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Effect of Elemental AI in MSWI ash when used as a Supplementary Cementitious Material

Rosaida Dolce

Supervisor: Prof. dr. ir. Nele De Belie, Prof. dr. ir. Milena Marroccoli, Prof. Dr. Ir. Antonio Telesca
Counsellor: ir. Aneeta Mary Joseph

Master's dissertation submitted in order to obtain the academic degree of Master of Science in Civil Engineering

Department of Structural Engineering
Chairman: Prof. dr. ir. Luc Tarwe
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Preface

Fristly, thanks to Prof. Nele De Belie, Prof. Marroccoli and Prof. Telesca for gave me the opportunity to improve my knowledge and myself through this laboratory research experience in Belgium.

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Rosaida Dolce

June 2016, Gent

Introduction

In this research MSWI (Municipal Solid Waste Incinerator) is used as the replacement of cement. The final product must have appropriate characteristics. Thus, different treatments are studied to improve the physical and chemical qualities of the concrete. In particular, the effect of Elemental Al was studied.

The amount of Municipal Solid Waste (MSW) increases with growing urbanization and industrialization. However, it is a relevant problem all over the world. Especially, in countries where there are limited landfill sites. To reduce the quantity to be landfilled, a large amount of MSW is incinerated. It gives about 70% of mass reduction and 90% of volume reduction of MSW. But MSWI ash is rich in heavy metals and salts. The use of MSWI ash without proper treatment may cause serious environmental problems. Therefore, the chemical composition of MSWI can be characterized through different processes: XRF (X-ray fluorescence), TGA (Thermogravimetric Analysis), ASR (Alkali silica Reaction) and Elemental aluminium. Finally, the concrete is tested in compressive strength of mortar. The research will test the quality of concrete with Supplementary Cementitious Material (SCM), using ashes from the Indaver Incinerator (Antwerp, Belgium).

Effect of Elemental Al in MSWI ash when used as a Supplementary Cementitious Material

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Abstract

Several controversy concerning the management of MSW (Municipal Solid Waste) and their environmental issues. To reduce the volume of waste about 70-90% the process used is the incineration. However, the material resulting from the plant are produced by an uncontrolled process, therefore they have hazardous chemical composition. To replace MSWI as the raw material in concrete, they should be treated with different process. In this research the ashes (from INDAVER) were treated with water, NaOH and Carbonate and after submitted to the compress strength test, TGA (Termogravimetric Analysis) and ASR (Alkali-Silica Reaction, with glasses aggregate) to evaluate the quality. Relevant the role of the Elemental Al, for this analysis new set up was realize. Results conduced that the MSWI was appropriate to replace raw materials in concrete after treatments.

Keywords: Municipal Solid Waste Incineration, Bottom Ash, Fly Ash, Concrete, Supplementary Cementitious Material, Elemental Al

1.INTRODUCTION

Municipal Solid Waste (MSW) management is a major environmental problem all over the world. In most of the developed countries, scientific waste management protocols are adopted, and thus reduce the residual wastes to a minimum (Qiao, Tyrer, Poon, & Cheeseman, 2008)(Ferraris et al, 2009). Nevertheless, with increase in the population growth, urbanization and technological/economic development, the disposal of residues is becoming a more serious issue (Wiles, 1995). Around 1,3 billion ton of MSW are generated globally each year (World Bank). The volume of MSW globally is projected to doubled by 2025. In the past, the majority of waste was disposed in the landfills but this has led to an increase of environment issue ,

health concerns and reduction of vacant land (Sawell et al., 1995). From this comes the purpose of this research: the reuse of MSWI (Municipal Solid Waste Incineration) in the cement to reduce the consumption of raw materials and the landfills. However, Bottom & Fly ashes are not produced by an industrial controlled process, thus they have many constituents making them unsuitable to be used in cement as such. Elemental aluminium, chlorides, sulphates and heavy metals are the disadvantageous constituents in the ashes. So some beneficiation methods are tested for its suitability to be used as a supplementary cementitious material.

2.MATERIALS

Normal concrete is composed of cement, sand, water and aggregates. The aim of this research is to replace the aggregates by bottom, fly ashes and glasses. Three types of bottom ashes, with different grain size (Figure 1), and one type of fly ash (from Indaver, Antwerp, Belgium) was used to casting mortars for all different tests made in this study.

ASHES	SIEVES (mm)	DATE OF PRODUCTION
BA 6/15	6-15	January 2016
BA 2/6	2-6	January 2016
BA 0/2	0-6	March 2016
FA	fly ash	Fresh

Table 1. Samples

One types of waste grinding glasses was used for Alkali Silica Reaction and the strength test. For all mortar bars was use CEM I (from VVM Rieme, Belgium) and standard sand EN 196-1.

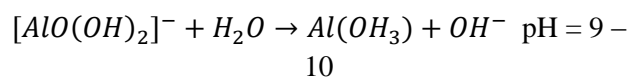
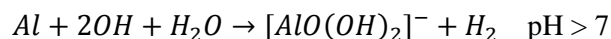
3.METHODS

Grinding samples

To use ashes as an SCM, it was necessary to grind samples BA 6/15, BA 2/6 and BA 0/2. FA was fine enough. All ashes was ground in the ball mill for 15 min in pulverisette mill.

Washing with water

Elemental Al reacts with water and releases hydrogen gas in alkaline environment. This treatment can possibly reduce the expansion due to elemental Al and some soluble salts such as chlorides and sulphates. Occurs the following chemical equation (Saikia et al. 2015):



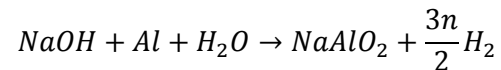
Washing of ashes with water was done as follows: 500g of ash was mixed with 1 liter of water and was

mixed daily for 1 minute for 7 days. After washing the samples were dried in the oven at 105 °C temperature for 24 h.

Washing with NaOH

Elemental Aluminium reacts with NaOH, and follows the stoichiometric equation given below. The reaction is much faster, than with water, releases hydrogen thus reducing the expansion when mixed with cement. The ash samples were immersed in 0.5M solution of sodium hydroxide (atm. Pressure 20°C) for 7 days at 20 °C. Then the samples was dried in the oven, T=105 °C for 24 hours, and then ground in ball mill to fine powder.

The following equation explain the process (Pera et al, 1996):



Accelerated carbonation

It is reported in literature that carbonation can reduce the solubility of elemental aluminium in water, and thus reduce the reaction and also the amount of hydrogen gas produced. This is facilitated by carbonation of various phases in the ash, encapsulating the aluminium in the process (Arickx et al, 2006) Carbonation of ground ash was done at a CO₂ concentration of 10% and a temperature of 20°C. The samples stayed in that condition for 7 days.

Compressive strength

Compressive strength test was conducted in mortar bar specimens of size 40 mm x 40 mm x 160 mm prepared according to NBN EN 12390-2:2009. For each mix, the 28 day strength is determined as an average of three specimens. The water cement ratio for standard sand mortar specimens was 0.5, and those for glass aggregate specimens was 0.55. The compressive strength R_c is in megapascals from:

$$R_c = \frac{F_c}{1600}$$

Where, R_c is the compressive strength, in megapascals; F_c is the maximum load at fracture, in newtons; A is the area of the platens or auxiliary plates (40 mm \times 40 mm), in square millimetres.

Oberholster Test

Oberholster Test is used to determinate the potential alkali-silica reactivity of aggregates, conforming to NF P 18 594. The samples used in this test are made with glasses, the test start one day after casting. First, must took measure of samples length and put in the apparatus; mix 400g of NaOH with 10 L of H₂O and put it inside it; attend until the temperature reach 80°C and after 1 h took the measures and took it again all days for 20 days, to monitored the expansion. If the expansion is more than 0.1% that means potential ASR.

Specific Gravity

Le Chatelier flask test method determinates the density of ashes. To evaluate Specific Gravity should do several measurement, used ASTM Standard C 188-95 (2003).

TGA

Thermogravimetric Analysis (TGA) was conducted for all types of ashes and in cement paste samples, after hydration for 28 days. The paste samples were crushed to powders and subjected to freeze dry, and subsequently kept in vacuum for 7 days to remove the evaporable water content and prevent carbonation or other contamination. They were heated under a nitrogen flow rate of 30 ml/min, starting from 30°C until 950°C.

XRF

The XRF (X-Ray Fluorescence) is a spectroscopy technique to identify the chemical elements of the sample, by analyzing X-rays emitted from it as a result of atomic excitation with appropriate energy. The values were carried out in the laboratory of INDAVER, in Antwerp.

Laser Diffraction

Laser diffraction is a standardized method according to the International Standard ISO 13320 to determine the fineness of the ground ash. To do this analysis has been used Mastersizer 2000.

Elemental Al

To determinate how much elemental aluminium there are in each samples, there is not official directive. A new setup was realized to evaluate the reaction of elemental aluminium with NaOH to for hydrogen. Hydrogen released replace water and the difference in water volume indicates the quantity of elemental aluminium in the ash.

Fill 2 L round bottom flask with water, weight it and immerse in the water facing downwards. Connect the bottom ash flask to the water filled flask using a tube to collect the hydrogen gas. Fill the flask on the bottom with 20 g bottom ash, and the top measuring bottle with 1 M NaOH. Open the stop cock and allow NaOH to pour down and keep the solution in motion using magnetic stirrer. The experiment during 2 days for one samples.

4. RESULTS

Material properties

From Laser Diffraction, all bottom ashes have similar size distribution, the highest point of each bell is around 10 μ m, it correspond to a volume of 4%. Fly ash has a double bell curve, suggesting that there are two size ranges in fly ash (Table 3).

	Refractive Index	Absorption	Weighted Residual %
BA 6/15	1.57	1	0.441
BA 2/6	1.57	1	0.242
BA 0/2	1.57	1	0.296
<i>FA</i>	<i>1.57</i>	<i>0.01</i>	<i>0.366</i>

Table 2. Laser Diffraction results

XRF analysis is fundamental technique to understand the chemical composition. In the following Table 5 there are the more relevant elements of the ashes.

	BA 6/15	BA 2/6	BA 0/2	FA
Cl	2030.15	1409.94	8621.17	34905.1
S	1718.99	2182.45	9552.91	22644.28
K	647.0464	732.05	982.95	854.23
Al	2734.5	2501.69	2273.37	1946.44
Cd	2.7	0	3.17	13.34
Cu	1098.39	1807	1702.65	6968.24
Fe	10605.48	15388.09	19058.99	14917.8
Mg	180.33	280.96	237.58	151.97
Pb	1611.97	2177.81	1120.51	4547.97
Zn	4264.43	7238.87	4359.45	8509.63
Ca	9570.91	13228.87	17258.19	18250.57
Si	34755.33	28008.13	19698.3	8984.36
Hg	3.713	7.5482	3.5	3.18
Ni	53.33	72.28	108.01	116.62
Sb	29.94	42.13	44.17	113.81

Table 3. XRF

Thermogravimetric analysis was conducted to understand the relative contents of volatile components in hydrated cement paste and ashes. Sudden increase in slope cannot be seen at 400 degree and 600 degree which represents calcium hydroxide and calcium carbonate, which are the usual phases in cement paste. Rather, a gradual slope is seen from 400 to 600 degree, which can indicate all the phases calcium hydroxide, calcium magnesium carbonate and calcium carbonate.

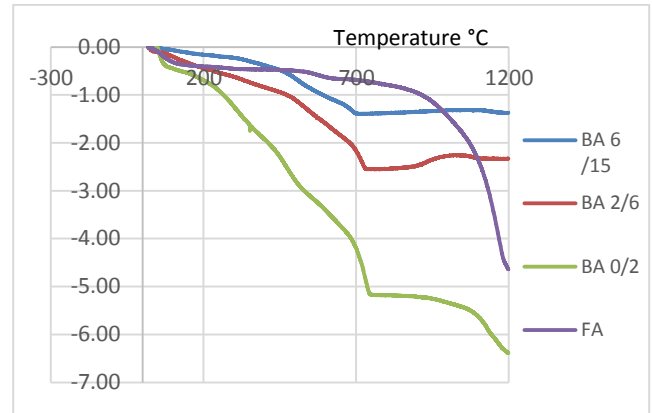


Figure 1. TGA

The analysis on the presence of elemental Al in Ashes is an experimental procedure. From the values obtained from the first sample, as expected, BA ash 6/15 reveals a low presence of elemental Al. At the results is the average of two test for each ashes.

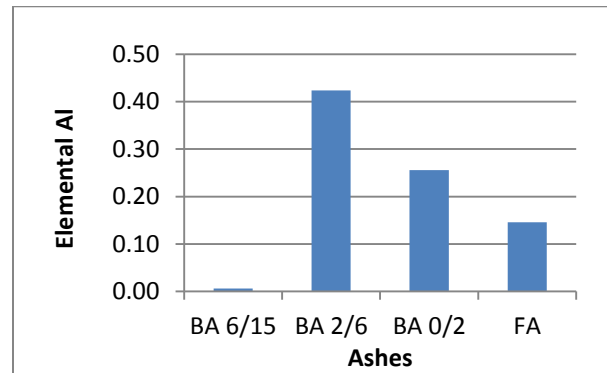


Figure 2. Elemental Al

The different treatment techniques adopted for reducing expansion are washing with water, washing with alkali (NaOH) and accelerated carbonation at 10%. The following graph (Figure 3) explains clearly the effect of different techniques adopted. All the washing techniques did not prove helpful in reducing the expansion, since the aluminium in ash was covered with other phases in ash, and thus not available for reaction with neither water or NaOH. Accelerated carbonation also failed to encapsulate the aluminium since the size of particles are too low, for carbonation of other phases to cover the aluminium in the ash.

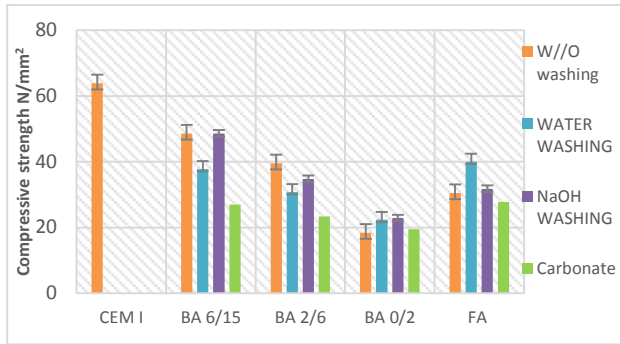


Figure 3. Compressive Strength Test

From the figure below, it can be seen that even after treatments expansion remains the deciding factor of compressive strength of mortar, and thus none of the treatment methods proved to be effective.

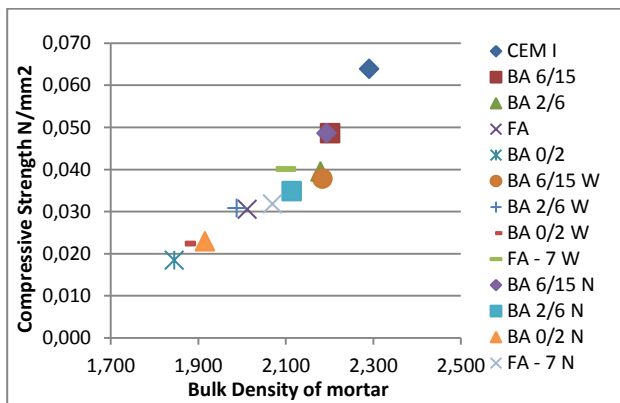


Figure 4. Compressive strength related to bulk density

The Oberholster test is an accelerated test that gives an indication of the alkali reactivity of aggregate. The values obtained prove that BA &/15 had the largest expansion and CEM I the lowest. But also FA did not have an high expansion. Although aluminates have effect of reducing the alkali silica reaction, the increased diffusivity due to high porosity caused by elemental aluminium overpowered its effect, and caused more expansion for specimens with ash replacement.

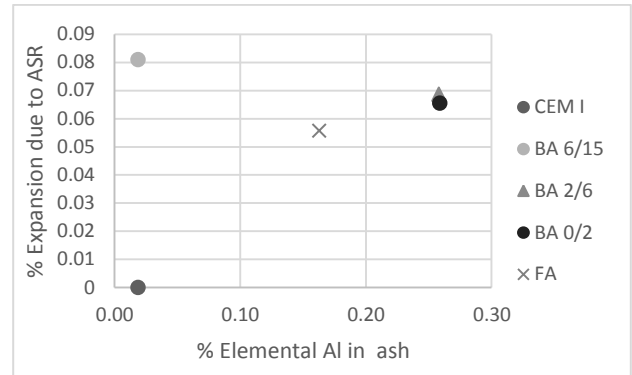


Figure 5. ASR Expansion related to % of Elemental Al

The percentage of portlandite in cement paste was determined by tangent method (Kocaba, 2010), and is shown in the following Figure 6.

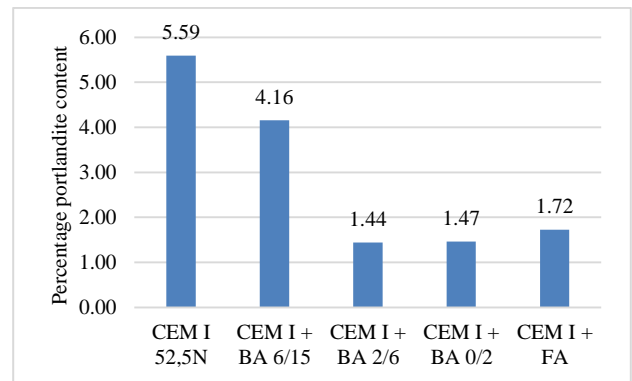


Figure 6. Percentage portlandite content

The maximum pozzolanic reaction is seen for BA 2/6 fraction, and minimum is for 6/15 fraction. This can be an indication of the reactivity of the ashes.

5. CONCLUSION

Expansion affects strength the most. None of the treatment techniques proved effective for reducing the expansion. In case of washing techniques, the ashes were not ground before washing. So most of the elemental Al present were encapsulated by other phases and were not available for reaction with alkali or water. Since the carbonation was done after grinding, Al particles and ash particles were separate, and the carbonated phases could not encapsulate the Al particles.

Least expansion was observed for CEM I sample. For ash replaced samples also, expansion was less than 0,1% despite high porosity due to expansion. This may be due to pozzolanic reaction and presence of Al, and also some comparison can be accommodate in the high porosity.

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List of abbreviations and symbols

ASR Alkali Silika Reaction

BA Bottom Ash

BCR Brussels Capital Region

C Carbonation

FA Fly Ash

G Glasses

GCM Global Center Magazine

GHG Greenhouse Gas

LD Laser Diffraction

PD Calorific value

PCA Portland Cement Association

PCI Lowest Calorific Value

PCS Higher Calorific value

MSW Municipal Solid Waste

MSWI Municipal Solid Waste Incinerator

N Treated with NaOH

SCM Supplementary Cementitious Material

TGA Thermogravimetric Analysis

XRF X-ray fluorescence

W treated with Water

D_i density of isopropanol

F_c maximum load at fracture

M mass of ash

M_i mass of isopropanol

P_{mc} maximum continuous capacity of the plant

R_c compressive strength

R_f flexural strength

T_c storage time

V_a volume of ashes

V_i volume of isopropanol

V_u Useful volume

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Chapter 1 LITERATURE REVIEW

1.1 INTRODUCTION

Municipal Solid Waste (MSW) management is a major environmental problem all over the world. In most of the developed countries, scientific waste management protocols are adopted, and thus reduce the residual wastes to a minimum (Qiao, Tyrer, Poon, & Cheeseman, 2008)(Ferraris et al, 2009). Nevertheless, with increase in the population growth, urbanization and technological/economic development, the disposal of residues is becoming a more serious issue (Wiles, 1995). The Treaty of Amsterdam has made the principle of sustainable development and a high level of environmental protection as a top priority. Due, European Union has adopted Directive 2008/98/CE of 19 November 2008, to protect the environment and human health to focus on the importance of proper waste management, recovery and recycling techniques to reduce pressure on resources and improve their use. Nevertheless, with increase in the population growth, urbanization and technological/economic development, the disposal of residues is becoming a more serious issue (Shih, Chang, & Chiang, 2003). Around 1,3 billion ton of MSW are generated globally each year (World Bank). The volume of MSW globally is projected to doubled by 2025.

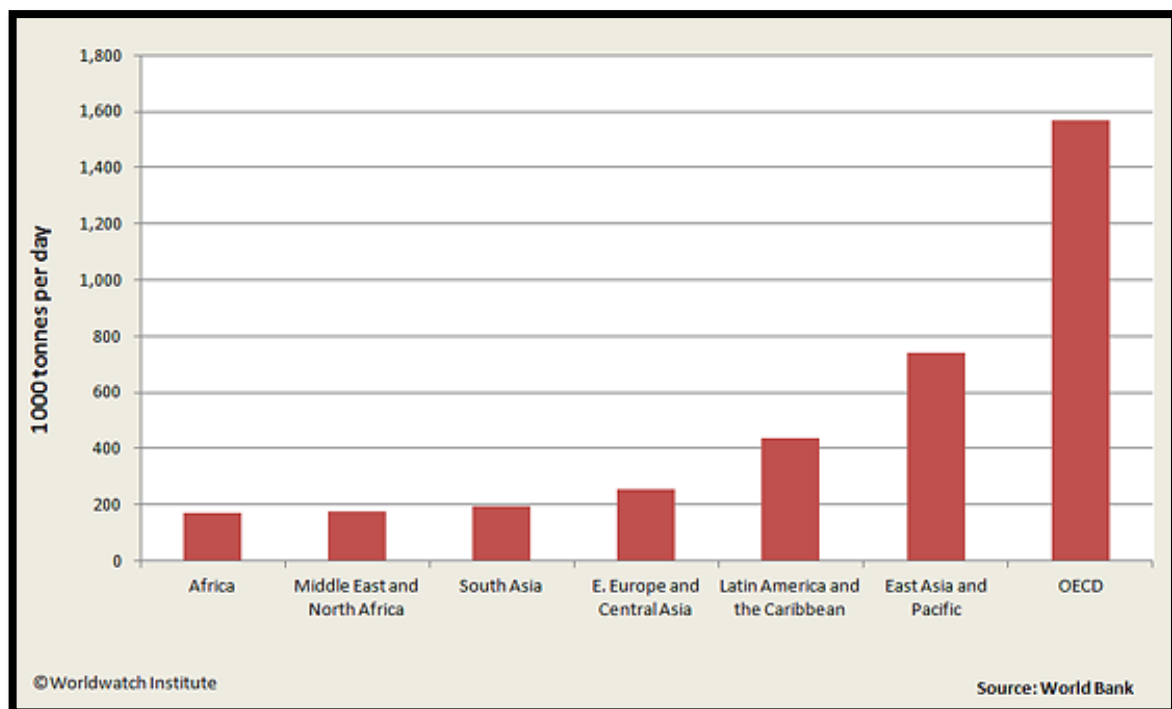


Figure 1. World MSW production (World Bank)

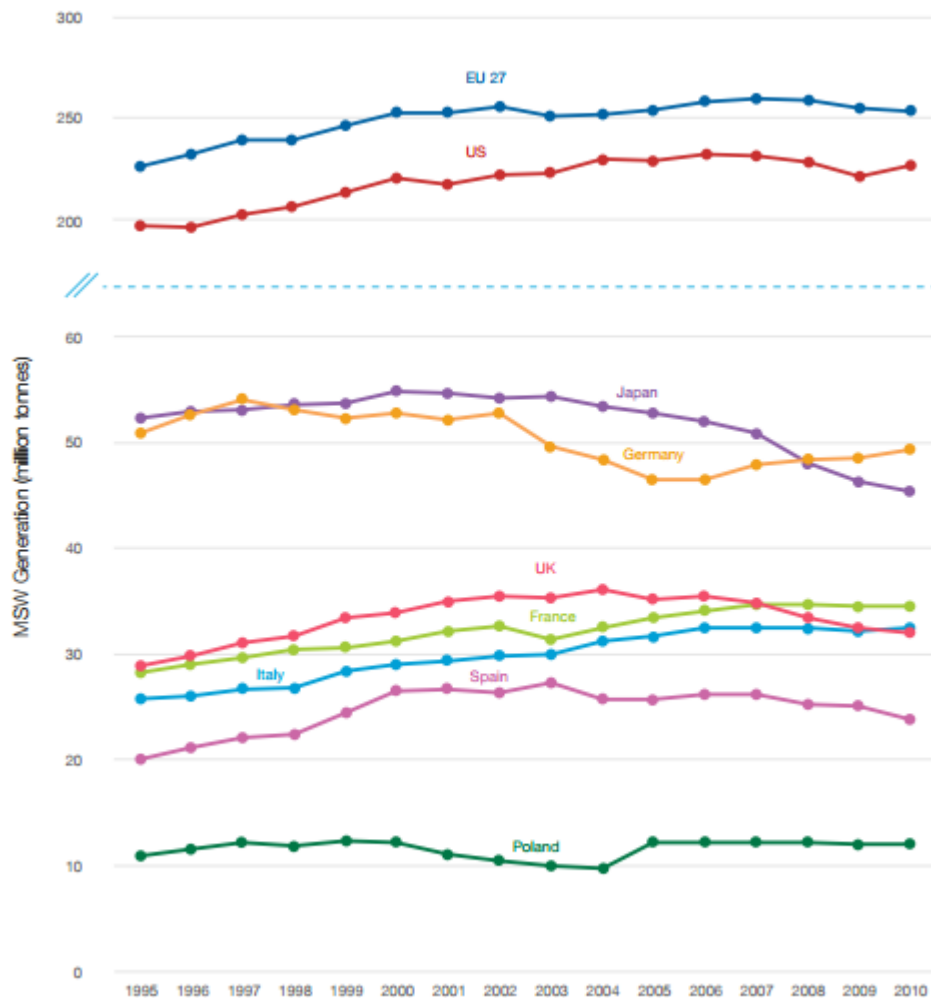


Figure 2. Trends in MSWI since 1995 in high-income countries

The management of this mass of waste involves a series of environmental issues:

- infiltration of nutrients, heavy metals and other toxic compounds from landfills;
- use of land as a dumping ground;
- greenhouse gas emissions generated by landfills and treatment of organic waste;
- air pollution and toxic by-products generated by incinerators;
- water and air pollution;
- increased transport carried by lorries

In the past, the majority of waste was disposed in the landfills but this has led to an increase of environment issue , health concerns and reduction of vacant land (Sawell et al., 1995). Figure 3 identifies the net greenhouse gas direct and avoided emission, from the management of MSW from 1990 to 2020, in the different treatment options: recycling, incineration, landfilling and transportation (European Environment Agency).

