Figure 4.2.2-1: a) Trial three DDL-NaOH specimens. b) Trial four DDL-NaOH specimen.

4.2.3 POTASSIUM ACTIVATED GROUP, DDL-KOH

DDL-KOH group specimens behaved consistently poorly throughout the four trials (Table 4.1.4-1). Trials One and Two produced very little changes in the specimen outcome as detailed in the results subchapters 4.1.1. and 4.1.2.. In both trials the resulting samples stuck to the mold and crumbled when demolded; they were also observed to be moist and bear the likeness of wet soil once broken. This appears to indicate that the change in mixing speed (Table 4.1.4-2) does not affect the solidity if the specimens.

Trial three, while also unsuccessful, showed a slight change in the samples. These now had a rigid top layer similar to that observed in DDL-NaOH samples from Trials One and Two (Figure 4.2.3-1 a)). In the DDL-NaOH discussion it was theorized that the change to wooden molds improved the aeration of the mixture, thus yielding better results; however, the fact that only the top most section of DDL-KOH samples exhibited solidity instead indicates that the increased curing time (Table 4.1.4-2) might have had a more beneficial effect. In contrast, the sample that was demolded after 48+ days shows that too long an exposure to humid environments has the reverse effect and actually turns the sample into incohesive, wet dirt. It can be theorized that a maximum effectiveness curing period must exist before the material starts to deteriorate.

Trial four had very much the same effect on DDL-KOH as it did on DDL-NaOH. The specimens broke down into piles of dry soil-like material upon demolding and showed very little cohesion (Figure 4.2.3-1 b)). The same argument can be made that the quick transition from the 95% relative humidity chamber to the 65% relative humidity chamber (Table 4.1.4-2) ended the hydration and polycondensation reactions still developing in the mixture, thus, negatively affecting the internal consistency of the resulting samples.

The diffractogram (Appendix C – DDL-KOH) from the X-Ray Powder Diffraction Analysis on a DDL-KOH specimen from Trial four also points in the same direction as the one for DDL-NaOH from the same trial. A pronounced decrease on alite and phyllosilicates' relative proportions is evident, comparing with the diffractogram of the base mortar, which indicates the successful dissolution of the aluminosilicate phases by the Potassium Hydroxide activator. The occurrence of several Calcite related peaks, however, seems to indicate a poor dissolution of the OPC phase in the precursor, and consequently, a poor hydration reaction of the same elements which are responsible for the creation of the C-A-S-H gel. This could explain the lack of rigidity in the specimens obtained from the procedural trials. An anhydrite phase in the diffractogram, again, corroborates this theory.

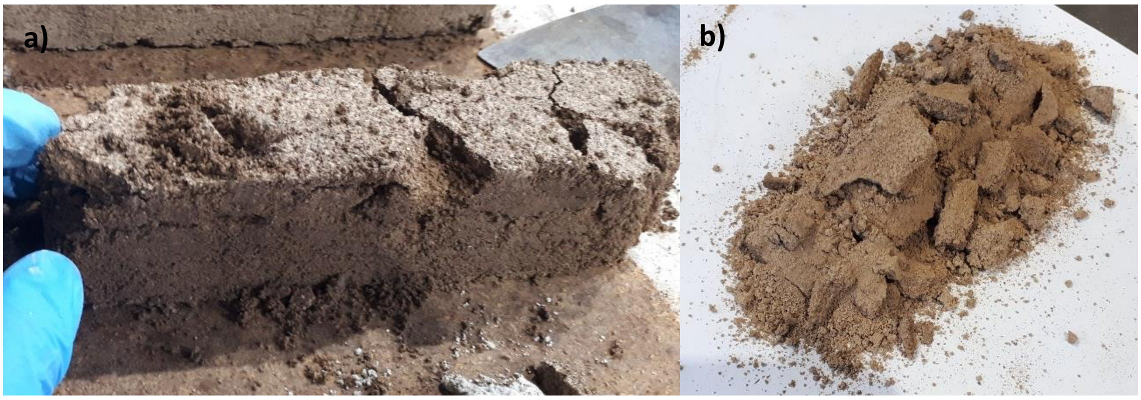


Figure 4.2.3-1: Trial three DDL-KOH specimen. b) Trial four DDL-KOH specimen.

