

**MASTER**

**Physical-chemical upgrading and use of bio-energy fly ashes as building material in the concrete industry**

Doudart de la Grée, G.C.H.

*Award date:*  
2012

[Link to publication](#)

**Disclaimer**

This document contains a student thesis (bachelor's or master's), as authored by a student at Eindhoven University of Technology. Student theses are made available in the TU/e repository upon obtaining the required degree. The grade received is not published on the document as presented in the repository. The required complexity or quality of research of student theses may vary by program, and the required minimum study period may vary in duration.

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain

**Take down policy**

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

EINDHOVEN UNIVERSITY OF TECHNOLOGY

# Graduation Project

---

Physical-chemical upgrading and use of bio-energy fly ashes as building material in the concrete industry

**ing. Guillaume Doudart de la Grée**

*27/6/2012*

---

# Graduation Project

---

## Physical-chemical upgrading and use of bio-energy fly ashes as building material in the concrete industry

ing. Guillaume Doudart de la Grée

27/6/2012

**Author** ing. G.C.H (Guillaume) Doudart de la Grée  
**Address :** Heereindsestraat 5  
5741RB  
Beek en Donk  
The Netherlands  
**Student number:** S090076  
**E-mail** [Gdoudart@hotmail.com](mailto:Gdoudart@hotmail.com)

**University:** Eindhoven University of Technology  
**Address:** Den Dolech 2  
Postbus 513  
5600 MB  
Eindhoven  
The Netherlands  
**Tel:** 31(0)40-247 9111  
**Fax:** 31(0)40-245 6087  
**URL:** <http://www.tue.nl>



**Supervisors:** Prof.dr.ir. H.J.H. (Jos) Brouwers  
Dipl. Eng. M.V.A. (Miruna) Marinescu – Florea  
**URL:** <http://josbrouwers.bwk.tue.nl>

**Internship:** Van Gansewinkel Minerals  
**Address:** Loswalweg 50  
3199 LG  
Maasvlakte Rotterdam  
Postbus 1016  
3180 AA Rozenburg  
The Netherlands  
**Tel:** +31 181 36 30 99  
**Fax:** +31 181 36 28 12  
**URL:** <http://www.vangansewinkel-minerals.nl/>



**Supervisor:** ir. A. (Arno) Keulen

## Preface

"I would like to thank my supervisors, starting with: Prof. Dr. ir Jos Brouwers, for his inspiring lectures and the opportunity to take part in this innovative project. Dipl. Eng. Miruna Florea, for her valuable advice and generous share of knowledge, but mostly for her enthusiasm that motivated me during the project, the encouragement to use and explore my abilities and expand my boundaries. ir. Arno Keulen for supporting and motivating me in every practical way, sharing his practical experience and helping me to collect relevant data for my research. Special thanks to Peter Cappon, for supporting and helping me when I was working in the laboratory and had some new crazy ideas. Together we were innovative and shared plenty of ideas and built different experimental set-ups. When looking back it was a significant learning process, during which I gained more enthusiasm for material science than I could ever imagine. There is a saying: *Time flies when you're having fun*, well for me that was definitely true".

Guillaume Doudart de la Grée

27-6-2012

## Summary

The aim of this research was to combine four different bio-energy fly ashes from bio-energy power plants in concrete mixtures. The roles of this type of fly ash in a concrete mixture as a binder (partly or totally replacing cement) or filler were investigated. First, physical and chemical properties of the different fly ashes are determined followed by the determination of unwanted contaminants and needed treatment methods. Second, tests are performed to indicate any improvement and if the use of bio-energy fly ash is promising. To draw conclusions, the obtained data is compared with reference coal combustion fly ash termed PKVA SMZ.

It was found that from the investigated bio-energy fly ashes, the bio-energy fly ashes delivered by HVC-Alkmaar have self cementitious and pozzolanic properties and Twence-Hengelo has pozzolanic properties. Physical and chemical properties like particle size distribution and oxide composition of the fly ashes vary enormous among each other and are also not really comparable with PKVA SMZ. The same applies for the amount of unwanted contaminants like chlorides and carbon. This all can however be related by the used fuel for the incineration plants and the used burning processes.

By using different treatment techniques like crushing, thermally and water treating bio-energy fly ash, it is tried to upgrade bio-energy fly ash to a material comparable with PKVA SMZ.

From the results in can be concluded that the thermal treatment and water treatment method reduce unwanted contaminants and not only make the material not hazardous, but they also increase the potential of the material as cement replacement. After treatment and crushing the bio-energy fly ash performs similarly as coal combustion fly ash.

## Table of Contents

Preface.....	3
Summary.....	4
Table of Contents.....	5
1. Introduction.....	8
1.1 Problem statement bio-energy fly ash.....	8
1.2 Problem definition.....	8
1.3 Objectives and research questions.....	9
1.4 Hypothesis.....	9
1.5 General approach.....	9
1.6 Structure of the report.....	9
2. Fly ash origin and types.....	10
2.1 Bio-power plant installations.....	10
2.1.1 History.....	11
2.1.2 Fuel.....	12
2.1.3 Process.....	13
2.2 The by-product fly ash in general.....	17
2.2.1 Coal combustion fly ash.....	17
2.2.2 Bio-energy fly ash.....	19
3. Concrete.....	20
3.1 Composition.....	20
3.1.1 Water.....	20
3.1.2 Cement.....	20
3.1.3 Aggregates.....	20
3.1.4 Filler and legislation.....	21
3.2 Properties of concrete and influence of fly ash.....	21
3.2.1 Fresh concrete.....	21
3.2.2 Hardening process.....	22
3.2.3 Hardened concrete.....	22
4. Bio-energy fly ash properties.....	24
4.2 Mineralogical properties.....	24
4.2.1 Fly ashes used in this study.....	24
4.3 Particle Morphology.....	25
4.4 Physical properties.....	26
4.4.1 Density.....	26
4.4.2 Colour.....	26
4.4.3 Carbon content.....	27
4.4.4 Fineness, PSD and SSA.....	28
4.4.5 Moisture content.....	31
4.5 Fly ash properties and legislation.....	31
4.5.1 Leaching value.....	32
4.5.2 Fly ash characteristics.....	33
4.5.3 Landfill.....	33
4.5.4 Building material.....	34
4.5.5 Regulation for fly ash.....	36
5. Cement.....	37
5.1 Composition.....	37
5.2 The hydration products.....	39

5.3	Hydration process (Barron, 2010).....	41
5.4	Hydration products during time.....	42
6.	Hydration of Portland cement with Fly ash.....	44
6.1	Tricalcium silicate and fly ash.....	44
6.2	Dicalcium silicate and fly ash .....	45
6.3	Effect Fly ash on the hydration of $C_3A$ and $C_4AF$ .....	45
6.4	Effect of fly ash on cement hydration .....	46
6.4.1	C-S-H content.....	46
7.	Effects of contaminants on cement hydration .....	47
7.1	Carbon content/loss on ignition test .....	47
7.2	Chloride content .....	48
8.	Treatment of bio-energy fly ash .....	50
8.1	Treatment methods.....	50
8.1.1	Sieving.....	51
8.1.2	Thermal treatment & Air-filtering.....	51
8.1.3	Metallic aluminium removal .....	52
8.1.4	Washing.....	52
8.1.5	Seperation/Grinding.....	53
8.2	Treatment evaluation.....	53
8.2.1	Carbon content .....	53
8.2.2	Chloride content in water .....	53
8.2.3	Chloride content of the solid material .....	53
9.	Results.....	55
9.1	Chloride removal (part one).....	55
9.1.1	Twence boiler fly ash (B1).....	55
9.1.2	Twence cyclone fly ash (B2) .....	57
9.1.3	Validation measurement .....	59
9.2	Chloride removal (part two).....	59
9.2.1	Twence boiler fly ash .....	59
9.2.2	Twence cyclone fly ash.....	60
9.2.3	HVC cyclone fly ash.....	61
9.2.4	HVC Filter fly ash .....	62
9.3	Treatment data particle size distribution .....	62
9.3.1	Twence boiler fly ash .....	62
9.3.2	Twence cyclone fly ash and HVC cyclone fly ash.....	63
9.3.3	Comparison PSD and SSA between original and treated bio-energy fly ash .....	64
9.4	Strength development.....	64
9.5	Side effects .....	69
9.5.1	Water treatment .....	69
9.5.2	Thermal treatment.....	69
9.5.3	Strength results.....	70
9.5.4	Scanning electron microscopy (SEM) .....	71
9.5.5	X-ray diffraction pattern (XRD).....	72
10.	Discussions and conclusions .....	75
10.1	Relations and differences.....	75
10.2	Treatment methods and reliability.....	75
10.2.1	Carbon removal.....	75
10.2.2	Water treatment .....	76
10.2.3	Method of measuring chloride content .....	76
10.2.4	Grinding.....	77

10.2 Strength results.....	77
10.3 Recommendations .....	79
References .....	80



# 1. Introduction

## 1.1 Problem statement bio-energy fly ash

Worldwide increased concern of the CO<sub>2</sub> emissions and dependency from fossil fuels leads to an increasing use of renewable energy sources in order to replace the use of fossil fuels and to decrease the greenhouse emissions. One of those renewable energy sources is 100% biomass that can be used as a replacement of coal in power plants. These so called bio-power plants use waste wood as fuel in their combustion room to produce heat. That energy is then consumed in steam turbines to generate electricity for own plant's need or supply to the electricity network of surrounding districts. This central method of electricity generation was already applied during the industrial revolution.

During that period of time, pulverized coal was used as fossil fuel and there was no awareness of the by-products exposed to the environment by the exhaust gases. However, those by-products of CO<sub>2</sub> emissions and air-polluting fly ashes increased health problems near the factories. When these problems were recognized, better installations were constructed to collect fly ashes using cyclone separators, electrostatic precipitators or bag houses to filter the exhaust gases. Also the combustion room processes improved resulting in development of less by-products. The collected coal combustion fly ashes were disposed at landfill sites. However, those responsible for disposal of fly ash are constantly seeking potential ash utilization options because of expensive costs and increasing production. Nowadays, fly ash can be used as ground stabilization under roads or applied in concrete mixtures due to its physical and chemical properties. Fly ash is a fine material that can be used as a filler in concrete mixtures and because of its pozzolanic activity it can be used as a binder and partly replace cement and therefore reduce the use of natural resources. However, fly ash has also disadvantages because of its contaminants like heavy metals and chlorides that can decrease the hydration degree of cement and reduce the strength of concrete structures.

The increase of using biomass for electricity generation in power plants leads to production of fly ashes different from the 'old fashion' coal combustion fly ash. These fly ashes created from burning biomass have different characteristics and properties in comparison to coal combustion fly ash.

## 1.2 Problem definition

Within the Netherlands, there is the need to increase the knowledge about the utilization of bio-energy fly ashes in concrete mixtures. So far the reuse of this type of fly ashes is not started because of the following reasons:

1. Bio-energy fly ash is a chemically and physically variable product which makes its combination with cement questionable. Particle size distribution, loss on ignition, density, specific surface area, leaching as well as its pozzolanic/cementitious properties need to be tested to confirm its suitability;
2. Bio-energy fly ash contains contaminants like lead, zinc and chromium and large amounts of chlorides that may have negative influences on the hydration of cement;
3. As replacement of cement, its slow pozzolanic activity influences the hydration process, consequently lowering the properties of concrete at early ages;

4. There is no worldwide agreement on the chemical and physical influences of fly ash in combination with concrete mixtures, which makes its application still uncommon;
5. So far there is no treatment method for contaminated fly ash to remove the contaminants and increase its pozzolanic activity that could make its utilization more cost-efficient and sustainable;

### 1.3 Objectives and research questions

The aim of this research is to combine bio-energy fly ash from bio-energy power plants in concrete mixtures. The role of this type of fly ash in a concrete mixture as a binder (partly or totally replacing cement) or filler will be investigated. The aim is to develop a more sustainable and cost-efficient concrete that gives by-products a second life and with that, reduces the CO<sub>2</sub> emissions of the cement production industry. In order to do so, bio-energy fly ashes need to be treated to remove unwanted particles so that it can be utilized in the concrete industry. The following objectives can be defined in accordance with the problem definition:

1. Determine the physical and chemical properties of the different fly ashes;
2. Remove unwanted contaminants in the bio-energy fly ashes by treatment to increase the reactivity in concrete mixtures.

### 1.4 Hypothesis

By means of a broad literature study, the following hypotheses are formulated:

1. After the treatment method described in Paragraph 8.1, the properties of the bio-energy fly ash used in concrete mixtures and mentioned in Chapter 4 are improved;
2. After washing and optimization the fly ashes will fulfil at least one of the requirements for use as a building material in shaped or non-shaped form as defined by the Building Material Decree, Paragraph 4.5.4.

### 1.5 General approach

To answer the described objectives, this research is structured into two parts. The first part (Chapters 1-7) is the theory based on literature study to obtain information, insight and data that can be used to set up the practical laboratory test and to better analyze the results. The second part (Chapters 8-11) consists of the practical experiments. This part describes the performed laboratory tests. Based on the experimental results, further optimization and tests are performed to meet the stated requirements and objectives.

### 1.6 Structure of the report

This report consists of two parts. The first part is the theory that describes origin of the different fly ashes, utilization, properties and legislation, based on a literature study. The second part will describe the practical part with the different laboratory tests performed, results and further optimization processes, ending by a discussion, conclusions and recommendations.

## 2. Fly ash origin and types

In this research different types of fly ashes are investigated. Each power plant has its own technology of the bio-energy fly ash generation. However, one thing they all have in common is that the generated bio-energy fly ashes cannot be reused because of its concentration of unburned components and harmful substances (metals and salts). To get more insight about fly ash in general, background information about the origin of the material and production is very important. In this chapter the background information of the fly ashes is provided.

### 2.1 Bio-power plant installations

The types of bio-energy fly ash used in this study were collected from the cyclone and electrostatic precipitators of two different power plants in the Netherlands. The reason for this approach is that fly ashes generated in power plants are inherently variable materials because of several factors. Among those are the type and mineralogical composition of the fuel, degree of pulverization, type of furnace and oxidation conditions including fuel ratio and the manner in which fly ash is collected, handled and stored before use.

Since no two utilities or plants may have all of these factors in common, fly ash from various power plants is likely to be different. The following types of bio-power plant fly ash are examined: cyclone fly ash (A1) and filter fly ash (A2) from HVC-Alkmaar, and boiler fly ash (B1) and cyclone fly ash (B2) from Twence-Hengelo. Using several types of fly ash, a more general approach of treatment and application might be found.

In HVC-Alkmaar, 170.000 ton waste wood (dry biomass) is incinerated every year, compared to 140.000 ton of waste wood incinerated by Twence-Hengelo. The incinerated waste of the HVC-Alkmaar is the same as the content of 20960 trucks that deliver the waste, and reduces the CO<sub>2</sub> emission by 100.000 ton per year, compared to fossil fuel which is equal to the annual emission of 500.000 cars. The bio-power plant of HVC-Alkmaar delivers 25 MW electricity, which is equal to the electricity use of 60.000 households and the produced heat can be used for 48.000 houses (HVC, 2009). An overview of the fuel incineration and by-products for the years 2008 and 2009 is provided in Table 1.

Table 1: Fuel incineration and by-products (DWMA, 2010)

Year	Installation	Incinerated fuel [ton]	Total waste	Bottom ash [%]	Fly ash [%]	RGR-salts [%]
2008	HVC-Alkmaar	171.829	8624	54	25	21
2008	Twence-Hengelo	137.440	12587	66	20	14
2009	HVC-Alkmaar	176.000	6485	29	50	22
2009	Twence-Hengelo	147.894	15766	66	22	11

### 2.1.1 History

The bio-power plants described in this study are built recently. Twence-Hengelo is in operation since 2007 and a year later HVC-Alkmaar started to operate. The reason for a development of bio-power plants is the increased concern of the CO<sub>2</sub> emissions worldwide.

In the Kyoto protocol, article 3 the climate change, or so called greenhouse effect, is one of the reasons to reduce the CO<sub>2</sub> worldwide by at least 5% compared to reference year 1990 in the period 2008-2012 (United Nations, 1998). This means a reduction of 50 Mton CO<sub>2</sub> for the Netherlands. The reduction is done by reducing 25 Mton CO<sub>2</sub> within the Netherlands and 25 Mton CO<sub>2</sub> outside the Netherlands because it is possible to reduce the obligation through actions in foreign countries. According to the 'Uitvoeringsnota Klimaatbleid 1 en 2' the reduction needs to be realized compared to the reference year 1990 (Tweede Kamer, 1999).

In the midterm evaluation the reduction of 25 Mton CO<sub>2</sub> within the Netherlands will be reduced to 20 Mton CO<sub>2</sub> within the period of 2008-2012. In addition to the Kyoto Protocol, the Dutch government has already shaped a policy 'Derde-energie nota' for the promotion of renewable energy (Wijers, 1995). It was stated that 10% of energy consumption in 2020 should come from renewable energy. Furthermore, the European guideline (Het Europees Parlement en de Raad, 2001) is promoting renewable power. The directive was to reach a target of 9% renewable electricity by 2010. In 2009 this goal was reached and did not decline in 2010. According to the "Landelijk afvalbeheersplan, 2009" (VROM, 2010) the aim of the Dutch government is to be one of the environmentally friendly and energy efficient countries in Europe and effectively use certain existing energy content in waste.

The macro economic survey 'bio based economy' performed in the Netherlands on behalf of the Energy Transition Platform for Green Materials concludes that large scale application of biomass might have a huge environmental benefit and longer-term positive economic impact of 5 and 8 billion euros per annum.

Biomass is considered a sustainable and renewable resource that can replace fossil fuels like coal and gas. Being a part of the CO<sub>2</sub> cycle, it reduces the CO<sub>2</sub>-emission because of its 'carbon neutral' origin. Thus, CO<sub>2</sub> released in converting biomass into energy does not contribute to the increase of the greenhouse effect. Therefore, biomass complies with the objective of the government for the reduction of the CO<sub>2</sub> emission and increased independency from fossil fuels. Furthermore, using waste as fuel, instead of using it as landfill, is more favourable for the environment because of preventing the emission of methane from landfills. The landfill generated gas methane is a greenhouse gas which is about 20 times more harmful than CO<sub>2</sub>. Therefore, the amount of the land filling with biodegradable waste and hence, the landfill gas emissions are being reduced in recent years. Between 1990 and 2006 the annual emission of landfill methane has decreased by more than 300 Ktons, from 572 Kton methane in 1990 to 257.6 Kton in 2006. This corresponds to about 6 Mton CO<sub>2</sub> in equivalent.

The Copernicus Institute (Utrecht University), in cooperation with the LEI (Wageningen UR), conducted a study on the economic effects of biomass. The survey provides some long-term macroeconomic scenarios for the use of biomass for bio-fuels, chemistry and electricity generation (Banse et al., 2009). The scenarios are designed for situations with high and low amount of biomass imported to the Netherlands from European countries and for situations with high and low levels of technological development. The study encourages

the ministry to pursue the scenario of high technology developments in large-scale import of biomass. The predicted effects of such a scenario by 2030 are: an additional annual turnover of 5 and 8 billion euros, 25% of the fossil fuels are being replaced by biomass, reducing greenhouse gas emissions by about 25%.

Every year the potential of bio-power plants is increased due to the reasons stated above. According to the recent Energy Report 2011 (CBS, 2011), the Netherlands is less dependent on fossil fuels and gradually switching to renewable energy. Figure 1 illustrates the breakdown by source of the total renewable energy production between 1990 and 2010.

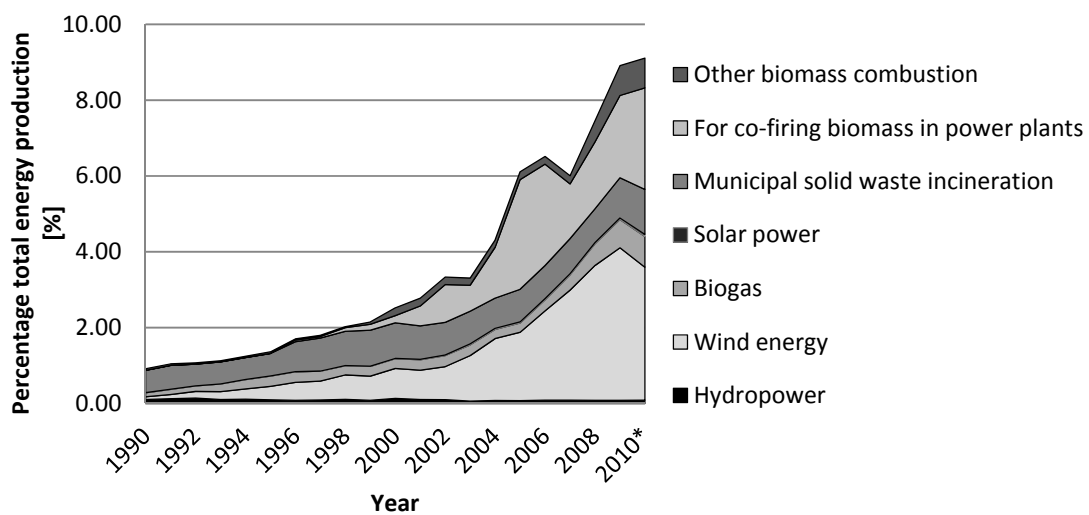


Figure 1: Renewable electricity 1991-2010 \*Preliminary results. (CBS, 2011)

### 2.1.2 Fuel

The fuel used in the bio-power plant of HVC-Alkmaar and Twence-Hengelo is a waste mainly consisting of wood. The wooden waste can be divided into three different classes, namely A-wood, B- and C-wood. A description and example for each class of wood are provided in Table 2. Not all these types of timber are suitable as fuel for the bio-power plants because of their components. Usually the wood waste used in the bio-power plants consists mainly of B-wood. Other compositions, such as beam grass, cocoa husks and residual products, nuts, shells and kernels are also used as fuel.

According to VROM (2010) "the minimum standard for manufacturing and processing of A- and B-wood is useful application". To be useful, the application of the wooden waste should satisfy certain requirements:

- By combustion, more energy is generated and recovered and then used in the combustion process; a portion of the generated energy must actually be used, either immediately in the form of heat, or after conversion in the form of electricity (C-228 / 00, paragraph 42);
- Most of the waste must be consumed during the operation and most of the energy generated must be recovered and used (C-228/00, paragraph 43). Because most of the waste must be incinerated, the waste has to consist of at least 50% organic matter;
- The installation that is using the fuel should not have the function/status of waste incineration.

The bio-power plant system meets these requirements, because more energy is recovered than what is used for production. Recovery takes place in the form of partly electricity and partly heat. In addition, the used biomass consists of more than 50% organic material. The system runs on A-wood when wood biomass in the form of wood chips is no longer available. This means that the power plant is not primarily designed for the incineration of waste, but to produce electricity and heat. This is very important because otherwise the class A and B wood could not be used according to the requirements described in (VROM, 2010).

Since no fossil fuel is involved, the electricity that is generated from the bio-power plants obtains the label of 100% green energy.

Table 2: Classification of wooden waste and description (VROM, 2010)

Class	Description	Example
Class-A	Unpainted and untreated wood	<ul style="list-style-type: none"> <li>- Beams</li> <li>- Stair components</li> <li>- Rafters</li> <li>- Battens</li> <li>- Pruning</li> <li>- Pallet wood</li> </ul>
Class-B	Wood products not mentioned in classes A and C, including painted, varnished and glued wood.	<ul style="list-style-type: none"> <li>- Hard-board</li> <li>- Soft-board</li> <li>- Chipboard</li> <li>- Wood fibreboard</li> <li>- Pressed wood</li> <li>- Furniture (except rattan)</li> <li>- Painted wood</li> <li>- Doors and frames (without glass and aluminium)</li> <li>- Not impregnated wood</li> <li>- Demolition Wood</li> <li>- Plywood</li> </ul>
Class-C	Impregnated wood and preserved wood (CC and CCA-wood); CCA wood also contains copper, chromium and arsenic, CC Wood contains copper and chromium, but not arsenic. Timber with other agents (fungicides, insecticides, boron-containing compounds, quaternary ammonium compounds) in order to prolong life.	<ul style="list-style-type: none"> <li>- Garden Fencing / fence parts</li> <li>- Sleepers</li> <li>- Meadow Poles</li> <li>- Green wood (wood used in playgrounds)</li> </ul>

### 2.1.3 Process

This section presents processes of wooden waste treatment for the HVC-Alkmaar and Twence-Hengelo power plants. Because these bio-power plants can have different process stages, an explanation is provided for the insight into the process of bio-energy fly ash extraction from waste products. Figure 2 presents the overall process that can vary for every power plant but in general the principle works as follows:

The waste travels from the combustion room to the boiler. The output is a boiler fly ash and a stream of air with small particles. This steam travels to an electrostatic filter where fly ash is collected and then to a fibre filter that collects further solid residue. After that, different steps of washing take place, additional water vapour with the clean gas is added and released in the atmosphere.

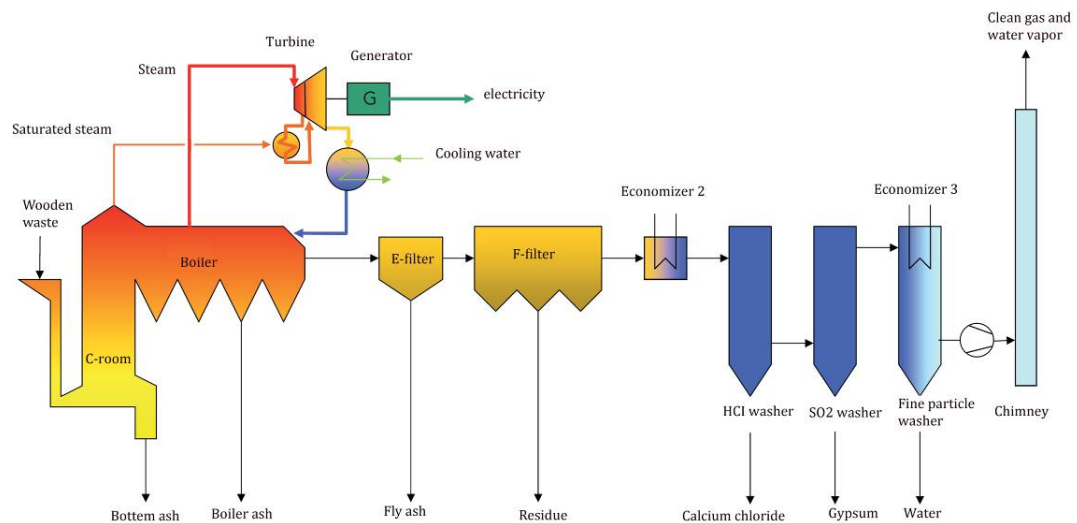


Figure 2: example of the processes in bio-power plant with grill oven (Afval Energie Bedrijf, 2006)

### 2.1.3.1 Supply

Waste wood is delivered by ship, train or truck and goes to the warehouse. Sometimes, the wood waste supplied by trains and ships first needs to be unpacked before it goes to the waste bunker. This can be performed automatically by special unpacking machinery.

### 2.1.3.2 Waste bunker

In the warehouse, fully automatic cranes equipped with a hydraulic polyp grab mix the supplied waste in the bunker. This is an important step because the supply comes from different factories that process different products and in order to minimize this effect, mixing is crucial. Afterwards, the wood is delivered from the bunker to the funnels, where the waste slides due to gravity into the combustion chamber.

### 2.1.3.3 Combustion chamber

There are different types of combustion chambers available for the incineration of waste. The two mainly used types are the grill oven (furnace) and the fluidized bed incinerators.

#### The grill oven used at the Twence-Hengelo bio-energy power plant

The grill oven consists of the following devices: moving tiles for the transport of waste materials; combustion zones; a water basin and an air suction system. The transport tiles can shift and tumble under an angle over each other and thus move the waste coming from the funnels over the surface of the grill. The waste then undergoes various stages of the combustion process, like drying, degassing, and finally burning under temperatures around 850 degrees Celsius. An overview of the grill is given in Figure 3. After a combustion time of around one hour, the solid combustion residues left on the grate (bottom ash) fall in a basin filled with water. The liquid level in the basin is regulated. Evaporated water is removed with the suction system for the combustion air. Besides cooling down the bottom ash, the basin is used to maintain the pressure in the combustion chamber (water seal). At the same time, extra air is coming through the air supply below the grills to cool them down and to provide oxygen for combustion. The amount of air, waste dosage and grill control device are controlled by an automatic process control system (automatic firing). The rest of the air is used as combustion air, which is functioning as a recirculation air blown over the grill in order to achieve proper turbulence and hence a better post-combustion, improving the

efficiency of the system. In some designs, the first part of these grills is cooled by water, which improves the durability of the system and facilitates the combustion because the supplied air now only fulfils the role of supplying oxygen and reduces the  $\text{NO}_x$  emission.