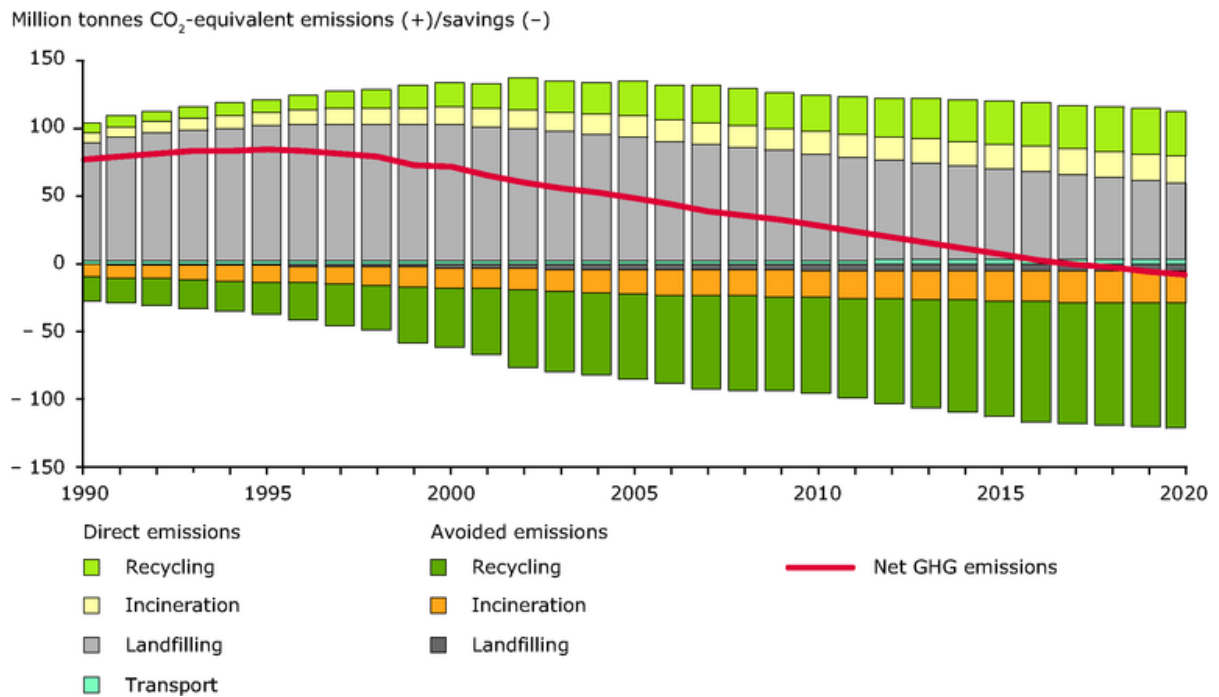


Figure 3. Modelled greenhouse gas emissions from MSW management in the EU

In the graphic, the two main factors responsible for bringing down net emissions are decreased methane emissions from landfill and increased avoided emissions through recycling (Sakai et al., 1996). The waste sources vary depending on the country and its economic situation. The countries of Western Europe produce a higher share of urban industrial waste compared to Central and Eastern Europe where mining and the main source of waste.

From this comes the purpose of this research: the reuse of MSWI (Municipal Solid Waste Incineration) in the cement to reduce the consumption of raw materials and the landfills.

1.2 MSW IN BELGIUM

In Belgium there are three different regions responsible of waste management planning and statistical reporting: Brussels Capital Region, Flanders and Wallonia. Brussels Capital Region produces 9% of the total MSW generated in Belgium and Wallonia 31% while Flanders 60% (total MSW generated in 2010 is about 5 million tonnes). Thus, each of the regions has their own strategies (EEA, 2013).

➤ Brussels Capital Region:

It has a high population density and level of urbanization and does not have enough space for effective waste management facilities. Two institutions are responsible for the Brussels Capital Region

Environmental waste management (waste prevention and management policy) and Agence Bruxelles Propreté (waste collection and processing of municipal waste). The management plan is built on five years, the main purpose is to indicate the various instruments to promote waste prevention.

➤ Flanders:

It has a long history of waste management (Parent et al, 2004), starting in 1986-90, with the opening of new landfill previous-related closure of the old. The plan was already included an extensive use of the incinerator and recycling. A second plan in force in 1991-95, focused on recycling to waste prevention. The Management Plan 1997-2001 regulating the maximum quantities of waste per inhabitant (255 kg / inhabitant in 1998 to 150 kg / inhabitant in 2010). In 2003-07 The measures become more restrictive (180 kg / habitant in 2003 to 150 kg / habitant in 2007). In 2007 71% of household waste were recycled and collected separately and only 4% was landfilled.

The plan for 2008-2015 has the following objectives: more environmentally beneficial consumption, no more than 560 kg of waste per person per year and not more than 150 kg of residual waste per person per year.

➤ Wallonia:

The 1991-95 plan promotes waste prevention, recovery of materials and energy and recycling, but only 15% of this collection was actually recycled. In 1998-2010 the municipal waste sent to incineration had an increase from 480,000 tons to 733,000 tons, the same for the biological treatment. In 2011 there was a reduction of Misiti household waste, but also an increase of bulky household waste (appliances, furniture...). A significant increase in incineration occurred between 2004 and 2008 and between 2008 and 2010. Finally, the rate of landfilling has dropped, especially in 2008 and 2010. The following graphics (Figure 4) show the different trends of each regions of Belgium. The further recycling increases is in Wallonia, for all three different types of waste.

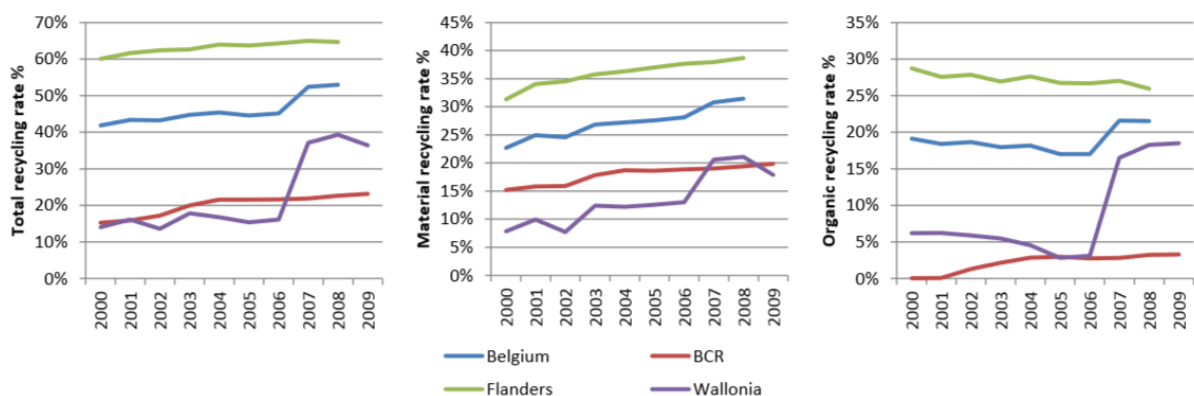


Figure 4. Recycling of MSW in Brussels Capital Region, Wallonia and Flanders, % (Eurostat 2012)

Analyzing the Belgium total recycling rate of MSW, and organic materials, should be noted that the percentage of recycled organic MSW is in decline, while the recycling of inorganic materials is rising. The rate of the national total recycling has increased, from 50% in 2001 to 57.24% in 2010 (456 kg MSW/capita).

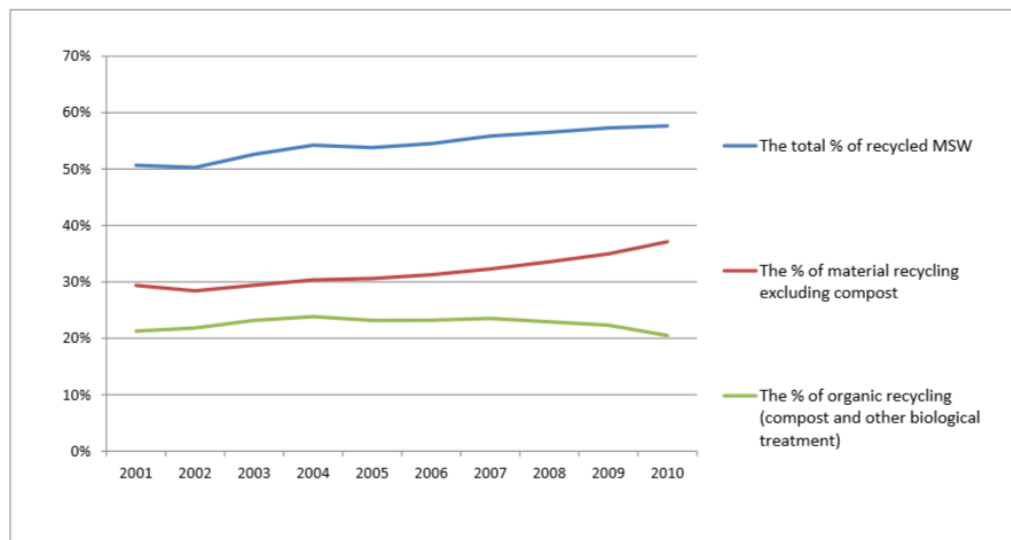


Figure 5. Recycling of MSW in Belgium, % (Eurostat 2012)

The goal of the EU 2020 is to recycle 50%, Belgium has achieved. Copenhagen Resource Institute has estimated the future recycling forecast, based on past data recorded by Eurostat 2012. The percentage are calculate as % of generated MSW. For 2020 the forecast is above 65%.

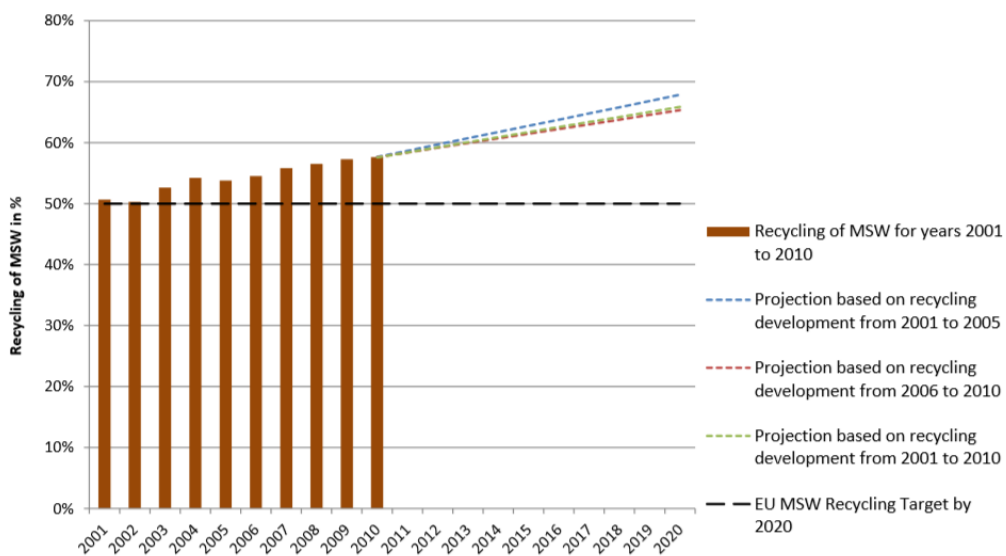


Figure 6. Future recycling MSW in Belgium, % (Copenhagen Resource Institute)

1.3 MSW MANAGEMENT TECHNIQUES

1.3.1 MSW Management

To optimize waste management, the European Commission decided to use an integrated management, that is the combination of activities, to reduce the consumption of natural resources and energy and to limit the environment and health risk (Aubert, Husson, & Sarramone, 2006). Integrated management provides a single "brain" that plans the entire system, the different stages and different technological options and organizational, knowing from the beginning what to recover, what reuse, where to put the fraction advancing and that cannot be recycled. There are 6 steps in the waste hierarchy management, placing prevention at the top and disposal (such as landfilling) as the least favored option.

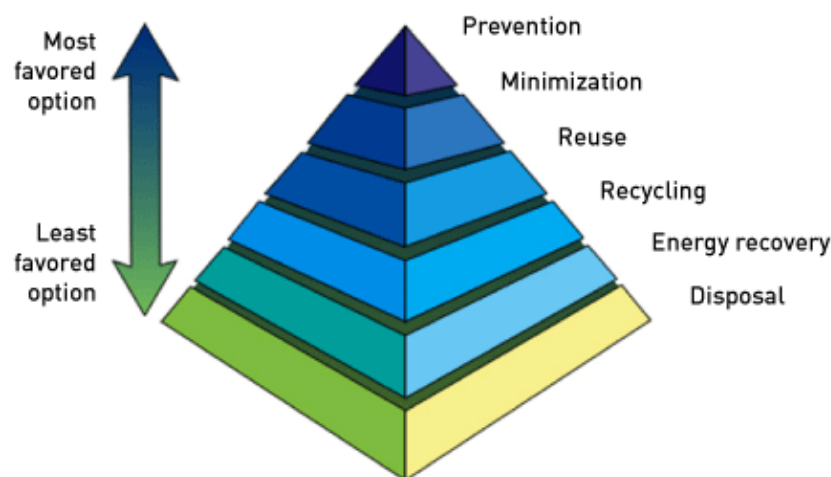


Figure 7. Hierarch of waste management

The necessity to introduce an integrate management arises because the disposal of waste cannot be satisfied trough only one type of intervention, but to a series of integrated "type actions", such as to ensure the disposal in the short and medium-long term. therefore, the MSW Integrated Management System consists of an organic complex of technologies, which are interrelated, able to integrate, territorially and functionally, the various subsystems of collection, transport, recovery and disposal.

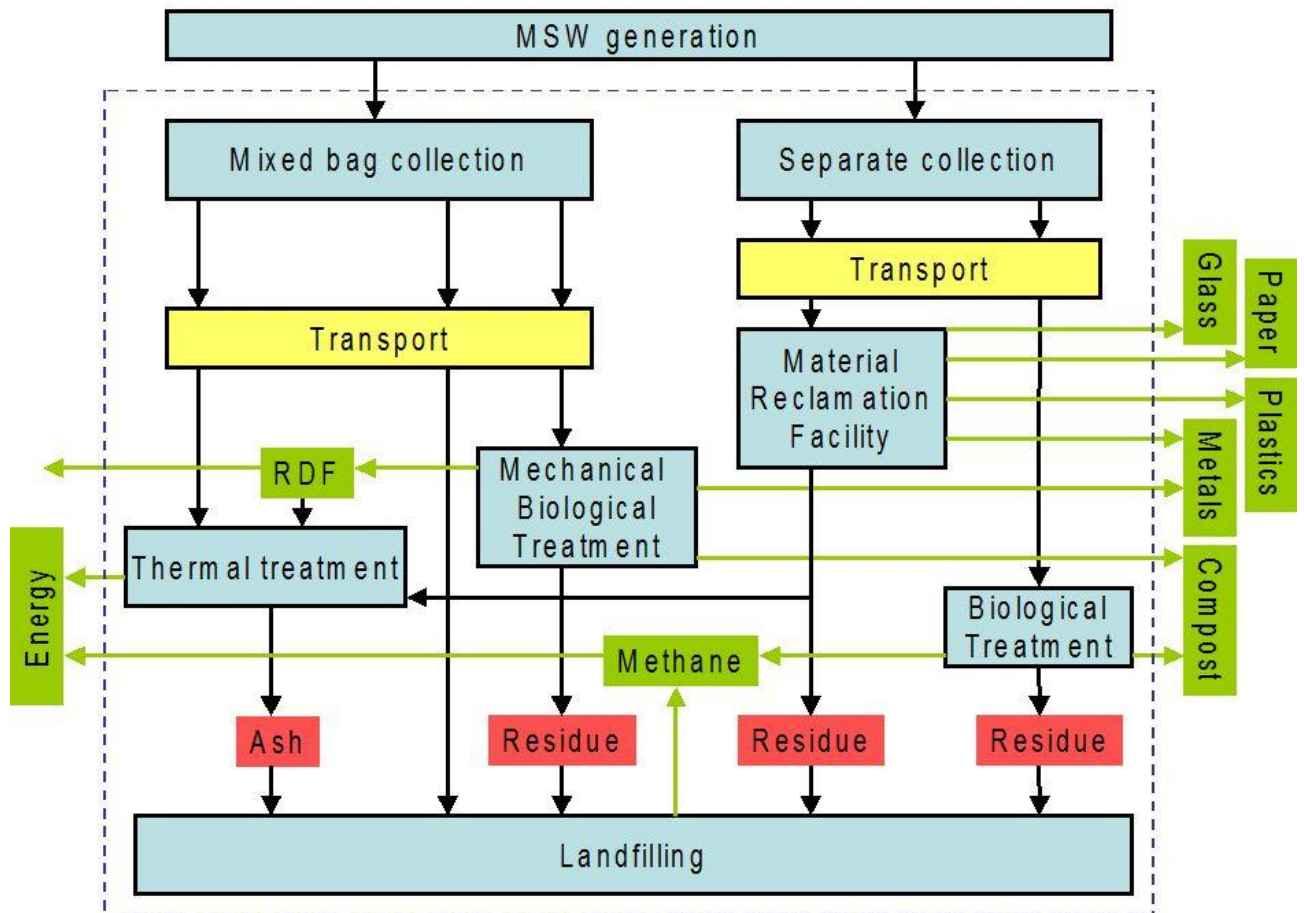


Figure 8. MSW Integrate Management

Waste management is divided into three basic parts:

- prevention of waste generation;
- waste recovery;
- waste disposal.

On the prevention of waste production, should be reduce the production and hazard level of waste:

- the development of clean technologies and the preservation of natural resources;
- the creation of less manufacture products, their use, their disposal do not increase the amount, the volume and dangerousness of waste;
- the development of techniques for elimination of hazardous substances in waste;
- determination of contract conditions that enhance the capabilities and technical expertise in the field of prevention of waste generation;
- the promotion of agreements and program contracts aimed at preventing the quantity and hazardous waste.

- recycling and other forms of recovery in order to obtain raw materials from waste;
- greater use of recovered materials;
- the use of waste as fuel.

Important assessments for an integrated management system are:

- achieve self-sufficiency in the disposal of non-hazardous urban waste in ATOs (ATO);
- allow the plant disposal closest to reduce the transport of waste is compatible with the use of specialist equipment;
- use the methods and technologies that can ensure a higher level of environmental and public health protection.

1.3.2 MSW Techniques

➤ **Separate waste collection** of waste is presented as a complex technology, based primarily on a set of procedures and equipment specifications. The set of procedures consists of several parts: the separation, the transfer, collection, control (and possible treatment), the start of the form provided for reuse or disposal. Separate waste collection is therefore able to play a central role in the recovery of resources from waste. It in fact allows to:

- recover materials still usable: separating from the undifferentiated mass of waste some components upstream of the ordinary collection, you can then recycle them much more easily;
- optimize the treatment and disposal of MSW returns aimed at resource recovery;
- prevent some dangerous components of MSW can be disposed of incorrectly and therefore pose a risk to the environment and to human health.

Furthermore, the achievement of high levels of selective collection involves a substantial savings in the management of the disposal system and leads to a more prolonged period of use of landfills and thus a greater duration of the relevant investments. There are different technological models of selective collection that can be classified both according to their interaction with the ordinary collection system of MSW and is based on the type of crops or materials to the type of use to which the selective collection addresses

➤ It defines the **composting municipal solid waste** the treatment technique that transforms the organic biodegradable fraction in a humified organic fertilizer, called compost, using the action of

microbial flora naturally present in the waste. The transformation of the organic substance takes place through a controlled aerobic biological decomposition process that develops according to three successive stages, respectively defined mesophilic, thermophilic and maturation, during which are active distinct bacterial and fungal species, actinomyces, in the presence of protozoans. Compost, rich in humic acids, the same ones that are found in the humus soil, finds its primary and beneficial use in agriculture as an organic fertilizer, corrective ie soil structure.

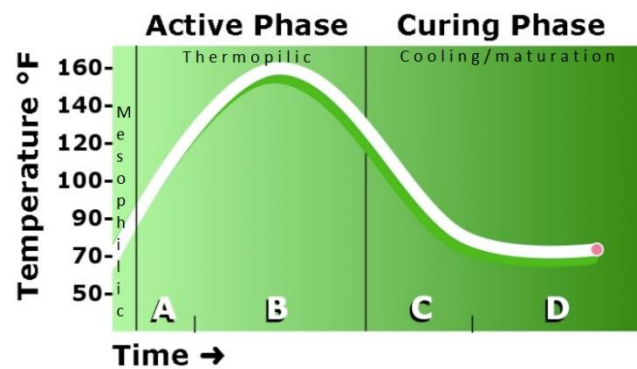


Figure 9. Temperature trend during the composting process

The composting plant, in addition to the organic phase, also includes a series of predominantly physical-mechanical nature of processes intended to facilitate the step of bioconversion, separate materials not subject to biological transformation or its inhibitors, improve the quality of the for a final product its most favorable marketing.

➤ To reduce the waste disposal volume, a large amount of MSW is **incinerated**, is currently receiving widespread attention. Incineration is a thermal treatment system, with the presence of air in excess and respect to the stoichiometric request, through a combustion process transforms solid waste into gaseous products containing suspended particles, ash and slag in the solid and energy (Alhassan, 2012). The strengths of this process are: treatment of waste of different nature and origin, volume reduction and energy recovery. On the other hand, several disadvantages challenge the incinerators, such high emission of CO₂ and other greenhouse gases, considerable operating cost and management of residues. The residues from combustion are classified into two categories: bottom ash (80%) and fly ash (20%). The problem is how to dispose incineration ashes (Muller & Rubner, 2006). The recycling of fly and bottom ashes is of increasing interest worldwide. The last 20 years, several studies address this issue. Yet, research on this topic is continuously developing.

