Recycling of concrete: Dehydration and reactivation of cement

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Abstract

Recycling of concrete: Dehydration and reactivation of cement
Keywords: cement, recycling, concrete, mortar, dehydration, reactivation

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The main objective is to compare different recycled mortars to conclude which one maintains better mechanical and thermal properties after the recycling process. The compared mortars are formed by a combination of different cement pastes (with Ordinary Portland Cement and blast furnace slag), different activation solutions (water and alkaline solutions) with different proportions of the water-to-cement ratio (water or other solution) and molarities.

The methodology followed starts with the preparation of cement pastes with fresh cement and water, which are heat up (dehydrated) and reactivated with other solutions (water and alkaline solutions, blast furnace slag and fresh cement, to analyse the influence of each product. The reactivated cement pastes are mixed with sand to prepare recycled mortars. These mortars are compared using mechanical test (compressive strength test) and doing a thermal study with a calorimeter and thermogravimetric analyser.

The results show that mortars after the recycling process do not achieve the same properties as fresh or new mortars. But it is seen that the addition of slags and alkalis increases the reactivity of recycled cement, but the compressive strength obtained with alkalis is very low. That is why the main conclusion is that the addition of alkalis gives less strength due to the low workability of the mortars. Also, cement without slags mixed with alkaline solutions does not react as much as mixed with water. In addition, a decrease of water (or other solution) content increases the compressive strength but decreases the reactivity of the mixture. And lower molarity increases the compressive strength, but no difference is seen in the reactivity when comparing it with higher molarity (comparison between 0.5 and 1M).

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PART I: Introduction to the recycling of cement

The first part is a description of all concepts about cement and concrete (production and chemistry) necessary to follow the present Master Thesis, as well as its objectives and organization. Also, there is a basic explanation about the procedure to recycle cement and the justification of the need of recycling cement nowadays. But why nowadays? To know the reason is necessary to understand one of the most popular calculation methods of environmental impact: Life Cycle Assessment, described at the end of the chapter.

Chapter 1: Introduction

1.1. General aspects of the industry of concrete

Concrete is used in construction and civil engineering mainly, but recently it has started being used in other applications thanks to the properties that confer new additives, i.e. concrete with fibres for countertops or tiles [1].

In addition, concrete made of Ordinary Portland Cement (hereafter "OPC") is one of the most important materials since the Industrial Revolution the 18th Century, arriving at 1.5-3 tons/year per capita in the industrial world. The main reason of this is its high compression or compressive strength -as noted above-, the simplicity of the extraction of materials and the process, as well as the fast velocity of fabrication and the easy way to mould it *in situ* [2]. Because of all these advantages, concrete is an unrivalled cheap material.

The process of fabrication of concrete, mortar, cement and other products of this sector generate however a lot of emissions to air (especially), water and soil. So, the main problem of using them is the environmental impact in almost all stages of its life: since the extraction of the raw materials to the waste treatment of the used products (explained in detail further on). Therefore, researchers are looking for new methods to reduce the environmental impact. One of the solutions proposed is using Construction and Demolition Wastes (CDW) as raw materials, because their waste treatment is a priority in the European Union -due to its volume (around 25-30% of the wastes generated in EU) and its high weight- and lots of the materials that compound them can be recycled [3].

1.2. Need of recycling and problem statement

As earlier pointed out, Europe has an issue with the waste treatment for CDW, but other problems are linked with the cement industry: the shortage of raw materials (i.e. limestone and clays) and the negative environmental impact due to mining by quarrying and the emissions released to the atmosphere. A solution to solve the issues with concrete waste and shortage of raw materials is by recycling concrete to produce new cement. By doing this, also the emissions related to the quarrying would be eliminated. It is complicated to eliminate *all* the emissions, because also the recycling process would emit, directly or indirectly, but it would decrease the absolute amount of pollutants emitted to the atmosphere.

 If one analyses the concrete sector, it is seen that it is the biggest of the world, in accordance with the European Pollutant Release and Transfer Register (hereafter "E-PRTR") [4]. Since 1950 the worldwide production of this sector increased almost 800% (Figure 1) but, as seen in Figure 2: World cement production in 2015 [7.], this situation is due to the fast growth of China in the last decades. The Figure 1 is taken form CEMBUREAU, the European Cement Association formed by all the national cement industry associations and cement companies in the European Union (except for Malta and Slovakia) and Norway, Switzerland, Turkey and Serbia [5].
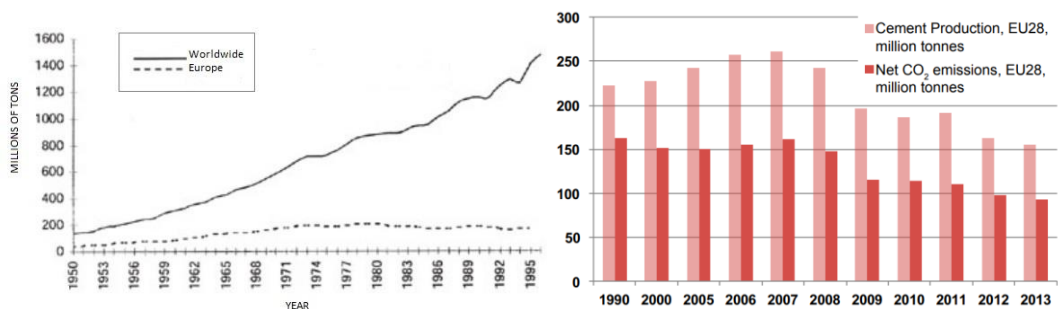
Figure 1: Evolution of cement production. Since 1950 to 1995 [6] (left), since 1990 to 2013 in EU [7](right).

Also, more recent information about the world cement production published is found in the E-PRTR web page (Figure 2), where it is shown that China produces around the 51.3% of worldwide production.
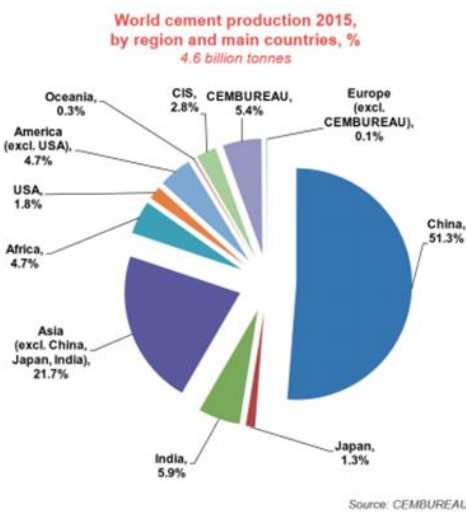
Figure 2: World cement production in 2015 [7].

According to the Lansink's Ladder waste hierarchy, the priorities of waste treatment should be: to reduce the consumption of the natural resources, re-use products (second-life products), recycle materials, valorisation of materials (energy recovery), incineration without energy recovery and lead wastes in landfill, as last option [8]. The problem is that the changes must be done in all the world because gaseous emissions are spread in the globe's atmosphere, so it must be a decision of all countries to make a real difference. This is a very difficult political issue.

The main problem with making an international policy is that industrialization in the 19 and 20th century of developed countries made them grew and evolved faster than other countries. This progress generated an important amount of pollution worldwide and nowadays these developed countries have realised the problems. So, the international policy they want to apply is to reduce emissions worldwide, but the problem is that undeveloped countries are now experiencing an industrialization period as the developed countries had decades ago, so denying undeveloped countries to evolve and grow to achieve the same point as the developed countries seems unfair because it maintains the underdevelopment of poor countries and the superiority of developed countries. However, trying to change the way the European industry works to improve the environment is better than continue as before, so implement recycling policies in the European Union is an important decision.

The CO_2 emissions to the atmosphere are the reason why the cement industry is so polluting, because they have an influence in global warming. The cement industry produces the 8% of worldwide emissions of CO_2, around 850 kg of CO_2 for one ton of clinker or 780 kg for one ton of Portland cement (see difference in section *1.2.1 Concrete and cement production*), of which mostly is due to the calcination of limestone: around 500 kg of CO_2/ton of clinker [9]. Analysing again the E-PRTR web page, it is found that the CO_2 emitted (using fossil fuel and biomass) was 107,367,000 tonnes in Europe during 2015 (Table 1). The real polluting CO_2 comes from the combustion of fossil fuels, but it is very difficult to know the real data if the facilities do not separate their emissions. The reason why the polluting CO_2 comes from fossil fuel is because biomass balance in CO_2 emissions is neutral: when biomass is burned, CO_2 is released into the atmosphere, but during the growth of organic matter, CO_2 is absorbed. In this way the cycle closes and the level of CO_2 emission in the atmosphere remains constant [10]. So, biomass energy does not contribute to climate change.

Table 1: Greenhouse gasses emissions of cement industry in Europe during 2015, adapted from E-PRTR [11]

Releases per country	Facilities	Air
Greenhouse gasses	187	
CH_4	1	140 t
CO_2 (biomass + fossil fuel)	**185**	**107,367,000 t**
HFCS (hydrofluorocarbons)	1	309 kg
N_2O	14	266.6 t
Non-specified greenhouse gasses	1	541,000 t

Besides CO_2, there are also other polluting gasses such as CH_4 which have a very high impact. To compare the emissions the following calculation must be done using the Global Warming Potential (GWP). GWP is a coefficient of the relative measure about the impact of greenhouse gasses in the heat trapped in the atmosphere. Because each gas has a different impact in the atmosphere warming, the GWP of a certain gas is normalised by the impact of the same amount of CO_2; in this way, different GWP can be comparable between gases. GWP compares the heat trapped by a certain gas with the heat trapped by the same amount of CO_2 in a specified period [12]. For example, in 20 years the relative impact of methane compared to carbon dioxide is [13]:

$$\textit{Comparable CH}_4 \textit{ emissions = Absolute CH}_4 \textit{ emissions} \cdot \textit{CH}_4 \textit{ GWP for 20 years =}$$
$$= 140 \ (t) \cdot 56 = 7{,}840 \ (t)$$

$$\textit{Comparable CO}_2 \textit{ emissions = Absolute CO}_2 \textit{ emissions} \cdot \textit{CO}_2 \textit{ GWP (reference) =}$$
$$= 107{,}367{,}000 \ (t) \cdot 1 = 107{,}367{,}000 \ (t)$$

When comparing the methane emissions, their real impact in 20 years is 56 times higher than CO_2 impact: the emission of 140 tonnes of CH_4 is equivalent to emitting 7,840 tonnes of CO_2, so the CH_4 is more polluting but the absolute amount emitted is much lower than CO_2. So, even comparing these results, the impact of the CO_2 emissions to the global warming is the worst. That is why focusing on CO_2 emissions is a more efficient decision.

1.3. Recycling of concrete

As explained before, nowadays the need for recycling concrete is a reality. The process of the production of OPC are discussed in detail and the chemical reactions are explained in Chapter 2: but the main idea of the recycling process is very basic: separating the different constituents of used concrete between completely inert and (somewhat) reactive materials (which can be reactivated to be used again). These useful constituents need to be transformed to a chemical structure similar to the raw materials: to achieve this, they are heated up to make the initial chemical phases appear again (called *dehydration of cement*). This recycled cement powder can be mixed with a solution and aggregates to produce concrete, following the same procedure as the first-life concrete. The step of mixing recycled cement with a liquid is called *reactivation of cement*, because the compounds give concrete its compressive strength again.

The main problem of recycling of concrete is the loss of compressive strength: the final compressive strength after the reactivation of cement is lower than the compressive strength of the used concrete (the initial one). So, a good way to reactivate the cement paste (without the loss of properties) is needed to achieve the aim of reduce the emissions. Also, it is important to point out that there exist different types of concrete with different requirements for the minimum compressive strength, so the recycled concrete can have another target than the concrete it is made of. According to International Building Code (IBC) (Section 1905.1.1) the minimum specified compressive strength for structural concrete is 17.3 MPa and lower compressive strength can be acceptable for non-structural concrete. For each application of the concrete there a compressive strength requirement, shown in Table 2.

Table 2: Compressive strength requirements [14]

Type or location of concrete construction	Specified MPa
Concrete fill (non-structural)	Below 13.8
Basement and foundation walls and slabs, walks, patios, steps and stairs	17.3 - 24.2
Driveways, garage and industrial floor slabs	20.7 - 27.6
Reinforced concrete beams, slabs, columns and walls	20.7 - 48.3
Precast and prestressed concrete	27.6 - 48.3
High-rise buildings (columns)	69 - 103.5

Recycled cement can be used in non-structural concrete due to the low compressive strength, but of course, the better solution is trying to achieve a higher strength. That is the reason why the objective of this Thesis is dehydrate the used cement and try to reactivate it with different solutions and aggregates.

Chapter 2:   State of Art

2.1. Concrete and cement production

As seen in Chapter 1, concrete is the most used construction material. It is composed by a granular skeleton of inert particles and a cement-based matrix that acts as binder for all the compounds. The matrix is cement or another binder, mostly mixed with water to activate the cement. The skeleton can be formed by lots of types of materials such as sand, gravel and stones of different granulometries. Ordinary Portland Cement is "hydraulic" because it reacts with water (explained below). Also, other active or inert additives can be added to confer other properties to the concrete, like resistance to specific environments. In the concrete sector, the mixture of cement and water (or other liquid) only is the "paste" and the sand, gravel or crushed stone is called "aggregate". If the paste includes more compounds than only OPC, it is called "glue". The difference between "mortar" and "concrete" is the size of the aggregates, the mortar having the finest ones like sieved sand or crushed rock (diameter < 9.55 mm) and the concrete having gravel or rock chippings, called "coarse aggregate" (9.55 mm < diameter < 37.5 mm) [15]. The creation of mortar or concrete is due to the hardening of the paste during a chemical reaction known as "hydration", which provides physical properties like high strength [16]. The hydration process is divided in two steps: dissolution of ions and precipitation of new solid phases [17]. So, first it is needed to know the compounds of the cement to understand the chemical reactions. To accelerate the reading, a specific nomenclature is used in the cement industry to name the compounds, seen between brackets with the chemical name and listed in Appendix I: Cement Chemist Notation.

As noted above, the cement is a binder (also known as conglomerate) manufactured basically by two inorganic materials: limestone and clay. The limestone is a sedimentary rock formed by different compounds such as calcium carbonate ($CaCO_3$ or Cc) or calcite (the mineral form), some traces of dolomite ($CaMg(CO_3)_2$) and other kind of carbonates, like siderite (iron(II)carbonate, $FeCO_3$ or Fc). Clay is a sedimentary rock formed by clay minerals (hydrous aluminium silicate minerals), quartz (silica, SiO_2 or S), metal oxides (the most important is the aluminium oxide, Al_2O_3 or A) and organic matter [18].

When the raw materials are extracted, the first step is to crush and grind the limestone into powder of 5-10 mm of diameter. The second step is called *Homogenization* and it starts when mixing the limestone with the clay, with conveyors and an industrial mill to achieve a mix of 0.5 mm of diameter. The mixture is calcined at 1,450 °C in a rotary kiln in the following step, called *Clinkerization*. The rotary kiln has two different parts: at low (1,300 °C) and high (1,450 °C) temperature. In the first one, the clay is dehydroxylised and limestone is decomposed into calcium oxide (C), all the reactions happen in the solid state mainly. In the second one, already about the 25% of the mixture is molten, so the creation of tricalcium silicates (C_3S) is the result of crystallization of the liquid phase, but the rest of the reactions happen in solid state: the

transformation into dicalcium silicates (C_2S), tricalcium aluminates (C_3A) and calcium ferro aluminates (namely, C_4AF but it is the average composition of C_6A_2F and C_6AF_2) [19].

The chemistry behind all the stages of the cement production is schematized below, from the raw materials until the hydration reaction in concrete [20]. The raw materials are limestone (Cc + Mc + Fc) and clay (S + A).

Eq. 1:   Rotary kiln: Cc + Mc + Fc + S + A → C_3S + C_2S + C_3A + C_4AF

Developed:
5Cc + 2S → C_3S + C_2S + 5c
Cc + A + F → C_3A + C_4AF

This product mixture of C_3S + C_2S + C_3A + C_4AF is the output of the kiln: Clinker, which is formed as granules of 1 to 3 cm diameter. The clinker needs to be cooled before being manipulated. Slow cooling generates that cements with more MgO become susceptible to expansion cracking due to the volume expansion of the slaking of MgO to $Mg(OH)_2$ [21]. But a supercooling of the liquid phase results the formation of a glassy phase in clinker with dissolved C_3A and MgO, which are less reactive, so it affects the setting characteristics of the cement. So, the cooling has to be done fast (18-20 °C per minute) [22], with the problem that achieving a lower temperature necessitates a refrigeration system which consumes more energy than cooling at room temperature, so more CO_2 is emitted to the atmosphere due to the energy needed. After the cooling, the clinker is milled and mixed with water to create the cement paste, which hardens due to chemical reactions: the hydration process. During mixing, gypsum is aggregated to the blend to decelerate the hardening time until 45 minutes. This is due to the reaction between gypsum and calcium aluminates: C_3A and C_4AF do not create hydration products that give strength to the cement (see section *2.3 Hydration of cement*). So, without gypsum, cement paste hardens so quickly that it is impossible to manipulate. Once it has been hardened, the cement maintains its stability and resistance even under water. Mortars and concretes can have other types of supplementary cementitious materials (SCMs) like fly ashes or blast furnace slag. The following image shows a chart with the steps of the industrial process of concrete manufacturing (Figure 3).
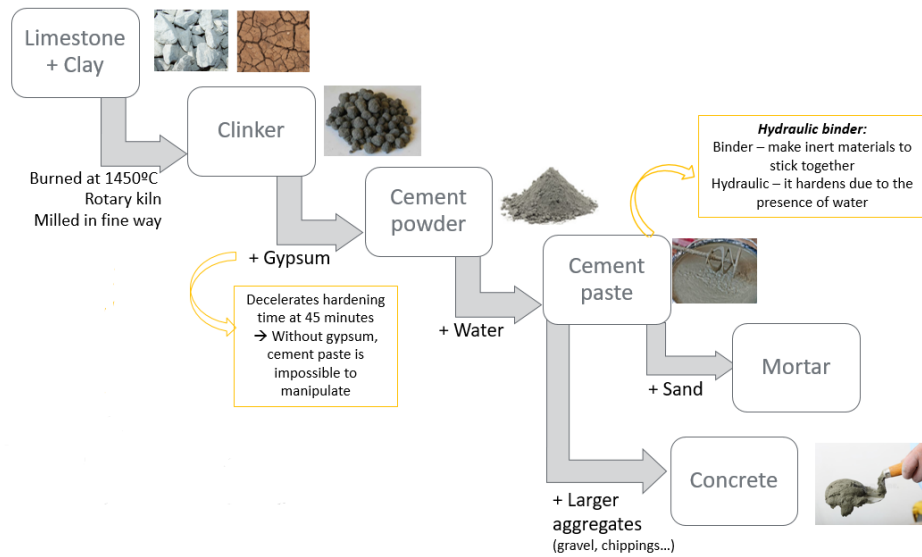
Figure 3: Chart with the steps of manufacturing of concrete.

The cement compounds are classified as main and minority compounds. The first group creates the matrix of the mixture and gives the name to the type of cement, explained below. The minority compounds are used in a maximum proportion of 5% of mass of the whole amount of cement - including both types [23]. So, for each type of cement, the proportions can be modified for the specific requirements. This will be explained below in the description of the European Standard EN 197-1.

2.2. Types of cement and aggregates, according to European Standard EN 197-1

As explained before, the type of cement depends on the proportions of its compounds. According to the European Standard EN 197-1, the main type of cement (CEM I, II, III, IV or V) indicates the compounds of the matrix and the second part of the name indicates other aggregates and their proportions. The table with all the nomenclature of the Standard EN 197-1 is in the Appendix II. CEM I is form of a 95-100% Ordinary Portland Cement (OPC) and 0-5% other minor additional constituents, which are impurities from the manufacture process. OPC is not always used in a pure form, reactive compounds, called supplementary cementitious materials (SCM) can be added. OPC with SCM mixtures are the other types of cement (CEM II, III, IV or V), depending on which SCM and their proportions. SCMs are blast furnace slag (BFS or GGBS), silica fume, pozzolanic ash or *pozzolana* (natural and natural calorized), fly ash (siliceous and calcareous), burn shale and limestone.

As explained in detail in Chapter 4: Materials, the binders tested in this study are CEM I (OPC) and CEM III (OPC and BFS). Therefore, the properties of BFS are going to be explained to understand this study. BFS is the by-product of the manufacturing process of pig iron. In this process, the raw materials are burnt in a blast furnace and its products are molten iron (used for steel making process) and its slag. This slag is quenched in water or steam to form a glassy product with granular form. The glassy product is dried and mill into fine powder. The composition of the BFS is SiO_2 and Al_2O_3 (clayey molten iron slag) mixed with coke, lime and magnesite, where SiO_2 and Al_2O_3 are acid oxides and CaO and MgO are alkaline oxides. The slag

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is considered acid when the ratio $CaO/SiO_2 < 1$ and normally it is from processes with low content in iron. The reason to choose mixing OPC with blast furnace slag is because they decrease the total hydration heat of the mixture and reduce the chemical reaction with alkalis, which give better durability thanks to avoid cracking so it provides high resistance to sulphates and sea water [24]. The reduction of the hydration heat is related to the filler effect, other property of SCMs which also it is seen in BFS. The filler effect is the partial replacement of space between cement grains by fine SCMs. It accelerates the hydration reaction of the clinker components by reducing the distance between particles [25], fine particles pack the spaces generating a higher packing density.

The properties of the binder are explained but the concrete is formed by the binder, aggregates and liquid. The aggregates most commonly used are sand, gravel, crushed rock or rock chippings. The difference between sand and gravel is the size: sand can cross a sieve of 4 mm and gravel cannot [26]. In this study, sieved sand has been used as aggregate to create the matrix (more details in Chapter 4: Materials). The importance of the sand in mortars is its capacity of decrease the shrinking due to the hardening of the binder to avoid cracking, because, as said before, the sand creates a skeleton and it occupies most of the mortar's volume [27].

The binder is mixed with water and aggregates (sand in this study) to create the mortar but sometimes the workability of the mixture is very low: a solid mixture is created instead of a paste. When this happens, another component can be added to make the mixture more liquid: a superplasticizer. The superplasticizers are additives that change the rheology of the mixtures, generating an increase of the workability of the mortars in fresh state [28]. This situation is created thanks to the dispersion of cement grains in the mixture, which cause two main consequences:

- A reduction of the water to cement ratio to achieve better strength and durability.
- An increase of the mortar's plasticity making it easier to handle during more time.

The main idea of how the plasticizer works is represented on Figure 4. The excessive addition of plasticizer causes a very high hardening time.
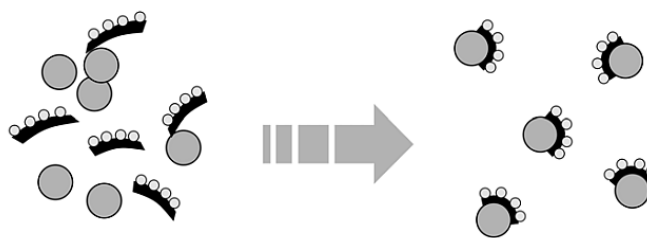
Figure 4: Effect of the plastizicers[29]

The difference between plasticizer and superplasticizer (a.k.a. high range water reducers) is that the second one has a strongest effect. There are different types of plasticizers and superplasticizers from the chemical point of view, they are divided in three generations: lignosulphonates (first generation), naphthalene and melamine sulphonates (second generation) and polycarboxylate ether-based superplasticizers or PCEs (third generation) [30]. The chemical structure of third generation is different because it is composed by macro molecules formed by main chains (backbone of carboxyl groups) with lot of side chains, which can be easily

modified to give the mortar specific properties depending on its application: for example, these superplasticizers can achieve a 40% of water reduction. In this study, the superplasticizer used was PCE. This type of superplasticizer can influence in other characteristics such as adsorption speed of the concrete, slump retention without retardation and subsequent fast strength development, early strength development with enough workability time, stickiness and viscosity. This polymer's backbone is responsible for the attainable water reduction and mixing time and the side chains determine the slump keeping capability of the superplasticizer, affected by an increasing number of side chains. The crucial factor is the limited space for carboxyl groups and side chains along the backbone [31].