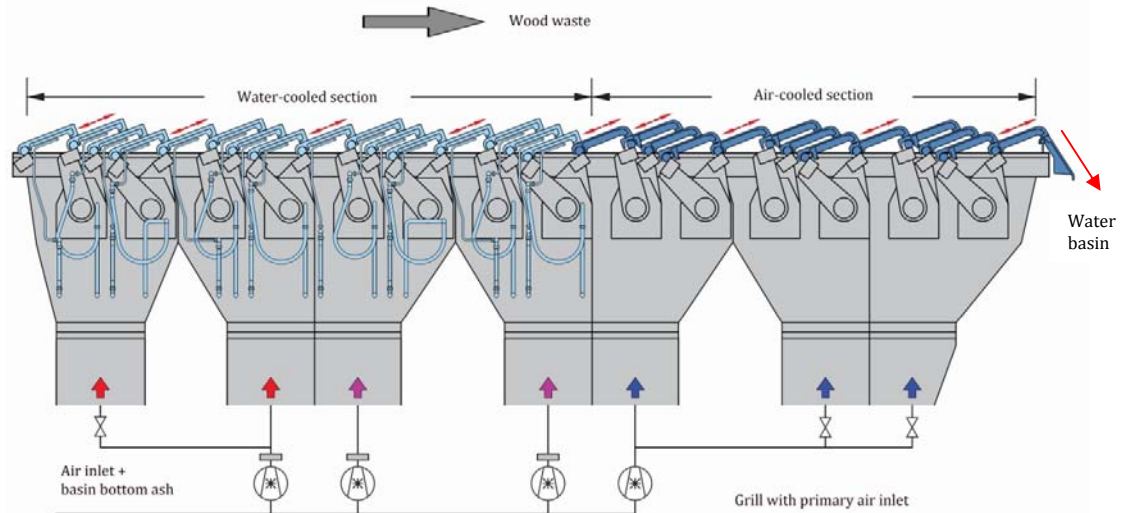


Figure 3: example of grill oven (Afval Energie Bedrijf, 2006). Arrows indicate hot and cold air inlets

In the design of the grill oven the focus should be on the following points:

- Sufficient distribution capabilities of the waste on the grill, so the covering of the waste on the grill should be as homogeneous as possible;
- Thorough mixing of the waste on the grill, so that combustion takes place as homogeneously as possible;
- Equal and adjustable air distribution across the grid zone, accordingly;
- Limitation of the primary combustion air and flue gases entraining dust and ash particles to reduce fly ash production;
- Proper control options for changing conditions so that an optimal combustion can be achieved.

In general, a sufficiently high temperature (above 850 degrees Celsius), the presence of oxygen (residual content of at least 6% in the flue gases), sufficient stand time (at least two seconds) and thorough mixing of the flue gases should provide a proper burning of the wood.

#### Fluidized bed incinerator used at the HVC-Alkmaar bio-energy power plant

In general, the biomass is fed to the fluidized bed, which contains a large amount of sand (an inert, non-combustible material). From the bottom combustion air is blown through the fluidized bed at high speed. The high volume of air passing the fluidized bed creates turbulence that ensures the complete combustion of the fuel particles. Also, by providing primary and secondary combustion air for a staged combustion and recirculation, the formation of the flue gas  $\text{NO}_x$  is reduced. Therefore, the combustion in the furnace can be characterized as a "low  $\text{NO}_x$ " process. A cyclone removes the solid and unburned particles from the flue gases and carries it back to the bed.

There are two main types of fluidized beds. In the first one, the velocity is chosen so that the sand and the fuel just perform a bubbling motion. This can be called a stationary fluidized



bed or a bubbling fluidized bed (BFB). In the second type, the speed of the airflow is further increased creating flows that are carrying sand and fuel. Such an installation is called a circulating fluidized bed (CFB). This system is used at HVC-Alkmaar. Compared to a BFB, CFB has the advantage that by the greater turbulence the heat transfer will be higher, that means a lower flue stream resulting in a highly efficient system. Figure 4 illustrates the principle of a fluidized bed combustion room. The disadvantages of the CFB are the higher use of electric power due to the need for an increased airflow and the higher dust concentration in the flue gas. Most of the dust, however, is simply separated from the flue gas in the cyclone. Unburned particles from the flue gases are going back to the combustion room. That process is controlled by the cyclone. After this, there is another cyclone that captures red-hot ash particles and ash particles greater than 10 microns. The fly ash that is removed by the cyclone is stored in closed fly ash silos.

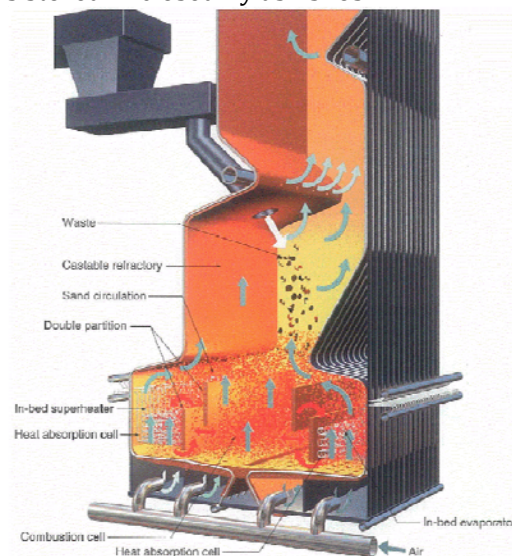


Figure 4: principle of a circulating fluidized bed combustion room

#### 2.1.3.4 Boiler

After the combustion room the flue gases pass first through the three sections (the radiant section) and then the fourth section (the convection part of the boiler), where the existing heat is recovered. In the first three sections, the gases release heat through radiation to the water tubes resulting in a steam production. The cooling of the gases occurs without direct contact between the gas stream and the heated surfaces of the boiler, in order to prevent corrosion. The amount of steam generated has the conditions of 90 bar and 500 degrees Celsius. During the passage of flue gas through the boiler the radiation decreases and more convective transfer takes place. During this process direct contact between flue gases and pipes is required. During all these processes the temperature is reducing and part of the ash in the gas is falling down. This so called bottom ash is then collected and stored in storage tanks.

#### 2.1.3.5 Power generation

From the process described above hot water and steam are produced. The steam can flow through a turbine to produce electricity. The hot water can be used for district heating, in which case transfer takes place through a heat exchanger. Also, the hot water can go to an evaporator to be converted in to steam. This steam can then be transported to the turbine.

### 2.1.3.6 Flue gas cleaning

For the separation of fly ash from the boiler outlet, an electrostatic filter is installed. This filter and the combination of the two-way ash handling system of the boiler make it possible to clean fly ash that can be reused. For the removal of dust a fine fibre filter is used. Dry powder (CaO or unslaked lime, or NaHCO<sub>3</sub> or sodium bicarbonate) is injected on the cloth filter to absorb fine particles and powdered limestone is added to prevent fire and explosions. The next cleaning step is to remove the acidic components and ammonia from the flue gases. This is done by a wet cleaning process with water.

So, in general, fly ashes in the grill oven are collected in the following way: in the boiler “big particles”, in the electrostatic filter and in the cloth filter, “small particles”. In the fluidized bed incinerator, fly ash is collected as follows: in the cyclone, “big particles” and in the electrostatic filter, “smaller particles”.

## 2.2 The by-product fly ash in general

Since ancient times, Romans, Chinese and Indians have used volcanic ashes and other similar natural and man-made materials to produce cementing materials by mixing with lime, volcanic ashes and pulverized burned bricks. In this way they produced cementitious mortars for the construction of ancient monuments that are still in existence today (Joshi & Lohtia, 1997). The term ‘fly ash’ appeared in literature in 1937. However, from 1914, data about the use of finely pulverized powdered coal (fly ash) as a pozzolan in concrete had been already published (Joshi & Lohtia, 1997).

Fly ash can be described as a fine material precipitated from the stack gases of burning solid fuels. In Europe the ash was always referred to as pulverized fuel ash, but in the United States this ash was termed fly ash because it escaped with the flue gasses of coal fuel power plants and “flew” into the atmosphere.

There are many types of fly ash produced from different installations:

- Coal combustion fly ash, from 1882, design Thomas Edison (NETL, 2011);
- Bio-energy fly ash, from 1971, (Dpcleantech, 2011);
- Paper-sludge fly ash, from 1990, (CDEM, 2011);
- Municipal Solid Waste Incineration (Destructor) fly ash, from 1874, design Albert Fryer (Herbert, 2011).

In this paragraph the first two types of fly ash are discussed.

### 2.2.1 Coal combustion fly ash

During the industrial revolution, the production of coal combustion fly ash started. The electric power plants created electricity from steam production. The steam was produced by burning 63 microns sized pulverized coal in a 1600 degrees Celsius fired combustion room (Hendriks et al., 1999)

The creation of coal combustion fly ash is illustrated in Figure 5, it starts from the moment when the mineral portion of coal is heated above the melting point. From that point, small drops are formed and when they are cooling down the formation of spherical fly ash particles begins. When the temperature of the particles is not above the melting point, less spherical fly ash particles are formed and more fused particles are detected as illustrated in the left part of Figure 6. This leads to less small particles of 10 microns and more porous fly ash particles as illustrated on the right part of Figure 6 (CUR, 1992). In general, the production of all fly ashes is similar to the formation of coal combustion fly ash.

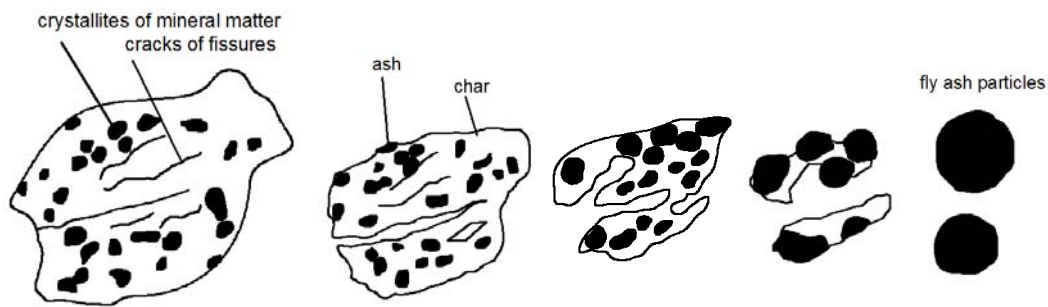


Figure 5: formation of coal combustion fly ash

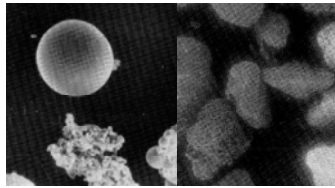


Figure 6: Left, "ideal" fly ash and fused particles. Right, less spherical: fine coal particles

Later, when air pollution problems were recognized, better installations were constructed to collect fly ash using cyclone separators, electrostatic precipitators or bag house filters as described in Paragraph 2.2. Depending on the collection system, varying from mechanical to electric precipitators or bag houses and fabric filters, about 85 to 99.9% of the ash from the flue gases is retrieved in the form of fly ash. Fly ash accounts for 75 to 85% of the total coal ash and the remainder is collected as bottom ash or boiler slag. The current annual production of coal combustion fly ash is about 500 million tons and forms 75-80% of the total ash production worldwide. Only 3 to 57% of this production is used worldwide (Joshi, 1979). The rest is landfilled, but this is not economically desirable because of high landfill costs, and environmental risks such as leaching to the ground, thereby creating water and also air pollution. However, the government in the Netherlands aimed to reuse the produced coal combustion fly ash from the beginning. This goal was achieved in 1988, when from the annual production of 712,400 tons fly ash, 98% was reused. This percentage represents the highest amount in the world (CUR, 1992). In 2007, 814.717 tons of fly ash were produced: 506.139 tons of fly ash were used as cement filler and concrete mixtures and 88.054 ton of fly ash were used in the production of pozzolanic cements. In total, this forms 73% of fly ash production (Vliegassunie, 2008). One of the cements is called "Portland fly ash cement" that is classified among other types as described in Figure 7.

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

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

Figure 7: Portland cement types conforming EN-197-1: Composition, specifications and conformity criteria for common cements

### 2.2.2 Bio-energy fly ash

The increase of using biomass for electricity generation in power plants leads to fly ashes different from the 'old fashion' coal combustion fly ash. The bio-energy fly ash created from burning biomass has different characteristics and properties in comparison to coal combustion fly ashes because of different combustion input and therefore, still need to prove their utilization in concrete mixtures. Their characteristics and properties will be further described in Chapter 4.

## 3. Concrete

Concrete has been used as a building material for ages. It consists of raw materials such as cement, aggregates like sand and gravel, water, additives and fillers. The properties of concrete can be characterized during three different phases: immediately after mixing “fresh concrete”, during the hardening process “young concrete” and the “hardened concrete”. These phases can be distinguished from each other by values of properties (e.g.: density, humidity, strength) that have an influence on the quality of the produced concrete.

### 3.1 Composition

Concrete is created when water is mixed with cement and aggregates, additives and fillers. With the correct proportion, voids in the mix are filled with sand and cement combines all the grains into one overall structure when it hydrates with water.

#### 3.1.1 Water

When a large amount of water is added to the mix, the excessive water does not take part in the cement hydration and seals the capillary pore structure. This leads to reduced strength and vulnerability of concrete to freezing, thus reducing its durability. In case of deficiency of the water, the cement cannot be completely hydrated resulting again in the strength and durability loss of the concrete product.

#### 3.1.2 Cement

A large amount of cement would increase the strength development in concrete and its durability. However, cement production generates CO<sub>2</sub> and is expensive because it consists of raw materials like calcite, clay, iron oxide and quartz needed to be firstly excavated and then heated. Therefore it is important to use cement as little as possible (no more than needed). Paragraph 5.1 describes the composition in detail.

#### 3.1.3 Aggregates

The aggregates consist of:

- Gravel 8-32 mm;
- Fine gravel 4-8 mm;
- Coarse sand 0-4 mm;
- Fine sand 0-1 mm;
- Stone powder 0-0,125 mm.

An ideal mix of aggregates would consist of an amount of small particles that would fit perfectly in the voids created by the bigger particles. Such a “perfect” mix however, is difficult to produce and is not necessary because pore space is needed for the hydration products. Still, fillers mostly finer than 0.125 mm are used for concrete mixtures, by that increasing the consistency of cement. The reason for that is the enlarging of the particle surface and the water retention capacity. In the presence of water, all the interfaces are drawn together. The particles seem to stick more together when finer particles are present resulting in the increased consistency. Applied aggregates and fillers have direct influence on the density of concrete. Depending on density, concrete can be divided into three categories:

- Light concrete, density 2000 kg/m<sup>3</sup> or lower;

- Normal concrete, density between 2000 – 2600 kg/m<sup>3</sup>;
- Heavy concrete, density 2600 kg/m<sup>3</sup> or larger.

### 3.1.4 Filler and legislation

According to NEN-EN-206-1 there are two types of fillers. The first type represents inert particles functioning as a filler without any chemical reaction in concrete.

The second type characterizes reactive fillers that have pozzolanic or hydraulic properties. Fly ash is related to the second category. The pozzolanic fillers form reaction products with the available calcium hydroxide ( $\text{Ca}(\text{OH})_2$  or CH) that is created by reaction of cement with water. The hydraulic properties of the filler are developed by reaction with the available cement minerals and formation of a denser pore structure, thus increasing the strength and durability (Joshi & Lohtia, 1997). Because of this, the second category can function not only as a filler but also as a binder. The binding function of a filler is further incorporated into the so-called k-value in the NEN-EN-206-1. This k-value is so far only available for the “old-fashioned” coal combustion fly ash in combination with CEM I 32.5 N, CEM I 32.5 R, CEM I 42.5 R, CEM III/A and CEM III/B. All other types should be implemented through a comparative study (equivalent concrete performance concept) to determine the binder function (see 5.2.5.2 and 5.2.5.3 of NEN-EN-206-1). The k-value is important because it determines the amount of fly ash that can be seen as binder (maximum 1/3 of total cement), and therefore reduces the minimum amount of cement required by NEN-EN-206-1, which is cost- and CO<sub>2</sub> reducing.

## 3.2 Properties of concrete and influence of fly ash

### 3.2.1 Fresh concrete

Concrete is a continuously transforming material. It starts from a mix varying from liquid form to earth-moist form, depending on the function and workability of the concrete mix. The definition of workability is the total properties of concrete that are important for a correct handling of the concrete mix in the circumstances. For example:

During a construction process with in situ concrete structures, the concrete should be pumped to the concrete structure and equally distributed along the surface, filling all of the corners and gaps. A low pumping ability means that the concrete cannot travel from the truck to the concrete structure when long distances or heights should be over passed (Figure 8).



Figure 8: Importance of the pumping ability and travel distance of a concrete mixture

A low workability means poor distribution of concrete while a high workability makes it more efficient. However, workability is not the only important parameter; the in-situ concrete should not segregate and the consistency should be high. Normally, for concrete with a high plasticity and a low consistency most of the heavy gravels may segregate to the bottom, thus resulting in a poor mixture and possibly affecting the concrete construction negatively, while a low plasticity and high consistency will decrease its ability to equally distribute along the surface.

Fly ashes can have an effect on the workability of the concrete mixtures when used as a filler, because their use mostly increases the specific surface area (depending on the particle size distribution) resulting in a higher water demand. On the other hand, fly ash used as a partial replacement of cement can decrease the water demand, because less cement is needed so less water is needed to hydrate. On the other hand, it will still need some water if it possesses pozzolanic properties, but less than cement hydration (Wang et al., 2012).

Fly ashes can also increase the water demand because of its lime and coal content, which adsorb water. Finally, fly ash can also increase the workability because of the available cenospheres and plerospheres that increases the fluidity (rolling effect) of the mortars. Therefore its effect on the water demand is strongly type dependent.

Fly ash influences the following aspects of workability: mix ability, transportability, flow behaviour, compact ability, stability, pumping ability, finishing and green strength. These important aspects will be considered during the preparing of the recipes.

### **3.2.2 *Hardening process***

The hardening process of cement paste is an important phase that determines the concrete qualities. In this phase concrete needs to be sealed in order to reduce the water evaporation. In addition, during the hydration of cement, heat is released while increasing the temperature within a large mass of concrete, since the heat is not quickly dissipated. The occurred difference in temperatures can cause internal stresses which may result in cracking. By using bio-energy fly ash in concrete, less hydration heat is released at the beginning because less cement is added. Bio-energy fly ash starts to hydrate later due to the slower pozzolanic reaction. Therefore, the hydration heat is spread out more over time. This results in less cracking but also in a decrease of early strength. Increasing the reactivity, resulting in a fast hardening could result in an increase of early strength.

### **3.2.3 *Hardened concrete***

Almost all properties of concrete are largely determined by its composition. The properties of concrete are: compressive strength, elastic deformation (in terms of the elastic modulus), permeability, porosity, wear resistance, density, relative humidity, frost resistance, colour and even the appearance.

To characterize the properties of concrete the following features can be used:

- Cement: type and amount;
- Aggregate: type, particle shape, particle size distribution and quantity;
- Additives: additives, fillers, dyes and fibres.

The compressive strength and sustainability are properties of concrete that are prescribed for each product and project by design institutes.

The compressive strength is important for the bearing capacity of the construction, which is influenced by the strength of the aggregate used and by the choice of the water-cement ratio and cement strength class. Furthermore, the composition of concrete will be determined by its application and related workability as mentioned in Paragraph 3.2.1. For a concrete wall a more liquid concrete mix is needed, while for a concrete brick an earth-moist concrete consistency is needed.

There are several reasons to use fly ashes in the concrete production. Coal combustion fly ash can provide cost savings, improved workability, better surface finishing, lower heat of hydration, improved long term or ultimate strength, reduced permeability, improved sulphate resistance and reinforcement corrosion prevention. On the other side, using coal combustion energy fly ash in concrete results in delayed strength gain, increased demand of air entraining agent with increasing carbon content in the fly ash, and slightly reduced resistance to scaling due to salts used for de-icing on concrete roads. So far it is believed that the same principle applies to bio-energy fly ash.



## 4. Bio-energy fly ash properties

Fly ash can be used in concrete as a filler or partial replacement of cement due to its particle-size distribution and pozzolanic properties as described in Paragraph 3.1.4. Pozzolans are defined as “*silicious and aluminous materials*” which in themselves possess little or no cementitious value. However will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. Some fly ashes with self cementitious properties react immediately with water (Joshi & Lohtia, 1997).

The mineralogical composition, crystalline and non-crystalline phases, particle morphology as well physical characteristics define largely the pozzolanic reactivity of fly ash. The physical characteristics of fly ash which affect concrete performance are loss on ignition, fineness, moisture content and specific gravity, and pozzolanic activity. These are the principal parameters for predicting the performance of fly ash in concrete.

### 4.2 Mineralogical properties

Fly ash consists of a glass phase and a crystalline phase. These phases can be recognized using the X-ray powder diffraction method. If structures are recognised, it is a crystalline phase. If the method does not detect structures, it is a glass phase. The glass phase is the reactive phase (pozzolan) consisting of alumina-silicates. Firstly, Portland cement in concrete needs to hydrate with water resulting in a formation of calcium hydroxide (lime). Then it reacts with the alumino-silicates presented in fly ash with the creation of cementitious compounds possessing adhesive properties. In contrast to pozzolanic fly ashes (Class F according to American standard test method (ASTM) C618), self cementitious fly ashes (Class C according to ASTM C618) are able to hydrate almost in the same way as Portland cement does. The degree of self hardening generally varies with the calcium oxide content of the fly ash.

#### 4.2.1 Fly ashes used in this study

In this study, six fly ashes will be used as follows:

- The first one is a cyclone fly ash, provided by HVC and termed A1;
- The second one is a filter fly ash provided by HVC and termed A2;
- The third one is a boiler fly ash, provided by Twence and termed B1;
- The fourth one is a cyclone fly ash, provided by Twence and termed B2;
- The fifth one is a commercial type, known as: PKVA SMZ (Class F) and is used as a reference fly ash coming from the coal combustion process and is termed R.

Table 3 presents the most important oxides present in the fly ashes; this is used for oxide engineering. In this method the oxides of different fly ashes are compared with a reference. This way an expectation can be made of how the material will react; the smaller the difference, the better the composition. The calcium oxide amount is lower in bio-energy fly ash than in cement but higher than in PKVA SMZ (R). On the other hand the amount of silicate is much higher in most of the bio-energy fly ashes compared to cement but lower than in the reference fly ash. This combination will result in a low C/S ratio which can have both negative and positive effects on the final product, depending on the ratio. Adding some gypsum will increase the CaO concentration and decrease the C/S ratio. In general the bio-energy fly ashes have more similarities from the point of view of oxide composition with cement than with the reference fly ash.

Table 3: Oxide composition of different fly ash types compared to reference fly ash type obtained by XRF

Oxide	HVC cyclone fly ash (A1) [%]	HVC filter fly ash (A2) [%]	Twence boiler fly ash (B1) [%]	Twence cyclone fly ash (B2) [%]	CEM I 42.5 N [%]	PKVA SMZ (R) [%]
MgO	2.7	2.1	2.7	3.2	1.6	1.9
Al <sub>2</sub> O <sub>3</sub>	7.6	3.7	6.4	5.5	5.8	22.3
SiO <sub>2</sub>	22.4	8.5	43.3	39.8	18.8	54.8
SO <sub>3</sub>	12.3	12.6	6.5	8.3	4.5	1.4
CaO	30.5	48.9	23.4	22.9	62.0	4.4
Fe <sub>2</sub> O <sub>3</sub>	5.2	2.5	3.9	3.7	3.6	8.4

### 4.3 Particle Morphology

While examining coal combustion fly ash with a scanning electron-microscope (SEM) it can be seen that it consists of small particles that are typically spherical and fused particles (Paragraph 2.2.1). These spherical particles can be very useful in concrete because of functioning as a lubricant between the irregularly shaped cement particles (CUR, 1992). There are however different spherical particles; the most common are described below:

- Cenospheres, small spherical particles that are hollow, owing to an entrapment of gases by the molten phase in the course of burning, representing about 20% of total fly ash;
- Plerospheres, the spherical hollow particles that contain entrapment of particles instead of gases.

Due to the low density of cenospheres, they are valuable for low density concrete production. Figure 9 presents reference fly ash under an Olympus SZX9 microscope with magnification of 150x and software package AnalisysIS 3.2.

For the separation of cenospheres and plerospheres from the fly ash drops of the water are used. The left picture illustrates reference fly ash under water and right picture on the surface of the water. On the surface of the water large amount of cenospheres and plerospheres can be clearly seen.

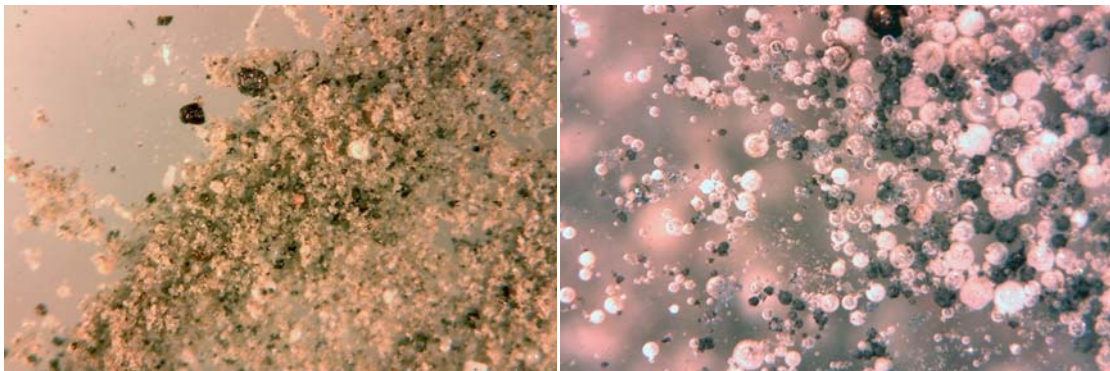


Figure 9: Left, PKVA SMZ fly ash (R) under water indicating small spheres and minerals. Right, PKVA SMZ fly ash (R) floating on water indicating low density spheres

Comparing Figure 9 with Figure 10 which presents Twence cyclone fly ash (B2) indicates that the bio-energy fly ash is much coarser and has almost no floating spheres but instead floating carbon particles. Also the particle size distribution is far greater than that of the reference fly ash which can indicate a lower pozzolanic activity.

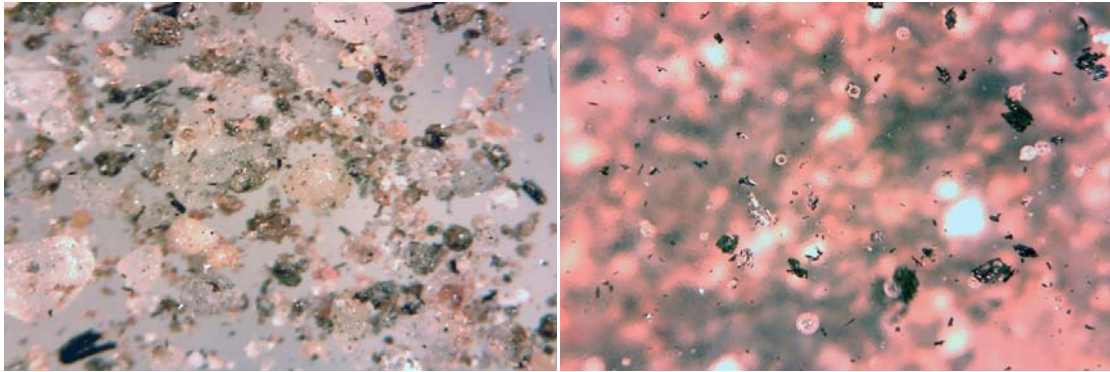


Figure 10: Left, Twence cyclone fly ash under water (B2), indicating coarse materials. Right, Twence cyclone fly ash (B2) floating on water indicating low density spheres and carbon particles

## 4.4 Physical properties

### 4.4.1 Density

Fly ash can be distinguished by its density. To measure the density, the fly ash is first dried in the oven at a temperature of 105 degrees Celsius according to NEN-12880 for 14 hours in order to remove adsorbed water. Table 4 presents the different densities of fly ash measured with a Micromeritics AccuPyc II 1340 gas pycnometer under conditions of 20.6 degrees Celsius with three purges and a cell volume of 108.23 cm<sup>3</sup> and expansion volume 74.003 cm<sup>3</sup>. The obtained densities are quite high comparing to coal combustion fly ashes that are around 2.1-2.4 g/cm<sup>3</sup> but still lower than cement ( $\pm 3.1$  g/cm<sup>3</sup>). The lower density of PKVA SMZ is probably due to the cenospheres and plerospheres as described in Paragraph 4.3.

Table 4: Density of fly ash from the bio-energy power plants

	HVC cyclone fly ash (A1)	HVC filter fly ash (A2)	Twence boiler fly ash (B1)	Twence cyclone fly ash (B2)	PKVA SMZ (R)
Density [g/cm <sup>3</sup> ]	2.73	2.59	2.65	2.68	2.36

### 4.4.2 Colour

Bio-energy fly ash can also be classified by colour. This quality is important for aesthetic reasons but can also be used to distinguish particles that are containing a large amount of iron oxide and coal particles. These particles are dark, blackish in colour. Changes in the concentration of these particles can affect the colour as can be observed from the next section "carbon content". Figure 11 presents four different bio-energy fly ashes investigated in this research. The fly ashes supplied by Twence are much darker than the ones from HVC, which indicates a higher carbon content. The HVC fly ashes are more sticky and consisting of clumped particles. The Twence cyclone fly ash has a consistency more like fine distributed powder (particle size <0.125 mm) and the Twence boiler fly ash – like mix of fine distributed powder and coal dust. For aesthetic reasons the amount of fly ash that is used can have influence on the colour output of the concrete. In the pictures below only unburned coal particles (black) can be distinguished from the samples, other unburned particles have a similar colour as the rest of the sample and are therefore hard to detect visually.

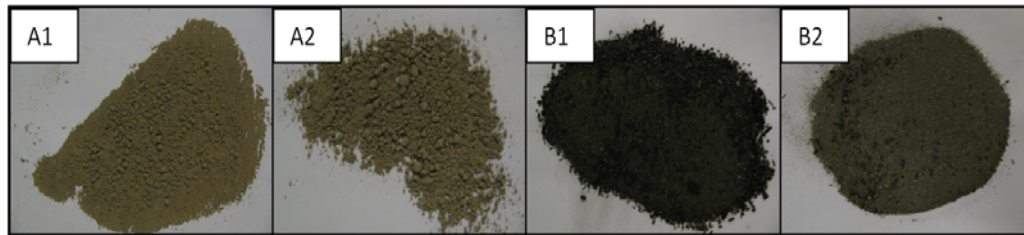


Figure 11: Pictures of the four different fly ashes (2010) Where A1(=HVC cyclone fly ash), A2= (HVC filter fly ash), B1(= Twence boiler fly ash), B2(= Twence cyclone fly ash)

#### 4.4.3 Carbon content

The carbon contents of the four bio-energy fly ashes are presented in Table 5. The Twence boiler fly ash has a large amount of unburned coal as also illustrated in Figure 11 and Table 6. This can be due to the combustion installation of the grill oven instead of a fluidized bed oven, where a less efficient combustion takes place. The fact that the Twence cyclone fly ash and HVC ashes have a comparable amount of loss on ignition (LOI), and is not illustrated in Figure 11, is probably because the LOI of Twence is mostly carbon; while in the HVC ash consist of other elements.