4.3 Characterization of DDL.ECM Projeção

DDL.ECM Projeção is a standard OPC mortar containing approximately 60% weight content of natural hydraulic lime. This value is backed up by the X-Ray Fluorescence analysis results detailed in Table 4.2.3-1, where the CaO and 'Loss on Ignition' (LOI) values add up to roughly that amount. The mortar also contains a noticeable amount of MgO which is attributed to dolomite coming mixed with the calcite used in the industrial process that makes these lime-based products. The small amount of Fe_2O_3 comes from iron sources added in the same process when making the OPC clinker in the mortar. Additionally, the high values of both Al_2O_3 and SiO_2 are due to the fine aggregate in the mortar's composition as these tend to be aluminosilicate materials.

Table 4.2.3-1: Simplified DDL.ECM Projeção Mortar chemical composition table. The full table can be seen in Appendix B.

Element	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**
% Weight	0.437	2.727	10.324	22.295	0.062	0.975	0.039	1.193
Element	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**Sr**	**Ba**	**LOI**	**Total**
% Weight	37.251	0.426	0.019	1.861	0.133	0.022	22.180	**99.944**

From the chemical composition data presented in TABLE, it is possible to locate DDL.ECM Projeção on a ternary diagram for characterizing cement precursors. The results seen in Figure 4.2.3-1 predict that C-A-S-H gel formation would be favorable when using this precursor, which is to be expected of an OPC based material with such a high CaO content. This is in accordance with expectations for alkali activation of blended systems.

Ternary Diagram Composition:

- Al_2O_3: 14.776%
- SiO_2: 31.909%
- CaO: 53.315%

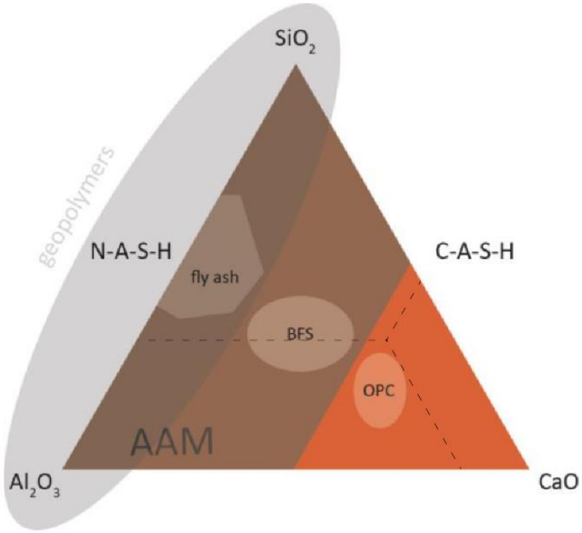


Figure 4.2.3-1: Ternary diagram for the cateforization of Alkali Activated Material precursors. Adapted from Garcia-Lodeiro et al. (2015b)

Aside from the obvious hydraulic lime, DDL.ECM mortar contains a number of mineral phases that can be identified through analysis of X-Ray Powder Diffraction (XRD) patterns (Appendix C - DDL). Main minerals are calcite and alite, followed by quartz and feldspars. Phyllosilicates and Al and Fe oxides/hydroxides are also present. These later are related to the clays used as fine aggregate in the mortar to add consistency. Calcite, as well as its polymorph, vaterite, point to the incomplete calcination of the limestone in process of creating the OPC clinker used in the mortar.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This dissertation provided not only a way to find the practical solution to an industrial case study, but it was also a valuable opportunity to further develop knowledge in both theoretical fundaments of cement engineering and laboratory methodologies associated with the subject. Ultimately, the benefit for either the industrial sector and the scientific community comes in the form of data gathered from the results of the whole process and the conclusions derived from those.

Although much was learned in the course of writing this thesis, it must be stated that not all previously stipulated goals could be achieved. The primary goal which was to evaluate the possibility of improving DDL.ECM Projeção mortar's thermal insulation properties by using alkali activation methods was unsuccessful. As was stated in sections 4.1.1. through 4.1.4. of the results subchapter, the experimental procedure failed to produce a large enough variety of specimens viable for testing, consequently making it impossible to answer the primary problem question.

The properties included in the sub-objectives associated with the goals of the thesis are, as stated in section 3.2.1. of the Planification subchapter (3.2.), Thermal conductivity, Compressive strength, Capillary water absorption and Response to Acid Dissolution. As a direct consequence of the lack of viable test samples, the evolution of these properties could not be measured, and the objectives could not be met.

The second goal of this thesis, to ascertain whether a product originated from the alkali activation of DDL.ECM Projeção mortar is technically viable, can be considered fulfilled to the best of the experiment's attempts. The brittle and crumbly specimens produced in trials one through four of the procedure stand as evidence that further testing is required before a proper working product can be achieved from the activation of the subject mortar using alkali activation methods.

