Fly ash from coal and biomass for use in concrete

Origin, properties and performance

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Fly ash from coal and biomass for use in concrete

Origin, properties and performance

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Aan de oevers van Babylons stromen zaten wij neer en de gedachten aan u, Sion,
vervulde ons hart met weemoed (naar Psalm 137)

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LIST OF BOXES

LIST OF ABREVIATIONS

AFM	ash forming matter
AI	Activity index
ar	as received
BE	back-scattered electron
BMP	biomass pellets
CCSEM	computer controlled scanning electron microscopy
CR	cacao residues
CRE	co-combustion experiment with mainly cacao residues
CF	cattle feed
Daf	dry and ash free
DW	demolition wood
EDX	energy dispersive X-ray
EXT	Extraction
e/e	energy on energy base
EPC	Equivalent Performance Concrete
ESP	Electro Static Precipitator
HPC	High Performance Concrete
ICP(-MS)	Inductively Coupled Plasma (Mass Spectrometry)
LHV	Lower Heating Value [MJ/kg]
LOI	Loss on ignition
MBM	meat and bone meal
MBME	co-combustion experiment with mainly meat and bone meal
MS	Municipal sewage sludge
MSE	co-combustion experiment with municipal sewage sludge
MSEref	reference combustion experiment for municipal sewage sludge
MWe	Electric capacity in Mega Watts
MW_{th}	Thermal capacity in Mega Watts
OC	ordinary concrete
PD	Poultry litter
PK	Palm kernels
PKE	co-combustion experiment with palm kernels
PS	paper sludge
PSE	co-combustion experiment with mainly paper sludge
PSEref	reference combustion experiment for paper sludge
REF	reference coal fly ash
SEM	Scanning Electron Microscopy
SRF	Solid Recovered Fuel
WD	Wood (not contaminated)
WPP	Wheat Pollard pellets
WPPE	co-combustion experiment with wheat pollard pellets
XRD	X-Ray diffraction

LIST OF SYMBOLS

µm	micrometer (m^{-6})
MJ	megajoule
MW	megawatt

VOORWOORD

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Deze dissertatie was een grote operatie, met diverse hindernissen onderweg. Het bleek geen brug te ver. Het heeft echter wel aanzienlijk langer geduurd dan gepland. De stelling van het thuisfront dat het daarmee niet afwijkt van andere privé projecten, kan door de promovendus niet verworpen worden.

Arnhem, 31 augustus 2017

Angelo Sarabèr

1 INTRODUCTION

1.1 General

The Romans were probably the first in history using concrete at large scale for their construction works. Pozzolans together with lime were used as binder in their concrete. The pozzolans, mainly volcanic ashes and ground ceramic bricks and tiles, react with lime to form water resistant, durable reaction products. The Roman architect and author Vitruvius gave already prescriptions how to produce good quality concrete based on pozzolans [1.1]. Also in modern times pozzolans are used to produce concrete. The most well-known modern synthetic pozzolan is coal fly ash. This material is a fine powder of mainly spherical glassy particles, derived from burning of pulverized coal. It has pozzolanic properties and consists essentially of SiO_2 and Al_2O_3 [1.2]. Pozzolanic materials do not harden when mixed with water but, when finely ground and in the presence of water, they react at normal ambient temperature with dissolved calcium hydroxide to form strength developing calcium silicate and calcium aluminate components. These components are similar to those which are formed in the hardening of hydraulic materials [1.3].

Coal fly ash is used as raw material for concrete since decades. The first comprehensive study to the role of fly ash in concrete goes back to 1937 [1.4]. In 1948-1953 the Hungry Horse Dam in the Rocky Mountains (see figure 1.1) was constructed with 3 million m^3 of concrete, whereby 35% of the Portland cement was replaced with fly ash [1.5]. This is probably the first big project using coal fly ash for concrete. Since the reintroduction of coal fired power plants in the Netherlands fly ash is used for concrete at large scale. Much research has been carried out on the properties of fly ash and on concrete with fly ash. This resulted in national regulations [1.6-1.10] and later also European regulations [1.11] to assess the quality of the fly ash in view of its use in concrete and mortar. Fly ash is able to replace a significant part of cement in concrete. This replacement has in general a positive influence on workability, sustainability (less primary materials, reduction of carbon foot print) and enhanced durability (see further 2.1). Only in EU (15) 7,654,000 tons of fly ash were used in concrete in 2010 [1.12].

Figure 1:1: Hungry Horse dam: concrete with 35% replacement of cement with fly ash [1.13]

Co-combustion of biomass in coal fired power stations was introduced to reduce CO_2 emissions in the second half of the nineties of the last century. Co-combustion means that in the existing power plants other fuels are fired together with coal. In this case the share of coal in the fuel mix is ≥50% m/m. Initially, co-combustion was limited, but with increasing share, questions rose about the performance of the concrete made with this fly ash and the necessary requirements to ensure the quality. These questions are caused by the lack of (systematic) knowledge of the relation between the ash forming matter in these biomasses, the formation of ash in the boiler and the properties of the generated fly ash. Due to co-combustion the content of several components in the fly ash will change compared to standard coal fly ash. Especially phosphor, potassium and calcium will increase. The amount of phosphorus is normally limited to about 1% m/m (as P_2O_5) in fly ash from 100% coal. Co-combustion may lead to about 5 % m/m or even more phosphorus. Phosphorus that is present as phosphate is also known as a retarder of cement hydration and, therefore, a critical component for the performance of concrete. Calcium as unburnt lime may cause unsoundness[1] of concrete, while potassium is one of the reaction compounds in the alkali silica reaction (ASR). To maintain the large scale utilization of fly ash in concrete with its benefits, systematic knowledge of the relation between the fuels, the combustion process, the properties of fly ash and the performance of concrete with this fly ash is necessary. This succession is given in figure 1.2 (A and B).

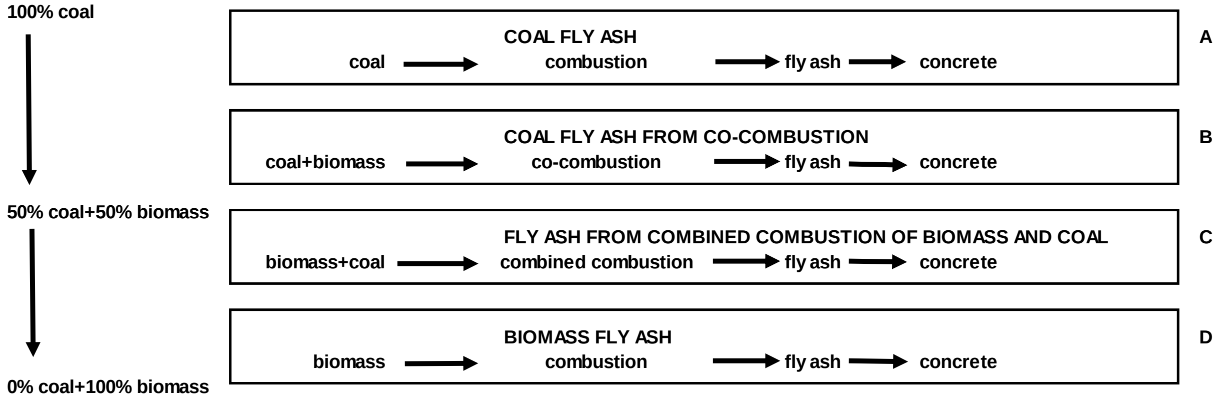

Figure 1:2: Steps from fuel to concrete for fly ash from coal and/or biomass

A further development is that more biomass than coal is fired in a power plant (figure 1.2, succession C and D). In this case the share of coal is <50% m/m. In general, wood is the only biomass with sufficient availability and technical suitability to be (co-)fired more than 50% in the large scale pulverized coal boilers. Therefore, above 50% biomass combustion only wood will be considered. Up to 50% co-combustion of wood, the wood ash content in the resulting fly ash is limited due to the low ash forming matter[2] of wood compared to coal (see figure 1.3 and section 2.5). This fly ash may be suitable for use as pozzolan in concrete. Ash from wood has high concentrations of CaO, P_2O_5 and K_2O and low concentrations of Al_2O_3 compared to ash from coal. Above about 70%, the contribution of

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[1] Unsoundness or volume instability of concrete occurs as expansion with or without formation of cracks.

[2] Ash is defined as the solid mineral residue from a complete fuel combustion (see NEN-EN 14588: 2010. Solid biofuels terminology, definitions and descriptions). In practice the term *ash content* is used to express the amount of ash that will be formed after combustion. In this thesis the term *ash forming matter* will be used to express that ash as such is not present in the fuel itself but only a residue of the fuel after a combustion.

wood in the fly ash will strongly increase and thereby influence the composition and the properties for use in concrete. The suitability and the role of such fly ash has to be (re)considered (sequence C and D).

