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Municipal solid waste incineration (MSWI) ashes for greener concrete

Master's project for the Master Program of Structural Engineering and Building Technology

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ABSTRACT

Owing to the varying characteristics of municipal solid waste incineration (MSWI) ashes and the lack of harmonized standards and regulations, a substantial portion of MSWI ashes are simply used as landfilling cover at the present, which can be better utilized in the viewpoint of sustainability. This study aims at using and developing experimental methods to assess the reactivity of MSWI ashes under alkaline activation to evaluate their potential use as a binding agent.

A new test, solution test, was developed in this work and performed on two kinds of MSWI ashes. The results were compared to an existing method, R^3 test. The solution test and R^3 test involve different activators, such as $Ca(OH)_2$, $NaOH$ and KOH. The reactivity of the reacted mixtures were mainly determined by thermogravimetric analysis (TGA).

The experiment results from R^3 test revealed that a concrete pore solution environment was not able to activate RISE BA (bottom ash) and STENA BA. Portlandite did not act as a good enough activator. The experiment results from the solution test showed that $NaOH$ and KOH activators added in order to reach a pH of 14, were able to activate RISE BA in addition to SLAG. However, STENA BA were still inert.

KEY WORDS:
Alkaline activation, bottom ashes, greener concrete, reactivity assessment, thermogravimetric analysis

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Preface

Tests have been performed from January 2019 to May 2019. The project has been carried out at the Department of Architecture and Civil Engineering, Division of Building Technology, Building Materials, at Chalmers University of Technology, Sweden.

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Arnaud Glikson and Sara López Menéndez

Acronyms

BA	Bottom ashes
$CASH$	Calcium aluminosilicate hydration gel
CH	$Ca(OH)_2$: potassium hydroxide or Portlandite
CM	Cementitious material
CSH	Calcium silicate hydration gel
DTG	Derivative thermogravimetric
IC	Ion Chromatography
ICP	Inductively coupled plasma
$(K,N)ASH$	Potassium or sodium aluminosilicate hydration gel
MSWI	Municipal solid waste incinerator
OPC	Ordinary Portland cement
PDA	Particle distribution analysis
RISE	Research institutes of Sweden
SAI	Strength activity index
SCM	Supplementary cementitious material
TG	Thermogravimetric
TGA	Thermogravimetric analysis

Notations

$Ca(OH)_{2,measured}$	Amount of Portlandite in raw materials
$CH_{normalised,CH_{added}}$	Normalised value of Portlandite per gram of ashes removing the initial content of Portlandite
$CH_{normalised}$	Normalised value of Portlandite per gram of ashes
$CH_{residual,anhydrous}$	Amount of Portlandite rescaled to an anhydrous solid fraction
$CH_{residual,measured}$	Amount of Portlandite in the hydrated paste
C_{init}	Initial concentration of the stock solution that is prepared for IC analysis
C_j	Concentration of the standards solution prepared for the IC analysis where j refers to the kind of dilution
C_3S	Alite
H	H_2O: water
$H_2O_{bound\%,Rise,series\ x}$	Chemically bound water of RISE BA where x refers to the series number
$H_2O_{bound\%,Slag,series\ x}$	Chemically bound water of SLAG where x refers to the series number
$H_2O_{bound\%,X,series\ 1}$	Chemically bound water of a kind of ashes for series 1 in R^3 test, where X refers to the kind of ashes

$H_2O_{bound\%,X,series\ 2}$	Chemically bound water of a kind of ashes for series 2 in R^3 test, where X refers to the kind of ashes
M	Alkaline specie
M_{CH}	Molecular mass of Portlandite
M_{CaCO_3}	Molecular mass of calcite
M_{CO_2}	Molecular mass of CO_2
M_{H_2O}	Molecular mass of H_2O
M_i	Molecular mass where i refers to the kind of compound
$m_{introduced,i}$	Amount of solid powder introduced to prepare the stock solution for the IC analysis where i refers to the kind of alkaline specie
$m_{solid,Y}$	Amount of powder involved in the solution test mix design where Y refers to the time
$m_{105°C,cooled\ down\ from\ 350°C}$	Weight measured at $105°C$ after a drying at $305°C$ for 2 hours
$m_{105°C,stablized}$	Weight measured at $105°C$ after a drying at $105°C$ for 24 hours
P_{ashes}	Percentage of ashes in the solid mix design
$P_{CH_{added}}$	Percentage of Portlandite added to the mix design
$RD_{series\ x}$	Relative difference between SLAG and RISE BA chemically bound water in R^3 test, where x refers to the series number
$RD_{X,series\ 1/X,series\ 2}$	Relative difference about chemically bound water in R^3 test for a same kind of ashes between series 1 and 2, where X refers to the kind of ashes considered
RISE BA KOH Y X	Bottom ashes from RISE mixed with KOH where Y refers to the waiting time and X to the series number of solution test
RISE BA NAOH Y X	Bottom ashes from RISE mixed with $NaOH$ where Y refers to the waiting time and X to the series number of solution test
RISE BA X	Bottom ashes from RISE where X refers to the series number
RISE BA	Research institutes of Sweden bottom ashes
S	SiO_2 : silica
S_i	Compressive strength for a given design
SLAG BA X	Slag Merit 5000 where X refers to the series number
SLAG KOH Y X	Slag Merit 5000 mixed with KOH where Y refers to the waiting time and X to the series number of solution test
SLAG NAOH Y X	Slag Merit 5000 mixed with $NaOH$ where Y refers to the waiting time and X to the series number of solution test

STENA BA KOH Y X	Bottom ashes from Stena mixed with KOH where Y refers to the waiting time and X to the series number of solution test
STENA BA NAOH Y X	Bottom ashes from Stena mixed with $NaOH$ where Y refers to the waiting time and X to the series number of solution test
STENA BA X	Bottom ashes from STENA where X refers to the series number
STENA BA	Stena bottom ashes
V_2	Final volume of the dilution
V_{flask}	Volume of volumetric flask
$V_{liquid,Y}$	Volume of alkaline solution involved in the solution test mix design where Y refers to the waiting time
$V_{sampling}$	Volume of sampling after centrifugation in solution test
$V_{stock\ solution\ to\ collect,j}$	Volume of stock solution collected to prepare the standard solution for the IC analysis where j refers to the kind of dilution
$V_{water,j}$	Volume of water to add to complete the dilution of the standard solution for the IC analysis where j refers to the kind of dilution
$W_{600°C}$	Weight of the remaining fraction after a drying at $600°C$
$WL_{H_2O,CH}$	Weight loss of water associated to the decomposition of Portlandite
$WL_{H_2O,CH_{added}}$	Weight of the water chemically bound in the initial content of Portlandite added to the mix design
$WL_{CO_2,CaCO_3}$	Weight loss of CO_2 associated to the decomposition of calcite

1 Introduction

1.1 Background

Since the prohibition of using combustible waste for landfilling in Sweden in 2005 [1], this waste has been used as fuel for heat and electricity production. When the waste is burnt, it remains left-over materials that are non-combustibles. Those by-products of the burning process are called bottom ashes (BA) and fly ashes. The main difference between these two kinds of ashes is the size of the particles, which bottom ashes are coarser than fly ashes. In the case of bottom ashes, they are usually mixed with sand, stones and mud that are also non-combustible materials [1].

After the burning process, bottom ashes are mostly made of minerals and metals, as shown in Figure 1.1 [2].

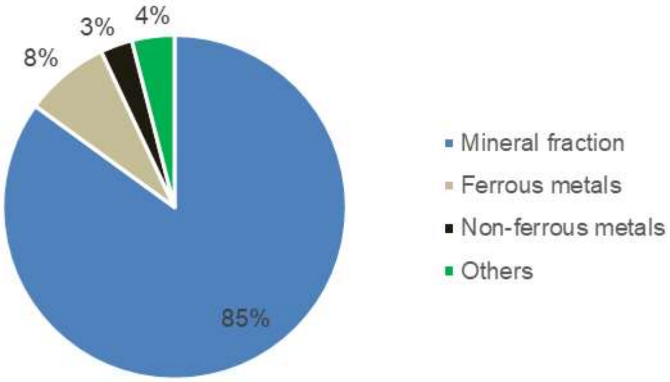

Figure 1.1: Composition of bottom ashes after the burning process [2].

A recovery of valuable metals is generally carried out up to 80% of the total amount of metals. After that, the remaining part of bottom ashes are used either in landfilling or as an aggregate in road constructions, replacing sand or gravel [2].

The total of waste (municipal, commercial and industrial) that are incinerated in plants in Europe is about 93 million tons per year. Once the burning process is completed, approximately 20% by weight is converted into bottom ashes [2], which is about 19 million tonnes per year. Sweden is ranked the sixth place in Europe with the largest amount of incinerated wastes. Figure 1.2 shows that, in 2016, Sweden incinerated 6 million tons of waste resulting in the production of approximately 1.2 million tons of bottom ashes [3]. In Figure 1.2, only European countries with more than 1 million ton of incinerated wastes were considered.

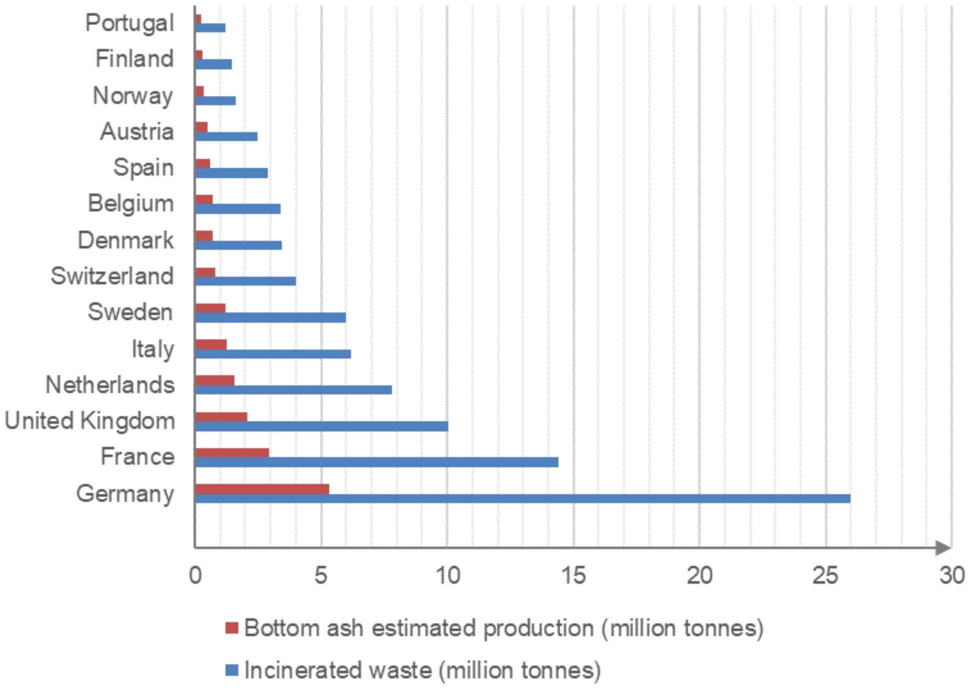

Figure 1.2: Bottom ash: amount produced in Europe in 2016 [3].

Sweden is one of the pioneer countries that municipal solid wastes are incinerated for energy production. Although the modern incineration technique can convert a substantial portion of municipal solid wastes to energy, a considerable number of residues are still left in the form of fly ash and bottom ash. Owing to the varying characteristics of these municipal solid waste incinerator (MSWI) ashes and the lack of harmonized standards and regulations, a substantial portion of MSWI ashes is simply used as landfilling cover at the present, which can be better utilized in the viewpoint of sustainability.

In 2011, the European commission introduced a roadmap where it is clearly expressed, that *"By 2020, waste is managed as a resource. Waste generated per capita is in absolute decline. Recycling and re-use of waste are economically attractive options for public and private actors due to widespread separate collection and the development of functional markets for secondary raw materials. More materials, including materials having a significant impact on the environment and critical raw materials, are recycled. Waste legislation is fully implemented. Illegal shipments of waste have been eradicated. Energy recovery is limited to non-recyclable materials, landfilling is virtually eliminated, and high-quality recycling is ensured."* [4].

The landfilling average in European Union was about 37% of the municipal waste produced in 2011 [5]. Following the guidelines endorsed by the European commission, member states succeeded to reduce landfilling reaching a European Union average of 22% in 2016 [5].

The guidelines previously considered became targets, and for 2030 there are some goals in the European Union that should be achieved: [6]

- Reducing landfilling to a maximum of 10% of municipal waste by 2030.
- Encourage other techniques to discourage landfilling.
- Economical encourage to sell green products on the market.

This project echoes these guidelines by studying the potential of bottom ashes as a functional binding agent within the concrete production. If such characteristics are demonstrated, landfilling could be reduced, and a greener concrete could be developed.

1.2 Aims and scope

This project aims at finding applications of MSWI ashes as functional compositions in concrete production to increase the added value of MSWI ashes and reduce the quantity of ashes for landfilling.

To achieve the general aim, two specific research questions have been studied.

1. What kind of tools and methods can be used and developed to assess the reactivity of MSWI ashes in a relevant way?
2. To what extent MSWI ashes are of interest when it comes about using them as a binding agent?

To answer the research questions, it is necessary to assess the reactivity of different kinds of MSWI ashes in an alkaline medium for the consideration of their potential use as alkali-activated binders. The reactivity must also be examined in a typical concrete pore solution environment to obtain close-to-reality results when it comes about replacement of part of the clinker by MSWI ashes.

1.3 Methodology

In the project, experimental investigations have been carried out to identify chemical activities of ash particles under different alkaline conditions and supply evidences of gel formation.

The investigation of chemical activities has been led into two different experiments. Moreover, in this task, two types of MSWI bottom ashes, supplied by Research institutes of Sweden (RISE) and Stena Metall, were studied after being sieved to a smaller size by the supplier.

Broadly speaking, experimental studies can hardly be based on real systems. Within a real system, different steps can occur at the same time and products from different stages can coexist, making any analysis laborious and inaccurate. Hence, it is necessary to simplify real systems, carrying out main assumed steps separately by using products that would have been previously created as reagents. In this work the different experiments carried out to study the reactivity of the ashes follow that principle.

The first experiment developed for the first time in that study, the “solution test”, aims at studying the potential of a supplementary cementitious material (SCM) for alkali-activated binders. It involved bottom ashes that was mixed in different types of highly alkaline solutions ($NaOH$ and KOH). Through the chemical analyses of filtrates by ion chromatography (IC) and thermogravimetric analysis (TGA), the pozzolanic/alkali-activities were determined by measuring ion concentrations and chemically bound water.

The second experiment carried out was is the R^3 test, which was recently developed by the scientific community as a standard test. The ashes were also tested according to the R^3 method to determine the reactivity of MSWI ashes in a typical concrete pore solution environment. The parameters measured were the content of chemically bound water and the Portlandite consumption.

The obtained results were compared with a known material, slag, which has been proven having high reactivity, thus enabling relevant comparisons.

Finally, the two tests conducted in this work were contrasted according to the methodology used, and the results obtained.

2 Literature research

2.1 Pozzolanic materials

2.1.1 Definition

One must understand the difference between hydraulic properties and pozzolanic properties. On one hand, hydraulic properties are related to the capacity of a material to develop binding properties in presence of moisture. On the other hand, a material displaying pozzolanic properties has the capacity to react chemically with alkalis in presence of moisture to form cementitious compounds provided with hydraulic properties [7].

Natural or artificial pozzolans, such as fly ash, burnt clay, volcanic ash and so on, are mostly composed of a reactive silica (SiO_2) and alumina (Al_2O_3). It must be noticed that a pozzolanic material itself has no hydraulic properties, which means that when being put into water, a pozzolanic material will not initiate a hydration process and participate to the hardening spontaneously. It needs to be activated [8].

For instance, in a concrete pore solution environment, Portlandite $Ca(OH)_2$, a by-product of the hydration reaction of clinker, will combine with the silica (SiO_2) of a given pozzolanic material to create tricalcium silicate as known as alite (C_3S). Once that step is done, the normal hydration reaction takes place. As it can be seen, it is necessary to activate the pozzolan (here with Portlandite). Chemical reactions that occur are the following ones (Eq(2.1) and Eq(2.2)) [9]:

$3CH + S \to C_3S + 3H$: pozzolanic reaction *Eq(2.1)*

$C_3S + 5.3H \to C_{1.7}SH_4 + 1.3CH$: hydration reaction *Eq(2.2)*

When clinker is consumed, Portlandite is created and the alkalinity of the medium is increased and thus the pH is increased. For high values of pH, silica and alumina will start to dissolve into the basic aqueous medium and form hydrates by combining with calcium. Thus, the pozzolanic reaction consumes the Portlandite. As a benchmark, chemical compounds of fly ash start breaking down when the pH reaches 13.2 [8].

2.1.2 Reactivity

Pozzolanic materials differ from each other according to their reactivity. In other words, their efficiency depends on how fast chemical compounds, such as silicon (Si) and aluminum (Al) will be disintegrated. Broadly speaking, what can be settled is that, the larger the amorphous phase, the greater the reactivity of pozzolans is. An amorphous phase is characterized by a high content of stored energy that is just waiting for being released. This is generally due to a fast cooling process from high temperatures (where the mineral addition is liquid) to a normal temperature. Molecules and ions do not have time to arrange themselves in the most stable state they could have reached. That is why crystalline phases display very low reactivity due to the stability of chemical bonds that have been created. The fineness of pozzolanic particles also allows a higher reactivity by increasing the available space for reaction sites [9].

In order to get a higher reactivity, pozzolanas can be activated in various way [10]:

- A mechanical activation can be achieved by crushing pozzolanas into smaller particles to augment the specific surface.

- A thermal activation can be done by higher curing temperatures than the ambient one (for instance a curing at $40^{\circ}C$). Higher temperatures are obviously related to accelerated chemical reactions. Another kind of thermal activation is calcination. By heating the pozzolanic material up to a very high temperature, a more amorphous phase can be built up by storing energy.
- A chemical activation consists on incorporating specific chemical components in order to enhance the dissolution rate of the mineral addition.

In the scope of that work, reactivity of bottom ashes will be mostly studied by mean of a chemical activation using alkali solutions. Therefore, a deeper background about alkali activation will be provided in the following part.

2.2 Alkali activation

2.2.1 Alkali activators

It exists different chemical components based on an alkali metal that enable a chemical activation. They can be sorted in six different groups, as shown in Figure 2.1, where the activators the most commonly used are the alkalis MOH and the silicates $M_2O.nSiO_3$,where M refers to the alkaline specie [11]:

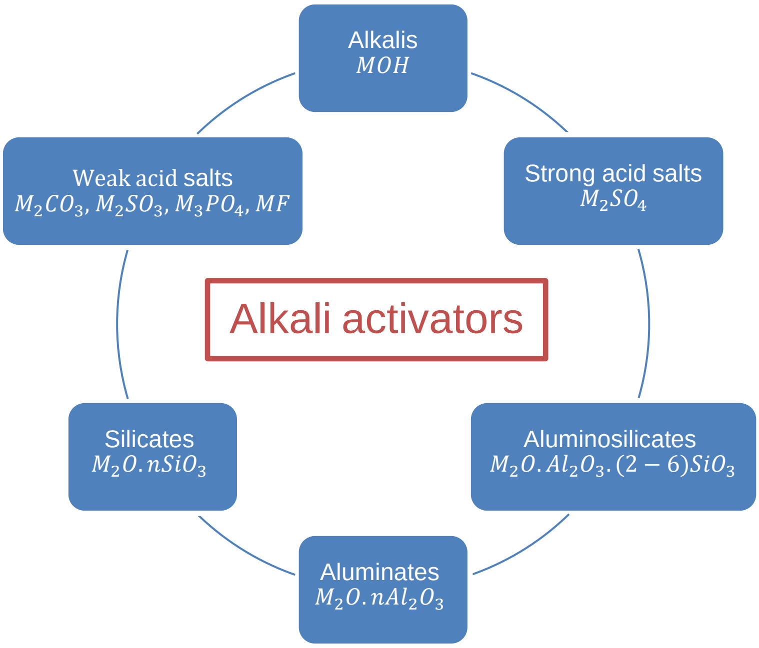

Figure 2.1: Different types of alkali activators.