According to the European Standard 196-1, the water to cement ratio on mass in mortars and concretes must be the following one:

$$\frac{\text{water}}{\text{cement}} = 0.5$$

However, in lot of literature [32, 33, 34] it is found a water to cement ratio of 0.4 in the procedure of cement pastes and mortars. This is due to the flowability of the mixture: the paste does not have the aggregates that create the matrix in the mortars, so the water needs to be reduced to achieve a suitable flowability (avoiding a very liquid paste). When preparing mortars with low cement ratios happens the opposite: it is too solid and difficult to manipulate. In these scenarios, the superplasticizer must be used in the mixture, in a maximum quantity of 0.3-0.6% of cement mass [35] of the cement final mass. A low water to cement ratio leads to high strength but low workability and a high water to cement ratio leads to low strength, but good workability. The relation between strength and water to cement ratio is shown below.
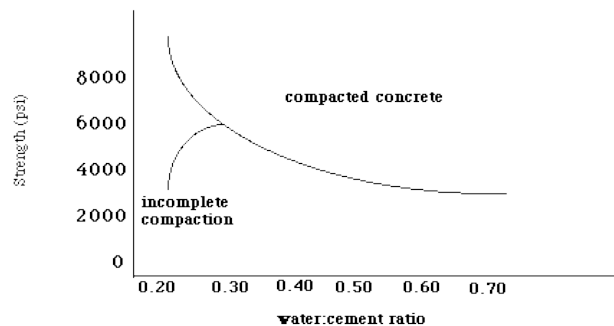
Figure 5: Relation between strength and water to cement ratios in mortars [36]

As seen, a water to cement ratio below 0.3 causes an incomplete compaction and the compacted concrete is considered with highest ratio. Trying to achieve the maximum strength but maintaining the workability is the reason why a 0.4 w/c ratio is used normally for reference.

2.3. Hydration of cement

The hardening of cement paste is called *setting* when it is superficial and *curing* when it is completed due to the internal cohesion. In both cases, it is due to the hydration of calcium aluminates and silicates (C_3A, C_3S, C_2S) which are soluble in water. The first part of the hydration process is the dissolution of the ions of cement into the water. This solution is no longer pure water, so it is called "pore solution", because the place it occupies will be the pores when the cement hardens. During the dissolution, the pore solution starts being saturated because the

alite (C_3S), tricalcium aluminate (C_3A) and gypsum (CsH_2) have more solubility than the other compounds -belite (C_2S) and ferrite (C_4AF), which means that alite's rate of hydration is slower. This is the reason why alite contributes to early strength and belite to the late strength in mature cement or concrete. This saturation of the pore solution generates the precipitation step, in which the products precipitated (a.k.a. hydration products) are created by the hydration reaction: the reactants combine with hydroxyl groups of water (OH^-) so they generate new products and because their most stable phases are solid, this means that the solid phases have the lowest free energy in these conditions.[37]. When the precipitation starts, the remaining reagents can continue dissolving and precipitation from the saturated solution continues. So gradually the hydration products will form a continuous matrix, binding everything together. Hydration of both silicates (alite and belite) generates portlandite (calcium hydroxide, CH) and calcium silicate hydrate gel ($C_{1.7}SH_x$ or C-S-H) due to the following reactions (Eq. 2, Eq. 3) [38]:

$$Eq.\ 2:\ C_3S + (1.3+x)H\ \rightarrow\ C_{1.7}SH_x + 1.3CH$$

$$Eq.\ 3:\ C_2S + (0.3+x)H\ \rightarrow\ C_{1.7}SH_x + 0.3CH$$
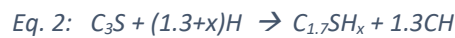
The tricalcium aluminate (C_3A) is more soluble than tricalcium silicate (alite, C_3S) so, if the reaction occurs in pure water, calcium aluminate hydrates are formed (C-A-H or $C_xA_yH_z$) and the final product is called hydrogarnet (C_3AH_6). The hydration of calcium aluminate (C_3A) is done in two steps (Eq. 4, Eq. 5), the two intermediate products are different types of calcium aluminate hydrates (Eq. 5) that react to yield the final product when the internal temperature is above 30°C.

$$Eq.\ 4:\ 2C_3A + 21H\ \rightarrow\ C_4AH_{19} + C_2AH_8$$

$$Eq.\ 5:\ C_4AH_{19} + C_2AH_8\ \rightarrow\ 2C_3AH_6 + 9H$$

The second reaction is more slowly (Eq. 5) than the first one, which is very rapid and exothermic. During the first reaction in water (Eq. 4), the cement paste hardens in few minutes after mixing, creating a condition called "flash set". To prevent it, it is necessary to add gypsum (dehydrated calcium sulphate, CsH_2). Due to its high solubility, gypsum generates a fast releasing of calcium ions (Ca^{2+}) and sulphates (s, SO_4^{2-}) into the pore solution; these ions react to create hardened cement paste (HCP) while precipitating (Eq. 6), which becomes primary ettringite or just ettringite ($C_6As_3H_{32}$). After, the ettringite generates a protective membrane that reduces hydration rate. Below the reaction when adding gypsum is shown:

$$Eq.\ 6:\ C_3A + 3CsH_2 + 26H \rightarrow C_6As_3H_{32}$$
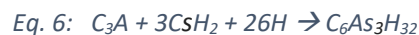
If gypsum reacts completely before C_3A, the concentration of sulphates in the pore solution is very low, so an unstable compound called monosulphoaluminate or secondary ettringite forms ($C_4As_3H_{12}$). This different solid phase (with less sulphate) occurs due to the following reaction:

$$Eq.\ 7:\ 2C_3A + C_6As_3H_{32} + 4H\ \rightarrow\ 3C_4As_3H_{12}$$
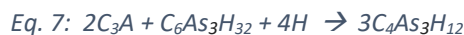
Reactions of Eq. 6 and Eq. 7 are exothermic, both contribute to the hydration heat, explained below. The hydration of the last clinker phase, ferrite (calcium ferro aluminates, C_4AF) is very similar to the hydration of the calcium aluminates but slower. The different is some aluminium

in the final products is substituted for iron depending on the conditions and the composition of the C_4AF (Eq. 8).

$$Eq.\ 8:\quad C_4AF + 3C\bar{s}H_2 + 21H \rightarrow C_6(A,F)\bar{s}_3H_{32} + (F,A)H_3$$

$$Eq.\ 9:\quad C_4AF + C_6(A,F)\bar{s}_3H_{32} + 7H \rightarrow 3C_4(A,F)\bar{s}H_{12} + (F,A)H_3$$

Where (A,F) means aluminium with variable quantity of iron and (F,A) means iron with variable quantity of aluminium. $(F,A)H_3$ is an amorphous phase forms in small amounts to maintain stoichiometry. Due to the substitution between aluminium and iron, the products are not pure primary ettringite (AFt) neither monosulphoaluminate (secondary ettringite, AFm), so they have other names to difference them: AFt and AFm, respectively, where *m* means one sulphate ion and *t* trisulphate. In OPC where C_3A and C_4AF are mixed, it is assumed that the products are never going to be pure, so normally it is used the nomenclature indicated before (AFt, AFm).

The qualitative amount of every compound during the curing time is shown in the Figure 6 Temporal evolution of the hydration products (Kurtis, 1995), the portlandite (CH) and ettringite (AFt) appear during the first 3-6 hours in low quantities due to the fast hydration of C_3A and C_3S (Eq. 2 and Eq. 4), in that moment the creation of C-S-H gel becomes more important due to the hydration of C_2S (Eq. 3) which also generate more CH. Also, calcium aluminates hydrated (C-(A,F)-H or C-A-H) starts reacting to yield ettringite (AFt) in a combination of the reaction IV, V and VI: it is seen an increase of the quantity around 6 hours in Figure 6 Temporal evolution of the hydration products (Kurtis, 1995) The quantity of ettringite (AFt) remains constant for 3 days, when it starts to decrease and monosulphoaluminate (AFm) starts increasing, this situation is due to the decrease of gypsum in the mix (Eq. 6 and Eq. 7). At 2 days, the quantity of gypsum is barely nothing that is why AFt yields completely to AFm. During all the hydration process (or curing) there is a decrease of porosity due to the precipitation of hydration products thanks to the saturation and disappearance of the pore solution.
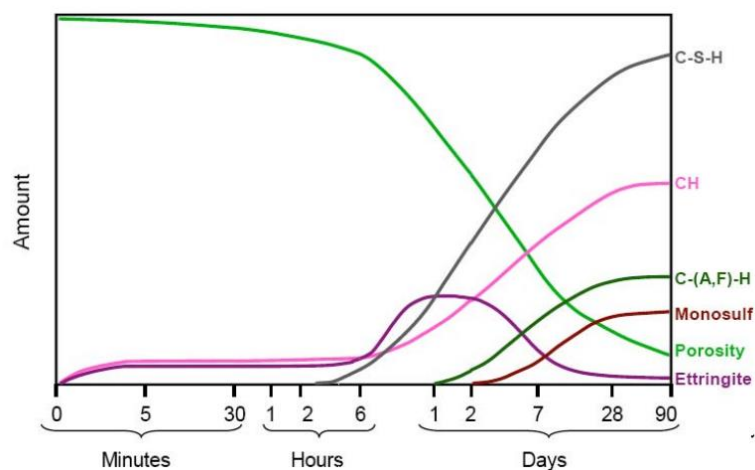
Figure 6 Temporal evolution of the hydration products (Kurtis, 1995)

The C_2S and C_3S constitute the 75-80% of the total weight of the OPC that is why the properties of the OPC are determined by the difference of percentage in C_3S and C_3S. While the hydration reaction occurs, the amount of alite and belite decrease because the creation of C-S-H gel and CH. That is why it is very important to know the age of the concrete for the recycling process: if

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the concrete is young (few days), its quantity of alite and belite would be higher than if it is old (28 days or more) and the reactivity of the recycled cement would increase because it depends on these compounds.

While converting one phase to another with less free energy, there is a release of energy normally as heat and reaction is defined as exothermic. In the opposite situation, when the reaction captures energy is called endothermic. In the cement chemistry, the exothermic heat of the reaction of hydration is named as "hydration heat" and there is a hydration heat for all the reactions described before. Thermal analysis is a useful technique to determine the heat flow to detect the different hydrated fractions or phases of cement. One of these techniques used in the present work is isothermal calorimetry, in which the heat flow of the hydration reaction can be measured during a certain time at constant temperature. The general representation of the isothermal calorimetry data in OPC shown below (Figure 7):
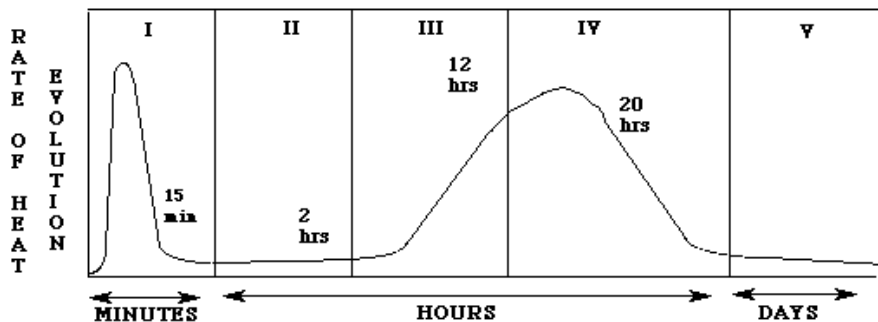
Figure 7: Schematic of the rate of hydration or heat evolution as a function of time [39]

The information obtained with the rate of hydration is the chemical kinetics and it is possible to divide the hydration process in 5 basic stages. As noted before, some of the compounds are highly soluble, so there is a very fast stage (Stage I) in the first minutes of contact of water and cement, when cement starts to dissolve. This stage is very fast because the water creates a thin amorphous layer of CH and C-S-H gel around the particles of cement, which prevent the cement to continue the dissolution (a.k.a. hydration reaction) as faster as before. In the Stage II, named "induction period", almost no reaction occurs. There is not an agreement about the reason of the ending of this stage yet. The Stage III and IV represent the start of crystallization process (nucleation) and grown of crystals. The Stage III and the first part of IV (the curve until the first peak) represents the high ratio of hydration of the tricalcium sulphate (C_3S), explained in Eq. 2. The maximum peak lasts no more than 24 hours from the mixing; this is the maximum heat released per time and depends on the temperature and the size of the cement particles. In the second part of the Stage IV there is a fast decrease of the heat flow. During all this stage, the hydration products, i.e. CH and C-S-H, deposit quickly and continuously so, at the end of it, around the 30% of the cement has been hydrated. This fast deposition is done in the pore solution, which means that the porosity of the cement decreases very fast (as seen in Figure 6), increasing the strength slightly. In this point, the microstructure is formed by unreacted cores of cement particles surrounded of a layer of hydration products. The final stage is Stage V, called "diffusion-limited reaction period", in which the dissolved ions of the cement move to the pores to precipitate and the water of the solution diffuses until the unreacted cement cores to

generate more ions and continue the hydration. This process starts to slow down when the layer becomes thicker.

2.4. Dehydration and reactivation of cement

Basically, recycling of cement means to modify the hydration products found in used concrete to achieve unreacted products (clinker phases) and reactivate them with water, understood as *rehydration* or *second cycle hydration*, to start the crystallization process and precipitate the hydration products again (the *rehydration* products).

It is important to point out that concrete, as noted above, is a mixture of cement paste and inert aggregates like sand, so the reactivation only makes sense for the cement paste. In the present work, fresh (or *unhydrated*) cement has been mixed with water to create cement paste ("hydrated cement"), that has been milled into powder. This powder has been dehydrated to be transformed into clinker phases again and later, it has been mixed with different activation solutions (water and alkalis) to reactivate and yield new hydration products: and this is the recycled cement, which should have similar mechanical properties as first cycle hydrated cement.

Figure 8: Basic flow chart of steps for recycling cement

There are different researches about the yield from hydrated to dehydrated cement, because, depending on the temperature of dehydration, it occurs degradation of different compounds. Next, these degradations are going to be explained and later, it will be justified the activation solutions chosen to reactivate the dehydrated cement.

The hydration products found in hydrated cement depend on the age of the concrete as seen in *Figure 6* Temporal evolution of the hydration products (Kurtis, 1995) When the cement has been curing for 2 days, it can be found C-S-H gel mainly, portlandite (CH) and ettringite (AFt). As noted above, in 7 days most part of the ettringite yields to monosulphoaluminate (AFm), also calcium ferro-aluminates hydrates (C-(A,F)-H) appears and C-S-H gel and portlandite (CH) continue increasing. The stages of decomposition can be divided in three or four different steps: 100-200, 450, 650-750 °C. According to C. Alonso and L. Fernandez [40], the decomposition temperatures for a 70 days old cement are interpreted as follows:

- Below 100 °C, ettringite decomposes
- At 100 °C, the free water of the pore solution start evaporating
- Below 200 °C, increase of portlandite (CH) due to the presence of condensate water
- From 100-250 °C, water of C-S-H gel is lost
- At 200 °C, C-S-H gel starts transforming into nesosilicate (Ca_2SiO_4)
- At 250 °C, most of the bond water is lost

- Below 450 °C, progressive increase of calcite (Cc)
- At 450 °C, dehydrated C-S-H phase yields to a modified C-S-H phase

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- At 450 °C, portlandite (CH) and calcite (Cc) react to lime (CaO, C)

- At 650 °C, total decomposition of calcite (Cc): CaCO3 → CaO + CO2
- At 750 °C, C-S-H gel has completely change into a nesosilicate with belite (C_2S) stoichiometry close to larnite (belite mineral form), but less crystalline
- At 750 °C, portlandite (CH) and calcite (Cc) are converted totally into lime (C)

In the present Thesis, the hydrated cement paste is 3 days old, so it is partially hydrated, which means that all the phases were shown but in different quantities (Figure 6). This is the reason why the cement has been dehydrated at 500 °C for 2 hours, according to C. Alonso and L. Fernandez, to maintain some reactive compounds like calcite and C-S-H phase. Also, they conclude that anhydrous phases, like belite, remain unaltered during heating.

In the next step of the recycling of cement, the dehydrated cement has been milled to achieve more specific surface for the reactivation. The reactivation of the dehydrated cement with an activation solution is necessary to recrystalize the calcite, portlandite and ettringite, and to yield C-S-H gel again from the nesosilicate formed at 200 °C. To reactivate the cement, in the present thesis it is used water and alkaline solutions, because alkaline activators stimulate latent properties of different cement aggregates and compounds. Alkalis activate aluminosilicates, creating a paste with a reasonably short period of setting and curing. Also, pozzolana has more reactivity in alkaline environment to react with lime at ambient temperature and form compounds possessing cementitious properties [41]. So, for these reasons the alkaline solutions chosen for the present Thesis have two different molarities (0.5 and 1 M) to compare its influence and different types of alkalis: sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and sodium sulphate (Na_2SO_4). It has been decided to work with sodium compounds because the properties of sodium and potassium compounds are similar because both alkali metals, and potassium has less availability in the market and more cost than sodium ones [42, 43].

2.5. Aim and research objectives: research questions

When analysing all the information given before, the aim of this Master Thesis is to make a comparison of different mortars to conclude which one maintains better mechanical and thermal properties in its second life cycle. The compared mortars are formed by combination of different cement pastes (with Ordinary Portland Cement and blast furnace slag) and different activation solutions (water and alkaline solutions).

So basically, the different analysis done are the following ones:

- Quantity of blast furnace slag in recycled cement paste: comparison between *cement:slag ratios* of 300:0, 300:100 and 300:220.
- Type of activation solution in recycled cement and molarity: comparison between water, sodium hydroxide 1M, sodium carbonate 1M, sodium sulphate 1M and 0.5M.
- Influence of using fresh OPC to activate cement paste: comparison between specimens with 100% dehydrated cement (non-activated) and 90% dehydrated cement + 10% fresh cement (activated).

2.6. Master Thesis organization

The present Master Thesis is organised in six Parts (Introduction, Experimental, Results and discussion, Conclusions, Future work and Bibliography) plus Appendices. Following the Part I, there are the descriptions of the materials, equipment and methods used to achieve it. Then, the discussion of the results and the conclusions of the experiments done. Finally, the future work proposed to continue the research and the references consulted.

Chapter 3: Environmental impact calculation method

3.1. Life Cycle Assessment

Life Cycle Assessment or Life Cycle Analysis (LCA) is a design technique made for investigating and evaluating the environmental impact of a determined product or service during all the stages of its life: since the extraction of the raw material, to the production, distribution, consumer use and its end of life (reuse, recycle, valorisation or waste management). The importance of this technique has appeared due to the increased awareness of the environmental protection the society lives nowadays. Thanks to this technique, it is possible to know the potential environmental impacts, needed to quantify the use of a resource (such as energy, raw materials and water) and the environmental emissions generated because of the analysed product or service. About the emissions, it is important to highlight that the LCA is not a risk measurement technique, because it does not evaluate the exposition to the emissions. The LCA quantify the emissions, but to know the real impact it is needed to know the location and the way they are emitted. So, for example, the LCA is useful to quantify the differences between two fabrication processes of the same product or to know the environmental impact of buying a new product or second-hand product ("which one is more polluting?"). Answering these questions is required to create an improvement on the processes.

The framework documents used in this technique are the international standards ISO 14040:2006 (Environmental management: Life Cycle Assessment. Principles and framework) and ISO 14044:2006 (Environmental management: Life Cycle Assessment. Requirements and guidelines), in which it is described the importance of the LCA, its definition, methodology and critical review. Some of the utilities of the LCA is the creation of the Environmental Product Declaration (EPD) and Environmental Footprint, necessary ways to quantify the environmental impact. The EPD is also regulated by the ISO 14025:2010 which modifies ISO 14025:2006.

The idea of Life Cycle Assessment appears on the explanation of Circular Economy (CE). The CE is an economic strategy to reduce the consume of raw materials, energy and natural resources as well as the huge production of wastes society creates. To achieve this aim, CE aspires to close the economic fluxes or loops of the resources. This is understood as maintaining the value of all the products and resources during their life time by reducing, re-using and recycling them; this is called the theory of the "3 R". The importance of this theory is following it in its order: first, we should try to reduce the amount of products and resources (water, energy) we use, because maybe they are not necessary; second, we should try to re-use the products or resources that are absolutely needed for living, for example with second-hand market or industries symbiosis

(the waste of a company could be the resource for another one) and third, if the product cannot be re-used, it is needed to be recycled. Recycling is the last of the options because it consumes energy and creates wastes also. An explanation chart can be found below (Figure 9).

That is why CE challenges industries to redefine products and services. And, for this reason, industries need to use the LCA tool to evaluate which strategy or combination of strategies (reduce, re-use, recycle) is the best option for each product or service.

Figure 9: Circular economy chart. Source: Ellen MacArthur, 2017

The vision of the industry that CE defends is seen in this Master Thesis: try to find a way to recycle cement and concrete and give them other life. And LCA is a widely used technique for the calculation of the impact of the cement and concrete [44, 45, 46], that is why it could be useful to calculate the differences with the impact of recycled concrete and its uses in the society.

PART II: Experimental

The second part is focused on the description of the experimental methodology followed in the present Thesis: from the materials used and the theoretical explanation of the characterization techniques to the exposition of the design of the experiment.

Chapter 4:   Materials

The materials used in the present thesis are different types of cement, aggregates and activation solutions. The details are listed below:

4.1. Solid materials

The different cementitious materials used to create the binders are exposed below. Also, their main characteristics are pointed out.

- CEM I 52.5N, Heidelberg's *Milke® classic*: 95-100% pure OPC

Table 3: Characteristics CEM I from Heidelberg

Compounds [wt%]		Compressive strength at 2 days (MPa)
Alite	54.50	
Belite	20.25	26.3
Tricalcium aluminate	7.00	
Ferrite	7.91	

- CEM I 52.5R, SECIL's *HES LA*: 99% pure OPC

Table 4: Characteristics CEM I from SECIL

Compounds [wt%]		Compressive strength at 2 days (MPa)
Portland clinker	99 (Gypsum: 5wt%)	44.0
Siliceous fly ashes	1	

- Plasticizer, SIKA's *Viscocrete®*

- Blast Furnace Slag, ORCEM's *ECO$_2$cem®*

Table 5: Characteristics BFS

Compounds	
CaO [wt%]	37.54
SiO$_2$ [wt%]	34.30
MgO [wt%]	8.79
Al$_2$O$_3$ [wt%]	13.74

Fe_2O_3 [wt%]	0.43
Mn_2O_3 [wt%]	0.27
Cl^- [wt%]	0.015
S^{2-} [wt%]	0.66
SO_3 [wt%]	0.04
Na_2O [wt%]	0.30
K_2O [wt%]	34.30
Na_2O equivalent [wt%]	0.70
$CaO+MgO+SiO_2$ [wt%]	80.63
$(CaO+MgO)/SiO_2$ [wt%]	1.35
Loss of ignition 975 ^{o}C [wt%]	0.10
Non-soluble residue [wt%]	0.27
Glass content [wt%]	99.00

Also, to produce the mortars is needed aggregates, as explained in the Introduction. The only aggregate used during this study was:

- Sieved Rhine river sand from Belgium, sieve between 0.2 - 0.85 mm

4.2. Reactivation solutions

To reactivate the dehydrated cement powder to produce recycled mortars is necessary to use some liquid. Because the aim of this study is also trying to understand better the reactivation, different types of solutions were used to this reactivation.