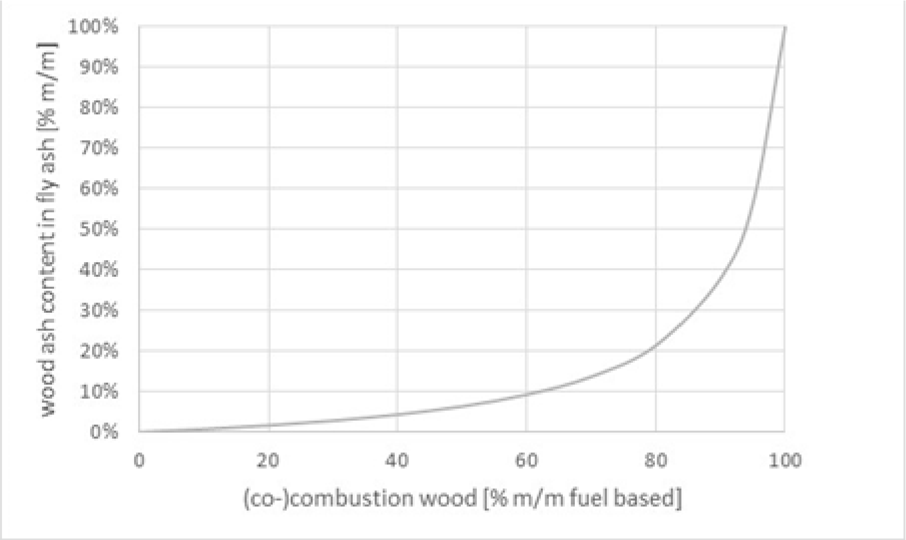

Figure 1:3: Relation between the share of wood in the fuel and the wood ash content in the generated fly ash (indicative)

Besides technical aspects, the use of fly ash from co-combustion and from combined combustion of wood and coal should also fit within corporate social responsibility. Especially the sustainability of this use and the way it fits with the ideas of circular economy are relevant. Sustainability is defined in the UN report ‘Our Common Future’ (1987) that states: Sustainable development seeks to meet the needs and aspirations of the present without compromising the ability to meet those in the future. In the concept of a circular economy the value of products and materials is maintained as long as possible. Generation of waste and use of resources is minimised. Resources are kept within the economy when a product has reached the end of its life, to be used again and again without loss of its performance [1.14].

1.2 Objectives and goals

Fly ash from coal combustion is widely used in concrete because of its contribution to strength development of concrete and its benefits regarding the improvement of workability, sustainability and durability. The properties of fly ash and the properties of concrete with fly ash have been well investigated. These investigations were the basis for the technical regulations to assess the quality for its use. Because of the concern about climate change more and more biomass is co-fired to reduce the CO_2 emissions of coal-fired power plants. This means that the fly ash is not only derived from the ash forming matter in coal, but also from different types of biomass. To keep fly ash as a valuable resource for concrete it is essential to create thorough understanding of the relation between the composition of the biomass fuel, the combustion process, the properties of fly ash and concrete made with this fly ash. This understanding is essential for the development of an adequate quality assessment.

The goals in this PhD thesis are *to create thorough understanding of:*

- The relation between the fuels, being biomass with or without coal, the combustion process, and the properties of the generated fly ash and the technical performance of concrete made with this fly ash and
- The impact of (co)combustion of biomass on the sustainability and circularity aspects of the use of this fly ash in concrete.

The following questions have to be answered to achieve these goals:

1. Which is the effect of co-combustion of biomass on the properties of fly ash?
2. Can these properties be explained by the composition of the fuel and the combustion process?
3. Which effects has co-combustion of biomass on the performance of concrete made with this fly ash. Can this be explained by the properties of the fly ash?
4. Which are the properties of fly ash from the combustion of biomass (wood) with or without coal? Can this be explained by the composition of the fuel and the combustion process?
5. Are fly ashes from the combustion of biomass (wood) with or without coal able to act as a pozzolan in concrete? If not can these fly ashes be used in concrete in a different way?
6. To what extent does the use of fly ash from co-combustion of biomass (wood) fit within the concept of circularity?

Basic preconditions in this PhD thesis are:

- Only (co-)combustion in pulverized coal boilers fired with hard coal or biomass will be investigated. As a consequence, (co-)combustion in lignite fired boilers and other type of boilers like fluidised bed and grate-fired boilers are not considered. Co-combustion is further limited to direct co-combustion (see appendix A)
- Herbaceous and annual growth material will not be considered in this study, because these types are not widely used on a large scale in pulverized coal boilers
- Combustion of >50% of biomass will only be assessed for wood as this is the only biomass with sufficient availability and technical suitability to be fired in the large scale pulverized coal boilers
- The use of fly ash as pozzolan will only be assessed for the combination with Portland cement. Combinations with other cements like blast furnace slag cement and alumina cement are not considered.
- The focus of the dissertation will be on technical and sustainability aspects.

1.3 Research strategy

Several steps can be distinguished in this PhD dissertation. The research strategy is summarized in figure 1.4.

Literature study co-combustion fly ash and wood fly ash (chapter 2)

A literature study has been performed to get a state-of-the-art about of the origin and composition of biomass, the reactions during ash formation and the effects of co-combustion of biomass on the properties of fly ashes and on the performance of concrete.

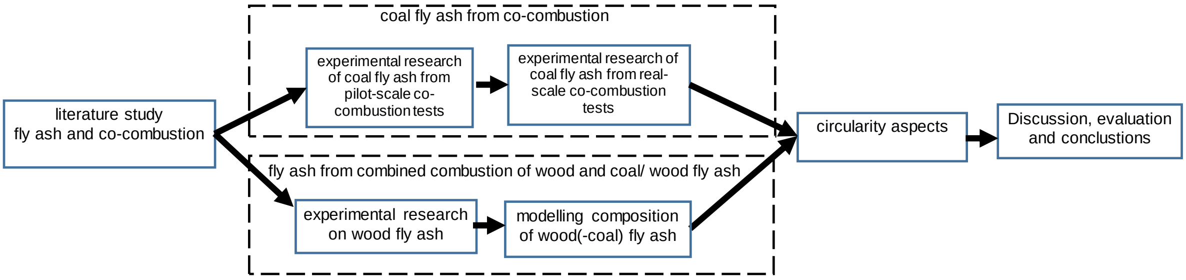

Figure 1:4: Research strategy of this PhD dissertation

<u>Experimental research of coal fly ash from pilot-scale co-combustion tests (chapter 3)</u>
As first step of an extensive experimental study on the relation between co-combustion and fly ash quality, co-combustion experiments were performed in a 1 MW_{th} test boiler (pulverized coal boiler) to generate fly ashes for further research. One reference test with Paso Diablo coal was performed and nine co-combustion tests were performed with this Paso Diablo coal and one secondary fuel at three different co-combustion percentages. Poultry litter, demolition wood and Solid Recovered Fuels[3] (SRF) were selected for these tests. The generated fly ashes were physically, chemically and mineralogically characterized. The fly ashes were investigated in view of their use in concrete. The results of this experimental research were published in Fuel Processing Technology [1.15].

<u>Experimental research of coal fly ash from real-scale co-combustion tests (chapter 4)</u>
As second step, co-combustion fly ashes were investigated from full-scale co-combustion experiments in several Dutch power plants. The involved secondary fuels were several agricultural residues, meat and bone meal, paper sludge and municipal sewage sludge. The generated fly ashes were physically, chemically and mineralogically characterized. The fly ashes were investigated in view of their use in concrete. The results of this experimental research were also published in Fuel Processing Technology [1.16].

<u>Experimental research of wood fly ash (chapter 5)</u>
Fly ashes from combustion of wood were characterized by physical, chemical and mineralogical methods. The fly ashes were investigated in view of their use in concrete. The characterization also provided information about the combustion process as input for chapter 6.

<u>Modelling fly ash from combined combustion of wood and coal (chapter 6)</u>
This step involves the prediction of the chemical composition of fly ash from combined combustion of wood and coal using the concept of relative enrichment factors. Thereby the existing KEMA Trace model ® is used incorporating the information from literature and analyses performed in this thesis.

<u>Circularity of the use of fly ash from (co-)combustion of biomass (chapter 7)</u>
The impact of the use of fly ash from (co-)combustion of biomass on the technical and biological cycle was investigated.

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[3] Fuel which consists of the separated high caloric fraction from municipal solid waste.

Discussion, evaluation and conclusions (chapter 8 and 9)

The last two chapters presents a comprehensive evaluation and discussion and general conclusions of this dissertation.

1.4 References

[1.1] Lamprecht, H.-O, 2001. Opus Caementitium. Bautechnik der Römer. 5th edition, pp 33-47. Verlag Bau+Technik. Düsseldorf. Germany.

[1.2] NEN, 2012. NEN-EN 450-1. Fly ash for concrete. Part 1: Definition, specifications and conformity criteria. Page 6.

[1.3] NEN, 2011.EN 197-1 Cement - Part 1: Composition, specifications and conformity criteria for common cements. Page 11.

[1.4] Malhotra, V.M. and Ramezanianpour, A.A. (CANMET). 1994. Fly ash in concrete. Second edition. Ministry of Supply and Services. Canada. Page 2.