In this project, the activation was done by three kinds of alkalis MOH type: $NaOH$, KOH and $Ca(OH)_2$. Therefore, what follows will be developed according to these activators.

$NaOH$ and KOH have a higher solubility than $Ca(OH)_2$, that is why they are better activators. Nevertheless, $Ca(OH)_2$ remains an interesting activator because it is a by-product of clinker hydration. [8]

2.2.2 Binding systems

2.2.2.1 Alkali-activated binders

The alkali-activated binders are made of a mix of a cementitious material with an alkali activator such as $NaOH$ or KOH. The very first study about alkali-activated binders was initiated in 1930 by mixing slag with a solution of KOH. However, 1940 marked the first large scale study of aluminosilicate materials activated with alkaline solution by experimenting different mix of slag with $NaOH$ solution [12].

Glukhovsky [13] brightened the understanding of such binder systems in 1967 leading to a sorting of alkali-activated binders in tow broad categories: low and high calcium systems. Low calcium systems are characterized by pure aluminosilicate materials such as fly ash, metakaolin or natural pozzolans. The fact that calcium is missing in such systems, leading to the formation of the so-called $(K,N)ASH$ gel, potassium or sodium aluminosilicate hydration gel. In opposition, significant or high calcium systems, with slag for instance, conduct to the formation of $CASH$ gels, calcium aluminosilicate hydration gel [13]. The hydration products of high calcium systems are more or less the same as for ordinary Portland cement (OPC), and such systems have been fully studied[8].

Low calcium systems have been further studied, and the term of geopolymer appears for the first time in the work of Davidovits in 1982, describing the hydration products created by aluminosilicates materials mixed with alkaline activators.

From that point, more and more papers have been published in that field, and now the chemistry and phenomenon behind the alkali activation are better described [14].

2.2.2.2 Hybrid cements

Researches have also been carried out on hybrid cement which aluminosilicate materials were mixed with ordinary Portland cement (OPC). Although Portlandite created by the hydration of cement helps the dissolution of aluminosilicates by creating a basic medium, stronger alkali activators might still be needed. Indeed, the greater the replacement of clinker is, the lower the Portlandite formation will be. In addition, Portlandite has a low solubility rate, meaning that the pH is limited to 12.3. Products of hydration are $(K,N)ASH$ and $CASH$. For a hybrid Portland cement, these two of gels coexist. Nevertheless, when both calcium ions and sodium or potassium ions present in the solution, the $(K,N)ASH$ turns into a $CASH$ structure when $pH > 12$. The calcium cations replace the alkali cations and the system reaches a more stable state [15].
It is important to understand that supplementary cementitious materials (SCM) are expected to be used as a replacement of OPC in order to reduce the carbon footprint and the cost of production [12].

2.2.2.3 Other binding systems

Other systems, such as pure aluminosilicates and alkali activators, have been studied, by adding reactive lime to compensate for the lack of calcium. The results of such systems are the production of $(K,N)ASH$ and $CASH$ gels [12].

Moreover, in practice, aluminosilicates materials are prone to contain reactive silica but not always reactive alumina. That is why another kind of systems called alkali-activated calcium aluminate blended cement have been studied, which reactive alumina and lime are added [16].

2.2.3 Gel formation process

Having a look on silica (SiO_2), one can notice that all varieties of silica are practically insoluble in pure water ($pH = 7$). However, silica can dissolve decomposing into ions if it is immersed in a strong basic aqueous solution. An example of strong base which is highly soluble in water is sodium hydroxide ($NaOH$). Another relevant example displaying similar properties could be potassium hydroxide (KOH) [17].

One of the first relevant model for the formation of gels under alkaline conditions has been proposed by Glukhovsky and Krivenko by the end of the 20th century [13] and the process of gel formation is described as:

$$= Si - O^- + M^+ \rightarrow = Si - O - M \qquad \text{Eq(2.3)}$$

$$= Si - O - M + OH^- \rightarrow = Si - O - M - OH^- \qquad \text{Eq(2.4)}$$

$$= Si - O - M - OH^- + Ca^{2+} \rightarrow = Si - O - Ca - OH + M^+ \qquad \text{Eq(2.5)}$$

where M refers to the alkali cation.

More recently, the mechanisms of the formation of alkali activated binders have been further described through three main steps: dissolution of silica and alumina, rearrangement and diffusion, and formation of polymers and hydrates.

2.2.3.1 Dissolution of silica and alumina

First, alkali hydroxides, such as sodium hydroxide or potassium hydroxide, break down the solid network into soluble species (mainly alumina and silica) within the aqueous medium [18]. It leads to the generation of $-Si - OH$. The cation from the alkali agent counterbalances the negative charge so that the reverse reaction is blocked [13].

In the case of silica, it can be seen easily in Figure 2.2, that the higher the pH, the greater the solubility of silica. Moreover, for such high pH, different species coexist such as $Si(OH)_4$, $[SiO(OH)_3]^-$ or $[SiO_2(OH)_2]^{2-}$.

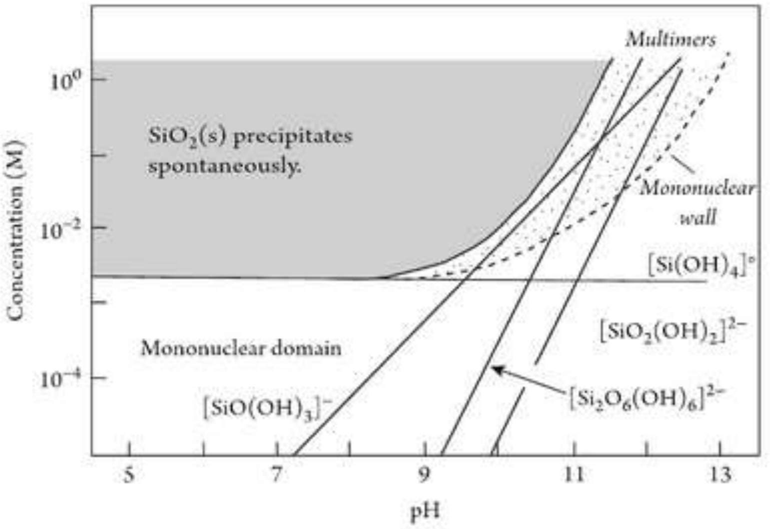

Figure 2.2: A solubility and speciation diagram for silica as a function of pH [19].

Chemical reactions involved are [20]:

$$SiO_2 + 2H_2O \leftrightarrows Si(OH)_4 \qquad \text{Eq(2.6)}$$

$$Si(OH)_4 + OH^- \leftrightarrows [SiO(OH)_3]^- + H_2O \qquad \text{Eq(2.7)}$$

$$[SiO(OH)_3]^- + OH^- \leftrightarrows [SiO_2(OH)_2]^{2-} + H_2O \qquad \text{Eq(2.8)}$$

Concerning the dissolution of alumina, it has been shown that, in basic solutions, the predominant ion specie is $[Al(OH)_4]^-$ [19]. Figure 2.3 shows the speciation diagram for alumina in function of the pH.

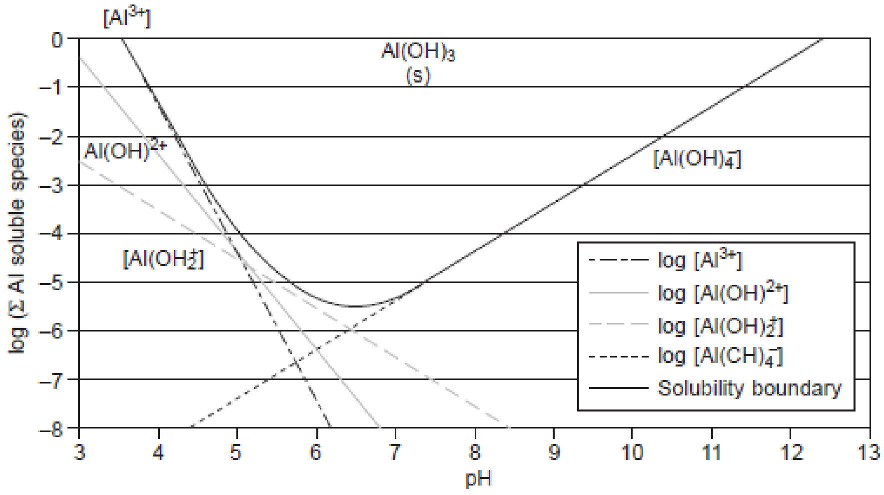

Figure 2.3: A solubility and speciation diagram for alumina as a function of pH [21].

The chemical reaction involved is [19]:

$$Al_2O_3 + 3H_2O + 2OH^- \leftrightarrows 2[Al(OH)_4]^- \qquad \text{Eq(2.9)}$$

2.2.3.2 Rearrangement and diffusion

The second step is the result of an accumulation of ionic species in solution. Contacts among species become more likely to happen. A process of rearrangement and diffusion of soluble species takes place, which results in the formation of a colloidal suspension [10].

2.2.3.3 Formation of polymers and hydrates

Finally, the growth of particles by condensation reactions leads to the formation of polymers and hydrates[10] [18]. Precipitation of the different clusters created in the previous stage gives hardened properties [13].

Besides, one of the possible polymerisation reactions in a basic medium involving aluminosilicate materials is presented in Figure 2.4.

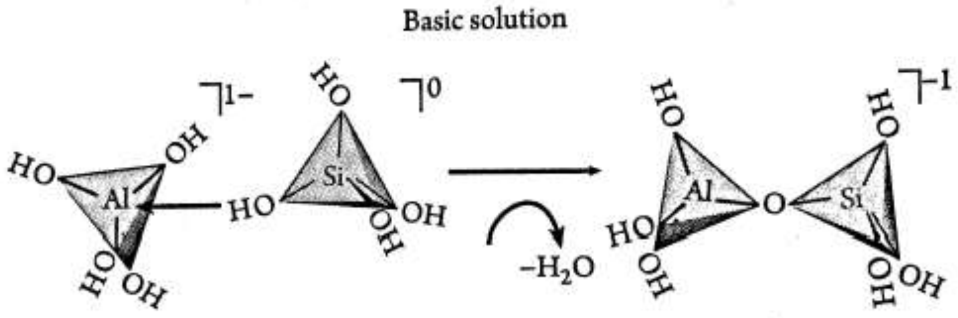

Figure 2.4: Formation of aluminosilicate clusters by condensation reaction in a basic aqueous solution [19].

As mentioned previously, many species are going to coexist in a basic alkali solution, such as $Si(OH)_4$, $[SiO(OH)_3]^-$, $[SiO_2(OH)_2]^{2-}$ or $[Al(OH)_4]^-$. One parameter that can prevent those monomers to bond with another is the electrostatic repulsion. This repulsion is in practice countered by cations that carry positive electric charges. The size of cations is then a parameter that might influence the polymerization rate. Moreover, repulsive forces can be reduced if the cations are larger and act as a screen. Knowing that potassium (K) has a bigger atomic number than sodium (Na), it is expected sodium to be more efficient than potassium [19].

Nevertheless, another comment of interest is that sodium ion (Na^+) has a higher charge density than that of potassium ion (K^+). Moreover, Na^+ has a smaller size than that of potassium ion for the same positive electric charge of $+1$. Thus Na^+ is more likely to bind with negative sites of water molecules rather than with K^+. K^+, with a more dispersed charge density, will link more easily with highly negative silicate monomer sites. Thus, in the case of K^+, water is less bound than that for Na^+. Therefore, Na^+ cations are meant to display a better gel formation [21].

2.2.4 Gel structure

Figure 2.5 illustrates a possible structure of hydrated silicate gels [7].

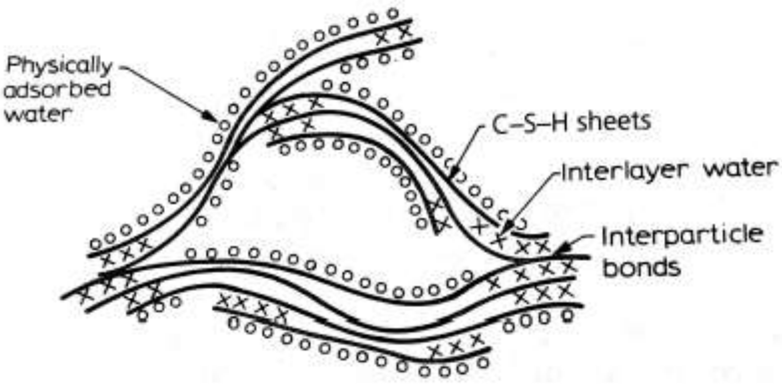

Figure 2.5: Probable structure of hydrated silicates [8].

The $C - S - H$ sheets are the result of the polymerization process, seen in section 2.2.3.3. They consist of water molecules that are chemically bound to aluminosilicates with inter and intra layers of calcium ions to ensure the electrical neutrality. Other cations such as sodium or potassium can behave in the same manner as calcium ions, leading to $(K,N)ASH$ sheets for instance. Chemically bound water is also defined as water that is non-evaporable below $105°C$ [8].

The structure of $C - S - H$ cannot be entirely described without mentioning the physically bound water which is held by gel particles. Two kind of physically bound water must be distinguished as it can be seen in Figure 2.5. Water can be either physically adsorbed by the surface forces or retained in between $C - S - H$ sheets as interlayer water [8].

Finally, free water is contained in the capillary pores created by the arrangement of $CASH$ layers [8]. This water hasn't reacted.

Up to this point, three kinds of water have been identified according to how it is held to $C - S - H$ sheets: chemically bound water, physically bound water and free water [8].

In this study, the content of chemically bound water is of interest since it enables to get an idea of the amount of gel created during the polymerization/hydration process.

2.3 Existing reactivity tests

In order to assess the reactivity of presupposed cementitious materials, different methods have been developed and used through the past years. Two main families of tests can be identified: direct and indirect methods [22]. The difference in between these two kinds of tests lies in the parameters that are studied. For a direct evaluation, the measured parameters are directly related to the material tested. It gives information about the material itself, for instance the quantity of calcium fixed, or the heat released during the reaction. Indirect parameters refer to the study of chemical and physical characteristics of the hardened paste that are impacted by the reaction of such materials. It can be the strength under compressive load as an example [22].

In this study, R^3 test is focused because it was the last one introduced by the scientific community in 2016 [23] and is currently subjected to a large scale of studies in many laboratories [24]. Moreover, this test is the only direct methods that reproduces a concrete pore solution environment to study the potential use of a supplementary cementitious material (SCM) for hybrid cements. That is the main reason why other testing methods were not included even if they all have their own advantage and limitations.

All the existing methods rely on the activation of a SCM by Portlandite. The limitation of such tests lies in the low alkalinity provided by Portlandite which has a low solubility in water. A too low alkalinity might not be able to activate energetically stable raw material such as bottom ashes. That is why a new direct reactivity test is developed in this study: the “solution test”. This test involves a higher alkalinity by using stronger chemical activators and provides more info in the same time frame as the R^3 test to better characterize the reactivity of a potential cementitious material. Details of solution test are given in section 3.2.

A non-exhaustive list of the existing methods is presented in what follows.

2.3.1 Direct reactivity test

2.3.1.1 R^3 test

The reactivity rate is assessed by means of thermogravimetric analysis. Since this test has been carried out in this study, an accurate description of the principle is provided in section 3.3.

2.3.1.2 Frattini test

The Frattini test is the first one to stand as a direct general reactivity assessment method that appeared in 1950 and is described in the European standards (EN 196-5) [25].

The procedure consists adding cementitious materials (mix made of 80% of ordinary Portland cement (OPC) and 20% of material to test) into distilled water with a water to solid ratio of 5. The OPC hydrates create Portlandite that is then supposed to be consumed by the material to test.

The curing conditions are 8 days at $40°C$. At the end of the waiting time, a filtration must be carried out to analyse the concentration of Ca^{2+} and OH^- that are in the filtrate by titration. Results are reported in a graph $[Ca^{2+}]$ in function of $[OH^-]$ where the solubility curve of Portlandite is also plotted. If results are below the solubility curve, it means lime has been consumed and pozzolanic reaction occurred [25].

2.3.1.3 Modified Chapelle test

The modified Chapelle test is an update of the Chapelle test developed in 1967. The only difference lies in the material to lime ratio. Initially the ratio was $1:1$ but it changed to $1:2$ in the modified Chapelle test. It has been noticed that a $1:1$ ratio could underestimate the reactivity of pozzolans because of a too low concentration of lime during the test. That is why the modified test has been developed with a higher lime content. As the initial Chapelle test, this modified method is a direct reactivity evaluation, and is nowadays standardized by the French (NF P18-513) and the Brazilian (NBR 15.895/10) standards [26].

The procedure involves $1g$ of material to test, mixing with $2\ g$ of reactive lime (CaO) into $250\,mL$ of distilled water for $16h$ at $90°C$. The aim is to quantify the lime consumption, that is to say the $Ca(OH)_2$ fixed to the material to test. To do so, a titration must be carried out [22].

2.3.1.4 Saturated lime test

The saturated lime test follows the principles of the Frattini test, but it displays less variability. The ordinary Portland cement is added, providing a reservoir of Portlandite which is necessary for the pozzolanic reaction. In the saturated lime test, Portlandite is not a product of hydration reaction, but a reagent with a known quantity [25].

The experiment requires $1g$ of material to test dissolving into $75\,mL$ of saturated lime solution at $40°C$ for 1, 3, 7 and 28 days. Then, similar like in the Frattini test, the filtrate after filtration is analysed to get the concentration of $[OH^-]$ and $[Ca^{2+}]$. Unlike in the Frattini test, since the amount of calcium hydroxide is known from the beginning, the exact amount of $Ca(OH)_2$ consumed can be derived [25].

2.3.1.5 Conductivity and pH test

Conductivity and pH test have been lately reconsidered by Tashimaa et al. in 2014 [27]. The principle involves mixing $1\ g$ of SCM in a $50\,mL$ solution saturated in slaked lime ($Ca(OH)_2$) with excess of slaked lime in solid state. Different slaked lime to cementitious material ratios were studied [27]. During the hydration process, $Ca(OH)_2$ is consumed and the ion concentrations of $[Ca^{2+}]$ and $[OH^-]$ are decreasing progressively, thus effecting the conductivity and the pH. Those two parameters can then be measured at different time to assess the reactivity rate of cementitious material.

2.3.2 Indirect reactivity test

2.3.2.1 Strength Activity Index (SAI)

The SAI test measures the compressive strength after 28 days of hardened pastes to quantify the reactivity of supplementary cementitious material (SCM).

The mix design consists of water, sand and ordinary Portland cement, where 20% of the OPC is replaced by the SCM to test. A reference mix must also be casted with 100% of OPC to compare results [25]. The reactivity is then assessed using

$$SAI\ (\%) = \frac{S_i}{S_{ref}} * 100 \qquad \text{Eq(2.10)}$$

where S_i refers to the compressive strength of a given mix design, and S_{ref} refers to the compressive strength of the reference mix.

Since the SCM to OPC ratio is 5, it is admitted that a Strength Activity Index (SAI) above 0.8 means that a pozzolanic reaction occurred [25].

2.3.2.2 Electrical resistivity test

The cement paste develops a solid network and becomes more and more hardened over time. Hence, pores and connections to one another are reducing accordingly. Since pores contain ions, electrical properties such as resistivity and capacitance factor are directly impacted by the hardening process and can be measured at different times [28].

The mix design is like the one within the SAI test. A reference mix must also be casted with 100% of OPC to compare results [28].

2.3.2.3 Calorimetry test

Chemical reactions that occur during hydration process are exothermic. Thus, the greater the hydration reaction, the larger the heat release. Therefore, the cumulative heat release can be measured and compared to a benchmark for different kinds of mix design to assess the reactivity rate of SCMs as done by Avet et al. [23].

3 Experiments

3.1 Raw materials

All chemical components that were used are listed with their lab grade in Appendix 3: Chemical products used.

Two different kinds of bottom ashes were studied in this work, bottom ashes from Stena Metall (STENA BA) and bottom ashes from Research Institutes of Sweden (RISE BA). To study the reactivity of bottom ashes, a commercial slag was used here as a benchmark to a better interpretation of results (Figure 3.1).