According to NEN-EN-450 the LOI is allowed smaller than 5%.

Table 5: LOI for the four different fly ashes obtained by X-ray fluorescence (XRF) from 2011

Bio-power plant	HVC cyclone fly ash (A1)	HVC filter fly ash (A2)	Twence boiler fly ash (B1)	Twence cyclone fly ash (B2)	PKVA SMZ (R)
LOI 2011 mass percentage [%]	0.5	0.5	18.7	1.2	3.9

As illustrated in Figure 11, the Twence fly ashes contain black coal particles. To investigate the amount, the fly ashes are visually observed. Firstly, fly ashes are sieved from 500 to 125 microns to remove the large unburned coal particles and to investigate their amount. It is found that Twence boiler fly ash (B1) consists of 13.1% coarse carbon particles and that the carbon particles also remain in the lower sieve diameters as illustrated in Figure 12 (visual analysis) and presented in

Table 6 (measured). However, the Twence cyclone fly ash (B2) has only 0.7% coarse carbon particles in the 500 micron sieve diameter and the carbon particles are almost entirely filtered out using the 125 micron sieve diameter as illustrated in Figure 13 (visual) and presented in Table 7 (measured). Remaining fly ash <125 microns presents 41.5% of total amount of fly ash which means that it is much more suitable for application in concrete than the B1 based on finer particles that are reacting faster and have less/non carbon content.

Table 6: The sieve diameter, mass percentage and carbon content for Twence boiler fly ash (B1)

Sieve diameter [μm]	Mass percentage [%]	Volume percentage [%]
500	13.1	14.09
300	19.2	19.06
250	8.3	8.21
200	14.9	14.78
125	24.9	24.77
<125	19.5	19.09
Total	100	100

Table 7: The sieve diameter, mass percentage and carbon content of Twence cyclone fly ash (B2)

Sieve diameter [ $\mu\text{m}$ ]	Mass percentage [%]	Volume percentage [%]
500	0.7	1.34
300	5.7	21.45
250	6.2	20.30
200	11.3	19.56
125	34.5	18.31
<125	41.5	19.03
<b>Total</b>	<b>100</b>	<b>100</b>

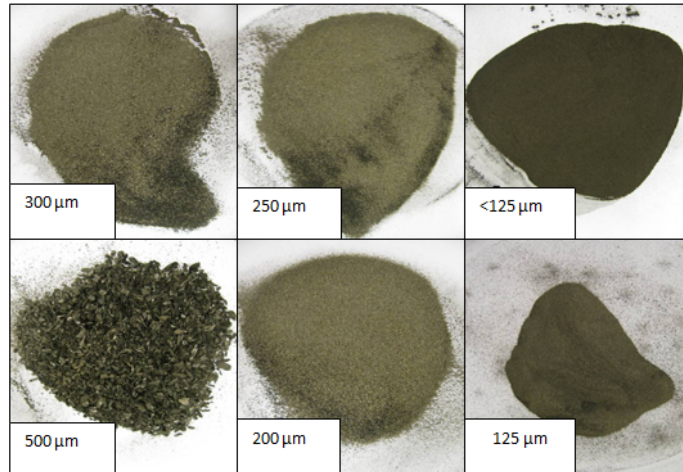


Figure 12: Sieved Twence boiler fly ash (B1) ash from 500 to <125  $\mu\text{m}$

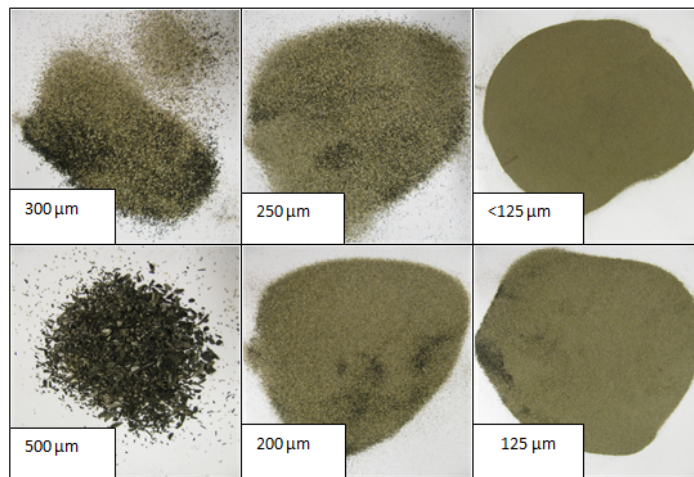


Figure 13: Sieved Twence cyclone fly ash (B2) from 500 to <125  $\mu\text{m}$

#### 4.4.4 Fineness, PSD and SSA

A larger amount of particles smaller than 45 microns can result in a better packing and more pozzolanic activity. More pozzolanic activity is due to reaction kinetics: finer particles react faster, and is not due to the fact that finer particles consist of more spherical glass particles and therefore more pozzolanic activity (Fraay, 1987). Also the workability of the concrete mix will be higher because smaller particles result in a higher H $\ddot{a}$ germann flow size (CUR, 1992) as described in Paragraph 3.2. For other fly ash types a large percentage of

particles larger than the 45 microns has been reported to have a negative effect on the 28 day and 90 day strengths of normally cured Portland cement fly ash mortars (Mehta, 1984; Diamond, 1985).

Fineness is one of the primary physical characteristics of fly ash that relates to its pozzolanic activity (Joshi, 1970). When examining fly ash for its particle size distribution (PSD) the NEN-EN-450 sets the limit of 40% for the maximum amount of fly ash retained on the 45 micron mesh sieve on wet sieving, as a quality control measure. Figure 14 illustrates (PSD) for five different types of fly ash measured with a Mastersizer 2000 using the laser diffraction method. Figure 15 presents the percentage of particles that are passing through a sieve subdivided from 100% (everything passes) to 0% (nothing passes). The X-axis presents the particle size distribution with increasing dimensions from left to right, while the Y-axis represents a volume percentage from the total sample increasing from the bottom to top. This data is summarized in Table 8.

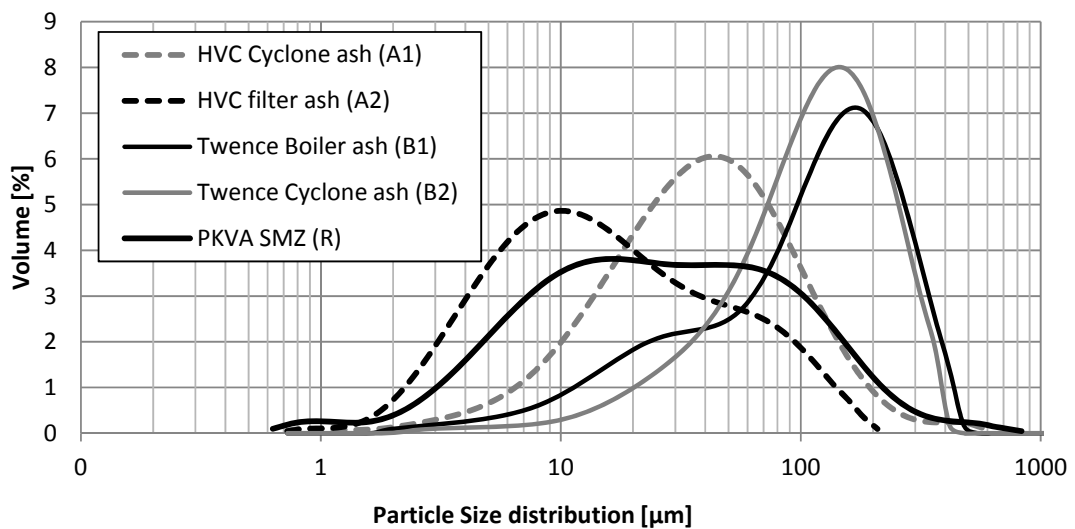


Figure 14: Particle size distribution (PSD) of the six fly ashes

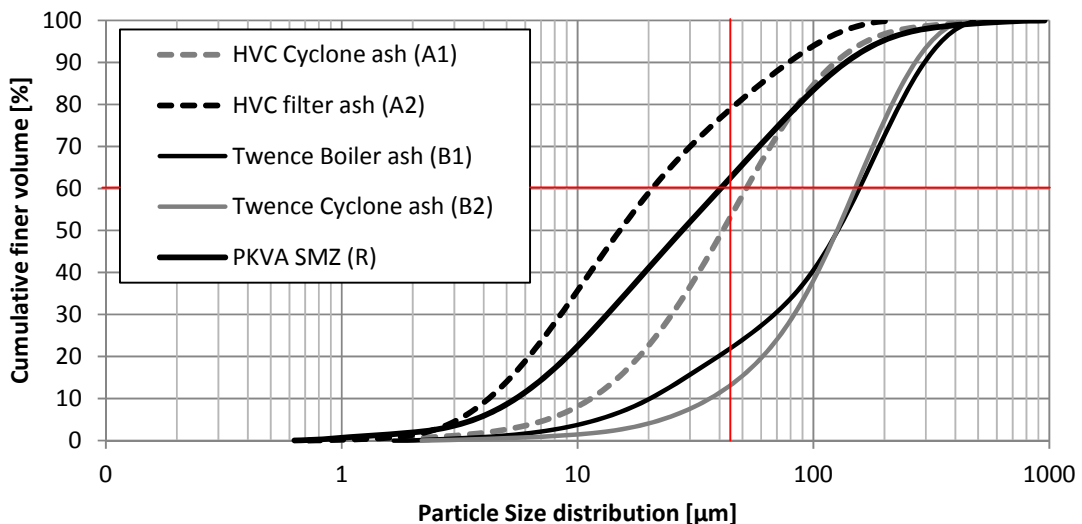


Figure 15: Cumulative finer volume of the fly ashes. The lines at size of 45 microns and volume of 60% indicate the break point between good and less positive quality of fly ash as described by NEN-EN-450

Table 8: Cumulative finer volume table of different fly ashes

	HVC cyclone fly ash (A1)	HVC filter fly ash (A2)	Twence boiler ash (B1)	Twence cyclone ash (B2)	PKVA SMZ (R)
<b>d(min.) [μm]</b>	0.7	0.7	1.7	2.2	0.6
<b>d(0.10) [μm]</b>	10	3.8	18	8.7	5.0
<b>d(0.50) [μm]</b>	38	13	110	110	25
<b>d(0.60) [μm]</b>	47	19	138	130	30
<b>d(0.80) [μm]</b>	75	40	202	187	106
<b>d(0.90) [μm]</b>	110	69	255	235	120
<b>d(max.) [μm]</b>	631	209	479	417	832

The fly ashes from Twence examined with the Mastersizer are sieved to a maximum particle size of 250 microns. However, from the results presented in Figure 15, about 10% has still a larger size. This is due to the fact that some particles are needle-shaped so if they are lying horizontally on the sieve they will be stopped, but falling vertically they will slip through the sieve.

As the graph illustrates, the fly ash of HVC is finer than the fly ash of Twence. This can be related to the burning process where HVC reduces the waste for the combustion room into small fragments. As expected, the HVC filter fly ash (A2) has a larger amount of small particles than HVC cyclone (A1). This can be explained by the fact that gasses with fly ashes coming from the combustion room are first collected with the cyclone (HVC) or boiler (Twence), collecting the bigger particles and after that the bag filter (HVC) or cyclone (Twence) collect the remaining fly ashes. However, the Twence boiler has finer particles than the A1 which in general was not expected; this could be mainly carbon dust (useless ingredients of fly ash).

Comparing the result with PKVA SMZ (R), A1 is a bit coarser while A2 is a bit finer. Probably mixing these two fly ashes will create a fly ash that is almost identical to that of the reference fly ash.

To have a clear view of the particles Scanning Electron Microscopy (SEM) is performed. The (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In this research a Philips XL 30 ESEM-FEG, equipped with GSE, SE, BSE detectors, EDX SEM is used to observe the external morphology of the fly ashes.

In Figure 16 the images are presented of HVC cyclone (A1) situated on the left, in the middle Twence boiler (B1) and on the right HVC filter (A2). From these images it can be concluded that A1 has very small particles compared to B1, which is also concluded from the PSD in Figure 14 and Figure 15. However, as the PSDs indicate there is an increase of particles smaller than 10 microns when comparing HVC ashes with B1. According to (CUR, 1992) regarding coal-combustion fly ash an increase of particles smaller than 10 microns would indicate a higher amount of spherical particles. For the bio-energy fly ashes this is not observed indicating again that bio-energy fly ash is of an entirely different nature. This is

even enhanced by the picture of A2 illustrating irregularly-shaped particles even for particles smaller than 10 microns.

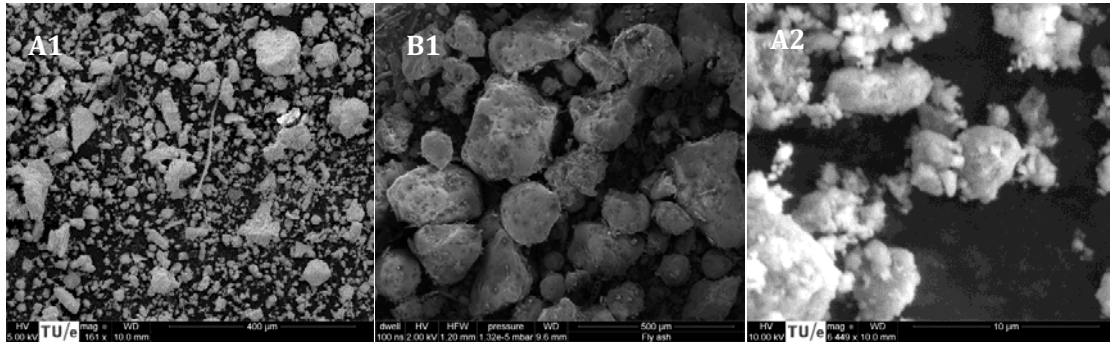


Figure 16: SEM images. Left, HVC cyclone fly ash (A1). Middle Twence boiler (B1). Right, HVC filter fly ash (A2)

For using fly ash as a filler, fly ash should contain small particles of spherical forms instead of the fused forms as mentioned in Paragraph 2.4.1. So far A2 fulfils this requirements and the requirements of NEN-EN-450 for maximum retained fly ash on the 45 micron sieve as described in Paragraph 4.5.5.

The fineness of fly ash is also defined by a specific surface area (SSA) per unit of mass. If the surface area is very large a considerable amount of small particles forming large active area are available. However, the effect of increase in specific surface area beyond 6000  $\text{cm}^2/\text{g}$  is reported to be insignificant (Joshi & Marsh, 1986). Table 9 presents the specific surface area of the fly ashes measured with the Mastersizer 2000 Ver. 5.60. This method, however, does not account the surface associated with the shape of the particles. According to this method the specific surface area of Twence fly ashes is much smaller compared to the reference or HVC fly ashes.

Table 9: Specific surface area (SSA) of fly ashes

Bio-power plant	HVC cyclone fly ash (A1) [ $\text{cm}^2/\text{g}$ ]	HVC filter fly ash (A2) [ $\text{cm}^2/\text{g}$ ]	Twence boiler fly ash (B1) [ $\text{cm}^2/\text{g}$ ]	Twence cyclone fly ash (B2) [ $\text{cm}^2/\text{g}$ ]	PKVA SMZ (R) [ $\text{cm}^2/\text{g}$ ]
Specific surface area	1160	2690	382	559	2090

#### 4.4.5 Moisture content

It is important that the ashes consist of less than 3% moisture to prevent caking and packing, especially if fly ashes have self cementitious properties (Joshi & Lohtia, 1997). The water can react with these particles forming hydration products, which can in turn react with the remaining fly ashes. The fly ash is then less cementitious and pozzolanic active when used in concrete mixtures.

### 4.5 Fly ash properties and legislation

Fly ashes from different power plants have variable amounts of each constituent element due to the applied combustion process and fuel type. The fly ash is seen as a waste and should not be hazardous in order to be landfilled and the best option when possible is to utilize it in a building material production.

As described in Paragraph 2.1.2, the fuel used in the bio-energy power plants mainly consists of B-wood and can be composed of many different products (e.g. window frames



made from timber). However, these products all have their own manufacturing process and finishing (e.g. paint or impregnation). This has influence on the quantities of different elements in wood and eventually in fly ash.

The wood is coming from trees growing in different forests. In these forests it grows while accumulating substances from the soil. Some species like alder, birch, poplar or willow can absorb toxic metals like Al, Cd, Cu, Fe, Mn, Mo, Ni en Zn (Port of Antwerp, 2000-2006). This ability can even be used to immobilize toxic metals in ground (termed: Phytoremediation) (Glimmerveen, 1996). The soil can for instance be polluted by the existing groundwater. Far from the forests the groundwater can be polluted by human and natural activities such as industries and cars, volcanoes and mines. The origin of these contaminants can be initiated far back in time.

Thus, it is not obvious if fly ashes from bio-energy combustion are less polluted than fly ashes from coal combustion power plants. In the current chapter the fly ashes are characterized and the legislation providing hazardous limits of contaminant products is described. It is required for landfill or reuse of fly ash to take out the potentially detrimental substances in order to avoid any harmful influence on the environment and the health of the people.

#### 4.5.1 Leaching value

To qualify the fly ash, a leaching test is performed. The leaching values for elements are determined by NEN-5773 using a column test. In this test the liquid flows through the solid sample. The amount of that liquid should be at least two times the volume of the solid sample, but less than ten times. The emission values stated in the Landfill Ban Decree (VROM, 2010) are defined by a relative amount of liquid to solid (L/S) equal to ten. However, this amount is hard to obtain for powder samples. In that case a L/S equal to two can be applied and finally extrapolated to ten (VROM, 2007):

$$E_{\frac{L}{S}=10} = E_{\frac{L}{S}=y} * \frac{1-e^{(-K*10)}}{1-e^{(-K*y)}} \quad (1)$$

Where:

$E_{L/S=10}$ : the cumulative leaching of a building material, soil or sludge at a ratio of liquid and solid (L/S) of ten;

$E_{L/S=y}$ : the cumulative leaching of a building material, soil or sludge with a L/S value equal to y, which is equal or higher than two, but lower or equal to ten;

K: material-dependent constant representing a measure of the rate of leaching. The values are given in Table 10.

Table 10: K-unit per element

Element	K	Element	K-unit
Antimony	0.04	Nickel	0.25
Arsenic	0.01	Selenium	0.16
Barium	0.17	Tin	0.10
Cadmium	0.32	Vanadium	0.04
Chrome	0.25	Zink	0.28
Cobalt	0.13	Bromide	0.51
Copper	0.27	Chloride	0.65
Lead	0.18	Fluoride	0.26
Molybdenum	0.38	Sulphate	0.33

### 4.5.2 Fly ash characteristics

Table 11 presents the maximum and minimum values of elements for different bio-energy power plant fly ashes. These values are obtained with X-ray fluorescence (XRF) and reported according to standard leaching test described in Accreditation Program Building Materials Decree AP04 (Accreditatiecollege Bodembeheer, 2008). The samples for the concentration measurements are collected twice per year at the corresponding power plant. It can be seen that for each plant the concentration of the components is varying. This is because of the different fuel types, the combustion process and the collecting point of each plant, as mentioned in Chapter 2. The content of certain elements in samples is reported in milligrams of element per kilogram of dry matter (mg/kg ds).

Table 11: Elemental composition of different fly ashes, values obtained by XRF

Element (symbol)	HVC cyclone fly ash (A1) [mg/kg ds]	HVC filter fly ash (A2) [mg/kg ds]	Twence boiler fly ash (B1) [mg/kg ds]	Twence cyclone fly ash (B2) [mg/kg ds]
Aluminium (Al)	17000	32000	9900-13000	13000-30000
Antimony (Sb)	110	67	28-49	65-300
Arsenic (As)	94	66	16-34	37-160
Barium (Ba)	160	150	80-770	130-780
Bromide (Br)	420	130	<15-59	15-150
Cadmium (Cd)	22	14	3.6-10	11-28
Calcium (Ca)	270000	140000	40000-96000	67000-190000
Chloride (Cl)	83000	23000	990-5600	5300-27000
Chromium (Cr)	270	240	88-130	130-280
Fluoride (F)	2.1	5	<2-6.8	6.9-100
Potassium (K)	16000	12000	9500-20000	9900-20000
Cobalt (Co)	20	21	13-19	16-23
Copper (Cu)	890	830	210-380	210-620
Mercury (Hg)	3.5	0.81	<0.05-0.09	0.14-2.5
Lead (Pb)	3800	2400	370-1100	970-4200
Magnesium (Mg)	8500	9700	6600-16000	10000-16000
Manganese (Mn)	1300	1200	590-920	1100-2600
Molybdenum (Mo)	11	8.8	4.6-5.8	7.1-13
Sodium (Na)	11000	12000	4100-6300	4500-8100
Nickel (Ni)	37	52	27-42	37-66
Selenium (Se)	4	4	<4-<4	<4-9.4
Silicon (Si)	440	540	410-4600	390-1600
Strontium (Sr)	470	500	180-340	320-740
Sulphate (SO <sub>4</sub> <sup>2-</sup> )	6100	7200	9800-15000	11000-16000
Tin (Sn)	34	45	18-38	33-97
Vanadium (V)	30	39	23-27	39-45
Tungsten (W)	16	29	13-35	29-62
Zinc (Zn)	3000	4600	1100-3300	2700-10000
pH	12.4	12.6	12.6-12.9	12.6-12.8

### 4.5.3 Landfill

The fly ash can be seen as a waste or building product. Both products need to fulfil certain requirements. The Landfill Ban Decree contains requirements that classify waste streams into inert, non-hazardous and hazardous. If the sample does not fulfil these requirements, it cannot be used even for landfill, before it undergoes a certain treatment. The leaching values of the different fly ashes from the bio-power plant compared to the classifying values according to the landfill decree are presented in Table 12. It can be seen that almost all the leached quantities of elements in the fly ash are non-hazardous. Only the chloride, lead and

sulphate contents are far above the limit that they cannot go to landfill before having a pre-treatment to remove unwanted elements. The cleaning process can be chemical treatment, immobilization or with washing techniques, as will be described in Chapter 7.

Table 12: Classification of Inert, Non-hazardous, Hazardous and No-landfill elements in the fly ashes (L/S = 10)

Elements	Inert [mg/Kg ds]	Non-hazardous [mg/Kg ds]	Hazardous [mg/Kg ds]	No-landfill* [mg/Kg ds]	HVC cyclone fly ash (A1) [mg/Kg ds]	HVC filter fly ash (A2) [mg/Kg ds]	Twence boiler fly ash (B1) [mg/Kg ds]	Twence cyclone fly ash (B2) [mg/Kg ds]
<b>(Sb)</b>	<0.06	0.06-0.7	0.7-5	5<	0.33	0.33	0.33	0.33
<b>(As)</b>	<0.5	0.5-2	2-25	25<	0.96	0.96	0.48	0.48
<b>(Ba)</b>	<20	20-100	100-300	300<	16.73	88.88	1.30	2.07
<b>(Cd)</b>	<0.04	0.04-1	1-5	5<	0.04	0.04	0.02	0.02
<b>(Cl<sup>-</sup>)</b>	<800	800-15000	15000-25000	25000<	21000	80000	5764	12628
<b>(Cr)</b>	<0.5	0.5-10	10-70	70<	0.41	0.41	3.27	0.23
<b>(F<sup>-</sup>)</b>	<10	10-150	150-500	500<	9.30	8.09	4.57	17.35
<b>(Cu)</b>	<2	2-50	50-100	100<	0.55	1.7	0.22	0.22
<b>(Hg)</b>	<0.01	0.01-0.2	0.2-2	2<	0.01	0.02	0.00	0.00
<b>(Pb)</b>	<0.5	0.5-10	10-50	50<	0.86	1.52	0.28	30.37
<b>(Mo)</b>	<0.5	0.5-10	10-30	30<	1.18	0.87	3.67	1.84
<b>(Ni)</b>	<0.4	0.4-10	10-40	40<	0.41	0.1	0.23	3.03
<b>(Se)</b>	<0.1	0.1-0.5	0.5-7	7<	0.43	0.21	0.23	1.22
<b>(SO<sub>4</sub><sup>2-</sup>)</b>	<1000	1000-20000	20000-50000	50000<	15000	15000	25915	16545
<b>(Zn)</b>	<4	4-50	50-200	200<	13.84	11	3.94	11.39

\*Materials that fulfil this category first need a pre-treatment before disposed on landfill

#### 4.5.4 Building material

If the fly ash is intended for application in building production it should also fulfil other requirements stated in the Building Material Decree (BMD) (VROM, 2007). This decree divides the building materials into different categories:

- Shaped building materials;
- Non-shaped building materials without insulation-management-control (Dutch: IBC-measures);
- Non-shaped building materials that need IBC-measures, this is an IBC-building material. (This is to prevent leaching into the environment).

To distinguish if a building material belongs in the “shaped” group, the following requirements should be satisfied:

- The smallest element in the material should have a volume of at least 50 cm<sup>3</sup>;
- The material needs to in a solid shape.

In other words, the building materials should consist of large shaped volumes and should not show abrasion (wearing).

The materials that do not fulfil these requirements are automatically referred to the “non-shaped” group. An example is ashes and granulates. If the materials cannot be applied without IBC measures, they belong to the non-shaped IBC building materials.

The requirements of the BMD encompass maximum composition and leaching values. The considered elements are those which are mainly available in building materials and can influence the soil quality.

Fly ash is a non-shaped building material because it is in powder form. When fly ash is applied into concrete blocks it will become a shaped building material. This concrete block will need to fulfil the requirements that are associated with shaped building materials.

In Table 13 the considered fly ashes are compared with the requirements for a non-shaped building material determined for L/S = 2 by BMD (VROM, 2007). The grey colour highlights values that are sufficient for using in a non-shaped building material. The dark grey colour illustrates the elements that are above the limit. All these materials need to undergo treatment to remove the detrimental substances. However, if it is impossible to fulfil all the non-shaped building material requirements it can be used in a shaped building material, part of the elements will then be immobilized and therefore not hazardous substances anymore (Eijk, 2001). In general there are three sorts of materials:

- The ones that fulfil all this requirements and can be used without any treatment;
- The ones that do not fulfil all this requirements and need to be treated;
- The ones that do not fulfil all these requirements but can be put in a shaped building material where the elements will be immobilized and fulfil the requirements for shaped materials.

Table 13: Non-shaped building material requirements compared with the fly ash values (L/S = 2)

Elements	Value (BMD)	A1 (HVC F)	A2 (HVC C)	B1 (TB)	B2 (TC)
(Sb)	0.16	0.17	0.17	0.078	0.1
(As)	0.9	0.48	0.48	0.1	0.73
(Ba)	22	48.21	9.07	0.46	0.01
(Cd)	0.04	0.02	0.02	0.01	0.1
(Cr)	0.63	0.23	0.23	1.4	0.1
(Co)	0.54	0.32	0.32	0.1	0.1
(Cu)	0.9	0.96	0.31	0.1	0.001
(Hg)	0.02	0.01	0.00	0.001	11
(Pb)	2.3	0.83	0.47	0.1	1
(Mo)	1	0.51	0.70	2	1.3
(Ni)	0.44	0.23	0.23	0.1	0.42
(Se)	0.15	0.11	0.23	0.078	0.2
(Sn)	0.4	0.35	0.35	0.2	0.1
(V)	1.8	0.43	0.43	0.1	5.2
(Zn)	4.5	0.99	7.89	1.8	80
(Br <sup>-</sup> )	20	559.59	310.88	0.46	9200
(Cl <sup>-</sup> )	616	108432.54	28823.84	4200	7.6
(F <sup>-</sup> )	55	4.57	5.25	2	8300
(SO <sub>4</sub> <sup>2-</sup> )	1.730	1993.42	2990.13	13000	0.1

#### 4.5.5 Regulation for fly ash

The NEN-EN-450 describes legislations for coal combustion fly ash concerning fly ash properties like particle size distribution and chemical composition. It is stated that the pozzolanic activity of fly ash is determined by the content of  $\text{SiO}_2$  (sand) and  $\text{Al}_2\text{O}_3$  (clay), and that the reactive form of  $\text{SiO}_2$  should be at least 25% (m/m).

Additional requirements are:

- Loss of ignition  $\leq 5\%$  (m/m);
- Chloride content  $\leq 0.10\%$  (m/m) = 1000 (mg/kg);
- Sulphate content  $\leq 3.0\%$  (m/m) = 30000 mg/kg;
- Free calcium oxide  $\leq 1.0\%$  (m/m) = 10000 mg/kg.

Physical requirements are assessed as follows. At first, the maximum sieved residue on the 45 micron sieve is  $\leq 40\%$  (m/m). Secondly, the strength loss by replacing 25% of the cement by fly ash in concrete mixtures should be less than 25% after 28 days and 15% after 90 days.

## 5. Cement

### 5.1 Composition

Cement is used as a binder in concrete. Cement needs to meet requirements that are defined in European standards such as NEN-EN-197-1 and additional standards (NEN-EN-197-4 and NEN-EN-14216).

Raw materials like  $\text{CaCO}_3$  (calcite in the form of limestone),  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  (clay, shale),  $\text{Fe}_2\text{O}_3$  (iron oxide)  $\text{SiO}_2$  (quartz in the form of silica) are used in the production of Portland cement. The raw materials are ground and mixed in certain proportions and burned at 1450 degrees Celsius forming particles known as clinker. After that, the clinker is cooled down and ground to a fine powder. In Figure 17 the process and formation of clinker phases is illustrated. Finally, some gypsum is added to form Portland cement.

The cement industry has its own notation for the common oxides. Table 14 provides a description of the oxides and used notations.