[1.5] Lutze, D and vom Berg, W., 2010. Handbook on fly ash in concrete. Second edition. Verlag Bau+Technik. Page 9 and page 81-82.

[1.6] CUR, 1983. Application of Portland fly ash cement and fly ash in concrete. CUR-recommendation 1. Gouda (in Dutch).

[1.7] CUR, 1987. Fly ash in concrete. CUR-recommendation 12. Gouda (in Dutch).

[1.8] CUR, 1991. Fly ash for mortar and concrete. CUR-recommendation 26. Gouda (in Dutch).

[1.9] CUR 1999. Application of fly ash in mortar concrete. CUR-recommendation 70. Gouda (in Dutch).

[1.10] CUR 2003. Application of fly ash in concrete, mortar and grout. CUR-recommendation 94. Gouda (in Dutch).

[1.11] NEN, 1994. NEN-EN 450-1. Fly ash for concrete. Part 1: Definition, specifications and conformity criteria.

[1.12] ECOBA, 20. Production and Utilization of CCPs in 2010 in Europe (EU 15)

[1.13] US Bureau of Reclamation, 2016. www.usbr.org. Downloaded on October 4th 2016.

[1.14] European commission, 2015. Circular Economy Package: Questions and Answers. Fact sheet.

[1.15] Sarabèr, A.J., Co-combustion and its effects on fly ash quality; pilot-scale experiments. In: Fuel Processing Technology 104 (2012) pp 104-114.

[1.16] Sarabèr, A.J., Co-combustion and its effects on fly ash quality; real-scale experiments. In: Fuel Processing Technology 124 (2014) pp 68-82.

2 LITERATURE STUDY

This literature study gives a state-of-the-art of the knowledge on (co-)combustion of biomass and the properties of fly ash and its use in concrete. First, in section 2.1 and 2.2 a description is given of the generation of coal fly ash, the fuel (coal), the conversion process, the properties of the ash and its use in concrete. The sections 2.3-2.5 describe the same issue for fly ash from (co-) combustion of different types of biomass. In section 2.6 an evaluation of the state of the art knowledge is presented, thereby answering the research questions as far as possible and identifying the remaining questions.

2.1 Generation of fly ash

2.1.1 General

In 1974 the last Dutch coal mine closed its doors and the use of coal in the Netherlands decreased to an absolute minimum (see figure 2.1). The first oil crisis in 1973-1974 caused a reconsideration of the use of fuels for electricity in the Netherlands. This lead to the re-introduction of coal, but now from a geopolitical point of view. The re-introduction was possible by the realization of new coal fired power plants and by the conversion of existing oil and gas fired units to coal firing.

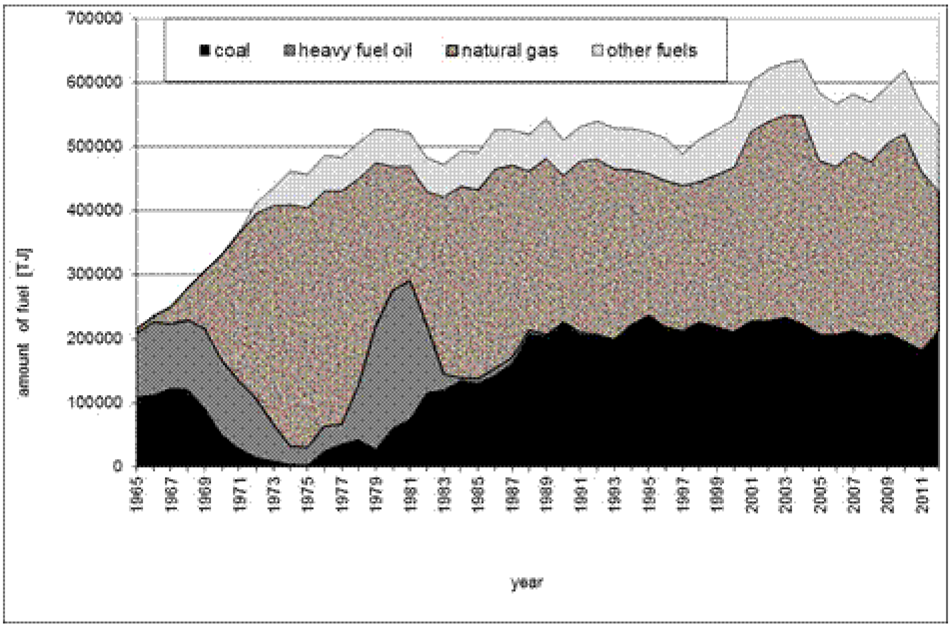

Figure 2:1: Development of the use of fuels for power generation in the Netherlands [2.1]

In 2002 the Dutch power companies and the government agreed to reduce the greenhouse gas emissions of coal-fired power plants by signing the covenant "Coal-fired power plants and CO_2 reduction". The power companies committed themselves to reduce the greenhouse gas emissions by replacing coal with biomass [2.2]. This lead to the introduction of a wide range of secondary fuels. Co-

combustion reached a maximum of 13% on an energy base (overall average) in 2005 [2.1]. In 2013 the Energy Agreement for sustainable growth (Energieakkoord) was signed by the government, the power sector and many other parties, whereby the use of renewable energy will increase to 14% in 2020 (wind, solar and biomass). In this agreement it is also stated that maximum 25 PJ output (corresponding with 6944 GWh) will be generated with biomass in coal-fired power stations [2.3].

Biomass is not only co-fired in coal fired power stations, but is also fired in several former pulverized coal-fired power plants which are converted to fire 100% wood. Examples are the power station Centrale Rodenhuize in Belgium (180 MW_e), Drax in the United Kingdom (2 units of each 660 MW_e) and Avedøre in Denmark (793 MW_e and 918 MW_{ht}).

2.1.2 Generation of coal fly ash in pulverized coal boilers

All Dutch coal fired power plants are using pulverized coal boilers (see figure 2.1). Pulverised coal fired boilers are in use since 1920 [2.4]. The typical aspect of this boiler is that pulverized coal is pneumatically transported into the combustion chamber and combusted in a cloud. This is only possible if the grain size of the coal is sufficiently reduced (grain size <100 μm; 70-95% < 75 μm). Pulverized coal is injected into the combustion chamber through the burners. The boiler has normally a flue gas exit temperature of about 1050-1300 °C [2.4, 2.5]. The temperature in the flame itself reaches temperatures in excess of 1700°C as shown by recent calculations by DNV GL for a Dutch coal-fired boiler [2.6]. Other sources mention even temperatures around 2000 °C. The average residence time of an ash particle in the boiler is 1-3 seconds. A residence time of about one second is suggested for instance by Baxter [2.7] for older boilers with a low burn-out. The main part (about 85-90 % m/m) of the ash that is produced during the combustion process, leaves the boiler with the flue gasses; the other part falls directly or indirectly (after slagging) to the bottom of the boiler (furnace bottom ash). The ash particles are removed by electrostatic precipitators (ESP). After removal, the fly ash is collected and pneumatically transported to the storage silos. From there it is transported by ships and trucks to the market.

Secondary fuels can be put into the combustion system using various ways. The simplest way is to add the secondary fuel into the coal transport system before the coal mill. Further, treated biomass can be put into the transport system between the coal mill and the burner. A more advanced way, especially for higher co-combustion percentages, is to use a dedicated burner for secondary fuels.

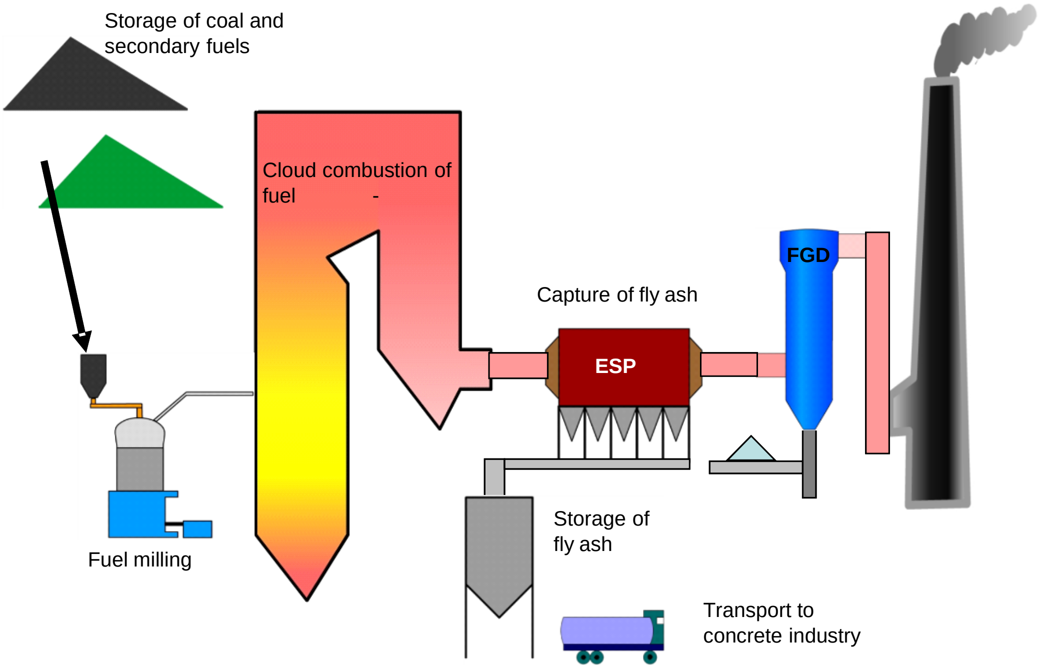

Figure 2:2: Principle of pulverised coal fired boiler [2.8]