1.4 HOW AN INCINERATOR PLANT WORKS

The ashes used in this study came from INDAVER, in Antwerp, Belgium. Indaver is responsible for waste management in more than 30 locations in Belgium, Germany, Ireland and the Netherlands. The Indaver Group manages around 5 million tonnes of waste every year, using the best available techniques for the treatment of this waste. They recover as many materials and as much energy as possible and they want to contribute to the transition to a circular economy that uses materials and energy more intelligently (Qiao et al., 2008).

Incineration is a thermal treatment system that, through a combustion process with the presence of air in excess with respect to the stoichiometric request, transforms solid waste into gaseous products containing suspended particles, ash and slag in the solid and energy in the form of heat was (Bertolini, 2004). With the incineration is obtained the greater reduction in the volume of the treated waste with production of a sterile solid residue. Compared to other systems of treatment, incineration requires the least effort of the surface and the implant is placed close of the area served with obvious benefits on the waste transport costs. It should also be pointed out that the incineration can treated together waste of different nature and origin: urban, sewage sludge, hospital and industrial. There is also recovery energy from the hot combustion fumes (Youcai, Lijie, & Guojian, 2002).

1.4.1 Combustion principles.

Combustion is an exothermic chemical reaction in which energy is released as heat. The solid waste is substantially characterized by four parameters:

- Calorific
- Moisture content
- Ash content
- of airborne solid percentage.

It defines calorific value (P.C.) the amount of heat that develops as a result of the total combustion of unit mass of waste under conditions of temperature and standard pressure. In particular, there are a higher calorific value (PCS) and a lower calorific value (PCI), the first considers the heat of condensation contained in the products of combustion (steam) and its cooling in liquid phase, until the temperature standard. This water is formed mainly by moisture of the mass in combustion and in smaller proportions of the water resulting from the reaction between hydrogen and oxygen in the air of rejection. The components of the waste characterized by a higher calorific value are the predominant

composition of cellulosic materials (paper and cardboard) and plastics. However, these contribute to raising the P.C. of waste, but the presence of elements causing pollution and corrosion of components of the combustion plants. The knowledge of the moisture content, and its variations, is fundamental for describing the combustion process, since the process does not take place until the refusal loses its water content. The ash content is the residual material which is found at the end of the complete combustion of the waste sample. They contain the inert materials (metal residues, glass, ceramic materials, etc.). Finally, the volatile solids are defined the combustible fraction of the waste that evaporates when heated to high temperatures in the absence of air; the remaining fraction of the combustible material is defined fixed residue, or fixed carbon. The composition of MSW can be outlined, in relation to the combustion, as a sum of a fraction of the fuel, the moisture content and the ash content: Tanner of the ternary diagram (Figure 10), provides a graphical representation. In the diagram it is shown the area where the waste characteristics allow the self-sustenance of combustion itself; A is water in %, R are ashes in %, C are combustible materials in %.

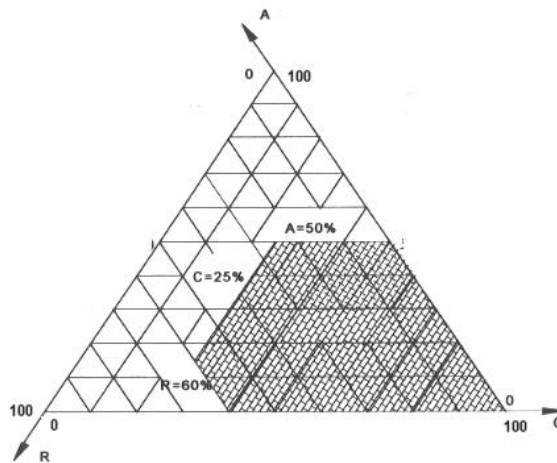


Figure 10. Tanner triangular diagram

The diagram of following Figure 11, represents the relationship between the P.C.I., the moisture content and the percentage of ash, providing a broad indication of the greater or lesser capacity for incineration of waste.

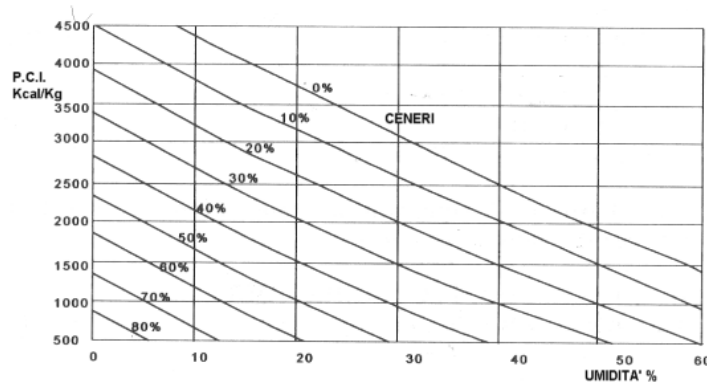


Figure 11. caloric value P.C.I. for humidity and the ashes of MSW

1.4.2 Treatment cycle

In the incineration treatment cycle can be identified the following main steps:

- Acceptance and accumulation;
- Supply;
- Combustion;
- Heat recovery;
- Treatment of combustion residues.

The mentioned steps are represented in the schematic sectional view of Figure 12 and are also present equipment of the incineration plant. This scheme is grate incinerator from INDAVER, in Antwerp, Belgium.

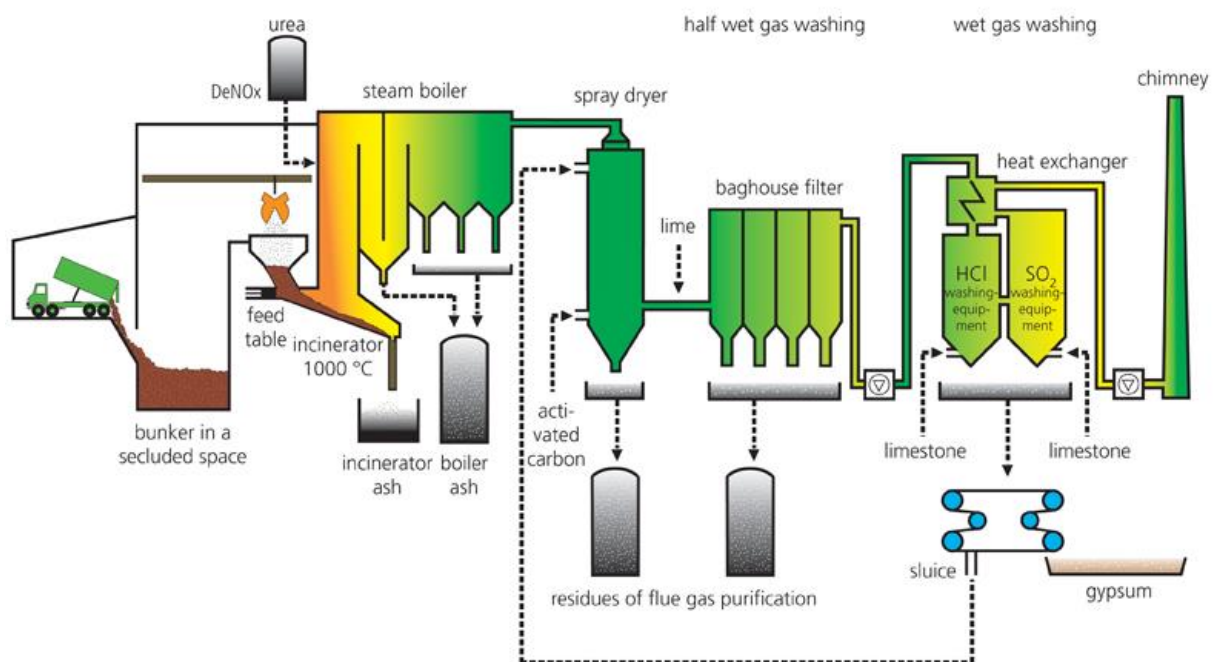


Figure 12. Grate incinerator scheme from INDAVER

➤ *Acceptance and accumulation*

After registration and weigh on a suitable weighing to automatic operating bridge, the vehicles involved in the collection and transport to the waste, arrive at the pit of accumulation where pour its content. The pit accumulation acts as lamination in waste flow, variable over time, and allows a continuous feed and constant phase incineration. Its useful volume (V_u) is calculated on a basis of a storage time (t_c) of not less than two days of production of the waste, the maximum continuous capacity of the plant (P_{mc}) in t/h, and taking into account the specific weight of the waste in the pit (γ_s) of 0,3-0,4 t / m³:

$$V = \frac{P_{mc} \cdot 48}{\gamma_s} \quad (1)$$

The walls are smooth but be smooth, to avoid the storage of materials and facilitate cleaning operations, and are coated with special products hardeners rubs protection; the bottom is waterproofed and equipped with sump of the washing water collected.

➤ *Supply*

The supply of the furnace takes place with a mechanical arm with a bridge crane that allows its movement in both transversal and longitudinal. The mechanical arm also carries out a mixing of the contents in the pit so that the characteristics of the waste to be incinerated are the most homogeneous as possible. The waste raised is transferred to the large hopper. So the supply conduit placed between the hopper and the oven must have sufficient length to form a rejection column which acts as upper plug in the oven and thus prevents the release of smoke.

➤ *Combustion*

The incineration takes place in special furnaces formed by a grid floor and a combustion chamber, and develops, the three phases, described before: drying, ignition and combustion coexist. Drying is caused by the hot gases of combustion or pre-heated air, by radiation and convective effects generated from the oven walls. The combustion of the waste and of the gases generated during the drying and thermal decomposition is mainly influenced by three factors: the time (a detention time must be

assured sufficient to the completion of chemical reactions), turbulence (an adequate degree of turbulence It promotes contact between the reactants and a more rapid completion of the process) and the temperature (complete combustion requires values not lower than 750-800 ° C, having the upper limit of 1,000-1,100 ° C in order to prevent melting of the ashes). When the temperature decreases, the ashes fused create solidify in vitreous masses, the slag, which, adhering on the grid and on the walls of the combustion chamber, damaging the materials constituting the oven, hampering the orderly functioning.

The field of functioning of a furnace can be represented by the diagram (Figure 13) following in which shows the flow of the waste (t / h), and the thermal potential, or thermal load, Gcal / h.

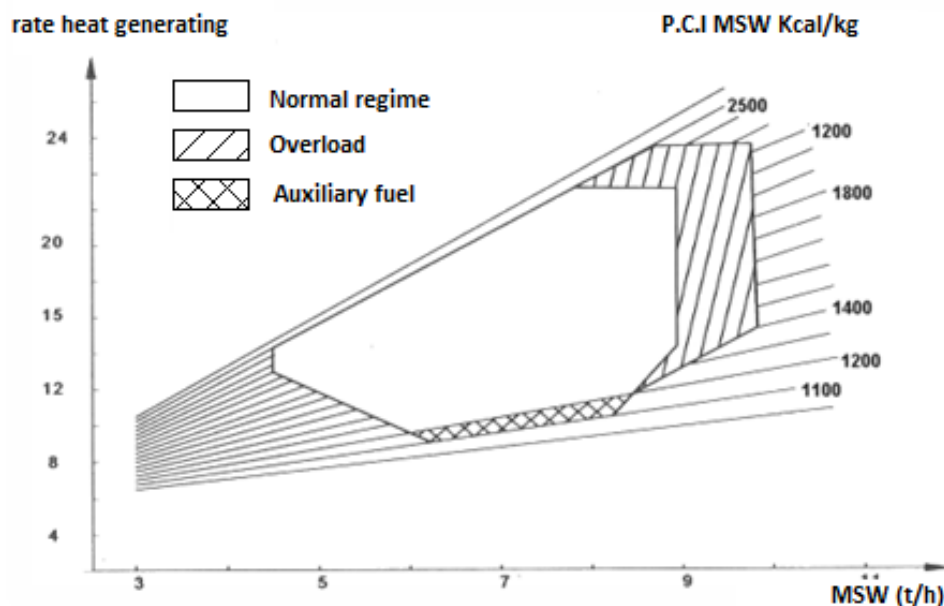


Figure 13. Field of functioning of a furnace

Known P.C.I. of the waste, one can determine the quantity to be treated per hour in normal operating conditions thus avoiding to resort to the use of auxiliary fuels or overload the oven. The delimitation of the field of operation considers the flow of combustion air and of the most suitable operating temperatures, with regard to the thermal load, and an adequate flow of waste ensuring coverage of the grid but which does not exceed at the same time values for which a complete combustion is not ensured.

➤ **Combustion chamber**

The combustion chamber in which is housed the grid has, in addition to the mouth of the waste input, two openings: the first top to the exit of the combustion gas, the second lower for the evacuation of the ash and the slag. Above the grid there is a heat radiation on the layer of waste reshuffled by the grid. The chamber is made, with refractory materials lined with insulating layers to ensure the maintenance of operating temperatures inside the oven of about 1,000 ° C. While the combustion chamber normally includes metal walls cooled by water (water-jacket), connected with the boiler of the boiler, which also allow to obtain a higher heat production. The combustion chamber is equipped with an ignition system with oil burner or gas to automatic operation methane, is used for the starting of the oven is in the case in which the implant are received solid waste with low calorific value, less than 1,000 kcal / kg. The proportioning of a combustion chamber is correlated to the specific thermal load, the values of which are normally comprised between 100.000150.000 kcal / m³h. The amount of air required for the combustion process is extracted from the pit of accumulation of waste and fed into more conduits, with the aid of centrifugal fans.

In INDAVER there are two different types of Combustion chamber:

- **Grate Furnace (for BA)**

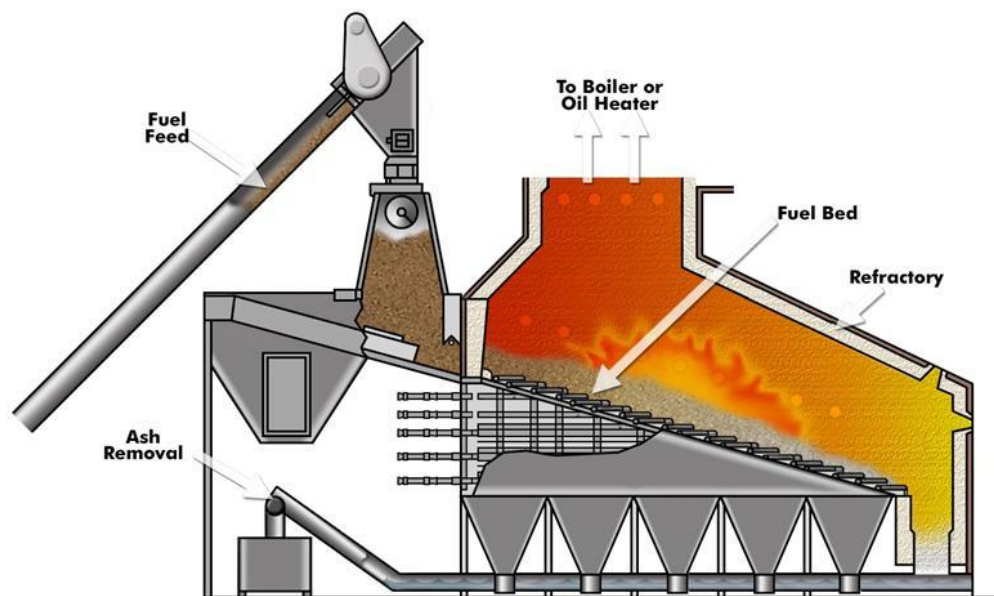


Figure 14. Grate furnace

- **Fluidized bed furnace (for FA)**

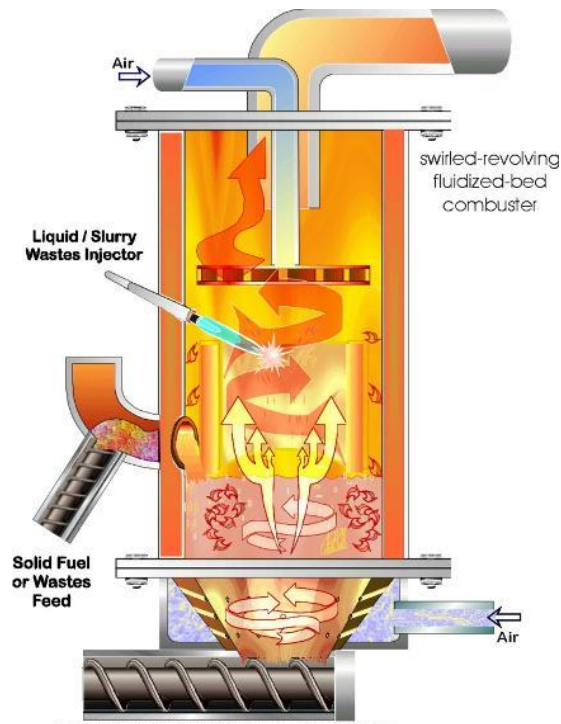


Figure 15. Fluidized bed furnace

➤ **Heat recovery**

In the recovery of the heat from the combustion gas is used in practice to a heat exchanger in which the hot fluid (smoke) transmits heat to the cold fluid (water) due to the difference in temperature. The system essentially comprises the following units: a superheater fed with the saturated steam produced in the boiler which allows to increase the temperature up to 500 ° C; the boiler body of which rate of the cooling surface may be located in the combustion chamber, after coating with silicon carbide to protect it from the action of the flame; an economizer in which the water supply is preheated to a temperature a little lower than that of vaporization, with a simultaneous further lowering of the temperature of the fumes that stabilizes around 200-300 ° C. The schematic process cooling and heat recovery is illustrated in the following Figure 16.

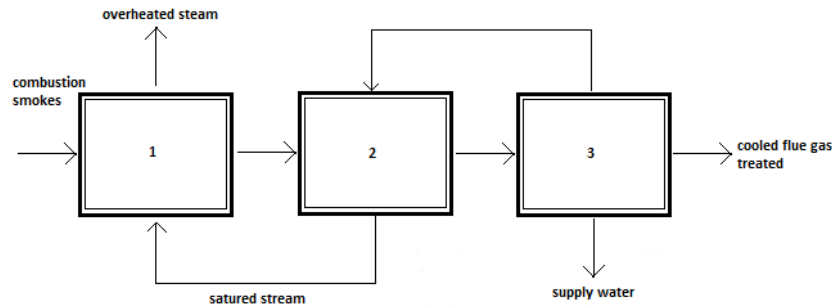


Figure 16. Diagram of a heat exchanger with steam production

The transformation of solid waste into thermal energy in the form of heat makes available a variable steam quantity between 1.5-3 tonne for tonne of MSW, depends on the calorific value and the moisture content of the waste. Such steam can be used as it is or converted into electricity or used for both purposes. The steam conversion, and then into electrical energy thermal energy involves the use of a steam turbine, in which the thermal energy is transformed into mechanical energy and a generator to convert mechanical energy into electrical energy.

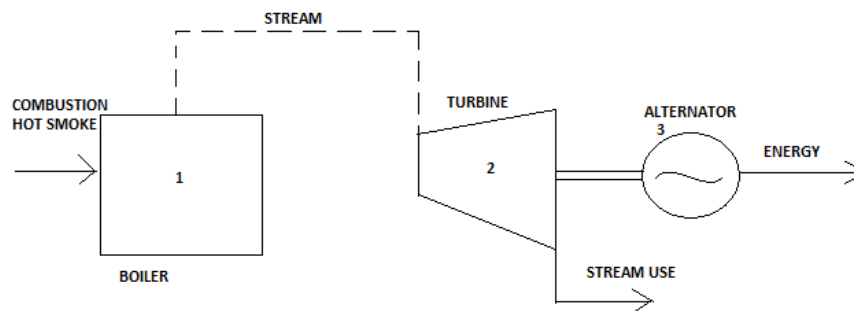


Figure 17. Diagram of a type of cogeneration plant for the production of electrical and thermal energy: 1) Boiler, 2) Turbine, 3) Alternator

The set turbine-generator, is characterized by conversion efficiency around 20%, corresponding to a ratio between the heat supplied and energy produced approximately 4,500 kcal / kWh. In the overall efficiency of a conversion system to be considered heat loss during the process leading to a reduction of an average of between 8-10%.

1.5 MSWI ASH AS SUPPLEMENTARY CEMENTITIOUS MATERIAL

1.5.1 Cement

➤ *Cement consumption*

Ordinary Portland cement is the major construction material throughout the world. A report released by the Portland Cement Association (PCA) indicates that cement consumption among developed economies increased by roughly 9.2 million metric tons in 2015, followed by another 9 million ton increase in 2016.

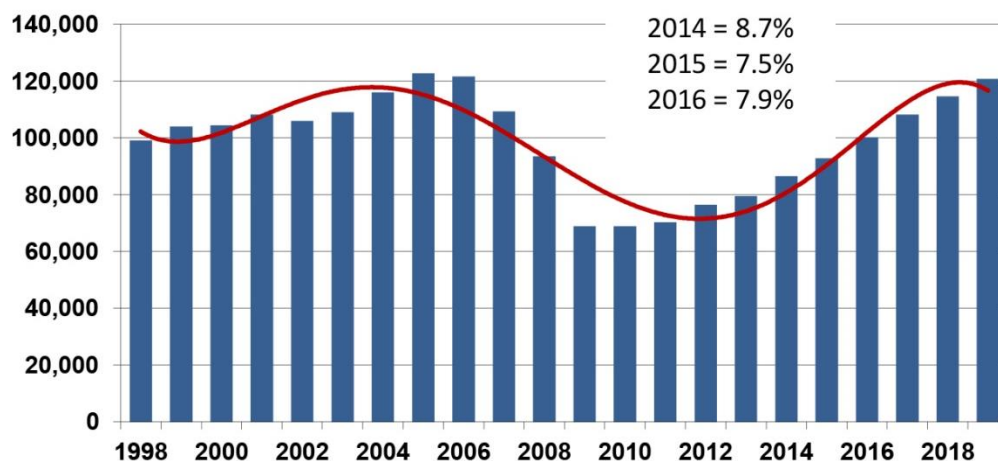


Figure 18. Portland cement consumption- thousand metric tons

The global cement consumption is closely linked to the growth and progress of country. It depends on several factors like demand, raw material reserves and economic condition. The cement industry has changed in recent years. The major potential is Switzerland and China, the emerging market, it represent approximately 90% of the worldwide market today while western Europe and North America account for most of the remainder. This has opened many markets to competition, consolidation and technical progress. In the follow Figure 18 there are a ranking of top 10 global cement companies (Global Center Magazine, Statista 2016).

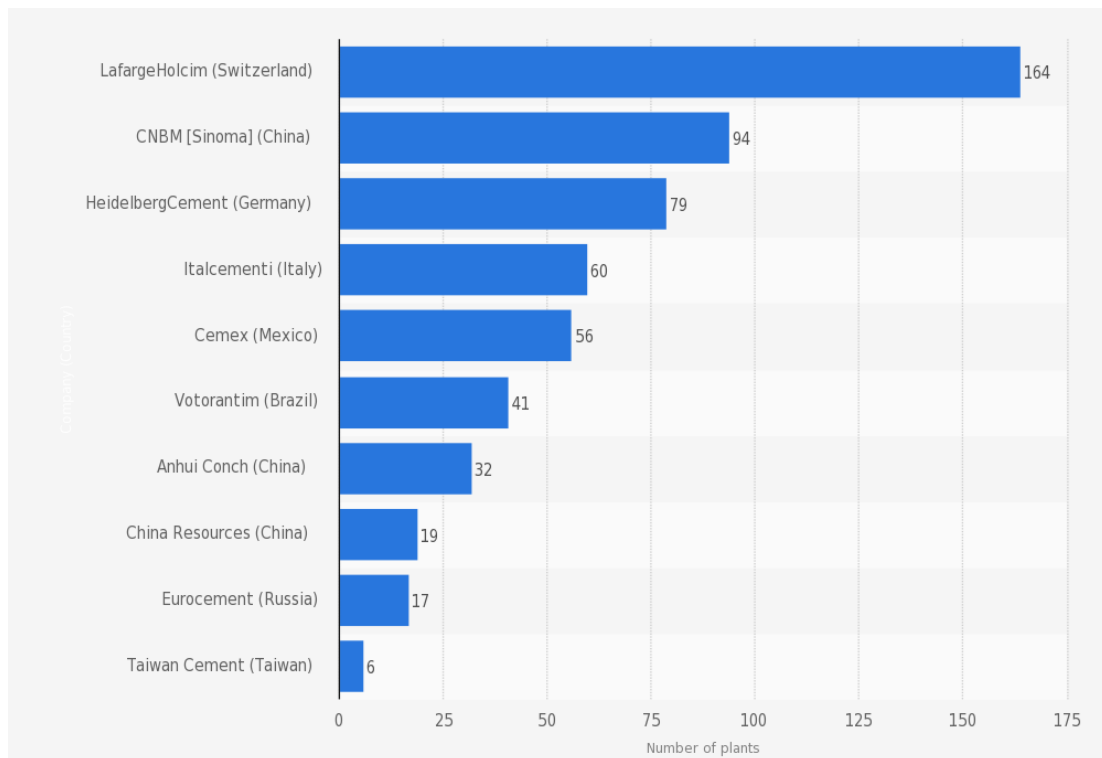


Figure 19. Numbers of plants of top cement producers in 2015 (Statista)

➤ *Cement in Belgium*

Belgium has five integrated cement plants, quite all are located close to the French border to the southwest. The other plant is located at Lixhe in the east, close to the borders with Germany and the Netherlands. Belgium consumed 6000000 tonnes of cement in 2010, although it also exported 1.676150 tonnes. Over 95% of the exports were destined for the EU, mainly to France and the Netherlands. In 1980 the Netherlands took 71% of Belgian cement exports, but by 2005 this had halved to just over 35%. Much of the exports now head to France, which took just 0.4% of Belgian cement exports in 1980, but 44% in 2005. Of the cement produced in Belgium, nearly 20% was used in civil works, 36% was used in residential construction and 44% was used in non-residential construction. The clinker substitution rate was 47.3%.