MATERIALS

It is important to recalculate the molarities of the activating solutions because the moles of Na^+ is not the same in all solutions, which means that sodium carbonate and sulphate are have twice the amount of Na^+ than sodium hydroxide:
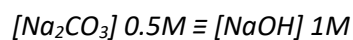
$$[Na_2CO_3]\ 0.5M \equiv [NaOH]\ 1M$$

The liquids were:
- Distilled water
- Sodium hydroxide (NaOH), 1M (0.5M $[Na_2CO_3]_{equivalent}$), powder > 99% pure, Honeywell Fluka
- Sodium carbonate (Na_2CO_3), 1M, powder 99.5% pure, Honeywell Fluka
- Sodium sulphate (Na_2SO_4), 1M and 0.5M, powder > 99% pure, VWR PROLABO

PREPARATION OF SOLUTIONS

The preparation of all the alkaline solutions were made following the same procedure. First, the quantity needed for each solution is weighted in a precision scale. Later, the solid is put in a medium baker with 75-100 ml of water. A glass rod is needed to mix it. Starting the solution in this way, the water became saturated soon and it can be transferred to a bigger baker to

continue the mixing with a magnetic stirrer and a magnetic stir bar. The process of solving the majority of the solid by hand, separate the saturated solution and put more water avoid the creation of big solid particles in the bottom that can be difficult to solve or take too much time. The solution must be dissolving for 5 minutes at least to be sure that everything is mixed. When there are no particles in it, the solution can be transferred to a volumetric flask, where more water in added to achieve the total volume.

STORAGE

After putting the solutions in the volumetric flask, they were transferred to plastic recipients with hermetic cover to storage them. The sodium hydroxide reaction is exothermic, so the solution must be kept in the volumetric flask until it gets cooler, later it can be transferred to the plastic recipient.

Chapter 5:   Methods

5.1. Characterization techniques

The aim of this Thesis is to compare mechanical properties between recycled cements with different composition and activation solutions. A proper comparison needs information of different thermal and mechanical analysis to have a real data of the samples. For this reason, the techniques used in this Thesis are calorimetry, thermogravimetric analysis and compressive strength testing. In the present headland these techniques are explained to have a global idea about the information they can provide, in this way it is possible to design the experimental method that must be followed, explained in the next headland (5.2 Design of the experiment).

5.1.1.   Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is used to record the mass loss of a sample over time when the temperature changes. It is a type of thermal analysis, which has been used for many years to detect the amorphous fraction of hydrated material (complementary method to X-Ray Diffraction) [47]. With the mass loss, different physical phenomena can be studied, like phase transitions, as well as chemical phenomena like thermal decomposition, oxidation/reduction reactions, inter alia. TGA is used for the analysis and the thermogravimetric analyser. In the present study, TGA Q5000 Thermal Analyser (TA Instruments, U.S.A.) was used, which can achieve 1200 °C.

The operation of the TGA requires a calibration of the pan where the sample is located, with a previous disinfection of it with a Bunsen burner. The sample must be hardened cement (not paste) and no more than 25 mg. There are pans of different materials; for this Thesis it can be used Platinum-HT pans for temperatures below 700 °C and alumina pans for more than 700 °C. The atmosphere to heat up the samples was nitrogen. Hi-resolution TGA was performed by heating up to 500, 600 and 700 °C with a heating rate (ramp) of 10 °C/min, resolution of 5 and sensitivity of 3. The method used followed the following temperature profile:

- Equilibrate at 60 °C
- Isothermal for 5 min at 60 °C

- Ramp 10 °C /min for 600 °C
- Isothermal for 2 h at 600 °C
- Equilibrate at 60 °C

5.1.2. Calorimetry

The calorimetry is the science that studies the changes of state variables related with the heat transfer of a body. It is also referred to the act of measuring the heat flow between a body and the surroundings. So basically, it is needed to determinate the changes in internal energy (reaction and combustion energy) and enthalpy.

The release of heat is an important property of cement reaction hydration, that is why it has been used since the early 20th century to characterize and study cements. Today, there are four types of calorimeters in use for measurements of heat of hydration: solution calorimetry, semi-adiabatic calorimetry, adiabatic calorimetry, and isothermal (heat conduction) calorimetry. In this study, isothermal calorimetry has been used because it has been found (Lars Wadsö, Markus Arndt) that results from solution calorimetry and isothermal calorimetry agree well for Portland cements [48].

Isothermal calorimeters measure thermal power (heat flow rate). A small sample (1–10 ml) is placed in contact with a heat flow sensor, which is in contact with a heat sink. The heat leaves the sample by heat conduction and a well-designed experiment will be essentially isothermal (typically having temperature changes less than 0.1 °C at the main hydration peak) [49]. The equipment used in this study was TAM Air 8-channel, a chip-based fast scanning calorimeter (FSC).

The procedure of the calorimetry starts with measuring a baseline during at least 30 minutes. The glass ampoules are filled by the cement paste and prepared for the calorimeter (more details in Design of the experiment5.2 Design of the experiment). Later, the ampoules must be put inside each channel. This part has to be done as fast as possible, because while opening each channel few turbulences of heat flow are recorded in the data, but they are not due to chemical reactions. Each sample has to be put after another, due to the situation explained with the het flow changes, the channels do not have to be opened at the same time. To introduce the ampoule in the channel, first it is necessary to open the cover and take the fixture with a hook, later the ampoule is introduced in the channel and the fixture in put in the top of it. Finally, the cover in put again.

5.1.3. Mechanical test

The standard recommends do different types of test depending on the final use of the concrete. But compressive strength is one of the most important engineering properties of concrete, so in this study, this test has been done. Concrete has relatively high compressive strength, but much lower tensile strength, that is why it is usually reinforced with strong materials in tension, like steel (do not applicable at this study). The compressive strength or stress test consists in measuring the maximum amount of compressive load a material can bear before fracturing. The

test piece, usually in the form of a cube, prism, or cylinder, is compressed between the platens of a compression-testing machine by a gradually applied load [50].

Very low-strength (14 MPa or less) concrete is normally used as lightweight concrete, achieved by adding air, foams, or lightweight aggregates, with the side effect that the strength is reduced. Concrete compressive strength for general construction varies from 15 MPa to 30 MPa and higher in commercial and industrial structures [51]. 40 MPa concrete is more durable, but more expensive. Higher-strength concrete is often used for larger civil projects and strengths more than 40 MPa are used for specific elements of construction, for example, lower floor columns of high-rise concrete buildings may use concrete of 80 MPa.

The equipment used were Instron 5900R and Instron 5881H, with spherical seatings load cells. The specimens tested were cylindrical moulds of 60 mm of height and 33 mm of diameter, with the *ratio height/diameter* or H/D = 1.82, approximately. Each batch was formed by 5 specimens. And two batches were prepared of each type of concrete, to test the strength at 2 days and 7 days -except batches that were seen with very low strength after the first results, which were tested only at 7 days. The method used during the experiments was define by a compressive extension of 2 mm/min.

5.2. Design of the experiment

With all the information given up to this point, it is possible to create the design of the experiment, to plan the tests and the lab work to achieve the objectives. So basically, there design is composed for two differenced parts: the experimental procedure to create the specimens and samples, and the tests needed to be done in every stage of the experimental procedure. The experimental procedure and the tests needed are shown below and all details for every stage are explained following.

i.   PRODUCTION OF FRESH CEMENT PASTE (HYDRATED CEMENT) → TGA / CALORIMETRY
ii.   SYNTHESIS OF RECYCLED CEMENT POWDER (DEHYDRATED CEMENT) → TGA / CALORIMETRY
iii. PRODUCTION OF MORTARS (REHYDRATED CEMENT + AGGREGATES)
iv.   PRODUCTION OF SPECIMENS (CURING AND PREPARATION FOR TESTS) → COMPRESSIVE STRENGTH TEST

5.2.1. Production of fresh cement paste (hydrated cement)

First, TGA was done for fresh cement powder (before hydration of cement). To do it, the method explained in the point *5.1.1 Thermogravimetric Analysis* was followed. The results are shown and compared to the others in *Chapter 6: Results and comparison of samples.*

Later, the hydrated cement paste was prepared with a water to cement ratio of 0.4, because no aggregates were added, it was not necessary to use the same w/c ratio as the mortars, as explained in the Introduction. The pastes were cured for 3 days in air at 25 °C with a deviation of ±2, so some reactive compounds were in the mixture.

Also, isothermal calorimetry was carried out for hydrated cement paste. This technique was used to know the heat flow during the hydration reactions in the mortars. A certain water to cement ratio is required to do these experiments. So, for calorimetry, a w/c ratio of 0.5 was

used. To create the mixtures, the European standard EN196-1 was used as a guide, but not all the steps could be followed (for example, different type of mixers were used). In the calorimetry, the ampoules used were 20 millilitres and made of glass, but the paste quantity was 10 g. A mixer *Heidolph* model *RZR 2041* and a steel paddle stirrer with small holes was used for mixing the cement and water. Because the calorimetry measures the heat flow during the whole hydration reaction, it is very important to mix the materials in the ampoules and introduce them in the calorimeter immediately. For this reason, the cement powder was introduced in all the ampoules and the exact quantity of the different liquids (water in the fresh cement paste and water or alkalis in recycle cement paste) were prepared in separated beakers. Between mixing one paste and another, the mixer must be cleaned with water and paper.

The mixture described in the European standard EN 196-1 is prepared with a Hobart mixer (in the present thesis other mixer was used) and the steps start by mixing water and cement at the different speeds of Hobart mixer -low (1), high (2), superhigh (3)-: at low speed for 30 seconds, mixing at high speed for 30 seconds, stop mixing to collect the paste of the sides of the recipient and finally, mixing at for 60 seconds. Because the ampoules of the calorimeter are smaller than the bakers used to do mortars following the Standard, the mixture procedure followed in this thesis was mixing the paste at 1600 rpm for 1 minute.

After the mixing, the ampoules must be closed to seal the aluminium cap and a lifting eyelet must be put in the centre of the cap; thank to them, the ampoule can be put inside the channels of the calorimeter using a hook.

The procedure of mixing the cement with water to do the cement paste which later was dehydrated is the same as in the calorimetry, because the European Standard must be followed, but with different quantities and recipients. The quantity needed for mechanical test were 2 kg of fresh cement powder and 800 g of tap water to achieve the water to cement ratio of 0.4, and the mixer used was from *Heidolph*, model *RZR 2102 control* and a centre hole type blade for dispersion with plate shape made of steel, of 4 centimetres of diameter. The mixture was prepared in a beaker of 2 litres and later the paste was transferred into plastic recipients of 0.5 litres. The recipients were only filled less than ¼ to make the crushing easier.

5.2.2. Synthesis of recycled cement powder (dehydrated cement)

The hydrated cement paste cured for 3 days at room temperature in closed recipients. When this time passed, the blocks of hydrated OPC were put in the oven at 500 °C for 2 hours, with a ramp of heating of 30 minutes from room temperature to requested temperature and a slow cooling to room temperature again. Later, they were crushed manually with a hammer, milled with a mortar and stored in hermetic bags inside a barrel.

The blast furnace slags used in mortars were dehydrated following the same procedure that the OPC paste; it was stored in desiccators for a few days and in hermetic plastic bags later. When needed, the dehydrated OPC powder (crushed hardened paste) was mixed with the dehydrated slag to create the recycled cement powder. The temperature's profile followed during the heating is represented in Figure 10.
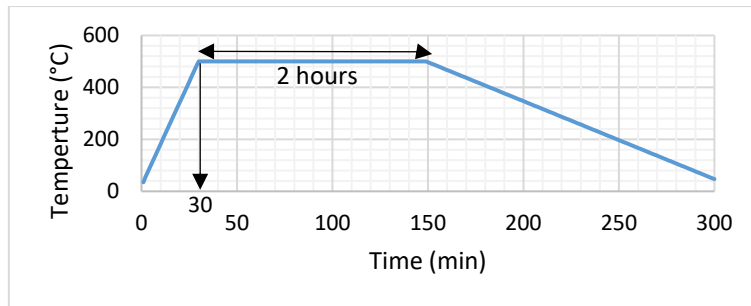
Figure 10: Representation of the heating profile followed during time

5.2.3. Production of recycled mortars (rehydrated cement + aggregates)

This point must be divided in the different types of mortars, because not all of them had the same proportions of materials. For this reason, an overall explanation about the procedure of creating mortars is going to be explained firs and later the different quantities used in each batch are pointed out.

The mixing of the mortar must follow the European Standard -as the cement paste. So, the procedure was almost the same as the preparation of the hydrated cement paste, with the difference of the addition of sand during the mixing. Also, the same mixer was the same model: *RZR 2102* from *Heidolph* with the same blade. The differences of the procedure followed in the present study and the mortar preparation explained in the Standard were: the absolute quantities and the samples tubes. The steps followed used the Standard as reference, these are: mixing cement and the solution at 800 rpm for 60 seconds, add sand regularly, mixing at 1800 rpm for 60 seconds, stop mixing to collect the paste of the sides and bottom of the recipient and return it to the centre and finally, mixing at 1800 rpm for 60 seconds.

The tubes used in the present Thesis were cylindrical instead of prismatic because they are smaller, more manageable and to do the compressive strength test is not necessary the prismatic ones. So, because the recipients were different, the absolute quantities also (but maintaining the proportions):

3:1 = sand : cement → sand/cement = 3 = 450 (g sand)/ 150 (g cement powder)
2:1 = cement : water → liquid/cement = 0.5 = 150 (g cement powder) / 75 (g liquid)

While doing the first mortars, a problem with the workability appeared because it was not a paste, it was very solid and granulated, so it was added more water to compensate and create a proper paste able to work with. The total quantity added was 16.5 g, so the final amount was 91.5 g of water. To do a comparison between the results, few batches were prepared with the same proportion of water (or activation solution), so the resulting water content ratio was:

w/c = 91.5 g / 150 g = 0.61

So, the Tables 1-6 show the batches with different characteristics: different water content ratio and activation solution used. Different batches were prepared for the mechanical test: for 2 days

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and 7 days of curing. The calculation for the quantities needed for the proportions *300:100* and *300:220* of *100% dehydrated* cement and *90% dehydrated + 10% new* were:

<u>100% dehydrated cement + blast furnace slag</u>

> 300 g cement + 100 g slag = 75% cement + 25% slag
> → For 150 g of total mix: 112.5 g cement + 37.5 g slag
>
> 300 g cement + 220 g slag = 58% cement + 42% slag
> → For 150 g of total mix: 86.54 g cement + 63.41 g slag

<u>90% dehydrated cement + 10% fresh (new) cement + blast furnace slag</u>

> 300 g cement (90% dehydrated + 10% new) + 100 g slag =
> = 75% cement (90% dehydrated + 10% new) + 25% slag
> → For 150 g of total mix:
> 112.5 g cement (90% dehydrated + 10% new) + 37.5 g slag =
> = 101.25 g dehydrated cement + 11.25 g new cement + 37.5 slag
>
> 300 g cement (90% dehydrated + 10% new) + 220 g slag =
> = 58% cement (90% dehydrated + 10% new) + 42% slag
> → For 150 g of total mix:
> 86.54 g cement (dehydrated + new) + 63.41 g slag =
> = 77.88 g dehydrated cement + 8.65 g new cement + 63.41 slag

The name given to identify the samples is form with different parts: *Cem* is referred to CEM I (OPC) from SECIL, Cem^H is referred to CEM I (OPC) from Heidelberg; the following number indicate the OPC proportions; *F* indicates the presence of 10% of fresh cement (unhydrated) in the binder; BFS_{number} indicates the proportions of blast furnace slag. These proportions numbers come from the ratios of *cemen:slag 300:220* kg and *300:100* kg, which were suggested by the partners of this project. All the nomenclature used is in Appendix III.

Table 6: Quantities of materials in batches activated by water with w/c 0.61 for 2-day test.

Proportions and characteristics	Name given	Water (g)	Sand (g)	Dehydrated OPC (g)	Dehydrated BFS (g)	Fresh OPC (g)
300:0 Heidelberg w/water	$Cem^H_{300}slag_0(H_2O)_{0.61}$	91.66	450.68	150.13	-	-
300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{0.61}$	91.50	450.20	112.51	37.49	-
300:220 w/water	$Cem_{300}slag_{220}(H_2O)_{0.61}$	91.57	450.12	86.53	63.40	-
300:100 w/new cement	$FCem_{300}slag_{100}(H_2O)_{0.61}$	91.50	450.01	101.27	37.52	11.25
300:220 w/new cement	$FCem_{300}slag_{220}(H_2O)_{0.61}$	91.53	450.21	77.88	63.42	8.66

Table 7: Quantities of materials in batches activated by water with w/c 0.61 for 7-day test.

Proportions and characteristics	Name given	Water (g)	Sand (g)	Dehydrated OPC (g)	Dehydrated BFS (g)	Fresh OPC (g)
300:0 Heidelberg	$Cem^H_{300}slag_0(H_2O)_{0.61}$	91.50	450.69	150	-	-
300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{0.61}$	91.64	450.27	112.44	37.48	-
300:220 w/water	$Cem_{300}slag_{220}(H_2O)_{0.61}$	91.44	450.82	86.54	63.44	-

Table 8: Quantities of materials in batches activated by alkaline solution with w/c 0.61 for 2-day test.

Proportions and characteristics	Name given	Alkaline solution (g)	Sand (g)	Dehydrated OPC (g)	Dehydrated BFS (g)
300:100 w/sodium hydroxide 1M	$Cem_{300}slag_{100}(NaOH)_{0.61}$	91.53	450.41	112.59	37.50
300:220 w/sodium hydroxide 1M	$Cem_{300}slag_{220}(NaOH)_{0.61}$	91.54	450.01	86.72	63.47
300:100 w/sodium carbonate 1M	$Cem_{300}slag_{100}(Na_2CO_3)_{0.61}$	91.64	450.99	112.56	37.57
300:220 w/sodium carbonate 1M	$Cem_{300}slag_{220}(Na_2CO_3)_{0.61}$	91.55	450.58	86.58	63.47

Table 9: Quantities of materials in batches activated by alkaline solution with w/c 0.61 for 7-day test.

Proportions and characteristics	Name given	Alkaline solution (g)	Sand (g)	Dehydrated OPC (g)	Dehydrated BFS (g)
300:100 w/sodium hydroxide 1M	$Cem_{300}slag_{100}(NaOH)_{0.61}$	91.71	450.93	112.49	37.49
300:220 w/sodium hydroxide 1M	$Cem_{300}slag_{220}(NaOH)_{0.61}$	91.52	450.32	86.53	63.41
300:100 w/sodium carbonate 1M	$Cem_{300}slag_{100}(Na_2CO_3)_{0.61}$	91.49	450.73	112.52	37.50
300:220 w/sodium carbonate 1M	$Cem_{300}slag_{220}(Na_2CO_3)_{0.61}$	91.51	450.28	86.53	63.42

Due to the results obtained in the mechanical test, the next samples to test were changed from the original planning. First, the water to cement ratio "w/c" was changed to 0.5 instead of 0.61, so it was necessary to add the superplasticizer ViscoCrete® from Sika Group, which is used to achieve lower water content ratio on cement paste (which increases strength). The problem is it only works in water, not in alkaline solutions. So, other alkali was tested (sodium sulphate) and with lower molarity (1M and 0.5M) too, to see if there was any difference.

Also, samples of CEM I from Heidelberg with proportion *300:0* in *cement:slag* (AW) gave very bad results (discuss in Part III), so the 100% cement samples were repeated using other cement (CEM I from SECIL). So, the quantities used in the mortars activated by water are in *Table 10*: Quantities of materials in batches activated by water with w/c 0.5 for 2-day test, with lower

water content ratio and different blast furnace slag proportions. And in *Table 11*: Quantities of materials in batches activated by water and alkalis with w/c 0.5 for 7-day test, there are also the quantities for batches with alkalis for the 7-day test.

Table 10: Quantities of materials in batches activated by water with w/c 0.5 for 2-day test

Proportions and characteristics	Name given	Water (g)	Sand (g)	Dehydrated OPC (g)	Dehydrated BFS (g)
300:0 w/water	$Cem_{300}slag_0(H_2O)_{0.5}$	75.18	450.22	150.07	-
300:220 w/water	$Cem_{300}slag_{100}(H_2O)_{0.5}$	75.17	450.01	112.51	37.50
300:100 w/water	$Cem_{300}slag_{220}(H_2O)_{0.5}$	75.09	450.11	86.54	63.41

Table 11: Quantities of materials in batches activated by water and alkalis with w/c 0.5 for 7-day test

Proportions and characteristics	Name given	Liquid (g)	Sand (g)	Dehydrated OPC (g)	Plast. (g)	Dehydrated BFS (g)
300:0 w/water	$Cem_{300}slag_0(H_2O)_{0.5}$	75.31	450.02	150.01	0.47	-
300:0 w/sodium hydroxide 1M	$Cem_{300}slag_0(NaOH)_{0.5}$	75.13	450.12	150.12	-	-
300:0 w/sodium carbonate 1M	$Cem_{300}slag_0(Na_2CO_3)_{0.5}$	75.10	450.17	150.02	-	-
300:0 w/sodium sulphate 1M	$Cem_{300}slag_0(Na_2SO_4^{1M})_{0.5}$	75.07	450.19	150.04	1.24	-
300:0 w/sodium sulphate 0.5M	$Cem_{300}slag_0(Na_2SO_4^{0.5M})_{0.5}$	75.32	450.25	150.13	0.47	-
300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{0.5}$	75.38	450.04	112.52	0.48	37.52
300:200 w/water	$Cem_{300}slag_{220}(H_2O)_{0.5}$	75.03	450.13	86.55	0.47	63.43

The mixtures were put in the tubes to create the specimens for the mechanical test. This procedure is described below.

5.2.4. Production of specimens (moulding, curing, demoulding and preparation for test)

When the mixtures were prepared, the mortars were put in tubes or moulds of 60 mm of height and 33 mm of diameter, approximately. Later, the tubes were put in a vibration table during few minutes (to make air bubbles go out the mixture), closed and labelled. At 48 hours of curing the specimens need to be demoulded, but for the 2-days were demoulded and cut at 24 hours to let the water of the sword dry. This is possible because during the first hours, the cement paste starts to harden. The demoulding can be done easily if the tubes are internally painted with oil, but it could happen that that the demoulding is difficult: in this situation, a little hole

must be done in the bottom surface with a drill and the specimen can be pushed out from the tube using a compress air gun. When using the air gun, it is necessary to use gloves and safety glasses.

After the demoulding, the specimens must be prepared to do the mechanical test: the top and the bottom must be flat to do the compressive strength test, so the specimens must be cut with a diamond sword to achieve it. Because the sword uses water as cutting oil for cooling, the specimens become wet, so it is needed to dry them before the compression test: after the cutting, the specimens were put in an oven at 50ºC for 24 hours. When they are dry, the height and diameter of the specimens must be measured. This data will be necessary for the compressive strength test.

PART III: Results and discussion

Chapter 6: Results and comparison of samples

In the third part of the thesis, the results of the different cement pastes and concretes tested are shown. The binders tested in the calorimeter are prepared with fresh cement (OPC) with water and dehydrated cement (OPC or OPC with slags) with a reactivation solution: water and alkaline solutions (sodium hydroxide, sodium carbonate and sodium sulphate, all 1M and last one also 0.5M). Cement from the company is "fresh" or "unhydrated", after it is mixed with water and it is heat up until 500 °C, so it is called "dehydrated" and later it is mixed with a reactivation solution to become "hydrated", "rehydrated", "regenerated" or "reactivated".