Figure 3.1: Ashes tested in the experiment.

3.1.1 SLAG

3.1.1.1 Origin

The benchmark material chosen was SLAG MERIT 5000. Slag is known because of its high reactivity.

3.1.1.2 Chemical composition

Figure 3.2 shows the chemical composition of SLAG. It is mainly composed of silicon and calcium that represent more than 60% of the total mass. Secondary compounds that still constitute a significant part of SLAG are aluminium and magnesium, lining up 30% of the total mass.

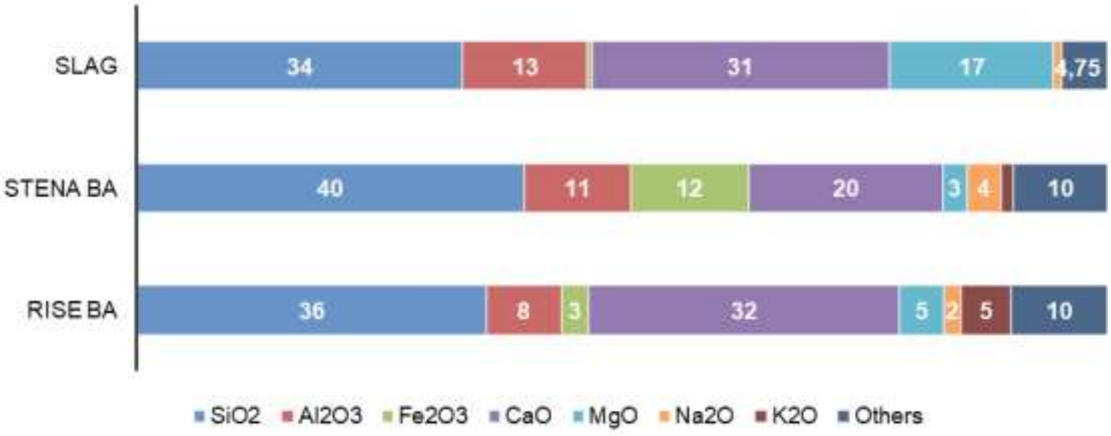

Figure 3.2: Chemical composition of raw materials.

3.1.2 RISE BA

3.1.2.1 Origin

This section is dedicated to the description of RISE BA provided by the Research Institutes of Sweden. RISE BA came from paper industry and they were basically burnt bark of trees.

3.1.2.2 Chemical composition

As it can be seen in Figure 3.2, the compounds with the biggest percentage were SiO_2 and CaO, representing more than $60\%$of the total mass. Secondary compounds still representing a significant percentage were Al_2O_3 and K_2O.

Regarding information mentioned previously, these ashes should perfectly display pozzolanic properties and cementitious value. However, the main question is the reactivity of these components (see section 2.1.2).

3.1.3 STENA BA

3.1.3.1 Origin

This section is dedicated to the description of STENA BA that were generated from incineration of municipal solid waste in a grate boiler. The ashes went through a water bath directly after the combustion and were collected from a landfill in Lidköping. They were then stored outside for one year. An excavator was needed to break the ash pile. They were collected two years ago.

The ashes were sieved into different particle size fractions by a device called the Stena Separator. The retrieved sample was the fraction $0 - 5000\ \mu m$. It was later milled till $355\ \mu m$ and metallic object were removed.

3.1.3.2 Chemical composition

Figure 3.2 shows the chemical composition of STENA BA. The main compounds were SiO_2 and CaO, as for RISE BA. Secondary compounds of interest were Fe_2O_3 and Al_2O_3.

3.2 Solution test

3.2.1 Aim of the solution test

The solution test aims at activating bottom ashes by putting them in a highly alkaline medium. Two different alkali activators, sodium hydroxide ($NaOH$) and potassium hydroxide (KOH), were tested.

The purpose of the solution test is to measure the chemically bound water content as well as the amount of oxides from bottom ashes dissolved at different times. Species of interest are silicon, aluminum, calcium, sodium and potassium because they constitute the main components involved in the formation of hydration products. Thus, their concentration levels constitute a good indicator. Moreover, since chemically bound water is incorporated in the chemical structure of hydrated products, it is also a relevant parameter to study when it comes about assessing reactivity of different materials.

3.2.2 Experiment procedure

The dissolution rate of ashes was studied for five different waiting times: 6 hours, 1 day, 2 days, 4 days and 7 days. It means that 10 samples must be done to study only one type of ashes (5 waiting times multiplied by 2 kinds of alkali solutions).

- **Preparation:**

To perform that test, two alkali solutions at $1\ \frac{mol}{L}$ were prepared, one with sodium hydroxide ($NaOH$) and the other with potassium hydroxide (KOH). The concentration of $1\ \frac{mol}{L}$ was chosen based on the work of Buchwald et al. [18] where it can be seen that increasing the concentration of $NaOH$ beyond $1\ \frac{mol}{L}$ doesn't impact on the dissolution rate of silica and alumina.

- **Mixing:**

Samples were done by mixing alkaline solution with ashes in a mass ratio equal to 20, as.

$$\frac{m_{alkaline\ solution}}{m_{ashes}} = 20 \qquad \text{Eq(3.1)}$$

- **Curing:**

Samples were set up in an automatic rotator for curing at a temperature of $40°C$. The rotation speed was fixed at 12 revolutions per minute. The constant rotating process was to ensure that particles were always in suspension in the solution. Hence, the surface available for ion exchanges can be optimized.

- **Setting up samples for ion concentration analysis:**

Once the waiting time was reached, the concerned samples were put in a centrifuge to separate the solid from the liquid phase. A part of the liquid phase was kept proceeding to an ion chromatography (IC) and an inductively coupled plasma (ICP) analysis later. The IC analysis was conducted to get the concentrations of sodium, potassium and calcium. The samples were stored at $40°C$ before doing the IC analysis. To avoid any carbonatation between the sampling and the IC or ICP analysis, a few drops of acids were added to reduce the pH below 3.

- **Setting up samples for thermogravimetric analysis (TGA):**

Only the solid phase of the seven-day waiting time was retrieved to determine the amount of hydration products by doing a thermogravimetric analysis (TGA). After the centrifugation process, a hydration stoppage was carried out on the solid phase. To do so, the RILEM TC-238 procedure, which a solvent exchange by isopropanol, was followed [29]. The principle of solvent exchange is that the free water is replaced by an organic solvent miscible with water, then the solvent is removed by evaporation. The purpose of the hydration stoppage is to remove the water physically bound to the solid phase in order to preserve the hydration product assemblage at a chosen time or degree of hydration. After such a process, only chemically bound water remains (see section 2.2.4). Once the hydration stoppage carried out, samples were tested with a TGA instrument.

The whole procedure is summed up in
Figure 3.3.

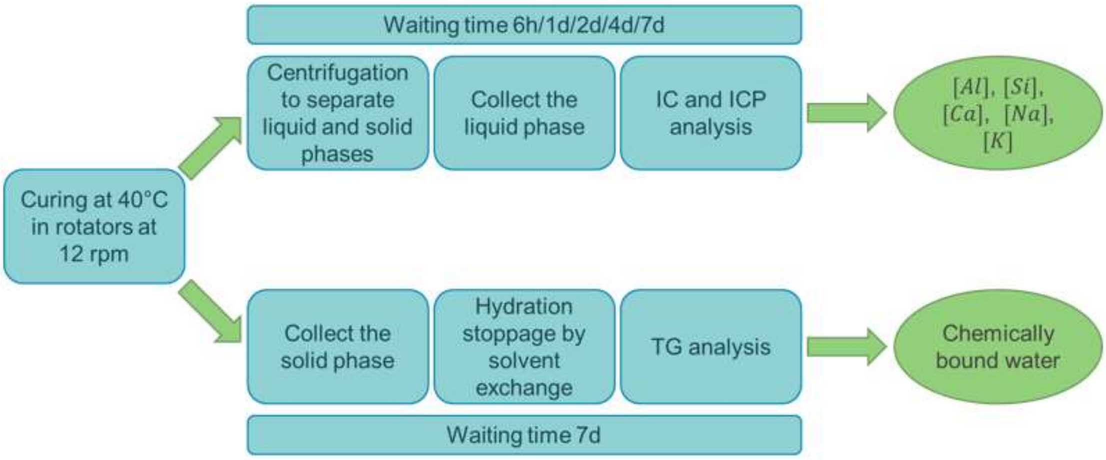

Figure 3.3: Solution test procedure.

More information about how to perform this experiment step by step is given in Appendix 1: Solution test protocol.

3.3 R^3 test

3.3.1 Aim of the R3 test

The aim of R^3 test is to use a simplified model to measure the reaction of a SCM by reproducing the environment of a real blended cement without incorporating any hydrated clinker phases [24].

R^3 stands for rapid, relevant and reliable.

- Rapid: results obtained in less than one week.
- Relevant: linear trends are obtained between bound water content and strength.
- Reliable: good reproducibility because of small standard deviations and no significant impact on the correlations.

The purpose of this experiment is to measure the chemical bound water created and the Portlandite consumption to assess the reactivity of different presupposed cementitious materials. As Portlandite is consumed during the pozzolanic reaction and water is incorporated in the chemical structure of hydrated products, both are good indicators that are relevant to study when it comes about assessing reactivity of different materials.

3.3.2 Experiment procedure

The procedure proposed by RILEM TC 267-TRM [30] was followed in this work.

- **Choosing a concrete pore solution environment:**

Different cement paste environments can be reproduced in this test. An environment related to a $LC^3 - 50$ cement paste mix design was the one selected for developing the R^3 test in this work. Figure 3.4 shows the composition of a $LC^3 - 50$ mix design compared to an ordinary Portland cement (OPC).

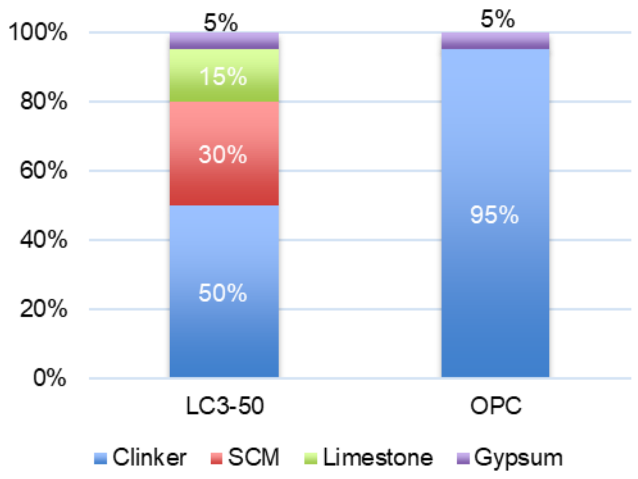

Figure 3.4: Mix proportions of LC3-50 compared to OPC.

Figure 3.5 shows the main components involved in the R^3 test. One can notice that the use of every component presented in the $LC^3 - 50$ mix design (except the clinker) is directly replaced by its by-product (Portlandite) after the hydration. Soluble alkalis are added to reproduce the concrete pore solution pH.

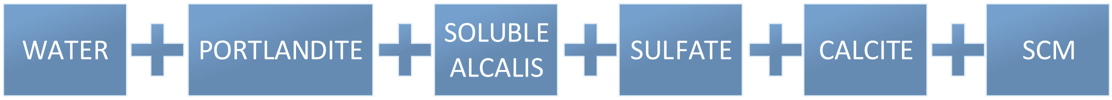

Figure 3.5: Main components.

- **Mixing:**

Figure 3.6 shows the final mix chosen in this study to reproduce a $LC^3 - 50$ concrete environment, which have been used by the RILEM TC 267-TRM [30].

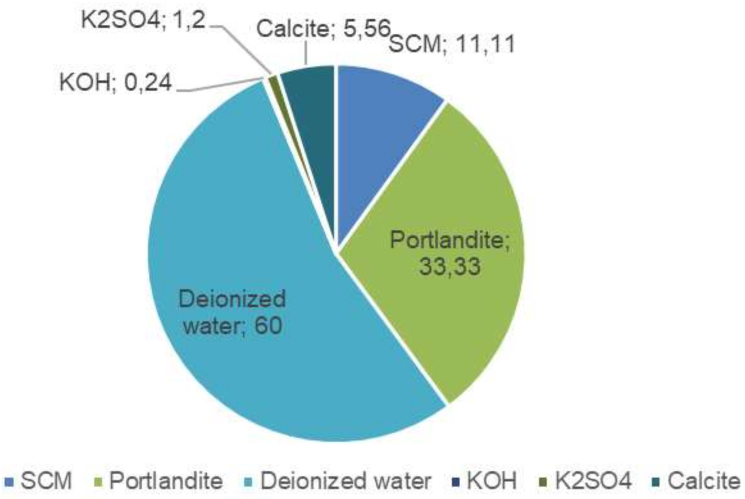

Figure 3.6: Ideal mix for LC3-50 environment.

Firstly, the water to solid ratio was fixed to be 1.2 in order to get a quick reaction which means more species dissolved and therefore more hydration products. Also, the ratio between Portlandite and SCM was chosen to avoid running out of Portlandite during the reaction process. Finally, the quantity of soluble alkalis and sulfates were adjusted to reproduce the environment conditions of a $LC^3 - 50$ mix design.

- **Curing:**

The R^3 pastes were cast in sealed plastic containers according to the mix design seen in Figure 3.6. Then, they were cured at $40°C$ for 7 days in an oven.

- **Setting up samples for chemically bound water determination:**

After seven days, samples were crushed and a hydration stoppage by oven drying was carried out on the crushed fraction collector. To get rid of the free water, samples were heated at $105°C$ until constant weight was reached according to "Report of TC 238-SCM: hydration stoppage methods for phase assemblage studies of blended cements—results of a round robin test" [31]. Then, collected samples were subjected to thermogravimetric analysis in a simple oven.

A more detailed explanation of the procedure to get the bound water consumption is explained in Appendix 2: $\boldsymbol{R^3}$ test protocol.

- **Setting up samples for Portlandite consumption determination:**

After the curing time, samples were crushed making sure that the crushed fraction was fine enough to go through a sieve of $1\ mm$. The collected fraction was subjected to a hydration stoppage using solvent exchange by isopropanol. The procedure described by Snellings et al. [29] was followed. Then, collected samples were tested with a TGA instrument.

A full explanation of this procedure is explained in Appendix 2: $\boldsymbol{R^3}$ test protocol.

The whole procedure is summed up in Figure 3.7.

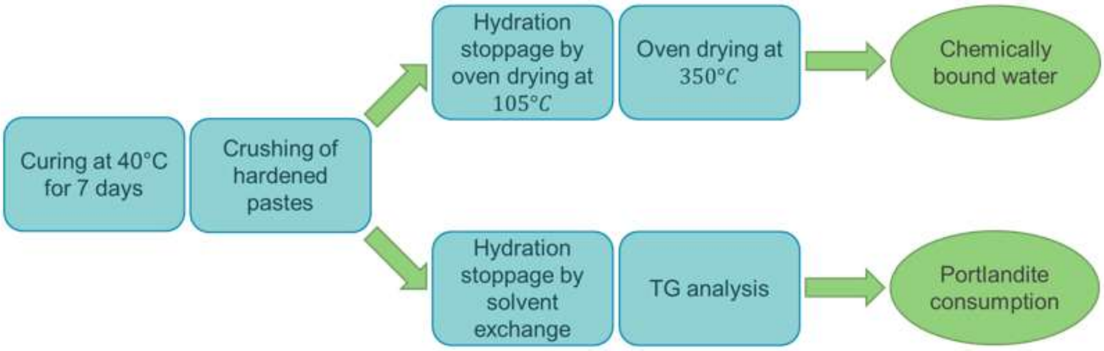

Figure 3.7: R^3 test procedure.

4 Measurement techniques

This chapter describes the working principle and testing protocol of TGA and IC that are used in this study.

All the instruments used in that study and their settings are described widely in Appendix 4: Instrument used and settings.

4.1 Thermogravimetric analysis (TGA)

TGA was used to determine and analyse the content of chemically bound water, the content of Portlandite and calcite.

4.1.1 Access solid composition

TGA technique enables to access relevant information about the composition of the sample tested. Information of interest that can be determined are presented in the following list.

- **Access the chemically bound water of gels:**

Phases $CASH$ or $(K,N)ASH$ that are built during hydration reactions mainly decompose between $105°C$ and $300°C$ A secondary range of dehydration between $650°C$ and $800°C$ has been reported, but it is very low and can be neglected compared to the first range of dehydration [32].

Thus, the chemically bound water can be determined by measuring the difference between the weight right after hydration stoppage and the weight at the temperature of interest. The temperature of interest depends on cases. Notwithstanding, as a general guideline, it should be noticed that the weight losses beyond $550°C$ are not of interest since decarbonation is then the main phenomenon at stake. Therefore, the temperature of interest is generally picked up below that upper limit of $550°C$.

- **Access the Portlandite content:**

Portlandite dehydrates between $400°C$ and $600°C$ according to [32]:

$$Ca(OH)_2 \rightarrow CaO + H_2O \qquad \text{Eq(4.1)}$$

Consequently, the weight loss associated to the release of water molecules enables to derive the Portlandite content.

- **Access the calcite content:**

Calcite decomposes above $600°C$ according to [32]:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{Eq(4.2)}$$

Consequently, the weight loss associated to the release of carbon dioxide molecules enables to derive the Portlandite content.

4.1.2 Use of TGA to analyse raw materials

Raw ashes were tested with a TGA instrument.

It appeared that RISE BA and STENA BA had weight losses related to initial contents in Portlandite and calcite. Water associated to Portlandite dehydration was measured using the tangent method [32]. The Portlandite content was then calculated using:

$$Ca(OH)_{2,measured} = WL_{H_2O,CH} \cdot \frac{M_{CH}}{M_{H_2O}} = WL_{H_2O,CH} \cdot \frac{74}{18} \qquad \text{Eq(4.3)}$$

Carbon dioxide related to calcite decarbonation was evaluated using here as well the tangent method [32]. The calcite content was then derived using:

$$CaCO_3, measured = WL_{CO_2,CaCO_3} \cdot \frac{M_{CaCO3}}{M_{CO2}} = WL_{CO_2,CaCO_3} \cdot \frac{100}{44} \qquad \text{Eq(4.4)}$$

4.1.3 Use of TGA in solution test

In the solution test, the chemically bound water was derived testing samples with TGA instrument.

Chemically bound water determination method:

In the solution test, the only reagents were water, ashes, and alkali hydroxide. It was important to mention that there was no water already bound to any of these reagents. Therefore, the chemically bound water was derived taking the difference between the weight at $105°C$ and at $550°C$.

Here the weight loss interval considered starts at $105°C$ but not at the weight right after hydration stoppage, because in practice there is still a little free water remaining after hydration stoppage. As explained before, taking a temperature beyond $550°C$ is not relevant because of decarbonation, as seen in section 4.1.1 .

4.1.4 Use of TGA in R^3 test

The chemically bound water and the Portlandite consumption were derived in the R^3 test.

Chemically bound water determination method:

A thermogravimetric analysis in a high temperature oven was done to determine the chemically bound water in the R^3 test.

In the R^3 test, the main reagents were water, Portlandite, calcite and a SCM. One must understand that the water which is already bound to Portlandite is not of interest since this type of water has not been chemically fixed during the hydration reaction of the ashes.

Consequently, in the R^3 test, the chemically bound water content was calculated between the weight after drying between $105°C$ and $350°C$ because Portlandite dehydrates beyond $400°C$ as seen in section 4.1.1 .

Figure 4.1 illustrates a simplified graph showing the temperature profile of the procedure in function of the time.