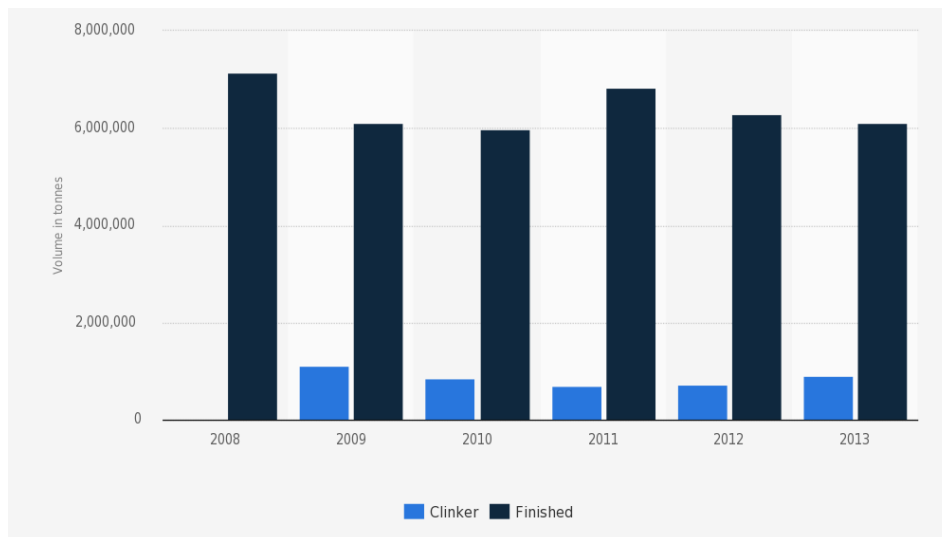


Figure 20. Cement produced in Belgium from 2008 to 2013, by type (in tonnes), (British Geological Survey, Statista)

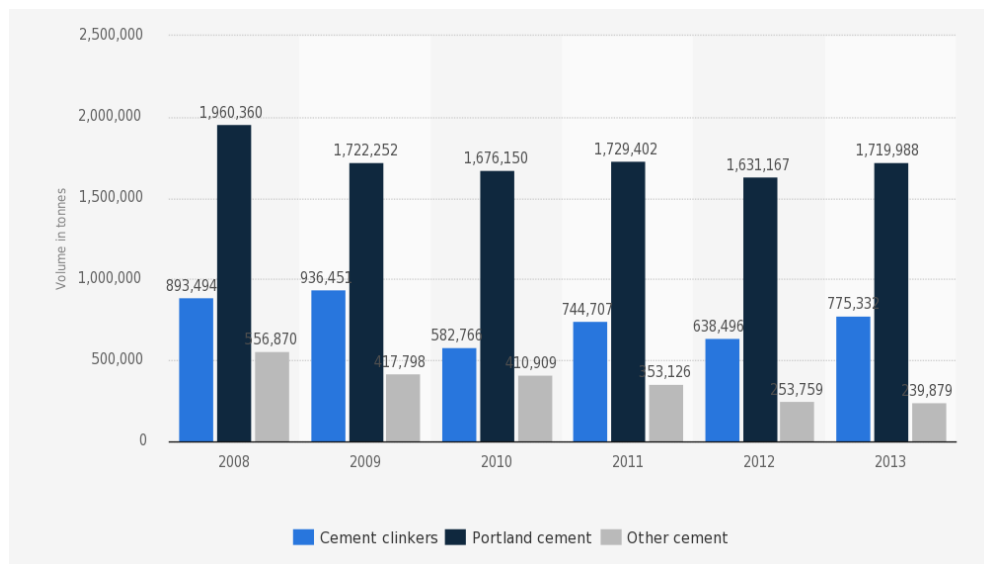


Figure 21. Volume of cement exported Belgium from 2008 to 2013, by type (in tonnes), (British Geological Survey, Statista)

➤ Cement constituents

Clinker is produced from raw materials, such as limestone and clay, they are crushed, homogenised and fed into a rotary oven. The clinker burn at temperature of 1450°C which is needed to form the new compounds. Clinker consists mainly of calcium-, silicium-, aluminium- and ironoxides. In the next phase the cement is grinding in a mill. Gypsum and other additional materials are added to the clinker. All constituents leading to a homogenous and fine powder. Cement, aggregates and other suitable materials are mixed with water to produce concrete. When water is added to cement, it reacts and forms a glue which binds together the other main constituents of concrete.

1.5.2 Supplementary Cementitious Material (SCM)

Supplementary cementitious materials are those materials which have a behavior that is hydraulic pozzolan. The pozzolanic activity is conventionally described as a measure of the degree of reaction in time between a pozzolan and Ca_2 or $\text{Ca}(\text{OH})_2$ in the presence of water (Snelling et al), physical surface adsorption is not considered part of the pozzolanic activity, because no irreversible molecular bonds are formed in the process (Takemoto and Uchikawa 1980). The driving force at the base of the pozzolanic activity is the difference in Gibbs free energy between the first stages and the final reaction, while the reaction kinetics are governed by the barrier of activation energy which must be exceeded in order to proceed in the reaction (to Felipe et 2001). SCM represents a wide variety of materials that vary in origin, chemical and mineralogical composition. The most widely used classification is Massazza (2001). They differ mainly in two main categories, it depends from the origin, natural or not. In the first category the characteristics can vary only through processes such as sieving or grinding processes, while SCM of artificial origin can be produced and made deliberately, just as the combustion ash. In the same group there can be a large variability of the physico-chemical properties. The figure shows a typical variation of the most used groups of SCM.

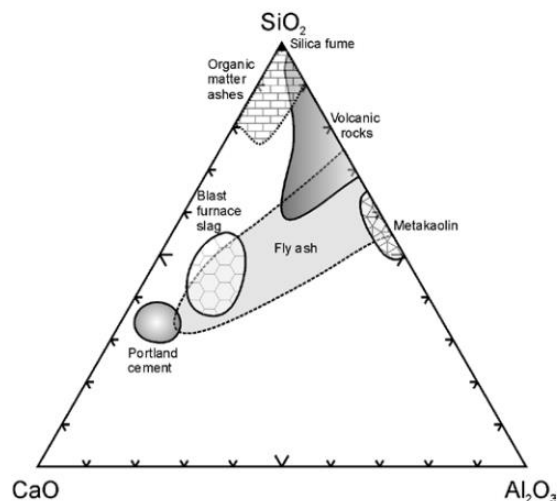


Figure 22. Ternary $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ diagram (wt% based) situating the chemical constitution of the major

When pozzolanic materials are added to cement, the silica (SiO_2) reacts with free lime released during the hydration of cement and forms additional calcium silicate hydrate (CSH) as new hydration products, this improves the mechanical properties of concrete (Ganesan2007). The use of SCM has several advantages, first, the economic gain; second, lowering of greenhouse gas emissions emitted during the production of a normal concrete and especially the improvement of durability and of the final product.

1.5.3 MSWI as SCM

Due to increase cement consumption in the world, the cement industry aims to sustainable development. The aim is to reduce its fuel and raw material requirements and subsequent emissions. There are different SCM materials as regards Portland cement: silica fume, fly ash, slag, natural pozzolans, etc (Papadakis, Antiohos, & Tsimas, 2002). Fly ash has been recognized as a pozzolanic constituent (Joshi and Lothia 1997). In Europe, different countries had good result, then generally the conclusions lead to proper evaluation of the samples functionality (Krammart & Tangtermsirikul, 2004).

- *Present hurdles using MSWI as SCM*

The quality of ashes depends of the processing, the burning temperatures, the coal type and other factors (to. Sakai et 2005). The physical and chemical characteristic are very variable, depending on the process they undergo.

Not all types of ashes can be used, such as some ashes from a France incinerator, the results was not satisfactory(Aubert et al., 2006). But the same authors of the last study has good result from other MSW in another study (Aubert et al., 2006). Therefore, if the MSWI are properly pretreated is possible the solve the issues. (Saikia et al., 2015). Generally, the hurdles encountered are: Elemental Al, Chlorides and sulphates and heavy metals.

- Elemental Al

The presence of elemental Al in concrete due to an increase in volume, then an expansion of the cement(Mangialardi, Paolini, Poletini, & Sirini, 1999), (Pecqueur et al, 2000).

- Chlorides and Sulphates

When in concrete are found higher percentages of sulphates at 0.4-0.6% degradation Concrete can be attributed to sulfate attack(Mulder, 1996), (Pera, Coutaz, Ambroise, & Chababbet, 1997).

- Heavy Metals

They are toxic, so if they enter into the environment and therefore in our organism in doses higher than those tolerable entail serious effects. Heavy Metals require a long time for the leaching (Tang, Florea, Spiesz, & Brouwers, 2014) (Mangialardi, 2003)

In Europe, different countries, after treatment, had good result, then the conclusions lead to proper evaluation of the samples functionality (Krammart & Tangtermsirikul, 2004).

1.6 TECHNIQUE TO DETERMINATE POZZOLANICITY

The pozzolan are silica or silica-alumina substances that can reacting at atmospheric temperature with the calcium hydroxide to form compounds cementing. They are divided into natural and artificial. Natural ones can be of volcanic origin, or mixed, while the artificial ones are constituted by fly ash or by the silica fume which is the by-product resulting from the reduction process of the quartz in pure silicon metal in electric arc furnaces for the production of silicon or iron-silicon alloys. The pozzolanic cement is obtained by grinding the clinker and pozzolan with chalk (Zheng, 2016). The hydration of cement, pozzolanic leads to the same of the Portland cement hydration products, with the difference that is less than the content of C_2S and C_3S to which it must be the mechanical strength at early age (Bertolini et al 2004). As regards the long curing, the mechanical strength of pozzolanic cement is very similar or even superior to that of Portland cement; this is due to the fact that unalterable amount of calcium hydrate (C-S-H silicate), products for the relatively slow reaction between lime and pozzolan, is to be added to that obtained by hydration of C_3S and C_2S . The amount of pozzolan addition to Portland cement clinker and gypsum during the grinding for the production of pozzolanic cement can vary from 10 to 40%, especially in relation with the reactivity of the pozzolan (Qia et al, 2008). If a less pozzolanic material is added to the cement it is necessary to added it in significant proportions otherwise the mechanical strength would be very low. If the pozzolan is a good reactivity, the cement has better properties during processing. Specifically, there are two tests to evaluate it: TGA or pozzolanicy test.

The **pozzolanicy test** is carried out by mixing 20 g of cement and 100 ml of water at 40 ° C for 8 days. To evaluate the results it is necessary to know the solubility at 40 ° C of the calcium hydroxide in a solution whose alkalinity varies from 35 to about 100 mol OH- per liter (UNI EN 196-6: 1991). After 8 days the samples should be filtered through a 2.7 μ m, after diluted HCl with methyl orange indicator, to regulate pH to 12.5, then titration with 0.03 M EDTA solution. The results in the graph explain if the sample is pozzolanic or not.

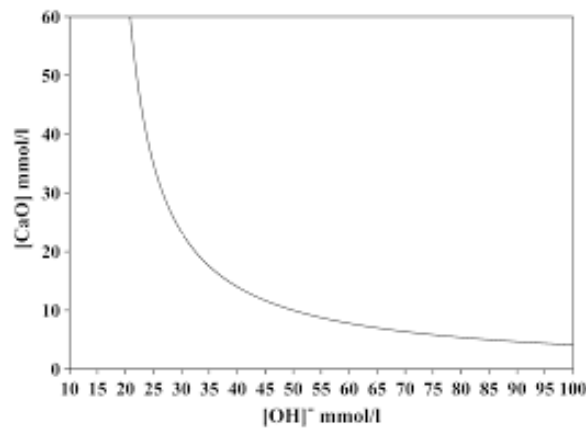


Figure 23. Graph of Pozzolanicity Test

TGA (Termogravimetric Analysis) measuring the weight of a substance while it is subject to heating with controlled temperature growth (Leemann et al, 2015). The use of thermogravimetric conditions depend on the information to be obtained. However the first experiment which is usually performed to quickly characterize the decomposition of a material with formation of volatile products, consists of a heating in an inert gas current with increase of the temperature of 10 ° C / min. The results of the experiment are normally described and represented in terms of percentage of residue sample weight, depending on the heating temperature (Afshinnia & Rangaraju, 2015). Portlandite content in each cement paste sample can be determined and the reactivity of ash can be indirectly determined from the portlandite consumed.

1.7 ASR (ALKALI SILICA REACTION)

The reaction Alkali - Silica (ASR Alkali - Silica Reaction) is due to the expansive phenomena destructive to concrete (Leemann et al., 2015). The ASR reaction was discovered in the late '30s, but only made explicit in 1940 by T.E. Stanton, who first described it as a reaction between the cement and aggregates in concrete. It is now known that the reaction takes place in the high pH of the solution in the pores of concrete (Rajabipour et al, 2015). This aggressive solution attacks the siliceous minerals present in the coarse aggregate and fine. The reaction alkali - silica substantially involves the aggregates that contain a particular form of silica, capable of reacting with the alkali (sodium and potassium), coming from the concrete or from the external environment, to produce an expansive reaction. Each granule of reactive aggregate equipped of silica poorly crystallized or amorphous, swells when in contact with water and alkali (Murlidhar, Mohamad, & Armaghani, 2016).



Figure 24. Example of ASR in the concrete

The reaction between the alkali and siliceous aggregates produces a reactive silicate gel that can absorb mainly water, and so swell (Chappex & Scrivener, 2012). This swelling can cause a cracking state strongly influenced by the presence of constraints (geometry of the structure, arrangement of armor) and the level of existing stress states (Figure 24). When these expansive forces exceed the tensile strength of concrete can occurrence breaking (cracking) (Davies & Oberholster, 1988). The typical crack scene is called "a spider web" with randomly distributed cracks from which the gel can leak whitish. The alkali-aggregate reaction occurs much faster and more intensively as increase in relation to the increase of: sodium and potassium in the aqueous phase that fills the capillary pores of the cement paste: a content of more than 3 kg / mc is considered dangerous, the relative humidity and the amount of siliceous aggregates.

Chapter 2 MATERIALS

In this research mortars samples are used to test compressive strength and ASR and paste samples for TGA. For testing ASR, sand fine aggregates was replaced with glass aggregates.

Normal concrete is composed of cement, sand, water and aggregates. Three types of bottom ashes, with different grain size (6/15; 2/6; 0/2)mm, and one type of fly ash was used to casting mortars for all different tests made in this study. One types of grinding glasses was used for Alkali Silica Reaction and the strength test. Details of each material are given in this chapter.

2.1 CEM I 52.5

The cement used in this study was collected from VVM Cement in Rieme, Belgium. In this plant there are a number of different cement types, the material taken is CEM I 52.5, it has higher strength. This cement is conform to the norm NF P 15-317:2006 (PM), NF P 15-318:2006 (CP1/CP2), NF P 15-319:2014 (ES) (Annex 1), through AFNOR Certificate (France). Portland cement contains 95-100% of Portland cement clinker, with addition of 5% natural gypsum as bonding regulator, commonly grounded in ball mill.



Figure 25. CEM I from VVM

2.2 MSWI ASHES

The ashes used in this study was collected from INDAVER, in Antwerp, Belgium. Indaver is responsible for waste management in more than 30 locations in Belgium, Germany, Ireland and the Netherlands. The Indaver Group manages around 5 million tonnes of waste every year, using the best available techniques for the treatment of this waste. They recover much energy as possible.



Figure 26. Indaver Plant

In this plant were taken four different ash samples with different sieves (Table1), following the information about each samples:

Table 1. Samples collected in Indaver

ASHES	SIEVES (mm)	DATE OF PRODUCTION
BA 6/15	6-15	January 2016
BA 2/6	2-6	January 2016
BA 0/2	0-6	March 2016
FA	fly ash	Fresh



Figure 27. Samples collected

The binders used was five:

- CEM I
- CEM I + 25% BA 6/15
- CEM I + 25% BA 2/6
- CEM I + 25% BA 0/2
- CEM I + 25% FA

2.3 AGGREGATES

Aggregates are a fundamental component of concrete. They don't contribute to the chemical processes of gripping and hardening, but they are essential for the resistance, deformability and durability of the concrete

2.3.1 Grain size distribution of sand

Confirm to the NBN EN 196-1 (2005) for casting mortars was used CEN-NORM SAND DIN EN 196-1. The standard sand shall comply with the particle size distribution specified, as determined by sieve analysis on a representative sample of sand of total mass not less than 1345 g, as in the Table 2. Sieving shall be continued until the amount of sand passing through each sieve is less than 0,5 g/min.

Table 2. Requirements of EN 196-1

Requirements of EN 196-1	
Square mesh Size (mm)	Cumulative (%)retained
0.08	99 ± 1
0.16	87 ± 5
0.5	67 ± 5
1	33 ± 5
1.6	7 ± 5
2	0

The moisture content shall be less than 0,2 % determined as the loss of mass of a representative sample of sand after drying at 105 °C to 110 °C to constant mass and expressed as a percentage by mass of the dried sample.



Figure 28. Standard sand

2.3.2 Grain size distribution of glass aggregates used

To evaluate the alkali silica reaction was used mortars casting with glasses in place of sand. To have the same grain size of the standard sand, 25 Kg of waste bottles of different colors was washed with water and dry in the oven (T=105°C) for 48h.



Figure 29. Waste bottles



Figure 30. dry bottles in the oven 105°C

After drying, the bottles were crushed in the Jaw Crusher apparatus, and then sieved to obtain the required size distribution.



Figure 31. Crushed bottles

The bottles were sieved to obtain the same grain size distribution as standard sand.



Figure 32. Sieves bottles

2.4 MORTARS

Mortar bars was used for several test, following their composition:

- CEM I
- 75% CEM I + 25% BA 6/15
- 75% CEM I + 25% BA 2/6
- 75% CEM I + 25% BA 0/2
- 75% CEM I + 25% FA
- CEM I + Sand ratio 1:3 + w/c 0.5

These samples were used for compressive strength test and ASR.



Figure 33. Concrete mortar bars

Cement paste was used for TGA, following the binders were used in w/c 0.5:

- CEM I
- 75% CEM I + 25% BA 6/15
- 75% CEM I + 25% BA 2/6
- 75% CEM I + 25% BA 0/2
- 75% CEM I + 25% FA

Chapter 3 METHODS

3.1 GRINDING OF ASHES

To use ashes in the concrete, it was necessary to grind samples of size 6-15mm, 2-6 mm, 0-2 mm. FA was fine enough. Planetary ball mill was used for grinding, 12 balls of 1.5 cm was used to grind 100 g each of ash. 6/15 and 2/6 fraction was ground for 15 min and 300 rpm and 0/2 fraction for 5 min for same duration.



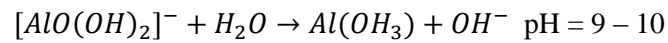
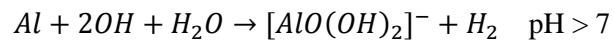
Figure 34. Grinding samples

3.1 TREATMENTS METHOD

The ash produced is a residual of incineration of municipal solid waste, and thus is not produced by an industrial controlled process. As a result, it has many constituents making it unsuitable to be used in cement as such. Elemental aluminium, chlorides, sulphates and heavy metals are the disadvantageous constituents in the ash. So some beneficiation methods are tested for its suitability to be used as a supplementary cementitious material. The following treatment methods have been tried:

➤ Washing with water

Elemental Al reacts with water and releases hydrogen gas in alkaline environment. This treatment can possibly reduce the expansion due to elemental Al and some soluble salts such as chlorides and sulphates. Occurs the following chemical equation (Saikia et al. 2015):



Washing of ashes with water was done as follows: 500g of ash was mixed with 1 liter of water and was mixed daily for 1 minute for 7 days. After washing the samples were dried in the oven at 105 °C temperature for 24 h.



Figure 35. Ashes washed with water

➤ Washing with NaOH

Elemental Aluminium reacts with NaOH, and follows the stoichiometric equation given below. The reaction is much faster, than with water, releases hydrogen thus reducing the expansion when mixed with cement. The ash samples were immersed in 0.5M solution of sodium hydroxide (atm. Pressure 20°C) for 7 days at 20 °C. Then the samples was dried in the oven, T=105 °C for 24 hours, and then ground in ball mill to fine powder.