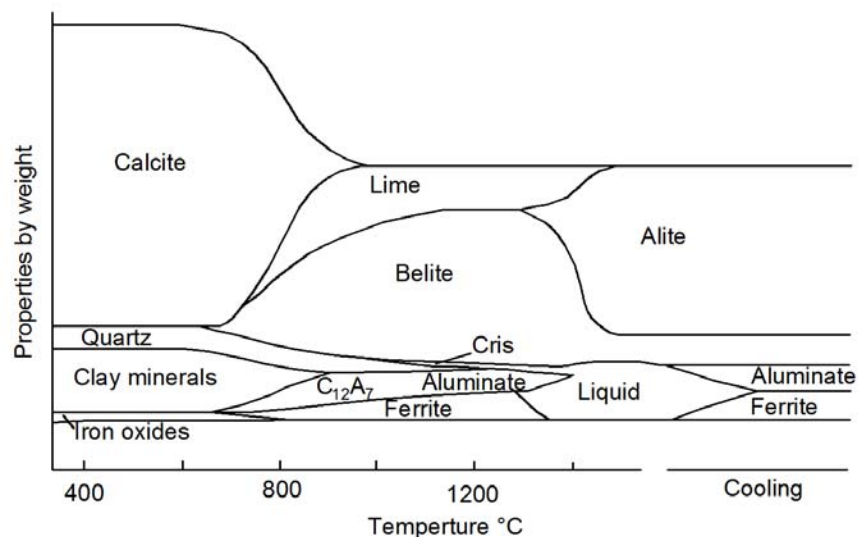


Figure 17: Schematic diagram showing the variations in type contents of phases during the formation of Portland cement clinker (Taylor, 1997)

Table 14: Oxides that are found in Portland cement with cement chemistry notation

Oxide	Symbol
$\text{CaO}$	C
$\text{SiO}_2$	S
$\text{Al}_2\text{O}_3$	A
$\text{Fe}_2\text{O}_3$	F
$\text{SO}_3$	$\bar{S}$
$\text{H}_2\text{O}$	H
$\text{CO}_2$	$\bar{C}$
$\text{MgO}$	M

The oxides interact with each other forming series of more complex compounds. Table 15 describes five mineral compounds that usually are regarded as the major constituents of cement and which undergo hydration.

Table 15: main compounds of Portland cement

Compounds	Actual Formula	Name	Mineral Phase
C <sub>3</sub> S	3 CaO • SiO <sub>2</sub>	Tricalcium silicate	Alite
C <sub>2</sub> S	2 CaO • SiO <sub>2</sub>	Dicalcium silicate	Belite
C <sub>3</sub> A	3 CaO • Al <sub>2</sub> O <sub>3</sub>	Tricalcium aluminate	Celite
C <sub>4</sub> AF	4 CaO • Al <sub>2</sub> O <sub>3</sub> • Fe <sub>2</sub> O <sub>3</sub>	Tetracalcium alumino ferrite	Ferrite
C $\bar{S}$	CaSO <sub>4</sub> (• 2H <sub>2</sub> O)	Calcium sulphate	Gypsum

The potential composition of Portland cement is based on the work of R.H. Bogue and others (Neville, 2004) referred to as ‘Bogue composition’ that describes the percentage of main compounds in cement by:

$$\begin{aligned}
 x_{C_4AF} &= 3.043x_F && (2) \\
 x_{C_3A} &= 2.650x_A - 1.692x_F \\
 x_{C_3S} &= 4.072x_C - (7.600x_S + 6.718x_A + 1.430x_F + 2.852x_{\bar{S}}) \\
 x_{C_2S} &= 2.867x_S - 0.754x_{C_3S} \\
 x_{C\bar{S}} &= 1.701x_{\bar{S}}
 \end{aligned}$$

where C is computed as the total CaO minus the free lime (estimated as 0.7% from ENCI measurements in 2012).

The general composition of the main compounds of cement is illustrated in Table 16.

Table 16: Composition limits of Portland cement (Neville, 2004)

Oxide	Content [%]
CaO	60-67
SiO <sub>2</sub>	17-25
Al <sub>2</sub> O <sub>3</sub>	3-8
Fe <sub>2</sub> O <sub>3</sub>	0.5-6.0
SO <sub>3</sub>	2.0-3.5
MgO	0.5-4.0
Alkalis	0.3-1.2

A summary of the pattern of formation and hydration of cement is given in Figure 18.

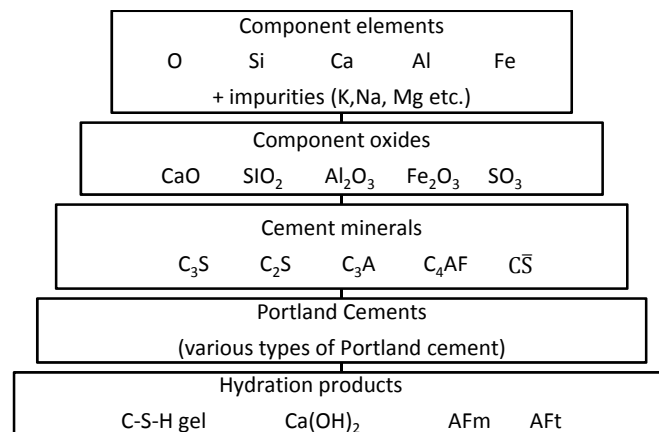


Figure 18: Pattern of formation and hydration of cement (Taylor, 1997)

Chemically, the hydration of Portland cement consists of a series of reactions between individual clinker minerals, calcium sulphate and water, which proceed both

simultaneously and successively at different rates and influence each other. The following factors determine the kinetics of the hydration process:

- The phase composition of the clinker and the type and quantity of foreign ions incorporated in the crystalline lattices of the individual clinker minerals;
- The processing history of the clinker, including the heating rate, maximum burning temperature and cooling rate;
- The quantity and form of calcium sulphate present in the cement;
- The fineness of the cement;
- The technology employed for comminution (process in which solid materials are reduced in size, by crushing, grinding and other processes) of the cement;
- The water/cement ratio of the mix;
- Curing conditions (air or water curing);
- The hydration temperature;
- The presence of chemical admixtures in the mix.

The hydration progress depends on:

- The rate of dissolution of the involved phases;
- The rate of nucleation and crystal growth of the hydrates to be formed;
- The rate of diffusion of water and dissolved ions through the hydrated material already formed.

## 5.2 The hydration products

Hydration occurs in different forms and there is a divergence of opinions between researchers about the chemical equations. This depends on the conditions, cement type, or different analyze techniques, temperatures etc. Furthermore the complete hydration process is not clearly known, a lot of different results are found. Below a short description is given for the main hydration process as in reality much more will happen because of different compositions in the cement compounds and interaction between each other.

Two primary mechanisms occur when hydration happens.

- **Through solution** involves dissolution of anhydrous compounds to their ionic constituents, formation of hydrates in solution, and eventual precipitation due to their low solubility;
- **Topochemical** or solid-state hydration - reactions take place directly at the surface of the anhydrous cement compounds without going into solution.

When water is added to cement, the dissolution of cement grains occurs. This results in a growing ionic concentration in "water" which is now a solution. The ionic concentration forms compounds in the solution and after reaching their saturation point, compounds precipitate out as hydration products (solids).

To describe the hydration of silicates and aluminates a review of Brouwers (2005) is used, which compared 60 types of cement to create a general model presented in Table 17.

Table 17: Main hydration products of cement at 100% RH

Name	Equation	Main hydration product
Tricalcium silicate	$C_3S + 4.5H \rightarrow C_{1.7}SH_{3.2} + 1.3CH$	C-S-H gel, CH
Dicalcium silicate	$C_2S + 3.5H \rightarrow C_{1.7}SH_{3.2} + 0.3CH$	C-S-H gel, CH
Tricalcium aluminate	$C_3A + C\bar{S} + 14H \rightarrow C_4A\bar{S}H_{14}$	SO <sub>4</sub> -AFm
Tricalcium aluminate	$C_3A + CH + 21H \rightarrow C_4AH_{22}$	Hydroxi-AFm
Tricalcium aluminate	$C_3A + 3C\bar{S} + 36H \rightarrow C_6A\bar{S}_3H_{36}$	AFt (Ettringite)
Tetracalcium aluminoferrite	$C_4AF + 2C_3S + 22H \rightarrow C_6AFS_2H_{18} + 4CH$	C-A-F-S-H hydrogarnet, CH
Tetracalcium aluminoferrite	$C_4AF + 2C_2S + 20H \rightarrow C_6AFS_2H_{18} + 2CH$	C-A-F-S-H hydrogarnet, CH



In this model, the probability of C-A-F-S-H hydrogarnet and CH formation is included, formed from the reaction between ferrite phases and calcium silicates. This because ferrite has been found in hydrogarnets and the resulting calculated products could be formed by the hydration of Tetracalcium alumina ferrite and calcium silicates in cement, which is according to the author more likely than the reaction of  $C_4AF$  with water and/or  $C\bar{S}$ .

### 5.2.1 *Tricalcium silicate*

Over 60% by mass of most cements comprises the tricalcium silicate ( $C_3S$ ). This mineral is the most important one as it controls the setting and hardening of cement. In combination with water,  $C_3S$  hydrates into two hydration products, Calcium Silicate Hydroxide (C-S-H) and calcium hydroxide (known as CH or  $Ca(OH)_2$ ). During the hydration, CH forms with water calcium and hydroxide. During the acceleration period see also Paragraph 5.1.2,  $Ca(OH)_2$  concentration in the liquid phase attains a maximum, at this time it begins to decline, crystalline calcium hydroxide starts to precipitate as described by:



The hydration of  $C_3S$  can be accelerated by the addition of anhydrite, gypsum or fine inert calcium carbonate.

### 5.2.2 *Dicalcium silicate*

Over 20% by mass of most cements comprises dicalcium silicate ( $C_2S$ ). The hydration of dicalcium silicate is associated (same as tricalcium) with the release of calcium and silicate ions into the liquid phase (water) and is similar to that of  $C_3S$  even though the whole process progresses more slowly. However, (for example) the hydration amount is significant lower than that of  $C_3S$  with the same degree of hydration.

### 5.2.3 *Tricalcium aluminate*

The other 10% of hydration products are aluminates (coming from  $C_3A$ ) in the form of main products of hydroxy-AFm, monosulfo-aluminate and ettringite. Despite their little amount these products are crucial for cement because the reactions with them are affecting the hydration of the calcium silicates phases. Comparing to  $C_3S$ , the hydration of  $C_3A$  is very fast. However, a very rapid hydration of  $C_3A$  prevents cement to develop sufficient strength. Therefore gypsum in the form of calcium sulphate dihydrate ( $CaSO_4 \cdot 2H_2O$ ) is added to slow down the hydration speed of  $C_3A$ .

There are two main hydration product types generated by the reaction of  $C_3A$  with water in the presence of calcium sulphates, AFm and AFt described in equation four.



The most commonly considered AFm compound is monosulfate,  $C_4A\bar{S}H_{14}$ . The AFt phase is represented by ettringite,  $C_6A\bar{S}_3H_{36}$ . Ettringite crystallizes in the form of well-developed prismatic or acicular crystals. Monosulfate crystallizes in the form of thin hexagonal plates.

### 5.2.4 *Tetracalcium aluminoferrite*

The remaining 10% of the composition of CEM I is  $C_4AF$ . The reactivity of the ferrite phase may vary in a wide range and depend on the Al/Fe ratio. As soon as there is insufficient amount of gypsum to convert all of the  $C_4AF$  to ettringite, silicate hydration is slowed down. The reaction mechanism of the ferrite phase implies that in the presence of ferrite less C-S-H and more CH are formed than without ferrite (Brouwers, 2005). Through the hydration of  $C_4AF$  a hydrogarnet will be formed, as explained in Paragraph 5.2.

## 5.3 Hydration process (Barron, 2010)

The hydration of Portland cement materials is exothermic. This variation of hydration heat can be monitored using a calorimeter, which helps to visualize the heat evolution curve. This curve can be divided in four different stages presented in Figure 19.

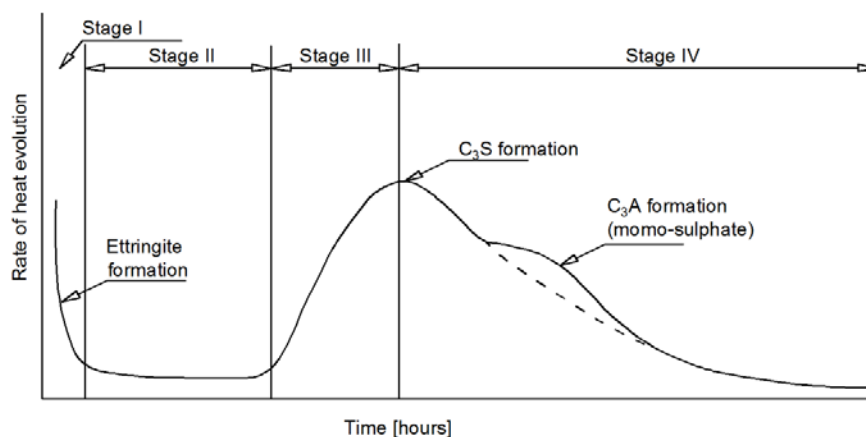


Figure 19: Rate of heat evolution (Mindess & Young, 1981)

### 1. "Pre-induction period" (lasting a few minutes)

Immediately when cement gets in contact with water, a rapid dissolution of ionic species into the liquid phase and the formation of hydrate phases starts. Alkali sulphates present in the cement dissolve completely within seconds, contributing  $K^+$ ,  $Na^+$  and  $SO_4^{2-}$  ions. Calcium sulphates (gypsum) dissolves until saturation, contributing  $Ca^{2+}$  and additional  $SO_4^{2-}$  ions.  $C_3S$  dissolves and a layer of C-S-H phase precipitates on the cement particle surface which eventually slows down the hydration of  $C_3S$  and  $C_2S$ . As the C/S ratio of the produced hydrate is lower than that of  $C_3S$ , the formation of C-S-H phase is associated with an increase of the  $Ca^{2+}$  and  $OH^-$  concentration in the liquid phase. At the same time, silicate ions enter also the liquid phase, although their concentration remains very low. The fraction of  $C_3S$  hydrated in the pre-induction period remains low (2 to 10 %).  $C_3A$  dissolves and reacts with  $Ca^{2+}$  and  $SO_4^{2-}$  ions present in the liquid phase (mostly from gypsum), yielding ettringite (AFt) that also precipitates on the cement particle surface and eventually slows down the hydration of  $C_3S$  and  $C_2S$ .  $C_3A$  hydrates in the pre-induction period around 5-25 %. The concentration of  $Al^{3+}$  in the liquid phase remains very low.  $C_2S$  reacts in the pre-induction period, yielding a C-S-H phase and contributing to the  $Ca^{2+}$  and  $OH^-$  concentration in the liquid phase.

The early fast hydration reaction appears to be slowed down due to the deposition of a layer of hydration products at the cement grain surface. In this way a barrier is formed between the non-hydrated material and the bulk solution, causing a rise in the concentration of dissolved ions in the liquid phase in immediate contact with the non-

hydrated material to values approaching the theoretical solubility of the anhydrous compound. The main products in this stage are ettringite and CH (Hewlett, 2004).

2. “Induction period” (or Dormant stage)

After a short period of fast hydration, the overall hydration rate slows down for a period of a few hours. In this period the hydration of all clinker minerals progress very slowly. Different authors describe different theories about the induction period. Taylor (1997) describes the following theories: “Impermeable hydrate layer theory”, “Electric double layer theory”, “Nucleation of  $\text{Ca}(\text{OH})_2$  theory”, “and Nucleation of C-S-H theory”. In general the “Impermeable hydrate layer theory” assumes the creation of a barrier layer that prevents the reaction of non reacted cement because of the prevention of water penetration to the inorganic oxide in the cement grains. In the end of the Dormant stage, cracks are formed and dissolution of the layer ensures that hydration accelerates. This theory of barrier layer formation is worldwide excepted (Taylor, 1997).

3. “Acceleration period”

In this period the progress of hydration accelerates again and is controlled by the nucleation and growth of the resultant hydration products. The rate of  $\text{C}_3\text{S}$  hydration accelerates and the 'second-stage C-S-H' starts to be formed. A noticeable hydration of  $\text{C}_2\text{S}$  starts. Because of the calcium hydroxide in the liquid phase, the concentration of  $\text{Ca}^{2+}$  in the liquid phase gradually declines. The calcium sulphate becomes completely dissolved and the concentration of  $\text{SO}_4^{2-}$  in the liquid phase starts to decline, due to the formation of the AFt phase. In this period 30% of the cement is hydrated forming CH and C-S-H due to  $\text{C}_3\text{S}$  which is largely available in cement.

4. “Deceleration period” (Post-acceleration)

In this period the hydration rate slows down gradually by the slow penetration of  $\text{H}^+$  through the C-S-H to the anhydrous  $\text{CaO}$  and  $\text{SiO}_2$  and the penetration of  $\text{Ca}^{2+}$  and  $(\text{SiO}_4)^{4-}$  to the  $\text{OH}^-$  ions left in the solution, as the amount of still non-reacted material declines and the rate of the hydration process becomes diffusion-controlled. During this final stage hydration slowly continues, hardening the cement paste. The contribution of  $\text{C}_2\text{S}$  to this process increases with time and, as a consequence, the rate at which additional calcium hydroxide are formed declines. After the supply of calcium sulphate becomes exhausted, the  $\text{SO}_4^{2-}$  concentration in the liquid phase declines. As a consequence, the AFt phase that has been formed in the earlier stages of hydration starts to react in a through-solution reaction with additional  $\text{C}_3\text{A}$ , yielding monosulfate. At sufficiently high initial water/cement ratios the hydration process progresses until all of the original cement becomes consumed. However, the residue of larger cement particles may persist even in mature pastes. At low water/cement ratios the reaction may stop in the presence of significant amounts of non-reacted material, due to the lack of sufficient amounts of water needed for the hydration process.

## 5.4 Hydration products during time

The formed hydration products from the time zero until 90 days is presented in Figure 20, in the first minutes, ettringite is created by  $\text{C}_3\text{A}$  dissolving in the liquid and reacts with  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions present in the liquid phase which are produced by  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  hydration. At the same time CH products are formed by the  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  hydration.

After a few hours the formation of the C-S-H phase follows the hydration of alite and belite. After a fast initial formation of small amounts associated with the hydration of  $C_3S$  in the pre-induction period, the amount of C-S-H increases only slowly in the induction period.

From a few hours to one day, the formation of hydration products accelerates. The formation of ettringite by  $C_3A$  in the presence of calcium sulphate  $CaSO_4$  slows down because of the consumption of  $CaSO_4$ . Because of this,  $C_3A$  will react with ettringite resulting in monosulfate. While monosulfate formation is increased, the ettringite content declines.

Though the whole process the porosity (empty spaces) is decreasing because the hydration products are filling the voids in the concrete.

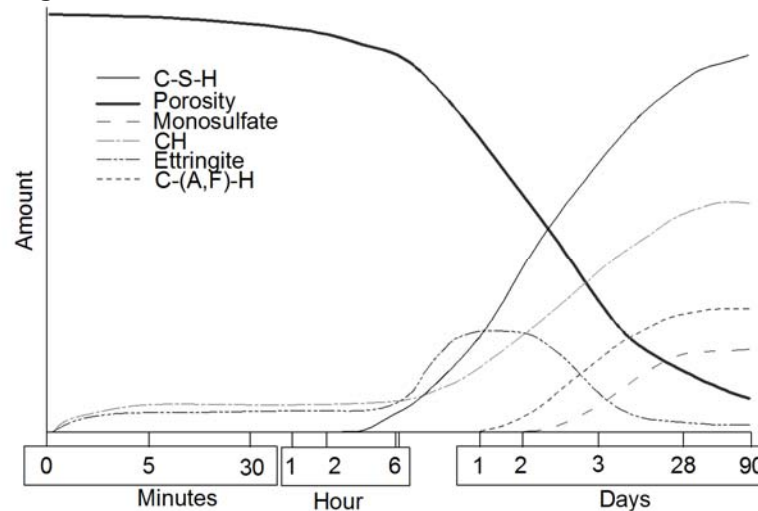


Figure 20: Introduces different hydration products in time where  $C_4AF$  and  $C_3A$  are the first hydration products and almost completely hydrate during time (Kurtis, 2011)

Typical hydration kinetics of pure clinker minerals ( $C_3A$  without and with added gypsum) hydration at ambient temperature are illustrated in Figure 21. During the first hours the “early age” strength development is caused by  $C_3S$ . Due to its slow reaction,  $C_2S$  contributes to the ‘long term’ strength development of cement.

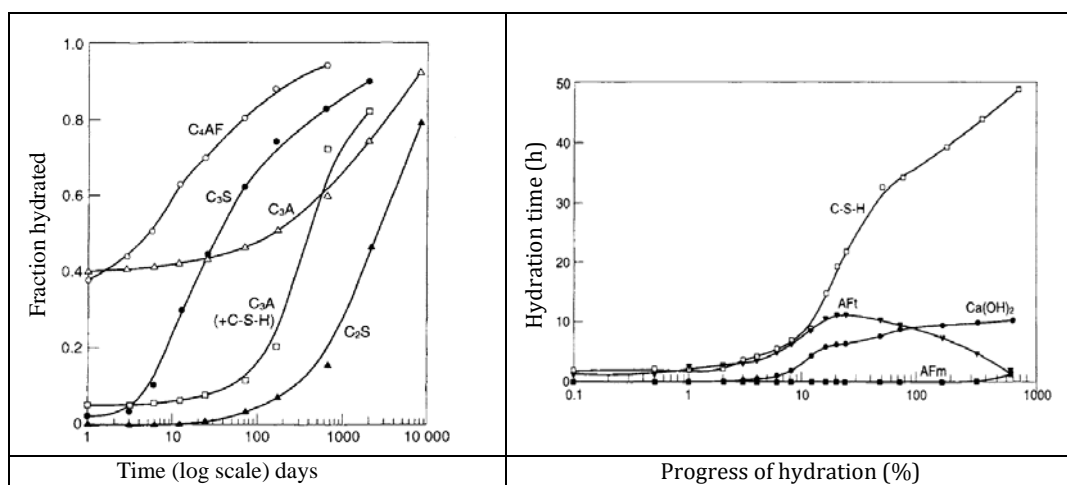


Figure 21: Typical hydration kinetics of pure clinker minerals (Hewlett, 2004)

## 6. Hydration of Portland cement with Fly ash

The pozzolanic activity of fly ash is due to the silicate and aluminate phases of fly ash in combination with the  $\text{Ca(OH)}_2$  that is formed during cement hydration which together produce calcium silicates and aluminate hydrates ( $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$  and  $\text{C}_3\text{A}$ ) (Hewlett, 2004). However, the hydration and pozzolanic reactions do not occur independently. Water, soluble alkalis, sulphates, calcium and organics from the fly ash may affect the surface reactions and the nucleation and crystallization processes, especially in the early stages of cement hydration. Similarly, the pozzolanic reactions will depend on the amount of calcium, alkalis, sulphates, silicates and aluminates released into the liquid phase from cement and fly ash.

Different authors describe various influences of fly ash in combination with Portland cement (PC). This can vary up to:

- Retarding influence (Diamond, 1981);
- Acceleration of hydration of PC (Costa & Massazza, 1983).

This difference is mostly due to the different chemical and physical properties of the used fly ash in the research. Also the hydration of  $\text{C}_3\text{S}$  is can be delayed due to changes in ionic composition, which affects the dissolution of  $\text{C}_3\text{S}$ . If for example more gypsum is present, more  $\text{Ca}^{2+}$  is present in the liquid phase; this can also be happening with fly ash producing  $\text{Ca}^{2+}$ : eventually less  $\text{C}_3\text{S}$  hydrates because there is no need for  $\text{Ca}^{2+}$ . If all the  $\text{Ca}^{2+}$  reacts with  $\text{C}_3\text{A}$  and also gets absorbed by the fly ash particles, the speed of  $\text{C}_3\text{S}$  hydration will increase. It may be clear that it is not sure which ionic change will occur. Below are some conclusions described by different authors. It can be stated that there is more known and explained about the positive reactions than about negative reactions which, also occur but are hardly understood.

### 6.1 Tricalcium silicate and fly ash

It is found that  $\text{C}_3\text{S}$  reacts faster with fly ash than without in both Pre-induction period and Acceleration period (Takemoto & Uchikawa, 1980; Costa & Masazza, 1981);. After 24 hours  $\text{C}_3\text{S}$  is hydrated for 55% in the presence of fly ash compared to 38% pure  $\text{C}_3\text{S}$ . This is due to the fly ash particles that can absorb  $\text{Ca}^{+2}$  and provide additional surface on which C-S-H gel can precipitate. In consequence, the dissolution of  $\text{C}_3\text{S}$  because of increasing provision of  $\text{Ca}^{+2}$  to the liquid and less C-S-H gel formation near  $\text{C}_3\text{S}$  because otherwise it would disturb the water penetration and therefore the hydration of  $\text{C}_3\text{S}$ .

Fly ash was also found to accelerate the polymerization of hydrated silicates; about 60 % of Si in the C-S-H of  $\text{C}_3\text{S}$  fly ash paste was present as polymers compared with 40 % for pure  $\text{C}_3\text{S}$  paste (Wesche, 1991). When 4% gypsum is added, the hydration speed decreases at early ages but increases at later ages. This is due to the increasing provision of  $\text{Ca}^{+2}$  and therefore  $\text{C}_3\text{S}$  reacting less, but when fly ash is also reacting (absorbing  $\text{Ca}^{+2}$ ) the  $\text{Ca}^{+2}$  content reduces and  $\text{C}_3\text{S}$  reacts faster. If the amount of added gypsum is increased (8%) the hydration decreases in all stages because a large amount of  $\text{Ca}^{+2}$  is present in the liquid phase.

Fly ash in combination with PC also has an influence on the  $C_3S$  and  $C_2S$  hydration ratio. After 18 months  $C_3S$  is fully hydrated in the  $C_3S$ -fly ash mix, compared to the partly hydrated in pure  $C_3S$  paste. The opposite happened for  $C_2S$  hydration products.

It is also found that the hydration heat curve of  $C_3S$  in combination with fly ash is changed. The heat hydration peaks are retarded and are less high. This could be due to the delay of nucleation and hydration of  $Ca(OH)_2$  and C-S-H by the soluble aluminate species released from fly ash (Wesche, 1991). A significant delay of more than 12 hours in the maximum heat evolution peak in the presence of fly ash was also found by Ogawa et al. (1980). Fly ash decreases the  $Ca^{+2}$  and silicate concentrations in the liquid phase of hydrating  $C_3S$ -fly-ash significantly (20 and 50%, respectively).

Fly ash is expected to affect the composition of C-S-H produced in the hydration system. Small amounts of AFt and AFm phases were found at 7-28 days and within 3 months all the Fe, Al and  $SO_4^{2-}$  supplied by the fly ash were incorporated in the C-S-H gel.

The pozzolanic reaction of fly ash however starts later. The glass phase particles need to be cracked but this depends on the amount of alkali (pH-value) in the concrete mix, which is depending on the amount of  $OH^-$  ions present in the liquid. The layer of  $Ca^{+2}$  and C-S-H gel around the fly ash prevent reaction of fly ash particles. In a later stage when the pore water has a lower  $Ca^{+2}$  content (because it was consumed for production of ettringite) and the pH value is higher (resulting in dissolution of the glass phase), less C-S-H is created around fly ash particles because the formation of hydration products is more near the cement grain. Fly ash can therefore start reacting and consuming CH. Also more hydration products are created, resulting in an increasing temperature; a higher temperature will increase the reaction of fly ash.

It appears that the CH content is increased when fly ash and PC are combined. This is due to the acceleration of the hydration of  $C_3S$ . After the pozzolanic reaction of fly ash starts, it gradually consumes CH and this decreases the CH content (Taylor et al., 1985).

## 6.2 Dicalcium silicate and fly ash

For the  $C_2S$  hydration product, different opinions are formulated. It is found that the  $C_2S$  can have two acceleration periods, around four and 30 days. It is also found that it has no effect on the hydration until 28 days. However, Sakai et al. (2005) found that the  $C_2S$  hydration is accelerated up to 91 days and after that retarded. This is due to the formation of dense hydration products on the surface of  $C_2S$ .

## 6.3 Effect Fly ash on the hydration of $C_3A$ and $C_4AF$

Fly ash is a more effective retarder of  $C_3A$  and  $C_4AF$  hydration compared to the same amount of gypsum.  $SO_4^{2-}$  and  $Ca^{+2}$  dissolved from fly ash may partly explain the retarding effect of fly ash. Analyzing the liquid phase of the hydrating system showed that saturation in terms of gypsum occurred with a few seconds of water being added to fly ash.

The interaction of fly ash with  $C_3A$  probably involves the following process (Wesche, 1991):

- Adsorption of sulphate ions, which reduces its active dissolution sites;
- Formation of ettringite at an early age, which reduces available migration of sulphates;
- Migration of sulphate ions and stabilization of hexagonal structures.

Pozzolanic materials including fly ash accelerate not only the formation of ettringite and its conversion to monosulfoaluminate, but also the hydration of  $C_3A$  in the presence of gypsum. Higher amounts of alkalis in the pozzolanic materials promoted the formation of cubic hydrates. The formation of ettringite and its conversion to monosulfoaluminate were retarded by  $Ca(OH)_2$ . Fly ash increased the dissolution of CH and hence the hydration of  $C_3A$  by providing surface for ettringite precipitation and  $Ca^{2+}$  absorption (Uchikawa et al., 1985).

## 6.4 Effect of fly ash on cement hydration

Lukas (1976) found that fly ash in combination with PC increases the formation of  $Ca(OH)_2$  in pastes up to three days of hydration and attributed it to the accelerated hydration of  $C_3S$  in cement. The  $Ca(OH)_2$  content decreases with time, indicating that it had been used for the pozzolanic reaction of fly ash. It was found that the degree of hydration of  $C_3S$  in a cement-fly ash paste was higher than in pure cement pastes from one day onwards. Also, Ghose & Pratt (1981) reported a retardation of both  $C_3A$  and  $C_3S$  heat evolution peak maxima for cement fly ash pastes.