2.2 Fly ash from coal

2.2.1 Origin

Coal can be defined as a combustible, sedimentary organic rock, which is composed mainly of carbon, hydrogen and oxygen. It is formed from vegetation, which has been consolidated between other rock strata and altered by the combined effects of pressure and heat over millions of years to form coal seams (definition used by the World Coal Institute). A coal layer is often a part of a regular succession of sediments (a so-called cyclothem) like sand, shale, feldspar, limestone etc. The coal layer itself may also contain interlayers with these materials and inclusions of foreign material. It is conceivable that also after processing of the coal, a certain amount of these components is still present in the coal and not in the rejects. In general the term mineral matter is used for these components. Mineral matter can be defined as the sum of the minerals and inorganic matter associated with coal [2.9].

This mineral matter can be present (see also figure 2.3) in four basic forms [2.10]:

1. Excluded mineral grains, which break free of the coal during milling. These grains are relatively large.
2. Included mineral grains which are retained in the coal during milling and tend to be smaller.
3. Organically bound elements, which are distributed within the different organic components in coal (macerals). These elements are liberated during the combustion process
4. Salts dissolved in water in the coal.

Lower rank coals[4], like lignite and sub-bituminous coals, contain relatively more organically bound elements and dissolved salts, than in higher rank coals (bituminous coals) [2.9]. In this study the term ash-forming matter is preferred instead of mineral matter. It covers the same components but also S, and carbon as far as it ends in the ash (fly ash or furnace bottom ash) instead of the flue gasses.

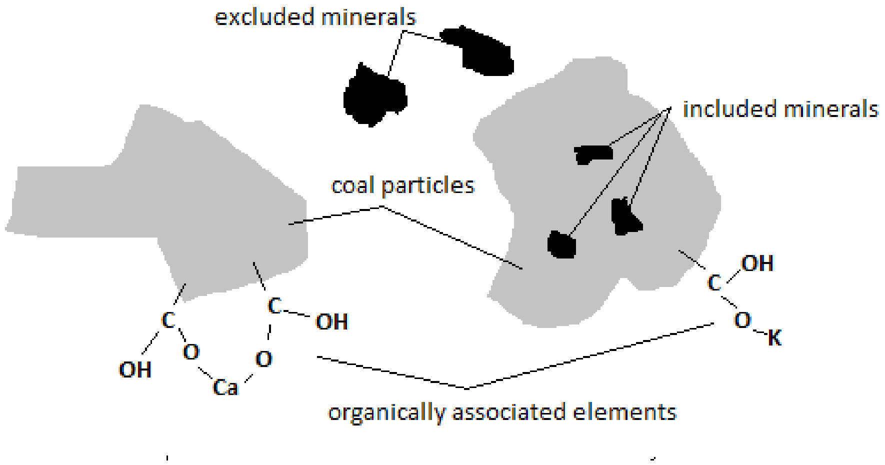

Figure 2:3: Distribution of mineral matter in coal (after [2.11])

Coal contains most of the elements of the periodic system, but the concentration may be very low. The concentrations of Al, Ca, Fe, K, Mg, and Si in ash from hard coal are in the range 1-32 % m/m [2.12]. Ba, Sr, Na, P, It and S are present in lower concentrations; in the range 0.1-1% m/m (see appendix B). Other elements of the periodic system are below 0.1% m/m and are more relevant for environmental and health properties than for the technical properties of concrete. The mode of occurrence of first two groups of elements in coal is described below.

Aluminium and silica are present in coal in different silicate and alumina silicate minerals. The clay minerals and quartz are usually about 60-90 % of the total mineral matter in coal [2.4]. Quartz is a very common silicate mineral in coal. Other pure silicates in coal are chalcedony and opal, but these are of minor importance. The clay minerals are mainly kaolinite, illite, montmorillonite and mixed-layers of illite and montmorillonite. Other alumina silicate minerals in coal are feldspars and mica (mainly muscovite). Feldspars are represented by K-feldspars and plagioclases. The latter have a predominantly sodium-rich composition. *Barium* can be present in several minerals, but barite seems to be the most important one [2.9, 2.15]. *Iron* is mainly present in coal as pyrite, ankerite, and siderite and to a less extent as marcasite and hematite [2.11; 2.15]. The major iron-bearing mineral in Northern Hemisphere coals is typically pyrite, while it is usually siderite in the Southern Hemisphere [2.16]. *Calcium* in coal is present in the inorganic matter, but a small amount is also present in the organic phase. In higher rank coals only a small part of the ash-forming elements Na, K, Ca and Mg are organically bound [2.17]. Calcium is mainly present as calcite and dolomite and to a lower extent in other minerals like aragonite, ankerite, apatite and gypsum. After milling of the coal carbonate

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[4] Coal rank is a classification for coal, generally based on the content of volatiles. Lignite or brown coal is the lowest rank of coal (peat is not seen as part of the coal rank) . The highest in the coal rank are anthracite and graphite.

minerals tend to be present as excluded minerals (see figure 2.3) [2.16]. *Magnesium* can be present in several minerals like dolomite, chlorite and montmorillonite. The mode of occurrence of potassium is as illite, K-feldspar and to a lower extent in mica (muscovite, biotite) [2.11]. Much of the *phosphorus* occurs in coal as apatite [2.4]. Apatite in coal is usually Fluor apatite [2.13]. Alumina phosphate minerals have been found in a number of Australian and British coals [2.9; 2.18]. The presence of *sulphur* in coal is both organic and inorganic. A substantial share of sulphur is organically bound. Pyrite and markasite (FeS_2) are the principal minerals found in coal [2.9]. *Strontium* is mainly present in goyazite ($SrAl_3\ (PO_4)_2(OH)_5 \cdot (H_2O)$) and in minor quantities in strontianite ($SrCO_3$). Sr may also be present in calcite in some cases [2.13]. *Titanium* is mainly present as rutile and to a lower extent as anatase [2.4, 2.13-2.15, 2.19].

2.2.2 Combustion and ash forming processes

General

Basically, coal combustion consists of three steps:

- Drying and heating of the coal particle (see figure 2.4; reaction I).
- Devolatilisation and combustion of volatile matter (reaction II).
- Combustion of char (reaction III).

After entering the boiler, heating of the coal particles is caused by contact with hot flue gases and by radiation from the flames and the walls of the boiler. Moisture present in the coal evaporates almost instantaneous.

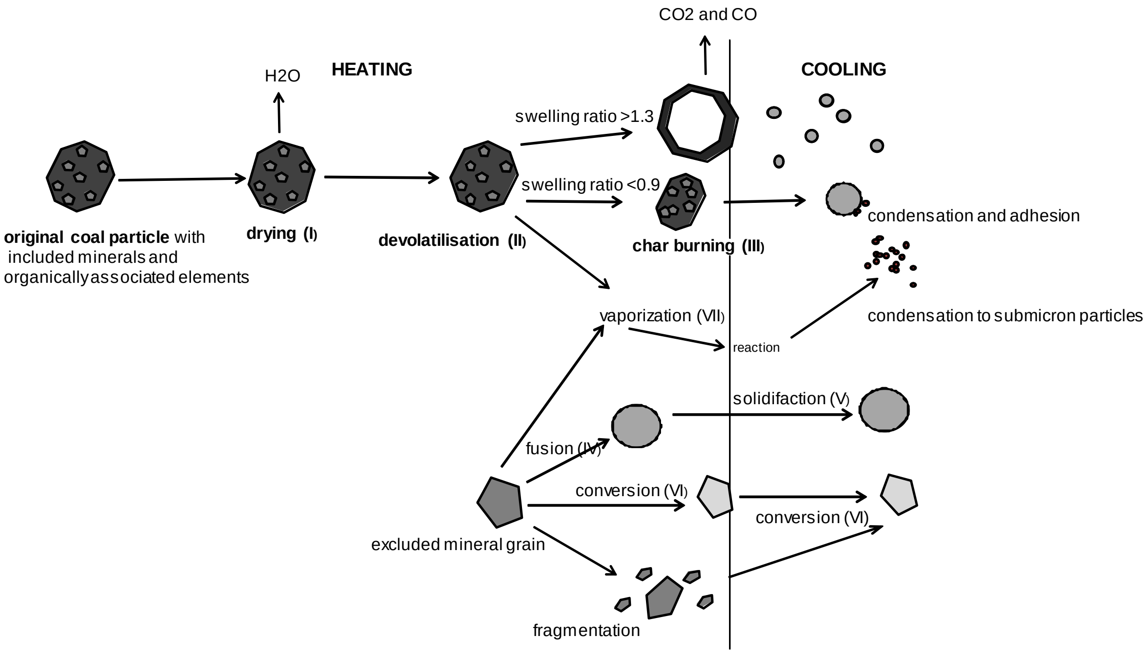

Figure 2:4: Coal combustion (step I, II and III) and ash-forming mechanisms during this combustion process (after [2.20]).