The following equation explain the process (Pera et al, 1996):

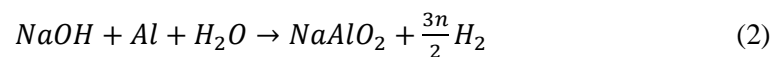




Figure 36. Ashes washed with NaOH

➤ **Accelerated carbonation**

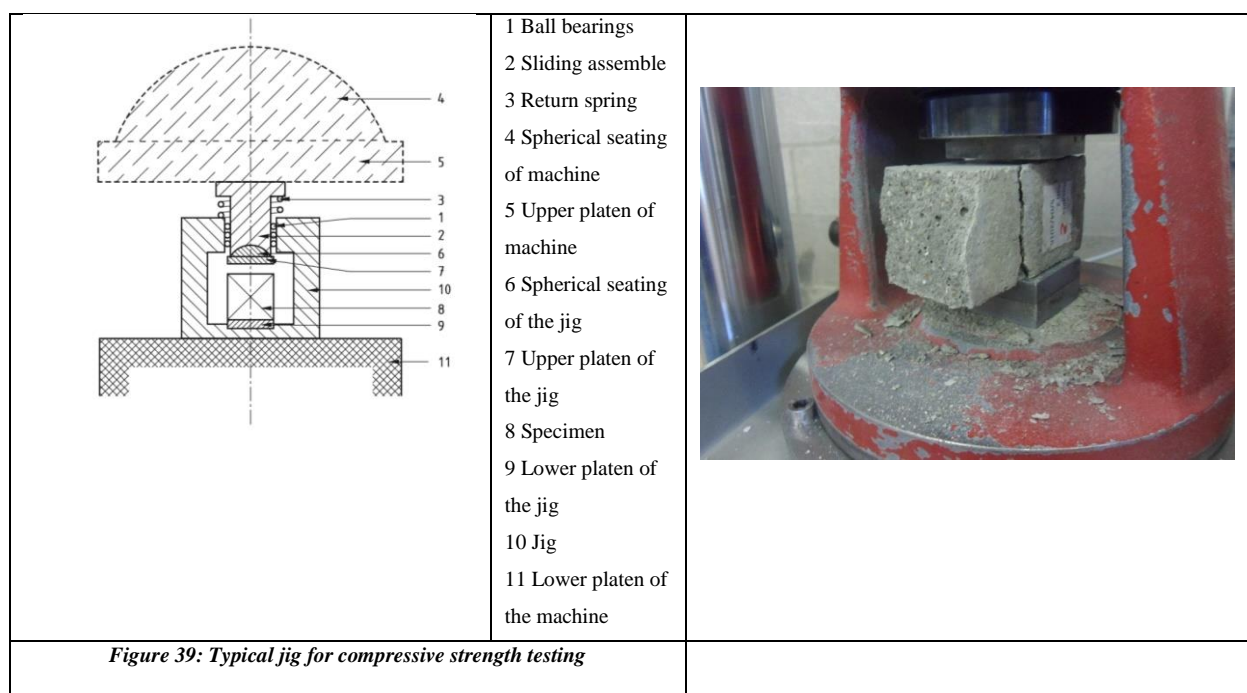
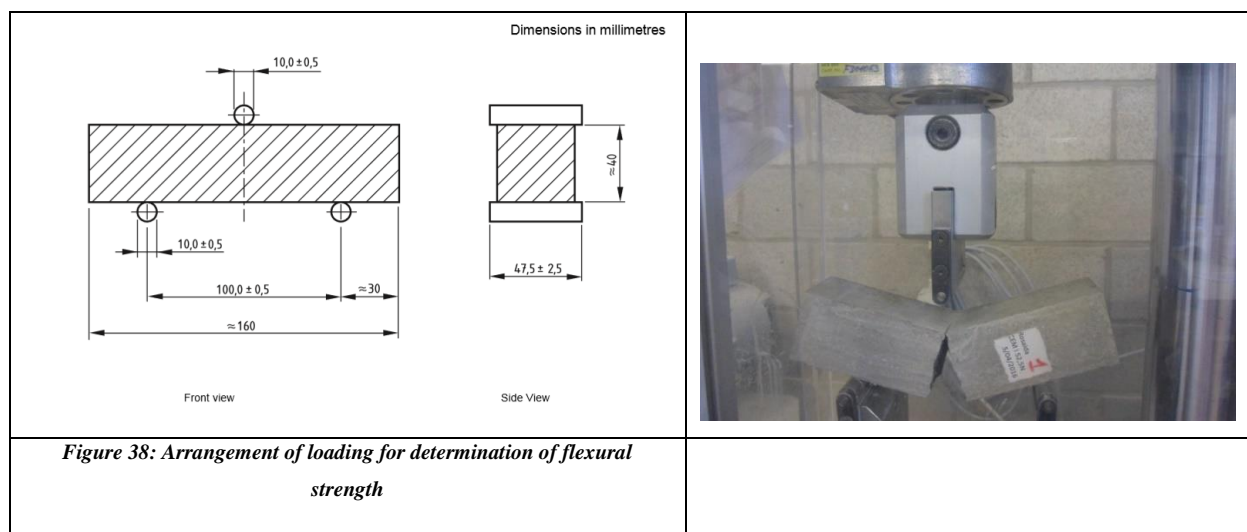
It is reported in literature that carbonation can reduce the solubility of elemental aluminium in water, and thus reduce the reaction and also the amount of hydrogen gas produced. This is facilitated by carbonation of various phases in the ash, encapsulating the aluminium in the process (Aricx et al, 2006) Carbonation of ground ash was done at a CO_2 concentration of 10% and a temperature of 20°C . The samples stayed in that condition for 7 days.



Figure 37. Carbonate chamber

3.2 COMPRESSIVE STRENGTH

Compressive strength test was conducted in mortar bar specimens of size 40 mm x 40 mm x 160 mm prepared according to NBN EN 12390-2:2009. For each mix, the 28 day strength is determined as an average of three specimens. The water cement ratio for standard sand mortar specimens was 0.5, and those for glass aggregate specimens was 0.55. The prepared specimens were moist cured for 28 days at a relative humidity of 100%, and then tested for strength. The apparatus for measuring the compressive strength of specimen is shown in Figure 38-39. In the apparatus, the prism was placed with one side face on the supporting rollers and with its longitudinal axial normal to the support, as show in the Figure.



Conforming to NBN EN 196-1, the three vertical planes through the axes of the three rollers shall be parallel and remain parallel, equidistant and normal to the direction of the specimen under test. One of the supporting rollers and the loading roller shall be capable of tilting slightly to allow a uniform distribution of the load over the width of the specimen without subjecting it to any torsional stresses. The flexural strength R_f is calculated in megapascals from:

$$R_f = \frac{1.5 * F_f * l}{b^3} \quad (3)$$

where:

R_f is the flexural strength, in megapascals;

b is the side of the square section of the prism (mm);

F_f is the load applied to the middle of the prism at fracture, in newtons;

l is the distance between the supports (mm)

The compressive strength R_c is in megapascals from:

$$R_c = \frac{F_c}{1600} \quad (4)$$

where

R_c is the compressive strength, in megapascals;

F_c is the maximum load at fracture, in newtons;

1 600 is the area of the platens or auxiliary plates (40 mm × 40 mm), in square millimetres.

3.3 OBERHOLSTER TEST

Oberholster test is used to determinate the potential alkali-silica reactivity of aggregates, conforming to NF P 18 594. The samples used in this test are mortars with glass aggregate to induce ASR, the test start one day after casting. First, must took measure of samples length and put in the apparatus; mix 400g of NaOH with 10 L of H₂O and put it inside it; attend until the temperature reach 80°C and after

1 h took the measures and took it again all days for 20 days, to monitored the expansion. If the expansion is more than 0.1% that means potential for ASR.



Figure 40. Samples in ASR apparatus

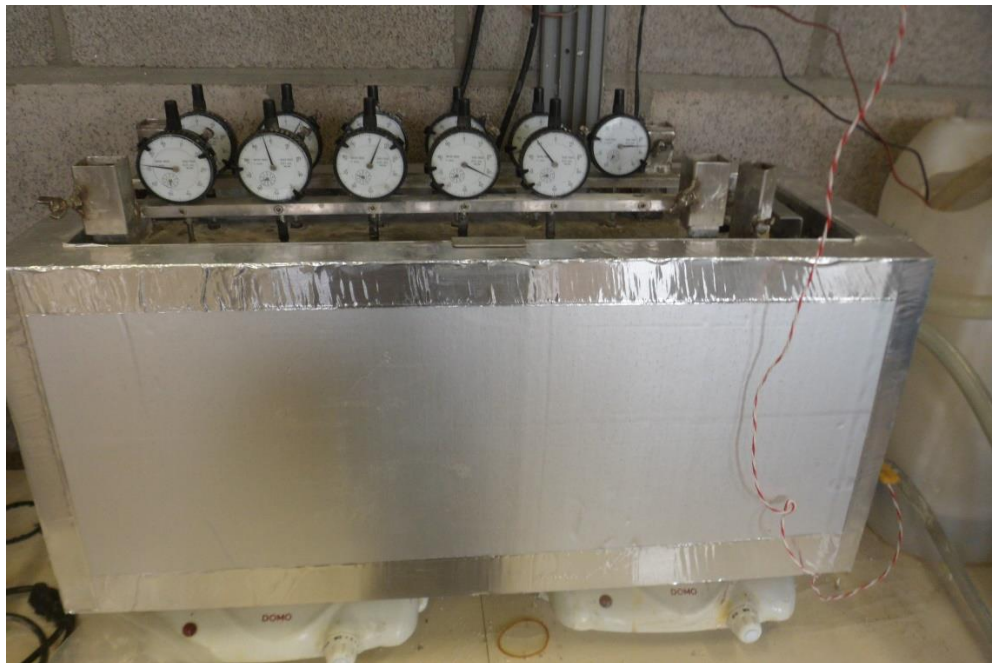


Figure 41. Oberholster test

3.4 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric Analysis (TGA) was conducted for all types of ashes and in cement paste samples, after hydration for 28 days. The paste samples were crushed to powders and subjected to freeze dry, and subsequently kept in vacuum for 7 days to remove the evaporable water content and prevent carbonation or other contamination. They were heated under a nitrogen flow rate of 30 ml/min, starting from 30°C until 950°C.

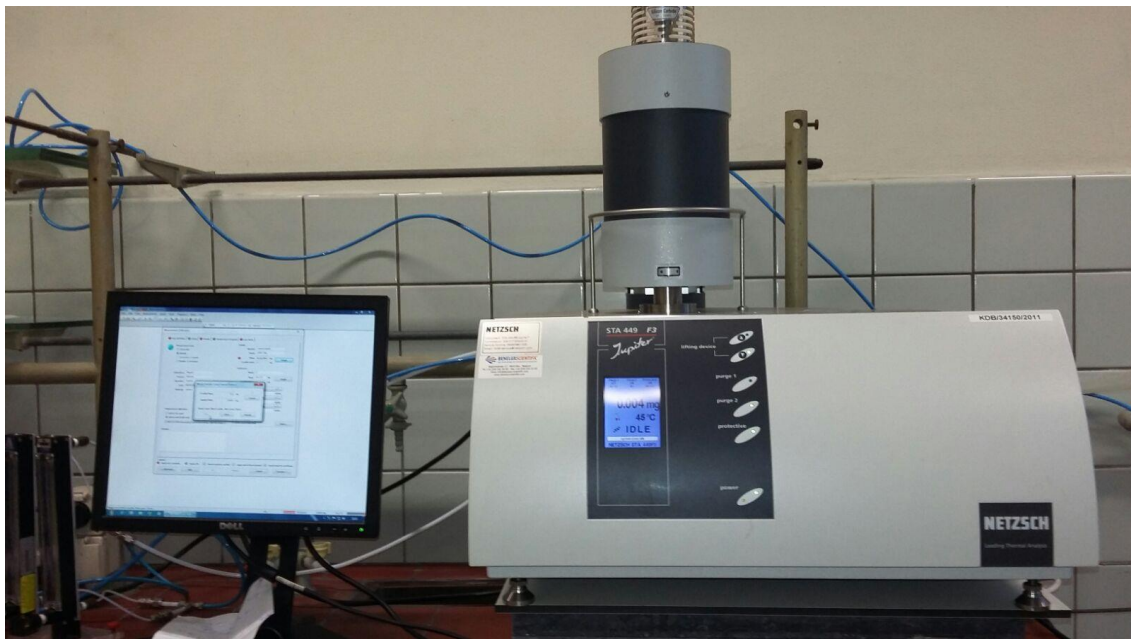


Figure 42. Netzsch for TGA

3.5 DENSITY OF ASHES

Le Chatelier flask test method determines the density of ashes. To evaluate Specific Gravity should start with several measurements, used ASTM Standard C 188-95 (2003). Following the calculations.

Density of isopropanol:

$$D_i = \frac{w_5 - w_4}{100} \quad (5)$$

Mass of ash:

$$m = w_2 - w_1 \quad (6)$$

Mass of isopropanol:

$$m_i = w_3 - w_2 \quad (7)$$

Volume of isopropanol:

$$V_i = \frac{w_3 - w_2}{D_i} \quad (8)$$

Volume of ash:

$$V_a = 100 - V_i \quad (9)$$

Density of ash:

$$D_a = \frac{m}{100 - V_i} \quad (10)$$



Figure 43. Samples to determinate density of ashes

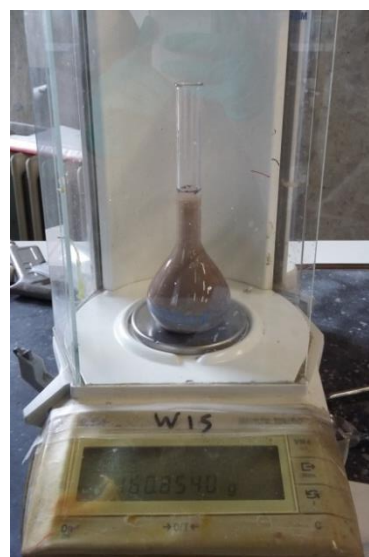


Figure 44. Le Chatelier method

3.6 XRF

The XRF (X-Ray Fluorescence) is a spectroscopy technique to identify the chemical elements of the sample, by analyzing X-rays emitted from it as a result of atomic excitation with appropriate energy. The analysis is non-destructive because it does not require any type of sample preparation, it can operate in the air and does not alter in any way the material analyzed. The X-radiation impinging on the sample has a maximum energy of a few tens of keV and the information that is obtained comes from the more superficial layers of the sample, that is, from those that the re-emitted radiation characteristic can pass through.

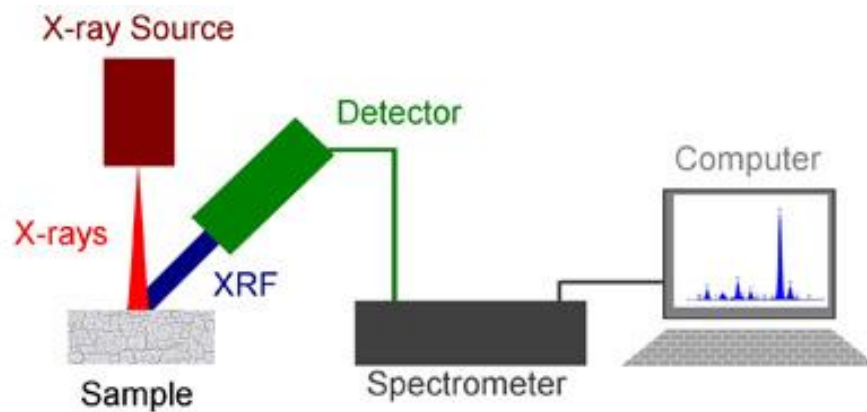


Figure 45. XRF process

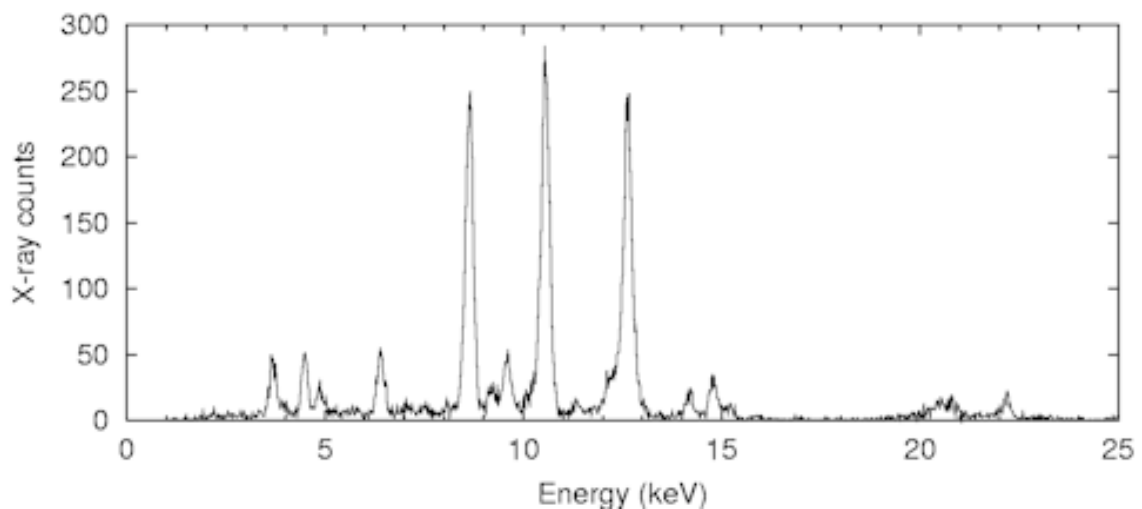


Figure 46. X-ray counts

3.7 LASER DIFFRACTION

The technique of laser diffraction particle size is based on the principle that particles illuminated by a laser beam scatter light at an angle related to their size. With decreasing particle size, the angle observed scattering (diffusion) logarithmically increases. The scattering intensity also depends on the size of the particles decreases and, with a good approximation, in relation to the surface of the cross-section of the particle. Simplifying, larger particles scatter light with tight corners and high intensity, whereas small particles with wider corners and low intensity. In 1999 (the last review was in 2009), the International Organization for Standardization (ISO) has published the ISO13320 an independent guide that describes how an exhaustively for particle size by laser diffraction system. Data analysis is covered the use of Mie Theory and Fraunhofer approximation, and rated the field of applicability of each. Mie theory was developed to predict the way light is scattered by spherical particles, if the way light passes through, or is adsorbed by, the particle. If the size of the particle, and other details about its structure, are known, the scatter light can be predicted. Each dimension of the particle has a different characteristic of the dispersion pattern.

To do this analysis has been used Mastersize 2000, it makes measurement and then analyze the data automatically.



Figure 47. Mastersize 2000

3.8 ELEMENTAL ALUMINIUM

To determine how much elemental aluminium there is in each sample, there is no official directive. A new setup was realized to evaluate the reaction of elemental aluminium with NaOH to form hydrogen. Hydrogen released displaces water and the difference in water volume indicates the quantity of elemental aluminium in the ash.

A 2 L round bottom flask was filled with water, the weight of flask was measured and then it was immersed in the water facing downwards. Then flask was connected to the water filled flask using a tube to collect the hydrogen gas. After the flask on the bottom was filled with 20 g bottom ash, and the top measuring bottle with 1 M NaOH (200 ml). The stop cock was open to allow NaOH to pour down and keep the solution in motion using magnetic stirrer. The experiment was conducted for 2 days for each sample.

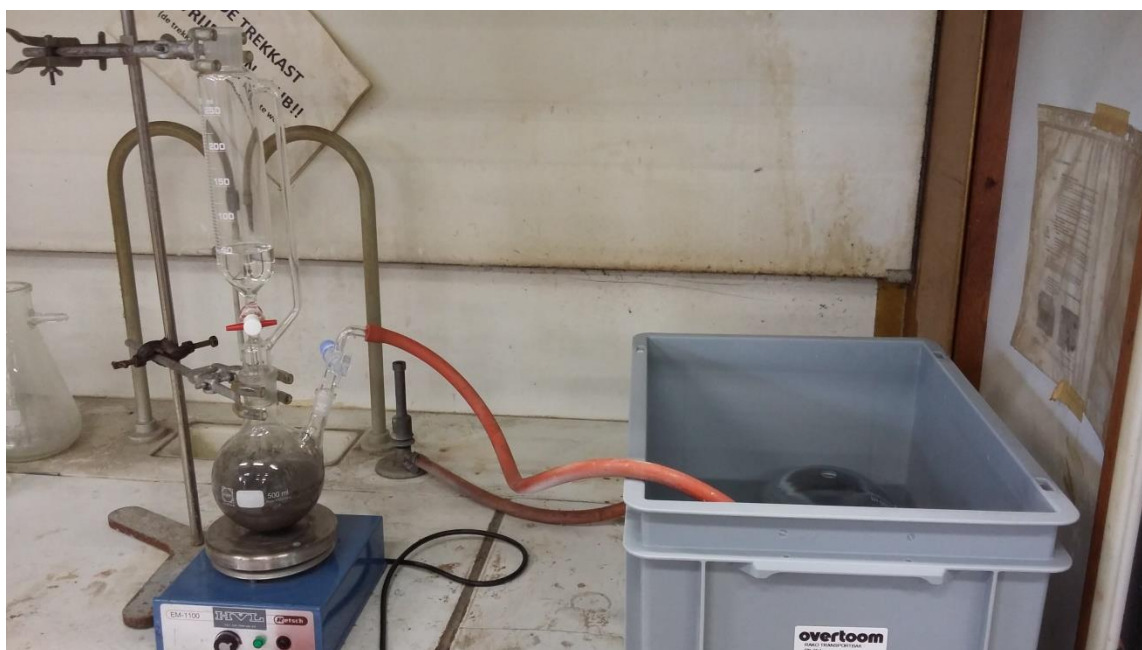


Figure 48. Elemental AL set up



Figure 49. ASR – Before and after 1 h BA 6/15

Chapter 4 RESULTS

4.1 PHYSICAL CHARACTERIZATION OF THE MATERIALS

The different materials used for the research and its source has already been explained in Chapter 3.

The results of physical characterization tests on these materials are given below.

4.1.1 Grain size distribution of sand






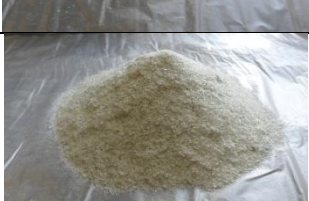


Standard sand conforming to NBN EN 196-1 (2005) was used for casting mortar bars and testing strength using W+B DB250/15 Testing Machines. Glass aggregates of same size distribution was used for testing durability to alkali silica reaction. Thus, the standard sand was sieved and the weights retained on each sieve was measured and the same was replicated for glass aggregates. The sieve size distribution of both the samples are given below in Table 3.

Table 3. Sand grading

SIEVE SIZE	Weight Retained (g)	% Retained (weight retained*100/Total)	Cumulative % retained	% Passing (100 - % Retained)	% Passing (tot - previous weight * 100) / tot
2	0.45	0.03	0.03	100.0	99.97
1.4	300.2	22.21	22.24	77.8	77.76
1	204.15	15.10	37.34	62.7	62.66
0.5	401.75	29.72	67.06	32.9	32.94
0.125	412.6	30.52	97.59	2.4	2.41
0.09	24.9	1.84	99.43	0.6	0.57
0	7.7	0.57	100.00	0.0	0.00
Total	1351.75				

Table 4. Glass used as fine aggregate

GLASSES SAND		
SIEVE SIZE	Weight Retained (g)	Photos

> 2	425.6	
2	0.45	
1.4	300.2	
1	204.15	
0.5	401.75	
0.125	412.6	
0.09	24.9	
<0.09	7.7	
Total	1351.75	

The grading of sand in mortar is important because it affects strength and workability of the mortar. Comparing the two graphs (Figure 50-51), the grading of aggregate use in this study is analogue to the D curve. D trend has a medium sand trend.

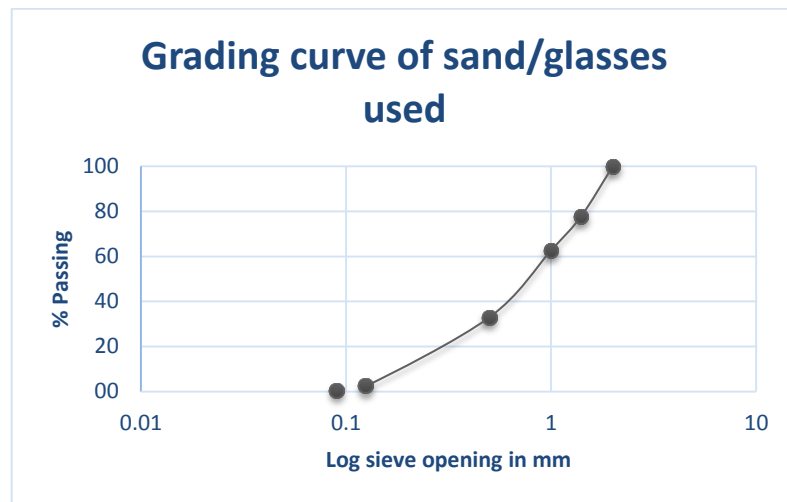


Figure 50. Grading curve of fine aggregate used for mortar

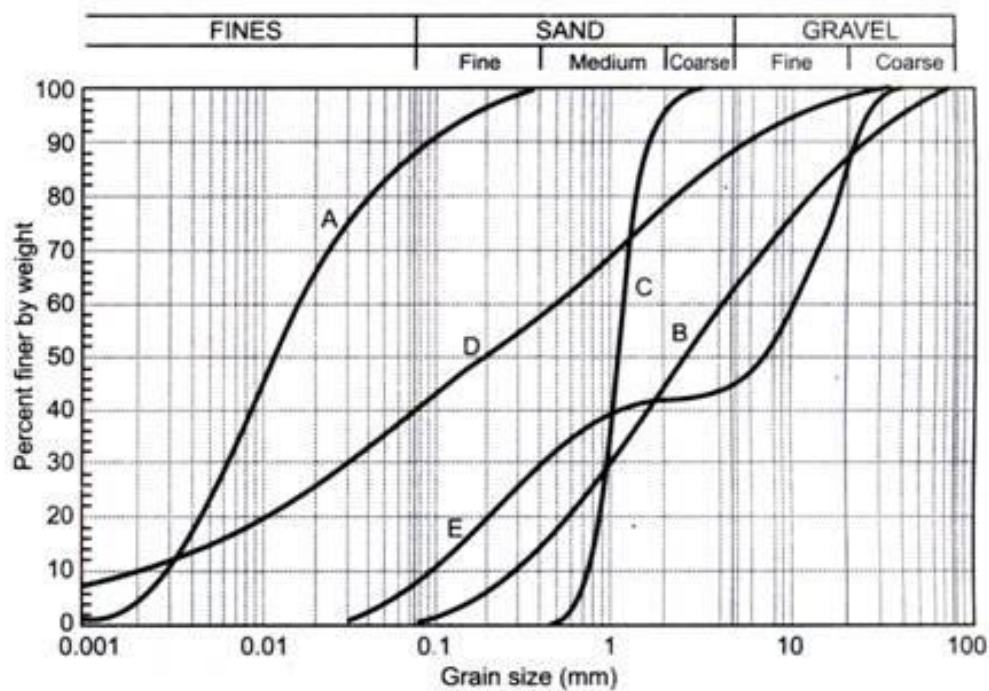


Figure 51. Aggregate Grading Curve (Soil Classification System)

4.1.2 Laser Diffraction

Laser diffraction is a standardized method according to the International Standard ISO 13320 to determine the fineness of the ground ash. Malvern Mastersizer 2000 was used (Malvern Instruments Ltd, 2007). The result from the analysis is the relative distribution of volume of particles in the range of size classes. Frequency curve – this is calculated by differentiating the result-under/cumulative

undersize curve. The frequency curve is particularly useful for displaying the results to show the “modes” or peaks in the graph. The peak of the frequency curve gives the modal diameter, the most commonly occurring particle diameter.