From chapter 4., Results and Discussion, a couple notions on the subject became evident, while others remained arguably unanswered. It was made obvious by Trial Four that alkali activated mixtures produce significantly worse results if not given enough curing time in humid environments. As such, in regard to parameter ‘Curing Conditions’, it can be concluded that early transitions to dry environments, and consequentially the shutting down of ongoing reactions in the curing mixture, are severely prejudicial to the consistency of the final product.

Another evident find is that high mixing speeds produce better quality specimens in control groups while no clear evidence was found on the effect it may have in alkali activated groups. Similarly, the effect of the material used in the molds remains unknown, mostly due to the coupling of different parameter changes switching from Trial Two to Trial Three, which makes it harder to verify which is more influential.

The effects of parameter ‘Time’ remain poorly understood in this matter, mostly due to insufficient testing and results. The increased performance of the alkali activated groups in Trial three when compared to the other trials might be related to the extra time spent curing before demolding, however there is not enough data to extrapolate a correlation from.

The parameter ‘Alkali Activator’ is one based upon which some conclusions can be drawn. As observed in Trial Three, Sodium Hydroxide activated samples can consolidate given the right conditions, even if the resulting material is more fragile than expected. This was not observed in samples activated with Potassium Hydroxide, which behaved very poorly throughout the four trials, although with a slight performance increase in Trial Three as well. The conclusion taken from here is that NaOH activated samples develop physical strength more quickly than KOH activated groups at early ages of curing.

5.2 Recommendations for Future Studies

While this dissertation has come to an end, there is still plenty left to be discovered. The potential of Alkali Activated Materials is immense, and the world has only recently opened its eyes to the myriad possibilities this scientific area still holds. Thus, it is proposed that further studies on the subject should be conducted taking into consideration some of the recommendations detailed in this final subchapter.

From section 3.1.2. in Chapter 3., DDL.ECM Projeção was characterized as an OPC based mortar containing high amounts of CaO and favoring the development C-A-S-H gels. Alkali Activated Cement studies using OPC based materials as precursors are expected to use starting materials containing SiO_2, CaO and Al_2O_3 contents of at least 20% in order to be defined as hybrid or blended cement systems. This mortar does not meet these requisites as the amount of Al2O3 present is of only ~10.3%. This coupled with the dominant CaO content when compared to the remaining two indicates that the viability of alkali activation of this mortar is low unless certain compensation measures are taken beforehand to balance the chemical composition of the system. Taking this information into account, it is recommended that further studies experiment with the addition of aluminosilicate aggregate to the base mortar in order to achieve an ideal chemical composition and obtain better results from the alkali activation procedure. Another recommendation would be to try different activator solutions including Sodium Silicate coupled with an alkali hydroxide in an effort to add more SiO to the system.

As for the laboratorial procedure, it is recommended that more detailed parameter grids are elaborated in the future with the goal of understanding the role of each one of them on the properties being evaluated. The parameter ‘Mixing Speed’ must also be reevaluated with attention to the recommended preparation methods of the mortar used to avoid unexpected behavior of the samples. Another recommendation is that stochiometric calculations are run taking into consideration the chemical composition of the precursor to ensure the concentration of alkali reagents in the activator is 100% effective in the reaction. Lastly, larger sample batches are recommended using individual molds as this would simplify demolding individual specimens without disturbing adjacent samples.