As soon as the drying process is completed, temperature rises to pyrolysis temperature. If the pore system does not allow steam to escape in time out of the particle, causing steam pressure inside, fragmentation of coal particles may occur. The degree of fragmentation depends on the heating rate and pore system (structure and shape). The heating rate of pulverized coal flames exceeds 10^4 ºC/s [2.20].

Devolatilisation is initiated at temperatures between 450 and 500 °C. For biofuels this temperature is considerably lower, about 350 °C. The release of volatile matter is a complex mechanism of chemical reactions and diffusion processes, depending in many parameters like particle size, temperature, residence time, coal composition and the environment of the particle in terms of gas composition and pressure. During devolatilisation many coals have a plastic stage. During this process bubbling and swelling are common phenomena. Due to these processes, resulting char particles have different morphologies (more or less porous coal char). The char starts to burn when the temperature of the char is high enough and there is sufficient oxygen around and in pores of the char particle [2.20].

During the combustion process many different reactions regarding ash formation take place in a very short time. Basically, these reactions can be divided in three different groups (see also figure 2.4):

1. Vaporization and condensation of organically bound elements. Reactions belonging to this group contribute to the formation of very fine particles and to condensation of compounds on the surface of ash particles and several parts of the boiler (VII in figure 2.4). In lower rank coals inorganic elements, which are organically bound, like Ca, Mg, K and Na, tend to vaporize during combustion. Vaporization is influenced by the temperature of the coal particle, the volatility of the compound and the atmosphere around the coal particle which may contain both reducing and oxidizing zones. During the gaseous phase reactions may take place between gaseous compounds. Vapour will be condensed to fine particles with sizes in the range of 0.02-0.2 µm. These submicron particles can adhere to and coat larger ash particles.
2. Fusion with or without (limited) coalescence. These reactions (IV in figure 2.4) may occur if one or more melted phases are present during the combustion process. The properties of the char particle (structure and swelling ratio) determines to what extent one big ash particle is being formed or many smaller ones. See also figure 2.5, where a particle is shown consisting of char with spherical sub particles, as relicts from melting during combustion. The melted phases mainly originate from the clay minerals (illite and kaolinite) and to feldspars.
3. Conversion, other than melting, of included and excluded minerals. These conversion reactions include decomposition, oxidization, phase transformation etc.

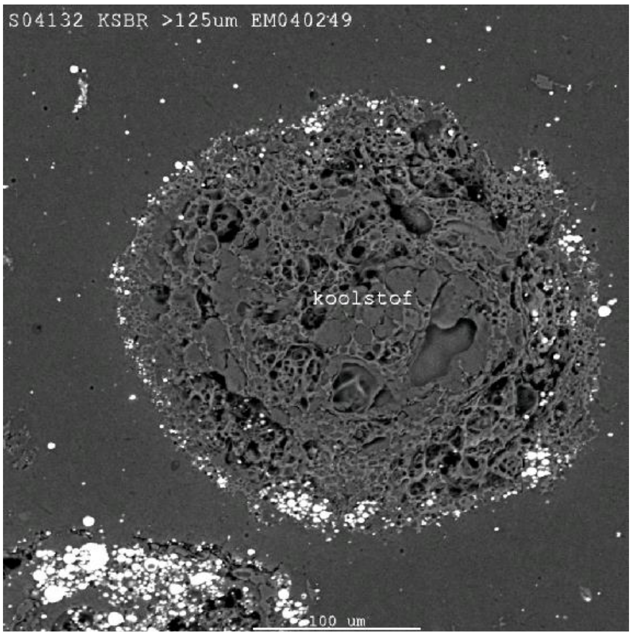

Figure 2:5: Fly ash particle consisting of char with spherical sub particles mainly at the surface. Example of incomplete char burn-out whereby the included minerals were melted during combustion.

So-called *excluded minerals* (see figure 2.4) do not coalesce, but remain as individual particles [2.20] due to the low probability on collision. Fragmentation of excluded minerals may occur due to the thermal shock during the combustion process.

Below a description is given of the reactions related to the most abundant minerals in coal:

Behaviour of Illite

When heated, adsorbed water is lost from illite ($KAl_2(AlSi_3O_{10})(OH)_2)$) between 100-200°C [2.21]. At 550-600°C the hydroxyl groups are removed. At higher temperatures (from about 1000°C) mullite ($3Al_2O_3.2SiO_2$ - $2Al_2O_3.SiO_2$) and quartz will be formed [2.22] and illite will lose its crystal structure. With increasing temperature, a molten phase will be formed, whereby mullite and quartz will dissolve. At 1400°C all mullite and quartz will be dissolved in the molten phase. According to [2.23], loss of potassium due to vaporization will not occur during heating (during heating experiments in a laboratory scale reactor up to about 1200°C).

Reaction of kaolinite

Kaolinite ($Al_2SiO_5(OH)_4$) will also lose some of its adsorbed water on heating to 100-120°C, while the remainder is lost at temperatures up to 400°C. Between 550-600°C combined water from the hydroxyl groups is removed whereby an amorphous phase is formed, known as metakaolin. Above 800°C the structure is further disrupted and cannot be reconstructed by rehydration [2.21]. Metakaolin remains unaltered up to 950-1000°C. Above these temperatures mullite starts to form [2.22]. Above 1500°C mullite is the only stable phase. With increasing temperature more liquid will be formed and mullite will be dissolved (see figure 2.6). It is stated that the higher the kaolinite content in the coal, the higher the mullite content in the fly ash [2.24].

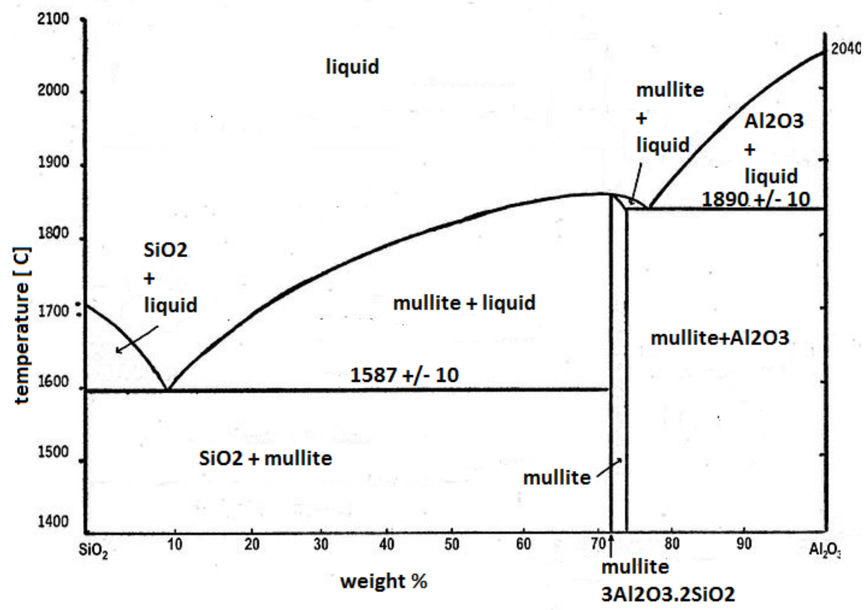

Figure 2:6: Phase diagram for the system Al_2O_3-SiO_2 [2.25]

Reaction of feldspar

When K-feldspar (microcline) was heated up 800 °C in an ash fusion test [2.22], the K-feldspar and the contaminants quartz and kyanite were relatively unaffected. Heating up to 1600 °C resulted in complete vitrification.

Decomposition of calcite

Each carbonate mineral has its specific threshold temperature where thermal decomposition occurs. Limestone (calcite) decomposes into CaO (lime) and CO_2. The dissociation temperature of calcite is 896-910 ˚C (at 1 atm pressure, 100% CO_2 in atmosphere) [2.26, 2.27]. It is known from lime production that lime particles are more or less reactive depending on the original limestone properties (like particle size and impurities) and the calcination process (temperature). The temperature profile in the calcining zone and the rate of heat exchange between the gases and the limestone particles are the main process parameters [2.28]. During transport of the flue gases in the power plant from the boiler to the ESP lime particles in the fly ash may react at the surface with components in the gas phase, like CO_2, [2.29] and SO_2. [2.4].

Decomposition of dolomite

The decomposition of dolomite occurs at higher temperatures than pure $MgCO_3$. The calcination of dolomite is more variable than that of limestone due to its variable chemical composition. It decomposes in two steps. The first decomposition step is:

$Ca(Mg)(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2$.