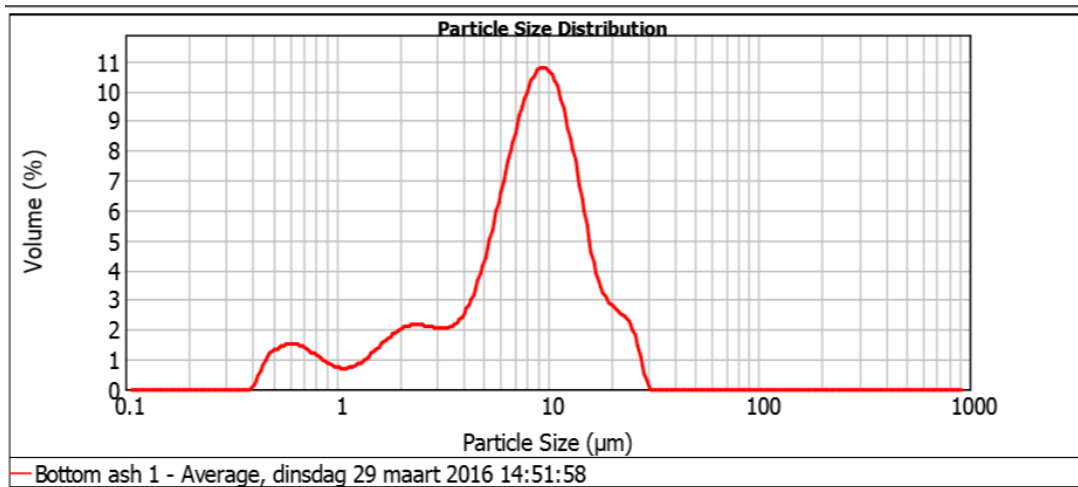


Figure 52. Laser Diffraction - difference graph, BA 6/15

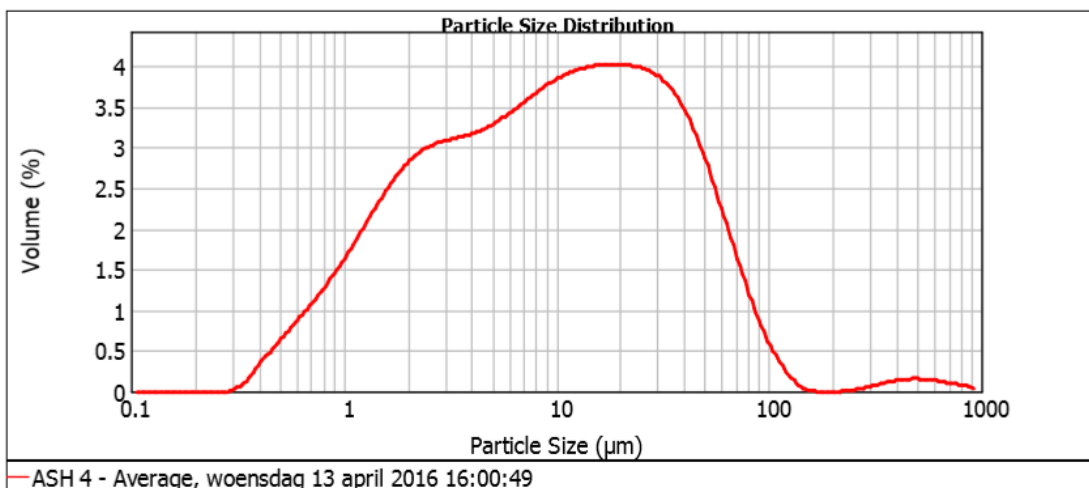


Figure 53. Laser Diffraction - difference graph, BA 2/6

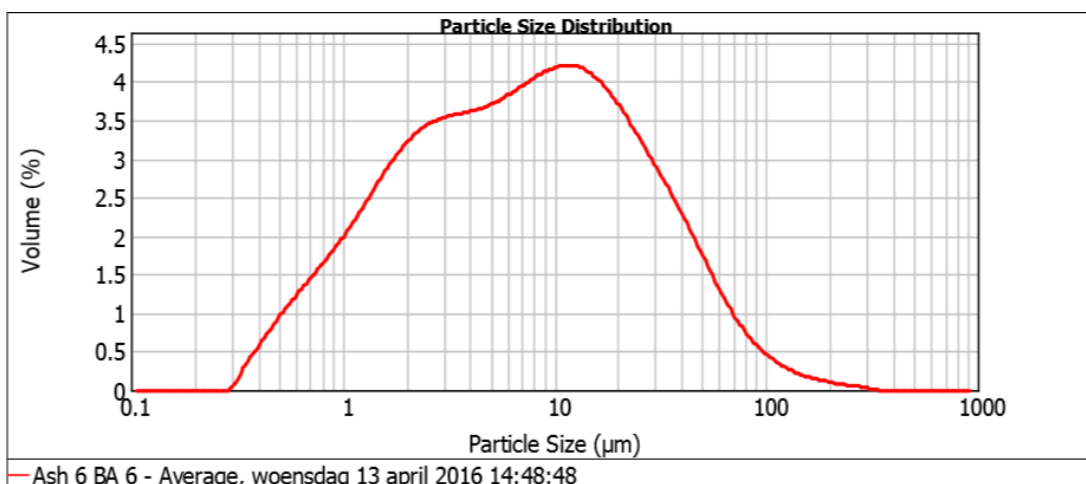


Figure 54. Laser Diffraction - difference graph, BA 0/2

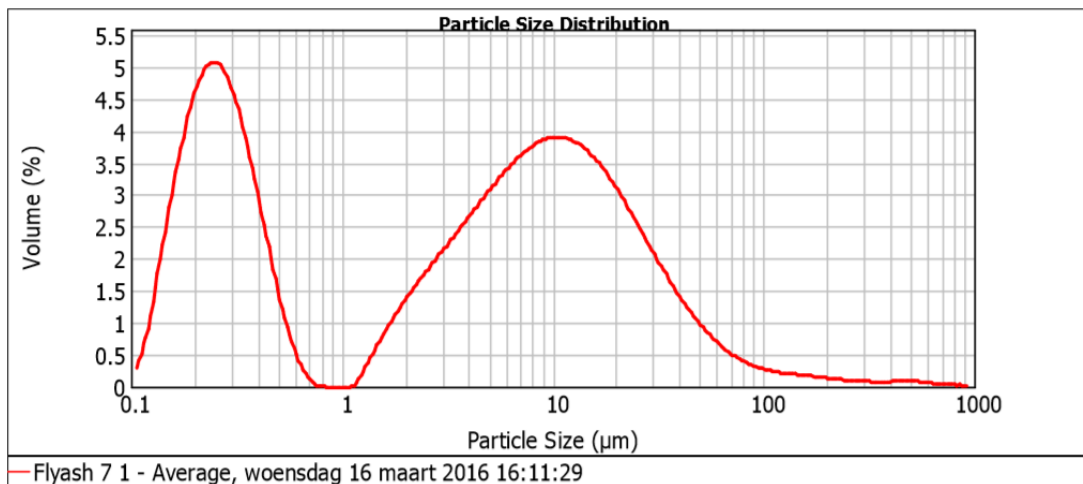


Figure 55. Laser Diffraction - difference graph, FA

All bottom ashes have similar size distribution, the highest point of each bell is around 10 µm, it correspond to a volume of 4%. Fly ash has a double bell curve, suggesting that there are two size ranges in fly ash.

The residual indicates how well the calculated data, in that case the values obtained are acceptable since they are less than 1%.

Table 5. Laser diffraction results

	Refractive Index	Absorption	Weighted Residual %
BA 6/15	1.57	1	0.441
BA 2/6	1.57	1	0.242
BA 0/2	1.57	1	0.296
FA	1.57	0.01	0.366

A graphic representation of particle size distribution can be seen in Figure 56. All the bottom ashes have similar fineness, and fly ash is having much higher specific surface area, especially due to the smaller sized fraction in it.

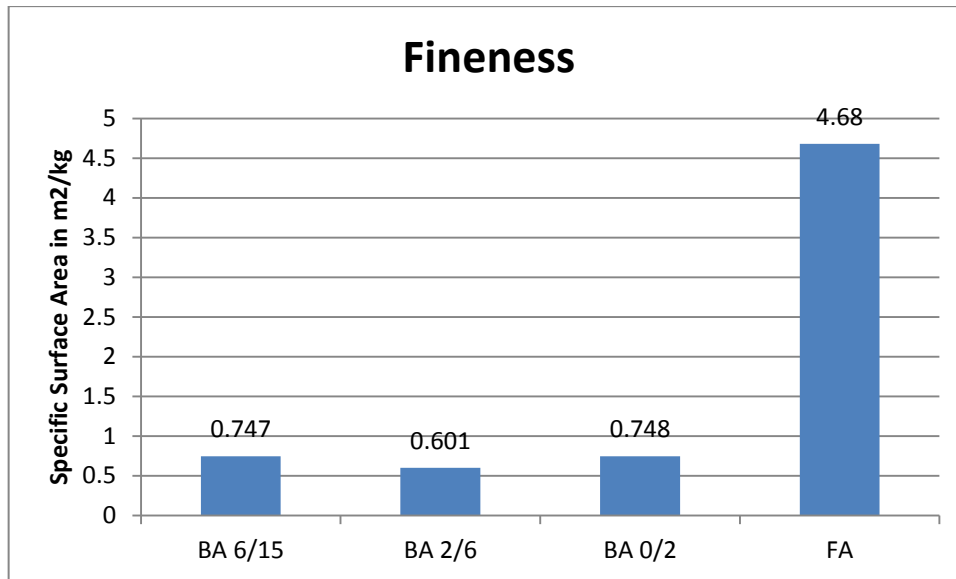


Figure 56. Fineness

4.1.2 Specific Gravity of ashes

The specific gravity of different ashes were determined used ASTM Standard C 188-95:2003(C188, 2011). The Calculation are in the Annex 2. From the calculation the values of Specific gravity are almost the same for each of the bottom ashes, and is highest for fly ash. It indicates that the density of fly ash is higher, and thus the crystallinity is also higher.

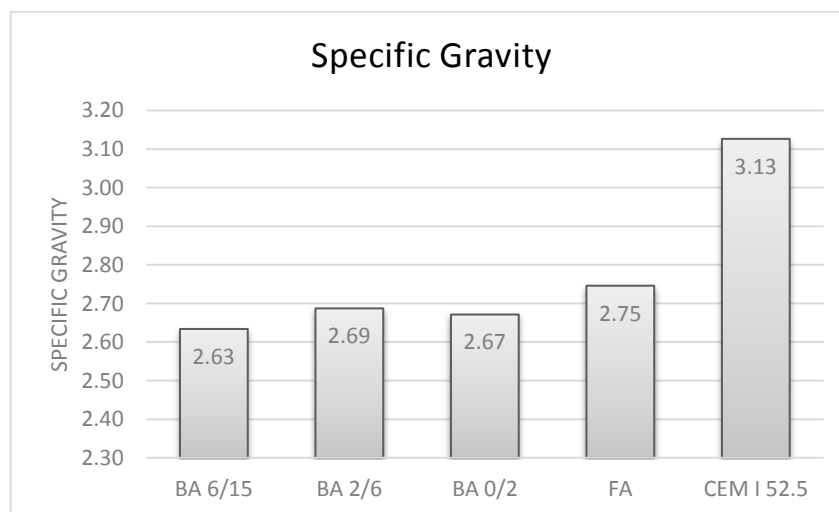


Figure 57. Specific gravity

4.2 CHEMICAL CHARACTERIZATION OF THE MATERIALS

4.2.1 XRF

XRF analysis is fundamental technique to understand the chemical composition. The following results (Table 6) were carried out in laboratory of INDAVER in Antwerp about normal ashes and ashes washed with water.

Table 6. XRF results

	BA 6/15	BA 2/6	BA 0/2	FA	BA 6/15-W	BA 2/6-W	BA 0/2-W	FA-W
Cl	2030.15	1409.94	8621.17	34905.1	901.37	1231.89	6669.08	14179.22
S	1718.99	2182.45	9552.91	22644.28	1171.94	1450.35	6830.59	23352.34
K	647.0464	732.05	982.95	854.23	665.31	681.47	946.62	527.09
Al	2734.5	2501.69	2273.37	1946.44	2664.03	2123.22	2223.01	1868.24
Cd	2.7	0	3.17	13.34	1.8991	1.77	4.24	9.32
Cu	1098.39	1807	1702.65	6968.24	1611.27	2389.31	2637.53	6793.65
Fe	10605.48	15388.09	19058.99	14917.8	12297.37	15324.44	21223.88	15246.13
Mg	180.33	280.96	237.58	151.97	207.91	281.37	227.8	165.27
Pb	1611.97	2177.81	1120.51	4547.97	595.3293	932.04	1241.76	4343.88
Zn	4264.43	7238.87	4359.45	8509.63	1958.34	7187.22	4527.53	8606.48
Ca	9570.91	13228.87	17258.19	18250.57	11146.64	13043.37	15702.49	19377.67
Si	34755.33	28008.13	19698.3	8984.36	31419.59	29759.18	22662.68	8867.88
Hg	3.713	7.5482	3.5	3.18	2.56	5.56	5.67	0
Ni	53.33	72.28	108.01	116.62	57.06	83.3	108.36	93.74
Sb	29.94	42.13	44.17	113.81	34.52	36.02	50.15	95.23

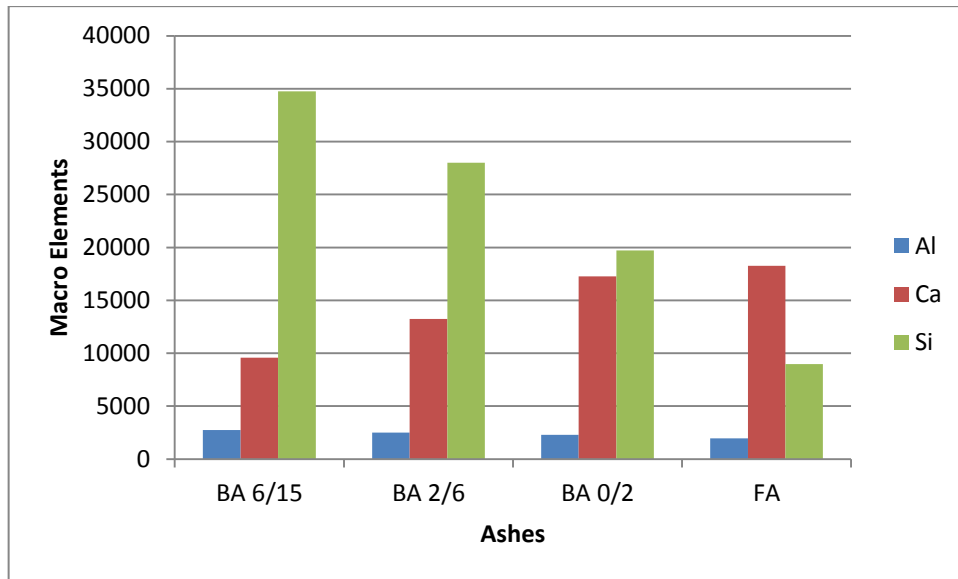


Figure 58. XRF Macro Elements

The relative proportion of different macro elements in different ashes can be seen in Figure 58. As the size of the fraction decreases, silica content also decreases. This can be attributed to high hardness of silica minerals compared to others. On the other hand calcium content is increasing through decreasing size of fraction. Alumina content is almost same for all the fractions under study.

The relative proportion of micro elements which are relevant for the use of ash in cement is shown in Figure 59. Chlorides has two main effects when coupled with cement. It acts as an accelerator of hydration reaction. But also, it acts as a corrosive agent for reinforcement corrosion. So high amount of chlorides in cement is considered to be detrimental. It can be seen from Figure 59 that chloride content is higher in smaller size fraction, especially in fly ash.

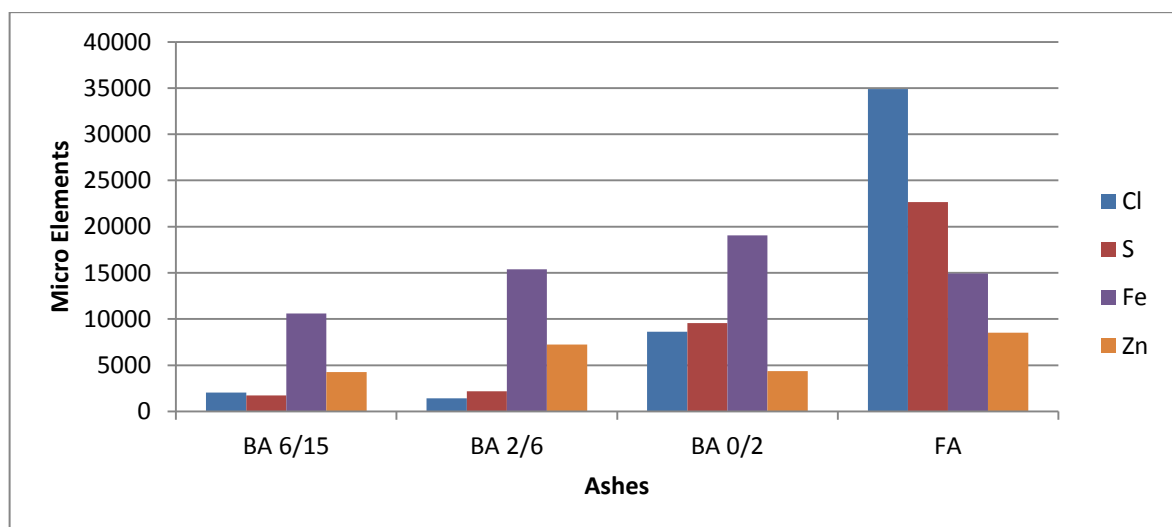


Figure 59. XRF Micro Elements

Sulphur is present in the form of sulphates. Small amount of sulphates, to around 5% by weight of cement is beneficial to cement to prevent flash setting. But high sulphates content can cause internal sulphate attack, or delayed ettringite formation especially when concrete is subjected to high temperature curing. So, if high amount of sulphates are present in the ash, it should be compensated during addition of gypsum in cement.

The composition of ashes with respect to heavy metals is shown in Figure 60. It is important in environmental point of view. The heavy metals can get leached into the ground water, and if consumed by biological creatures in high amount it can prove harmful. Some amount of heavy metals get fixed by encapsulation during cement hydration. So it is important to perform leaching tests in mortar and concrete, and the heavy metal content of ashes is less relevant.

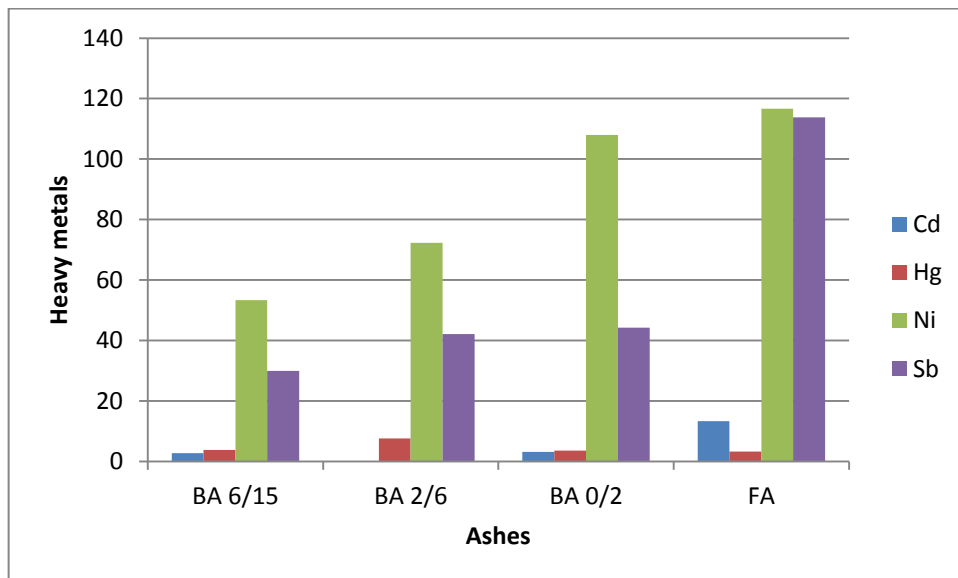


Figure 60. XRF Heavy metals

4.2.2 TGA

Thermogravimetric analysis was conducted to understand the relative contents of volatile components in hydrated cement paste and analyze the contents of them in cement paste and ashes. 50 g of ash was used to conduct TGA. Sudden increase in slope cannot be seen at 400 degree and 600 degree which represents calcium hydroxide and calcium carbonate, which are the usual phases in cement paste. Rather, a gradual slope is seen from 400 to 600 degree, which can indicate all the phases calcium hydroxide, calcium magnesium carbonate and calcium carbonate.

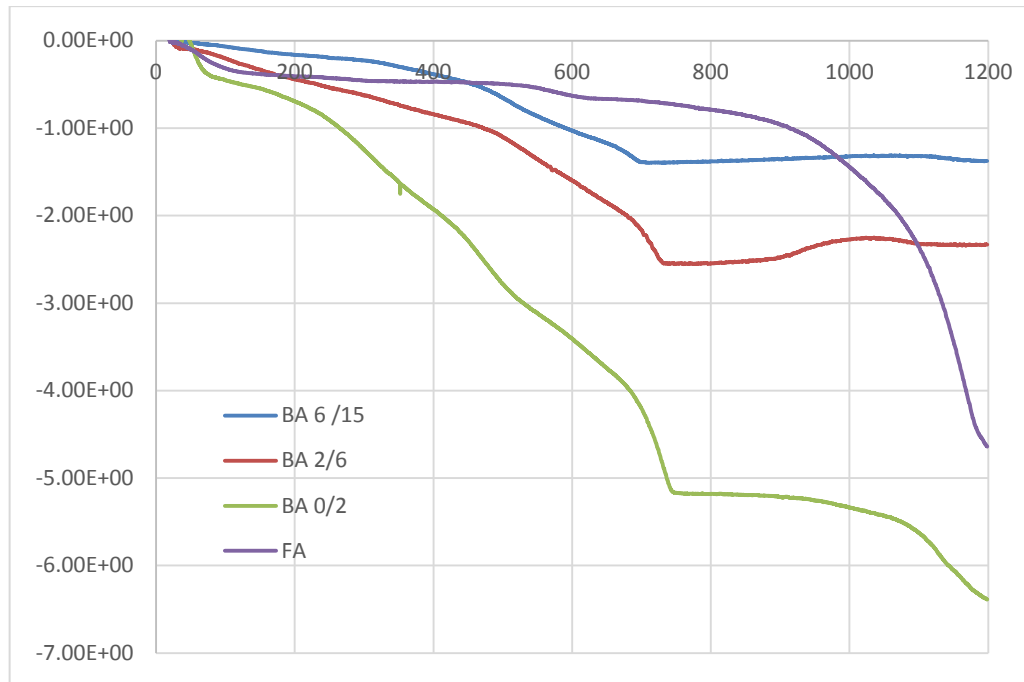


Figure 61. TGA of ashes

4.2.3. Elemental Al

The analysis on the presence of elemental Al in Ashes is an experimental procedure. From the values obtained from the first sample, as expected, BA ash 6/15 reveals a low presence of elemental Al. Al the results is the average of two test for each ashes.