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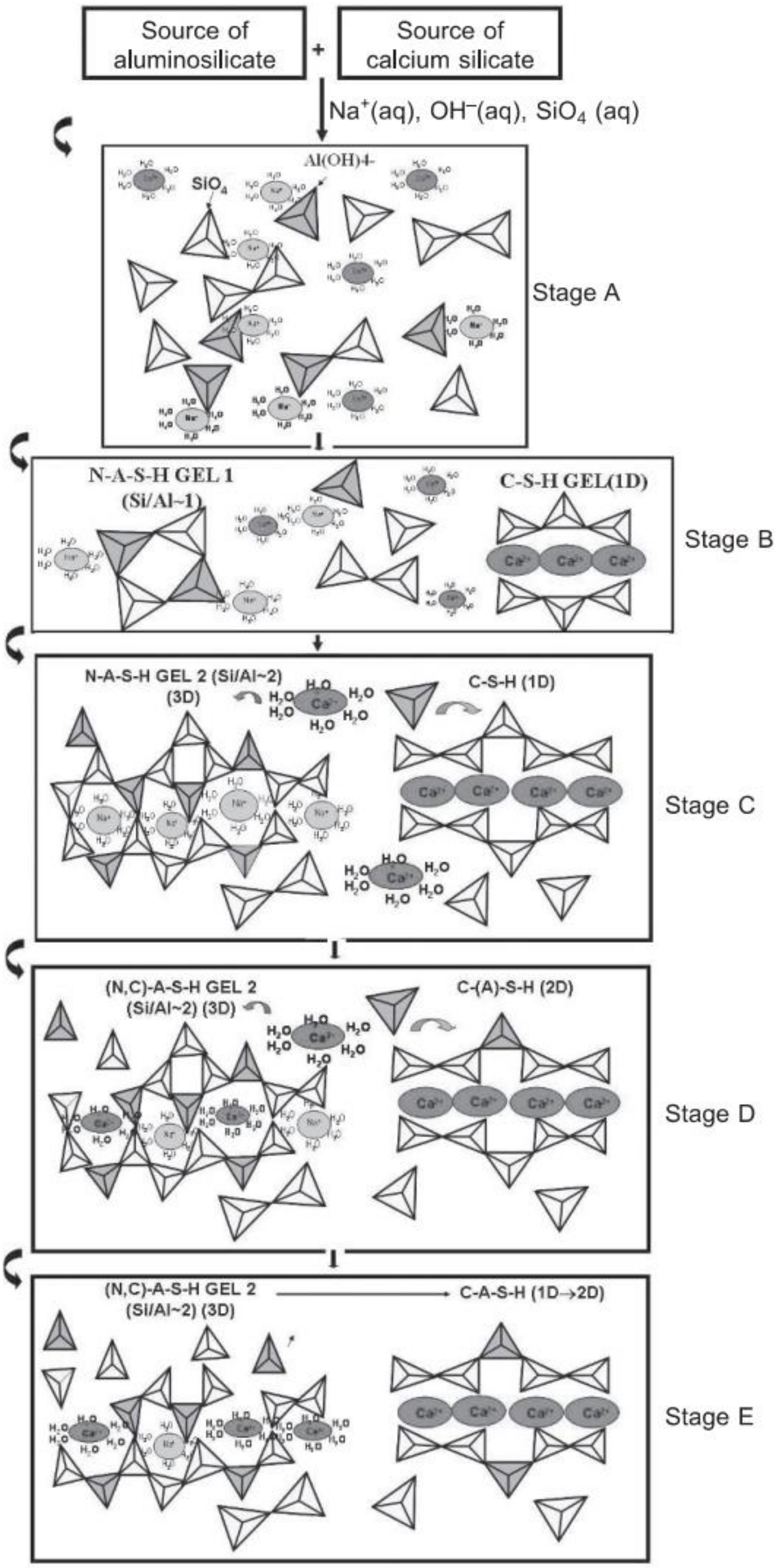
Appendix A - BLENDED ALKALI ACTIVATION MODEL FOR A LOW CALCIUM SYSTEM (30% OPC) ACTIVATED WITH NAOH, ADAPTED FOM GARCIA-LODEIRO ET AL. (2013A).



Appendix B – X-RAY FLUORESCENCE OF DDL.ECM PROJEÇÃO

Universidade de Aveiro
Departamento de Geociências
Results quantitative - OMNIAN 37
4 de abril de 2018

Fábio Matos
DDL

Na2O	MgO	Al2O3	SiO2	P2O5	SO3	Cl	K2O	CaO	TiO2	MnO	Fe2O3	Sr	Ba
(%)	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**
0.437	2.727	10.324	22.295	0.062	0.975	0.039	1.193	37.251	0.426	0.019	1.861	0.133	0.022