This may occur in the temperature range 510-750˚C (at 1 atm pressure, 100% CO_2 in atmosphere). This is followed by the decomposition of the calcite component into CaO (lime) and CO_2 [2.28].

Decomposition of siderite and ankerite

Siderite ($FeCO_3$) decomposes at 580° C into CO_2 and FeO. FeO which will be further oxidized at about 600°C [2.21] to hematite. Ankerite ($Ca(Fe,Mg)CO_3$) decomposes at higher temperature range, namely 700-800°C.

Decomposition of pyrite and marcasite

The combustion process of pyrite and its dimorph marcasite is very complex. During the heating experiments of Reifenstein whereby a sample of pyrite was heated, pyrite was oxidized to hematite (αFe_2O_3) and maghemite (γFe_2O_3) in the range up to 800° C [2.22]. Fe_2O_3 and Fe_3O_4, magnetite ($Fe^{II}Fe_2^{III}O_4$) are the final combustion products, together with gaseous SO_2. Fe_2O_3 is the stable form of iron oxide beneath 1388°C; above this temperature Fe_3O_4 (magnetite) is the stable form. However, already at 1200°C magnetite was found in the research of Vassileva and Vassilev [2.24]. The disappearance of hematite will be due to conversion to magnetite and dissolution in the melts that exist with increasing temperature. The melting point of pure magnetite is 1594°C [2.21].

Thermal behaviour of Quartz

At about 573° C (atmospheric pressure) the transformation from α quartz (trigonal system) to β quartz (hexagonal) occurs [2.21]. Further transformations occurs from β quartz to tridiymite (orthorhombic) at 867° C and to crystoballite (cubic) at 1470 °C. The melting point of crystoballite is 1713° C. The results of the experiments of Vassileva and Vassilev, [2.24] and Mitchell and Gluskoter [2.30] show that quartz exists at temperatures above the conversion temperature of quartz to tridiymite or even to cristobalite [2.22] due to the apparently slow conversion.

2.2.3 Properties

As already stated, fly ash is defined as a fine powder of mainly spherical glassy particles, derived from burning of pulverized coal, which has pozzolanic properties and consists essentially of SiO_2 and Al_2O_3. The spherical morphology of the particles is related to the formation of the molten alumina silicate phase during the combustion process. The droplet form is obtained if the viscosity of this molten phase is sufficiently low. Due to the fast cooling process after the boiler, the melt transforms mainly into a glass structure whereby the droplet form is frozen. The average particle diameter of Dutch coal fly ash is 13-22 μm. Particle density is about 2300 kg/m^3. The main components are SiO_2, Al_2O_3, Fe_2O_3 and CaO and to a lower extent Na_2O, K_2O, TiO_2, P_2O_5 and MgO (remark: the concentrations of these components are expressed as oxides, but this does not imply that they are always present in this form). The average concentration of these components in coal fly ash found in the literature and measured in Dutch coal fly ash is presented in table 2.1. Besides these components also trace elements are present (see Appendix B). The main trace elements are Ba, Mn and Sr, but also to a less extent B, V and Zn [2.14, 2.31]. These trace elements are only relevant for environmental and health aspects.

Table 2.1: Concentration of main components in coal fly ash as described in literature [2.32] and measured in Dutch coal fly ash[5] over the period 1995-2000 [2.33]

Parameter	Literature	Dutch
SiO_2	36-59	55±3.5
Al_2O_3	20-35	27±2.6
Fe_2O_3	3-19	7.3±1.7
SiO_2+ Al_2O_3+ Fe_2O_3	-	89±2.3
CaO Total	1-12	4.5±1.7
CaO free	-	0.31±0.23
MgO	0.7-4.8	1.5±0.45
Na_2O	0.1-3.5	0.6±0.40
K_2O	0.5-6	1.6±0.54
P_2O_5	-	0.77±0.40
Cl	-	<0.01
SO_3	0.1-2	-
Loss on ignition[1]	0.5-5	5.3±2.4

[1]) Loss on Ignition is a measure for the amount of unburnt carbon in fly ash. Unburnt carbon consists of non-combusted, pyrolised fuel. The loss on Ignition is determined by igniting a sample of fly ash at (950 ± 25) °C in an oxidizing atmosphere for 1 hr [2.51]. Per definition, Loss on Ignition is the weight loss of the sample before and after this treatment, expressed as percentage of the original sample.

The main reaction product is an amorphous phase consisting of alumina-silicate glass, which is about ca 65% by mass of the total fly ash. This phase is responsible for the pozzolanic properties. Furthermore, other mineral phases are present, which are enlisted in table 2.2. Some of these minerals originate directly from the coal (like quartz); others are synthesized during the combustion process (like mullite). This list is derived from a literature study of qualitative X-ray diffraction analyses of coal fly ashes [2.34].

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[5] Data originates from quality control of Dutch coal fly ashes produced in the period 1995-2000. This period is chosen as hardly any co-combustion was practiced. All concentrations are expressed as oxide with exception of Cl and loss on ignition.

Table 2.2: Overview of common and less common mineral phases in Dutch coal fly ash as determined with qualitative X-ray diffraction [2.34]

Group	Classification	Phases
0	Non-crystalline and organic phases, always present*	Amorphous phases (alumina-silicate glass) Unburnt matter (pyrolised fuel)
1	Crystalline phases, nearly always present	Anhydrite ($CaSO_4$) Free lime (CaO) Quartz (α-SiO_2) Hematite (α-Fe_2O_3) Mullite ($Al_6Si_2O_{13}$)
2	Crystalline phases, sometimes present	Calcite ($CaCO_3$) Magnetite (Fe_3O_4)
3	Crystalline phases, incidentally present	Periclase (MgO) Rutile (TiO_2) Corundum (Al_2O_3) Sillimanite (Al_2SiO_3) Feldspars

* identified using gravimetric and/or chemical methods

2.2.4 Use of coal fly ash in concrete

The use of fly ash has several advantages. First of all, cement replacement by fly ash improves the workability of fresh concrete [2.34, 2.35]. The enhanced workability is generally attributed to the fact that fly ash is largely composed of smooth spherical particles. Also, fly ash behaves inert in the plastic stage of concrete and mortar.

Coal fly ash has pozzolanic properties, which means that it will react with Portlandite, as reaction product of the hydration of cement, to form calcium silicate hydrates. In this way fly ash contributes to the strength development of concrete. These pozzolanic properties depends on several factors, especially the glass content and the specific surface of this glass phase. The pozzolanic behaviour in mortar and concrete depends on several external factors, especially cement properties, water-binder ratio, curing temperature, time and fly ash/cement ratio. The contribution increases with time (see figure 2.7), which can be explained by the increasing pH of the pore water to attack the glass structure.

Box 1.1 How to measure pozzolanic behaviour of coal fly ash?

The pozzolanic behaviour of fly ash in mortar and concrete can be quantified using different parameters. The most direct method of quantifying the pozzolanic behaviour is to measure the amount of reaction product from the pozzolanic reaction. However, it is complicated to perform this in practice. An indirect method is to measure the consumption of calcium-hydroxide or the consumption of the glass phase. Another, more pragmatic approach is to measure the influence of the pozzolanic behaviour on the compressive strength of mortar or concrete. There are several concepts for quantifying the contribution of the pozzolanic reaction on the strength. The k-value and the activity index are the most widely used.

The k-value indicates the contribution in concrete reaching the same strength as the reference concrete without added fly ash. This concept is used in the European standard for concrete (EN 206). The other concept is used in the European standard for fly ash in concrete (EN 450) and is defined as the relative compressive strength (as percentage) of a fly ash cement mortar compared to the strength of standard cement mortar. In the fly ash cement mortar, 25% of the cement is replaced by fly ash. The activity index is normally measured after 28 and 91 days.

Activity index $X = \sigma'_{cfm} / \sigma'_{cm} * 100$ [%]

Whereby:
σ'_{cm} = compressive strength of a standard mortar with Portland cement as binder
σ'_{cfm} = compressive strength of a standard mortar whereby 25% of cement has been replaced by fly ash to be tested

The EN 450 standard requires that the activity index is at least 75% and 85% after 28 and 91 days respectively.
The mix composition of the standard mortar is:

- 450 gram of Portland cement (or 112 gram of fly ash and 338 gram of Portland cement)
- 1350 gram of sand
- 250 gram of water

As indication, the activity index of both a commercial limestone filler and a commercial ground granulated blast furnace slag has been determined. The activity index after 28 days was 75% and 89% respectively. The activity index of coal fly ash with the same cement sample (CEM I 52,5 R) is about 84% (standard deviation is 4%).