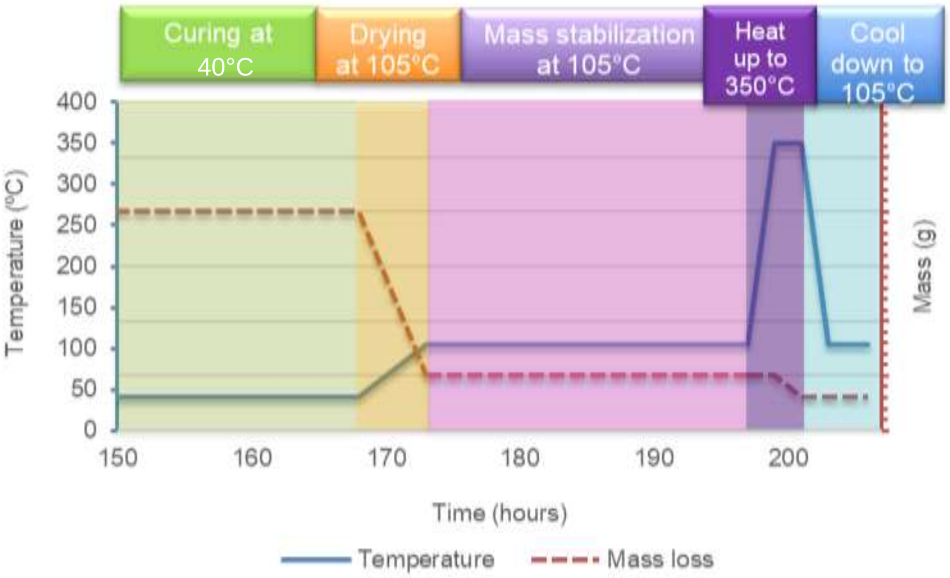

Figure 4.1: R^3 method procedure.

Then the chemically bound water was derived as follow:

$$\text{Bound water (\%)} = \frac{\mathrm{m}_{105°\mathrm{C,stablized}} - \mathrm{m}_{105°\mathrm{C,cooled\ down\ from\ 350°C}}}{\mathrm{m}_{105°\mathrm{C,stablized}}} \cdot 100 \qquad \textit{Eq(4.5)}$$

<u>Portlandite consumption determination method:</u>

In the R^3 test, the Portlandite consumption was derived testing samples with a TGA instrument.

The water chemically bound to Portlandite ($WL_{H_2O,CH}$) was directly derived using the Tangent method described in “A Practical Guide to Microstructural Analysis of Cementitious” [32].

From that value, the amount of Portlandite ($CH_{residual,measured}$) in the hydrated paste was calculated using the ratio between the molecular mass of Portlandite ($M_{CH} = 74\ \frac{g}{mol}$) and water ($M_{H_2O} = 18\ \frac{g}{mol}$) [33].

$$CH_{residual,measured} = WL_{H_2O,CH} \cdot \frac{M_{CH}}{M_{H_2O}} \qquad \textit{Eq(4.6)}$$

However, one must notice that the weight of the solid phase before and after hydration was not the same since water was bound to it. Therefore, results need to be rescaled to an anhydrous solid fraction: the fraction that was remaining after a drying at $600°C$ ($W_{600°C}$) where all the water chemically bound was released. The rescaled value ($CH_{residual,anhydrous}$) were obtained as follow [34]:

$$W_{600°C} \rightarrow 100\%$$
$$CH_{residual,measured} \rightarrow CH_{residual,anhydrous}$$

$$\Rightarrow CH_{residual,anhydrous} = \frac{CH_{residual,measured}}{W_{600°C}} \cdot 100\% \qquad \textit{Eq(4.7)}$$

Finally, a normalised value of Portlandite content per gram of ashes ($CH_{normalised}$) was derived. That normalisation was done based on the initial content of ashes (P_{ashes}) introduced in the mix design [34]. In the case of the R^3 test, the percentage of ashes in the solid mix design was $P_{ashes} = 21.60\%$.

$$P_{ashes} \rightarrow 100\%$$
$$CH_{residual,anhydrous} \rightarrow CH_{normalised}$$

$$\Rightarrow CH_{normalised} = \frac{CH_{residual,anhydrous}}{P_{ashes}} \cdot 100\% \qquad Eq(\ 4.8)$$

However, for a better pertinence, the normalised value calculated just above should consider the initial content of Portlandite introduced in the mix design. That normalised value ($CH_{normalised,CH_{added}}$) was obtained as follow [34]:

$$CH_{normalised,CH_{added}} = \frac{CH_{residual,measured} - (WL_{H_2O,CH_{added}} \cdot \frac{M_{CH}}{M_{H_2O}}) \cdot P_{CH_{added}}}{W_{600°C}} \cdot \frac{1}{P_{ashes}} \cdot 100\%$$

Eq(4.9)

$P_{CH_{added}}$ is the percentage of Portlandite added in the mix design.
Within this study: $P_{CH_{added}} = 64.79\%$.

$WL_{H_2O,CH_{added}}$ was the water chemically bound in the raw Portlandite added initially in the mix design. One must notice that once that content of water was multiplied by the ratio $\frac{M_{CH}}{M_{H_2O}}$, the result might not be 100%, because of the probable dehydroxylation of a part of the Portlandite which was exposed to CO_2 of the atmosphere. However, the data was not given in this study. Thus, the Portlandite used was assumed as pure as indicated on the bottle ($WL_{H_2O,CH_{added}} \cdot \frac{M_{CH}}{M_{H_2O}} = 95\%$).

4.2 Ion chromatography analysis

IC was used to determine and analyse ion concentrations.

4.2.1 Access ion concentrations

The IC analysis was used to get the intensity of different ions in the solution. This method was developed in the end of the 20th century, replacing efficiently the titration method for the determination of ion concentrations in solutions. It is less laborious than titrations which is fastidious and prone to interferences.

However, the intensity measured by the IC cannot be directly related to a concentration. Therefore, standard solution with known concentration must be studied first to relate a peak intensity or a peak area to a concentration.

4.2.2 Use of IC in the solution test

The concentration of sodium, potassium and calcium were studied in the solution test with the IC technique.

Ion concentrations determination method:

Five standard solutions were prepared to plot a standard curve. Moreover, one must notice that the order of magnitude required to measure concentrations with IC was around the millimole per liter. Thus, the five standard solution concentrations were $0{,}01\ \frac{mmol}{L}$, $0.1\ \frac{mmol}{L}$, $0.5\ \frac{mmol}{L}$, $1\ \frac{mmol}{L}$ and $2\ \frac{mmol}{L}$ for each ion of interest.

A detailed explanation of how were prepared the standard solutions is provided in Appendix 1: Solution test protocol.**¡Error! No se encuentra el origen de la referencia.**

Once the standard solutions were prepared and analyzed in the IC the standard curves were plotted as shown in Figure 4.2 and Figure 4.3.

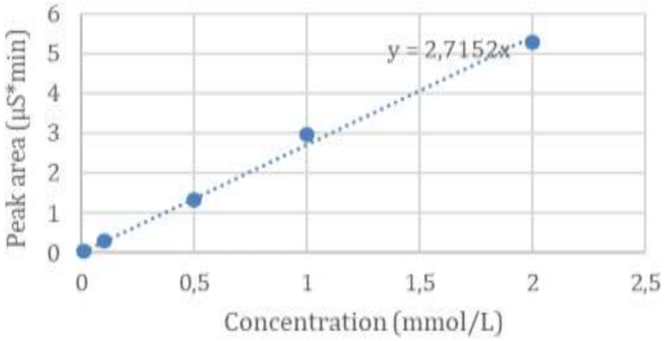

Figure 4.2: Standard curve for sodium.

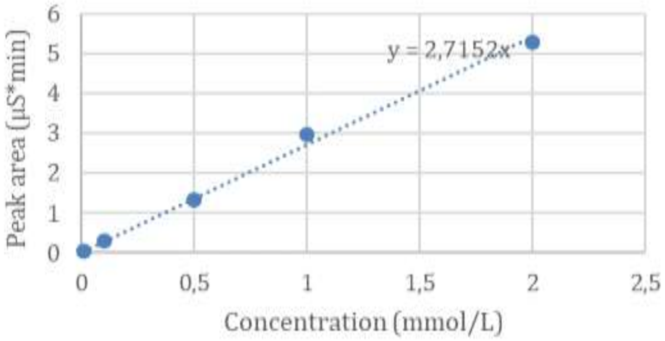

Figure 4.3: Standard curve for potassium.

Samples with unknown concentrations were analyzed relating their peak intensity with a concentration by using the standard curves. Nevertheless, samples were diluted to be in the range of standard concentrations. Therefore, it is necessary to have an idea of the concentration of species in solution. For sodium and potassium, the initial concentration was $1\ \frac{mol}{L}$. Assuming the concentration was still close to that value after the experiment, a dilution was carried with a factor of 1000, which the concentration was reduced to $1\ \frac{mmol}{L}$ to fit the IC work frame.

5 Results

5.1 Raw materials characterization

5.1.1 Particle size

After a particle distribution analysis (PDA), it can be obtained the size distribution as well as the grading curves from the bottom ashes provided. These curves were shown in Figure 5.1 and Figure 5.2.

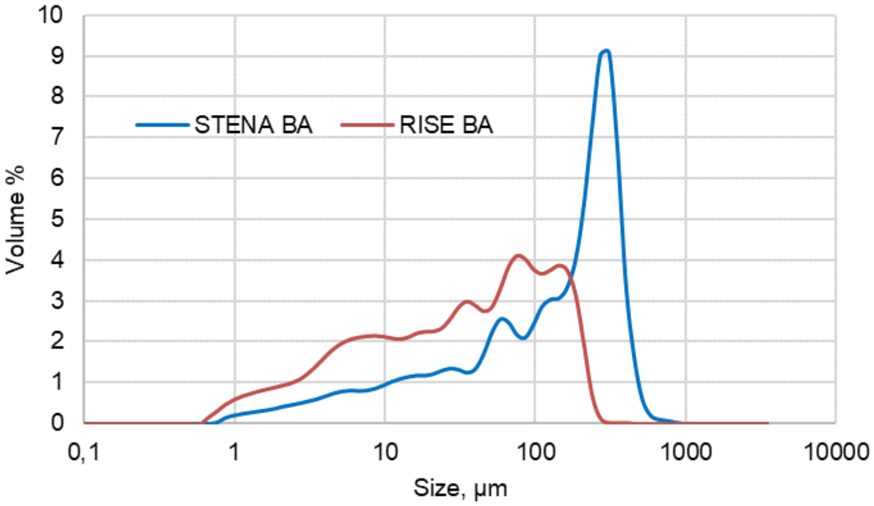

Figure 5.1: Size distribution curves.

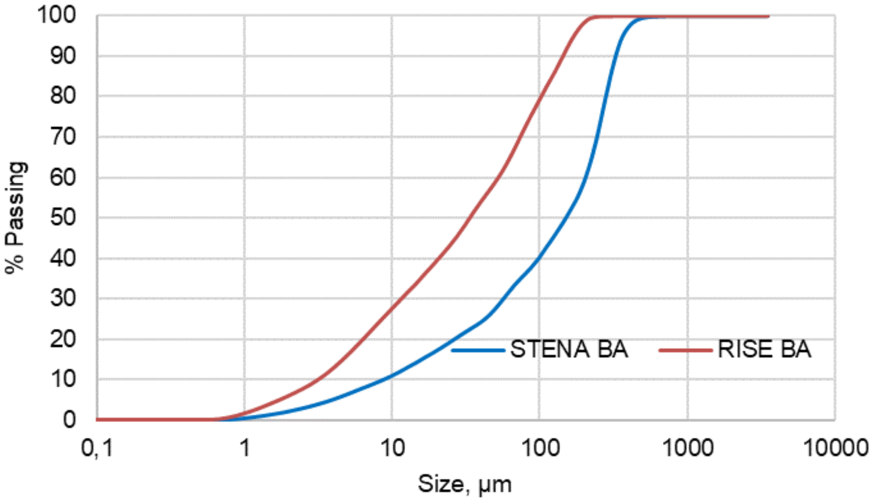

Figure 5.2: Grading curves.

As seen in Figure 5.1 and Figure 5.2, the diameter of RISE BA particles varied between $0.6\ \mu m$ and $250\ \mu m$. The distribution was more homogeneous than that of Stena BA. As key values, 50% of the ashes had a diameter above $33\ \mu m$, the specific surface area was $2525\ \frac{cm2}{g}$, and the particle diameter average was $58\ \mu m$.

In Figure 5.1 and Figure 5.2, the diameter of STENA BA particles varied between $0.6\ \mu m$ and $355\ \mu m$. The distribution was quite disparate within this range, where a peak can be observed for a particle diameter of $310\ \mu m$. As key values, 50% of the ashes had a diameter above $170\ \mu m$, the specific surface area was $1046\ \frac{cm^2}{g}$ and the particle diameter average was $172\ \mu m$.

The SLAG had a specific surface area of $5000\ \frac{cm^2}{g}$. Supposing a density value was between 2 and $2.5\ \frac{g}{cm^3}$, the average grain diameter can be obtained by:

$$S = \frac{3}{\rho \cdot r} \qquad \text{Eq(5.1)}$$

According to it, the diameter can vary between 4.8 and $6\ \mu m$.

The median particle diameter for each kind of ashes was indexed in Table 5.1. One can observe that the diameter of particles was rather different from one kind of ashes to another. This parameter makes the comparison between different ashes more complicated. However, an additional sieving process was not done because of practical reasons. Indeed, ashes that have been given are also studied by others and our results might be more useful if the same particle size was kept for comparison.

Table 5.1: Particle size of each addition studied.

Kind of ash	Particle diameter average (μm)
SLAG	$4.8 - 6$
RISE BA	58
STENA BA	172

5.1.2 Thermogravimetric analysis

RISE BA and STENA BA were also analyzed by thermogravimetric analysis (TGA). According to the TGA and derivative thermogravimetric (DTG) curves in Figure 5.3 and Figure 5.4, it can be established that RISE BA contained a small portion of Portlandite and calcite; while STENA BA contained a small amount of calcite.

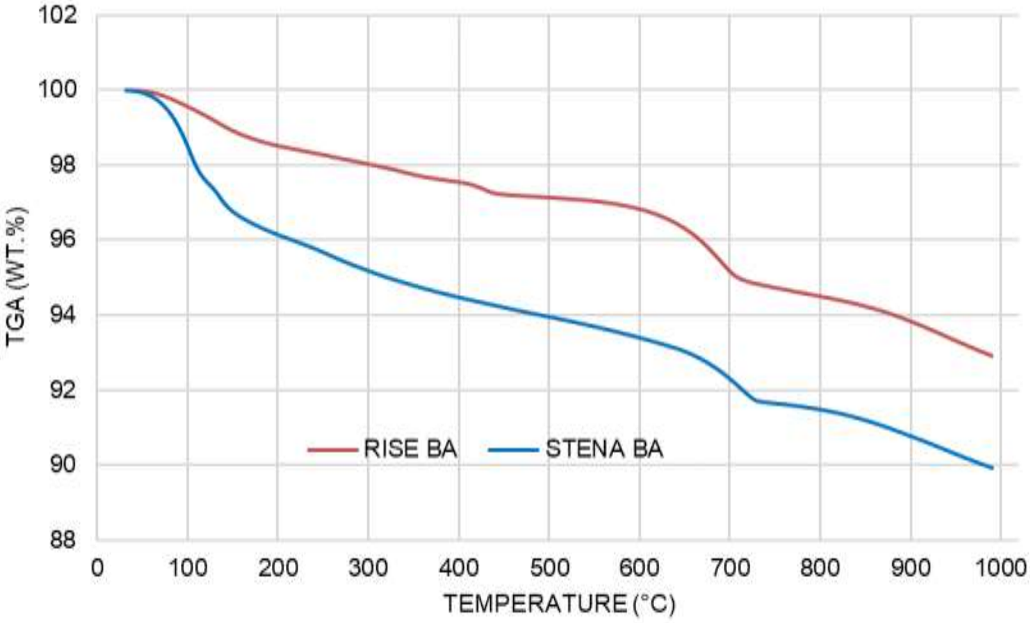

Figure 5.3: TGA bottom ashes.

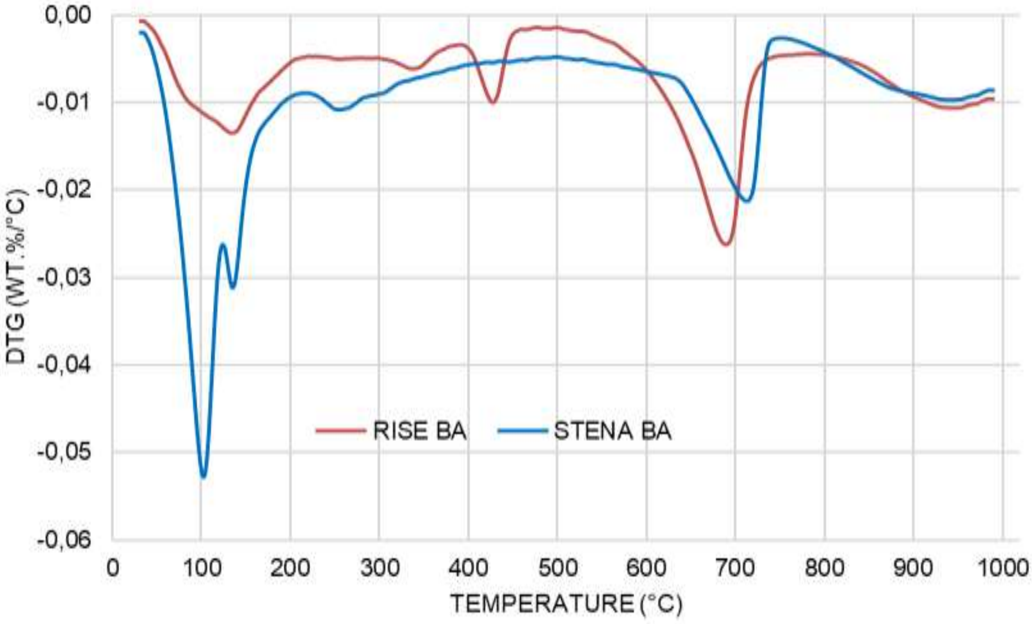

Figure 5.4: DTG bottom ashes.

For RISE BA the peak observed between $393°C$ and $453°C$ corresponded to the water released from calcium dioxide $Ca(OH)_2$. Another peak in between $560°C$ and $720°C$ can be observed. This peak corresponded to the decomposition of calcite ($CaCO_3$) into CaO and CO_2.

In addition, the results from TGA showed that STENA BA contained a certain initial content of moisture (6.8%). Still from TGA (Figure 5.3) and DTG (Figure 5.4) curves, a peak can be observed between $635°C$ and $743°C$. This peak corresponded to the decomposition of calcite ($CaCO_3$) as seen for RISE BA.

According to Lothenbach et al. [32] and following methods explained in section 4, the contents of Portlandite and calcite can be derived and results were presented in Table 5.2.

Table 5.2: TGA results for bottom ashes.

	Portlandite	Calcite
RISE BA	0.8346%	3.0796%
STENA BA	–	2.1046%

5.2 Solution test

For the solution test, two series were carried out with exactly the same parameters from one series to another one in order to obtain comparable results to analyse.

5.2.1 Observation of the mixed samples

Figure 5.5 shows the pictures taken during the experiment after 7 days of waiting time. It enlightened that SLAG displayed the best reaction rate while STENA BA seemed to react less than both SLAG and RISE BA. The amount of hydrated products was larger for SLAG than that for STENA BA. Moreover, the mixture of RISE BA was closer to SLAG than to STENA BA.

Figure 5.5: Samples at 7 days in solution test.

5.2.2 TGA results

Results of the first series are presented in Figure 5.6 and Figure 5.7. Results of the second series are presented in Figure 5.8 and Figure 5.9.