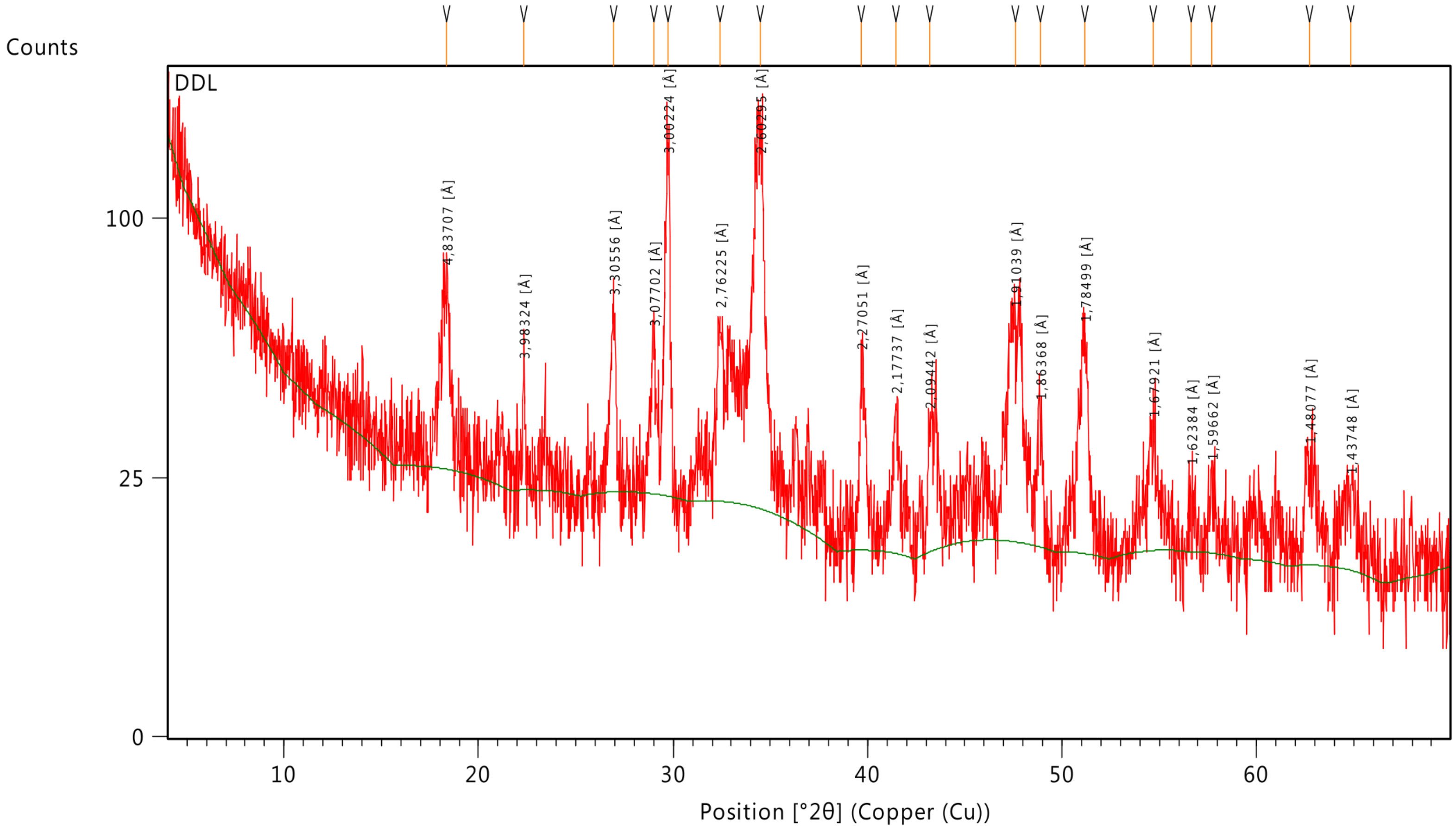
LOI
(%)
22.180

Results quantitative - Pro-Trace 2018
ND=<Min.LLD(ppm)

Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Y
(ppm)	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**
16.7	74.1	47.8	6.6	30.0	26.9	32.3	10.7	ND	8.7	ND	ND	67.5	8.2
Zr	**Nb**	**Mo**	**Ag**	**Cd**	**Sn**	**Sb**	**Te**	**I**	**Cs**	**La**	**Ce**	**Nd**	**Sm**
(ppm)	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**
39.3	7.7	3.1	ND	ND	5.5	ND	ND	ND	7.2	27.9	43.4	16.3	ND
Yb	**Hf**	**Ta**	**W**	**Tl**	**Pb**	**Bi**	**Th**	**U**					
(ppm)	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**	**(ppm)**					
ND	ND	ND	ND	ND	46.1	ND	11.9	8.4					