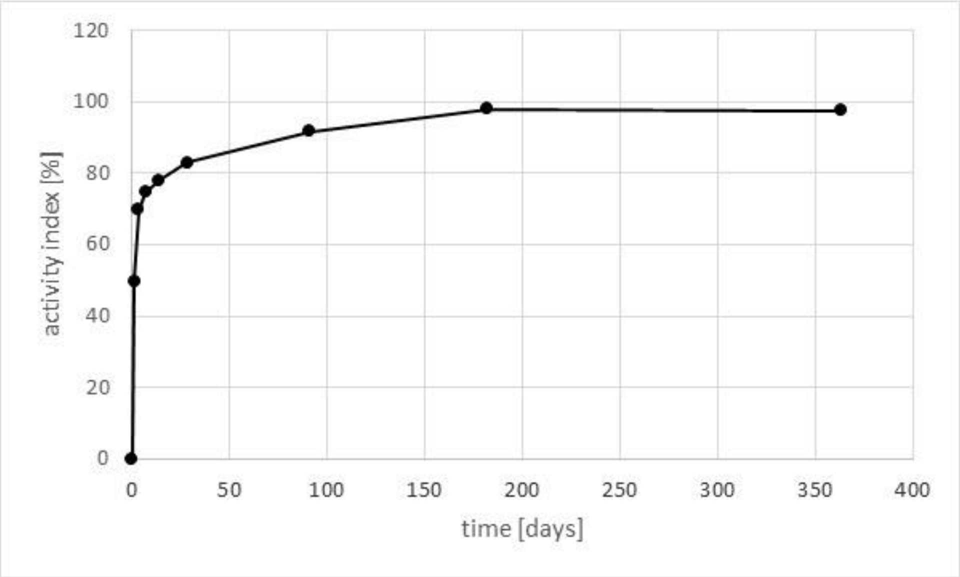

Figure 2:7: Pozzolanic behaviour, expressed as activity index, as function of time (see also Box 1.1). Tested on standard mortars with binder consisting of 25% fly ash and 75% Portland cement and water binder ratio=0.50 [2.36]

Another advantage of applying fly ash is reduction of the heat of hydration in mass concrete.

Under many conditions fly ash in concrete improves the durability of the concrete in the case of both external and internal attack [2.37]. Alkali silica reaction (ASR) is an important cause for unsoundness due to reactions between reactive aggregates and cement components. Pozzolans like fly ash are able to have a positive influence in suppressing this alkali-silica reaction [2.38-2.42]. Another type of internal attack is caused by extensive steam curing of concrete (above circa 70° C), which is related to expansion caused by delayed ettringite formation (DEF) [2.43]. The use of fly ash reduces the risks as shown by several researchers like, Ghorab and Heinz [2.43, 2.44].

The improvement of the resistance to external attack is mainly due to the denser pore size distribution, which reduces the ingress of ions. The resistance of concrete with fly ash against external sulphate attack is widely investigated. In sodium sulphate solutions at room temperature and at low temperature fly ash improves resistance compared to Portland cement [2.45-2.47]. This is not only due to the reduced permeability, but also because of the reduced content of C_3A and portlandite, which leads to less formation of ettringite. It has been shown that for the same compressive strength, the carbonation behaviour of concrete with fly ash does not significantly differ from the same concrete without fly ash, also under non-ideal storage conditions [2.48]. Another cause for corrosion is the ingress of chloride ions. The reduced permeability reduces the chloride diffusion in concrete. Over time the chloride diffusion is comparable to that of concrete with slag cement (CEM III\B) [2.49]. Freeze-thaw resistance (with and without de-icing salts) of concrete is an important issue in many countries. The freeze-thaw resistance of concrete with fly ash is comparable to that without fly ash both in the case with or without additional air pores, which is also confirmed by observations in practice [2.50].

The first European standard for fly ash, the EN 450 was launched in 1994. An overview of the requirements in the present EN 450 is presented in table 2.3, whereby the requirements are roughly classified to the main properties of concrete. The requirements concern mainly physical and chemical properties of fly ash to assure indirectly its performance in concrete, but also directly by examining initial hydration of fly ash cement paste (setting time) and the pozzolanic behaviour (activity index).

Table 2.3: Criteria [2.51] and properties[6] [2.33] for coal fly ash (category N, according to EN 450)

Concrete	Property	Unit	requirement	Range
Workability	loss on ignition (LOI)[1]	% m/m	≤ 5.0 (cat. A)	5.4±2.3
		% m/m	2.0 -7.0 (cat. B)	
		% m/m	4.0- 9.0 (cat. C)	
	fineness fraction > 45 μm 2)	% m/m	≤ 40	22±2.3
Setting and initial strength development	soluble phosphate (P_2O_5)	mg/kg	≤ 100	-
	total phosphate (P_2O_5)	% m/m	-	0.77±0.40
	initial setting	min.	2C 3)	51±26
Strength development	sum $SiO_2 + Al_2O_3 + Fe_2O_3$	% m/m	≥ 70	89±2.3
	reactive SiO_2	% m/m	≥ 25	42±6
	activity index 28 days	%	≥ 75	80±5.6
	91 days		≥ 85	93±6.5
Resistance to alkali silica reaction	total content of alkalis (Na_2Oeq)	% m/m	≤ 5.0	1.6±0.54
	reactive calcium oxide (CaO)	% m/m	≤ 10.0	4.5±1.7
Soundness/durability	sulphuric anhydride (SO_3)	% m/m	≤ 3.0	0.68±0.18
	free calcium oxide (CaO)	% m/m	≤ 1.5 4)	0.31±0.23
	Soundness 2)	mm	≤ 10	
	magnesium oxide (MgO)	% m/m	≤ 4.0	1.5±0.45
	chloride (Cl-)	% m/m	≤ 0.10	<0.01

1) Effects of higher LOI are: reduced workability and reduced efficiency of organic admixtures. See further 4.5.4.

2) The fineness shall not vary by more than ±10% from the declared value.

3) Initial setting of fly ash cement paste shall not be more than twice as long as the initial setting time of the test cement alone.

4) If the content of free lime is greater than 1.5 % by mass, the fly ash must be tested for conformity to the requirement for soundness. Soundness or volume stability. The European standard for coal fly ash in concrete uses the term soundness. The soundness is measured with the LeChatelier test.

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[6] Data originates from quality control of Dutch coal fly ashes produced in the period 1995-2000. In the case no data were available (initial setting, activity index, reactive SiO_2, and SO_3), data from the period 2009-2013 were taken.

2.3 Fly ash from co-combustion of biomass of vegetable origin

2.3.1 General

Biomass is defined as material of biological origin excluding material embedded in geological formations and transformed to fossil. Biomass can be classified in several ways. In this study biomass is divided based on the origin of the ash forming matter in the biomass, namely vegetable, animal or industrial origin (see figure 2.8). The resulting classification is slightly different from classification as normally used in the energy sector. Biomass from vegetable origin is further divided into:

- Wood and woody biomass. Examples are wood pellets, wood waste from commercial logging and harvesting and mill residues. Used wood, treated wood and waste wood, are excluded from this.
- Agricultural by-products, which are residues from food processing industry like olive residue, cacao husks peanut shells and rice husks. Oils and fats from vegetable origin are also included, but not of interest for their low ash forming matter.
- Herbaceous biomass, which is biomass from plants that has a non-woody stem and dies at the end of the growing season. Examples are straw, grass and maize
- Others like aquatic biomass (algae).

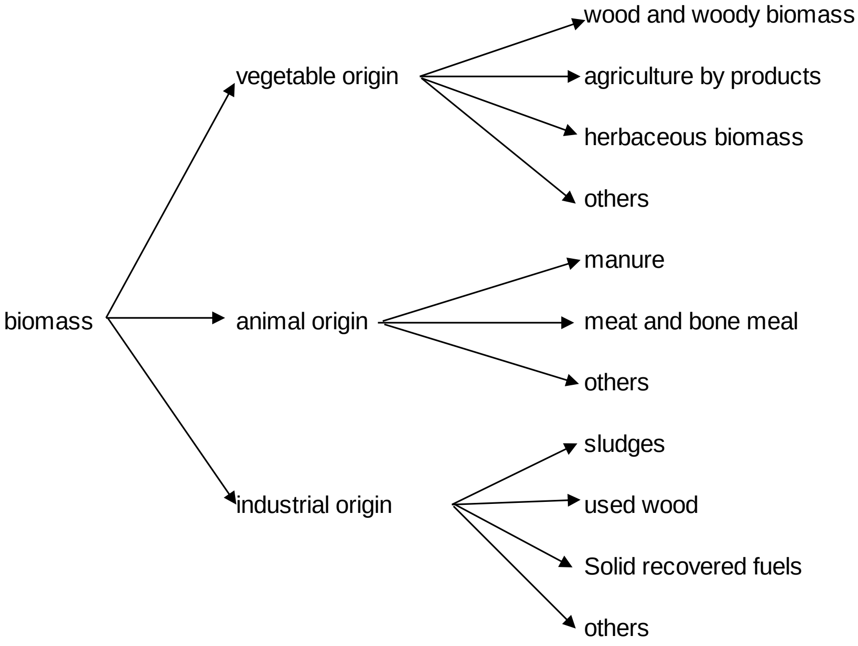

Figure 2:8: Classification of biomass used in this study. The classification is based on the (main) origin of the ash forming matter in the biomass.