First, the results from the thermogravimetric analysis are represented to analyse the hydrated material tested. Second, the reactivity study done with the calorimeter describes the hydration heat due to the chemical reactions that occur in the samples, using isothermal calorimetry as the characterization technique. Finally, the results from the compressive strength test are analysed and compared with each other and with the calorimetry results. It is important to explain the dehydration of cement in detail. Below, a general graph about the thermogravimetric analysis is shown and explained (Figure 11). CEM II paste of 1 day old has been chosen to explain the different steps of the TGA because they are represented very clearly in this paste. Also, the sample has been heated up until 800 °C to see what happens in all temperatures. As seen in the Figure 11, three main steps of weight loss are seen around 100 °C, 400 °C and 650-700 °C. As explained in *2.4 ¡Error! No se encuentra el origen de la referencia.*, in those temperatures there are different reactions, i.e. dehydroxylation and decarbonation, where the reactants decompose and the mass loss is recorded. The green line represents the weight loss in percentage and the blue one the derivative of the weight loss, which indicates the point of greatest rate of change on the curve. This is also known as the inflection point [52].
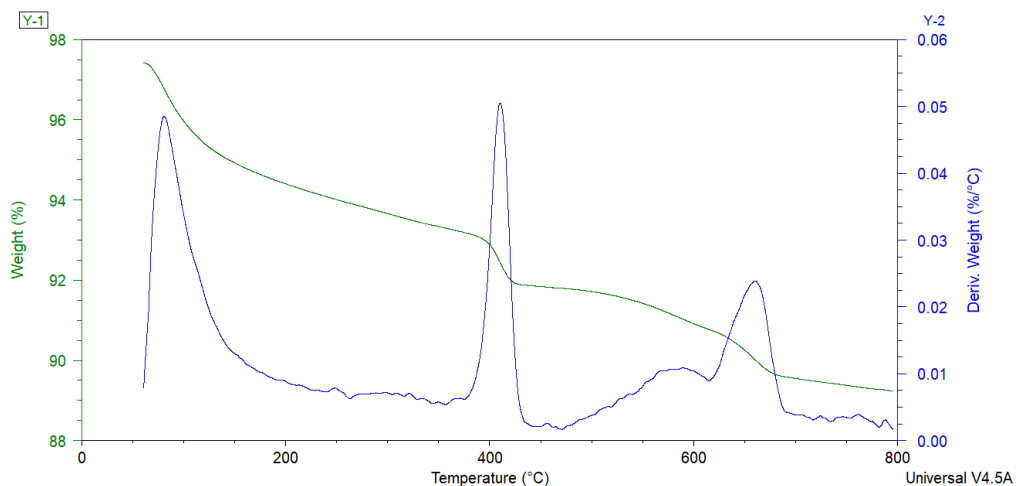

Figure 11: TGA to cement paste of 1 day old. Hubo's CEM II + water with a water to cement ratio of 0.4

Upon heating, a decrease in the weight loss is seen. In that part, ettringite starts dehydrating du to the evaporation of freewater so it begins to lose its crystalline form (around 80 °C to 100 °C).

At 100 °C, the free water evaporation geerates the dehydration of C-S-H gel. So, the first step seen around that temperature is the weight loss due to the free water. Between 100 °C and the next big step at 400 °C, part of the water steam condensates because there are sealed parts in the cement, so not all the vapour goes out the pores. This condensation of water reacts with the alite and belite that are still present in the mixture and generates an increase of portlandite and C-S-H. In the same time, the water still evaporating so the C-S-H gel starts dehydrating; the partially dehydrated C-S-H is a new form of a nesosilicate ($Ca_{1.5}SiO_{3.5} \cdot xH2O$) (Alonso and Fernandez, 2004). According to Alonso and Fernandez, around 400-450 °C, bond water is completely lost (which means that all phases are dehydrated). From the initial heating until the second main step, the reaction of the CO_2 gas present in the pores generates calcite (Cc, $CaCO_3$, $CaO \cdot CO_2$) due to the carbonation of lime, being the maximum increase of Cc at 450 °C. In that temperature, calcite and portlandite start reacting into lime. This reaction will be completed at 750°C. Also, around 700 °C, the calcite starts the decarbonation, reacting to CO_2 and lime again and the new nesosilicate created from C-S-H gel is completely formed.

All these steps are seen in hydrated cement paste but when the cement is dehydrated, the steps are not always seen. The study of TGA curves of pastes with cement dehydrated at different temperatures (100, 200, 450, 750 °C) [53] shown that when re-hydrating the dehydrated cement (called before *reactivation*), samples changed to crystalline composition, so some of hydrated forms were recovered: calcite, portlandite, ettringite and C-S-H gel. Initial belite (C_2S) and ferrite (C_4AF) remained unaltered during reactivation. But they concluded that in samples heated at 750 °C "weight losses are very low in the whole range of temperatures (…) indicating that during heating [*at 750 °C*] a complete chemical transformation of the cement paste has occurred", explaining that the only transformation seen in dehydrated samples at high temperatures is the transformation of the portlandite and calcite into lime. So, the reactivation of the dehydrated cement at 750 °C generate again portlandite, calcite and a C-S-H gel very similar to the initial; but no alite, belite or ettringite which give strength to the cement. For this reason, the dehydration of the cement paste has been done at 500 °C in the present study.

6.1. Results thermogravimetric analysis

The importance of the TGA in cement research and industry is to identify portlandite (CH), calcite (Cc), calcium aluminate hydrates (C-A-H, $C_xA_yH_z$), bond and free water. The different phases of the cement break down at different temperatures (as seen in the Introduction) to release bond water during their dehydration and CO_2 (in the case of decarbonation of calcite). These releases help to identify different phases present in the cement thanks to the weight loss observed and the derivatives curves quantify the proportions of the phases in the hardened cement paste.

In the present study, this technique has been used to identify the phases in fresh cement and in recycled mortars (prepared with regenerated cement previously dehydrated at 500 °C) prepared with different proportions of blast furnace slag (0Wt%, 25Wt% and 42Wt%) and reactivation liquids (water and alkaline solutions of different molarities), as well as the comparison with mortars activated with a 10% of fresh cement and water. Also, an old used concrete (more than 90 days) was analysed to perform as a reference.

First, when analysing fresh (unhydrated) CEM I from SECIL used in the majority of the mortars (Figure 12: TGA to fresh CEM I SECILFigure 12), the total mass loss is low (0.25%). This shows that the fresh cement is almost not hydrated. The first mass loss step starts at about 110 °C and might be linked to the first dehydration of the gypsum (dihydrate calcium sulphate) (Eq. 10). In the same figure, fresh cement powder is compared with fresh cement paste (hydrated, cement powder mixed with water) before dehydration. There it can be seen the hydrated phases this cement have, explained below.
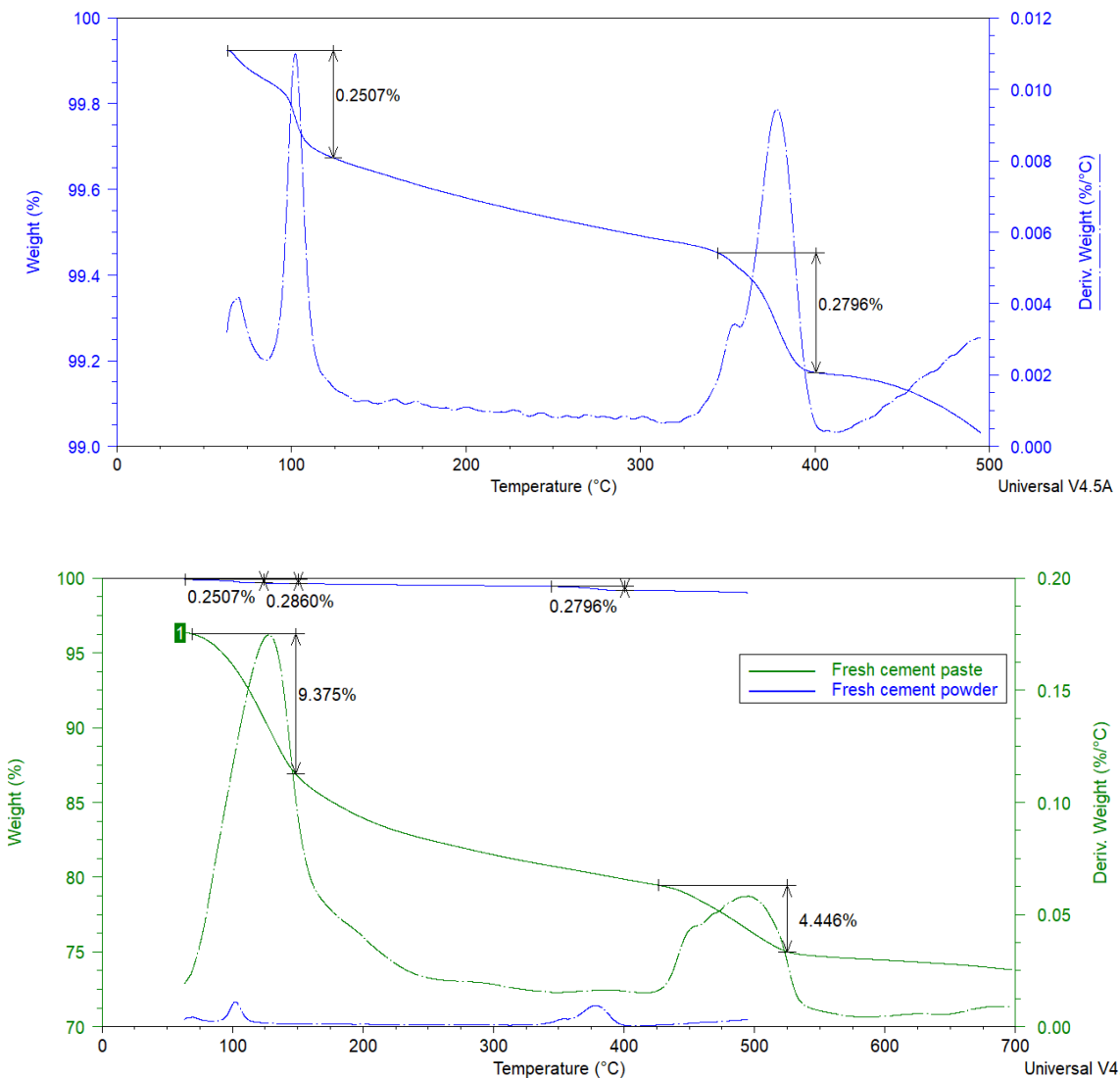
Eq. 10: $CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1.5H_2O + 0.5H_2O$

Figure 12: TGA to fresh CEM I SECIL: powder (up) and comparison between powder and paste (mixed with water) (down)

As explained in the beginning of Part III, around 100-150 °C it is seen the evaporation of free water of the pore solution and a partial dehydration of hydrated compounds like gypsum, which represent the 5% of the clinker, with a mass loss of 0.22%. Because this is fresh (unhydrated) cement, the step around 450 °C is very low: at this temperature the C-S-H gel dehydrates due to

the elimination of bond water of the gel and also the portlandite (CH) yields to lime (C) due to the reaction with calcium carbonate (Cc) and the portlandite dehydration, but the hydrated phases (C-S-H, CH) are not present in unhydrated cement, so their dehydration does not happen. In this step, the loss is a 0.35% of mass, indicating the cement powder does not have lot of portlandite (which is generated due to the presence of water).

The next analysis is between mortars of dehydrated CEM I but mixed with different solutions (water, sodium sulphates of different molarities, sodium carbonate and sodium hydroxide). These specimens had different ages and they are compared with a concrete of more than 90 days old (Figure 13).
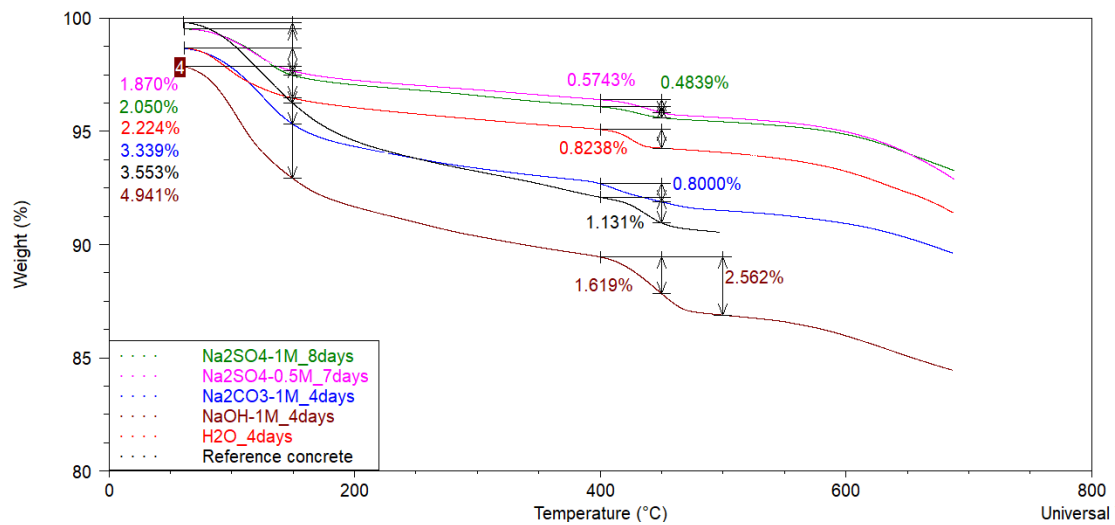

Figure 13: TGA for mortars with 100% of dehydrated CEM I from SECIL and different liquids used in the reactivation, different ages

There are seen in all the curves the two steps expected around 100 °C and 450 °C of evaporation of free water and dehydration of C-S-H in the first one and decomposition of portlandite and the change of crystalline form of C-S-H in the second one. At the first temperature, the maximum mass loss is seen in the younger mortar, prepared with sodium hydroxide (4.9%) with can be compared with the same age mortar prepared with sodium carbonate (with a mass loss of 3.3%) and mortar prepared with water (mass loss of 2.2%). Just as reminder, the solution of 1M of sodium carbonate acts like an equivalent solution of 2M of sodium hydroxide, because of the quantity of sodium, which means that the solution with sodium carbonate has less water than the others. It has less water, but it is seen that mortars with sodium hydroxide solution have bigger mass loss and mortars with water have less mass loss. The reason why sodium hydroxide generates bigger loss could be due to the presence of hydroxides (and not because the sodium): they can react with the calcium of gypsum to create portlandite, in which case the decomposition of gypsum would be seen in that step with the evaporation of free water.

To compare the influence of water it can be analysed the curves of mortars with sodium sulphate with different molarities: 1M and 0.5M. As seen, the mortar with more water (0.5M, pink curve) has less mass loss (1.9%) than with less water (1M, green curve) which has a 2.1% of loss. This situation is the opposite as expected, because it can be thought that if the mixture has less

water, less quantity is going to be evaporated. But the quantity of water is slightly different (solution with 0.5M has 0.89% less water) and mortar with less water has more sodium sulphate, so it seems that this alkali has an influence on this step.

The second step is the dehydration of portlandite and creation of new phase of C-S-H due to the elimination of bond water. As in the first step, the mortar with more mass loss (more portlandite) is prepared with sodium hydroxide (1.6%), followed by mortars with water (0.8%) and with sodium carbonate (0.8%). These mortars are younger than mortars with sodium sulphate, so their quantity of portlandite should be less than the older ones, but it is seen that the water loss due to the dehydration of portlandite is bigger, which means they have more portlandite. The other mortars have less mass loss; 0.5% mortar with sodium sulphate 1M and 0.6% with sodium sulphate 0.5M.

Comparing with same young age, mortars with sodium carbonate have smaller loss due to the reaction with portlandite to create sodium hydroxide and calcium carbonate (Eq. 11).

$$Eq.\ 11:\ Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$$

The analysis of the older mortars shows that mortar with less sulphates (0.5M, pink curve) has more mass loss (more portlandite) (0.5743%) than with more sulphates (1M, green curve) which has a 0.4839% of loss, even they are very similar. This could happen because the mortar with less sulphate has more water, so the clinker reacts with it to create more portlandite, even if this binder is one day younger (theoretically, young mortars have less portlandite).

The next analysis done with TGA is between mortars with 100% dehydrated binder (cement and blast furnace slag) and mortars with 90% dehydrated binder and 10% fresh OPC, to see if the activation with fresh cement affects the hydration products (Figure 14).
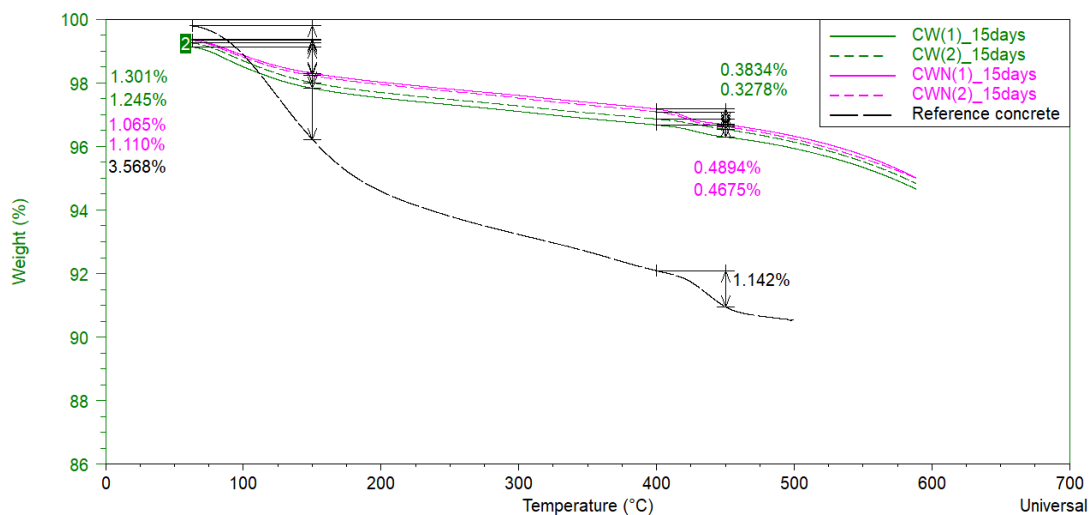

Figure 14: Influence of activation by 10% of fresh cement. TGA for mortars with 25% of slag, water and with (pink) and without (green) fresh or new cement, 15 days old.

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As seen in Figure 14, the tendency of the curves of the mortar with dehydrated binder activated with 10% of fresh cement (pink) is the same as the mortars with only dehydrated binder (green curve). The first step (evaporation of free water) is slightly bigger (more mass loss) for 100% dehydrated binder (1.2-1.3%) than for the dehydrated binder activated with fresh cement (1.1%). And the second step (dehydration of portlandite) is the opposite: the dehydrated binder has less mass loss (0.4-0.3%), which means less portlandite, than the dehydrated binder with fresh cement (0.5%). Because both types of mortars have same age, it can be understood that the mortar with 100% dehydrated binder has a slower hydration reaction, that is why it has more water and more less portlandite than the other at the same age.

The comparison of this binders with the fresh cement paste is shown in Figure 15. There it can be seen that the fresh cement paste is very hydrated, more than the concrete as expected, so this comparison cannot give lot of information.
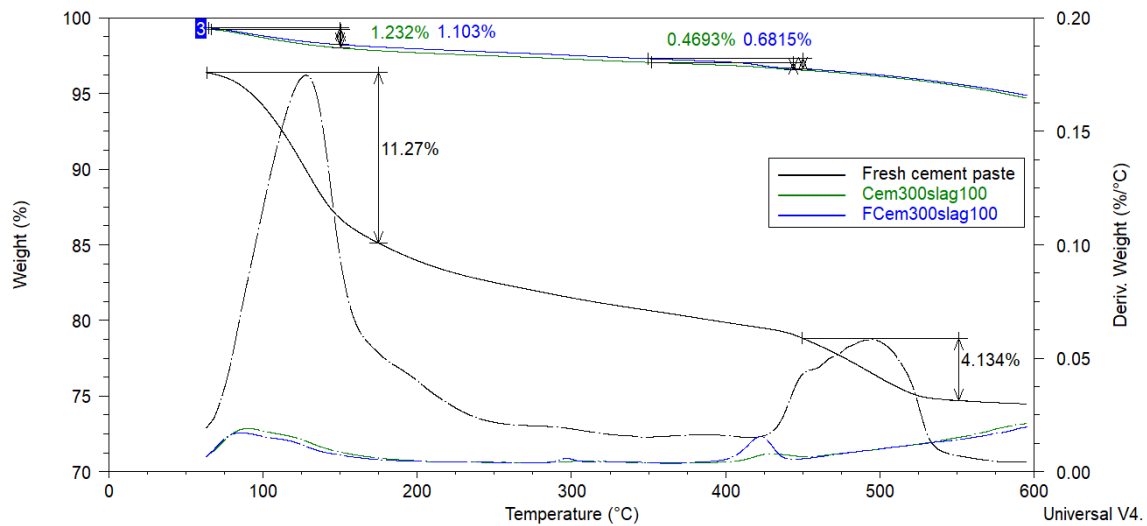

Figure 15: Influence of activation by 10% of fresh cement and comparison with fresh cement paste (black). TGA for mortars with 25% of slag, water and with (blue, FCem300slag100) and without (green, Cem300slag100) fresh or new cement, 15 days old

The next analysis is between dehydrated binders with 10% of fresh OPC to activate but with different proportion of blast furnace slag in their dehydrated binder (25% and 42% of dehydrated slag). The influence of dehydrated slag in binder can be seen with this comparison (Figure 16).
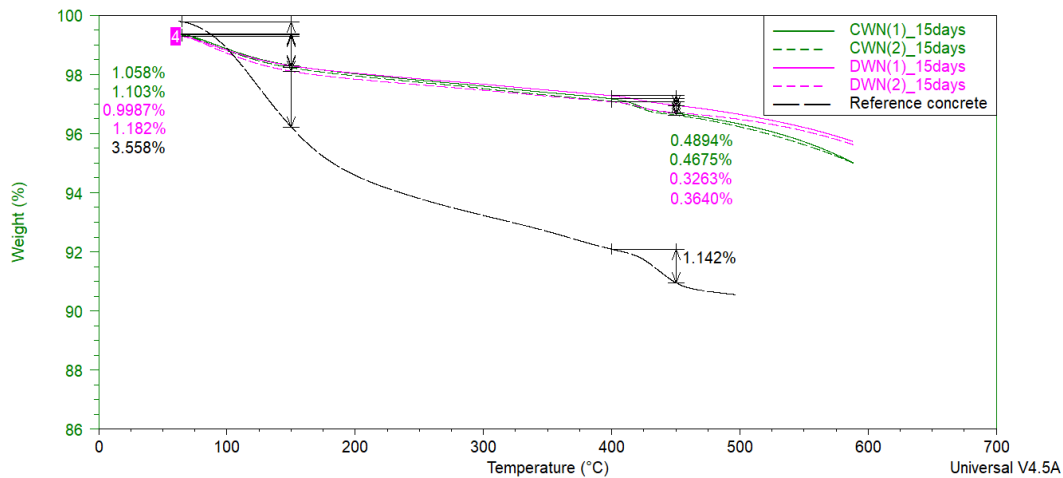
Figure 16: Influence of slag proportion. TGA for mortars with 10% of fresh cement, water and different prportion of slag, 15 days old

As seen, the evaporation of free water around 100 °C is barely the same, which means that both mortars have same quantity of free water in that moment. However, the dehydration of portlandite at 450 °C is different. In this second step, the dehydrated binder with less slag (more OPC) has a bigger step, which means it has more portlandite. This make sense because it has more OPC.