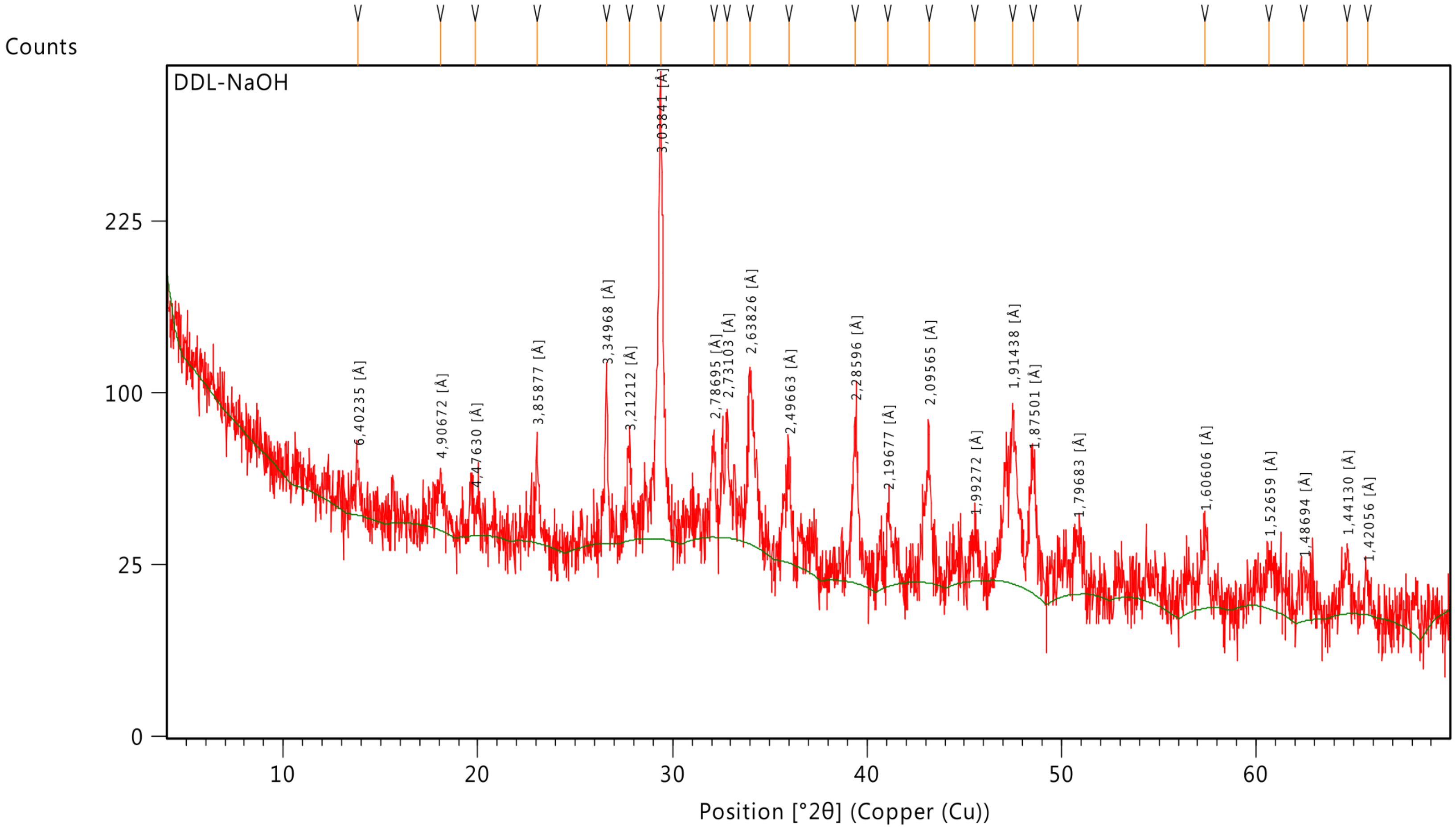
Appendix C - X-RAY DIFRACTOGRAMS FOR DDL (BASE MORTAR), DDL-NAOH (TRIAL FOUR) AND DDL-KOH (TRIAL FOUR) RESPECTIVELY.