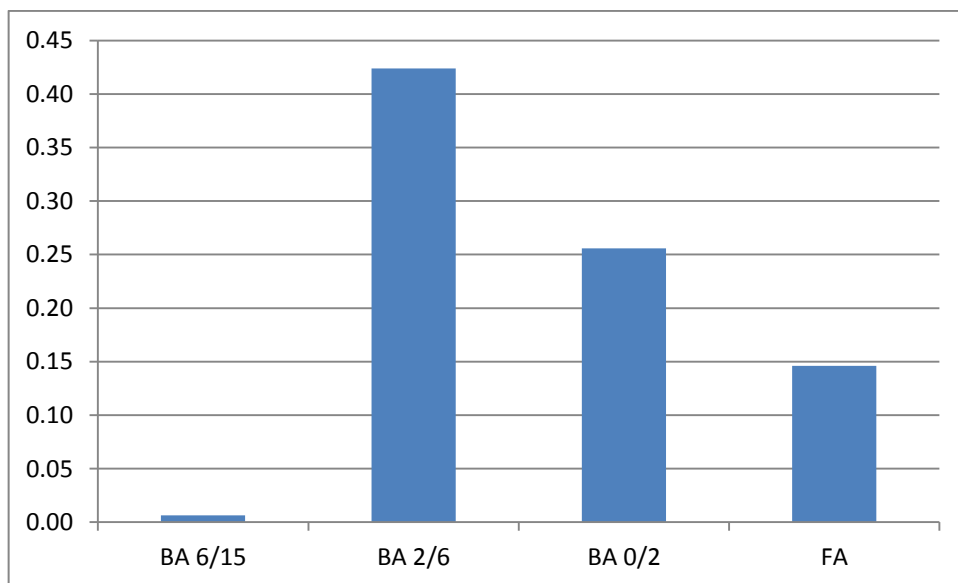


Figure 62. Percentage Elemental Aluminium in different ashes

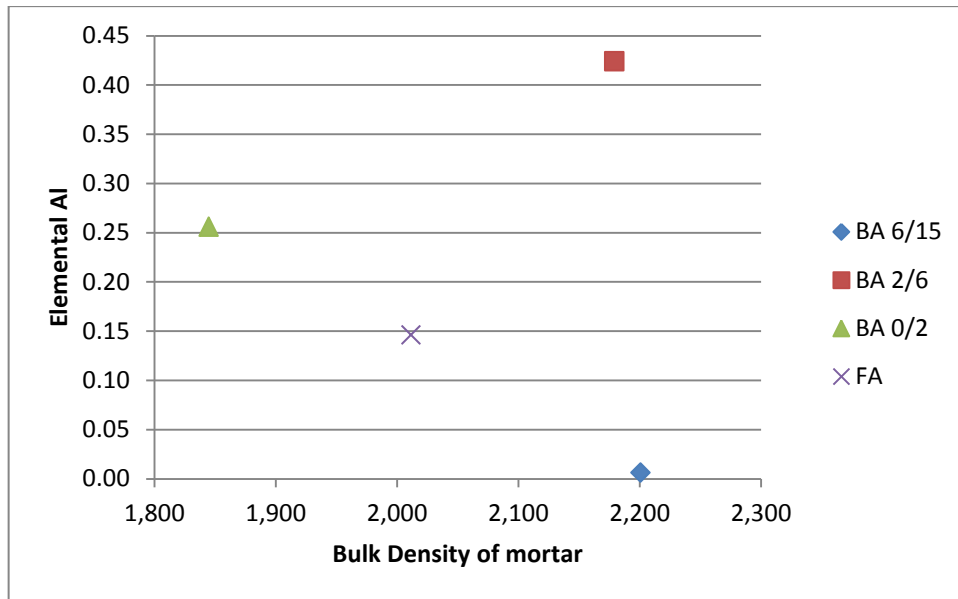


Figure 63. Elemental AI - Bulk density

4.3 COMPRESSIVE STRENGTH

For testing the mortar samples for their compressive strength was used EN 196 -1(EN 196-1). Test were performed on three samples for each mixture, which are moist cured for 28 days.

4.3.1 Compressive Strength for untreated ashes

Compressive strength test was conducted in mortar samples of size 40 X 40 X 160 mm, three specimens for each mix. CEM I 52.5N was used as control, and other binders were made by mixing 75% CEM I 52.5N and 25% ash. First the specimen was subjected to bending test, and broken into two halves, and compression test was conducted on the broken halves.

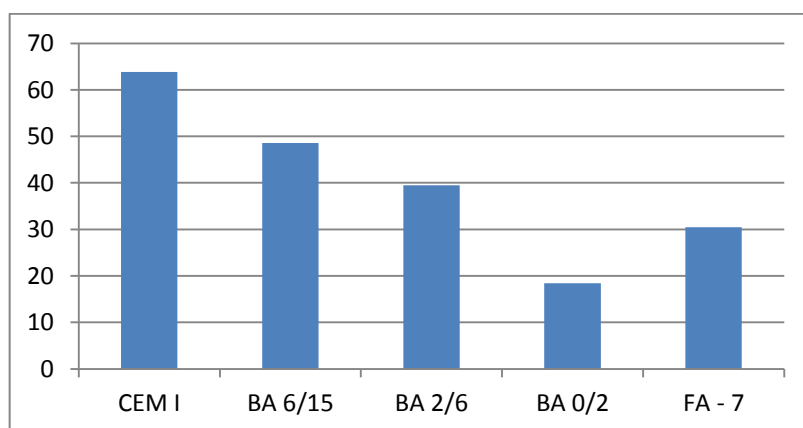


Figure 64. Compressive Strength Test- Concrete untreated

The average compressive strength of different mixes with untreated ashes are shown in Figure 65. It shows the effect of density on compressive strength. Here, bulk density is used as an indicator of the expansion.

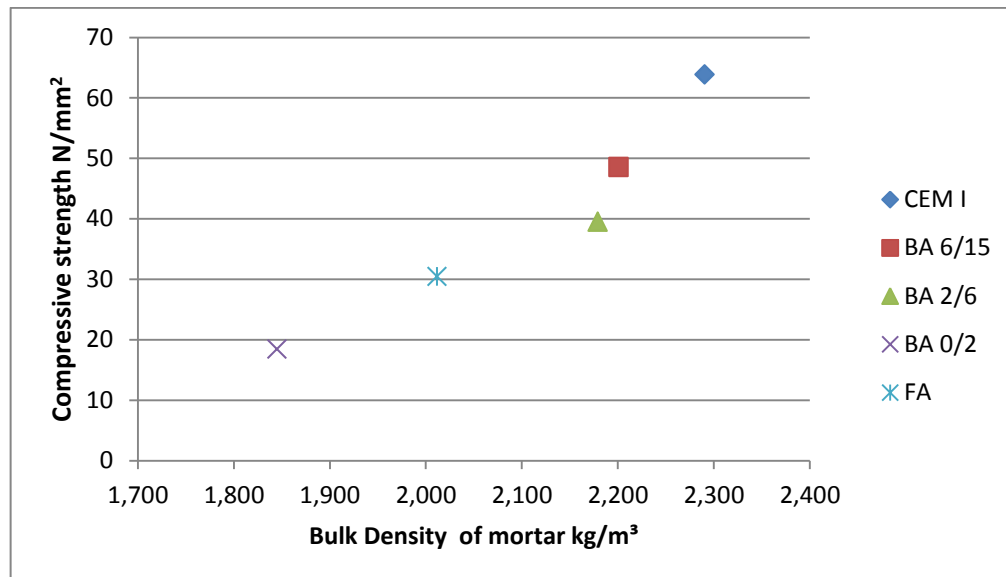


Figure 65. Compressive strength related to bulk density

It can be seen from the above figure that despite different composition and reactivities, the strength is mainly affected by the expansion. Thus it is very important to curb the expansion in mortars to achieve better strength. So different techniques to reduce expansion were tested and the results are shown in next section. Fasted tests need to be done.

4.3.2 Compressive strength for treated ashes

As previously explained in Chapter 3, the different treatment techniques adopted for reducing expansion are washing with water, washing with alkali (NaOH) and accelerated carbonation at 10%. The following graph (Figure 66) explains clearly the effect of different techniques adopted. All the washing techniques did not prove helpful in reducing the expansion, since the aluminium in ash was covered with other phases in ash, and thus not available for reaction with neither water or NaOH. Accelerated carbonation also failed to encapsulate the aluminium since the size of particles are too low, for carbonation of other phases to cover the aluminium in the ash.

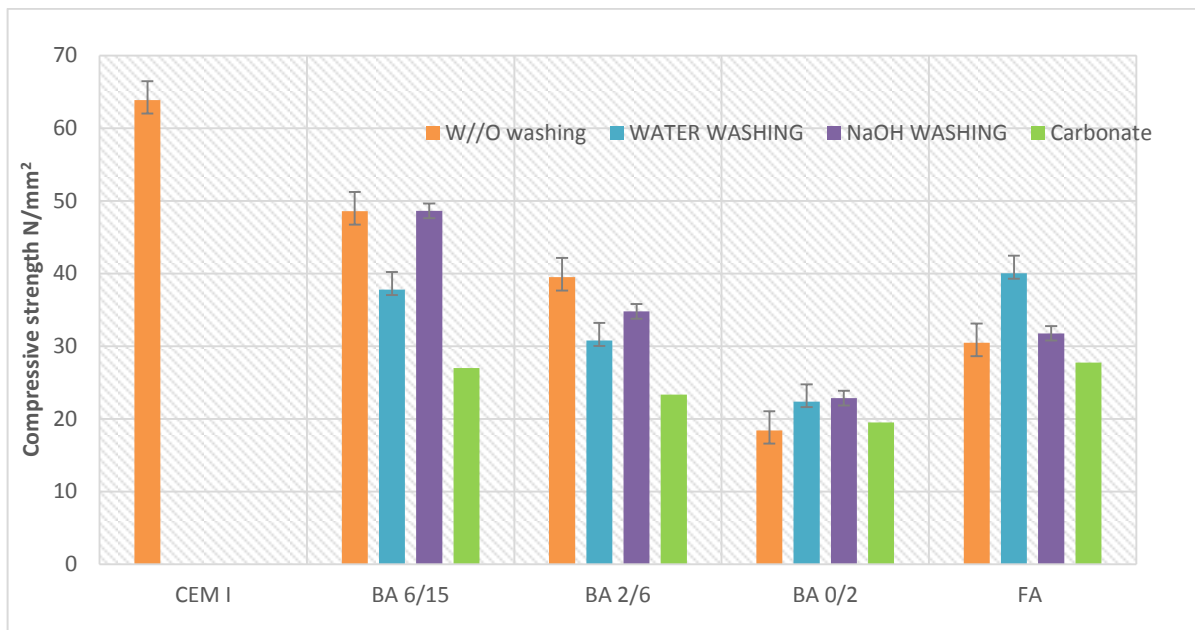


Figure 66. Compressive strength results

So, from the Figure 67 below, it can be seen that even after treatments expansion remains the deciding factor of compressive strength of mortar, and thus none of the treatment methods proved to be effective.

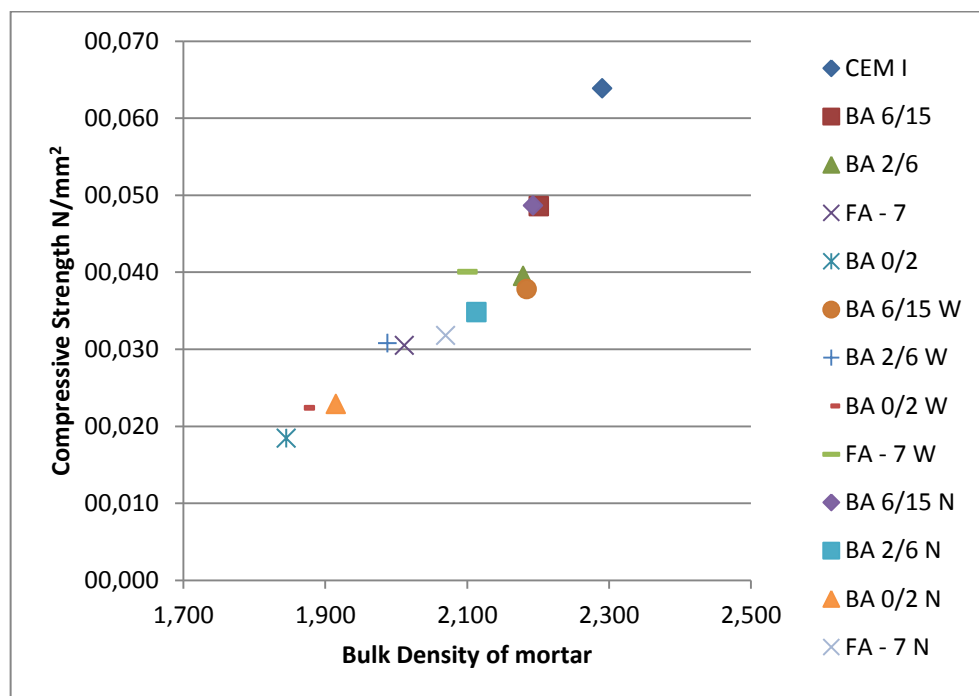


Figure 67. Compressive strength related to bulk density

4.3.3 ASR

In particular, three elements are harmful for the concrete: water, an alkaline environmental and silica containing aggregates. The Oberholster test is an accelerated test that gives an indication of the alkali reactivity of concrete. The values obtained prove that BA &/15 had the largest expansion and CEM I the lowest. But also FA did not have an high expansion. Although aluminates have effect of reducing the alkali silica reaction, the increased diffusivity due to high porosity caused by elemental aluminium overpowered its effect, and caused more expansion for specimens with ash replacement.

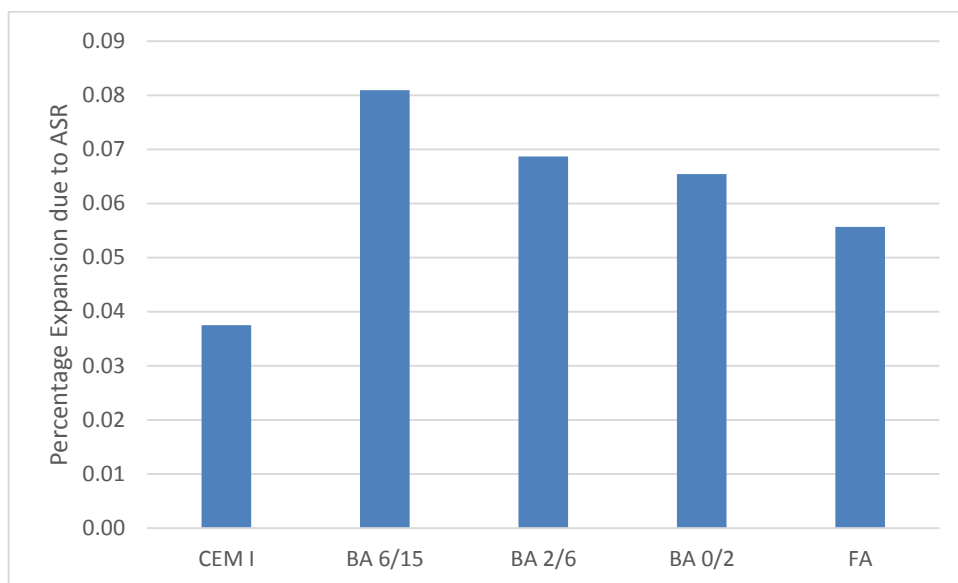


Figure 68. Percentage Expansion due to ASR

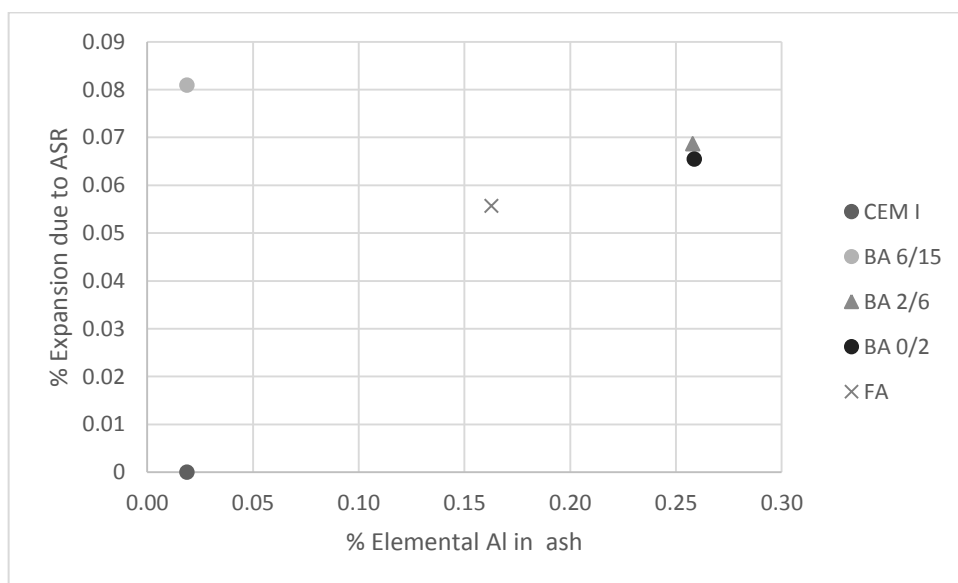


Figure 69. ASR Expansion related to % of Elemental Al

4.3.4 TGA of hydrated paste (pozzolanic reaction)

The following graphs was made from the results of TGA to evaluate the percentage of portlandite for each samples of ashes.

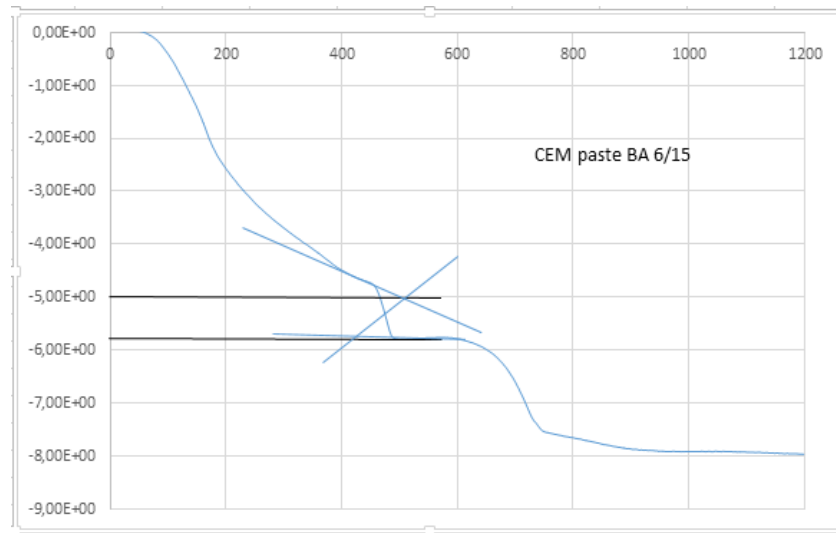


Figure 70. TGA Cement paste BA 6/15

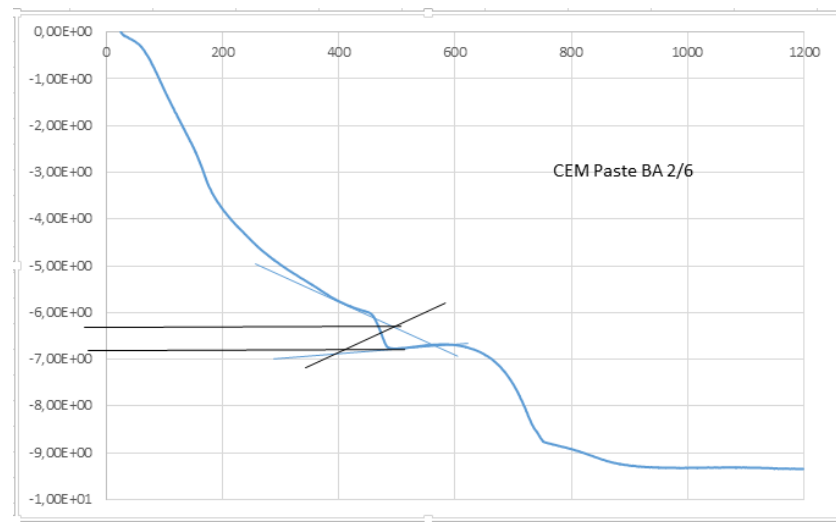


Figure 71. TGA Cement paste BA 2/6

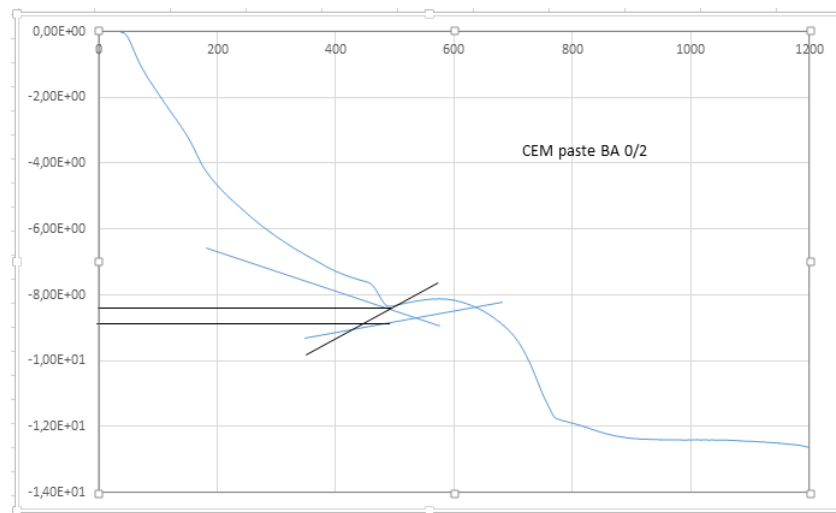


Figure 72. TGA Cement paste BA 0/2

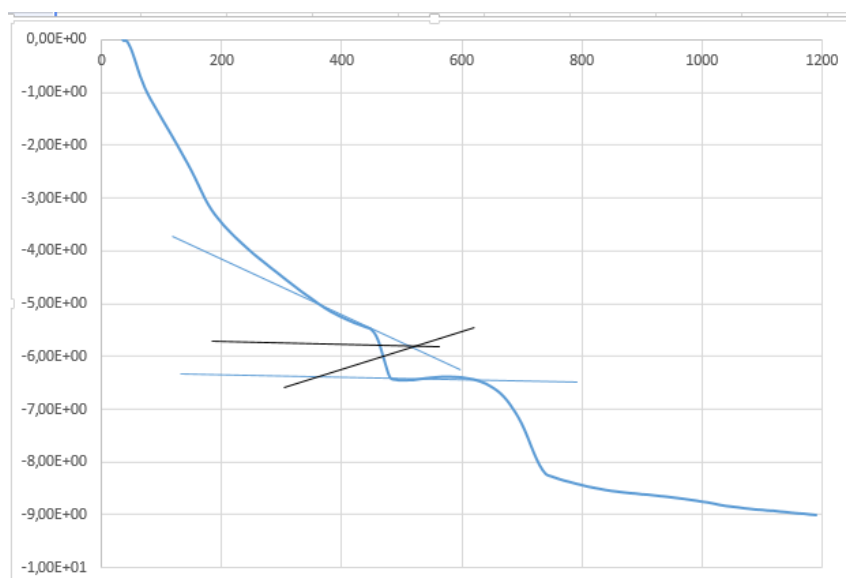


Figure 73. TGA Cement paste FA

The percentage of portlandite in cement paste was determined by tangent method (Kocaba, 2010), and is shown in the following Figure 74.