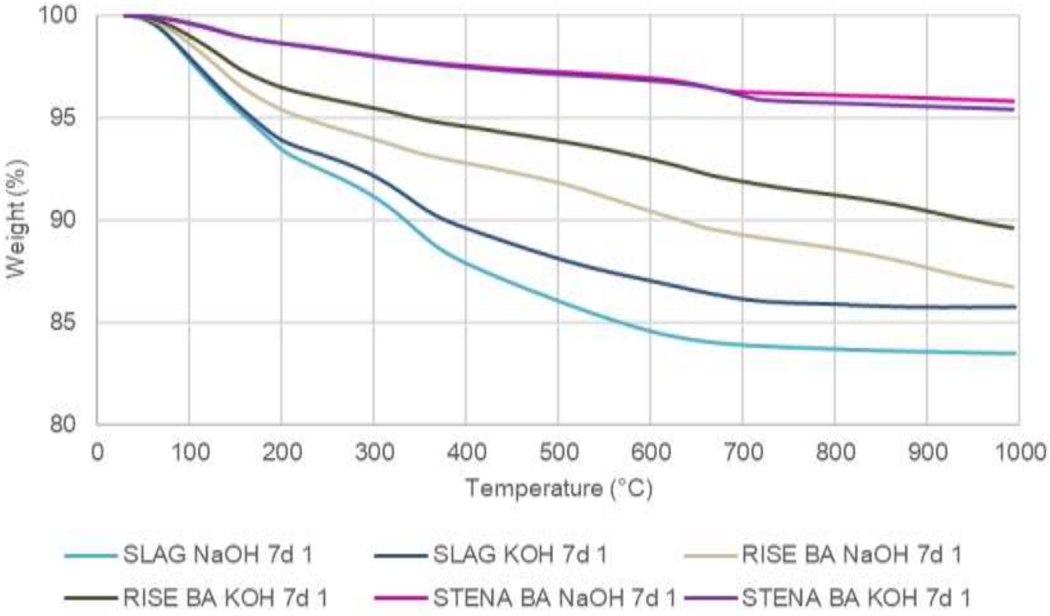

Figure 5.6: TGA results for solution test first series.

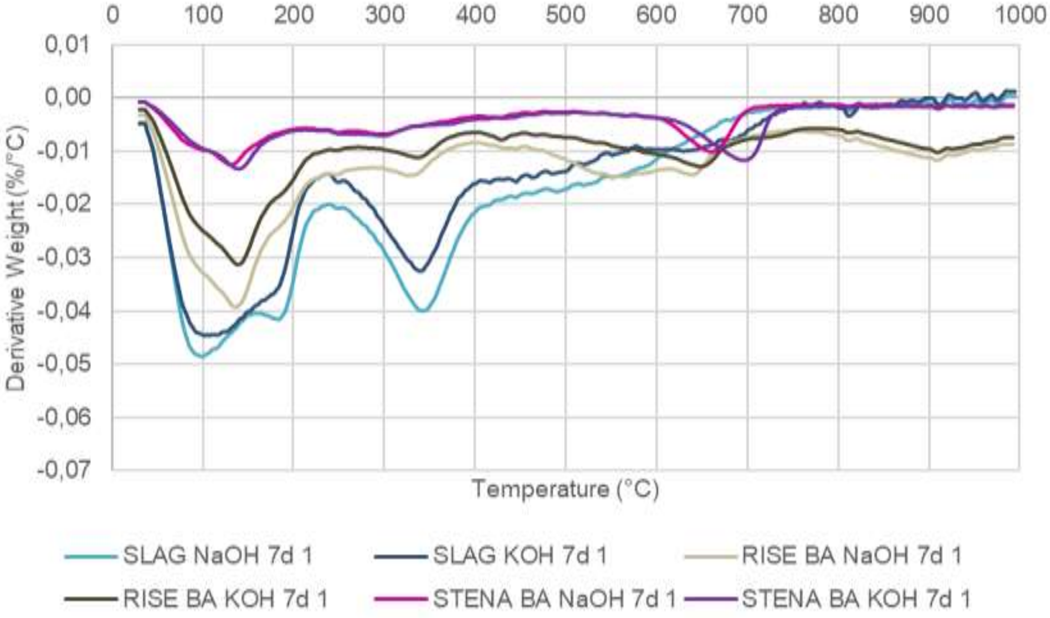

Figure 5.7: DTG results for solution test first series.

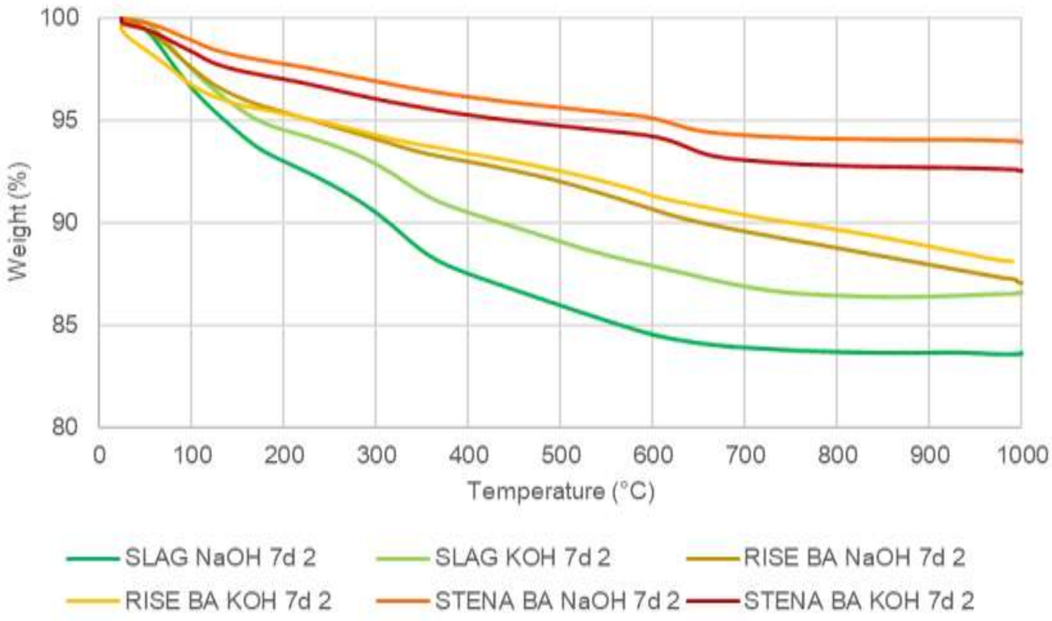

Figure 5.8: TGA results for solution test second series.

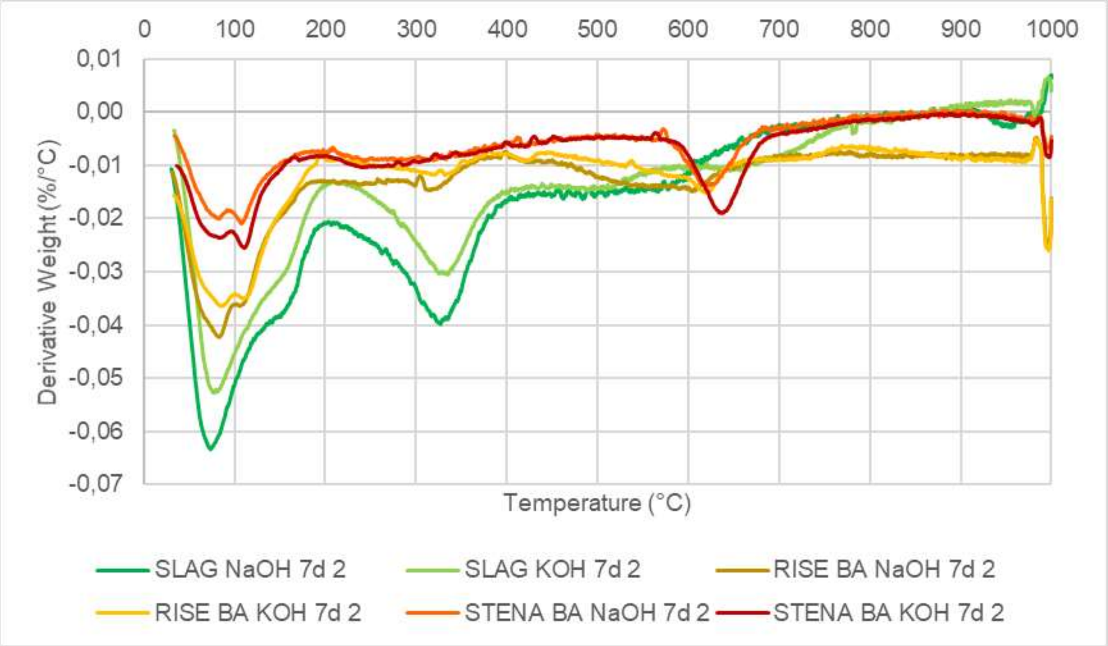

Figure 5.9: DTG results for solution test second series.

Figure 5.6, to Figure 5.9 clearly showed that the chemically bound water content was the highest for SLAG, and the lowest for STENA BA. Moreover, it seemed that samples subjected to $NaOH$ showed a higher content of bound water, therefore a higher content of built phases, while those subjected to KOH showed less bound water. Figure 5.7 and Figure 5.9 showed that the peaks related to samples cured with $NaOH$ were deeper for all kind of ashes under temperatures of $400°C$. The only exception that can be notice was that in the second series of STENA BA the peaks related to KOH were sharper (Figure 5.9).

Moreover, it must be noticed that for the same kind of ash, both TGA and DTG curves (Figure 5.6, Figure 5.7, Figure 5.8, Figure 5.9) have the same shape, independent of

$NaOH$ or KOH treatment. It showed that the same kind of phases were built, only the amount differed according to sodium or potassium conditioning.
In DTG curves (Figure 5.7and Figure 5.9), it showed that below $400°C$, the three kinds of ashes had the same peak locations even though the amplitude was different and small shifts can be noticed. Despite these differences, it might be concluded that the same kind of phases were built below $400°C$, independent of the types of ashes.

Peaks above $400°C$ were out of interests because phases of $(N,K)ASH/CASH$ were mainly decomposed above that temperature as explained in section 4.1.1 . However, looking at Figure 5.7 and Figure 5.9, one can notice that SLAG did not show any peaks above $400°C$ unlike RISE BA ad STENA BA. That can be explained in the following way. The chemical analysis of RISE BA revealed that there is an initial content of Portlandite and calcite. It explained peaks between $400°C$ and $550°C$ as well as the one above $600°C$ (see section 4.1.1). Similarly, the chemical analysis of STENA BA revealed that an initial content of calcite, which explained the peaks above $600°C$ (see section 4.1.1). As it can be observed in Figure 5.10 and Figure 5.11, a part of Portlandite and calcite were consumed during the reaction process, but it seemed it remains a little bit of them.

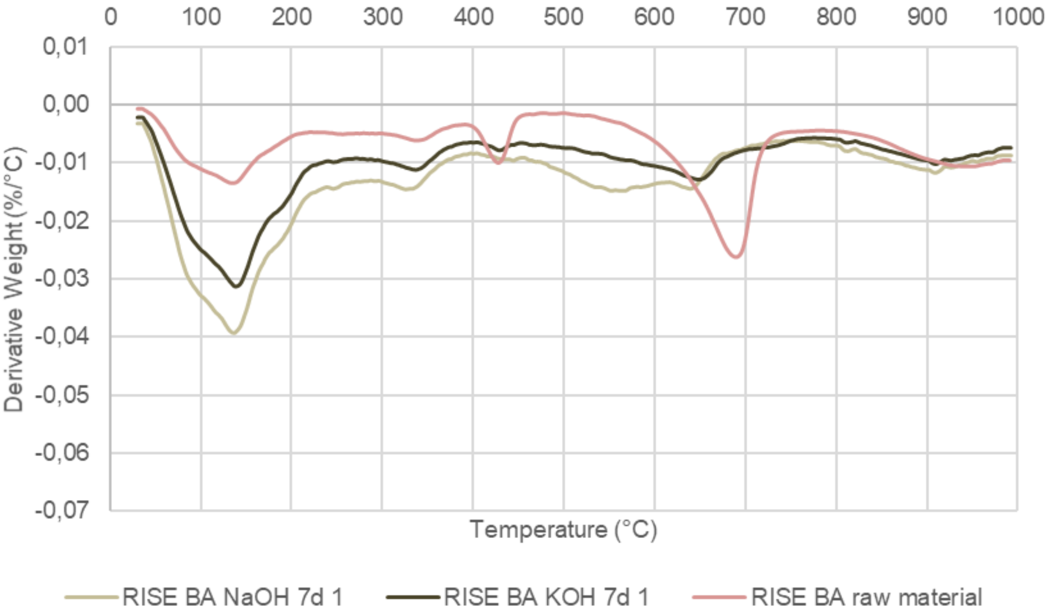

Figure 5.10: Comparing DTG results of RISE BA first series and RISE BA raw material.

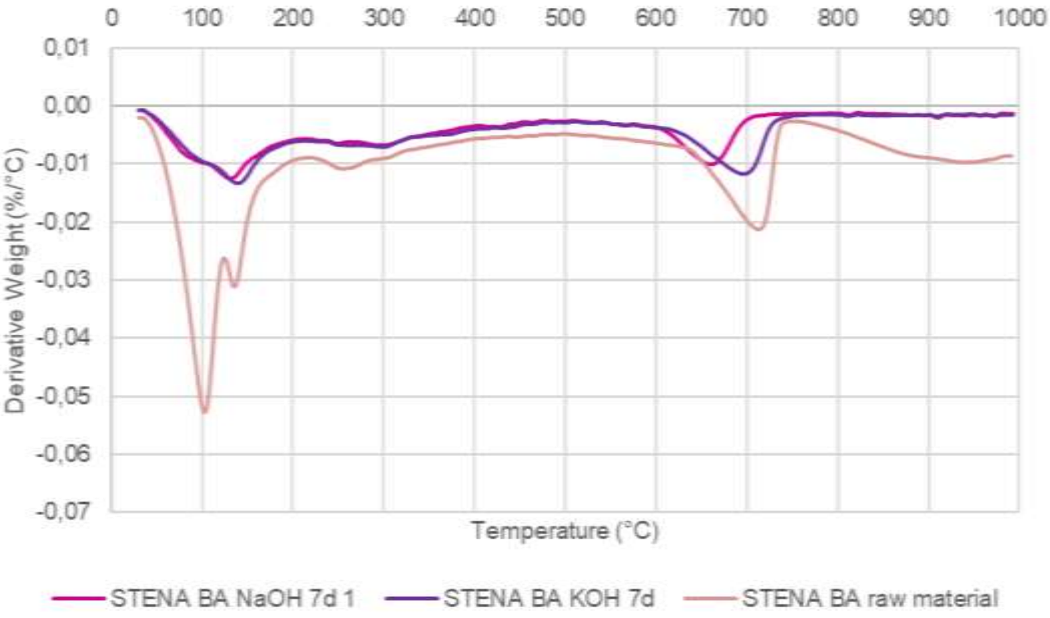

Figure 5.11: Comparing DTG results of STENA BA first series and STENA BA raw material.

5.2.3 Chemically bound water derivation

The chemically bound water was calculated according to the thermogravimetric (TG) results. According to the method explained in section 4.1.3 , the upper limit chosen was $550°C$. However, unlike in section 4.1.3 , the weight loss was not calculated by doing the difference between the weight at $105°C$ and $550°C$. An important fact must be considered that the heating rate of $10\ \frac{°C}{min}$ was a little higher, and the weight introduced in the TG instrument was not the same as in the first (around $50\ mg$) and the second series (around $10\ mg$). Details were reported in Appendix 4: Instrument used and settings. Those two parameters may shift the real range of the evaporation of free water as well as other peaks, as seen in Figure 5.12.

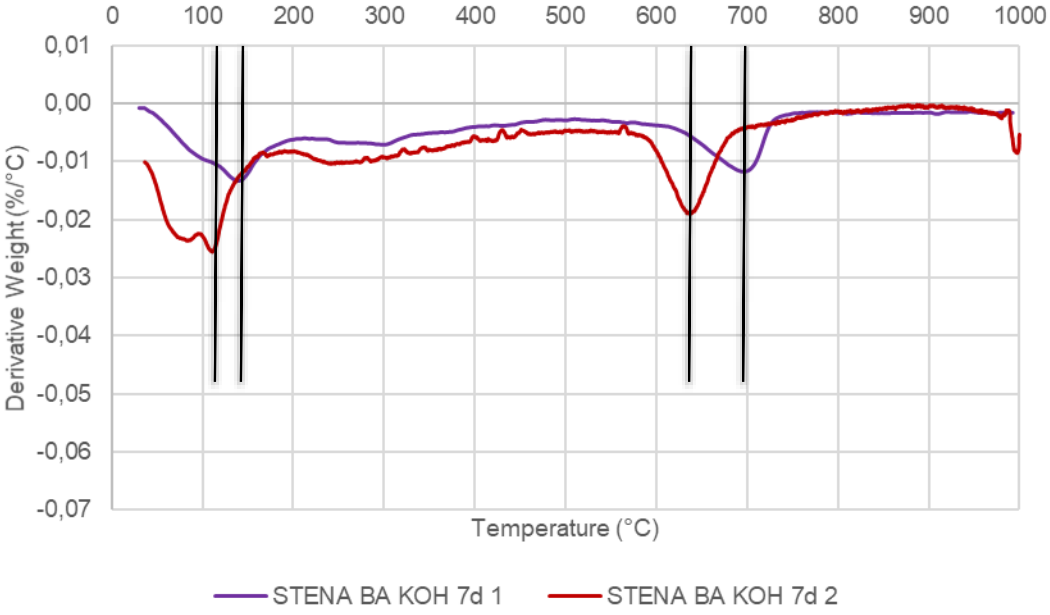

Figure 5.12: Peak shifts between STENA BA KOH series 1 and STENA BA KOH series 2 due to different weighs taken for TGA.

Therefore, the method consisted in taking the temperature associated to the deepest peak close to $105°C$ as the new reference for the evaporation of free water. Then the weight associated to the upper limit $550°C$ must be shifted as well according to the new reference. In this way, the same interval length can be kept for weight measurements. The weigh difference was therefore derived according to the new interval that was shifted. The procedure is exemplified in Figure 5.13.

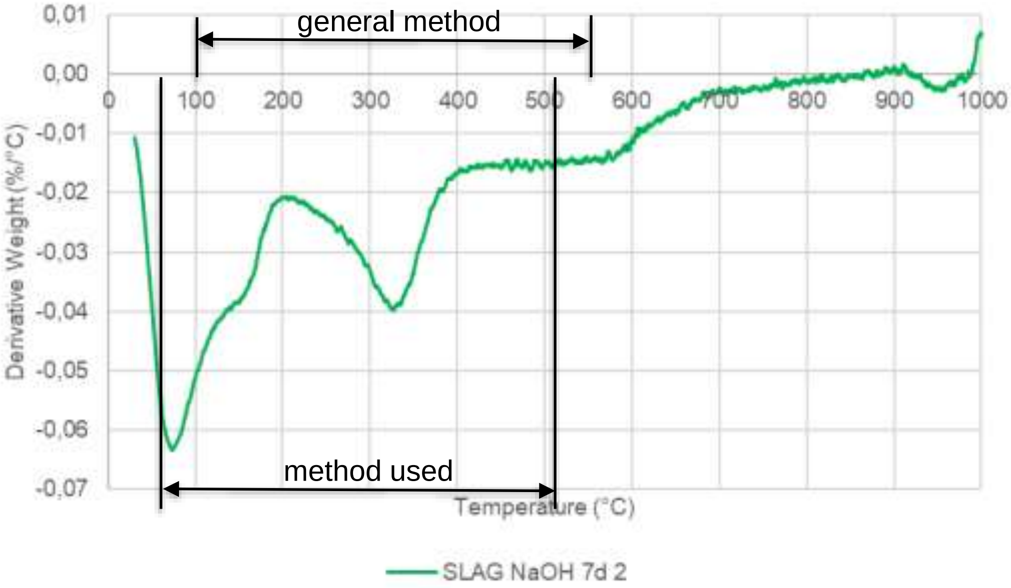

Figure 5.13: Difference between the general method and the method used.

Bound water content was derived accordingly. The results of an average between the two series is presented in Figure 5.14 .

From Figure 5.14, it confirmed that SLAG displayed the best reactivity and STENA BA the worst. STENA BA had a low content of bound water, meaning that they were not activated, by either potassium or sodium treatment.

When ashes were well activated, which was the case for SLAG and RISE BA, it showed that sodium behaved as a better activator.