By adding fly ash into the mixture, the amount of hydration products in the concrete is increasing as well as the concrete strength. However, that can only occur after cement starts to hydrate because of the need of  $Ca(OH)_2$ . Therefore, in the case of fly ash usage as a partial replacement for cement, the early strength is reduced but the long term strength may be equal to the one of plain cement, or even be higher. The rate of strength gain, however, depends upon the properties of fly ash and cement, mix properties, as well as the curing conditions of the fly ash concrete (Joshi, 1979)

### 6.4.1 C-S-H content

In a combination of PC with fly ash, C-S-H is produced by the hydration of PC and the pozzolanic reaction of fly ash with CH. Both C-S-H are different due to different reaction mechanisms (Killoh et al., 1989). The Ca/Si ratio for C-S-H in fly ash cement paste is expected to differ from that in cement paste, since C-S-H is also formed by the reaction of  $Ca(OH)_2$  with aluminosilicate phase of the fly ash. The decrease of Ca/Si ratio (which is not always a negative effect) of the inner hydrate can be attributed to an increase in the Si content. It is found that the Ca/Si ratio of C-S-H is lower near the pozzolan grains of fly ash as compared to the C-S-H near to  $C_3S$  (Ogawa et al., 1980).

Normally at early ages, the range of Ca/Si ratio is typically 1.2-2.3 for OPC pastes. At later ages it ranges around 1.60-1.85. C-S-H may be formed with Ca/Si ratios varying from 0.8 to about 1.75 in CEM I pastes (Taylor, 1997). This author also describes that some studies have indicated minimum Ca/Si ratios of 0.6-0.7. According to several authors the Ca/Si ratio of C-S-H close to fly ash particles is lower compared to ordinary PC mix. (Rayment, 1982; Taylor et al., 1985; Uchikawa, 1986). A lower Ca/Si ratio gives a more stable C-S-H gel which is a positive effect. The greater proportion of C-S-H gel in the hydrated fly-ash cement results in low permeability, which together with the reduction in the  $Ca(OH)_2$  content offers an explanation for the improved resistance to chemical attack, particularly by sulphates, observed for fly ash opposed to plain cement concrete. However, because of all this it is also possible that C-S-H gel can develop less because of low void space, resulting in a decrease of water penetration to the cement grain, which eventually reduces the strength of concrete.

## 7. Effects of contaminants on cement hydration

The use of bio-energy fly ash in concrete mixtures can not only have positive effects as described in Chapter 6 and other previous chapters, but some elements can also create structural damage. To minimize these negative effects the regulation of coal-combustion fly ash (NEN-EN-450) has been developed. In this chapter the importance and reasons are described for some of the regulations. The regulations are described in Paragraph 4.5.5 and consider: loss of ignition, chloride content, sulphate content and free calcium oxide content.

### 7.1 Carbon content/loss on ignition test

Loss on ignition (LOI) is defined as the mass loss that takes place when heating up materials to a temperature of 950 degrees Celsius according to NEN EN-196-2. In the first phase, water is evaporated, organic matter is combusted to ash and carbon dioxide at a temperature between 500 and 550 degrees Celsius. This LOI can be calculated using:

$$LOI_{550} = ((DW_{105} - DW_{550}) / DW_{105}) * 100 \quad (5)$$

where  $LOI_{550}$  represents LOI at 550 degrees Celsius (as a percentage),  $DW_{105}$  represents the dry weight of the sample after drying (usually 12–24 h at ca. 105 degrees Celsius) and before combustion, and  $DW_{550}$  is the dry weight of the sample after heating to 550 degrees Celsius (both in g). In a second phase, carbon dioxide is evolved from carbonate, leaving calcium oxide and LOI is calculated as:

$$LOI_{950} = ((DW_{550} - DW_{950}) / DW_{105}) * 100 \quad (6)$$

where  $LOI_{950}$  is the LOI at 950 degrees Celsius (as a percentage),  $DW_{950}$  represents the dry weight of the sample after heating to 950 degrees Celsius (Heiri et al., 2001). To calculate the LOI for fly ash the total mass loss of the dry weight up to 950 degrees Celsius needs to be considered.

Because the LOI has a high relation with the carbon content of bio-energy fly ash, a low LOI practically in most cases means low carbon content. A low carbon content of bio-energy fly ash is important because high carbon contents may lead to the following negative effects (van den Berg, 2006):

- Coarse coal particles can form galvanic elements with pre-stressed steel products. As a result, small electric circuits are created, which can cause corrosion of the reinforcement (pitting). Therefore, it is not often used in combination with pre-load and pre-tensioned steel. For that reason, high carbon fly ash can only be used in combination with CEM I, because it consists of less/no coal particles, while in CEM II a part of the clinker is replaced by fly ash or blast furnace slag that contain coal particles, 60% of which are smaller than 45 microns. In addition there is a requirement that the amount of fly ash particles larger than 212 microns should be less or equal to 3% (m/m) (NEN-EN-5950);
- The absorption of the cellulating agent by the carbon particles can prevent the formation of air bubbles, which can decrease the resistance of concrete to frost and de-icing salts and have an effect on the durability of concrete,
- Carbon acts as filler of the active pozzolanic matter in the fly ash, which is not desirable;



- Carbon particles absorb water and thus reduce the available water for the cement to hydrate.

## 7.2 Chloride content

Chlorides, especially  $\text{CaCl}_2$  were added in the past to concrete to increase the hydration rate. Later a negative effect was found-the corrosion of steel reinforcement. Chlorides reduce the durability of reinforced concrete. Steel reinforcement in concrete is protected against corrosion by the “passive layer” on the steel surface. This passive layer is created due to oxidation of the steel combined with a high alkaline environment. However, when a sufficient amount of chlorides reaches the steel reinforcement, corrosion starts reducing the quality and function of the steel reinforcement.

The bio-energy fly ashes contain large amounts of chlorides which makes it unsuitable to use in reinforced concrete. Most chlorides however are soluble and can be removed using water treatments. This approach will be further discussed in Chapter 8.

Chloride is formed from chlorine (halogen). When chlorine (Cl) gains an electron it forms an anion chloride ( $\text{Cl}^-$ ). From different studies including a complete review of Yudovich & Ketris (2005) it is known that coal ash can contain large amounts (more than 1000 ppm) of Cl-containing phases. The species of Cl occurring in coal ash are surprisingly varied. Among them are found:

- **Inorganic** saltlike NaCl and other chlorides, Cl-bearing silicates, carbonates, sulfides, as well as dissolved chlorides in pore moisture;
- **Organic**-associated Cl seems to predominate in coal. It may consist of two types. Firstly, (minor site (“true”  $\text{Cl}_{\text{org}}$ ) water-insoluble Cl-organic compounds, where Cl is covalent bonded with coal organic matter (Hodges et al., 1983; Saunders, 1980). Secondly, “semi-organic”Cl, as anion  $\text{Cl}^-$ , which is partly or fully water-soluble Cl that is sorbed on the pore surface of coal organic matter. Such form does not enter the coal organic macromolecule and may be exchangeable (Daybell & Pringle, 1958; Edgcombe, 1956; Gluskoter & Ruch, 1971; Saunders, 1980; Caswell et al., 1984; Pearce & Hill, 1986; Oakey et al., 1991; Huggins & Huffman, 1991; Spears, in press).

Furthermore it needs to be noted that small size coal particles can contain more chlorine than large size coal particles (Yudovich & Ketris, 2005).

All this information from the review of Yudovich & Ketris (2005) indicates that coal particles in fly ashes can contain large amounts of chlorine that can be represented by chlorides. In Chapter 8, further research is done on this phenomena and possible occurring problems when trying to wash out these chlorides.

Looking closer with X-ray diffraction (XRD) provides knowledge about the elemental composition of fly ashes. The analysis are performed using copper radiation with a step size of 0.02 degrees and 1-second count time. Pattern processing was done using EVA software and the ICDD pattern database. To find out which chlorides the fly ashes contain, a sufficient amount of chlorides should be available (content of >5%). For this reason HVC filter fly ash (A1) is used because it contains approximately 9% chlorides.

Figure 22 illustrates the XRD-pattern of original and water treated A1, to see which chlorides are present and if there is a relation with soluble chlorides. It can clearly be seen that the chloride content is mainly consist of KCl but also traces of  $\text{CaCl}_2$  and NaCl are

present. After treating with water, most of the chlorides are dissolved in water. However, the solubility of the Cl-containing phases are different. The solubility in water at ambient temperatures of  $\text{CaCl}_2$  (740 g/l) is much higher than that of  $\text{NaCl}$  (360 g/l) or  $\text{KCl}$  (344 g/l), while the solubility of  $\text{MgCl}_2$  (5.43g/l) is rather low.

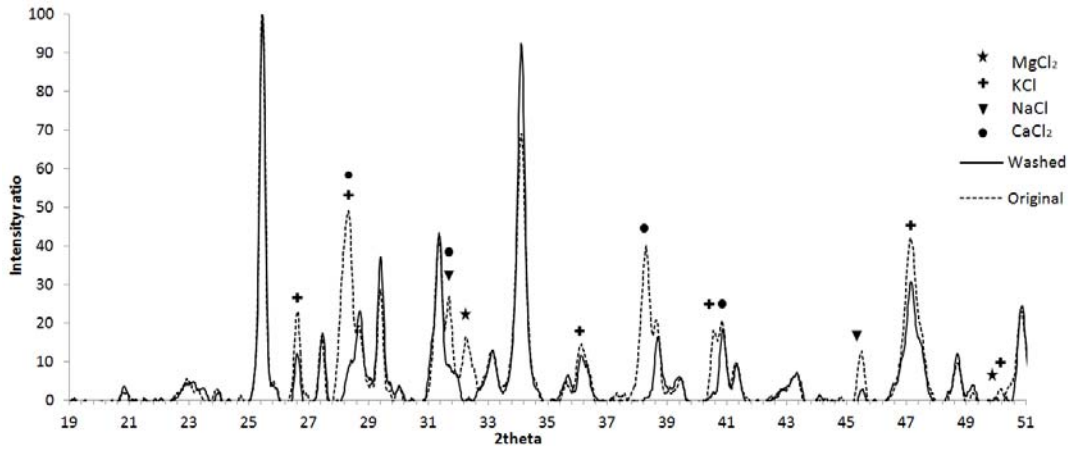


Figure 22: XRD pattern of HVC filter fly ash (A1), indicating different Cl-containing phases

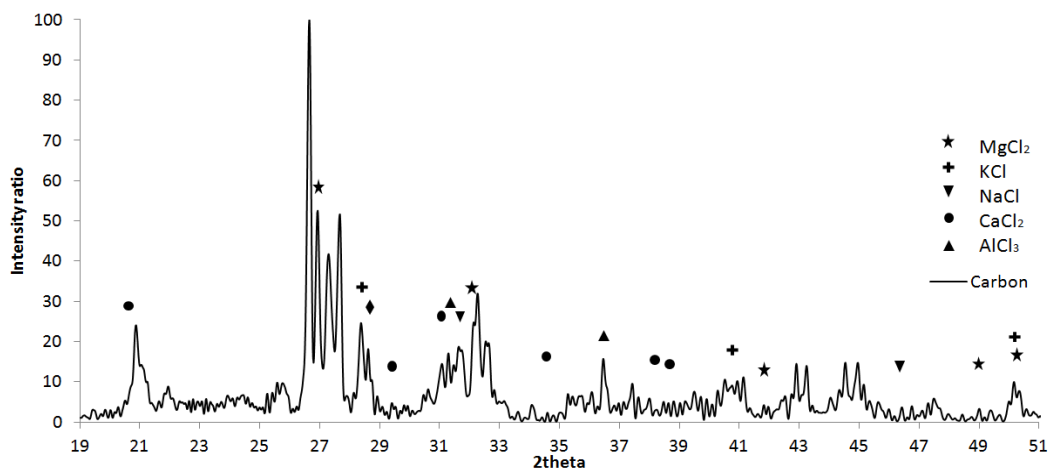


Figure 23: XRD pattern of Carbon from Twence boiler fly ash (B1)

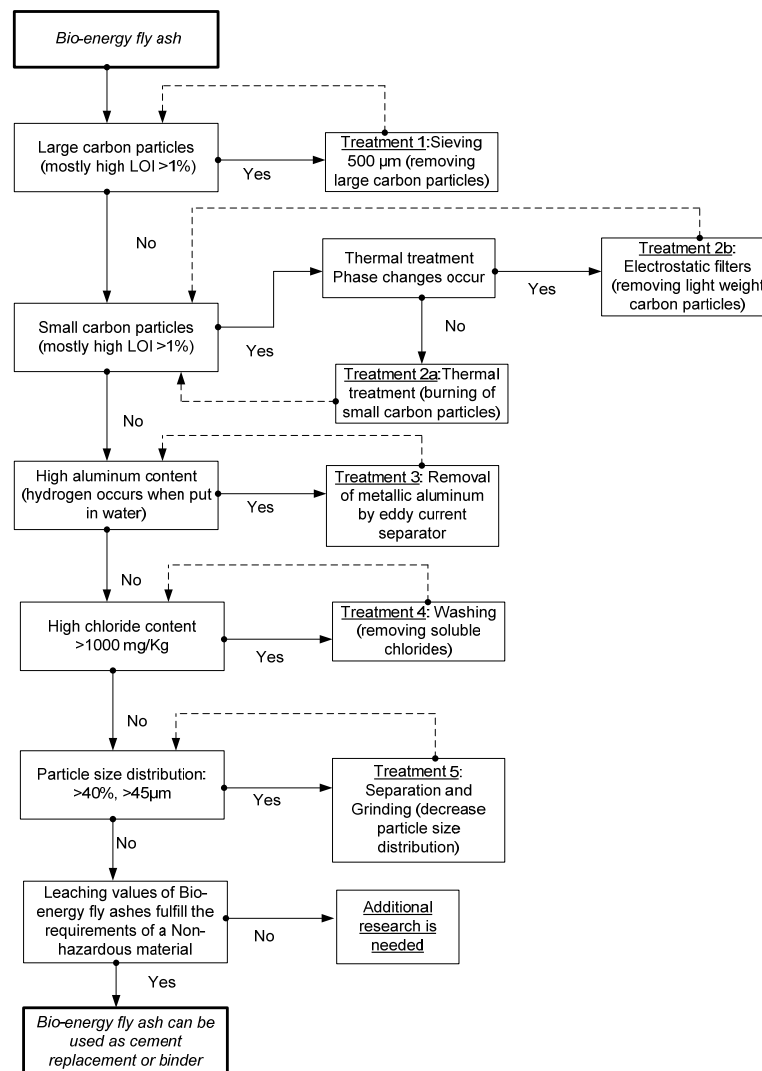
## 8. Treatment of bio-energy fly ash

The treatment of bio-energy fly ashes is divided into five different steps. These include the removal of big and small carbon particles, chlorides, metallic aluminium and fulfilling the requirements like particle size distribution and sulphates according to NEN-EN-450 and making the fly ash Non-hazardous or even Inert (as defined by the Landfill Ban Decree).

The removal of heavy metals will not be tested after these steps. However, after the water treatment almost all leachable metals should be removed. Remaining metals will be enclosed into the cement matrix as described by Eijk (2001). Removal of metallic aluminium will be described because internal swelling occurs increasing the porosity and decreasing strength.

### 8.1 Treatment methods

The treatments steps used in this research depend on the bio-energy fly ash and moreover the compounds which it consist of. In general the following treatment methodology can be used:



First, carbon particles are removed, because of the negative effect on the chloride removal. Secondly, the fly ash is washed using water treatments to reduce the soluble chlorides and aluminium content and in the end grinding can be performed to decrease the PSD and possible increase the reactivity of the bio-energy fly ashes.

### 8.1.1 Sieving

This treatment is needed for bio-energy fly ashes with a high content of carbon. Using a sieve of 500 microns, big carbon particles will be removed. In this way the LOI will be reduced, as well as the chloride content of the fly ash. The relation between removing carbon and chloride is already discussed in Paragraph 7.2.

### 8.1.2 Thermal treatment & Air-filtering

This treatment is needed for bio-energy fly ashes with high content of small carbon particles ( $<40\mu\text{m}$ ). These fly ashes can be recognized because of their black appearance, even after Treatment 1. For this treatment, two options (2a and 2b) are available. Treatment 2a is a thermal treatment. Treatment 2b is a separation by electrostatic filters (both for industrial use). However, in the lab the thermal treatment is performed by using an oven and electrostatic filters are replaced by a shaking device with air suction as presented in Figures 24 and 25. This measure should give similar end results as the above described industrial processes. The choice which method to use depends on whether there are phases present that can change when thermal treatment is used. A phase change can result in crystallisation which negatively affects the pozzolanic reactivity of the fly ashes, and should therefore be avoided. Phase changes are depending on the content of the fly ash, but can as an example consist of: formation of mullite, hematite and crystallisation of melilite or oxidation of magnetite. In general the reduction of the glass phase and increase of crystalline phase occur at temperatures above 700 degrees Celsius, resulting in a decrease of the pozzolanic activity (Fox, 2005)

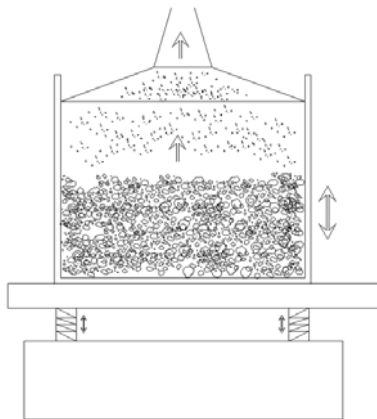


Figure 24: Shaking device with air suction



Figure 25: Heated fly ash in oven at 800°C

If there is a possibility of phase change, Treatment 2a is not an option and Treatment 2b can be applied. Treatment 2b uses a shaking mechanism with air exhaust. By shaking, the light coal particles are lifted up and removed using the air exhaust. When well calibrated, the removal of small light particles that are not coal should be limited. In Chapter 10, the difference between these two methods and the removal of small particles is further discussed.

### 8.1.3 Metallic aluminium removal

This treatment is only required when large amounts of metallic aluminium are present, which in contact with water will form hydrogen according to:



If this happens in the mortars, an increase in volume, resulting in an increase of porosity and decrease of compressive and flexural strength will take place. To remove the unwanted aluminium for industrial purpose, an eddy current separator can be used. In this way a powerful varying magnetic field separates the non-ferrous metals from the rest of the material. For lab use, the fly ash is stirred in water for 72 hours with a liquid to solid ratio of four. Afterwards, the liquid is filtered, flushed and dried according to the steps 2,3,4 which are described in Paragraph 8.1.4.

### 8.1.4 Washing

After this, water treatment is used to remove water soluble compounds mostly chlorides. For this, four steps are performed which are described below:

1. Fly ash in combination with demineralised water is shaken in bottles using a “Stuart reciprocating shaker SSL2” to remove soluble chlorides and metals as illustrated in Figure 25;
2. The water is separated from the fly ash using 15-30 micron filters as illustrated in Figure 26;
3. The remaining fly ash on the filter is flushed with demineralised water to remove remaining water with soluble minerals;
4. The remaining fly ash is dried to remove the available water content as illustrated in Figure 27.

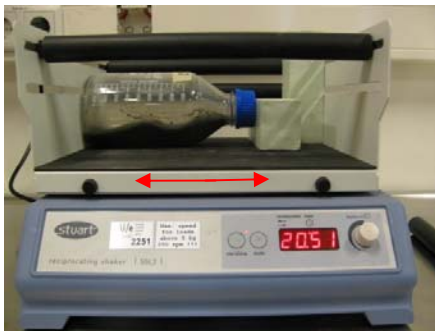


Figure 26: Shaking process



Figure 27: Filtering



Figure 28: Dried fly ash after filtering

The efficiency of the water treatment technique depends on the parameters stated below and will be discussed later.

- Temperature of water
- pH-value of water
- Water/solid ratio;
- Oscillation speed;
- Treatment time;
- Amount of flushing water;
- Filter size.

### 8.1.5 *Seperation/Grinding*

This last is used to create small particles using a ball mill (only for lab use), increasing the reactivity and filler effect of the particles. This results in an increase of pozzolanic activity at early curing ages, creating compacter concrete with a higher density and higher flexural and compressive strength.

## 8.2 Treatment evaluation

### 8.2.1 *Carbon content*

After Treatments 1 and 2 the carbon content can be measured using Thermogravimetric analysis with a NETZSCH STA 449 F1, where the weight loss at different temperatures can be linked to the removal of certain compounds including carbon.

### 8.2.2 *Chloride content in water*

From the washed sample, 3 ml of used water is taken and after filtering, two ml are taken using a "Macro 25ml pipette". The chloride content of the 2 ml together with additional demineralised water is then measured using titration with "Metrohm 785 DMP Titrino" with 0.01 M solution of silver nitrate as presented in Figure 29.



Figure 29: Metrohm 785 DMP Titrino

### 8.2.3 *Chloride content of the solid material*

For measuring the chloride content of solid materials, two grams solid material (bio-energy fly ash), together with 37 ml of demineralised water and 3 ml of nitric acid is combined in a bottle. The mix is then stirred using a magnetic stirrer on a heating plate of 45 degrees Celsius for 15 minutes. Afterwards, the solution is filtered and flushed until a volume of 100 ml is obtained. From this, 2-10 ml, depending on the chloride content, can be measured using Metrohm 785 DMP Titrino with a 0.01 M solution of silver nitrate. The chloride content is given by:

$$C_t = \frac{B_{100} * V * 35.5 * Z_{0.01}}{1000 * G_2 * P_{10}} \quad (12)$$

were  $P_{10}$  is the amount in the pipette in ml (used for determination of the concentration of chloride),  $B_{100}$  is the total volume of the solution (in ml),  $V$  is the titrated silver nitrate solution in ml and  $Z_{0.01}$  the concentration of silver nitrate in moles per liter (M).  $G_2$  is the used solid (bio-energy fly ash) in grams for making the solution and  $C_t$  the chloride concentration in g/g.

## 9. Results

This chapter describes the treatment data together with the effects and obtained final compressive and flexural strengths. During the measurements, assumptions are made, which are then assessed during the measurements. This data provides increased knowledge on how to perform the measurements and explanations of the obtained results. It should be stated that at the beginning most of the data did not meet the expectations. Because of this, the first paragraphs provide information about the measurements and improvements that were made, followed by a second paragraph with obtained data.

### 9.1 Chloride removal (part one)

#### 9.1.1 *Twence boiler fly ash (B1)*

In this first experiment with Twence boiler fly ash (B1), different treatment parameters and their influence on fly ash properties are investigated. In this case the fly ash is shaken for one hour with different temperatures (20 and 60°C), two different shaking speeds (120 and 240 rpm) and two different liquid to solid ratios (L/S = 2, L/S = 4). The chloride is measured by taking three ml water and measuring the chloride content by titration. The results are given in Table 18.

Table 18: Removed chlorides from Twence boiler fly ash with different parameters

Liquid to solid ratio	Original 20°C, 120 rpm [mg/kg]	Increased shaking speed 240 rpm [mg/kg]	Increased temperature 60°C [mg/kg]	Combination 60°C, 240 rpm [mg/kg]
L/S = 2	1957	2575	2091	2867
Percentage improved*	0%	+11.8%	+2.6%	+17.4%
L/S = 4	2043	2320	2320	2702
Percentage improved*	0%	+6.0%	+5.3%	+12.6%

\* This percentage is compared to the original 20 °C, 120 rpm values

The results in Table 18 present a large improvement by increasing the shaking speed compared to the original, especially for a liquid to solid ratio of two. The larger quantity of chlorides which are removable with an L/S = 2 can be explained by different theories. Firstly, because of gravity, particles are more attached to the bottom surface and the water pressure downwards reduces the movement of the particles, the so called “damping effect”. Secondly, when waves are close to the bottom surface, a higher turbulent flow is realized, the “mixing effect”. When the flow is further away from the bottom surface the waves have almost no influence on the particles and reduce the efficiency of dissolving chlorides.

The increase of temperature for L/S = 4 has a bit more advantage than for L/S = 2. It is believed that this is due to the rapid decrease in temperature of L/S = 2 and therefore has a shorter effect. A combination of increased temperature and liquid to solid ratio works well for removing chloride ions, because the positive effects cumulate.

In order to monitor the behaviour of the bio-energy fly ash in time, the chloride content of B1 is measured during one hour with a shaking speed of 120 rpm, extracting every 15 min 3 ml and adding 3 ml demineralised-water to keep the liquid to solid ratio constant. For each step the calculation is corrected for the removed content of chlorides in each three ml. In



order to observe differences between 2 samples, the bottles with a liquid to solid ratio equal to 2 and 4 are measured twice to check reliability (group A and B). Results are presented in figure 30.

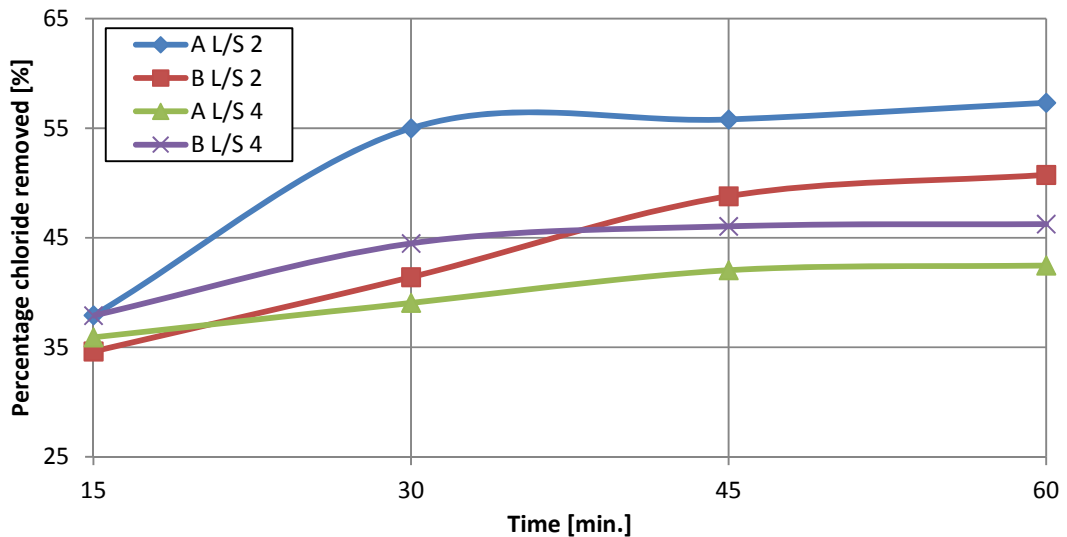


Figure 30: Chlorides removed from Twence boiler fly ash (B1) during 60 minutes with different L/S ratios

From Figure 30 it can be concluded that in time more chlorides are removed. However, the measurements are hardly repeatable. To evaluate the reliability of the previous results, a second test is performed. In this case, five bottles of Twence boiler fly ash (B1) are washed (TBw). The used fly ash is coming from the same bucket of 15 kg. From this bucket five samples of 100 grams are taken while mixing. The 100 gram is then put into bottles (A-E) which are shaken for one hour at a speed of 120 rpm and with L/S = 4 to test the repeatability. Furthermore, the chloride content in the used distilled water is measured three times to see if there is a large variability. The results are presented in Table 19.

Table 19: Investigation of five the same Twence boiler fly ash samples (A-E), to determine the chloride removal

L/S	Sample TBw (A) [mg/kg]	Sample TBw (B) [mg/kg]	Sample TBw (C) [mg/kg]	Sample TBw (D) [mg/kg]	Sample TBw (E) [mg/kg]
4	1980-1993	2153-2172	1997-2026	1852-1905	2149-2200
<b>Reduction*</b>	37.9-38.1%	41.2-41.6%	38.2-38.8%	35.4-36.5%	41.1-42.1%

\* Percentage removed is calculated from the original 5226 mg/kg

The results in Table 18 show that in every sample there is a deviation of results. Sample D is the worst case with a variation of 1.1%, the lowest difference is sample A with a variation of 0.3%. Comparing the samples and taking the lowest value of sample D and the highest value of sample E results in the worst case scenario with difference between the samples of 6.7%.

In order to investigate the quantity of chloride which is removed from Twence boiler fly ash by distilled water, the chloride content of solid Twence boiler fly ash (TBs) is determined. This is done for two pairs of measurements. The first one is a pure Twence boiler fly ash without any changes. The second one is a crushed Twence boiler fly ash. Samples 1 to 4 present the pure Twence boiler fly ash and Samples 5 to 8 - the crushed Twence boiler fly ash. Sample 9 is sieved, crushed and represents everything below 500 microns (87% of mass), while sample 10 is sieved, crushed and represents everything above 500 microns

(13% by mass). The results are presented in Table 20, where samples 9 and 10 together are assumed to constitute 100% (100% mass).

Table 20: Chloride content of solid Twence boiler fly ash

TBs 1 [mg/kg]	TBs 2 [mg/kg]	TBs 3 [mg/kg]	TBs 4 [mg/kg]	TBs 5 [mg/kg]	TBs 6 [mg/kg]	TBs 7 [mg/kg]	TBs 8 [mg/kg]	TBs 9 [mg/kg]	TBs 10 [mg/kg]
2680.3	2545.4	3553.6	2751.3	3714	3634.3	3738.2	3771.9	2855	2370
51.3%	48.7%	68.0%	52.6%	71.1%	69.5%	71.5%	72.2%	54.6%	45.4%

It can be seen that samples 1-4 contain less chlorides than samples 5-8, probably because not all chloride ions from these samples were dissolved. Probably some chloride ions contained in coal particles were not dissolved in water. This is in contrast to the samples 5-8 that are crushed, and therefore chloride particles were released and could be dissolved in water. Sample 10 is pure carbon that was on top of the 500 micron sieve and represents 13% by mass. Even this low content by mass contains almost 50% of the chlorides. This explains why samples 5-8 have more chlorides than sample 9, because a small part of carbon with chlorides was still present. Nevertheless, because of the small amount of two grams that is investigated, samples 5-8 are not a realistic representation of the chloride content in Twence boiler fly ash. However, it is believed that sample 9 together with sample 10 give a good representation. Moreover, this value is close to the results coming from the XRF analysis (990-5600 mg/kg). These results show that coal particles have a big influence on the chloride content of a fly ash, as chlorides attach and combine with coal particles as described earlier in Paragraph 7.2. These facts can explain the observed differences between the same samples. For that reason, further investigation is performed on Twence cyclone fly ash due to less carbon particles in its composition and should result in less fluctuation when measuring the chloride content in distilled water and pure fly ashes.