Date: 07-05-2018 Time: 09:07:14 File: DDL User: laraterroso



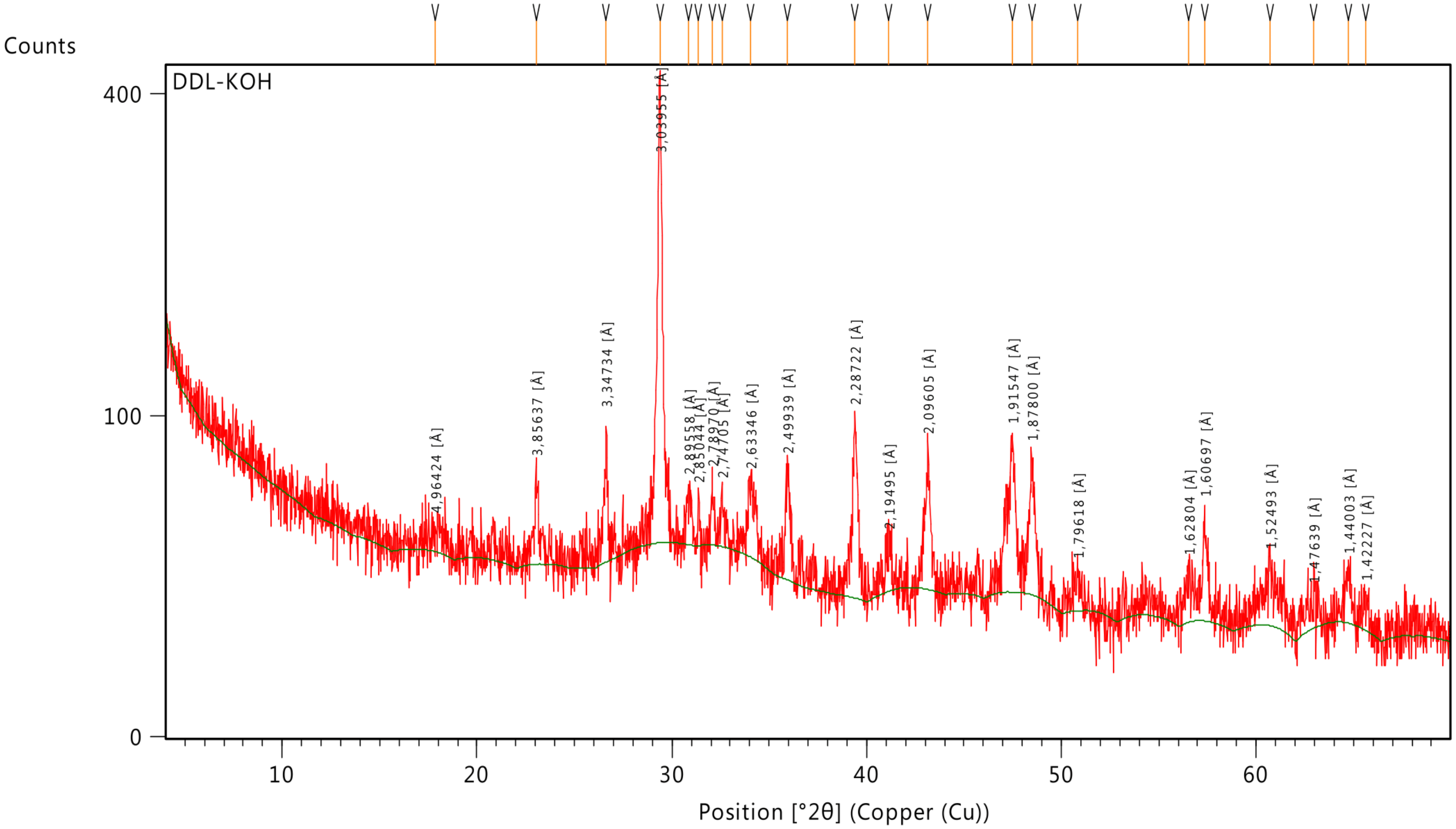
Page: 1 of 1

Date: 12-10-2018 Time: 14:17:58 File: DDL-NaOH User: laraterroso



Page: 1 of 1

Date: 12-10-2018 Time: 14:17:12 File: DDL-KOH User: laraterroso



Page: 1 of 1

Appendix D – DDL.ECM PROJEÇÃO TECHNICAL DATASHEET.

DDL.ECM PROJEÇÃO

Datasheet 601

Patent pending by:

AMORIM
universidade de aveiro

TECHNICAL DATA

DRY PRODUCT

Weight by package	8,5 kg
Dry bulk density (EN 1015-10)	310 to 360 kg/m³
Conservation	12 months

PASTE PRODUCT

Mixing water	96 % ±2 %
Mixing time	6 to 9 minutes
Yield	3 to 4 kg/m²/cm
Work time	30 minutes
Drying time	4 weeks
Cure time	6 months