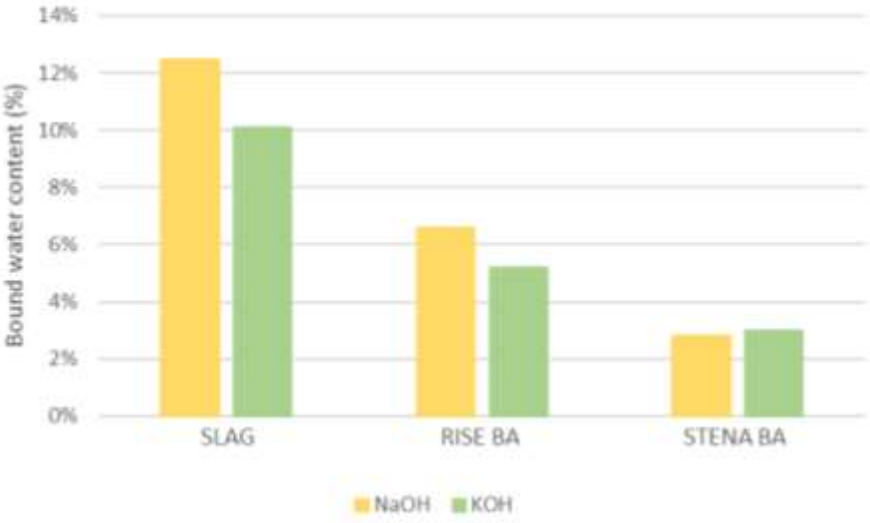

Figure 5.14: Chemically bound water content in solution test.

Table 5.3 presents the ratios of bound water content, taking SLAG as the reference. From these ratios, it was interesting to notice that RISE BA displayed quiet good properties, unlike STENA BA. STENA BA might have a too coarse particle size to enable a good reactivity. It would have been interesting to analyse those ashes with a finer particle size, but such finer STENA BA were not provided for this study.

Table 5.3: Bound water content ratios.

NaOH	RISE BA 1/ SLAG 1	0.52	STENA BA 1/ SLAG 1	0.18
	RISE BA 2/ SLAG 2	0.53	STENA BA 2/ SLAG 2	0.27
	Average	0.53	Average	0.22
KOH	RISE BA 1/ SLAG 1	0.46	STENA BA 1/ SLAG 1	0.22
	RISE BA 2/ SLAG 2	0.58	STENA BA 2/ SLAG 2	0.37
	Average	0.52	Average	0.30

5.2.4 Ion concentrations results

In this project, it was impossible to use an ICP instrument meaning that silicon and aluminum concentrations couldn't be measured. Another issue that must be noticed was the measurement of calcium concentration with IC. One must understand that the IC instrument analyses sodium, potassium and calcium at the same time. However, the concentration of calcium was so low compared to sodium and potassium that the IC instrument cannot measure the calcium content properly. Hence, only potassium and sodium concentrations were measured.

The first series showed that similar trends for these three kinds of ashes studied, as seen in Figure 5.15 and Figure 5.16. The initial concentration introduced for each mix design was 1 $\frac{mol}{L}$. After six hours, it appeared that the concentration was still close to that the initial value. At one day, the concentration drastically decreased. Here the concentration declined because the alkali agent reacted with ion species released from the ashes that are accumulated in the solution to create gels. In the case of SLAG and RISE BA, it can be observed that the final concentration at seven days was higher than the one at one day. This phenomenon can be explained by considering a high initial content of calcium in SLAG and RISE BA. At the beginning, the concentration of calcium ions was low because of the high alkalinity of the media. The dissolution of calcium reduced at the same time as the pH increased. When alkaline cation was consumed, the pH reduced (see section 2.2.3), and calcium can be dissolved. Once calcium was dissolved, it replaced the alkali cations in the gel structure to reach a stable state. That was why the concentration of the alkali cation raised again after one day. Nevertheless, the final concentration at seven days seemed to be stabilized and was lower than 1 $\frac{mol}{L}$, which indicated that sodium ions were consumed and incorporated in the gel structure.

It can also be seen in Figure 5.15 and Figure 5.16 that of these three types of ashes, the final concentrations were rather the same and cannot lead to any differentiation. What can be added was that there was no specific difference between sodium and potassium activation according to the concentration levels.

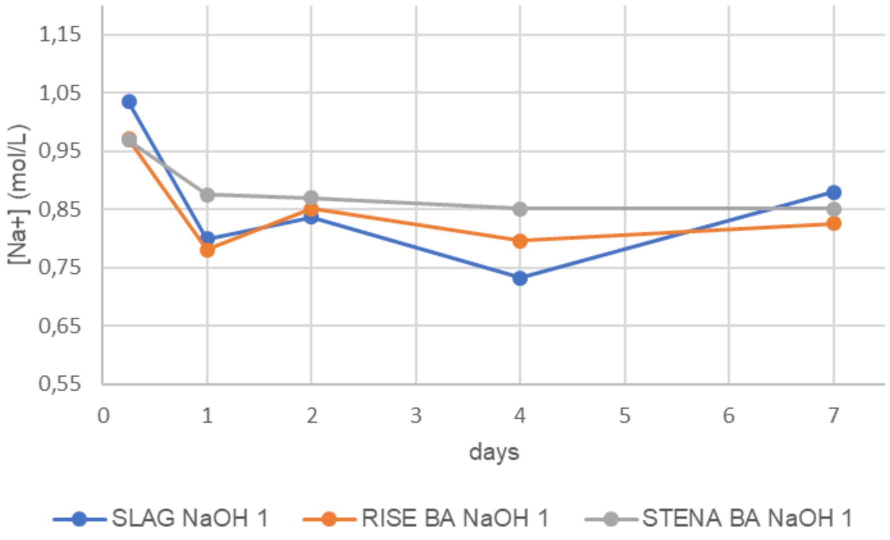

Figure 5.15: $[Na^+]$ *in function of the waiting time, first series.*

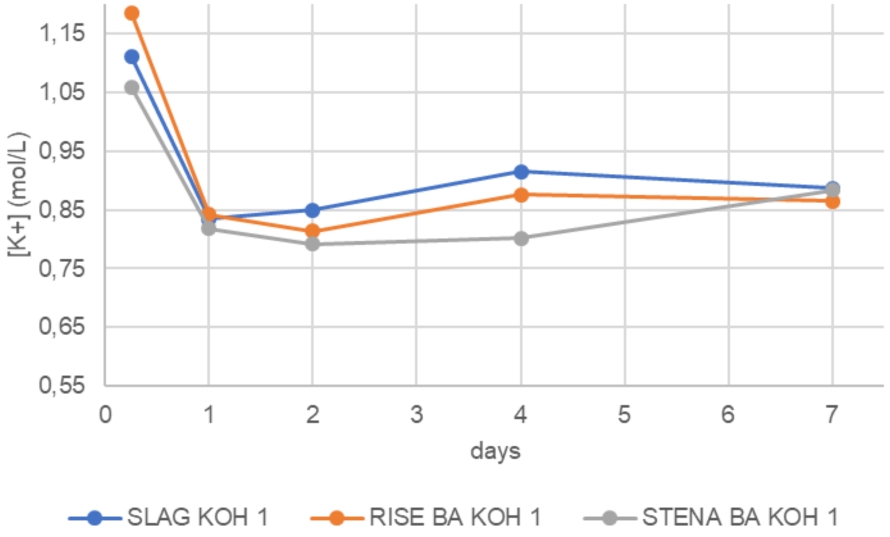

Figure 5.16: $[K^+]$ *in function of the waiting time, first series.*

The second series was interesting because the trends looked very different, at least in the beginning (Figure 5.17 and Figure 5.18). However, one must notice that the first series displayed a significant fall between six hours and one day. In addition, after one day, it raised again. It indicated that around those waiting times, concentrations varied a lot and would require more data points. In addition, the six hours waiting time was rather approximative because of logistic reasons (mainly the laboratory access) and can vary from six hours to eight hours between the first and the second series. That could explain why the concentration was lower at six hours for the second series. Considering all these remarks, the trends can be better related to the one from the first series and was exemplified in Figure 5.19 in the case of RISE BA under sodium activation.

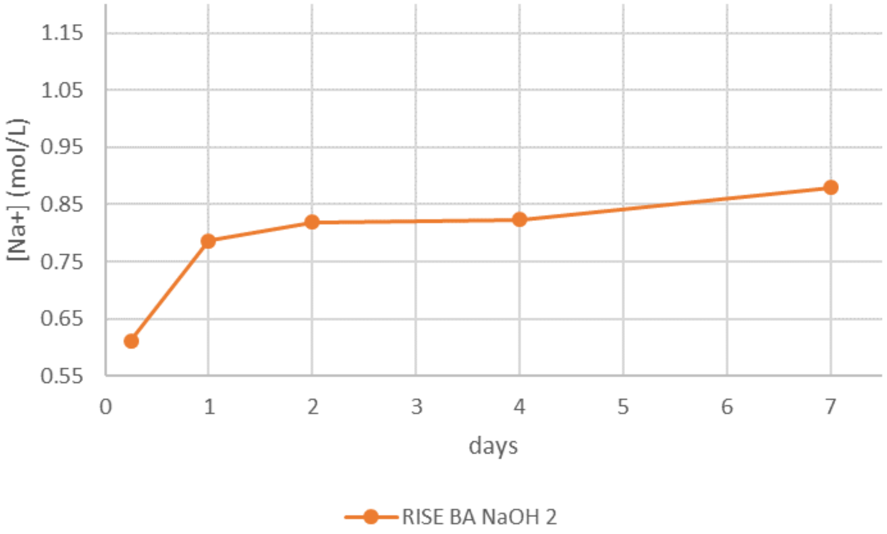

Figure 5.17: $[Na^+]$ *in function of thee waiting time, second series.*

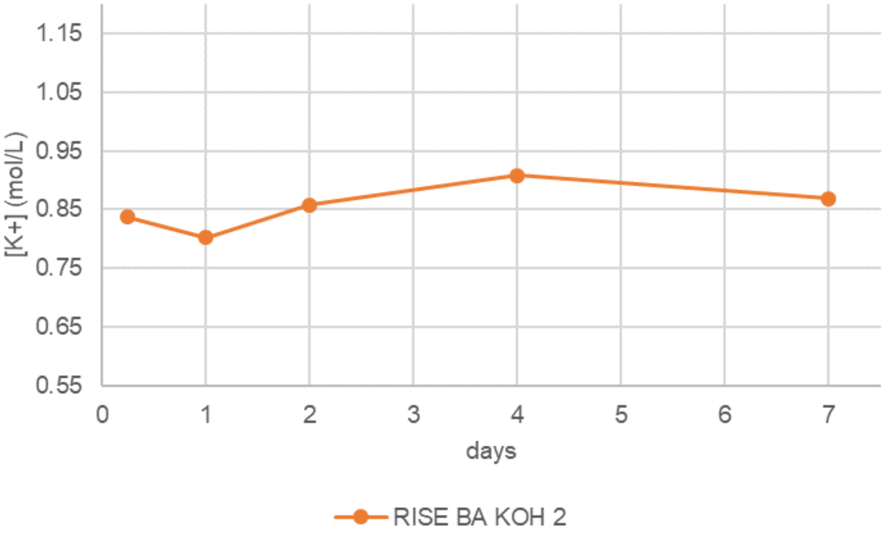

Figure 5.18: $[K^+]$ *in function of thee waiting time, second series.*

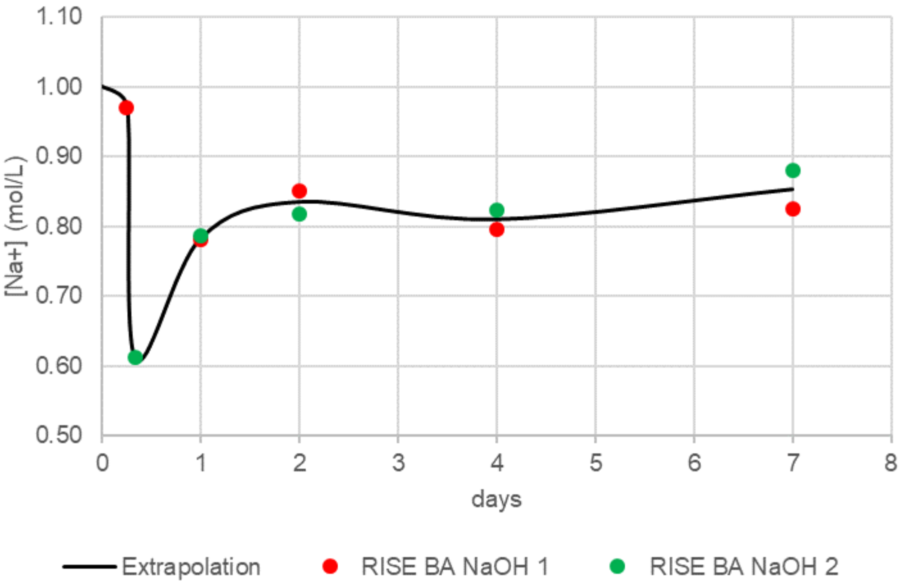

Figure 5.19: Probable trend of $[Na^+]$ *for RISE BA.*

5.3 R^3 test

Three series of experiment were carried out for each kind of ashes with exactly same parameters from one series to another one in order to obtain comparable results to analyse.

5.3.1 Observation of the mixed samples

Before any detailed analysis, a few comments must be made. First, impressions of the experiment are the following one. SLAG paste was the most hardened, behaving as a solid. RISE BA paste displayed also solid properties even if it could be felt that the paste was less hardened. STENA BA paste was in between solid and liquid. As a first assumption, it could be said that STENA BA ashes were not very reactive compared to others. Moreover, it could be seen that a part of STENA BA ashes was agglomerated in the bottom of the container, resulting in a heterogeneous paste (Figure 5.20).

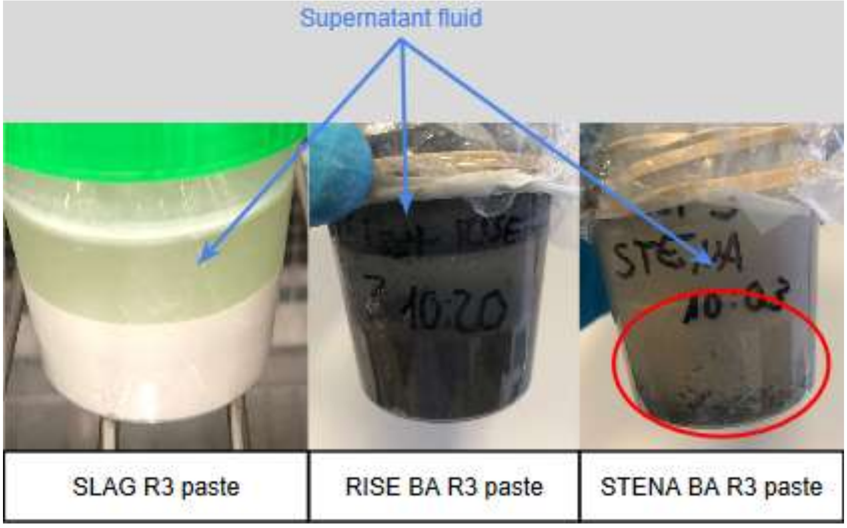

Figure 5.20: R^3 *pastes after 7 days of curing.*

5.3.2 TGA results

Results of the first series are presented in Figure 5.21 and Figure 5.22. Results of the second series are presented in Figure 5.23 and Figure 5.24. Results of the third series are presented in Figure 5.25 and Figure 5.26.

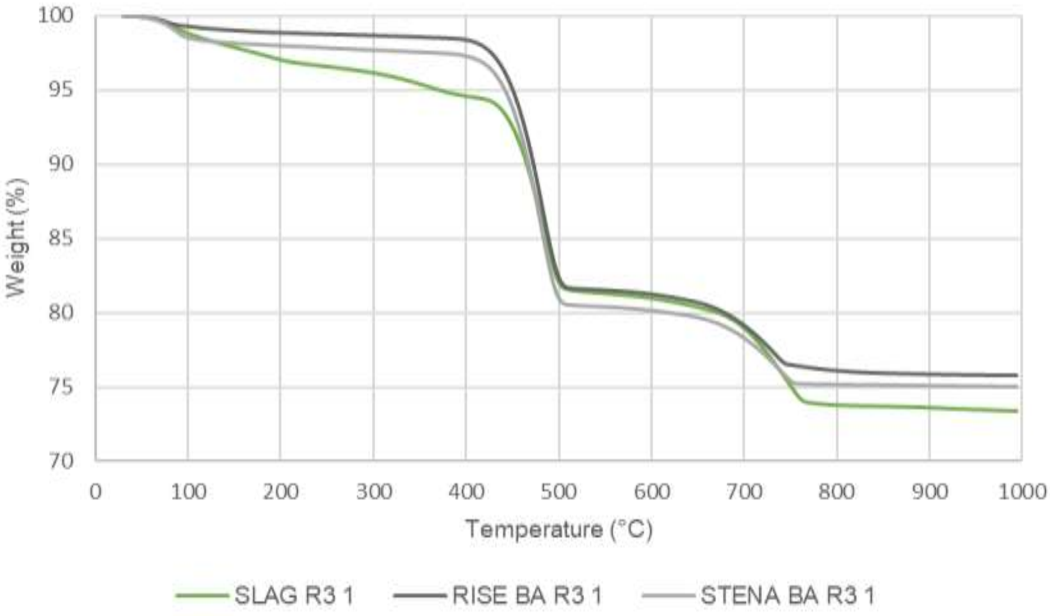

Figure 5.21: TGA results for R^3 test first series.

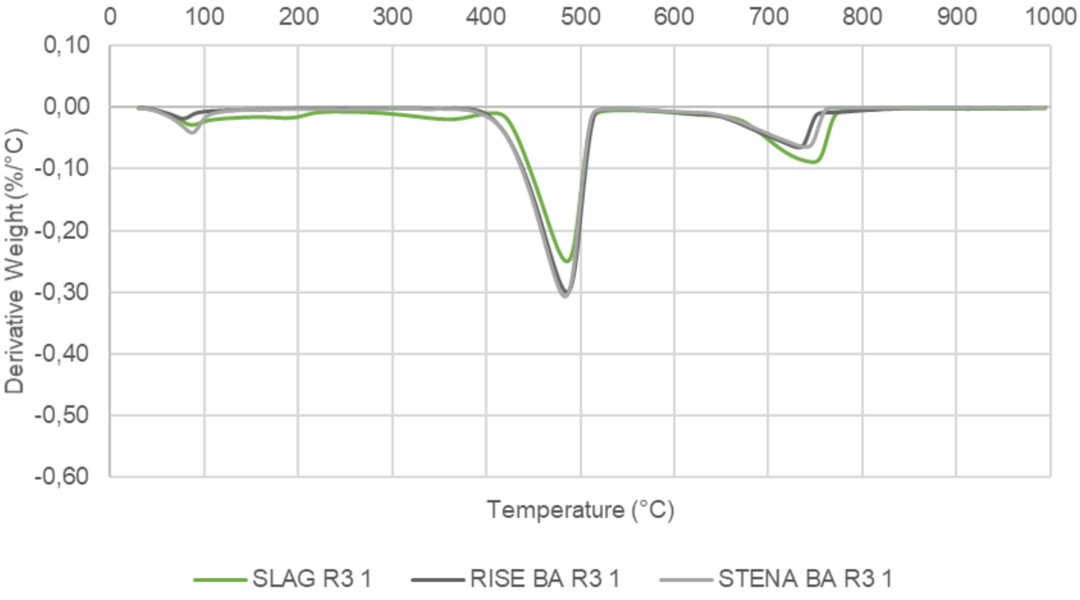

Figure 5.22: DTG results for R^3 test first series.