### 9.1.2 Twence cyclone fly ash (B2)

To investigate the quantity of removed chloride from Twence cyclone fly ash (B2), at first the initial chloride content of plain B2 is determined. This is done for two pairs of measurements. The first one is plain B2 without any changes. The second one is crushed B2. Samples TC1-TC3 present the plain B2 and samples TC4G-TC6G the crushed B2. Sample TCA represents the average of samples TC4G-TC6G and is taken as 100% chloride content because of the small differences between samples TC4G-TC6G. The results are presented in Table 21.

Table 21: Chloride content of solid Twence cyclone fly ash

TC1 [mg/kg]	TC2 [mg/kg]	TC3 [mg/kg]	TC4G [mg/kg]	TC5G [mg/kg]	TC6G [mg/kg]	TCA [mg/kg]
3887.3	4276.0	4020.4	4158	4090	4143	4130.8
94.1%	103.5%	97.3%	100.7%	99.0%	100.3%	100%

From Table 21 it can be stated that the difference between the original sample and crushed sample is very small. This is probably due to smaller content of carbon particles. The results are in contrast to Twence boiler fly ash, where a large difference was observed.

In order to monitor the behaviour of the bio-energy fly ash in time, the chloride content of four samples B2 are measured and presented in Figure 31. The four samples are divided into group A and B, both measured every 15 minutes for one hour long with a shaking speed of 120 rpm and two different liquid to solid ratios (L/S), namely 2 and 4.

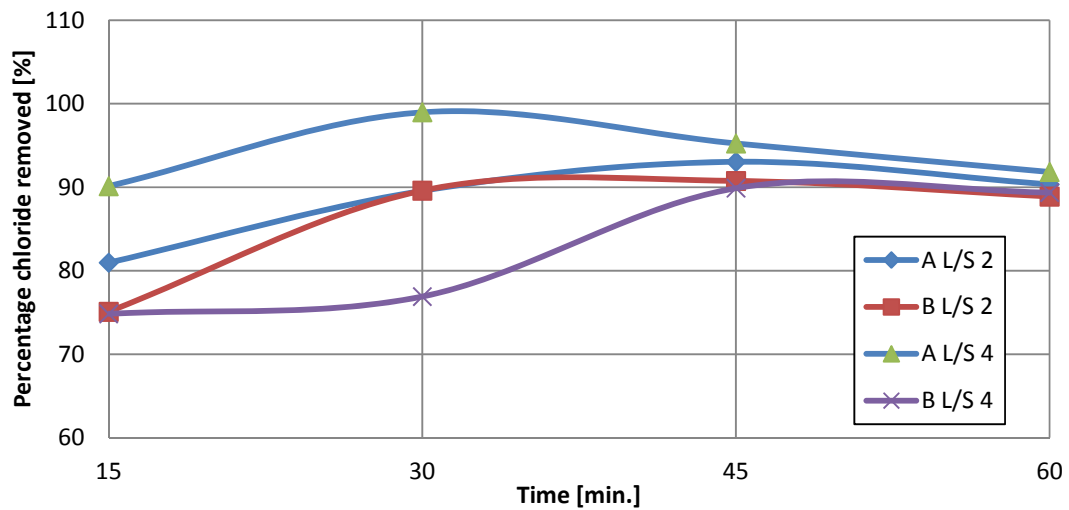


Figure 31: Chloride remove in Twence cyclone fly ash (B2) during 60 minutes with different L/S ratios

It was expected that with increasing time more and more chlorides would be removed. However, Figure 31 illustrates that there are still differences between the same-sample pairs, although this is already considerably reduced compared to B2. The reduced but still present inaccuracy can have different reasons. One of the first reasons would be that the chloride content in fly ash is not homogenously distributed, resulting in a difference in chloride removal. However, it can also be that the 3 ml from every sample are not representative for the total 400 ml that is used. This would explain why at 60 minutes all the results are in close agreement, because at this time the washing stopped and 50 ml of water was extracted for measuring the chloride content.

The following measurement is performed using a liquid to solid ratio of 2 and taking 25 ml samples instead of the three ml used to confirm this statement. Also the shaking speed is increased to 240 rpm because this would reduce the time to solve the chlorides in water, as mentioned in Table 18. Results are illustrated in Figure 32.

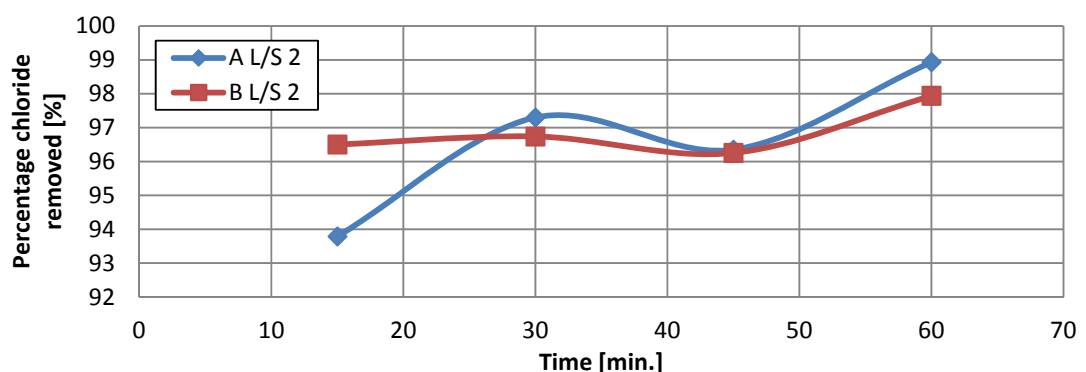


Figure 32: Chloride ions removed in Twence cyclone fly ash (B2) during 60 minutes with L/S = 2 and shaking speed of 240 rpm

The results presented in Figure 32 look more promising. Not only the discrepancy between the same-samples decreased, but close to 30 minutes more than 95% of chlorides are

removed. The fact that there is still a bit of shifting in the results during time could be explained by small measurement errors. The difference between these results is less than 5% and is assumed to be trustworthy. Therefore, further investigations for the other fly ashes are made using the knowledge that a large sample size of 25 ml of water is needed and that carbon particles have a large influence on the outcome of the washing technique because of possible chloride content.

### 9.1.3 Validation measurement

To test the reliability of the prediction of chlorides in solid samples, two different solutions of NaCl and CaCl<sub>2</sub> are mixed with CaO-SiO<sub>2</sub> in different ratios with a total sample size of 10 grams. Afterwards the chlorides are measured and results are analysed whether there is any discrepancy. The results are given in Table 22.

Table 22: Chloride content of NaCl and CaCl<sub>2</sub> solutions compared to measured values

Cl <sup>-</sup> [%]	Original NaCl [g]	Measured NaCl [g]	Difference [%]	Original CaCl <sub>2</sub> [g]	Measured CaCl <sub>2</sub> [g]	Difference [%]
2	0.33	0.25	-40.0	0.41	0.18	-44.0
4	0.66	0.53	-36.4	0.83	0.47	-29.2
6	0.99	0.70	-44.4	1.24	0.60	-39.0
8	1.32	0.95	-43.3	1.66	1.02	-35.8

In general the above results present an error of 40% in measuring the chloride content, but this is strongly related to the used chloride type. It can be seen that the difference of the highly soluble CaCl<sub>2</sub> is smaller than that of the less soluble NaCl. The reason for these differences can so far only be speculated about. Perhaps the time for dissolving (five-ten minutes) was too short, and that a longer mixing time is needed to dissolve all soluble chlorides. A similar trend is in fact visible when monitoring the dissolving rate of chlorides during time. From this it takes 30-60 minutes to have a stable result.

## 9.2 Chloride removal (part two)

### 9.2.1 Twice boiler fly ash

To ensure that the maximum chloride content will not exceed 1000 mg/kg the following treatment steps are carried out:

- 1) The bio-energy fly ash is sieved on a 500 micron sieve, to remove large coal particles;
- 2) The bio-energy fly ash is:
  - a. air filtered removing small coal particles;
  - b. thermally treated at 750 °C, to remove small coal particles.
- 3) Both samples described under step two are then washed using the water treatment.

The results are illustrated in Figure 33.

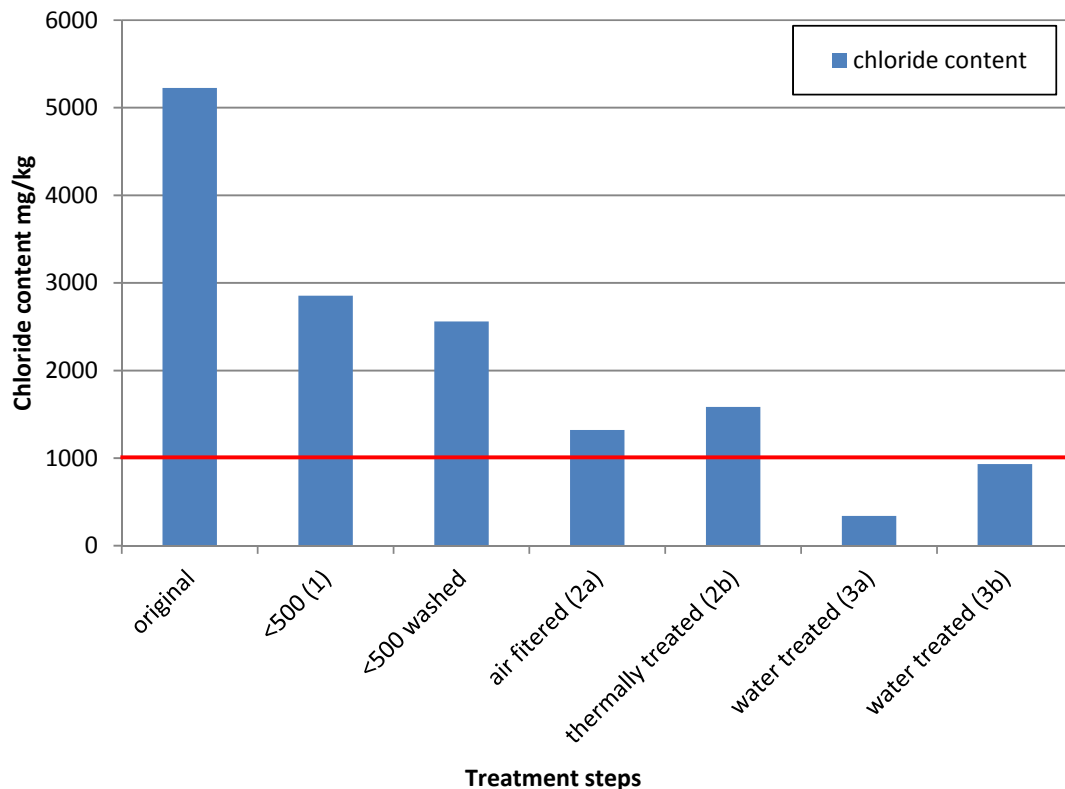


Figure 33: Chloride ions in Twence boiler fly ash (B1) before and after different treatment steps

The first step already reduced the available chloride content with 45%. This is due to absorbed chloride and chlorine in the carbon structure. Washing this fly ash will result in a total decrease of 51%. This is 6% lower than not washing, from which it can be concluded that washing has almost no effect as long as small carbon particles are still present. The soluble chlorides are somehow attached to the surface of the carbon particles and prevented to dissolve in water. Removing the small carbon particles using Treatment 2a or 2b results in a reduction of 75% and 70%, respectively, compared to the original fly ash. Washing this fly ashes results in a total reduction of 93% and 82%. This indicates that first removing the coal particles increases the removal of chlorides. Secondly, air filtering removes chlorides that are less soluble and with this decreases the remaining chloride content.

### 9.2.2 *Twence cyclone fly ash*

Because this fly ash only has large carbon particles the following steps are performed:

- 1) The bio-energy fly ash is sieved on a 500 micron sieve, to remove large coal particles;
- 2) The bio-energy fly ash is washed using the water treatment.

Results are illustrated in Figure 34.

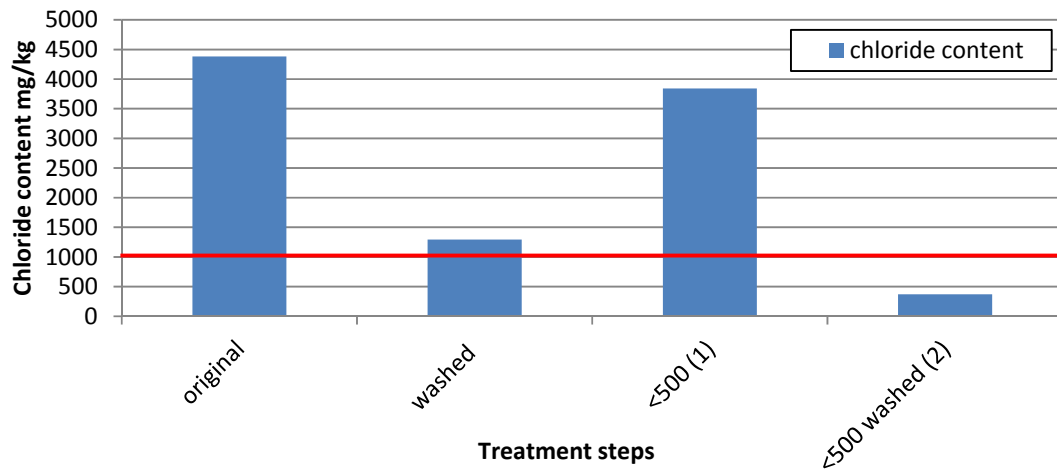


Figure 34: Chloride ions in Twence cyclone fly ash (B2) before and after different treatment steps

The chlorides in B2 ash are easily soluble and after treatment almost fulfil the maximum limit of 1000 mg/kg. When sieved with a 500 micron sieve, the chloride content is reduced by 12%. After sieving with a 500 micron sieve and water treatment only 9% of the chloride content remains, compared to 29% when washed without sieving. This means that by removing carbon the efficiency of the washing technique increases by 8%, and as a result the chloride content fulfils the stated requirements.

### 9.2.3 HVC cyclone fly ash

This fly ash has no carbon issues and therefore the water treatment could immediately be applied to fulfil the chloride requirements presented in Figure 35. However, before treatment almost all the metal aluminium is removed. This is done by putting the fly ash in a bottle with water using a liquid to solid ratio of four and shaking it for 72 hours.

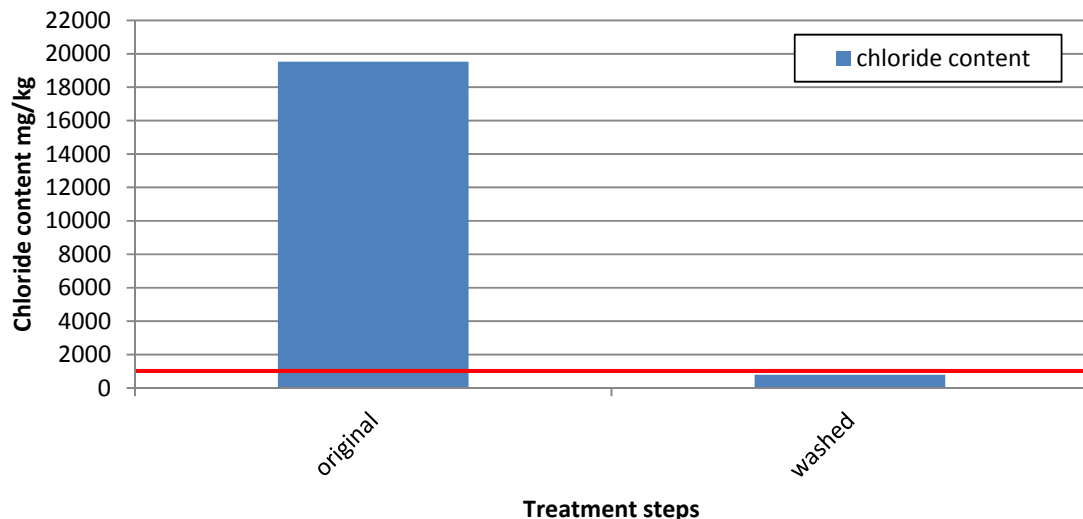


Figure 35: Chloride ions in HVC cyclone fly ash (A1) before and after treatment

After washing the chloride content is reduced by 96% and fulfils the stated requirements.

### 9.2.4 HVC Filter fly ash

This fly ash has (like HVC cyclone fly ash) no carbon particles and therefore can immediately be water treated. It also contains metallic aluminium, but because the water treatment was not successful further research has not been performed. As it can be seen from Figure 36, the chloride content of this fly ash is 86 times more than allowed. After treatment this amount is reduced by 80% but still it is too high to be used as cement replacement in concrete structures.

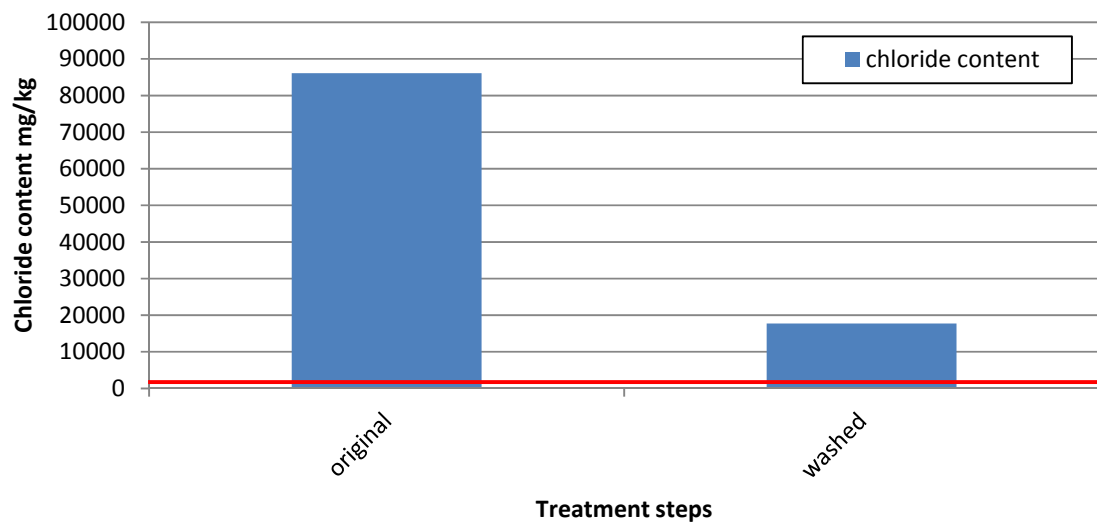


Figure 36: Chloride ions in HVC filter fly ash (A2) before and after treatment

## 9.3 Treatment data particle size distribution

The effect of removing small coal particles by thermal treatment or air filtering on the particle size distribution (PSD) will be discussed, as well as the effect of the water treatment. Furthermore, crushed bio-energy fly ash samples which fulfils the NEN-EN-450 and NEN-EN-5950 requirements as illustrated.

### 9.3.1 Twence boiler fly ash

In Figure 36 the effect of both thermal treatment (TBH) and air filtering (TBA) are illustrated, together with the original PSD of Twence boiler fly ash (B1). Also crushed TB (TBAG and TBHG) are present that fulfils the NEN-EN-450 and will be used for strength development in the following chapters.

It can be seen that there is almost no difference between the thermal and the air filtering treatment. Both PSDs are shifted to the right, indicating bigger particles due to the removal of the small coal particles. Looking at the grinded fly ash, 65% is smaller than 45 microns and 0.1% is bigger than 212 microns, fulfilling the stated requirements.

The effect of the water treatment on the PSD of this fly ash is illustrated in Figure 37. To obtain these results, the fly ash is first heated and ground and afterwards separated into two groups where one is water treated for comparison. The effect of the water treatment is negligible and only the soluble materials that are removed provide a small change in the PSD.

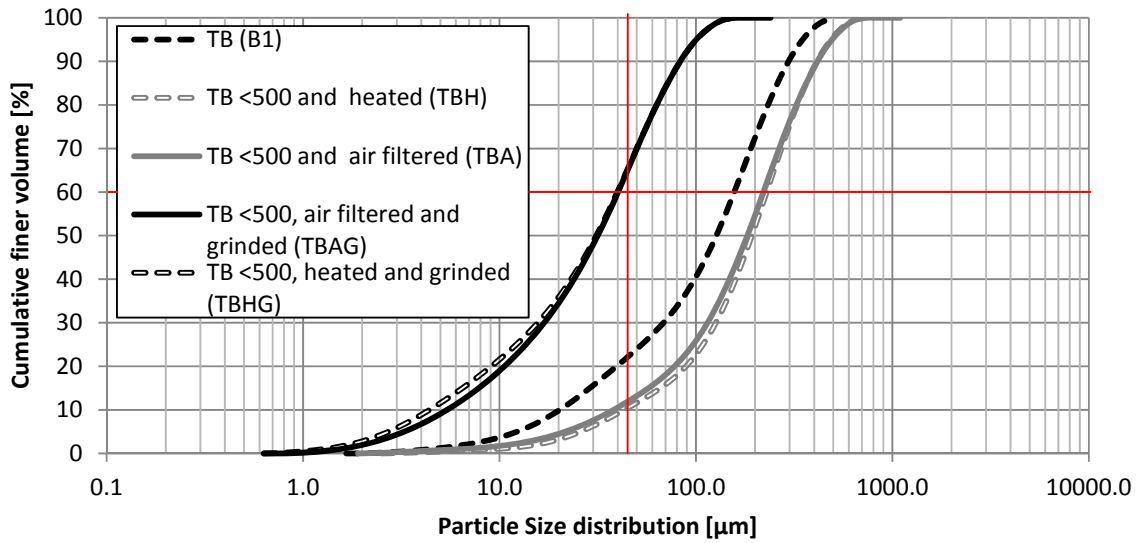


Figure 37: PSD TB before and after different treatment steps

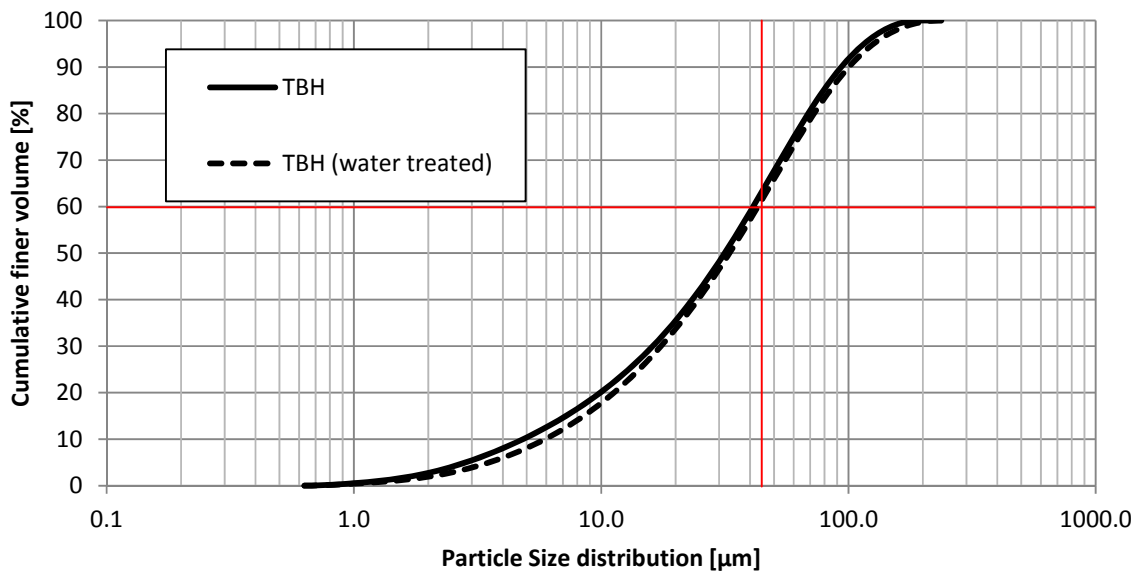


Figure 38: PSD Twence boiler thermally treated (TBH) before and after water treatment

### 9.3.2 Twence cyclone fly ash and HVC cyclone fly ash

Both Twence cyclone fly ash and HVC cyclone fly ash are water treated and ground. The results are presented in Figure 39. Also these two bio-energy fly ashes are fulfilling the stated requirements after successfully been water treated and ground.



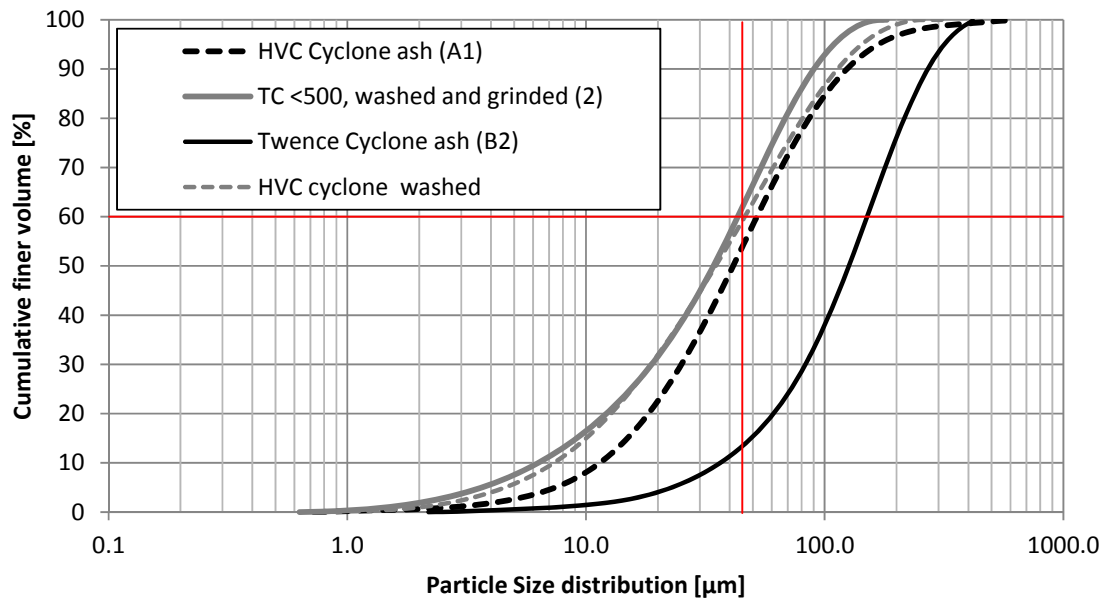


Figure 39: PSD of Twence cyclone (TC) and HVC (A1) before and after treatment

### 9.3.3 Comparison PSD and SSA between original and treated bio-energy fly ash

All data regarding particle size distribution (PSD) and specific surface area (SSA) of original (O) and treated bio-energy fly ashes (T) are described in Table 23. The treated bio-energy fly ash is the final bio-energy fly ash after all treatments steps including crushing.

Table 21: PSD and SSA data regarding original and treated bio-energy fly ashes

	HVC cyclone (A1)		Twence boiler (B1)			Twence cyclone (B2)		PKVA SMZ (R)
	(O)	(T)	(O)	(TH)*	(TA)*	(O)	(T)	(O)
<b>d(min.) [µm]</b>	0.7	0.7	1.7	0.7	0.8	2.2	0.7	0.63
<b>d(0.10) [µm]</b>	10	7	18	4	5	31	6	5
<b>d(0.50) [µm]</b>	36	34	110	31	31	110	34	21
<b>d(0.60) [µm]</b>	47	46	138	40	40	130	42	30
<b>d(0.80) [µm]</b>	75	80	202	63	63	187	68	63
<b>d(0.90) [µm]</b>	126	113	257	83	82	235	90	106
<b>d(max.) [µm]</b>	631	275	479	158	158	417	182	832
<b>SSA [cm<sup>2</sup>/g]</b>	1160	1370	382	1980	1720	559	1590	2090

\* TH = Twence boiler thermal treated and TA = Twence boiler air filtered

Table 23 indicates that still after crushing the bio-energy fly ashes PKVA SMZ have a smaller PSD and a larger SSA. However, there is a large improvement after treatment (for instance, the B1 d(0.90) decreases from 257 to 82).

## 9.4 Strength development

The Bio-energy fly ashes are used as 5%, 10% and 20% cement replacement. Mortars are produced using the standard method described in NEN-EN-196 and are cured under water for 28 days. The 7 day strength is not measured because of the slow reactivity of fly ash in general. The red line indicates PKVA SMZ and is used as a reference.

First the influence of the water treatment is investigated, replacing 5% and 20% of cement. Regarding flexural strength, the difference is negligible and in the order of magnitude of  $\pm 0.5$  MPa. Compressive strength results are presented in Figure 40 and Figure 41.