6.2. Reactivity study

The reactivity study was done to analyse the hydration heat and enthalpy of samples with a water to cement ratio of 0.5 principally, because it is the ratio used in the European Standard. Also, other important analysis is the influence of water in the mortars and in the hydration reaction, so few binders were tested with an excess and less water. Because the calorimetry analyses the chemical reactions, inert aggregates are not needed to be added to the mixture tested, such as sand. The main reactions cannot be seen properly in the representation of the data of 7 days, because they occur during the first and second day, so it has been decided to only use the first days' data, that is why the results obtained in the calorimetry were cut to scale the resolution of the graphics.

6.2.1. Reactivity of binders with water to cement ratio 0.5

The binders characterised in this section are detailed in Table 12 with the quantities of the materials used. In this part, binder with fresh OPC has been tested in the calorimeter to compare it with the other results: it is the only sample with fresh cement paste, the rest of the samples were prepared with dehydrated OPC at 500 °C. The first comparison than can be done is the analysis of the differences in the enthalpy of hydration of the binders (Table 13). The reaction's enthalpy is the heat absorbed or released during the period in which the chemical reaction occurs, in this case, the hydration enthalpy represents the enthalpy of all the chemical reactions that occur during the hardening of the cement paste.

Table 12: Quantities of materials in binders with w/c 0.5 for calorimetry.

Proportions and characteristics	Name given	Liquid (g)	Dehydrated OPC (g)	Dehydrated BFS (g)
300:0 w/water	$Cem_{300}slag_0(H_2O)_{0.5}$	3.350	6.672	-
300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{0.5}$	3.340	5.001	1.676
300:200 w/water	$Cem_{300}slag_{220}(H_2O)_{0.5}$	3.350	3.854	2.823
300:0 w/sodium hydroxide 1M	$Cem_{300}slag_0(NaOH)_{0.5}$	3.310	6.678	-
300:0 w/sodium carbonate 1M	$Cem_{300}slag_{100}(Na_2CO_3)_{0.5}$	3.380	6.675	-
300:0 w/sodium sulphate 1M	$Cem_{300}slag_0(Na_2SO_4^{1M})_{0.5}$	3.300	6.679	-
300:0 w/sodium sulphate 0.5M	$Cem_{300}slag_0(Na_2SO_4^{0.5M})_{0.5}$	3.310	6.67	-
300:0 w/water, w/c=0.36	$Cem_{300}slag_0(H_2O)_{0.36}$	2.678	7.363	-
			Fresh OPC (g)	
300:0 Fresh OPC w/water, w/c=0.5	$FCem_{300}slag_0(H_2O)_{0.5}$	3.342	6.698	
300:0 Fresh OPC w/water, w/c=0.4	$FCem_{300}slag_0(H_2O)_{0.4}$	2.868	7.169	

Table 13: Enthalpies of the hydration reaction in binders with w/c 0.5, in J/g of cement

Proportions and characteristics	Name given	Enthalpy (J/g dehydrated CEM I), at 2nd day
300:200 w/water	$Cem_{300}slag_{220}(H_2O)_{0.5}$	314.032
300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{0.5}$	296.271
300:0 w/water	$Cem_{300}slag_0(H_2O)_{0.5}$	263.391
300:0 w/sodium hydroxide 1M	$Cem_{300}slag_0(NaOH)_{0.5}$	234.543
300:0 w/sodium carbonate 1M	$Cem_{300}slag_0(Na_2CO_3)_{0.5}$	233.325
300:0 w/sodium sulphate 1M	$Cem_{300}slag_0(Na_2SO_4^{1M})_{0.5}$	255.577
300:0 w/sodium sulphate 0.5M	$Cem_{300}slag_0(Na_2SO_4^{0.5M})_{0.5}$	260.786

300:0 w/water, w/c=0.36	$Cem_{300}slag_0(H_2O)_{0.36}$	210.235
300:0 fresh OPC w/water, w/c=0.4	$FCem_{300}slag_0(H_2O)_{0.4}$	267.051
300:0 fresh OPC w/water, w/c=0.5	$FCem_{300}slag_0(H_2O)_{0.5}$	285.393

Comparing the enthalpies, the binder with higher enthalpy is prepared with 42% of slags and water, $Cem_{300}slag_{220}(H_2O)_{0.5}$, and the second one is with 25% of slags and water too, $Cem_{300}slag_{100}(H_2O)_{0.5}$. This means that slags increase the reactivity more that the alkaline solutions used in this study. Fresh cement (unhydrated, before dehydration) with water has higher enthalpy than dehydrated cement, which means that the dehydration generates a loss in the reactivity of the binder. The comparison between different water ration in fresh cement shown that binders with 0.5 are more reactive than binders with 0.4, both higher that dehydrated binders. So, a decrease of the water to cement ratio decreases the reactivity, could be that with less quantity of water than 0.5 not all the clinker phases react.

Between the rest of dehydrated cements without slags, binder with water ($Cem_{300}slag_0(H_2O)_{0.5}$) has higher enthalpy than binders with other solutions and also than binder with lower ratio ($Cem_{300}slag_0(H_2O)_{0.36}$). Comparing alkaline solutions, sodium sulphate generates higher heat than hydroxide and carbonate, in that order. More molarity in sodium sulphate solution creates lower heat (binder $Cem_{300}slag_0(Na_2SO_4{}^{1M})_{0.5}$) than binder of 0.5M, it could happen because solution with lower molarity have more absolute water and due to the effect of alkalis, which should be studied in detail. About the alkalis, sulphates react with C_3A and C_4AF to create AFt and AFm, so these reactions increase the total hydration heat. So, this alkali has a clear influence in the hydration heat.

Finally, binder of dehydrated OPC and with lower water to cement ratio has been compared ($Cem_{300}slag_0(H_2O)_{0.36}$). This binder has the lowest enthalpy, so the reactivity of the hydration reaction is lower, which could mean that not all the hydrated phases have been created after the reactivation or not all regenerated clinker phases were present before the reactivation.

First comparison shown is between the fresh (unhydrated) and dehydrated OPC pastes. Fresh OPC paste was prepared mixing water and cement directly from the company bag and dehydrated OPC paste by dehydrating the fresh OPC paste at 500 °C for 2 hours, as explained in *5.2 Design of the experiment*. Both pastes were prepared with a water to cement ratio of 0.5 - as suggested in the European Standard, reactivated with distilled water and without slags; the thermogram is shown in Figure 17. In all the thermograms, the heat flow is represented in darker curves and the enthalpy is represented in light curves. The reaction's enthalpy is represented as the area under the curve and calculated as the summation of enthalpies in every second during the reaction. So, it is the summation of the data from the beginning of Stage 3 (first minimum) to the end of the reaction. In this case, only the reactions during the first two days were analysed. To do these representations, the data has to be normalised by the total amount of OPC in each sample. Also in all these representations, the first sharp peak in the thermogram represents the second peak in the hydration reaction since the first peak ('dissolution peak' or Stage I) is so fast (first minutes of reaction) that cannot be recorded using this test.
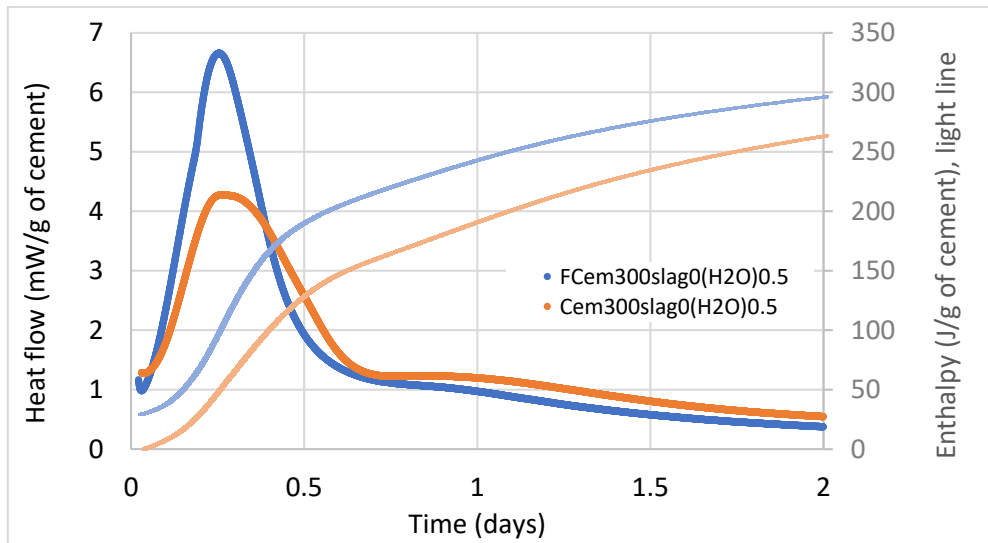
Figure 17: Reactivity of binders prepared with fresh (unhydrated) and dehydrated pastes, with a water to cement ratio of 0.5 and water. In blue fresh (unhydrated) OPC and in orange dehydrated OPC.

In Figure 17, the heat flow achieved in the second hydration peak (the first one seen in the thermogram) is higher for the fresh paste than for the dehydrated cement paste. This situation shows that clinker phases are not totally regenerated after the dehydration and reactivation of the cement, that is why the final reactivity is lower. Also, both enthalpies have the same tendency but being the enthalpy of fresh cement always higher, also seen in Table 13.

The next thermograms show the heat flow of the reactions in dehydrated cement (OPC or OPC with slags) and reactivated with different solutions (water or alkaline solutions). Next comparison is the influence of blast furnace slag in dehydrated binders with water (Figure 18).
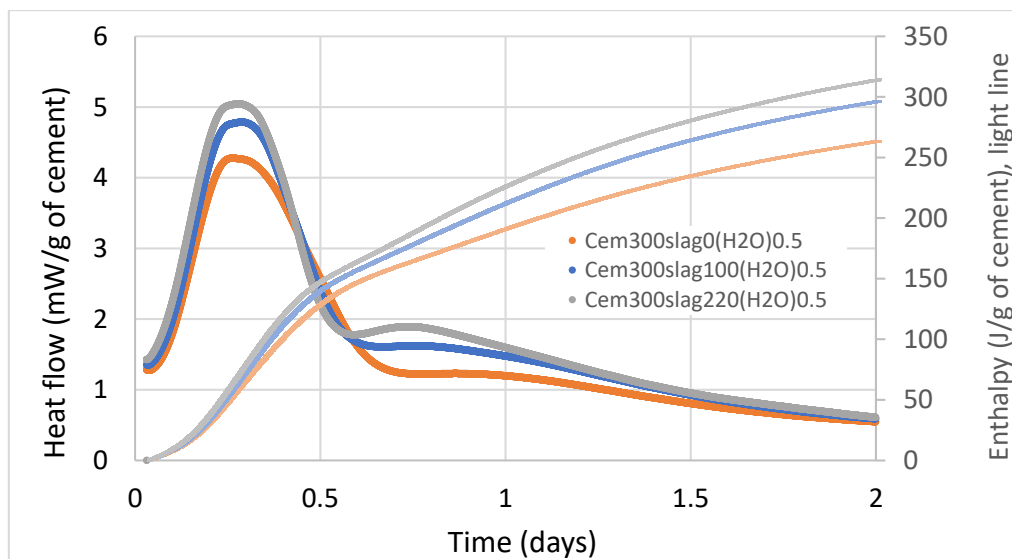

Figure 18: Reactions with water and different binders, w/c =0.5. In grey binder with more slag, in blue binder with less slag and in orange binder without slag.

Analyzing Figure 18, the presence of blast furnace slag increases the hydration heat and enthalpy (grey and blue lines). This situation happens due to the filler effect explained in *2.2 Types of cement and aggregates, according to European Standard* EN 197-1. Because the slags are fine particles, they are filling the spaces between OPC grans, which accelerate the reaction of the clinker compounds [54]. Comparing the second hydration peak (first one seen), binder without slag (orange curve) has lower hydration heat. Also, in these curves another broader peak (third on hydration reaction, but second on the graph) can be observed. This peak is bigger in binders with slags and very low -but not inexistent- in the binder without them. It represents the reaction of slags and portlandite, and the creation of more C-S-H gel. So, it can be concluded that the slags give more reaction products than only OPC. In the case of the curve of binder without slags (orange curve), the third peak of the hydration is lower but not flat; so, it can be the continuation of creation of portlandite and C-S-H, explained by the Stage IV: the unreacted cement cores move to the pore solution due to the diffusion of the water that goes inside cement grains (explained in *2.3 Hydration of cement*). This could happen due to an excess of water in the hydration reaction, so it will be developed in the comparison of water content in section *6.2.3. Influence of water to cement ratio in compressive strength*.

The next interesting comparison to do is the analysis of the influence of different solutions used to reactivate the cement. In this case, all binders were 100% dehydrated OPC.
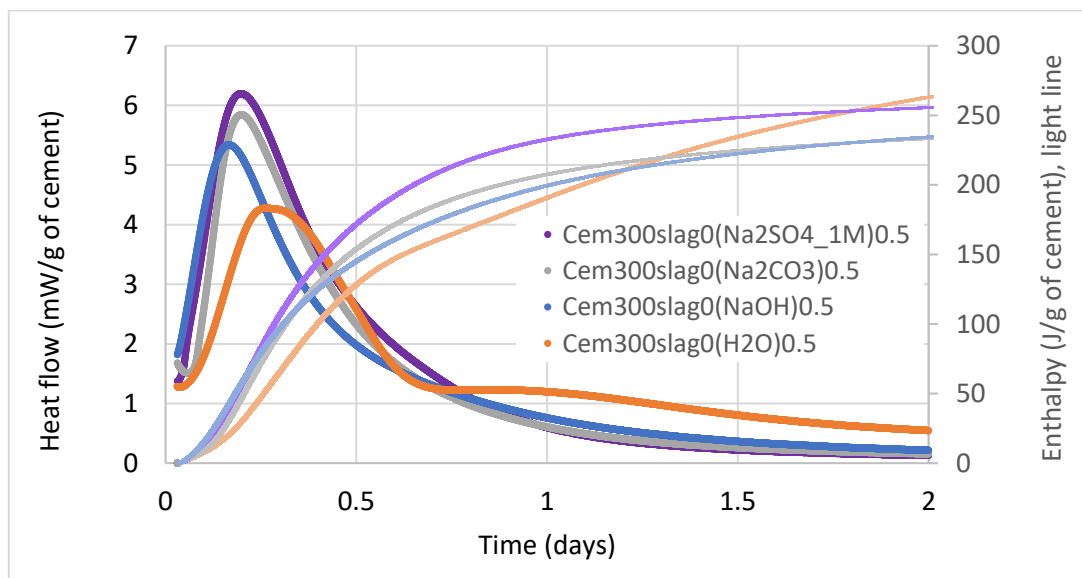

Figure 19: Reactions with different solutions used to reactivate cement using w/c = 0.5. Purple: Cem300slag0(Na2SO4^1M)0.5, grey: Cem300slag0(Na2SO3)0.5, blue: Cem300slag0(NaOH)0.5 and orange Cem300slag0(H2O)0.5.

As seen in Figure 19, the solution that generates the highest heat flow is the one with sodium sulphate (Cem$_{300}$slag$_0$(Na$_2$SO$_4$^{1M})$_{0.5}$, purple curve). As mentioned before, sulphates react with C$_3$A and C$_4$AF to create AFt and AFm, so these reactions increase the total hydration heat. The second highest heat flow is the reaction with sodium carbonate (binder Cem$_{300}$slag$_0$(Na$_2$CO$_3$)$_{0.5}$, grey curve). The carbonates react with the portlandite to yield to calcite and its reaction heat flow contributes to the total of hydration seen in the graph. The solution of sodium hydroxide has a smaller peak than the carbonate solution but a slightly higher enthalpy. And the heat flow

peak of the reaction with water is the smallest but this binder has the highest enthalpy, due to the third peak seen in the curve. This third peak (second in the graph) is seen in binders with water and binders with slag and carbonates, but not in binders with carbonates but without slag.

Other parameter compared during this thesis is the influence of the molarity in the alkaline solutions (Figure 20). To do this, two solutions of sodium sulphate with different molarities were used: 1M and 0.5M, in the binders $Cem_{300}slag_0(Na_2SO_4^{1M})_{0.5}$ and $Cem_{300}slag_0(Na_2SO_4^{0.5M})_{0.5}$, respectively.
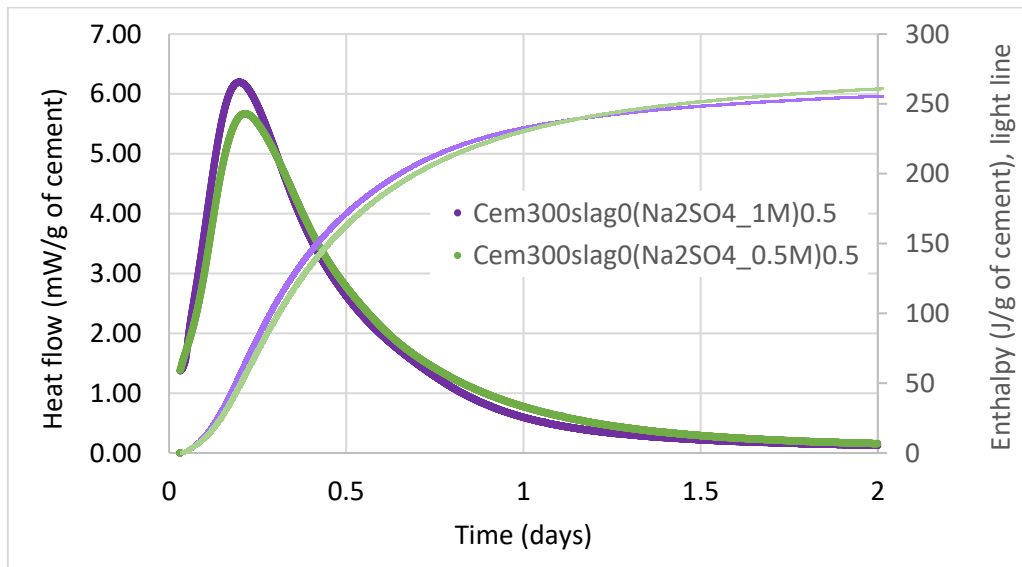

Figure 20: Reactivity of dehydrated binders without slags reactivated with sodium sulphate solutions of different molarities. In purple with 1M and green with 0.5M

As seen in Figure 20, solutions with both molarities have very similar tendencies. The only difference is solution with higher molarity has a higher maximum in the peak and tends to cero before, and its enthalpy is slightly higher. But both are very similar curves. For these reasons, it can be concluded that there is no difference between solutions of 1M and 0.5M, maybe lower or higher molarities and larger differences in molarities can give different results.

6.2.2. Reactivity of cement pastes with an excess of water

As seen in the previous section, the presence of water in the cement paste influences the hardening, so it could be interesting to analyse the heat flow and the enthalpy when the pastes have an excess of water. In this case, the water to cement ratio used was 1.5 and all the binders tested were dehydrated cement (two types of OPC and OPC with slags) and reactivated with different solutions. The quantities of the materials of the binders characterised in this section are detailed below (Table 14).

Table 14: Quantities of materials in binders with w/c 1.5 for calorimetry.

Proportions and characteristics	Name given	Liquid (g)	Dehydrated OPC (g)	Dehydrated slag (g)
300:0 Heidelberg w/water	$Cem^H_{300}slag_0(H_2O)_{1.5}$	6.17	3.93	-
300:0 Heidelberg w/sodium hydroxide 1M	$Cem^H_{300}slag_0(NaOH)_{1.5}$	6.16	3.90	-
300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{1.5}$	6.10	2.93	0.98
300:100 w/sodium hydroxide 1M	$Cem_{300}slag_{100}(NaOH)_{1.5}$	6.13	2.97	0.97
300:100 w/sodium carbonate 1M	$Cem_{300}slag_{100}(Na_2CO_3)_{1.5}$	6.14	2.92	0.97
300:220 w/water	$Cem_{300}slag_{220}(H_2O)_{1.5}$	6.11	2.26	1.65
300:220 w/sodium hydroxide 1M	$Cem_{300}slag_{220}(NaOH)_{1.5}$	6.13	2.24	1.65
300:220 w/sodium carbonate 1M	$Cem_{300}BFS_{220}(Na_2CO_3)_{1.5}$	6.18	2.25	1.66

The main hydration reaction happens during the first two days, but it continues slowly while the heat flow continues to decrease towards the baseline. Even the thermograms show the first two days, some binders were tested for 7 days to compare if there is lot of difference between the reactivity data from 2nd and 7th day. Knowing the enthalpy gives an idea of the extent of hydration that occurs in the paste. Table 15 shows the enthalpies of the hydration reaction in binders with an excess of solution.

Table 15: Enthalpies of all reaction in binders with w/c 1.5, in kJ/g of cement

Proportions and characteristics	Name given	Enthalpy (J/g dehydrated CEM I)		Increase (%)
		At 2 days	At 7 days	
300:0 Heidelberg w/water	$Cem^H_{300}slag_0(H_2O)_{1.5}$	192	244	27.1%
300:0 Heidelberg w/sodium hydroxide 1M	$Cem^H_{300}slag_0(NaOH)_{1.5}$	208	241	15.9%
300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{1.5}$	364	492	35.2%
300:100 w/sodium hydroxide 1M	$Cem_{300}slag_{100}(NaOH)_{1.5}$	386	496	28.5%
300:100 w/sodium carbonate 1M	$Cem_{300}slag_{100}(Na_2CO_3)_{1.5}$	441	563	27.7%
300:220 w/water	$Cem_{300}slag_{220}(H_2O)_{1.5}$	393	544	38.4%

300:220 w/sodium hydroxide 1M	$Cem_{300}slag_{220}(NaOH)_{1.5}$	447	608	36.0%
300:220 w/sodium carbonate 1M	$Cem_{300}slag_{220}(Na_2CO_3)_{1.5}$	521	744	42.8%

In general, binders with 42% of slags ($Cem_{300}slag_{220}$) have higher enthalpies and binders with 100% OPC from Heidelberg have the lowest. Comparing between solutions used to reactivate, sodium carbonate generates more heat than sodium hydroxide and water in the last position. This behaviour is the opposite that occurs with a water to cement ratio of 0.5 in binders without slags: in the previous case, binders without slags have more reactivity when react with water than with alkaline solutions. So, binders with slags get more reactivity when reactivating with alkaline solution and binders without slags (100% OPC) when are reactivated with water; i. e. $Cem_{300}slag_{100}(H_2O)_{1.5}$ has 364 J/g and $Cem_{300}slag_{100}(Na_2CO_3)_{1.5}$ has 441 J/g, and n the other hand, $Cem_{300}slag_0(H_2O)_{0.5}$ has 263 J/g and $Cem_{300}slag_0(Na_2CO_3)_{0.5}$ has 233 J/g. And even it is not the maximum, binders with slags have more reactivity with more water content: i.e. $Cem_{300}slag_{100}(H_2O)_{1.5}$ has 364 J/g and $Cem_{300}slag_{100}(H_2O)0_{0.5}$ has 296 J/g. So, the final order of highest enthalpies is (first one the highest):

i. With slags + excess of alkalis → around 400 J/g
ii. With slags + excess of water → around 360 J/g
iii. With slags + 0.5 of water → around 300 J/g
iv. Without slags + 0.5 of water → around 260 J/g
v. Without slags + 0.5 of alkalis → around 250 J/g

It is important to point out that an excess of heat (high enthalpy) could generate future cracking in concrete (less durability) and less resistance to sea water. Also, the BFS added in fresh cement decrease the total heat but, as seen with these results, BFS added in recycled cement increases it, so more studies should be done related with this topic.