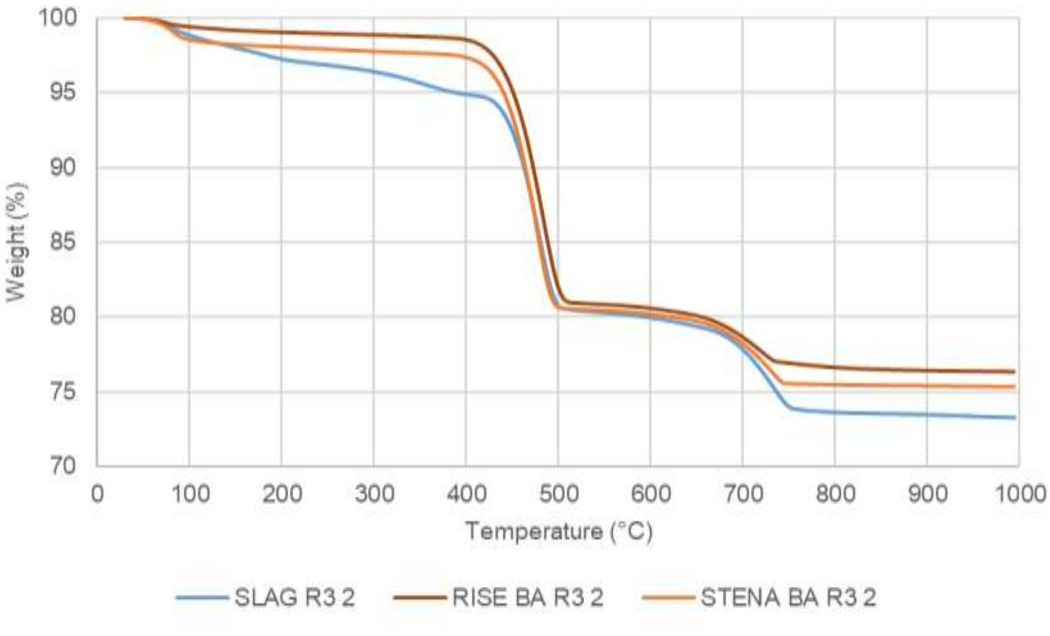

Figure 5.23: TGA results for R^3 test second series.

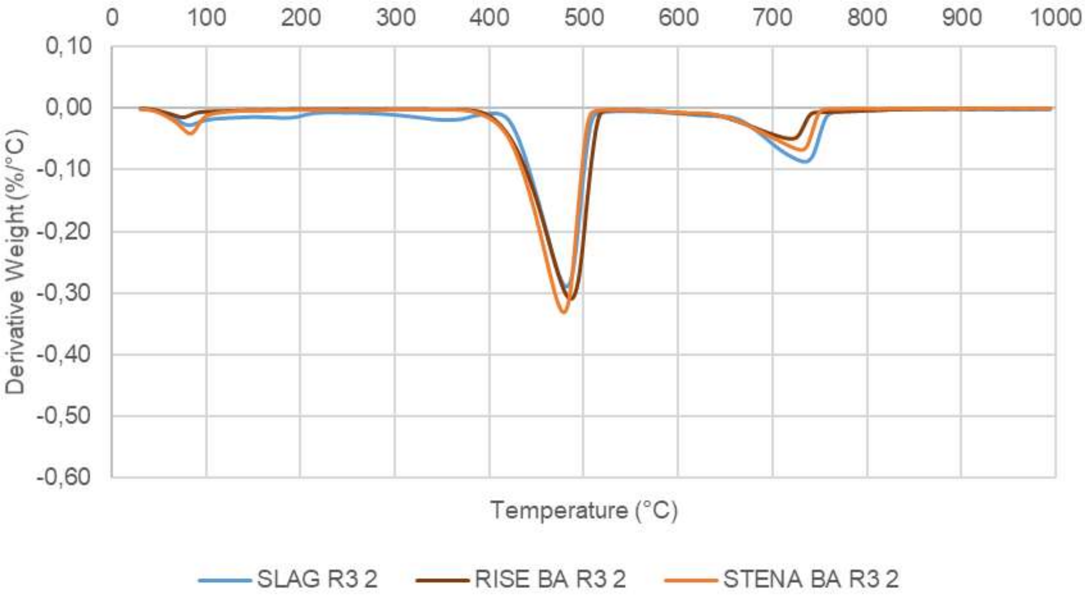

Figure 5.24: DTG results for R^3 test second series.

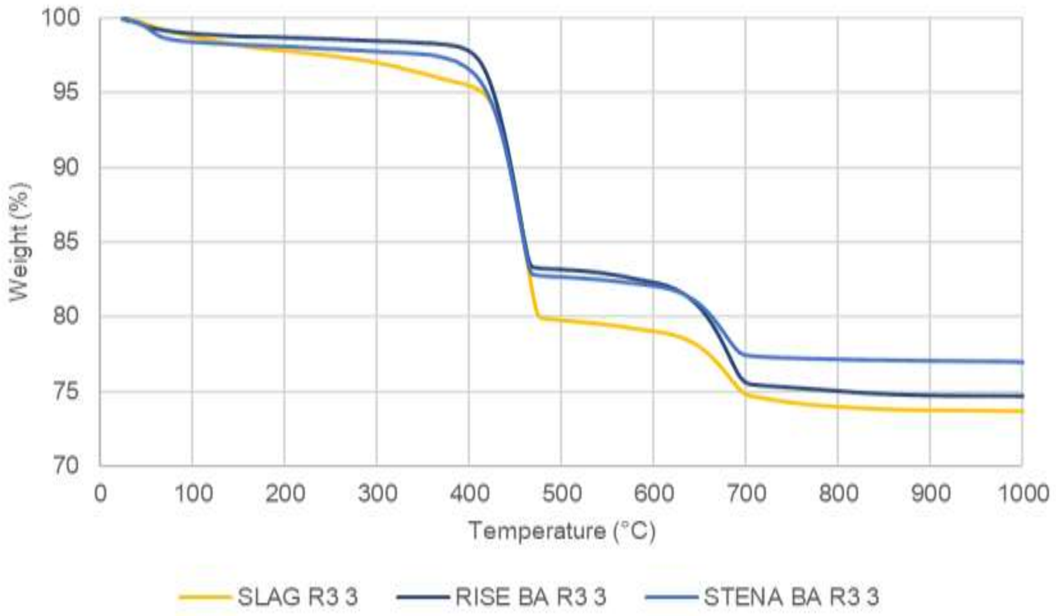

Figure 5.25: TGA results for R^3 test third series.

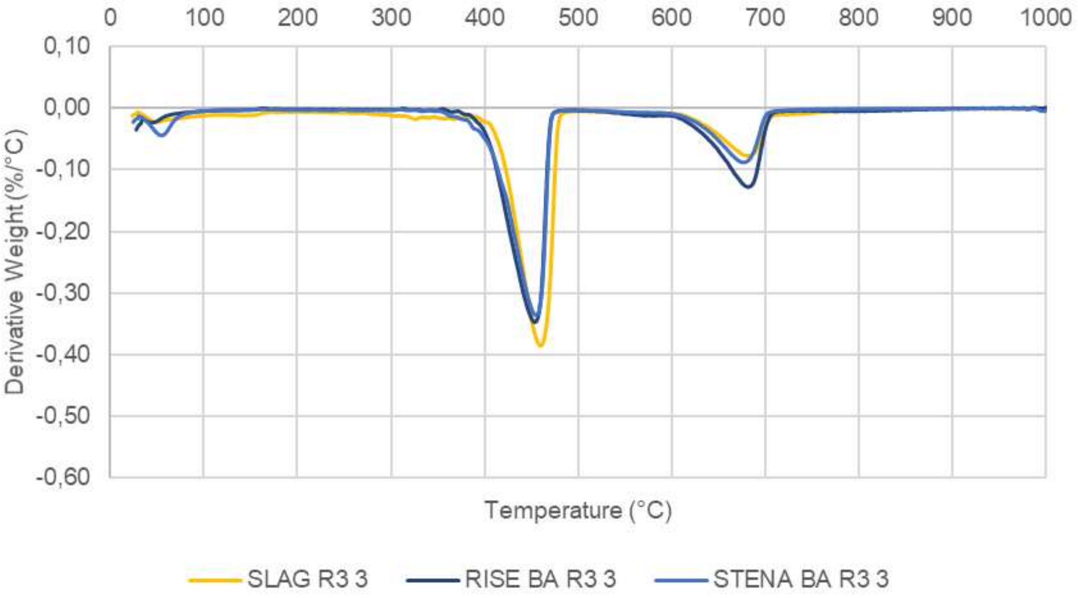

Figure 5.26: DTG results for R^3 test third series.

For SLAG, STENA BA and RISE BA, the main mass loss was located between $400°C$ and $500°C$, which corresponded to the release of the chemically bound water of Portlandite. The second significant mass loss was situated beyond $600°C$ and it referred to the decarbonation of calcite.

Another remark can be concerned for the weight loss around $100°C$ for the three kinds of ashes. One must notice that hydration stoppage by solvent exchange was carried out, meaning no more or only a few free water should remain. Samples were kept in a vacuum desiccator right after hydration stoppage. However, to be analysed, they had to be put into test tubes, therefore a little free water could enter the system again because of moisture. For STENA BA, the peak related to free water evaporation was the largest as shown in Figure 5.22, Figure 5.24 and Figure 5.26. It should be mentioned that solvent exchange might be less efficient because of the size of grains that hindered the isopropanol to penetrate to the core

Last comment concerning the TGA curves (Figure 5.21, Figure 5.23 and Figure 5.25) was that it was rather clear that between $105°C$ and $350°C$, only SLAG lost a significant amount of water. The curves of RISE BA and STENA BA were completely flat in that area. This implied that a concrete pore solution environment does not have enough alkalinity to activate RISE BA and STENA BA. In a concrete pore solution environment, Portlandite is the main one responsible for the alkalinity of the media rising the pH up to 12.3 which might not be enough to dissolve the energetically stable raw materials such as bottom ashes.

5.3.3 Chemically bound water derivation

The results obtained in the three series are presented in Figure 5.27.

Independent of the series, slag displayed the highest content of bound water, followed by RISE BA and finally STENA BA.

One important remark must be done related to Figure 5.27. To get the chemically bound water content, hydration stoppage by drying at $105°C$ was done until the mass stabilization was reached. The temperature used for the third series was a little above $105°C$ (it reached $120°C$) for a few minutes while the target temperature was set at $105°C$. Even if it was a short time, results might be impacted displaying lower content of chemically bound water, which was as a matter of fact the case here. However, even if the results were lower, the trend was the same as for the other series.

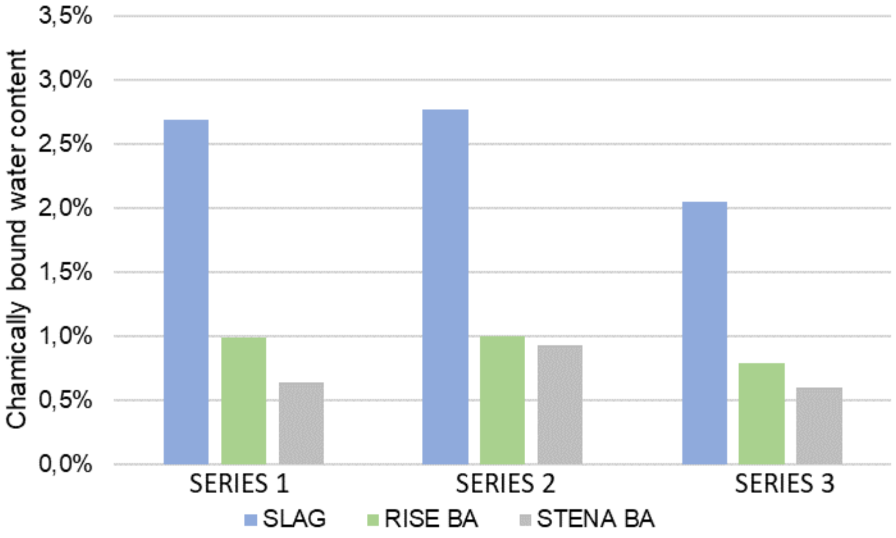

Figure 5.27: Chemically bound water content in R^3 test (oven drying).

A way to check if the third series was relevant, despite of the lower values that might come from the oven technical malfunction, was to calculate the relative difference between SLAG and RISE BA for a same series. SLAG bound water content was taken as a reference. The relative difference was derived as follow, where x refers to the series number:

$$RD_{series\ x} = \frac{H_2O_{bound\%,Slag,series\ x} - H_2O_{bound\%,Rise,series\ x}}{H_2O_{bound\%,Slag,series\ x}} \quad \text{Eq(5.2)}$$

In

Like in the solution test, bound water content ratios were calculated taking SLAG as the reference in Table 5.6. From these ratios, it can be observed that RISE BA and STENA BA were close to each other and were not very reactive compared to SLAG. The alkalinity of the medium might be too low to activate RISE BA and STENA BA.

Table 5.4, the relative difference was almost the same between the three series, meaning that the third series was relevant when SLAG was taken as a reference for comparison of the reactivity. In further into the two first series, the relative difference was very low comparing the bound water content for a same kind of ashes, except for STENA BA as in

Like in the solution test, bound water content ratios were calculated taking SLAG as the reference in Table 5.6. From these ratios, it can be observed that RISE BA and STENA BA were close to each other and were not very reactive compared to SLAG. The alkalinity of the medium might be too low to activate RISE BA and STENA BA.

Table 5.4: Relative difference between SLAG and RISE BA.

SLAG - RISE BA	Series 1	Series 2	Series 3
Relative difference	63%	64%	62%

Table 5.5. The relative difference was calculated as follow where X refers to the kind of ash:

$$RD_{X,series\ 1/X,series\ 2} = \frac{|H_2O_{bound\%,X,series\ 1} - H_2O_{bound\%,X,series\ 2}|}{MAX(H_2O_{bound\%,X,series\ 1}; H_2O_{bound\%,X,series\ 2})} \qquad \text{Eq(5.3)}$$

Like in the solution test, bound water content ratios were calculated taking SLAG as the reference in Table 5.6. From these ratios, it can be observed that RISE BA and STENA BA were close to each other and were not very reactive compared to SLAG. The alkalinity of the medium might be too low to activate RISE BA and STENA BA.

Table 5.4: Relative difference between SLAG and RISE BA.

SLAG - RISE BA	Series 1	Series 2	Series 3
Relative difference	63%	64%	62%

Table 5.5. Relative difference between series 1 and 2.

	SLAG	RISE BA	STENA BA
Relative difference	2.76%	1.17%	31.32%

Table 5.6: Bound water content ratios in R^3 test (oven drying).

RISE BA R3 1/SLAG R3 1	0.37	STENA BA R3 1/SLAG R3 1	0.24
RISE BA R3 2/SLAG R3 2	0.36	STENA BA R3 2/SLAG R3 2	0.34
RISE BA R3 3/SLAG R3 3	0.38	STENA BA R3 3/SLAG R3 3	0.29
Average	**0.37**	Average	**0.29**

5.3.4 Portlandite consumption

According to the formulas stated in section 4.1.4 , it can be seen in Table 5.7 that SLAG had the lowest Portlandite content, meaning that the pozzolanic reaction had been more intense than that for the other ashes. STENA BA and RISE BA results were close, sometimes overlapping each other, making it difficult to compare.

Another relevant comment was that SLAG obtained negative normalised values while those of STENA BA and RISE BA were positive (excepted for the third series).

Negative normalised values indicated that a part of the added Portlandite was consumed in addition of the one that might have been created by the release of calcium ions that were initially in the ashes. In the opposition, positive values indicated that the Portlandite added in the mix design was not used at all, or at least that more Portlandite was created than consumed.

These values enlightened once again that SLAG was activated by Portlandite unlike RISE BA and STENA BA.

Table 5.7: Detailed analysis of Portlandite consumption in R^3 test.

	$WL_{H2O,CH}$	$CH_{residual, measured}$	$W_{600°C}$	$CH_{residual, anhydrous}$	CH_{added_purity}	$CH_{normalised ,CHadded}$
SLAG R3 1	12.0%	81.0%	61.1%	49.5%	95%	-69.1%
SLAG R3 2	13.4%	79.9%	68.8%	55.0%	95%	-37.8%
SLAG R3 3	14.7%	79.0%	76.5%	60.5%	95%	-6.3%
RISE BA R3 1	16.3%	80.6%	83.1%	67.0%	95%	31.2%
RISE BA R3 2	17.2%	81.3%	86.9%	70.6%	95%	51.5%
RISE BA R3 3	14.8%	82.3%	74.1%	61.0%	95%	-3.0%
STENA BA R3 1	16.4%	80.2%	84.3%	67.6%	95%	34.7%
STENA BA R3 2	16.5%	80.2%	84.4%	67.7%	95%	35.6%
STENA BA R3 3	14.5%	82.1%	72.4%	59.4%	95%	-12.0%

5.4 Solution test versus R^3 test

It was interesting to plot the TGA results from both solution and R^3 tests for each kind of material studied. Figure 5.28to Figure 5.30 present the collective results.

The first comment that can be stated was that, for SLAG and RISE BA, the weight loss between $105°C$ and $350°C$ was more important in the solution test than in the R^3 test. That fact can be easily explained because of the higher alkalinity of the medium in the solution test. Indeed, in the solution test the pH was about 14, while in the R^3 test the pH was ruled by the Portlandite dissolution, which means it cannot be higher than 12.3. STENA BA did not display that much differences difference between the two tests in the tested range of temperature, which means that the activation, if it exists, was the same in the two tests.

However, in Figure 5.29 and Figure 5.30, in the range $105°C - 350°C$, it was rather clear that RISE BA and STENA BA were not activated at all in the R^3 test. On the contrary, SLAG displayed good reactivity, both in solution test and R^3 test.

Thus, Portlandite, the alkaline agent in the R^3 test, was not strong enough to activate RISE BA and STENA BA. The alkalinity of the solution test (fixed at $1\ \frac{mol}{L}$ at the beginning) was not high enough for STENA BA. However, that alkalinity enabled the activation of RISE BA. Both RISE BA and STENA BA were bottom ashes, which meant they went through the same kind of heating and cooling process in the furnace. Moreover, the chemical composition was rather similar. The only main difference lied in the particle diameter. STENA BA grains were coarser than that of RISE BA ($d_{50\%,STENA\ BA} = 170\ \mu m$ and $d_{50\%,RISE\ BA} = 33\ \mu m$). Therefore, it can be concluded that the particle size also played a role in the activation.

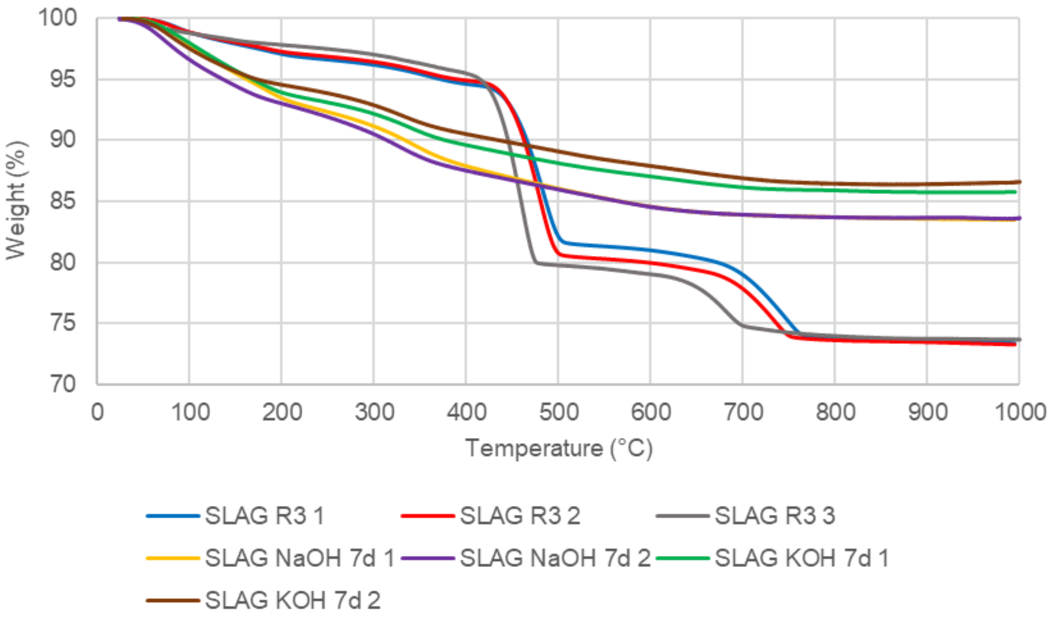

Figure 5.28: Comparing TGA results for SLAG between solution test and R^3 test.