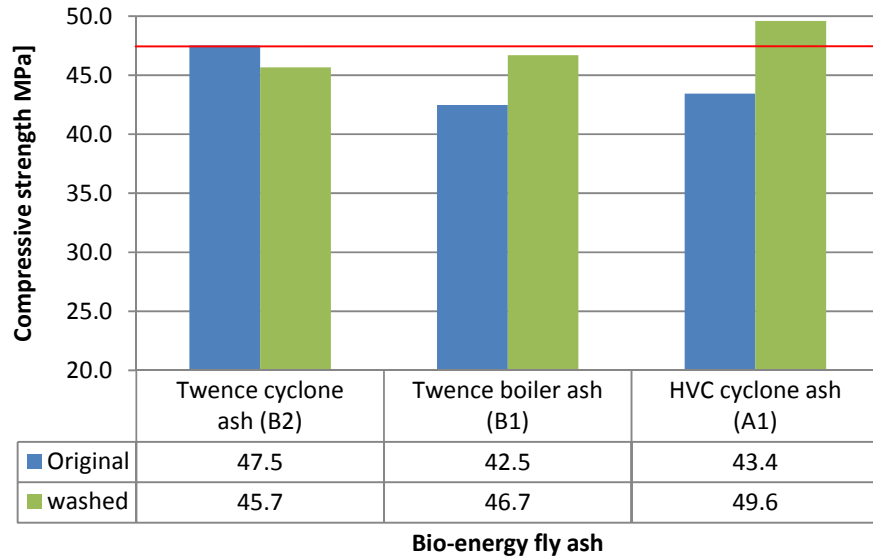


Figure 40: Effect of water treatment on the 28 days strength development using 5% bio-energy fly ash as cement replacement (PKVA SMZ (R) 47.5 MPa)

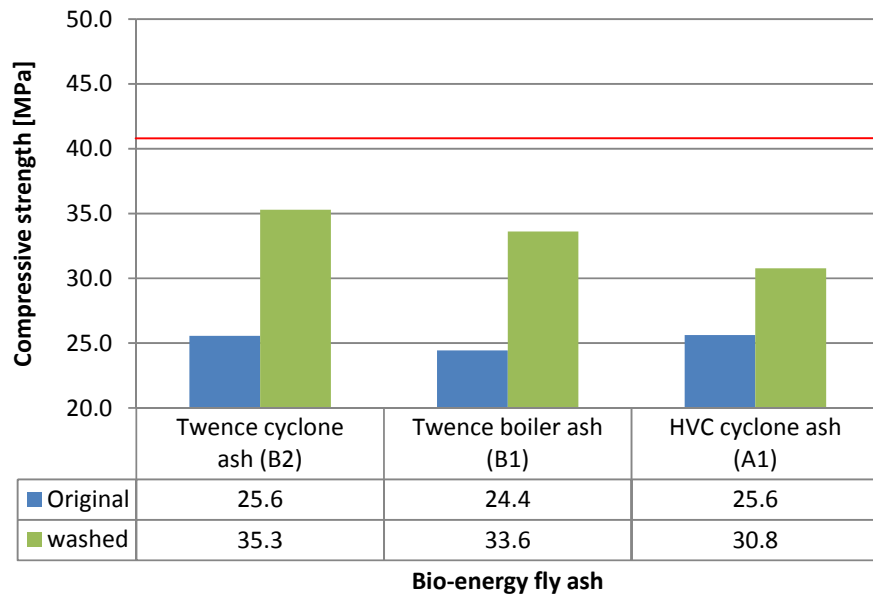


Figure 41: Effect of water treatment on the 28 days strength development using 20% bio-energy fly ash as cement replacement (PKVA SMZ (R) 41 MPa)

From Figure 40 and Figure 41 it can be concluded that in general the water treatment has a positive effect on the strength generation and further treatment can be performed. Only the 5% replacement with Twence cyclone fly ash seems to have a negative effect. This however can also be due attributed to the accuracy of the test.

Figures 42-47 illustrate the 5%, 10% and 20% replacement of cement by the different bio-energy fly ashes. The results are separated in original bio-energy fly ash, treated bio-energy fly ash (fulfilling the carbon and chloride requirements) and the afterwards ground bio-energy fly ash fulfilling the requirements for particle size distribution. Figures 42-44 show the measured flexural strength and Figures 45-47 – the compressive strength.

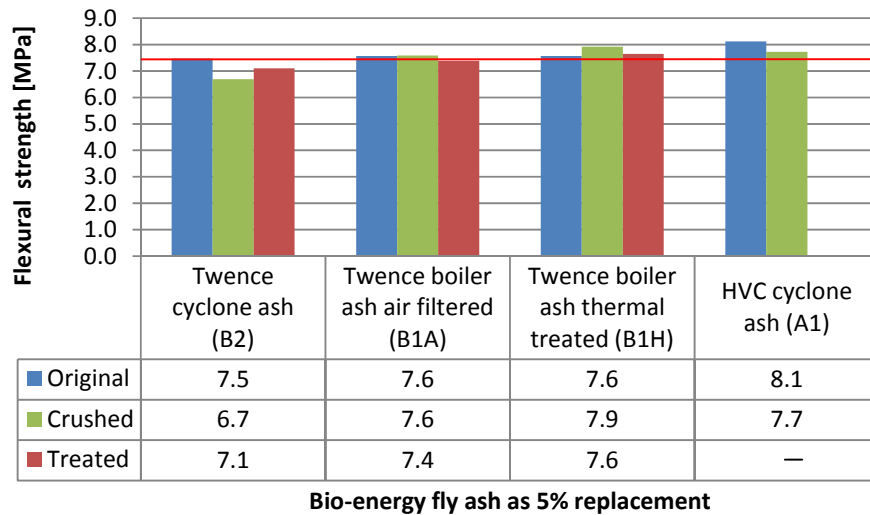


Figure 42: 28 days flexural strength development using 5% bio-energy fly ash as cement replacement before and after different treatment steps (PKVA SMZ (R) 7.5 MPa)

The 28 days flexural strength with 5% bio-energy fly ash as cement replacement seems to be almost the same as PKVA SMZ (R) and even close to that of CEM I 42.5 R (8.1 MPa). Thermally treated Twence boiler fly ash has the highest strength development, followed by HVC cyclone and Twence boiler air filtered fly ash. Twence cyclone fly ash seems to react negatively on treatment and the strength is decreased by 0.4-0.6 MPa.

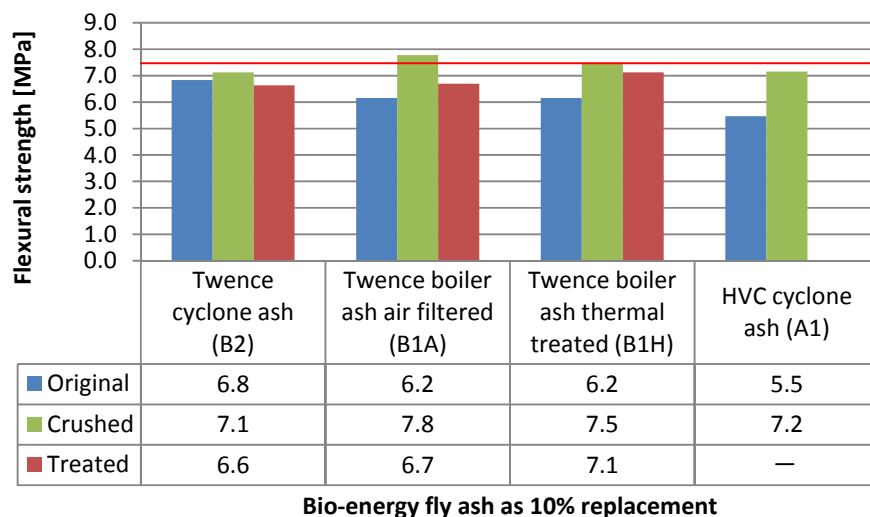


Figure 43: 28 days flexural strength development using 10% bio-energy fly ash as cement replacement before and after different treatment steps (PKVA SMZ (R) 7.5 MPa)

Figure 43 presents a small decrease of 28 days flexural strength for almost all bio-energy fly ashes (replacement level 10%) compared to the reference (R). However, the flexural strength of crushed particles is significantly increased compared to original flexural strength and is even comparable with the reference (R).

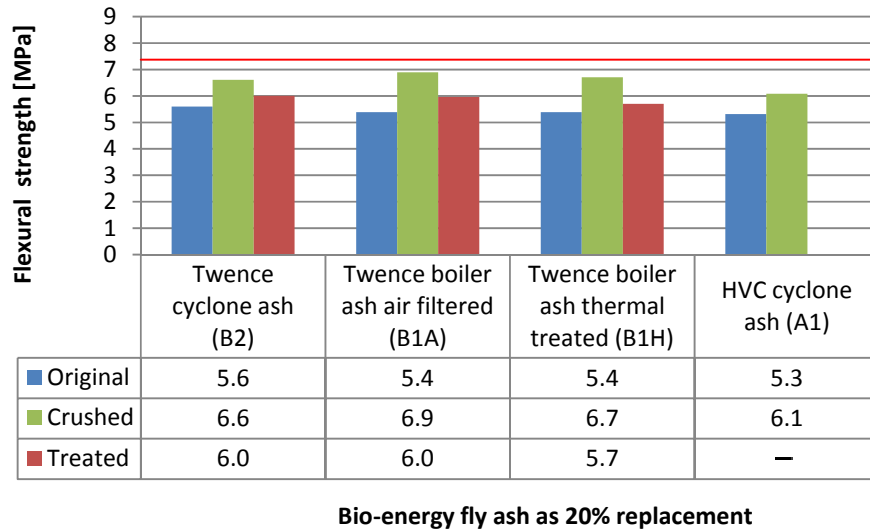


Figure 44: 28 days flexural strength development using 20% bio-energy fly ash as cement replacement before and after different treatment steps (PKVA SMZ (R) 7.2 MPa)

Figure 44 presents a decrease of 28 days flexural strength for all bio-energy fly ashes (replacement level 20%) compared to PKVA SMZ (R). Still crushed particles have a higher flexural strength for all bio-energy fly ashes compared to the reference flexural strength.

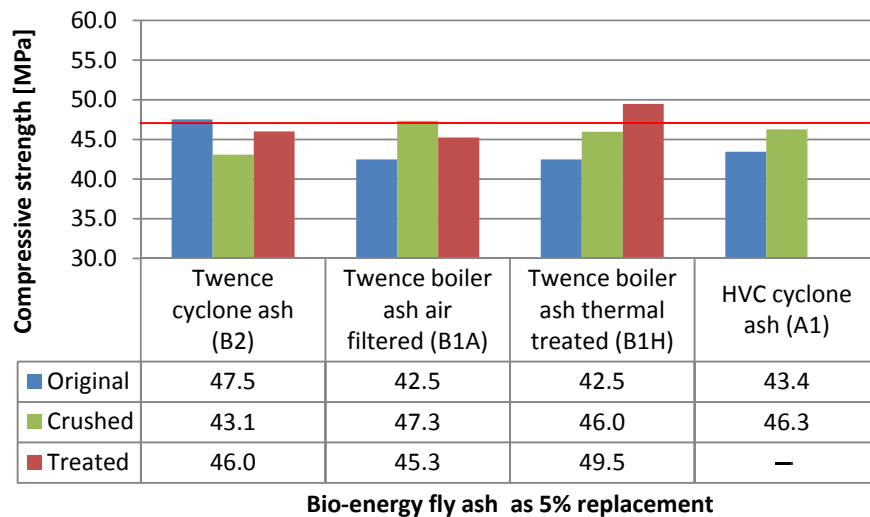


Figure 45: 28 days compressive strength development using 5% bio-energy fly ash as cement replacement before and after different treatment steps (PKVA SMZ (R) 46.9 MPa)

The 28 days compressive strength development using 5% bio-energy fly ash as cement replacement (described in Figure 45) illustrates comparable and even higher strength developments compared to the reference (R). Especially the two treated Twence boiler fly ashes are performing well. Twence cyclone and Twence boiler thermally treated fly ash are

examples that indicate that crushing not always increases the strength development compared to not crushed. The above results also indicate that the bio-energy fly ash has a binding activity because they develop a higher strength than the reference (R).

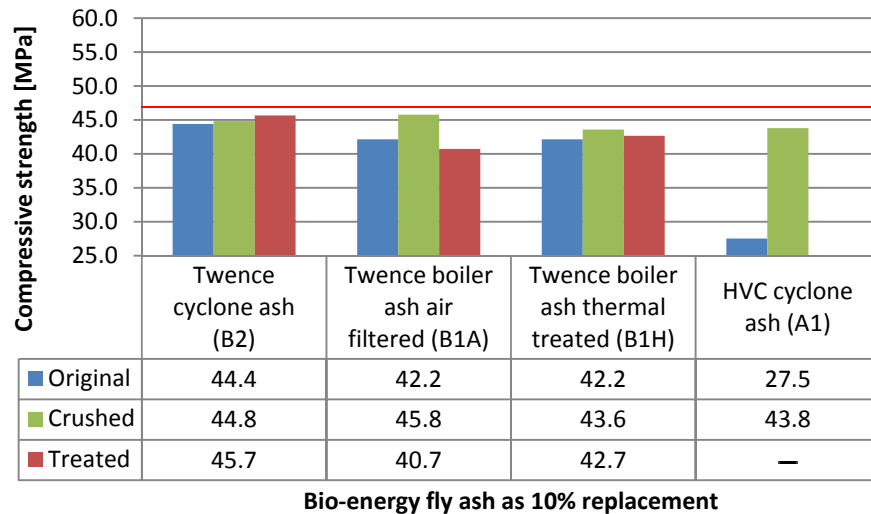


Figure 46: 28 days compressive strength development using 10% bio-energy fly ash as cement replacement before and after different treatment steps (PKVA SMZ (R) 46.1 MPa)

The 10% replacement is at all fronts lower than that of PKVA SMZ. HVC cyclone shows a high compressive strength development compared to the original.

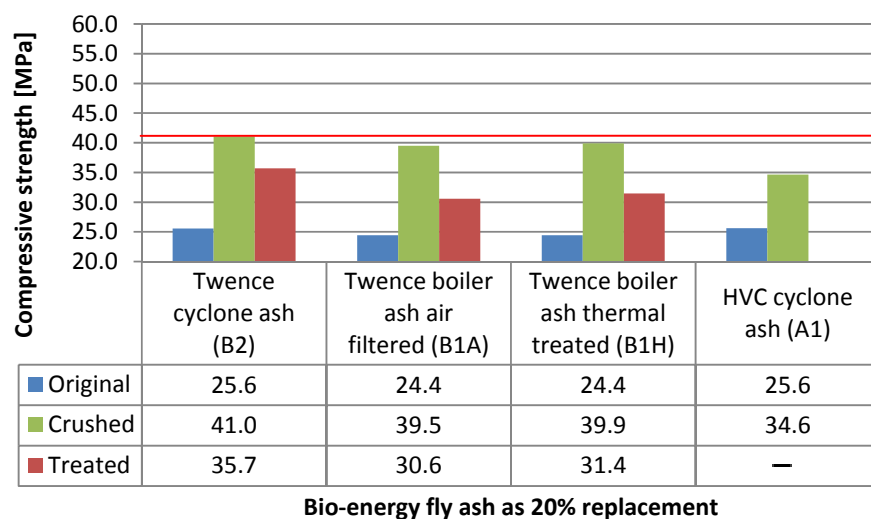


Figure 47: 28 days compressive strength development using 20% bio-energy fly ash as cement replacement before and after different treatment steps (PKVA SMZ (R) 41 MPa)

The Twence cyclone 28 days compressive strength with 20% replacement has similar results compared to the 10% replacement regarding the treated sample. It seems that crushing somehow affects the fly ash, creating lower strength results in all replacements. Furthermore, the strength results of the Twence fly ashes are comparable with the strength results of PKVA SMZ.

## 9.5 Side effects

This paragraph summarizes different experiments that got attention during the research because of interesting phenomena. It started by water treating the bio-energy fly ashes to investigate the effectiveness, followed by thermal treating all four bio-energy fly ashes and removal of metallic aluminium. Results are later investigated using scanning electron microscopy and X-ray powder diffraction.

### 9.5.1 Water treatment

That the water treatment did not always result in what was hoped (which can be clearly seen in Figure 48). The figure illustrates HVC filter fly ash (left) and HVC cyclone fly ash (right) after water treatment and separation of liquid and solid using a filter. The fly ashes are dried in the oven for 12 hours at 50 degrees Celsius.



Figure 48: Fixed HVC filter fly ash (left) and HVC cyclone fly ash (right) due to cementitious properties

The figure illustrates that the fly ash already possesses cementitious properties. The same applies for HVC cyclone fly ash, which is, however, easier to break (lower strength).

### 9.5.2 Thermal treatment

The thermal treatment also created some rather spectacular results as presented in Figure 49. After treatment at 750 degrees Celsius HVC filter fly ash completely clumped together into small granulates. After crushing this thermally treated fly ash is used as a cement replacement; low strength results were found, probably due to phase changes.



Figure 49: Thermal treated HVC filter fly ash after one hour in oven at 750 degrees Celsius

### 9.5.3 Strength results

A test was performed in order to investigate the strength results of thermally treated bio-energy fly ash, followed by a water treatment and crushing to particles smaller than 100 microns. Furthermore a longer curing time is tested for thermally treated and only water treated bio-energy fly ashes, to investigate if there is any pozzolanic activity after 28 days, the results are presented in Table 24.

Table 22: Strength development after 28 days of thermal treated bio-energy fly ashes

Bio-energy fly ash	28 days flexural strength [MPa]	28 days compressive strength [MPa]	60 days compressive strength [MPa]
HVC cyclone fly ash (A1) (20% replacement)	6.3	25.4	-
HVC filter fly ash (A2) (20% replacement)	5.5	35.5	36.2
Twence cyclone fly ash (A1) (20% replacement)	7.1	40.3	-
Twence boiler fly ash (B2) (20% replacement)	7.4	40.6	-
Twence boiler fly ash (B2) water treated (40% replacement)	3.7	18.7	23

Table 24 illustrates that the thermal treatment did not have a positive effect on the tensile, and especially not on the compressive strength, of HVC bio-energy fly ashes. Even after 60 days no pozzolanic activity is found. This indicates that hydration is hindered by thermal treatment. The small increase of 0.7 MPa can be seen as a measurement error. Twence boiler water treated fly ash with 40% replacement of cement illustrates an increase of 23%, which indicates that the bio-energy fly ash possesses slow pozzolanic reactions.

Further investigation of the effect of the water treatment on the strength development is done by increasing replacement. The results are presented in Table 25.

Table 23: 28 days strength development of water treated bio-energy fly ashes with different cement replacement percentages

Replacement [%]	28 days compressive strength [MPa]		28 days compressive strength [MPa]	
	HVC cyclone fly ash original (A1)	HVC cyclone fly ash water treated(A1)	HVC filter fly ash (A2) original	HVC filter fly ash (A2) water treated
5%	43.4	49.6	46.7	43.9
20%	25.6	30.8	40.8	33.7
30%	26.8	21.4	33.0	14.9
40%	19.9	15.9	23.0	5.0

Replacement [%]	28 days compressive strength [MPa]		28 days compressive strength [MPa]	
	Twence cyclone fly ash (B1) original	Twence cyclone fly ash (B1) water treated	Twence boiler fly ash (B2) original	Twence boiler fly ash (B2) water treated
5%	47.5	45.7	42.5	46.7
20%	25.6	35.3	24.4	33.6
30%	23.8	23.9	20.1	26.0
40%	13.7	17.5	16.1	18.7

It was found that the water treatment had an effect on HVC filter fly ash. This is due to the cementitious properties that it possesses. The effect on HVC cyclone fly ash was only observed above a replacement of 20%. Twence ashes are in general not affected. Only the 5% replacement of Twence cyclone fly ash is lower than expected.

### 9.5.4 Scanning electron microscopy (SEM)

HVC fly ashes seem to have cementitious properties. Still strength results show sometimes promising results and sometimes disappointing results, mostly depending on the treatment. To further investigate the effect of the water treatment, 1 hour water treated and 72 hours water treated HVC cyclone fly ash are investigated and compared with 1 hour and 24 hours water treated Twence boiler fly ash. The results are presented in Figure 50 and Figure 51.

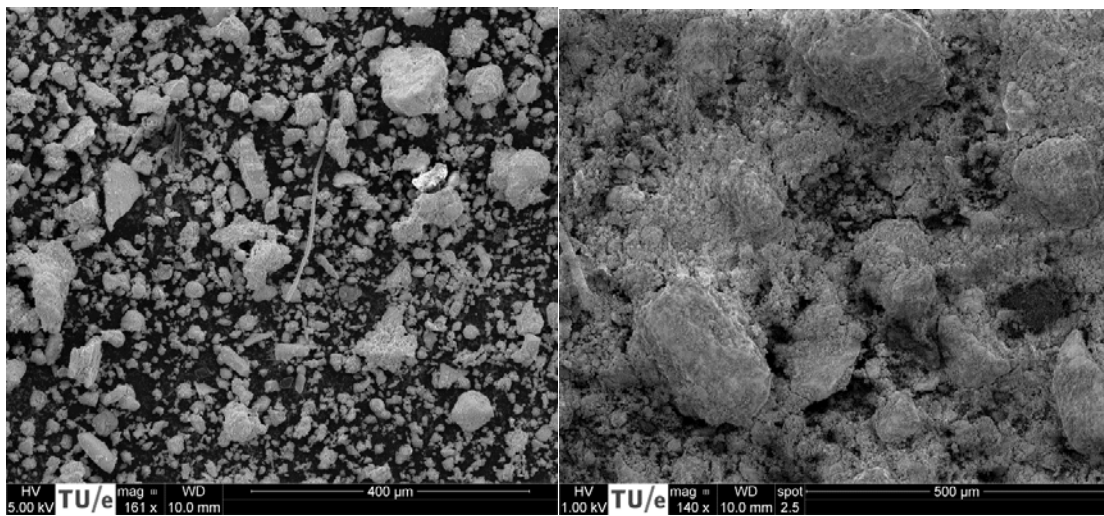


Figure 50: HVC cyclone fly ash after one hour of water treatment (left) and 72 hours of water treatment (right)

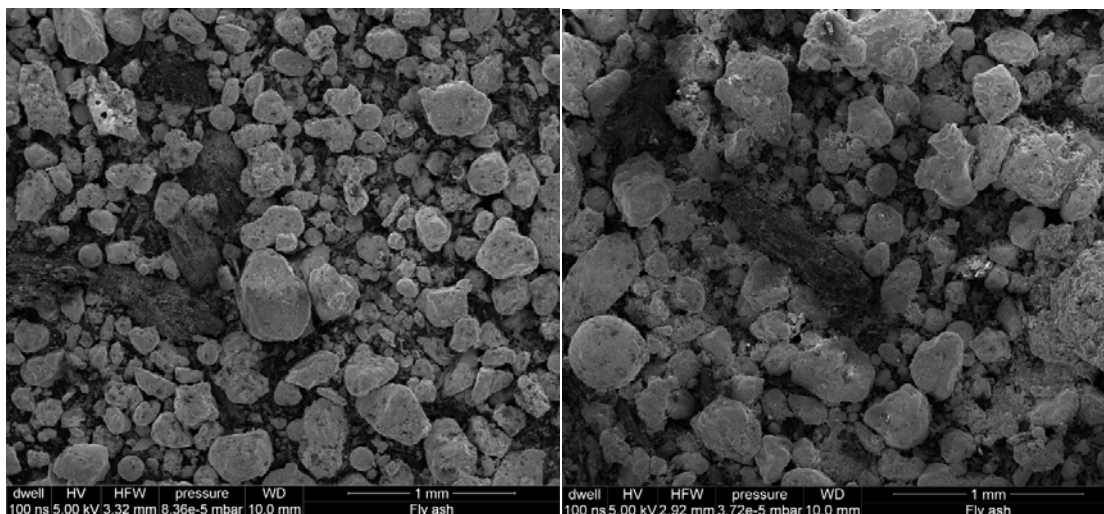


Figure 51: Twence boiler fly ash after one hour of water treatment (left) and 24 hours of water treatment (right)

After water treatment of one hour, almost no cementitious properties are found in both HVC cyclone and Twence boiler fly ash. However, after 72 hours of water treatment there seems



to be hydration products formed that completely cover the surface of the bio-energy fly ash particles. This result is not observed when water treating the Twence boiler fly ash. It seems that the three days of HVC cyclone water treatment to remove metallic aluminium has more effect than would be expected. This all seems to be caused by self-cementitious properties.

### 9.5.5 X-ray diffraction pattern (XRD)

The effect of different treatments like water and thermal treatment for bio-energy fly ashes are investigated using X-ray diffraction. The results of HVC filter fly ash are presented in Figure 52 and the results of HVC cyclone fly ash in Figure 53. Figure 54 presents the XRD-pattern of PKVA SMZ. The XRD-pattern of Twence boiler and Twence cyclone fly ash are illustrated in Figures 55 and 56, respectively.

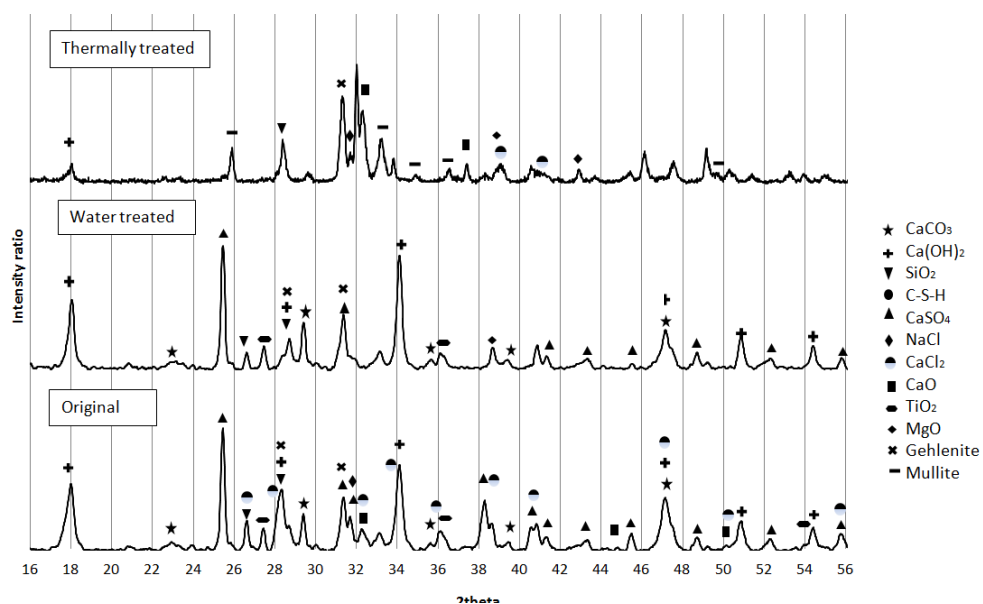


Figure 52: XRD pattern of original, water treated and thermally treated HVC filter fly ash

HVC filter fly ash contains phases like anhydrite ( $\text{CaSO}_4$ ), portlandite ( $\text{Ca(OH)}_2$ ), lime ( $\text{CaO}$ ), quartz ( $\text{SiO}_2$ ), chlorides ( $\text{CaCl}_2$  and  $\text{NaCl}$ ) and calcite ( $\text{CaCO}_3$ ). After water treatment the structure is similar and there is only an increase of  $\text{Ca(OH)}_2$  and a decrease of chlorides. When HVC filter fly ash is thermal treated at 750 degrees Celsius the structure is completely changed. Portlandite is reduced because of evaporated water and calcite is reduced because of release of carbon dioxide ( $\text{CO}_2$ ) and because of this free lime is increased. Anhydrite is also completely removed.

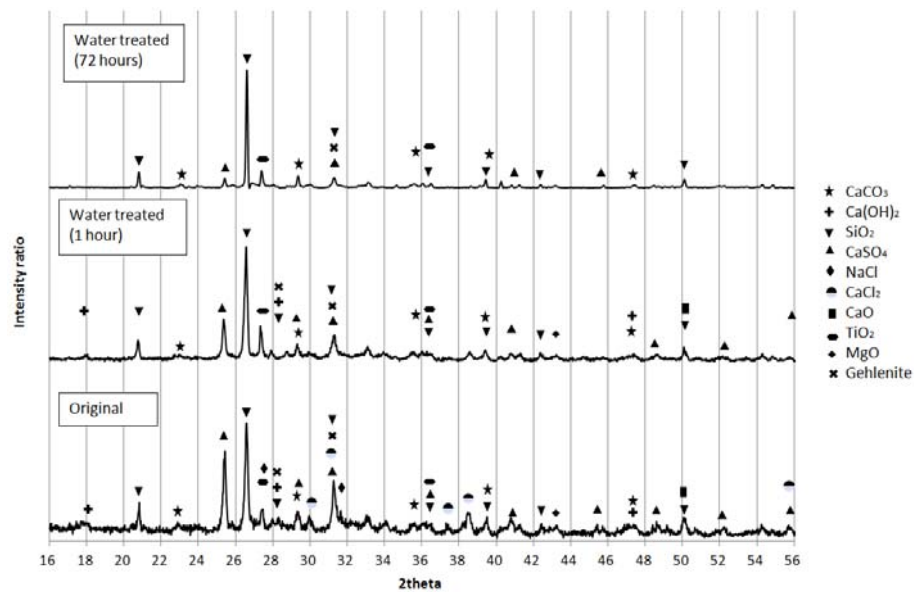


Figure 53: XRD pattern of original, one hour water treated and three hours water treated HVC cyclone fly ash

HVC cyclone fly ash compared to HVC filter fly ash contains similar phases of anhydrite (CaSO<sub>4</sub>), quartz (SiO<sub>2</sub>), chlorides (CaCl<sub>2</sub> and NaCl) and calcite (CaCO<sub>3</sub>), but less portlandite (Ca(OH)<sub>2</sub>) and lime (CaO). After water treatment there is a decrease of chlorides and anhydrite.

When HVC cyclone fly ash is water treated for 72 hours the structure is still comparable with the 1 hour water treated. Small changes are found in the available anhydrite and silicate. The main peaks are still those of quartz.