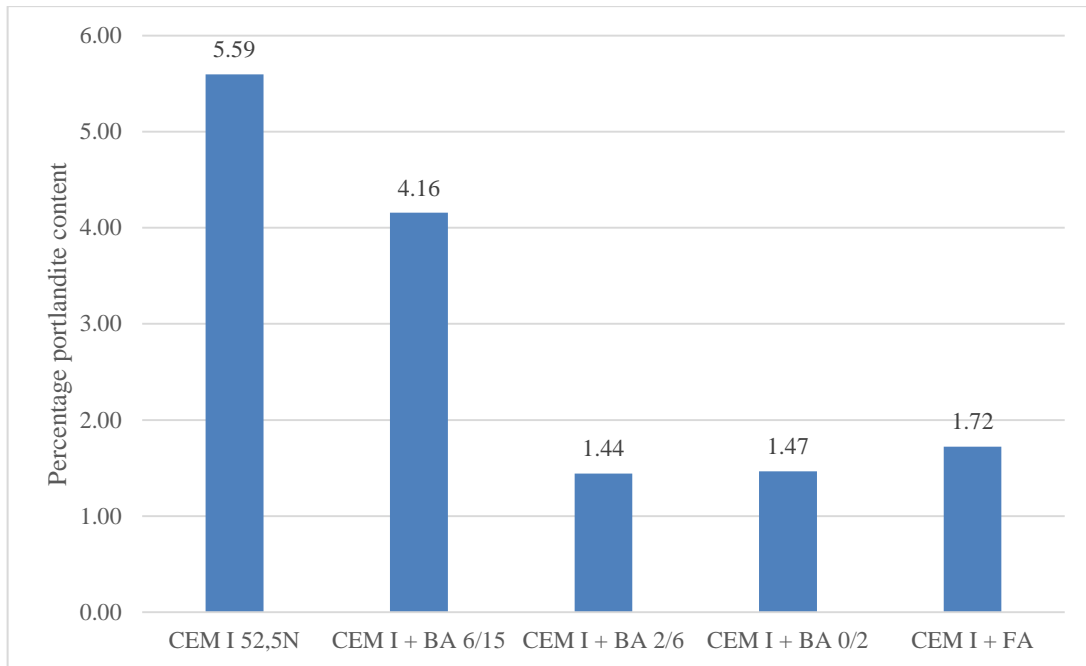


Figure 74. Percentage of portlandite

The maximum pozzolanic reaction is seen for BA 2/6 fraction, and minimum is for 6/15 fraction. This can be an indication of the reactivity of the ashes.

CH consumed was determinate with 75% CH in:

- CEM I
- CEM I + BA 6/15
- CEM I + BA 2/6
- CEM I + BA 0/2
- CEM I + FA

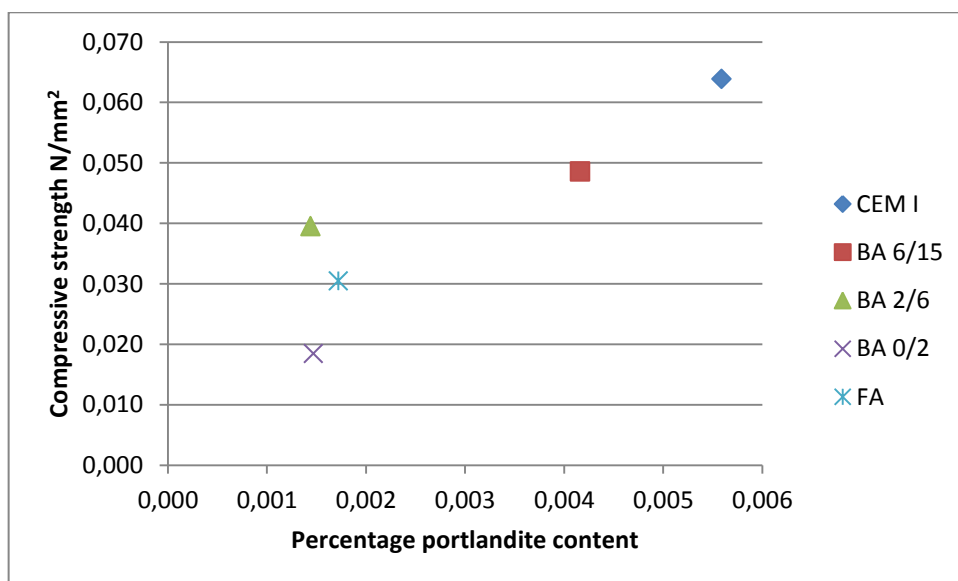


Figure 75. Percentage portlandite content

Chapter 5. CONCLUSION

The reuse of MSWI in concrete to reduce the consumption of raw materials and the landfills was investigated. Several analysis carried out on different ashes have given many and varied results.

The processes and the tests conducted were selected and manufactured according to the literature review, which was the starting point of this research built to fit the examined ashes. The combination of analytical choices includes many past research to give a more complete overview. And also an innovative subject was addressed: Elemental Al set up.

The analyzed BA 6/15 are the bigger incinerated fraction in this study. The fineness is $0.74 \text{ m}^2/\text{kg}$, as all the other bottom ashes, BA 2/6 is $0.601 \text{ m}^2/\text{kg}$ and BA 0/2 is $0.748 \text{ m}^2/\text{kg}$, contrast to $4.68 \text{ m}^2/\text{kg}$ of fly ash. With increasing fineness, the water demand increases and the workability decreases.

Even the specific gravity of BA has a range of 2.63-2.75, while FA has 3.13. The specific gravity of cement can be very variable, from 1.4 to 3.2. Therefore the obtained values are comparable to the cement's values.

In order to make any kind of evaluation on ashes samples is fundamental the chemical analysis. Through it, can be understand the chemical reactions that can take place to making mortars. Analyzing macro-micro elements and heavy metals, the BA 6/15 has less amount of hazardous chemical elements then the others BA. FlyAsh has highest values of this elements.

Highest value of portlandite is in CEM I, and the lowest value is for BA 2/6. This information comes from TGA. Thus, the maximum pozzolanic reaction is seen for BA 2/6 fraction and minimum is for 6/15 fraction.

The compressive strength of concrete was found to be affected mainly by expansion, and its effect is much higher than any other factor like fineness of ash or reactivity from TGA. Three treatment techniques were adopted to test the effect of it to curb expansion due to elemental Aluminium, but none of it proved to be effective.

The Oberholster test showed a largest expansion for BA 6/15 decreasing to FA, from 0.081% to 0.56%. thus considering the ASR, the best sample to consider are the FA. Despite the high porosity of sample due to expansion, the ASR expansion of the samples with ash replacement were found to be less than the prescribed limit 0.1%.

The new set up for Elemental Al has given well results, demonstrating the validity of its operation. BA 6/15 has a minimum quantity of Al. For the BA, highest Al in BA 6/15 increasing to lowest Al in BA 0/2.

The ashes samples compared to a reference concrete demonstrate slightly decrease in compressive strength for BA 6/15 and BA 2/6. While, the others samples have lower value. But in the other hand 0/2 BA and FA has the less expansion from ASR and less quantity of Elemental Al.

A results explain the capacity of the ash to be reused in the concrete, thanks to the values obtained from the various analyzes performed. More investigation should be done on the bottom ashes, to examine new applications. The Elemental Al set up can be improve with graduated cylinder to replace the flask.

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Annex 1 – CEM I 52.5 N CE NF



Contrôlé par la Ville de Paris
Secrétariat Technique :
Laboratoire d'Essais des Matériaux de la Ville de Paris
4, Avenue du Colonel Henri Rol-Tanguy – 75014 PARIS
Correspondant : Damien BALLAND
Correspondant AFNOR Certification :
Sébastien KOSTIC – 01 41 62 60 41

Certificat

Certificate

VVM nv
Monsieur VANHUMBEECK
Zwarteweg 49
Kaai 367

B-2030 ANTWERPEN
Belgique

Usine de : RIEME

Reconduction de la marque
NF-LIANTS HYDRAULIQUES

N° 1018.05 du 12.04.2016

est autorisée à apposer la marque NF en application des règles générales de la marque NF et du référentiel de certification NF-LIANTS HYDRAULIQUES (NF002) sur les emballages et lettres de voiture des produits suivants :

Désignation selon le référentiel NF002	Date de la 1 ^{re} admission	Teneur des constituants	Norme
CEM I 52,5 R CE NF	14.02.2014		NF EN 197-1 : 2012
CEM I 52,5 N CE NF	14.02.2014		NF EN 197-1 : 2012
CEM III/A 42,5 N CE NF	03.03.2015	S43	NF EN 197-1 : 2012
CEM III/B 42,5 N-LH/SR CE PM NF	03.03.2015	S69	NF EN 197-1 : 2012

Certains de ces produits sont également conformes à la norme NF P 15-317 : 2006 (PM), NF P 15-318 : 2006 (CP1 ou CP2), NF P 15-319 : 2014 (ES), pour les caractéristiques complémentaires mentionnées.

Cette décision atteste que ces produits sont certifiés conformes aux normes et aux exigences supplémentaires après évaluation par AFNOR Certification tel que spécifié dans le référentiel de certification NF-LIANTS HYDRAULIQUES. Elle est prononcée au vu des résultats des contrôles internes à l'entreprise, ceux-ci ayant été confirmés par les essais réalisés lors des visites effectuées par l'organisme de vérification et les essais réalisés en laboratoire extérieur.

Cette décision annule et remplace toute décision antérieure.

Ce droit d'usage de la marque NF est accordé pour une durée d'un an à compter de la présente décision, sous réserve des contrôles effectués par AFNOR Certification qui peut prendre toute décision conformément aux règles générales de la marque NF et au référentiel de certification NF-LIANTS HYDRAULIQUES.





Directeur Général
Franck LEBEUGLE



1/1

11 rue François de Provençal - 92571 La Plaine Saint-Denis Cedex - France - T +33 (0)1 41 62 60 00 - F +33 (0)1 49 17 93 08
SAS au capital de 18 181 000 € - 419 670 002 RCS Bobigny - www.marque-nf.com



Annex 2 – Table of Specific Gravity Test

SPECIFIC GRAVITY													
		x1	x2	BA 6/15		BA 2/6		BA 0/2		FA		CEM I 52.5	
Density of isopropanol	$(w5-w4)/100=$	0.7 8	0.7 8										
	$(x1+x2)/2=X$	0.78											
Mass of ash	$w2-w1=m$			43.1	41. 7	43.4	43. 1	43.4	43. 1	43. 5	43. 3	43. 1	43. 0
Mass of isopropanol	$w3-w2=$			65.1	65. 6	65.2	65. 5	65.3	65. 3	65. 3	65. 9	67. 2	67. 2
Volume of isopropanol	$(w3-w2)/x=y$			83.6	84. 2	83.7	84. 1	83.8	83. 8	83. 8	84. 5	86. 2	86. 2
Volume of ash	$100-y=$			16.4	15. 8	16.3	15. 9	16.2	16. 2	16. 2	15. 5	13. 8	13. 8
Density of ash	$m/(100-y)=$			2.6	2.6	2.7	2.7	2.7	2.7	2.7	2.8	3.1	3.1
Average				2.63		2.69		2.67		2.7 5		3.1 3	

Annex 3 – XRF Result

XRF								
	BA 6/15	BA 2/6	BA 0/2	FA	BA 6/15-W	BA 2/6-W	BA 0/2-W	FA-W
Cl	2030.15	1409.94	8621.17	34905.1	901.37	1231.89	6669.08	14179.22
S	1718.99	2182.45	9552.91	22644.28	1171.94	1450.35	6830.59	23352.34
K	647.0464	732.05	982.95	854.23	665.31	681.47	946.62	527.09
Al	2734.5	2501.69	2273.37	1946.44	2664.03	2123.22	2223.01	1868.24
Cd	2.7	0	3.17	13.34	1.8991	1.77	4.24	9.32
Cu	1098.39	1807	1702.65	6968.24	1611.27	2389.31	2637.53	6793.65
Fe	10605.48	15388.09	19058.99	14917.8	12297.37	15324.44	21223.88	15246.13
Mg	180.33	280.96	237.58	151.97	207.91	281.37	227.8	165.27
Pb	1611.97	2177.81	1120.51	4547.97	595.3293	932.04	1241.76	4343.88
Zn	4264.43	7238.87	4359.45	8509.63	1958.34	7187.22	4527.53	8606.48
Ca	9570.91	13228.87	17258.19	18250.57	11146.64	13043.37	15702.49	19377.67
Si	34755.33	28008.13	19698.3	8984.36	31419.59	29759.18	22662.68	8867.88
Hg	3.713	7.5482	3.5	3.18	2.56	5.56	5.67	0
Ni	53.33	72.28	108.01	116.62	57.06	83.3	108.36	93.74
Sb	29.94	42.13	44.17	113.81	34.52	36.02	50.15	95.23
Br	2.1147	33.1619	114.6961	548.4478	20.5228	20.7039	101.0652	429.6499
P	543.1227	1712.866	3181.71	3116.224	1148.9369	1706.1028	2807.239	3048.527
I	4.1495	2.8643	2.6409	10.162	1.4837	5.6475	5.4585	7.5717
As	82.3306	64.5889	9.2568	95.181	89.8834	68.0321	6.8662	97.2597
Ba	155.5765	228.4178	255.0009	293.3307	224.1385	245.2043	248.894	270.9964
Co	15.8693	39.3507	20.2592	14.209	16.1847	42.1126	20.9411	12.6035
Cr	144.1705	179.051	242.6401	154.9318	134.8881	213.6973	258.3642	161.5349
Mn	480.9191	960.5156	700.5367	595.4714	517.5449	1038.7253	749.7433	620.3037
Mo	6.4481	14.4106	19.8289	13.3413	8.1305	13.1925	16.5391	11.5671
Se	6.1544	10.3922	5.748	10.6759	5.3059	6.3609	5.5326	11.6635
Sn	37.047	54.2735	81.2852	103.5215	36.3055	45.7031	91.3389	103.1013
Tl	15.1742	14.5955	10.685	27.7651	8.8765	6.9953	12.4169	24.5355
V	23.4888	23.3637	26.376	26.464	20.7485	19.2086	26.9247	21.5298
Zr	198.4149	67.6008	67.9018	57.748	221.4679	75.1211	79.0467	57.9702
W	46.6755	14.685	17.0325	15.0538	13.7486	22.9945	35.7729	14.33
Ti	802.1877	971.5317	1441.384	1525.43	783.2431	973.6681	1405.148	1576.903
Th	25.2112	15.2931	20.5589	40.7068	28.0479	13.4972	22.2567	33.6452
Te	5.4033	4.5413	0	14.6339	0	4.9752	2.7366	11.5372
Sr	2103.058	2300.623	2362.828	2859.655	2461.3563	2147.2476	2310.6781	2841.517
Ga	10.5795	23.4316	6.8941	0	9.7442	24.7918	1.1534	0
Ge	2.8992	3.792	1.7456	0	0	5.057	0.3244	1.8032
U	19.0737	14.4525	14.4582	21.3519	16.5351	14.2196	13.2098	20.7948
Y	100.9635	96.8744	59.9311	73.3105	96.6576	89.7579	60.6788	75.2372
Pd	0	9.0127	4.9684	0.6983	0	3.9294	2.5123	2.0351
Rb	273.1015	119.0897	88.6713	145.1237	240.7513	113.7392	91.658	113.2586
Ag	0	3.8141	2.8796	8.2009	0	0	5.2638	5.7661

Annex 4 – Compressive Strength Test Concrete Untreated

NORMAL CONCRETE															
28 days - compression & strength															
	CEM I			BA 6/15			BA 2/6			BA 0/2			FA		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
height	40.2	40.3	40.4	41.7	41.9	41.1	40.3	40.5	40.0	44.8	44.2	43.7	43.4	44.0	43.3
width	40.2	40.3	40.2	40.1	40.1	40.3	40.3	40.1	40.4	40.2	40.2	40.4	40.4	40.2	40.3
length	161. 3	161. 7	162. 1	160. 8	160. 6	160. 3	161. 5	161. 6	161. 4	159. 9	160. 4	159. 7	160. 7	160. 1	161. 4
weight	597. 4	600. 8	602. 3	591. 0	590. 5	590. 1	571. 0	569. 8	569. 4	528. 4	526. 8	522. 2	564. 9	566. 8	571. 8
bulk density	229 3.0	228 4.8	229 3.5	219 4.9	218 8.7	221 9.0	217 9.0	217 0.6	218 7.6	183 4.4	184 7.3	185 2.7	200 3.8	200 2.9	202 8.0
AVER	229 0.4			220 0.9			217 9.1			184 4.8			201 1.6		
bending breaking load	2.4	2.6	2.5	2.1	1.9	2.3	1.7	1.7	1.7	1.5	1.2	1.2	1.6	1.8	1.7
bending strength	5.4	6.0	5.7	4.6	4.1	5.2	4.0	3.9	3.8	2.8	2.3	2.4	3.2	3.4	3.3
AVER	5.7			4.6			3.9			2.5			3.3		
compression breaking load 1	103. 1	99.2	106. 4	79.4	75.2	79.5	62.5	63.5	63.8	29.2	18.6	31.5	51.1	50.2	51.0
compression strength 1	64.5	62.0	66.5	49.6	47.0	49.7	39.1	39.7	39.9	18.3	11.6	19.7	31.9	31.4	31.9
compression breaking load 2	102. 0	99.7	102. 4	80.6	76.9	75.6	65.0	61.4	63.1	29.0	33.5	35.0	49.8	51.8	38.6
compression strength 2	63.8	62.3	64.0	50.4	48.1	47.3	40.6	38.4	39.4	18.1	21.0	21.9	31.1	32.4	24.1
AVER	63.8			48.6			39.5			18.4			30.5		
MAX	2.6			1.8			1.1			3.5			1.9		
MIN	1.8			1.6			1.2			6.8			6.3		

Annex 5 – Compressive Strength Test Concrete Treated Washing Ashes

WASHED ASHES												
28 days - compression & strenght												
	BA 6/15			BA 2/6			BA 0/2			FA		
	40.8	40.5	41.1	44.2	45.0	44.7	43.6	44.5	43.5	42.7	42.5	42.4
height	40.3	40.3	40.3	40.5	40.2	40.4	40.4	40.3	40.4	40.3	40.3	40.2
width	160.5	160.1	160.2	160.7	160.6	160.2	160.7	160.4	160.8	160.8	161.0	160.6
length	576.6	573.9	574.9	575.8	569.9	577.4	528.8	533.1	533.5	576.3	579.9	577.6
weight	2189. 2	2195. 2	2166. 7	2002. 0	1965. 0	1995. 6	1868. 2	1855. 2	1890. 3	2081. 3	2106. 5	2113. 5
bulk density	2183. 7			1987. 5			1871. 2			2100. 4		
AVER	2.1	2.1	2.4	1.9	2.1	2.0	1.8	1.9	1.7	2.1	2.6	2.2
bending breaking load	4.6	4.7	5.3	3.7	4.1	3.7	3.3	3.5	3.3	4.3	5.3	4.5
bending strenght	4.9			3.8			3.4			4.7		
AVER	62.1	58.8	62.1	47.1	46.1	53.5	32.8	35.6	37.8	62.4	64.2	65.1
compression breaking load 1	38.8	36.7	38.8	29.4	28.8	33.4	20.5	22.2	23.6	39.0	40.1	40.7
compression strength 1	61.3	59.9	58.6	52.5	45.4	51.1	34.0	35.3	39.2	63.3	65.0	64.6
compression breaking load 2	38.3	37.4	36.6	32.8	28.4	31.9	21.3	22.1	24.5	39.5	40.6	40.4
compression strength 2	37.8			30.8			22.4			40.0		
AVER	1.0			2.6			2.1			0.6		
MAX	1.2			2.4			1.8			1.1		
MIN	40.8	40.5	41.1	44.2	45.0	44.7	43.6	44.5	43.5	42.7	42.5	42.4

Annex 6 – Compressive Strength Test Concrete Treated with NaOH

WASHED WITH NaOH															
28 days - compression & strenght															
	GLASSES			BA 6/15			BA 2/6			BA 0/2			FA		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
height	39.1	39.6	39.8	41.0	40.8	40.2	42.2	42.4	42.5	41.9	43.1	41.4	41.9	42.1	42.2
width	40.1	40.0	40.0	40.2	40.0	40.3	40.2	40.3	40.3	40.5	40.2	40.3	40.1	40.3	40.4
length	161. 2	161. 2	161. 1	160. 5	160. 4	160. 2	160. 4	160. 3	160. 5	160. 1	160. 3	160. 1	161. 2	161. 1	160. 2
weight	482. 6	482. 2	486. 8	579. 9	572. 2	571. 5	577. 0	579. 5	577. 3	521. 2	521. 5	518. 6	559. 3	567. 0	565. 1
bulk density	190 7.7	189 2.1	189 6.6	219 3.8	218 0.8	220 4.4	212 1.1	211 8.6	209 9.9	192 0.2	188 0.6	194 4.5	206 6.4	207 5.4	206 7.0
AVER	189 8.8			219 3.0			211 3.2			191 5.1			206 9.6		
bending breakin g load	1.7	1.9	1.6	2.3	2.2	1.8	2.0	2.1	1.9	1.8	1.4	1.6	1.8	2.4	2.1
bending strenght	4.3	4.6	3.9	5.0	4.9	4.1	4.3	4.4	3.9	3.9	2.8	3.5	3.9	5.1	4.3
AVER	4.2			4.7			4.2			3.4			4.4		
compression breakin g load 1	35.3	37.4	37.4	73.5	72.8	68.4	55.1	55.3	56.2	36.6	38.3	36.1	51.9	50.6	49.2
compression strength 1	22.0	23.4	23.4	45.9	45.5	42.8	34.4	34.6	35.1	22.9	23.9	22.6	32.5	31.6	30.8
compression breakin g load 2	35.5	37.0	38.2	72.2	45.5	73.7	55.4	55.3	56.9	34.9	36.2	37.4	50.1	51.9	51.3
compression strength 2	22.2	23.1	23.9	45.1	66.4	46.0	34.6	34.6	35.5	21.8	22.6	23.4	31.3	32.4	32.0
AVER	23.0			48.6			34.8			22.9			31.8		
MAX	0.9			17.8			0.7			1.1			0.7		
MIN	1.0			5.8			0.4			1.0			1.0		

Annex 7 – Compressive Strength Test Concrete Treated with Carbonation

CARBONATE												
28 days - compression & strenght												
	BA 6/15			BA 2/6			BA 0/2			FA		
	1	2	3	1	2	3	1	2	3	1	2	3
height	47.3	47.6	46.8	47.7	47.7	46.9	45.0	45.2	44.1	44.4	44.4	44.6
width	40.2	40.3	40.5	40.3	40.4	40.2	39.9	40.1	40.0	40.3	40.2	40.4
length	160.8	160.2	160.8	160.5	161.5	161.3	161.5	161.1	160.5	160.1	160.3	160.2
weight	578.8	578.4	579.9	583.3	583.1	580.3	533.1	522.8	522.4	580.5	581.3	585.9
bulk density	1895.0	1884.1	1904.0	1893.1	1875.2	1910.6	1835.2	1792.1	1846.8	2029.1	2029.8	2033.8
AVER												
bending breaking load	1.9	2.0	1.9	2.0	2.3	2.1	1.5	1.6	1.5	1.9	2.1	2.0
bending strenght	3.1	3.3	3.2	3.2	3.7	3.3	2.8	2.9	2.9	3.5	3.9	3.8
AVER	1894.4			1893.0			1824.7			2030.9		
compression breaking load 1	41.5	43.0	41.8	27.3	31.6	42.4	31.9	29.6	31.6	43.8	44.3	42.5
compression strength 1	25.9	26.9	26.1	17.1	19.8	26.5	19.9	18.5	19.8	27.3	27.7	26.5
compression breaking load 2	41.4	46.3	40.3	45.2	42.3	35.4	33.4	28.1	32.6	46.0	44.4	45.4
compression strength 2	28.9	28.9	25.2	28.3	26.4	22.1	20.9	17.6	20.4	28.7	27.7	28.4
AVER	27.0			23.4			19.5			27.7		
MAX	1.9			4.9			1.4			1.0		
MIN	1.8			6.3			1.9			1.2		