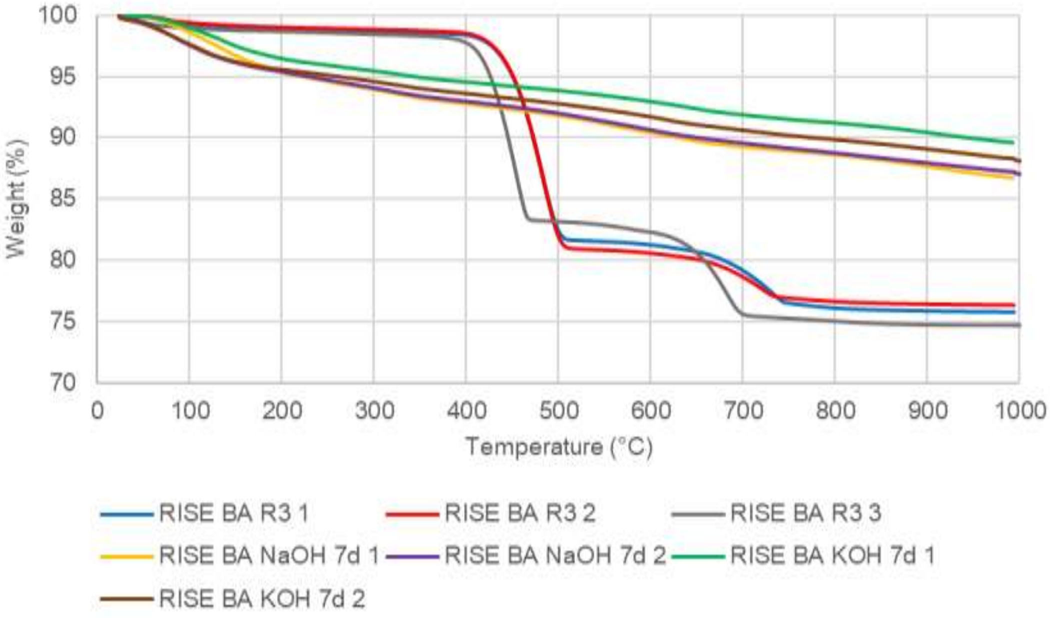

Figure 5.29: Comparing TGA results for RISE BA between solution test and R^3 test.

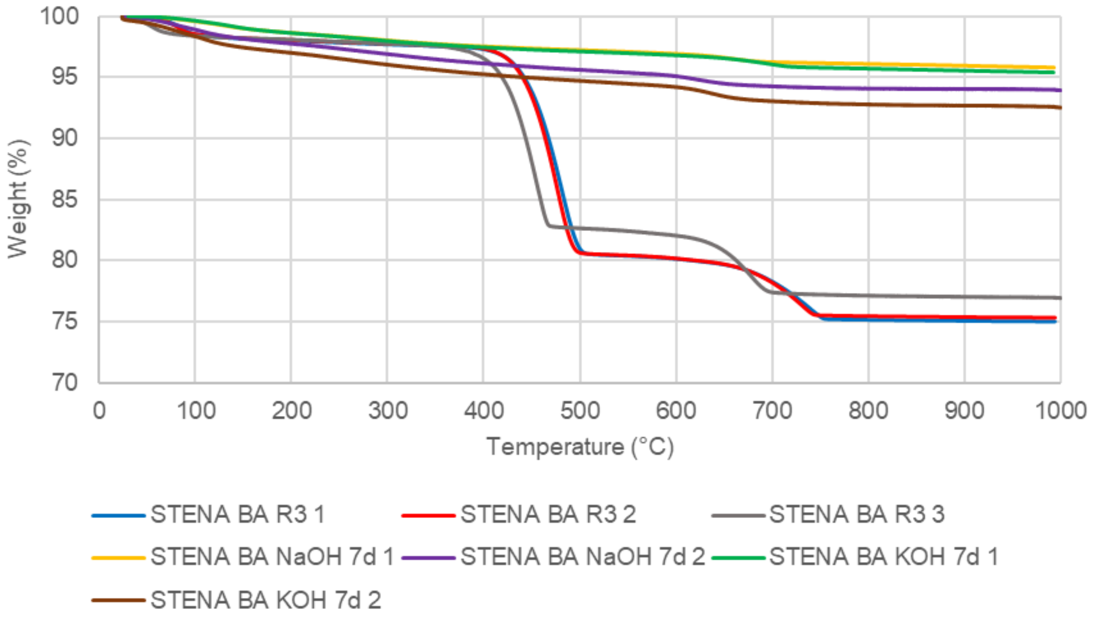

Figure 5.30: Comparing TGA results for STENA BA between solution test and R^3 test.

Comments made from Figure 5.28, Figure 5.29 and Figure 5.30 can also be stated from Table 5.8. It can be observed that the chemically bound water content derived for STENA BA was almost the same both in the solution test and in the R^3 test. Nonetheless, for RISE BA, an improvement in the chemically bound water content was substantial from R^3 test to solution test.

Table 5.8: Chemically bound water ratios in solution test and R^3 test

Bound water	**solution test**		**R3 test**
	NaOH	KOH	
RISE BA / SLAG	0.53	0.52	0.37
STENA BA / SLAG	0.22	0.30	0.29

6 Conclusion

Now it is time to go back to the first research question, which was: “What kind of tools and methods can be used and developed to assess the reactivity of MSWI ashes in a relevant way?”

The first experiment conducted in this study was the R^3 test, which aims at studying the potential use of bottom ashes for hybrid cements. Nowadays, alkali-activated binders based on stronger activators, such as $NaOH$ or KOH, are also increasingly considered in order to further reduce the CO_2 footprint and improve waste management. Thus, the second experiment, the solution test, has been developed for the first time in this study to answer these issues, providing a starting point for a reasonable reactivity assessment study.

The experiment results from R^3 test revealed that concrete pore solution environment was not able to activate RISE BA and STENA BA. Portlandite did not act as a good activator. Because Portlandite had a limited solubility into water, the pH was limited to 12.3, and the dissolution of energetically stable raw material such as RISE BA and STENA BA was impossible. Only SLAG, that is known to be highly reactive, was activated by Portlandite.

The experiment results from the solution test showed that $NaOH$ and KOH activators added in order to reach a pH of 14, were able to activate RISE BA in addition to SLAG. However, STENA BA was still inert. It was also shown that sodium hydroxide was a better activator than potassium hydroxide, comparing the amount of water chemically bound.

It is also interesting to answer the second research question which was: “To what extent MSWI ashes are of interest when it comes about using them as a binding agent?”

RISE BA and STENA BA were not displaying any activity within the R^3 test, meaning that a potential use in hybrid cement can be set aside. Based on the solution test, the same conclusion can be made for STENA BA for the development of an alkali-activated binder. However, RISE BA can be further studied for the development of an alkali-activated binder, proceeding to compressive strength tests at different ages for instance.

In this work, only two kinds of MSWI ashes were studied, but a lot of more different kinds of ashes are existing. The next step could be to experimenting others to enable better comparisons and create progressively a data base.

Before concluding this study, one must notice that, in addition of the type of activator, the specific area seemed also to play a role in the activation. Indeed, STENA BA have the lowest specific area and SLAG has the largest. Therefore, it could be interesting to repeat these experiments with finer particle sizes for RISE BA and STENA BA to see if Portlandite can be good enough to activate them. Thus, other possibilities could be explored for those ashes, using them in hybrid cements.

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Appendix 1: Solution test protocol

Here is established the detailed protocol for the solution test. Mix designs are presented in

Table 0.1.

- Prepare a solution of $NaOH$ and KOH of $1\ \frac{mol}{L}$.

Introduce in a test tube the amount of ashes necessary for each waiting time. As it can be seen in

- Table 0.1, for a waiting time of 7 days a test tube of $50\ mL$ is needed, for other waiting times one of $15\ mL$ is enough.
- Introduce $10\ \mathrm{mL}$ or $40\ \mathrm{mL}$ of NaOH or KOH solution in the test tubes.
- Seal the test tubes with their top and shake it to mix the solution with the ashes.
- Put the test tubes in a rotator at $40\,^{\circ}\mathrm{C}$ and wait according to the waiting time (6 hours, 1 day, 2 days, 4 days and 7 days).
- When the waiting time is reached, put the concerned samples in a spinner for a centrifugation process. When the solid and the liquid phase are separated, proceed to a sampling of $V_{sampling} = 5\ mL$ with a volumetric pipette.

Table 0.1. Mix designs for solution test.

Alkaline solution	$NaOH$	$NaOH$	$NaOH$	KOH	KOH	KOH
Raw material	SLAG	RISE BA	STENA BA	SLAG	RISE BA	STENA BA
$V_{liquid,6h,1d,2d,4d}\ (mL)$	10	10	10	10	10	10
$m_{solid,6h,1d,2d,4d}(g)$	0.521	0.521	0.521	0.524	0.524	0.524
$V_{liquid,7d}\ (mL)$	40	40	40	40	40	40
$m_{solid,7d}\ (g)$	2.082	2.082	2.082	2.094	2.094	2.094
$V_{sampling}\ (mL)$	5	5	5	5	5	5

- Introduce the sampling from the volumetric pipette into a volumetric flask of $50\ mL$ and add a little bit of deionized water.
- Acidify the volume collected to prevent ions from being carbonated. To do it, pour a few drops of nitric acid to ensure $pH < 3$.
- Fill the volumetric flask with deionized water to the mark.
- Mix the solution and ensure that the pH is still lower than 3.
- Introduce $10\ mL$ into a test tube and seal it with its top and with Parafilm paper.
- Keep the test tube inside an oven at $40\,°C$ until performing the IC analysis.
- For the last waiting time (7 days), collect the solid phase by filtering the remaining slurry after the last centrifugation.
- Install a vacuum filtration system using a Büchner funnel under a fume hood. The use of a fume hood is due to the use of highly volatile and flammable products such as diethyl ether and isopropanol.
- Fix the filter paper on the Büchner funnel and pour some drops of isopropanol on the filter to fix it. In order to fix it correctly it is recommended to open the tap and start doing the vacuum before pouring the drops.

- Take $3\,g\ \pm\ 0.1\,g$ from the crushed fraction ensuring the maximum size of grains after the crushing process are below $1\,mm$ diameter.
- Immerse the $3\,g$ of the crushed samples in $100\,mL$ of isopropanol for 15 minutes.
- Stir with a spatula the suspension and pour it on the filter, let the isopropanol percolate with the vacuum working.
- Bath the residue using approximately $20\,mL$ of isopropanol and after that do it again with approximately $20\,m$l of diethyl ether, still with the vacuum working.
- Put the residue and filter paper carefully on a plastic cup and dry for $8\min\ \pm\ 30s$ in a ventilated oven at $40\ \pm\ 5°C$.
- After drying, the powder collected can be kept in a low vacuum desiccator over silica gel and soda lime to avoid contamination from the environment.
- Analyze the powder doing a TGA. The powder in the TG instrument must be heated from room temperature to $1000°C$ at $10°\frac{C}{minute}$ and the system must be flushed with N_2.
- Derive the chemically bound water content.

Here is the procedure to proceed to the IC analysis.

Prepare the standard solutions. To do so, use Eq (0.1) to get the amount of $NaOH$ and KOH needed for a stock solution of $C_{init} = 100\ \frac{mmol}{L}$. Values are reported in

- Table 0.2. Introduce these quantities in a volumetric flask of $V_{flask} = 50\,mL$ and fill it with pure water till the mark.

Use the stock solution to prepare the five standard solutions with their respective concentration (see

Table 0.2: Stock solution preparation.

Solution at C_{init}	$NaOH$	KOH
$M_i\ (g/mol)$	39.997	56.106
$m_{introduced}\ (g)$	0.200	0.281

-

- Table 0.3) using Eq(0.1), Eq(0.2) and Eq(0.3), where i refers to NaOH or KOH and j refers to each of the four diluted solution (j=1 or 2 or 3 or 4 or 5).

$$m_{introduced,i} = C_{init} \cdot V_{flask} \cdot M_i \qquad \text{Eq(0.1)}$$

$$V_{stock\ solution\ to\ collect,j} = V_2 \cdot \frac{C_j}{C_{init}} \qquad \text{Eq(0.2)}$$

$$V_{water,j} = V_{flask} - V_{stock\ solution\ to\ collect,j} \qquad \text{Eq(0.3)}$$

- Collect the amount of volume $V_{\text{stock solution to collect,j}}$ for the desired concentration and introduce it in a volumetric flask of $50\,mL$. Fill the volumetric flask till the mark with pure water.
- Introduce $7\,mL$ of the dilution in the IC container with a volumetric pipette.
- Cork the IC container till there is no air inside the sample.

After preparing the standard solutions, here is the procedure to prepare the samples for the IC.

- Take the solution test sample that are in the oven at $40°C$.
- Fill each IC tube with $6.93\,m$L of pure water.

- Take a 2 or $3\ mL$ amount of the sample with the help of a $5\ mL$ syringe.
- Introduce the liquid collected in a test tube letting it go through a filter of $0.02\ mm$.
- Take $0.07\ mL$ from that filtered liquid with a volumetric pipette.
- Introduce it in the IC container and mix it with the pure water with the help of the volumetric pipette.
- Cork the IC container till there is no air inside the sample.
- Run the IC instrument.

Table 0.2: Stock solution preparation.

Solution at C_{init}	$NaOH$	KOH
$M_i\ (g/mol)$	39.997	56.106
$m_{introduced}\ (g)$	0.200	0.281

-

Table 0.3: Concentrations of the five standard solutions.

Data		
C1	2	$\frac{mmol}{L}$
C2	1	$\frac{mmol}{L}$
C3	0.5	$\frac{mmol}{L}$
C4	0.1	$\frac{mmol}{L}$
C5	0.01	$\frac{mmol}{L}$

Table 0.4: Preparing standard solutions from stock solution.

For $V_2 = 50\ mL$	Dilution at C1	Dilution at C2	Dilution at C3	Dilution at C4	Dilution at C5
$V_{\text{stock solution to collect,j}}$(mL)	1.00	0.50	0.25	0.05	0.005
$V_{water,j}$ (mL)	49.00	49.50	49.75	49.95	49.995

Appendix 2: R^3 test protocol

Firstly, here are explained the steps to follow in order to get the R^3 paste ready to analyse its bound water content and portlandite consumption.

- Mix the solid compounds: ashes $(11.11\,gr)$, portlandite $(33.33\,gr)$, K_2SO_4 $(1.2\,gr)$ and calcite $(5.56\,gr)$ in a plastic container.
- Dissolve the potassium hydroxide $(0.24\,gr)$ in the deionized water $(60\,gr)$ separately in a beaker.
- Pour the potassium hydroxide solution in the plastic container where there is the mix of powders and stir with a spatula to make it as homogeneous as possible.
- Seal the R^3 paste so created covering the plastic container with plastic paper in order to avoid any contamination or exchange from the environment.
- Leave the R^3 paste for curing in an oven at $40°C$ for 7 days.
- After the curing time, remove the supernatant liquid and crush the hardened paste that has formed with mortar and pestle. Depending on the sample and its consistence, the crushing can take more or less time. It is important to avoid taking edges and surfaces that has been exposed to air or supernatant solutions, due to the possible alteration of those parts. The crushing step should be done in less than 10 minutes.

Then, the complete procedure to get the bound water content is explained following these steps.

- Take approximately $6\,gr$ of the crushed fraction with a spatula and put it in a crucible.
- Cure it in an oven at $105°C$ for 24 hours in order to reach constant weight and write down the weight.
- Heat the sample up to $350°C$ and maintain that temperature for 2 hours.
- Let it cool down to $105°C$ and weigh again the sample.

Finally, here is the explanation of the procedure that must be followed in order to obtain the portlandite consumption.

- Install a vacuum filtration system using a Büchner funnel under a fume hood. The use of a fume hood is due to the use of highly volatile and flammable products such as diethyl ether and isopropanol.
- Fix the filter paper on the Büchner funnel and pour some drops of isopropanol on the filter to fix it. In order to fix it correctly it is recommended to open the tap and start doing the vacuum before pouring the drops.
- Take $3\,g \pm 0{,}1\,g$ from the crushed fraction ensuring the maximum size of grains after the crushing process are below 1mm diameter.
- Immerse the $3\,g$ of the crushed samples in $100\,mL$ of isopropanol for 15 minutes.
- Stir with a spatula the suspension and pour it on the filter, let the isopropanol percolate with the vacuum working.
- Bath the residue using approximately $20\,mL$ of isopropanol and after that do it again with approximately $20\,mL$ of diethyl ether, still with the vacuum working.
- Put the residue and filter paper carefully on a plastic cup and dry for $8\min \pm 30\,s$ in a ventilated oven at $40 \pm 5°C$.
- After drying, the plastic cup containing the powder collected can be kept in a low vacuum desiccator over silica gel and soda lime to avoid contamination from the environment.

- Analyze the powder doing a TGA. The powder in the TG instrument must be heated from room temperature to $1000°C$ at $10°\frac{C}{minute}$ and the system must be flushed with N_2.
- Derive the portlandite content using the tangent method.

Appendix 3: Chemical products used

Calcium carbonate ($CaCO_3$)
- Assay $\geq 99\%$
- Analytical reagent grade

Calcium hydroxide ($H_2(Ca0)_2$)
- Assay $\geq 95\%$
- Laboratory reagent grade

Diethyl ether (C_4H_{100})
- Laboratory reagent grade

Isopropanol (C_3H_8O)
- Assay $\geq 99.5\%$
- Laboratory reagent grade

Nitric acid 70% (HNO_3)
- Analytical reagent grade
- Density of 1.42

Potassium hydroxide (KOH)
- Assay $\geq 85.6\%$
- Analytical reagent grade
- Pellets

Potassium sulphate (K_2SO_4)
- Assay $\geq 99.5\%$
- Analytical reagent grade

Silica gel (O_2Si)
- General purpose grade
- Orange to green self-indicating
- Granule size $2.5 - 6\ mm$

Soda lime ($CaHNaO_2$)
- Laboratory reagent grade
- Not hygroscopic
- Particle size $1 - 2.5\ mm$ granules

Sodium hydroxide ($NaOH$)
- Assay $\geq 97\%$
- Reagent grade
- Pellets

Appendix 4: Instrument used and settings

- **Raw materials**

The TGA performed were done weighing $40-50\,mg$ of powder in $70\,\mu L$ alumina crucibles. The system was flushed with N_2 at $50\,\frac{mL}{min}$ and the heating rate was $10\,\frac{°C}{min}$ from 20 to $1000°C$. The instrument used was a "Mettler Toledo TGA/DSC 3+".

- **Solution test:**

<u>Chemically bound water determination:</u>

The TGA performed for the first series were done weighing $40-50\,mg$ of powder in $70\,\mu L$ alumina crucibles. The system was flushed with N_2 at $50\,\frac{mL}{min}$ and the heating rate was $10\,\frac{°C}{min}$ from 20 to $1000°C$. The instrument used was a "Mettler Toledo TGA/DSC 3+".

The TGA performed for the second series were done weighing $10-20\,mg$ of powder in alumina crucibles. The system was flushed with N_2 at $90\,mL/min$ and the heating rate was $10\,\frac{°C}{min}$ from room temperature to $1000°C$. The instrument used was a "TA instruments, TGA Q50/500".

<u>Ion concentrations determination:</u>

The instrument used for the two series was a "Dionex ICS-900 Ion Chromatography".

- **R^3 test:**

<u>Chemically bound water determination:</u>

The instrument used for the three series was a muffle furnace "Nabertherm L 9/12/B410".

<u>Portlandite consumption determination:</u>

The TGA performed for the first and second series were done weighing some $40-50\,mg$ of powder in $70\,\mu L$ alumina crucibles. The system was flushed with N_2 at $50\,\frac{mL}{min}$ and the heating rate was $10\,\frac{°C}{min}$ from 20 to $1000°C$. The instrument used was a "Mettler Toledo TGA/DSC 3+".

The TGA performed for the third series were done weighing some $10-20\,mg$ of powder in alumina crucibles. The system was flushed with N_2 at $90\,\frac{mL}{min}$ and the heating rate was $10\,\frac{°C}{min}$ from room temperature to $1000°C$. The instrument used was a "TA instruments, TGA Q50/500".