PERFORMANCE

Class (EN 998-1)	LW T
Compressive strength (EN 1015-11)	CS I
Flexural strength	0.37 N/mm²
Modulus of elasticity	≤ 400 N/mm²
Adhesion (EN 1015-12)	≥ 0.1 N/mm² - FP:B
Capillary water absorption (EN 1015-18)	W 1
Water vapour permeability coefficient (μ) (EN 1015-19)	≤ 15 kg/m².s.Pa
Thermal conductivity (λ10.dry) (EN 1745)	0.077 W/mK
Reaction to fire (EN 13501)	A2 – s1, d0
Durability	Varies according the conditions at the local of application
Colour	Grey

The indications and information are provided in good faith and reflect the last developments. DDL assures the consistent quality of the product, and is not liable regarding its application. Previous tests are recommended to verify the suitability of the product to the substrate and the environmental conditions at the local of application.

Date: April 2017 (version 1)

DESCRIPTION

DDL.ECM PROJEÇÃO (projection) is a premixed mortar, dry. It uses lime (slaked and natural hydraulic) and natural cement as binding materials, and properly calibrated aggregates. The core aggregate is cork, which ensures its light weight and high thermal resistance, suitable mechanical resistance and low environmental impact. It is free of dense graded aggregates. It is an industrial light thermal insulation mortar (LW / T1 – CS I – W1) for outdoor and indoor application. It is a coarse mortar to use in walls, columns, partitions and ceilings. **DDL.ECM PROJEÇÃO** has a suitable mechanical resistance and working time, good plasticity, low level of soluble and hydratable salts, good vapour permeability and low tendency to cracking. The binding, hydrated lime, is in conformity with EN 495-1. **DDL.ECM PROJEÇÃO** is in conformity with EN 998-1.

APPLICABILITY

DDL.ECM PROJEÇÃO was designed to provide thermal insulation or the elimination of the thermal bridges. The good thermal performance contributes greatly to the isolation of facades, and lowers the dew point. Therefore, it represents a good solution to interstitial condensation, assuring a high permeability to vapour. It can be applied in rehabilitation and restoration (stone, brick, and earth masonry), and in new constructions.

PREPARATION AND ENVIRONMENTAL CONDITIONS

Before applying **DDL.ECM PROJEÇÃO** the substrate must be clean of all dust, dirt and paint by brushing or chiselling. Salts, grease and other contaminants must also be removed. After the cleaning, the substrate must be wetted with clean water on the previous day of the application. Before the application on highly absorbent materials, the wetting must be repeated. Irregularities must be levelled by applying several layers of **DDL.ECM PROJEÇÃO**. DDL.ECM MANUAL can be used as a complement. The application must not be done when the temperatures are above 25 °C, nor below 5 °C. The relative humidity must be below 80 %. The application must not be done under strong wind. Until after three days post application, the mortar must not be exposed to rain, direct sunlight or frost.

APPLICATION AND RECOMMENDATIONS

To prepare **DDL.ECM PROJEÇÃO**, add 96 % (weight) of water. For every 8,5 kg of mortar add 8.1 litres of water. Mixing should take place with mechanical mixer, low spin (750 rpm) for 3 to 4 minutes, followed by high mixing (1500 rpm) for 3 to 5 minutes until a homogeneous paste is obtained.

Projection must be made with maximum thickness of 60 mm. When it starts setting, smooth the surface with appropriate tools. Between layers there must be a waiting period of 2 to 4 days for each 10 mm of thickness, and the lower layers must have a coarse surface to maximum adherence. Edges and wedges will probably require the use of appropriate profiles. Dilatation joint of the substrate must be respected. For accessible floors, the mortar must be reinforced with synthetic or natural nets in the external part of the layer. Not wetting the substrate can cause cracking. Saturation is neither recommended. Too much water mixing makes the mortar prone to cracking and the decreases its mechanical characteristics and durability. Equipment and tools must be washed with clean water. The product's pH is high; therefore the materials must be protected from alkaline damages.

Do not add any other products. The surface can be finished using DDL.CM FINISH with net reinforcement.

SAFETY, HEALTH AND STORAGE

Avoid contact with the eyes and skin. Use gloves and safety goggles. Keep away from children. Keep the bag well sealed and in a suitable place. Ensure the adequate transportation of the product. Keep the package in a safe place, do not use or store the product in extreme conditions of temperature, and keep it away from ice and humidity. Always keep in mind the applied legislations. For more information check the label and the safety data sheet.

DDL | Rua Póvoa de Baixo, 100, 4535-334 Paços de Brandão, Portugal | (+351) 964 203 409 | www.ddlarg.com | info@ddlarg.com