Other issue to analyse is the increase of the enthalpy from the 2nd day to the 7th. Binders with more slags shown a bigger increase of the total hydration heat when more days passed. This situation reinforces the idea that slags make the reactivity increase in recycled binders. Between type of solution, there is not seen a clear tendency, because depending on the binder, the lower and higher increase is seen in binders with different solutions.

From Figure 21 to Figure 25, the representations of reactivity of binders with different solutions (water, sodium hydroxide 1M or sodium carbonate 1M) are shown, so the comparison in each figure is between the different binders tested. Also, the data represented are normalised per gram of cement in each binder. The thermograms of the pastes mentioned in Table 14 and Table 15 are shown in that figures.
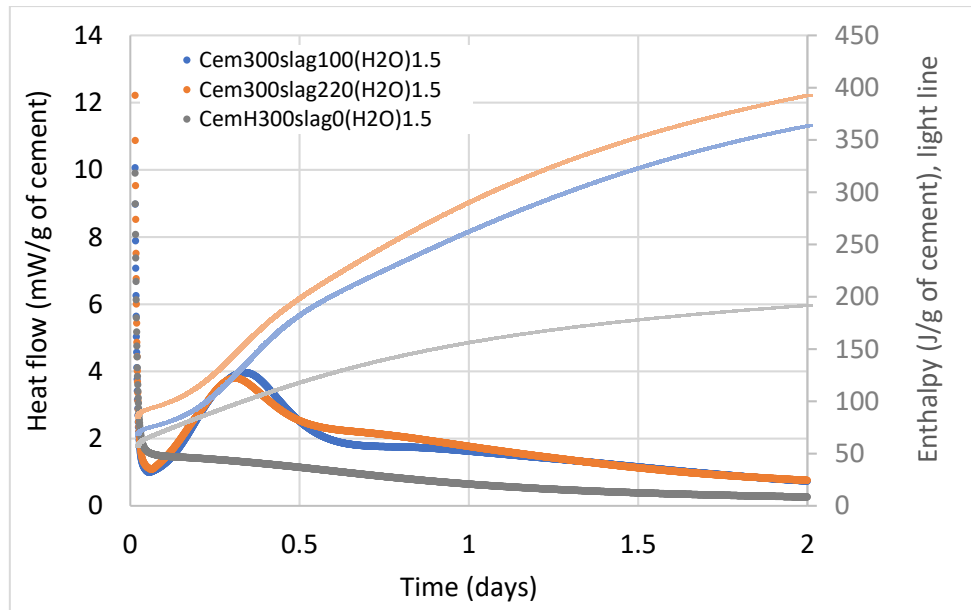
Figure 21: Reactivity of binders with excess of water. In blue Cem300slag100(H_2O)$_{1.5}$, orange Cem300slag220(H_2O)$_{1.5}$ and grey Cem^{H}300slag0(H_2O)$_{1.5}$

As seen in *Figure 21: Reactivity of binders with excess of water*Figure 21, the reaction of the binder of 100% dehydrated CEM I from Heidelberg (Cem$^H_{300}$slag$_0$(H_2O)$_{1.5}$) is extremely different from the others also containing BFS. Comparing with the theoretical information explained, it is seen that the reaction of hydration in this binder only has the first stage of heat flow and the reactions afterwards are not the same as the other binders. So, in the first minutes of contact with water, the dehydrated OPC from Heidelberg starts to dissolve because it shows the same tendency explained in the theoretical explanation of the Stages in calorimetry (*2.3 Hydration of cement*) but the formation of modified C-S-H phase never starts or is very limited (Eq. 3). Probably only the CaO dissolves but the other reaction steps are limited, with an enthalpy, thus the extent of reaction, lower than the other binders (Table 15).

The same situation also happened with sodium hydroxide 1M instead of water, so the problem is with this dehydrated cement. The problems could be the dehydration process or the storage of the dehydrated powder (but no differences were written down) or the chemical composition of this cement. So, binder of dehydrated CEM I from Heidelberg (Cem$^H_{300}$slag$_0$) has not the same tendency as the other binder's curves, which means the reaction happening in this binder is different from binders Cem$_{300}$slag$_{100}$ and Cem$_{300}$slag$_{220}$. Although the heat flow in the beginning is higher for 1M NaOH than for pure water, the total enthalpy is comparable. From these experiments it is clear that the regeneration of pure CEM I from Heidelberg (Cem$^H_{300}$slag$_0$) does not seem to be possible with heating at 500 °C. For this reason and for the results of the mechanical test, no further testing has been done with the binder of CEM I from Heidelberg.

Now, binder with 25% of slag (Cem$_{300}$slag$_{100}$) and 42% of slag (Cem$_{300}$slag$_{220}$) are going to be analyzed. It could already be expected that these binders had very similar thermograms because both have CEM I from SECIL and blast furnace slag. In the reaction with water (*Figure 21: Reactivity of binders with excess of water*Figure 21), the binder with a 25% of slag has lower enthalpy of

hydration than the binder with 42% and, when analyzing the graph, the first peak (production of modified C-S-Hl) is almost the same but in the Stage 4 (after the first peak), the binder with 42% of slag continues reacting and the heat flow decreases slowly, while the binder with 25% of slag has a faster fall after the peak and later follows the same tendency as the first binder. However, the difference in enthalpy is smaller [*(345.98-333.25)/333.25 = 3.8%*] than the differences in slag content [*(48-25)/25 = 92%*]. Theoretically, the long tail could be a second peak (smaller that the first one) which represent the production of secondary ettringite (AFm). Its creation is due to the existence of remaining calcium sulphate (gypsum) when all calcium aluminate (C_3A) has reacted to ettringite (AFt), so this could mean that in the binder with more slag ($Cem_{300}slag_{220}$) protects the cement from the gypsum, giving high resistance to the sulphates, but there are no lot of research about this, so more research is needed to figure this out.

In the reaction with sodium hydroxide 1M (Figure 22Figure 22: Reactivity of binders with excess of sodium hydroxide), the tendency of this figure is almost the same as Figure 21.
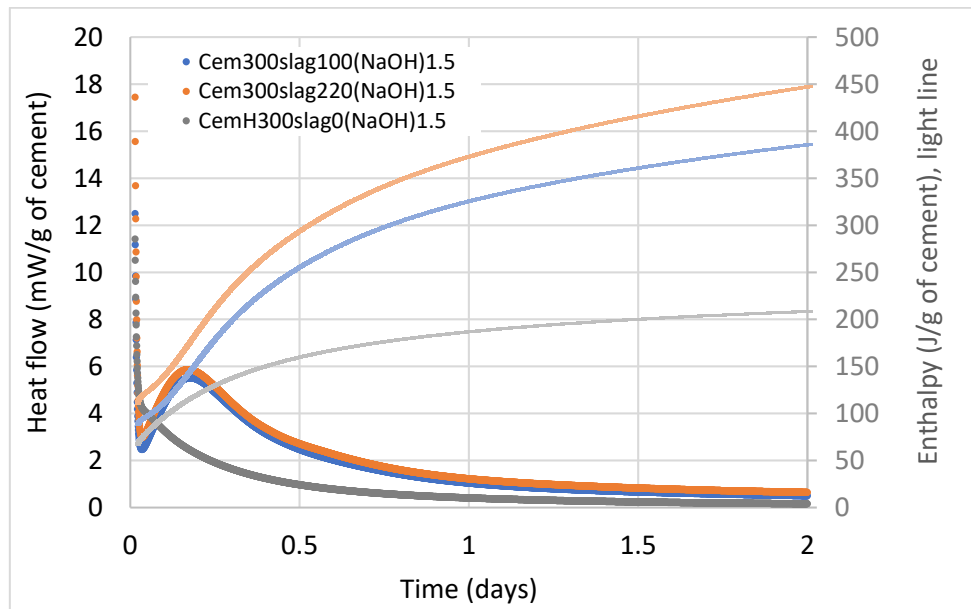

Figure 22: Reactivity of binders with excess of sodium hydroxide. In blue Cem300slag100(NaOH)$_{1.5}$, orange Cem300slag220(NaOH)$_{1.5}$ and grey Cem^{H}300slag0(NaOH)$_{1.5}$

It can be notice in Figure 22 that binder with less slag ($Cem_{300}slag_{100}$) is always less reactive than binder with more ($Cem_{300}slag_{220}$). In fresh cement pastes (before dehydration), presence of slag reduces chemical reaction with alkalis, because in the first reaction of OPC with slag, the slag is activated by the decomposition products of OPC. As such, more slag reduces the reactivity of the binder. But in the dehydrated cement however, the inverse seems to be true, as seen. The possible explanation is that the reactive phases of OPC have been reactivated to a limited extent.

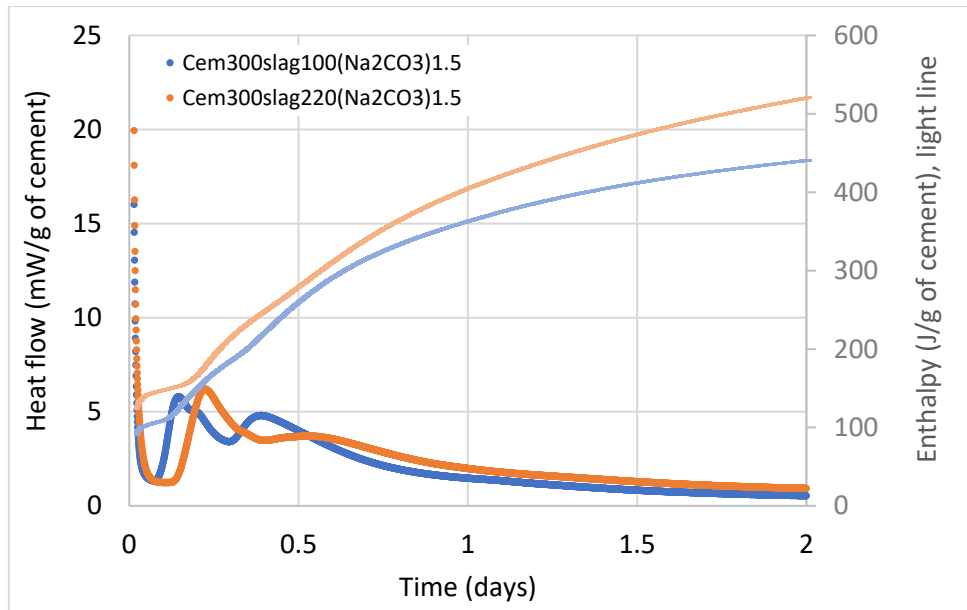The next comparison is between binders reactivated with a solution of sodium carbonate of 1M.

Figure 23: Reactivity of binders with excess of sodium carbonate. In blue Cem300slag100(H$_2$O)$_{1.5}$, orange Cem300slag220(H$_2$O)$_{1.5}$ and grey Cem^{H}300slag0(H$_2$O)$_{1.5}$

In the reaction with sodium carbonate 1M (Figure 23), both binders have two peaks in their heat flow but the binder with more slag (Cem$_{300}$slag$_{220}$) has the reactions retarded in time. Actually, the two peaks seen are the second and the third peak, because the first peak of the reaction is so fast that in cannot be seem, as explained in 2.3 Hydration of cement. Both binders with Na$_2$CO$_3$ have sharper peaks than reactions with water or NaOH, which means that carbonate accelerates the hydration reaction. This is also clear form the enthalpy which is about 10% higher than in the case of NaOH. Comparing the proportion of slag, it is seen that the second exotherm (which is the first seen in the calorimeter) is retarded but somewhat higher for the binder with more slag (Cem$_{300}$slag$_{220}$) and its third peak is less reactive -same behaviour than in the reaction with water. Also, binder Cem$_{300}$slag$_{220}$ is more reactive during the Stage 5 (decreasing of the heat flow).

The comparison between the solutions used to reactivate the cement is also an interesting analysis to do. So, the next graph shows the influence of different reactivation liquids in binder Cem$_{300}$slag$_{100}$ (Figure 24).
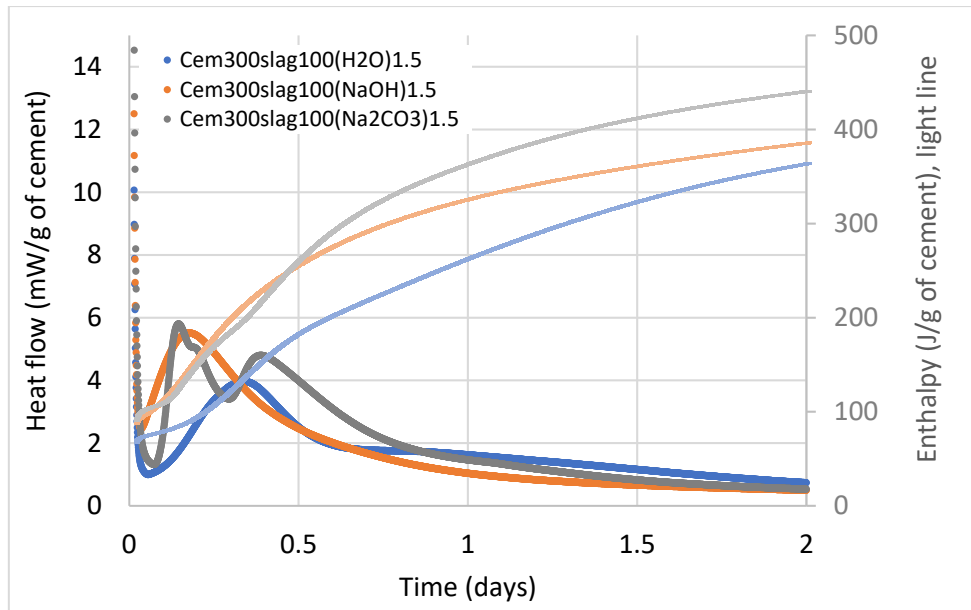
Figure 24: Reactivity of binders with 25% of slag and an excess of different solutions. In blue Cem300slag100(H₂O)₁.₅, orange Cem300slag100(NaOH)₁.₅ and grey Cem300slag100(Na₂CO₃)₁.₅
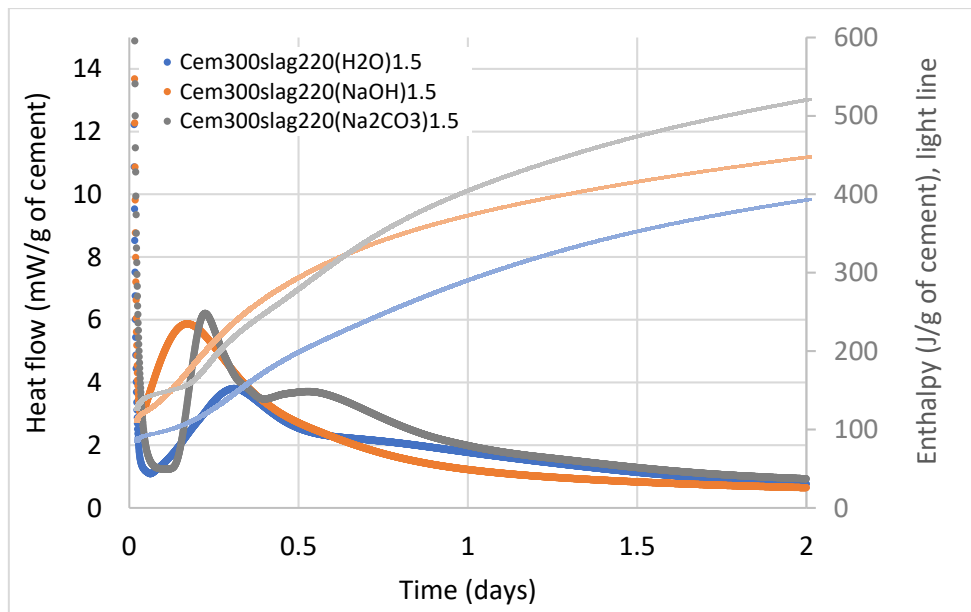

Figure 25: Reactivity of binders with 42% of slag and an excess of different solutions. In blue Cem300slag220(H₂O)₁.₅, orange Cem300slag220(NaOH)₁.₅ and grey Cem300slag220(Na₂CO₃)₁.₅

When analysing the binders $Cem_{300}slag_{100}$ with 25% of slag (Figure 24), the main difference noticed is the sharpness of the third peak (in the graph, the second) in the reaction with a solution of sodium carbonate of 1M (as seen also in the previous analysis), instead of the peak extended over a long period seen in water and the only peak seen in the reaction with the solution of sodium hydroxide 1M. The third peak in the reaction of hydration in fresh cement pastes is the creation of secondary ettringite (AFm). As explained in the part *2.3 Hydration of cement*, AFm appears when gypsum has reacted totally but some quantity of calcium aluminate

(C$_3$A) remains in the mixture, so C$_3$A reacts with ettringite (AFt) to yield AFm (Eq. 7). In binder Cem$_{300}$BFS$_{100}$, the fastest reaction to achieve the maximum of the second peak (the first seen in the graph), which represents the creation of modified C-S-H, is due to carbonate, but the reaction with sodium hydroxide starts first even though it does not reach the same heat flow. And the reaction with water is the slowest one and with less heat flow.

The next comparison is the influence of the solutions used in the reactivation in the binder Cem$_{300}$slag$_{220}$, with a 42% of slag (Figure 25). As seen, the tendencies of binders Cem$_{300}$slag$_{220}$ are very similar to the binder Cem$_{300}$slag$_{100}$. The difference notice between both binders is that binder with less slag has sharer peaks and its binder with carbonates has a faster hydration reaction, so slags accelerate the hardening when mixed with carbonates.

6.2.3. Influence of water to cement ratio in the chemical reactivity

The influence of water in enthalpy is compared in this section. For this reason, other paste of dehydrated OPC was prepared with a different water to cement ratio for the calorimetry test, with a w/c of 0.36, lower than the European Standard EN 197-1. Below there are shown the different enthalpies of the hydration reaction in each binder and their representation in the thermogram.

Table 16: Enthalpies of binders with 100% dehydrated cement and different water to cement ratios, J/g of dehydrated cement

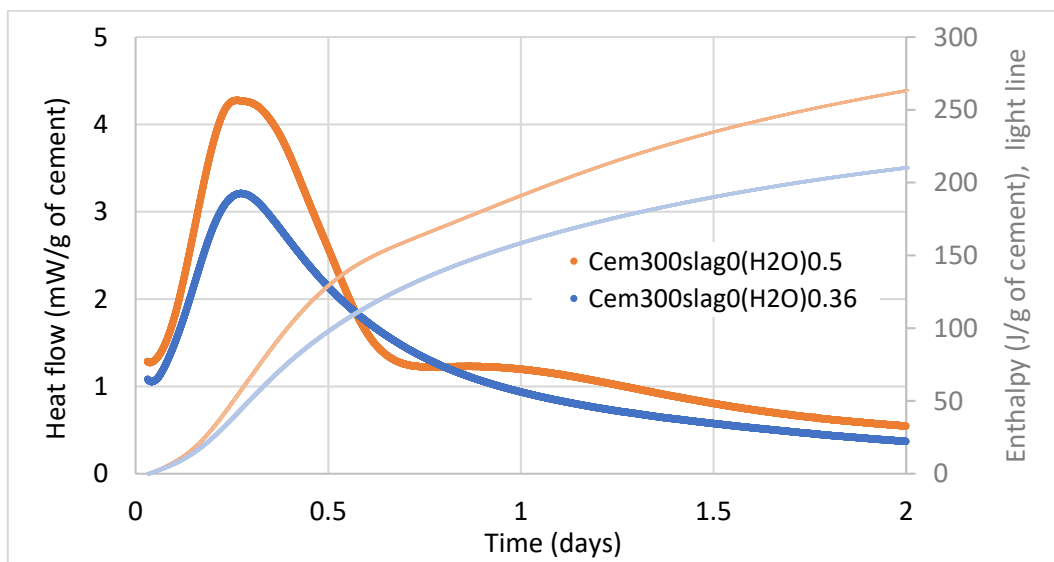| Proportions and characteristics	Name given	Enthalpy at 2nd day (J/g dehydrated CEM I)
300:0 w/water, w/c=0.5	Cem$_{300}$slag$_0$(H$_2$O)$_{0.5}$	208.60
300:0 w/water, w/c=0.36	Cem$_{300}$slag$_0$(H$_2$O)$_{0.36}$	165.10

Figure 26: Reactions with different water to cement ratio in binders with 0% slag. In orange w/c=0.5 and in blue w/c=0.36

The influence of water content in the heat flow is very important, as seen in Figure 26. The binder with w/c=0.36 has a lower peak and tends to zero faster that the binder with 0.5 (situation that happens when there are less hydration products, so lower strength can be achieved). Also, because the lack of water, the binder with 0.36 does not have the third peak (represented as second one in the graph). As said before, the creation of portlandite become slower when the layer around the cement grains star being very thick because the diffusion of water into the cement core becomes harder. But having more water makes that diffusion easier, so when the reaction is slowing down, the remaining water diffuses inside the cement cores and make the hydration products precipitate in the pore solution, reaction that is shown in this peak. However, it is important to point out that the enthalpies between them are not so different ($\Delta H=1.7$ kJ/g).

The comparison of different water content can be done also with binders with slags. Below there are shown the differences between water to cement ratio of 0.5 and 1.5: their enthalpies and the representation of the calorimeter data.