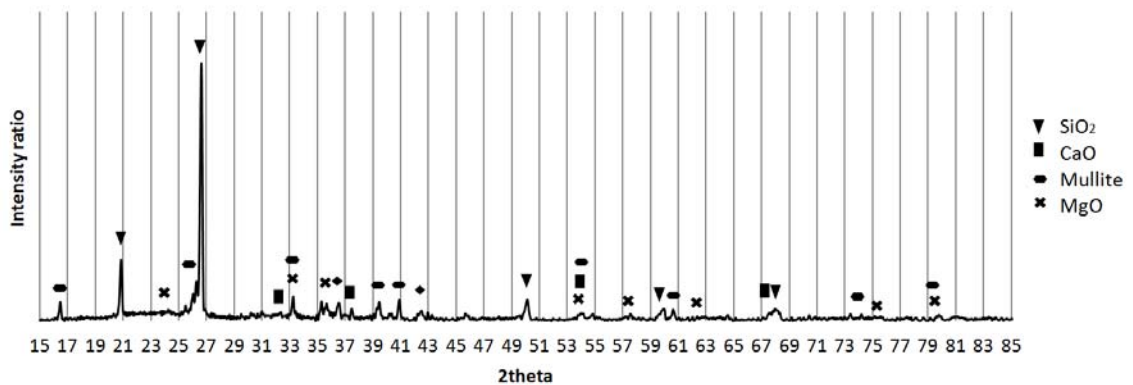


Figure 54: XRD pattern of PKVA SMZ (R)

PKVA SMZ mainly consist of quartz, free lime, mullite, magnesium oxide and hematite (Fe<sub>2</sub>O<sub>3</sub>).

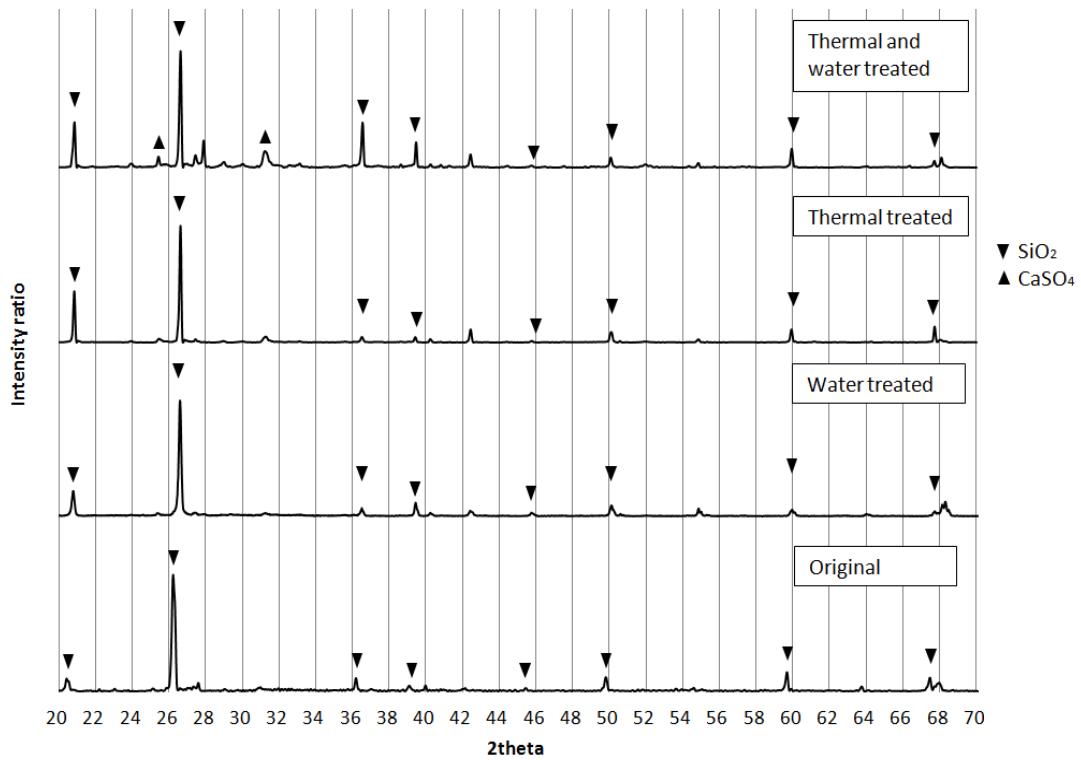


Figure 55: XRD pattern of original, water treated, thermally treated and thermally+water treated Twence boiler fly ash

Twence cyclone and Twence boiler have not only similar oxide composition but also X-ray diffraction patterns. Main peaks are quartz and other forms are not found, which means that they are in very low amount when compared to quartz.

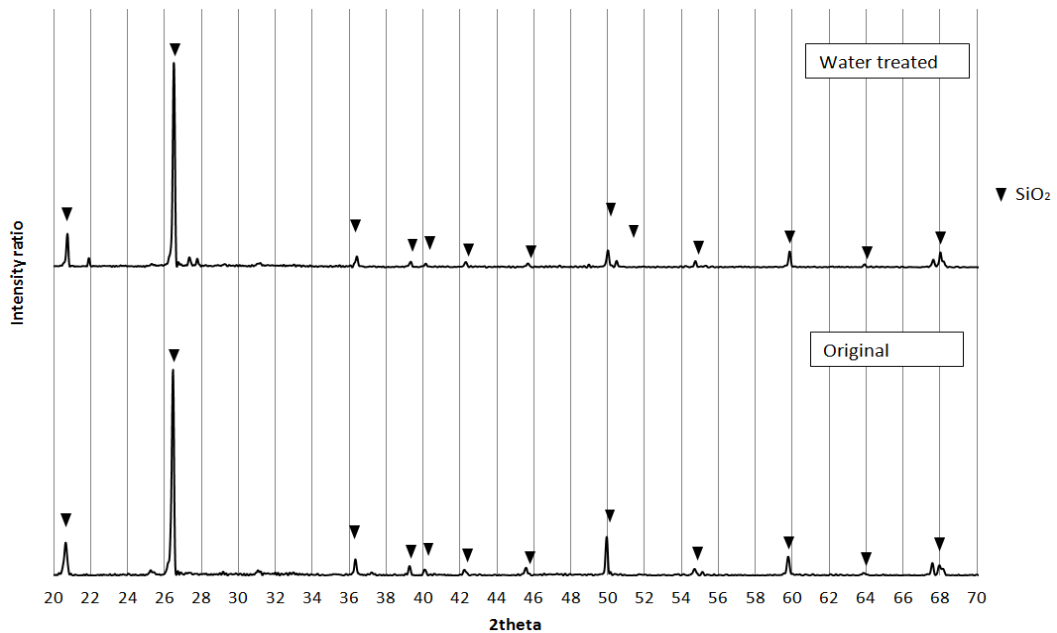


Figure 56: XRD pattern of original, water treated, thermally treated and thermally + water treated Twence cyclone fly ash

## 10. Discussions and conclusions

This section is divided into three different parts. The first part is about the bio-energy fly ashes, comparing with coal combustion fly ash. The second part is a discussion about the used treatment methods and reliability. The third part is about the obtained final results regarding treatment and strength results.

### 10.1 Relations and differences

During this research, working with different types of fly ash, it can be stated that the well known coal-combustion fly ash that has been used for decades is completely different than bio-energy fly ash or any types of fly ash described in this report. The benefits of coal combustion fly ash like a small particle size distribution, and the presence of cenospheres and plerospheres, increasing the workability and creating a denser structure do not naturally apply to bio-energy fly ash. Studying the physical and chemical properties, bio-energy fly ash has a larger particle size distribution with very little cenospheres and plerospheres. The larger particle size distribution would negatively affect the reactivity of bio-energy fly ash and would make it less suitable in concrete mixtures. Less cenospheres and plerospheres are leading to a material with higher density and less glassy phases.

Most of the bio-energy fly ash consists of fused particles with unburned coal particles that negatively affect the workability. These fused particles as well as coal particles can be related to the incomplete burning process, a process where the focal point is feeding the combustion room, keeping the fire and temperatures constant, resulting in waste streams that contain incompletely burned particles. These particles negatively affect the use of the fly ash in concrete mixtures, resulting in a need for different treatment methods making this material already more expensive than coal combustion fly ash. However, by not using the material in concrete mixtures it will be landfilled, which is not desirable because of increasing costs.

The use of the NEN-EN-450 as quality measure for bio-energy fly ash is debatable because actually we are talking about two different materials that are called "fly ash". Still the requirements regarding developed strength and chloride content can be applied because these are safety measures to ensure quality and have nothing to do with what type of material is used.

Finally, the content of bio-energy fly ash is like any type of waste continuously daily, weekly, monthly etc. depending on the waste streams that are put in the combustion room. It is therefore that continuously there is a need of chloride testing to ensure quality.

### 10.2 Treatment methods and reliability

#### 10.2.1 Carbon removal

Because of the high LOI of Twence bio-energy fly ashes, mainly due to high carbon content and the negative influence of carbon on the chloride removal of bio-energy fly ash, the carbon content needed to be reduced. After treatment the carbon content is significantly reduced and fulfils the LOI requirements. The reduction of the carbon content caused the removal of chlorides present in the carbon structure. Furthermore, it increased the efficiency of the water treatment to remove chlorides. When the carbon was still present,

the soluble chlorides were somehow attached to the surface of the carbon particles and prevented from dissolving in water. Due to the reduction of carbon, the chlorides could now dissolve in water.

### **10.2.2 Water treatment**

Optimization of the water treatment method was one of the biggest challenges during this research, because no information was available about water treatment of bio-energy fly ash to remove soluble elements. Available information about removing soluble elements from municipal solid waste was not applicable or incomplete. First results did not meet the expectations. After a lot of trial and error and trying to understand the chloride behaviour of bio-energy fly ashes in water, slowly reliable results came up. Still there is a lot of uncertainty about the water treatment. The influence of speed and time and temperature is not fully studied and can have enormous impact on the efficiency of the treatment. Until 30-60 minutes the removal of chloride ions was stable. For this research this was sufficient because when applying in an industrial environment, hours of water-treatments are increasing costs and decreasing the utilization. However, longer duration could remove chlorides with low solubility which would make the method more beneficial. During the treatment also other soluble elements are dissolved in the water, but this quantity has not been fully investigated, and perhaps increasing the time will have a positive effect on removing these elements. The same principle applies to the shaking speed or the increase of temperature. However, it also needs to be considered that the water treatment is not always beneficial, even if it is needed to reduce the chloride content.

Among the used bio-energy fly ashes, there are bio-energy fly ashes with cementitious properties, mainly due to the available free lime and anhydrite. Available free lime will, in contact with water, form portlandite that will ensure a high pH, activating the fly ash. Reducing the amount of free lime by washing will decrease the activation of fly ash and will result in a strength decrease. The available anhydrite will increase long term strength, but after a long water treatment the anhydrite is disappeared.

During the research it is found that the formation of portlandite takes time. Short time washing of around an hour would have less negative effect than a long duration of water treatment.

*All in all, this research shows that the method of water treating bio-energy fly ash to remove soluble elements is working, but still there is a need for further optimization to increase the removal of soluble elements and to ensure the reliability and efficiency of the method.*

So far, the water treatment used for non cementitious fly ashes indicates a positive effect on the strength development because of decreasing the concentration of contaminants that otherwise would have disturbed the cement matrix.

### **10.2.3 Method of measuring chloride content**

In this research two methods are used to test the chloride content of fly ash. Using data provided by the factory, the chloride content is known but can still differ from the original sample because it is not a homogenous material. To test the solid material, the method described in Paragraph 8.2.3 is used, that prescribes the use of nitric acid to dissolve types Cl-containing phases. Testing the chloride content of washed solid bio-energy fly ash and

comparing it to the obtained chloride concentration (which is obtained when measuring the chloride content of water from the water treatment), a difference of 500 kg/mg is found. In most cases there is less chloride in the water-treated fly ash than then would be expected when measuring the chloride content of the water.

The reason for this is not known, but the measured chloride content in water is a fact. The same was proven to be the case when measuring the chloride concentration of the solid-fly ash. From the validation study described in Paragraph 9.1.3 with known chloride concentration, indicates that only 55-70% is measured while the used chlorides are quite soluble. It is therefore not exactly known if the stated limit of 1000 kg/mg is indeed guaranteed when measuring the solid samples, it is only certain that the chloride concentration has dropped significantly.

#### **10.2.4 Grinding**

When grinding the materials, they fulfil not only the requirements described in NEN-EN-450 regarding particle size distribution (PSD), but also the requirements that the maximum percentage larger than 212 micron should not exceed 3% m/m (NEN-EN-5950), and the expected pozzolanic activity and workability. Such as earlier described, decreasing the PSD and increasing the specific surface area increases the reactivity of fly ashes and has a positive effect on the strength development during the first 28 days. It was expected that the strength results of crushed bio-energy fly ash would indicate higher strength results than not crushed bio-energy fly ash. However, from the obtained strength results the decrease in particle size distribution only has a significant effect when a high percentage of bio-energy fly ash is used. Upon 5% and 10% replacement the effect is barely visible and may indicate that bio-energy fly ash is not as sensitive to a decrease of particle sizes as the normal reference fly ash. Moreover, the grinding in order to reduce the particle sizes is an expensive method. Although in this research there was no investigation why the initial bio-energy fly ash from the two factories (Twence and HVC) have different particle size distributions. Two facts are known, HVC Alkmaar crushes its waste wood before incineration and it has a particle size distribution of 85% below 100 microns. If this would be the reason of a decrease in particle size distribution it could be preferable to first decrease the size of the waste that is incinerated in a more efficient way and thereby decreasing the size of the bio-energy fly ashes. The second fact is that both factories have a different incineration process, and because of the high carbon content of Twence Hengelo it can be concluded that the burning process of this factory is not complete enough, and probably also the reason of bigger particles.

## **10.2 Strength results**

Replacing cement with fly ash will in most cases result in a lower strength during the first 28 days. The more cement is replaced the less strength is developed. This is because the cement structure is disturbed by replacement by fly ash particles that are slowly reactive and therefore has fewer connections. When replacing 20% of cement with fly ash, and the initial 100% cement has strength of 50 MPa. The strength should be at least 40 MPa if not; the fly ash not only does not participate to the development of strength, but actually hinders cement hydration.

Comparing the replacement of cement with original not treated fly ash and washed fly ash indicates an increase of strength for most of the bio-energy fly ashes. Only Twence cyclone

fly ash has lower strength results at 5% replacement, and cementitious bio energy fly ashes such as HVC filter fly ash show a negative effect on the strength development after washing.

In general HVC cyclone fly ash is less promising at high replacement levels compared to Twence fly ashes. There are several reasons that can lead to lower strength results. In the original content of HVC cyclone fly ash there was a high amount of metallic aluminium and chlorides present. It is believed that the chlorides have no effect on the 28 days strength development and only affect the durability of the concrete when used with reinforcement. However, the available metallic aluminium, which in contact with water will create hydrogen, will increase the volume of the sample, resulting in an increase of porosity and decrease of compressive and flexural strengths. From earlier trials the removal of metallic aluminium by using water will take longer than 24 hours. From experiments it took 72 hours to remove the available metallic aluminium. The removed quantity was only visually observed, showing the formation of hydrogen up to the 72 hours. After this period of time no formation of hydrogen was observed. This is later confirmed when no deformation of the prisms was detected when measuring strength results. The effect of 72 hours of water treatment is further investigated using SEM and XRD.

SEM images of the 72 hours treated HVC cyclone fly ash illustrate the formation of hydration products on the surface of the particles. The nature of these hydration products is later investigated using X-ray diffraction, but could not reveal any explanation of a clear decrease of anhydrite. Still, because of these hydration products, treatment of HVC cyclone ash affects the strength results and is the reason that HVC cyclone ash for 20% replacement has a 5MPa lower strength compared to Twence fly ashes. If metallic aluminium could be removed by an eddy current separator and one hour of water treatment is not effecting the fly ash (as is believed due to earlier results), HVC cyclone can still have a potential as filler or as a partly replacement of cement, with the same properties as Twence fly ashes.

Comparing thermally treated Twence boiler fly ash with Twence air filtered boiler fly ash, comparable results are found for 20% replacement. Also the strength results of the crushed samples with different replacement percentages of 5% and 10% are similar.

The treatment of Twence cyclone only has effect for high replacement percentages of 20%. This is probably due to the following reason: in general a small replacement amount will not have much influence on strength results than larger replacement amounts. If treatment is really effective it is clearly visible by an increase in strength compared to the original, not treated bio-energy fly ash. For this sufficient amount of replacement is needed, which is clearly visible for 20% replacement because then the applied bio-energy fly ash really plays a roll.

*Observing the flexural and compressive strength results of bio-energy fly ashes show a material that has similar properties to those of reference PKVA SMZ. The effect of crushing the fly ashes to increase the reactivity is not always that effective as was initially thought.*

It is believed that the obtained strength results can be improved because of two effects during the creation of the samples. First, the water demand is kept the same for different replacement factors because it was uncertain if the bio-energy fly ash behaves the same as PKVA SMZ. From the strength results and the delayed strength increase in time, it seems that bio-energy fly ash indeed possesses pozzolanic properties and that the water demand therefore could be decreased. Second, the used jolting method described in NEN-EN-196-1

is believed to be insufficient. After crushing, a high porosity was found by insufficient removal of air bubbles. It is therefore preferred to use a vibration table.

Finally, normally the spherical shape of the fly ash particles produces a rolling effect at the point of aggregate contact, reducing friction and improving the fluidity of the cement paste. It was found that for treated bio-energy fly ash the spread of the crushed and not crushed bio-energy fly ash was good at all replacement factors, despite the coarse particles. This is an improvement because the spread of the original bio-energy fly ash was poor (probably due to trace elements and contaminants on the surface of the particles). This would indicate the need for plasticizers. Because of the good flow ability of the treated bio-energy fly ashes, plasticizers are never used.

### 10.3 Recommendations

During the research it was not possible to obtain all required results and discussed subjects in the literature study. The points described below and subsequent investigations could lead to better understanding and potential of the use of bio-energy fly ash as cement replacement.

Further analysis that could be performed:

- LOI content of treated bio-energy fly ash;
- Chloride content of treated bio-energy fly ash (XRF-data);
- Testing the efficiency of water treatment when removing known amounts of chlorides with similar pH-value as when water treating bio-energy fly ashes.
- Leaching test on treated fly ashes to conform that the bio-energy fly ashes are inert or non-hazardous;
- Leaching tests on created samples to test if they fulfil the requirements of non-shaped building materials;
- Analysis of chloride content of coal particles using SEM/XRF;
- Perform X-ray diffraction measurements with smaller step size (<0.02) and count time (<1.0) for more accurate results;
- X-ray diffraction on bio-energy fly ashes to investigate the quantity of amorphous or glass phases;
- X-ray diffraction on the created samples to investigate the hydration products.

Investigations that could be performed:

- Using K-factor to determine the required water cement ratio's;
- Use of plasticisers to see their effect on the strength development;
- Activation effect by adding free lime / other activators.



## References

Accreditatiecollege Bodembeheer, 2008. *Accreditatieprogramma voor keuring van partijen grond, bouwstoffen en korrelvormige afvalstoffen Onderdeel : Algemeen AP04 - A*. Gouda: Stichting Infrastructuur Kwaliteitsborging Bodembeheer (SIKB).

Advanced cement technologies, 2012. *Metakaolin*. [Online] Available at: <http://www.metakaolin.com/metakaolin> [Accessed 3 February 2012].

Afval Energie Bedrijf, 2006. *Méér waarde uit afval*. Amsterdam: Energie Bedrijf gemeente Amsterdam.

Banse, M., Faaij, A., Hoefnagels, R. & Dornburg, V., 2009. *Analysis of the Economic Impact of Large-Scale Deployment of Biomass Resources for Energy and Materials in the Netherlands*. Santiago de Chile: EnergieTransitie Platform 'Groene Grondstoffen'.

Barron, A., 2010. *Hydration of Portland Cement*. [Online] (1.11) Available at: [http://cnx.org/content/m16447/1.11/content\\_info](http://cnx.org/content/m16447/1.11/content_info) [Accessed 5 November 2011].

Brouwers, H.J.H., 2005. The work of Powers and Brownyard revisited: Part 2. *Cement and Concrete Research*, 35, pp.1922-36.

CBS, 2011. *Renewable electricity 1991-2010*. Den Haag: Centraal Bureau voor de Statistiek.

CDEM Minerals BV, 2003. *Top-Crete*. Product information. Geldermalsen: CDEM.

CDEM, 2011. *Company overview, Our History*. [Online] Available at: <http://www.cdem.nl/node/13> [Accessed 25 November 2011].

Changling, H., Osbaeck, B. & Makovicky, E., 1995. Pozzolanic reaction of six principal clay minerals: Activation reactivity assessment and technological effects. *Cement and Concrete Research*, 25, pp.1691-702.

Costa, U. & Masazza, F., 1981. Natural pozzolanas and fly ashes. *Material and Research Society: effects of fly ash incorporation in cement and concrete*, 16 November. pp.134-44.

Costa, U. & Massazza, F., 1983. Some properties of pozzolanic cements containing fly ashes. In ACI, A.c.i., ed. *Proceedings of the CANMET/ACI first international conference on the use of fly ash, silica fume, slag and other mineral by-products in concrete vol 1*. Detroit, 1983.

CUR, 1992. *Vliegas als vulstof in beton*. Gouda: Civieltechnisch Centrum Uitvoering Research en Regelgeving.

Diamond, S., 1981. Effects of two danish fly ashes on alkali contents of pore solutions of cement-fly-ash pastes. *Cement and Concrete Research*, 11, pp.383-94.

Diamond, S., 1985. *Selection and Use of Fly Ash for Highway Concrete. Joint highway Research Project*. West Lafayette, Indiana: Purdue University.

Doudart de la Grée, G.C.H., 2012. *Physical-chemical upgrading and use of bio-energy fly ashes as building material in the concrete industry*. Graduation report for master degree. Eindhoven: Eindhoven University of Technology.

Dpcleantech, 2011. *Biomass and waste to energy solutions*. [Online] Available at: <http://www.dpcleantech.com/about-dpcleantech/past-a-future> [Accessed 21 October 2011].

- DWMA, 2010. *Jaarverslag 2009. Monitoring reststoffen van de verbranding van afval, biomassa zuiveringslib [Monitoring residues from incineration of waste, biomass and sewage sludge]*. Annual report. Bunnik: Libertas Dutch Waste Management Association.
- Eijk, R.J.v., 2001. *Hydration of cement mixtures containing contaminants*. Twente: PrintPartners Ipskamp BV.
- Fox, J.M., 2005. Changes in fly ash with thermal treatment. In *Submitted for consideration in the 2005 World of Coal Ash*. Cleveland, 2005.
- Fraay, A., 1987. *Vliegas in mortels en beton, puzzolane werking, sterkte en duurzaamheid, vol. 1 en 2*.
- Ghose, A. & Pratt, P.L., 1981. Studies of the hydration reactions and microstructure of cement-fly-ash pastes. In Diamond, S., ed. *Material research society-in: Effects of fly ash incorporation in cement and concrete*. Boston, 1981.
- Glimmerveen, L., 1996. Should trees now be more actively used in the rehabilitation of heavy metal contaminated sites? *Aspects of Applied Biology*, 44, pp.357-61.
- Heiri, O., Lotter, A.F. & Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Paleolimnology*, 25, pp.101-10.
- Hendriks, C.F., Koppen, A.E. & Nijkerk, A.A., 1999. *De Bouwcyclus*. Best: Æneas BV.
- Herbert, L., 2011. *The chartered institution of waste management*. [Online] Available at: [http://www.ciwm.co.uk/web/FILES/About\\_CIWM/100\\_yrs\\_London\\_and\\_SE\\_centre.pdf](http://www.ciwm.co.uk/web/FILES/About_CIWM/100_yrs_London_and_SE_centre.pdf) [Accessed 30 November 2011].
- Het Europees Parlement en de Raad, 2001. *RICHTLIJN 2001/77/EG betreffende de bevordering van elektriciteitsopwekking uit hernieuwbare energiebronnen op de*. Brussel: Publicatieblad van de Europese Gemeenschappen.
- Hewlett, P.C., 2004. *Lea's Chemistry of Cement and Concrete*. 4th ed. Elsevier Science & Technology Books.
- HVC, 2009. *Publicaties*. [Online] Available at: [http://www.hvcgroep.nl/over\\_hvc/publicaties](http://www.hvcgroep.nl/over_hvc/publicaties) [Accessed 26 September 2011].
- Joshi, R.C., 1970. *Pozzolanic Reaction in Synthetic Fly ashes*. Ames: PhD Dissertation, Iowa State University.
- Joshi, R.C., 1979. Sources of Pozzolanic Activity in Fly Ashes. In *A critical Review. Proceedings, 5th international fly ash Utilization symposium*. Atlanta, Georgia, USA, 1979.
- Joshi, R.C. & Lohtia, R.P., 1997. *Fly ash in concrete : production, properties and uses*. Amsterdam: Gordon & Breach Science.
- Joshi, R.C. & Marsh, B.K., 1986. Some Physical, Chemical and Mineralogical Properties of Some Canadian Fly Ashes. *MRS Proceedings*, 86, pp.113-25.
- Killoh, D.C., Parrott, L.J. & Patel, R.G., 1989. Influence of Curing at Different Relative Humidities on the Hydration and Porosity of a Portland/Fly Ash Cement Paste, in Fly Ash, Silica Fume. In Malhotra, V.M., ed. *Slag and Natural Pozzolans in Concrete*. Detroit, 1989.
- Kinuthia, J.M., Wild, S., Sabir, B.B. & Bai, J., 2000. Self-compensating autogenous shrinkage in Portland cement-metakaolin-fly ash pastes. *Advanced Cement Research* 12, pp.35-43.

- Kurtis, K., 2011. *Lecture, Portland Cement Hydration*. [Online] Atlanta, Georgia Available at: <http://people.ce.gatech.edu/~kk92/hyd07.pdf>.
- Lea, F.M., 1970. *The Chemistry of Cement and Concrete*. 3rd ed. London: EDWARD ARNOLD PUBL.
- Lukas, W., 1976. *Matér. Constr.* 9. p.331.
- Mehta, P.K., 1984. *Testing and Correlation of Fly Ash Properties with Respect of Pozzolanic Behavior*. California: EPRI, Palo Alto.
- Mindess, S. & Young, J.F., 1981. *Concrete*. N.J.: Prentice-Hall: Englewood Cliffs.
- Murat, M., 1983. Hydration reaction and hardening of calcined clays and related minerals. *Cement and Concrete Research*, 13, pp.259-66.
- NETL, 2011. *History of Coaluse*. [Online] Available at: <http://www.netl.doe.gov/keyissues/historyofcoaluse.html> [Accessed 30 November 2011].
- Neville, A.M., 2004. *Properties of Concrete*. 4th ed. England: Pearson Education limited.
- Ogawa, K., Uchiwaka, H., Takemoto, K. & Yasul, I., 1980. The mechanism of the hydration in the system c3s-pozzolana. *Cement and concrete research* 10, V, pp.683-96.
- Port of Antwerp, 2000-2006. *Research project landscape mounds, App 06. Thesis "Broekpolder"*. [Online] Available at: [http://www.landscapingwithsediments.be/html/en\\_download.html](http://www.landscapingwithsediments.be/html/en_download.html) [Accessed 5 Oktober 2011].
- Rayment, P.L., 1982. The effect of pulverized-fuel ash on the c/s molar ratio and alkali content of calcium silicate hydrates in cement. *Cement and Concrete Research*, 12, pp.133-40.
- Sakai, E. et al., 2005. Hydration of Fly Ash Cement. *Cem. Concr. Res.*, 35(6), pp.1135-40.
- Services, P.I., 2011. *Cenospheres*. [Online] Available at: <http://www.primaryinfo.com/projects/cenospheres.htm> [Accessed 2011].
- Takemoto, K. & Uchikawa, H., 1980. Hydration of pozzolanic cement. In *7th international congress on the chemistry of cement*. Paris, France, 1980.
- Taylor, H.F.W., 1997. *Cement chemistry*. 2nd ed. New-York: ThomasTelford.
- Taylor, H.F.W., Mohan, K. & Moir, G.K., 1985. Analytical study of pure and extended portland cement pastes. *Journal of the American Ceramic Society*.
- Tweede Kamer, 1999. *Uitvoeringsnota Klimaatbeleid*. 's-Gravenhage: Sdu Uitgevers.
- Uchikawa, H., 1986. *J. Res. Onada Cement Company* 38.
- Uchikawa, H., Ogawa, K. & Uchida, S., 1985. Influence of character of clinker on the property of cement paste. *Cement and Concrete Research*, 15, p.561.
- United Nations, 1998. *Kyoto protocol to the United Nations framework convention on climate change*. Kyoto.
- van den Berg, P., 2006. *Beton technologie voor onderwijs en praktijk*. Betonvereniging / Cement & Beton Centrum.
- Vliegassunie, 2008. *Jaarverslag Vliegassunie 2007*. p.28.
- VROM, 2007. *Regeling bodemkwaliteit*. *Staatscourant*, 20 December. p.67.

- VROM, 2010. *Landelijk afvalbeheerplan 2009-2021. Naar een materiaalketenbeleid*. Den Haag: Ruimte en Milieu. Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer.
- Wang, Q., Feng, J. & Yan, P., 2012. The microstructure of 4-year-old hardened cement-flyash paste. *Construction and Building Materials*, 29, pp.114-19.
- Wesche, K., 1991. *Fly ash in Concrete Properties and Performance*. Rilem report 7. London: E & FN SPON The International Union of Testing and Research Laboratories for Materials and Structures.
- Wijers, G.J., 1995. *Derde Energie Nota*. 's-Gravenhage: Sdu Uitgeverij.
- Wild, S., Khatib, J. & Roose, J.L., 1998. Chemical and autogenous shrinkage of Portland cement-metakaolin pastes. *Advance Cement Research*, 10, pp.109-19.
- Yudovich, Y.E. & Ketris, M.P., 2005. Chlorine in coal: A review. *International Journal of Coal Geology*, 67, pp.127-44.
- Zhang, M.H. & Malhotra, V.M., 1995. Characteristics of a thermally activated alumino-silicate pozzolanic material and its use in concrete. *Cement and Concrete Research*, 25, pp.1713-25.