Table 17: Enthalpies for binders with slag and dehydrated cement and different water to cement ratios, J/g of dehydrated cement

Proportions and characteristics	Name given	Enthalpy (J/g dehydrated CEM I)
300:100 w/water, w/c=1.5	$Cem_{300}slag_{100}(H_2O)_{1.5}$	363.89
300:100 w/water, w/c=0.5	$Cem_{300}slag_{100}(H_2O)_{0.5}$	296.27
300:220 w/water, w/c=1.5	$Cem_{300}slag_{220}(H_2O)_{1.5}$	393.08
300:200 w/water, w/c=0.5	$Cem_{300}slag_{220}(H_2O)_{0.5}$	314.03

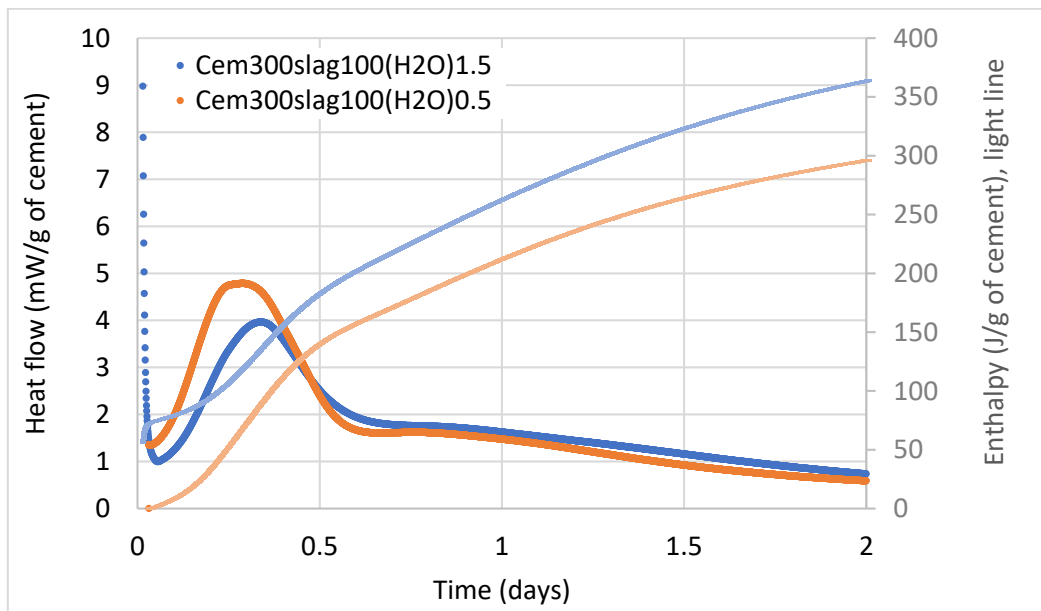*Figure 27: Reactivity with different water to cement ratio in binders with 25% slag. In organge w/c=1.5 andin blue w/c=0.5*
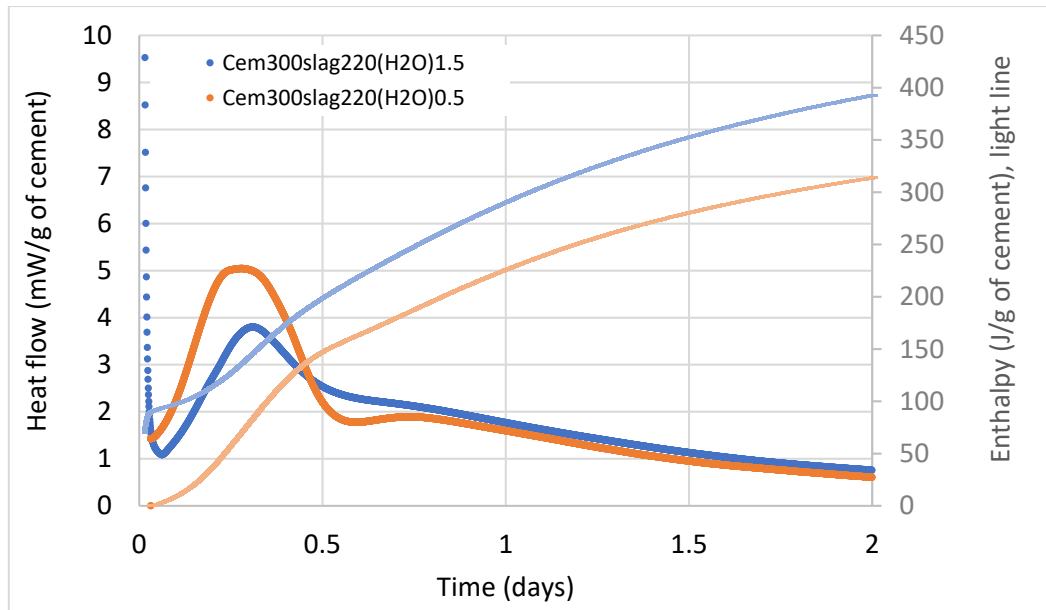
Figure 28: Reactivity with different water to cement ratio in binders with 42% slag. In organge w/c=1.5 andin blue w/c=0.5

As seen in Table 17, the enthalpies between same type of binders are not as similar as between binders with 100% OPC. The other difference is that in Figure 27 and Figure 28, the binders with excess of water (w/c=1.5) are less reactive than binders with less water (w/c=0.5); as reminder, in binders with 100% OPC, the one with 0.5 was more reactive than the ones with 0.36. So, here it can be pointed out that a very large quantity of water does not accelerate the hydration reaction. In all binders, it can be seen both peaks but with some differences: binders with less slag have their third peak very similar but one above other, and in binders with more slags, the curve of w/c=1.5 decreases continuously, without decrease very fast but maintaining both peaks.

As explained in *5.2 Design of the experiment*, the cement pastes prepared with fresh (unhydrated) cement were mixed with water with a w/c of 0.4, later they were cured for three days and heat up to 500 °C for two hours, to be finally mixed with other solutions or slags to reactivate the clinker phases, following a w/c ratio of 0.5. Because of the different ratio used for the fresh cement paste, it is very interesting to compare two pastes prepared with fresh OPC but with these two ratios: 0.4 and 0.5. This comparison is shown in Figure 29.

Figure 29: Reactivity of fresh cement pastes with different water to cement ratios: 0.4 and 0.5, both with water and without slags. In orange FCem300slag0(H₂O)₀.₄ and in blue FCem300slag0(H₂O)₀.₅.

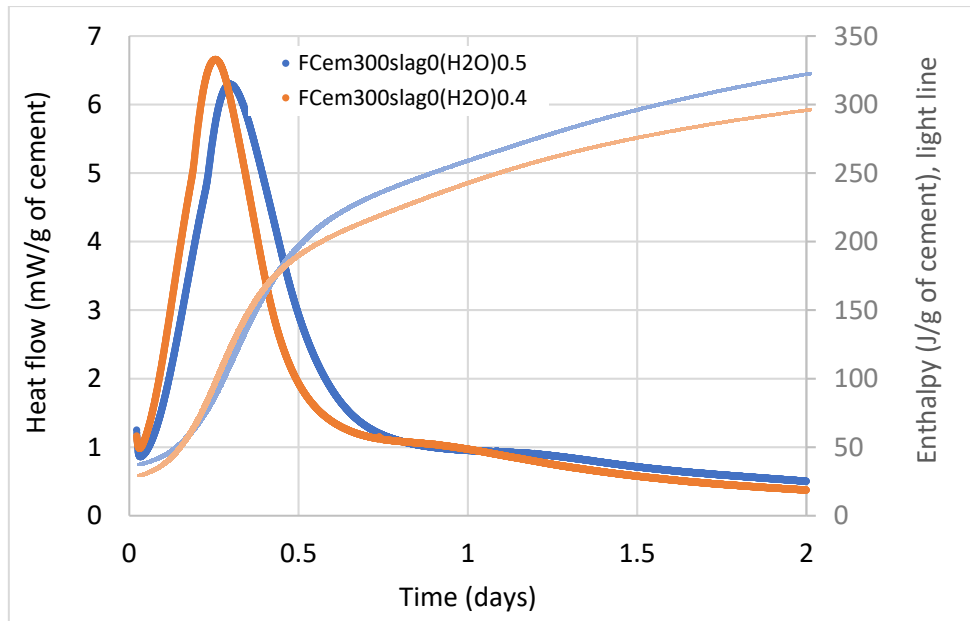The analysis of different water to cement ratios in fresh OPC (unhydrated, before dehydration) is seen in Figure 29: Reactivity of fresh cement pastes with different water to cement ratios: 0.4 and 0.5, both with water and without slags. In orange $FCem300slag0(H_2O)_{0.4}$ and in blue $FCem300slag0(H_2O)_{0.5}$.Figure 29 shows that binders with lower water content (w/c=0.4) has higher heat flow in the second peak of the hydration but lower hydration enthalpy at 2nd day. Also, this binder hydrates faster. So, less water in fresh cement pastes accelerates the hydration but give less reactivity, which in some cases could be interesting to avoid cracking.

6.3. Results compressive strength

The other main test to compare the specimens and determine if the concrete is good enough for the market is the compressive strength test, in which the maximum resistance of the concrete to breaking under pressure is measured. As explained before, the equipment used in these mechanical tests are Instron 5885H and Instron 5900R, where the load is measured during the compression of the specimens, so it is possible to know these properties during the compression of the specimen (seen as negative extension). Later the average of the maximum strength of all 5 specimens tested had to be calculated and only the data inside the 10% up and down of the average must be accepted as correct. So, the average is calculated again without the discarded data.

To know the influence of an excess of water, a water to cement ratio of 0.61 has been used instead of 1.5 in the compressive strength test. The following results are divided by the water to cement ratio in the specimens (w/c = 0.5 and w/c = 0.61) to compare the influence of every binder and solution used in the mortars. Later, the influence of the water content in the strength is also compared.

6.3.1. Compressive strength in specimens with a water to cement ratio of 0.5

Now, the results of compressive strength test for mortars prepared with a water to cement ratio of 0.5 are shown below. First, the study is focused on the analysis of mortars with different proportion of slags and reactivated with water; and later, the comparison of different liquids used to reactivate mortar with 100% of dehydrated CEM I from SECIL. In blue the strength at 2 days of curing and in orange at 7 days is shown.
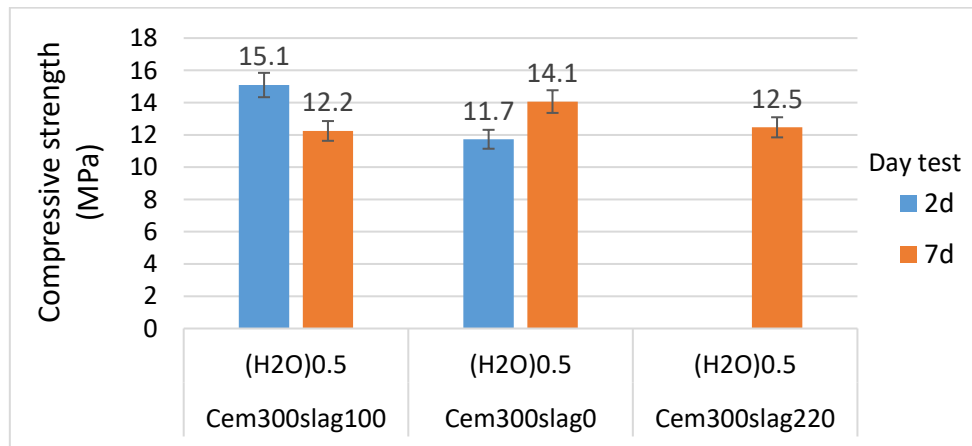

Figure 30: Comparison of compressive strength for different binders with water, w/c = 0.5

The influence of the proportion of blast furnace slag in the recycled binder of mortars reactivated with water is seen in Figure 30, where it is compared 100% of CEM I from SECIL (Cem$_{300}$slag$_0$), 25% of slag (Cem$_{300}$slag$_{100}$) and 42% of slag (Cem$_{300}$slag$_{220}$). The workability of these samples was better that other batches: they had paste texture instead of solid state, which gave a good flowability to mould them. It was seen during this procedure that the setting of these samples was not so fast as other batches (which were difficult to mould due to the creation of little stones in the paste). The data of 2 days of curing in specimens of mortar Cem$_{300}$slag$_{220}$(H$_2$O)$_{0.5}$ was lost due to a problem during the data extraction with the equipment. First of all, it is important to point out that the strength in Cem$_{300}$slag$_{100}$ at 2 days of curing is higher than at 7 days and theoretically, the strength rises with the days of curing, so the data from the 7-day compressive test in binder Cem$_{300}$slag$_{100}$ should not be taken account because they are not a reliable data. One explanation is that while demoulding the specimens from the tubes, few of the specimens broke: some quantity of material remained stick in the bottom of the tube, so the height of the final specimens was shorter than others (when cutting the sides to achieve them to be flat). So, the specimens did not have the optimal height to diameter ratio (which is h/D = 2, according to standard), it was lower which can be decisive when rely the results. Other explanation could be the air bubbles inside the specimens: in specimens with water, it was seen some holes when demould them. The specimens with holes were discarded but it is not possible to assure that the other specimens did not have not-visible holes inside.

The rest of compressive strengths are all in the same range. There is no explanation found for the lower strength of the sample with a low amount of slag after 7 days, compared to 2 days. As seen, the mortar reactivated with water with more strength is Cem$_{300}$slag$_0$(H$_2$O)$_{0.5}$ (0% slag) with 14.1 MPa, followed by Cem$_{300}$slag$_{220}$(H$_2$O)$_{0.5}$ (42% of slag) and Cem$_{300}$slag$_{100}$(H$_2$O)$_{0.5}$ (25% of

slag), which are very similar, so it has not a clear tendency. Besides, in the comparison of mortars with 0.61 of water content to cement, the tendency shown that the mortars with more strength are the ones with less slag, so we should expect that binder with 25% of slag has better strength that binder with 42% of it (Figure 32).

Below, the influence of the liquid used to reactivate the mortars prepared with dehydrated cement is analysed. In Figure 31, the results for mortars with binder $Cem_{300}slag_0$ and a solution of sodium sulphate 1M $(Cem_{300}slag_0(Na_2SO_4^{1M})_{0.5})$, sodium carbonate 1M $(Cem_{300}slag_{100}(Na_2CO_3)_{0.5})$, sodium hydroxide 1M $(Cem_{300}slag_0(NaOH)_{0.5})$ and water $(Cem_{300}slag_0(H_2O)_{0.5})$ at 2 and 7 days of curing are shown. The results obtained with sodium carbonate and sodium hydroxide are extremely low, 0.9 and 2.3 MPa respectively. And the strength with sodium sulphate is better but not so high as with water. In this point it is important to point out that during the preparation, the workability in these mortars was very bad due to the low water to cement ratio (considering "water" as any liquid). To help to the workability, 0.43 grams of superplasticizer (maximum amount recommended: 0.3-0.6% of cement mass [55]) were added to the mixture, but it only works with water, so the mortars prepared with alkaline solutions had a very bad workability. That is why the compressive strength in water is remarkably better than the rest and not due to the chemical reactions that happen during the curing.
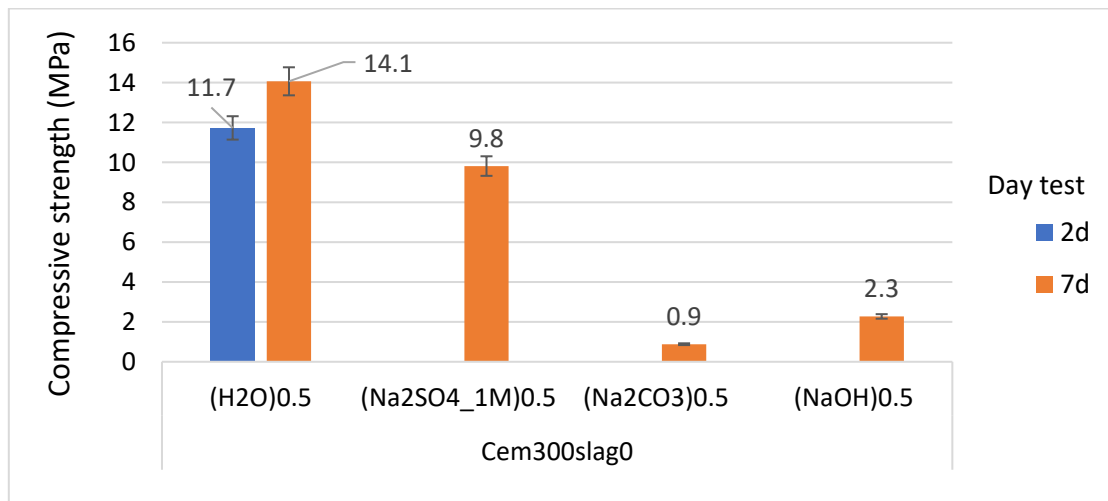

Figure 31: Compressive strength in mortars with 100% dehydrated CEM I from SECIL and different solution of 1M to reactivate

Below, some pictures about the look of the specimens of these mortars are shown (Figure 32Figure 32: Pictures of specimens of mortars with 100% of dehydrated CEM I from SECIL and sodium carbonate 1M (left) and 25% of slag, 75% of dehydrated CEM I from SECIL and water (right)).

Figure 32: Pictures of specimens of mortars with 100% of dehydrated CEM I from SECIL and sodium carbonate 1M (left) and 25% of slag, 75% of dehydrated CEM I from SECIL and water (right)

Due to these results shown before, the next step done was to analyse the influence of the molarity in the solution used to reactivate the mortars. So, the next solution compared was of sodium sulphate but 0.5M ($Cem_{300}slag_0(Na_2SO_4^{0.5M})_{0.5}$) and the results are shown below:
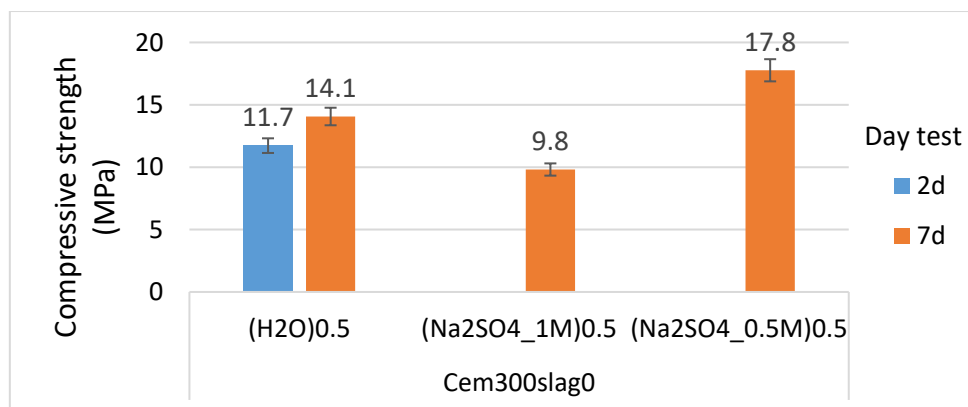

Figure 33: Influence of molarity in liquids used to reactivate the recycled mortars

As seen, the strength of mortars with alkaline solution but with less molarity that before had higher strength. First, it can be thought that this situation happens because a solution of 0.5M has more water content that a solution of 1M, but it is seen that mortars with solution of sodium sulphate 0.5M has more strength that mortars prepared with water, even thou mortar with water had superplasticizer, so their workability was better. This means that a little alkalinity in the solution helps to reactivate the cement inside the mortar.

The following tables (18-19) summarise all these results.

Table 18: Influence of blast furnace slag in mortars with water, w/c = 0.5

Type of binder	Name in graphs	Strength at 7 days	Strength at 2 days	Comments
100% CEM I SECIL (dehydrated)	$Cem_{300}slag_0(H_2O)_{0.5}$	14.1 MPa	11.7 MPa	Highest strength in 7-day test
75% CEM I SECIL (dehydrated) + 25% slag	$Cem_{300}slag_{100}(H_2O)_{0.5}$	12.2 MPa	15.1 MPa	7-days test data not reliable But, 2-days strength higher than with 0% slag
58% CEM I SECIL (dehydrated) + 42% slag	$Cem_{300}slag_{220}(H_2O)_{0.5}$	12.5 MPa	-	Higher than with less slag

Table 19: Comparison of strength between mortars reactivated with different liquids, w/c = 0.5

100% CEM I SECIL (dehydrated)		
Reactivation liquid		**Compressive strength**
Water	$Cem_{300}slag_0(H_2O)_{0.5}$	14.1 MPa
Sodium hydroxide 1M	$Cem_{300}slag_0(NaOH)_{0.5}$	2.3 MPa
Sodium carbonate 1M	$Cem_{300}slag_0(Na_2CO_3)_{0.5}$	0.9 MPa
Sodium sulphate 1M	$Cem_{300}slag_0(Na_2SO_4^{1M})_{0.5}$	9.8 MPa
Sodium sulphate 0.5 M	$Cem_{300}slag_0(Na_2SO_4^{0.5M})_{0.5}$	17.9 MPa
Coments		Better strength: 0.5M Na_2SO_4 But, water better than 1M of Na_2SO_4 Worst: NaOH and Na_2CO_3

6.3.2. Compressive strength in specimens with a water to cement ratio of 0.61

In the Figure 34, there is the comparison between binder with 100% of CEM I from Heidelberg ($Cem^H_{300}slag_0(H_2O)_{0.61}$) and binders of CEM I from SECIL and different proportions of blast furnace slag: 25% of slag ($Cem_{300}slag_{100}(H_2O)_{0.61}$) and 42% ($Cem_{300}slag_{220}(H_2O)_{0.61}$). The figure shows the strength of the mortars at 2 (blue) and 7 (orange) days of curing.
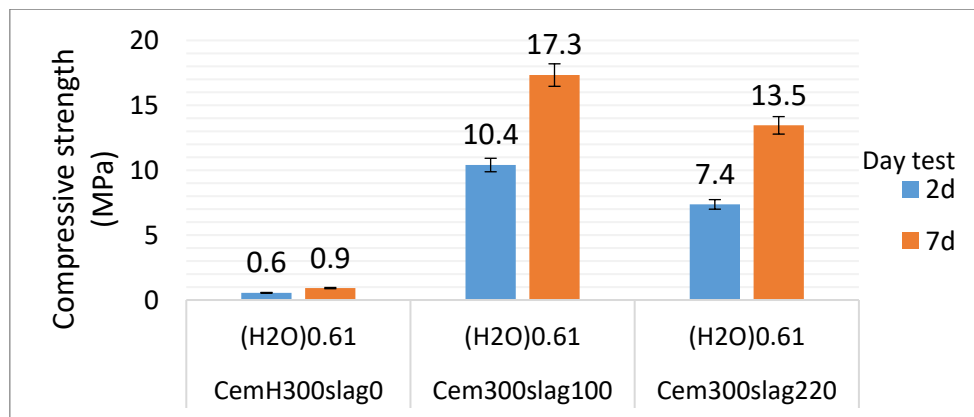

Figure 34: Comparison of compressive strength for different binders with water, w/c = 0.61

As seen in the reactivity study, the mortar $Cem^H_{300}slag_0(H_2O)_{0.61}$ has the lowest compressive strength. This binder showed during the calorimetry test that the reaction that occurs during the hydration is not the same (part is missing) as in the other binders and comparing with the result obtained in the mechanical test, it was decided to not continue working with it. It is important to point out that the problems seen in this mortar can be done by a wrong procedure during the dehydration, but no difference was written down, so it can be also for the type of cement.

Analysing the other mortars with water, we can see that the mortar with less slag in its binder ($Cem_{300}slag_{100}(H_2O)_{0.61}$) has higher strength that the other one with more slag

(Cem$_{300}$slag$_{220}$(H$_2$O)$_{0.61}$): it has 28.9% less compressive strength at 2 days of curing. These binders also follow this tendency at 7 days of curing. One explanation of this behaviour is that the more quantity of cement has the binder, higher strength achieves. Comparing these results with the reactivity study done during the calorimetry (Figure 21: *Reactivity of binders with excess of water*), it can be pointed out that the reaction of hydration in both binders is very similar -being a little more reactive when more quantity of slag is in the cement- (until the creation of C-S-H gel and portlandite) but the third peak (the second one in the graph), which represents the creation of secondary ettringite, is smaller in the binder with more slag. As explained in the Introduction, the secondary ettringite (AFm) is generated when the mixture runs out of gypsum (calcium sulphate). The strength results thus show that the link between calorimetry (or heat flow) and strength build up is not straightforward.

Binders with same proportion of slag but with a 10% of fresh (FCem$_{300}$slag$_{100}$(H$_2$O)$_{0.61}$, FCem$_{300}$slag$_{220}$(H$_2$O)$_{0.61}$) cement in their cement content and also with water were tested. The results are shown below in Figure 35. These batches only were tested at 2 days of curing.
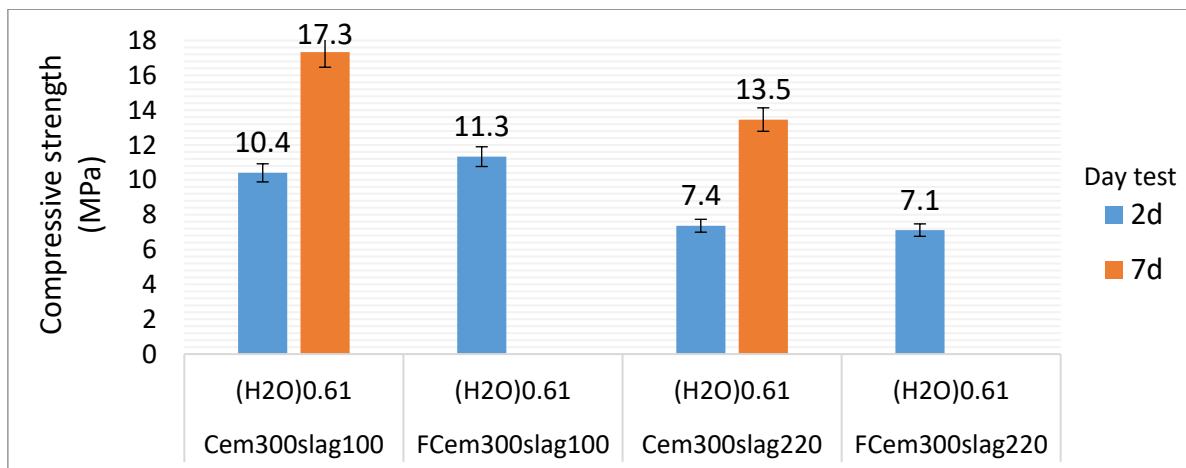

Figure 35: Influence of fresh cement in compressive strength for different binders with water, w/c = 0.61

As seen, the strength is higher in the binder with less slag (Cem$_{300}$slag$_{100}$(H$_2$O)$_{0.61}$) but a little lower in the binder with more slag. The extra activation given by the fresh cement should give more strength to the mortar, but the results show that is not always true. That is why more test should be done with a 10% of fresh cement, like the compressive strength test for 7 days of curing.

Also, mortars with alkaline solutions to activate the cement were tested. Figure 36 shows the results for mortars reactivated with a solution of sodium hydroxide of 1M ((NaOH)$_{0.61}$).
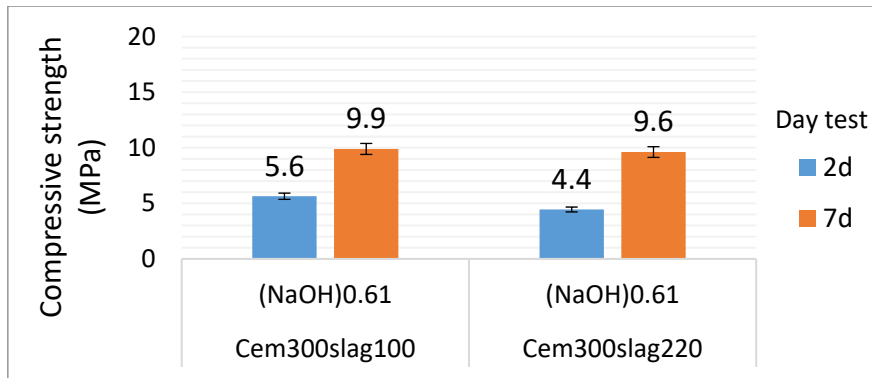
Figure 36: Comparison of compressive strength for different binders with sodium hydroxide, w/c = 0.61

As in the activation with water, the binder with less slag ($Cem_{300}slag_{100}(NaOH)_{0.61}$) has higher strength than the binder with more slag ($Cem_{300}slag_{220}(NaOH)_{0.61}$) even if the solution of reactivation is sodium hydroxide. The difference with water is that the strength is very similar between binders at 7 days of curing. Also, at 2 days of curing, strength in both binders is very low, as said before, the workability was very low, so the moulding was difficult due to the fast setting. Probably, this is the reason of the low strength. The solutions for this situation need to be study, but the addition of sulphates or the decrease of activator concentration could be tested; all of them will be discussed on Future work. The comparison between liquids in each binder is done further on.

In the reactivation with a solution of sodium carbonate of 1M, the results changed. As seen in Figure 37, the mortar with more slag ($Cem_{300}slag_{220}(Na_2CO_3)_{0.61}$) has more strength that the mortar with less slag ($Cem_{300}slag_{100}(Na_2CO_3)_{0.61}$), just the opposite situation seen in reactivation with water and sodium hydroxide.

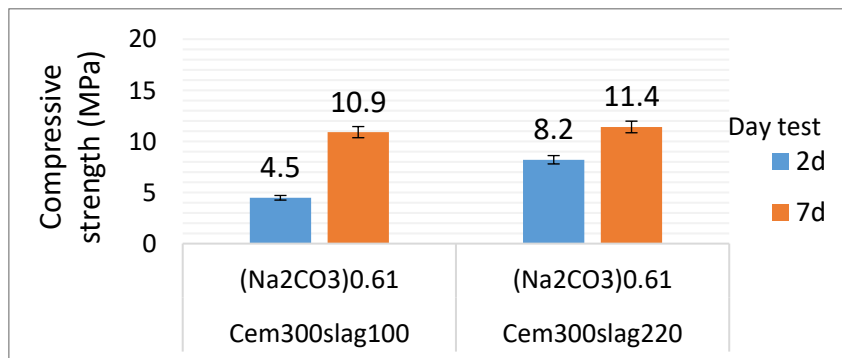*Figure 37: Comparison of compressive strength for different binders with sodium carbonate, w/c = 0.61, and dehydrated CEM I from SECIL*

Now, we can do the comparisons of the different reactivation solutions for each binder. First, the results for mortars with binder of less slag ($Cem_{300}slag_{100}$) are shown, being R for the solution of sodium carbonate 1M, S for sodium hydroxide 1M and W for water.
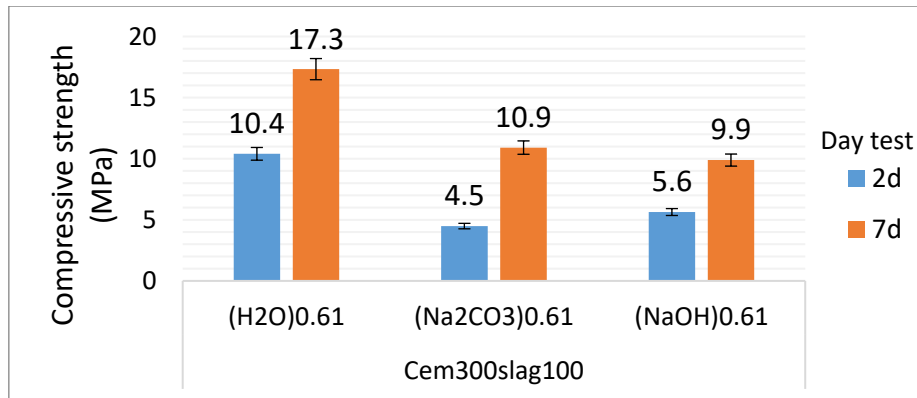
Figure 38: Influence of reactivation liquid in mortars with 25% of slag, w/c = 0.61

As seen in the Figure 38, the mortar with higher strength has been reactivated with water, followed by the reactivation with sodium carbonate and the lowest strength is in the mortars with sodium hydroxide in the strength at 7 days, but at 2 days the hydroxide gives more strength than the carbonates, but both are within margin of uncertainty, therefore it is not possible to know exactly their differences and distinguish them.

In the mortars with more slag in their binders ($Cem_{300}slag_{220}$), the comparison of the different liquids used in the reactivation of dehydrated cement paste is below.
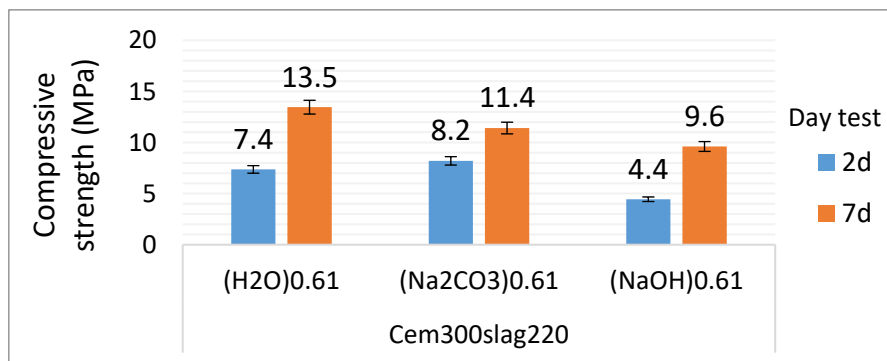
Figure 39: Influence of reactivation liquid in mortars with 42% of slag, w/c = 0.61

The same pattern seen in the reactivation in mortars with 25% of slag is seen in mortars with 42% of slag: water gives more strength, followed by sodium carbonate and the lowest strength is given by sodium hydroxide. The difference between NaOH and Na_2CO_3 activated samples is however larger in this case especially after 2 days. Conclusions of these results is exposed in the Tables 20-21.

Table 20: Influence of presence of fresh cement in binders with slags and water with a w/c = 0.61

Type of binder	Name in graphs	Strength at 7 days	Comments
75% CEM I SECIL (dehydrated) + 25% slag	$Cem_{300}slag_{100}(H_2O)_{0.61}$	10.4 MPa	

67.5% CEM I SECIL (dehydrated) + 7.5% fresh CEM I SECIL + 25% slag	$FCem_{300}slag_{100}(H_2O)_{0.61}$	11.3 MPa	Higher strength in mortar with less slag reactivated with fresh cement
58% CEM I SECIL (dehydrated) + 42% slag	$Cem_{300}slag_{220}(H_2O)_{0.61}$	7.4 MPa	Lower strength in mortar with more slag reactivated with fresh cement
51.92% CEM I SECIL (dehydrated) + 5.769% fresh CEM I SECIL + 42% slag	$FCem_{300}slag_{220}(H_2O)_{0.61}$	7.1 MPa	

Table 21: Comparison between binders and liquids used in reactivation with a w/c = 0.61

Reactivation liquid		75% CEM I SECIL (dehydrated) + 25% slag	58% CEM I SECIL (dehydrated) + 42% slag	Coments
		$Cem_{300}slag_{100}$	$Cem_{300}slag_{220}$	
Water	$(H_2O)_{0.61}$	17.3 MPa	13.5 MPa	Reactivation with water: better → cement less slag
Sodium hydroxide 1M	$(NaOH)_{0.61}$	9.9 MPa	9.6 MPa	Reactivation with NaOH: better → cement less slag
Sodium carbonate 1M	$(Na_2CO_3)_{0.61}$	10.9 MPa	11.4 MPa	Reactivation with Na_2CO_3: better → cement more slag
Coments		Reactivation better → water worst → NaOH	Reactivation better → water worst → NaOH	

6.3.3. Influence of water to cement ratio in compressive strength

All the graphical representations of the results are explained before, so in this point only the summary of the data is shown to do a comparison between the amount of water in the mortars' strength: the difference with w/c = 0.61 and w/c = 0.5.

Table 22: Comparison of strength between mortars with different w/c

Type of binder	Name in graphs	Strength at 7 days		Comments
		w/c = 0.5	w/c = 0.61	
75% CEM I SECIL (dehydrated) + 25% slag	$Cem_{300}slag_{100}(H_2O)_{0.5}$	12.2 MPa (*)	10.4 MPa	Clear tendency in both binders:
58% CEM I SECIL (dehydrated) + 42% slag	$Cem_{300}slag_{220}(H_2O)_{0.5}$	12.5 MPa	7.4 MPa	less water → more strength (as the theory says)

So, when the amount of water decreases the compressive strength in the mortar increase. This is because too much water will generate segregation of the sand from the binder (cement paste) because it does not participate in the hydration reaction of the cement [56].

PART IV: Conclusions

Chapter 7:   Conclusions

In this Chapter, all the conclusions that have seen said during all this Thesis are summarise. To organise them, this chapter is divided in different sections to analyse the influence of different issues separately.

DEHYDRATION PROCESS
- Dehydration process generates a loss in the reactivity on binders of OPC and OPC with slags, which have lower heat than fresh cement pastes.
- Not all regenerated (after dehydration) clinker phases are present before the reactivation.
- Not all the hydrated phases are present after the reactivation with solutions.

INFLUENCE OF SLAGS IN DEHYDRATED CEMENT AND CONCRETE
- Slags increase the reactivity of the hydration reaction of OPC more than alkaline solutions.
- Slags with water give higher compressive strength → Both help workability of the pastes

INFLUENCE OF ALKALIS IN REACTIVATION OF DEHYDRATED CEMENT
- Binders with slags are more reactive when mixing with alkalis instead of water.
- Binders without slags are more reactive when mixing with water than with alkalis.
- Mortars with alkaline solutions have less compressive strength than mortars with water → the dab workability of mortars with alkalis has a big influence on this
- Between alkalis, sodium hydroxide shows the worst compressive strength and sodium sulphate the best

INFLUENCE OF MOLARITY IN ALKALINE SOLUTIONS USED IN REACTIVATION OF DEHYDRATED CEMENT
- There is no difference of 1M and 0.5M in the chemical reactivity of the reactivation with sodium sulphate solutions.
- Mortars with 0.5M sodium sulphate solution has better strength than with water and with water better than with sodium sulphate 1M

INFLUENCE OF REACTIVATION WITH 10% OF FRESH OPC IN 90% OF DEHYDRATED CEMENT
- Mortars with 10% of fresh OPC have better compressive strength if binder has less slag (25%) than more slag (42%)

INFLUENCE OF WATER CONTENT IN REACTIVATION OF DEHYDRATED CEMENT AND FRESH CEMENT
- Decrease of w/c decreases the reactivity in dehydrated cements, it could be because not all clinker phases react with less ratio of 0.5.
- Decrease of w/c decreases the reactivity in fresh cement pastes -which in some cases could be interesting to avoid cracking- but accelerates the hydration reaction.
- Increase of w/c decreases the compressive strength: 0.5 better than 0.61

PART V: Future work

Chapter 8: Future work

This final chapter is thought to make suggestions about the future work the author thinks that needs to be studied and all the questions than cannot have been answer in this Thesis.

First of all, the presence of blast furnace slag has not the same behaviour depending on the composition of the binder and the solution used to reactivate the dehydrated cement. Also, it seems slags acts differently in fresh and dehydrated cement, so the comparison of these results with more test would be interesting to clarify this situation.

Second, the study of the influence of the molarity of alkaline solutions in dehydrated binders has been very concise in this study: solutions with molarities between 0.5 and 0.1 or less should be done to see exactly the influence of it.

Third, the exact effect of alkalis -in general- in the reactivation is not very clear, it would be interesting to do other types of tests like XRD to the mortars and pastes with the alkalis studied.

Fourth, the influence of the dehydration temperature has not been tested. Maybe lower temperature could achieve the same results with less energy consumption, or it could obtain better regeneration of the clinker phases to get more hydration products from the dehydration and higher strength.

Fifth, to achieve better workability in the mortars (which could resonate in the compressive strength), other procedure could be designed: i. e. curing of the specimens with pressure.

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APPENDICES

Appendix I: Cement Chemist Notation (CCN)

Table 23: Cement Chemist Notation (CCN)

Cement notation	Oxide formula	Chemical formula	Chemical name	Mineral name
C	CaO	CaO	Calcium oxide	Quicklime / Burnt lime / Lime
S	SiO_2	SiO_2	Silicon dioxide	Silica
A	Al_2O_3	Al_2O_3	Aluminium oxide	Alumina
F	Fe_2O_3	Fe_2O_3	Ferric oxide	Hematite / Rust
H	H_2O	H_2O	Water	-
M	MgO	MgO	Magnesium oxide	Periclase
N	Na_2O	Na_2O	Sodium oxide	-
s	SO_3	SO_3	Sulphur trioxide	Sulphate
c	CO_2	CO_2	Carbon dioxide	-
P	P_2O_5	P_2O_5	Phosphorus hemi-pentoxide	-
Cs	$CaSO_3$	$CaO \cdot SO_2$	Calcium sulphate	Andydrite
CH	$Ca(OH)_2$	$CaO \cdot H_2O$	Calcium hydroxide	Portlandite
Cc	$CaCO_3$	$CaO \cdot CO_2$	Calcium carbonate	Calcite
C_3S	Ca_3SiO	$3CaO \cdot SiO_2$	Tricalcium silicate	Alite
C_2S	Ca_2SiO_4	$2CaO \cdot SiO_2$	Dicalcium silicate	Belite / Larnite
C_3A	$Ca_3Al_2O_6$	$3CaO \cdot Al_2O_3$	Tricalcium aluminate	Celite / Aluminate
C_2A	$CaAl_4O_7$	$CaO \cdot 2Al_2O_3$	Dicalcium aluminate	-
C_4AF	$Ca_4Al_2Fe_2O_{10}$	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	Tetracalcium alumino ferrite	Ferrite
C_2AS	$Ca_2Al_2Si_2O_7$	$2CaO \cdot Al_2O_3 \cdot SiO_2$	Dicalcium alumino silicate	Gehlenite
CAS_2	$CaAl_2Si_2O_8$	$CaO \cdot Al_2O_3 \cdot 2SiO_2$	Calcium alumino di-silicate	Anorthite
AFt / $C_6As_3H_{32}$	$Ca_6Al_2S_3O_{18}$ $\cdot 32H_2O$	$(CaO)_3 \cdot Al_2O_3 \cdot (CaSO_4)_3$ $\cdot 32H_2O$	Alumina ferric oxide tri-sulphate	Primary ettringite
AFm / $C_4As_3H_{12}$	$Ca_4Al_2SO_{10}$ $\cdot 12H2O$	$(CaO)_3 \cdot Al_2O_3 \cdot CaSO_4$ $\cdot 12H_2O$	Alumina ferric oxide mono-sulphate	Secondary ettringite
C-A-H	-	$x\,CaO \cdot y\,Al_2O_3 \cdot z\,H_2O$	Calcium aluminate hydrate	-
$CS-H_2$	-	$CaSO_3 \cdot 2H_2O$	Calcium sulphate dihydrated	Gypsum dihydrated
C-S-H gel	-	$x\,CaO \cdot y\,SiO_2 \cdot z\,H_2O$	Calcium silicate hydrated gel	-

Appendix II: European Standard EN 197-1

Table 24: Types of cement described in EN 197-1

Main types	Notation of the 27 products (types of common cement)		Clinker	Blast-furnace slag	Silica fume	Pozzolana natural	Pozzolana natural calcined	Fly ash siliceous	Fly ash calcareous	Burnt shale	Limestone	Limestone	Minor additional constituents
			K	S	D[b]	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95-100	–	–	–	–	–	–	–	–	–	0-5
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	–	–	–	–	–	–	–	–	0-5
		CEM II/B-S	65-79	21-35	–	–	–	–	–	–	–	–	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	–	6-10	–	–	–	–	–	–	–	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	–	–	6-20	–	–	–	–	–	–	0-5
		CEM II/B-P	65-79	–	–	21-35	–	–	–	–	–	–	0-5
		CEM II/A-Q	80-94	–	–	–	6-20	–	–	–	–	–	0-5
		CEM II/B-Q	65-79	–	–	–	21-35	–	–	–	–	–	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	–	–	–	–	6-20	–	–	–	–	0-5
		CEM II/B-V	65-79	–	–	–	–	21-35	–	–	–	–	0-5
		CEM II/A-W	80-94	–	–	–	–	–	6-20	–	–	–	0-5
		CEM II/B-W	65-79	–	–	–	–	–	21-35	–	–	–	0-5
	Portland-burnt shale cement	CEM II/A-T	80-94	–	–	–	–	–	–	6-20	–	–	0-5
		CEM II/B-T	65-79	–	–	–	–	–	–	21-35	–	–	0-5
	Portland-limestone cement	CEM II/A-L	80-94	–	–	–	–	–	–	–	6-20	–	0-5
		CEM II/B-L	65-79	–	–	–	–	–	–	–	21-35	–	0-5
		CEM II/A-LL	80-94	–	–	–	–	–	–	–	–	6-20	0-5
		CEM II/B-LL	65-79	–	–	–	–	–	–	–	–	21-35	0-5
	Portland-composite cement [c]	CEM II/A-M	80-94	<————————————— 6-20 —————————————>										0-5
		CEM II/B-M	65-79	<————————————— 21-35 —————————————>										0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	–	–	–	–	–	–	–	–	0-5
		CEM III/B	20-34	66-80	–	–	–	–	–	–	–	–	0-5
		CEM III/C	5-19	81-95	–	–	–	–	–	–	–	–	0-5
CEM IV	Pozzolanic cement [c]	CEM IV/A	65-89	–	<———————— 11-35 ————————>				–	–	–	–	0-5
		CEM IV/B	45-64	–	<———————— 36-55 ————————>				–	–	–	–	0-5
CEM V	Composite cement [c]	CEM V/A	40-64	18-30	–	<——— 18-30 ———>		–	–	–	–	–	0-5
		CEM V/B	20-38	31-50	–	<——— 31-50 ———>		–	–	–	–	–	0-5

a   The values in the table refer to the sum of the main and minor additional constituents.
b   The proportion of silica fume is limited to 10 %.
c   In Portland-composite cements CEM II/A-M and CEM II/B-M, in pozzolanic cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement (for example see clause 8).

Appendix III: Nomenclature used in the Thesis

Table 25: Nomenclature of the present Thesis

Proportions and characteristics		Name
w/c = 0.5	300:0 w/water	$Cem_{300}slag_0(H_2O)_{0.5}$
	300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{0.5}$
	300:200 w/water	$Cem_{300}slag_{220}(H_2O)_{0.5}$
	300:0 w/sodium hydroxide 1M	$Cem_{300}slag_0(NaOH)_{0.5}$
	300:0 w/sodium carbonate 1M	$Cem_{300}slag_0(Na_2CO_3)_{0.5}$
	300:0 w/sodium sulphate 1M	$Cem_{300}slag_0(Na_2SO_4^{1M})_{0.5}$
	300:0 w/sodium sulphate 0.5M	$Cem_{300}slag_0(Na_2SO_4^{0.5M})_{0.5}$
	300:0 100% fresh OPC w/water	$Cem_0F_{300}slag_0(H_2O)_{0.5}$
w/c = 0.36	300:0 w/water, w/c=0.36	$Cem_{300}slag_0(H_2O)_{0.36}$
w/c = 1.5 (only in calorimetry, TAM Air)	300:0 Heidelberg w/water	$Cem^H_{300}slag_0(H_2O)_{0.61}$
	300:0 Heidelberg w/sodium hydroxide 1M	$Cem^H_{300}slag_0(NaOH)_{1.5}$
	300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{1.5}$
	300:100 w/sodium hydroxide 1M	$Cem_{300}slag_{100}(NaOH)_{1.5}$
	300:100 w/sodium carbonate 1M	$Cem_{300}slag_{100}(Na_2CO_3)_{1.5}$
	300:220 w/water	$Cem_{300}slag_{220}(H_2O)_{1.5}$
	300:220 w/sodium hydroxide 1M	$Cem_{300}slag_{220}(NaOH)_{1.5}$
	300:220 w/sodium carbonate 1M	$Cem_{300}slag_{220}(Na_2CO_3)_{1.5}$
w/c = 0.61 (only in mech. test and TGA)	300:0 Heidelberg w/water	$Cem^H_{300}slag_0(H_2O)_{0.61}$
	300:0 Heidelberg w/sodium hydroxide 1M	$Cem^H_{300}slag_0(NaOH)_{0.61}$
	300:100 w/water	$Cem_{300}slag_{100}(H_2O)_{0.61}$

	300:100 w/water, 10% fresh OPC, 90% dehydrated OPC	$FCem_{300}slag_{100}(H_2O)_{0.61}$
	300:100 w/sodium hydroxide 1M	$Cem_{300}slag_{100}(NaOH)_{0.61}$
	300:100 w/sodium carbonate 1M	$Cem_{300}slag_{100}(Na_2CO_3)_{0.61}$
	300:220 w/water	$Cem_{300}slag_{220}(H_2O)_{0.61}$
	300:220 w/water, 10% fresh OPC, 90% dehydrated OPC	$FCem_{300}slag_{220}(H_2O)_{0.61}$
	300:220 w/sodium hydroxide 1M	$Cem_{300}slag_{220}(NaOH)_{0.61}$
	300:220 w/sodium carbonate 1M	$Cem_{300}slag_{220}(Na_2CO_3)_{0.61}$