There are fifteen mineral elements which are essential for growth in higher plants. These can be divided (based on average concentration) in primary macro nutrients (N, P, K), secondary macro nutrients (Ca, Mg, S) and micronutrients (Fe, Mn, Zn, Cu, B, Mo, Cl, Ni, Co). The macronutrients are present in concentrations of 0.2-5 % or even higher, while micronutrient may be present at levels of

0.1-100 mg/kg [2.52]. The concentration of these elements in plants depends on several factors like the species, season of year, part of the plant and soil conditions. Furthermore, it is influenced by the way of harvesting, processing and pre-treatment. Due to these influence factors biomass shows a wide range of compositions.

The ash forming matter in biomass can generally be divided into four groups:

- Inherent in biomass, organically associated.
- Inherent in biomass, inorganically associated.
- Inherent in biomass as salts, ionically bound.
- Not inherent in biomass due to contamination, mainly inorganically associated.

Ca, Mg and K are mainly organically associated. E.g. Mg is a component in chlorophyll ($C_{55}H_{70}O_6N_4Mg$ and $C_{55}H_{72}O_5N_4Mg$) and K is dissolved in the cytoplasm of cells [2.53]. Phosphorus is a very important element for plant growth. It is a component of lipids, DNA and of ATP (adenosine tri phosphate), which is an essential component in the energy regulation of organisms. Reproductive parts of plants often contains relatively high concentrations of potassium and phosphorus as a supply before the uptake from the soil starts when new plants starts to grow from the seeds [2.54]. Contamination with soil during harvesting may increase the amount of ash forming matter, by increasing the amount of minerals like quartz, clays, feldspar, limestone etc.

2.3.2 Wood and woody biomass

The amount of ash forming matter in wood is relatively low. Woods of temperate zones contain 0.1-1.0% m/m, while those of tropical and subtropical zones contain up to 5% m/m ash forming matter [2.55]. There is a certain dependency of the ash forming matter (content and composition) of the location within the tree. See also table 2.4 as example of the variation of ash forming matter for four different Scandinavian species (all collected in midsummer from a small stand). The highest amount of ash forming matter is in the living parts of the tree: twigs, needles and the leaves (1.7-7.7% m/m), while stem wood has the lowest amount. Bark has also a high amount of ash forming matter, which is attributed to presence material from the environment (soil, dust).

Contamination with soil during harvesting will influence this sequence. The main components are Ca, K and Mg. In many woods up to 50% of the ash forming matter consists of Ca. In general, bark has high Ca contents related to sapwood. Mineral deposits in wood consist mostly of calcium carbonate, calcium oxalate or silicate. Silicon occurs in plants mainly in the form of silicic acid ($Si(OH)_{4\ aq}$) and precipitated as hydrated amorphous silica ($SiO_2.nH_2O$) in the leaves or needles. Ca is present in large amounts as calcium oxalate (CaC_2O_4) crystals in the bark and the foliage. Sulphur is present as sulphates or organic sulphur. The research of Werkelin et al showed that the elements K, P and S and mainly also Mg and Cl were enriched in the young and living parts of the trees. There was a strong correlation between the concentrations of K, P and S.

Table 2.4: Ash forming matter in four Scandinavian species [% m/m dry] [2.55]

	Spruce	Pine	Birch	Aspen
Stem-wood	0.2-0.4	0.2-0.3	0.2-0.5	0.2-0.5
Branch-wood	0.4-0.6	0.3-0.5	0.3-0.5	0.5-0.7
Stem-bark	2.4-2.9	1.9-2.6	2.2-2.8	3.7-4.4
Branch-bark	3.0-5.0	3.1-3.7	3.7-4.5	5.7-6.4
Twigs	1.9-2.7	1.8-2.6	1.7-2.3	3.3-4.4
Needles	4.3-5.8	2.4-2.6	-	-
Shoots/leaves	-	-	2.9-3.1	7.3-7.7

The chemical composition of ash from wood was summarized by Vassilev et al. They listed 28 varieties from literature [2.56]. There is a wide range of concentration for most of the elements. Also, the ash forming matter varied between 0.1 and 16.5 % m/m dry base (mean value 3.5% m/m dry). The alumina content of wood itself is low, as alumina will only be taken up to a limited extent as it is not a nutrient, but a phytotoxic component. Higher contents of alumina point to contamination of the wood with soil, dust of dirt. The bulk of ash from wood itself consists mainly of CaO, SiO_2 and K_2O. From the data summarized by Vassilev it can be derived[7]:

$CaO+SiO_2+K_2O > \approx 75\text{-}80$ % m/m if $Al_2O_3<5\%$
$CaO+SiO_2+K_2O+Al_2O_3 > \approx 80$ % m/m if $Al_2O_3\geq5\%$.

As these generic rules apply also to wood fuels with higher content of ash forming matters, part of the SiO_2 may also originate from contamination. A comprehensive collection of data of biomass and its ash is the Phyllis database [2.57]. The data of untreated wood are summarized in table 2.5. Fir, pine and spruce are taken for untreated wood as these are most relevant for large scale combustion. The data show that the main components of the ash forming matter are (in decreasing order) Ca, K and Si. The components P and Mg are present in lower concentrations. The components Ti, Na, Fe and Al are present in much lower amounts present. These are not considered as nutrients, with exception of Fe (micro nutrient).

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[7] The ash from Christmas tree and from fir mill residue are left beside in this approach. The former contains 11.7% SO_3 and the latter 29.8 % m/m Na_2O.

Table 2.5: Properties of untreated wood (fir, pine and spruce) [2.57].

Property	unit	min	max	median	mean	st.dev.	n
Moisture content	wt% (ar)	0	63	8.3	14.8	15.7	91
AFM	wt% (dry)	0.07	6.4	0.46	0.83	1.07	105
AFM at 550°C	wt% (dry)	0.08	4.4	1.88	1.76	1.41	20
AFM at 815°C	wt% (dry)	0.2	0.45	0.25	0.26	0.06	21
LHV	MJ/kg (daf)	16.2	25.0	19.0	19.0	1.01	124
Al	mg/kg (dry)	53	230	124	126	67.9	8
Ca	mg/kg (dry)	712	10 700	6 550	5 690	4 280	8
Fe	mg/kg (dry)	25	1 500	140	334	481	9
K	mg/kg (dry)	352	3 600	1 060	1 210	916	15
Mg	mg/kg (dry)	124	830	470	461	252	8
Na	mg/kg (dry)	18	640	43	107	174	12
P	mg/kg (dry)	7	910	260	335	327	8
Si	mg/kg (dry)	84	3 900	1 800	1 570	1 450	7
Ti	mg/kg (dry)	3	19	15	12.3	8.3	3
S	wt% (daf)	0	0.57	0.03	0.06	0.09	102
Cl	mg/kg (daf)	0	11 900	100	350	1 370	77

Key: AFM = amount of ash forming matter

According to heating experiments by Misra et al of wood to generate ashes[8] at low temperature, K volatilisation start in the range 800-900°C [2.58]. Ashes from all species show a decrease in K, S and B content from about 800 ˚C. The volatilization of K was about 5-37%, depending on the specie. When the sample was heated up to 1300°C, 63-97% of all potassium was volatilised. Mg, Mn, Al, Si and P were hardly or not volatilized. Also Zn was hardly volatilized, with exception of white oak and white oak bark. $Ca(OH)_2$, MgO, CaO, Ca_2MnO_4, Mg_6MnO_8, $K_2Ca_2(SO_4)_3$, K_2SO_4, Na_2CaSiO_4 and Ca_2SiO_4 were identified with XRD in ash from 1300˚C. Intermediate reaction products (at 600 °C) were $CaCO_3$, $K_2Ca(CO_3)_2$, $Ca(OH)_2$, MgO, $CaMn_3O_{10}$ (pine) and $K_2MgSi_3O_8$ (poplar). Na_2CaSiO_4 and $CaSiO_3$ may also be formed in wood ash from poplar. Werkelin et al investigated also ashes, which were prepared at 1000˚C for 4 hours from four Scandinavian wood species [2.59]. The ashes were analysed with XRD and SEM/EDX. Lime, periclase, $Ca_5(PO_4)_3OH$ (hydroxyapatite), K_2SO_4 (arcanite), $CaSiO_3$ (parawollastonite), $CaKPO_4$ and K_3PO_4 were identified. The last three components were found in spruce needles and spruce shoots. Olanders and Steenari performed also combustion tests with a mix of 50% bark+50% wood chips and a mix of 60% bark+40% wood in a laboratory fixed bed furnace [2.60]. The fuel mixes were first combusted at 400 ˚C, then heated to 650˚C and further with steps of 50˚C (30 minutes per step). In the range 800-1000˚C several components were identified. The strongest XRD peaks were from CaO and MgO and to a less extent K_2CaSO_4 and calcium silicates with or without K or Mg.

Siddique gave a review on the properties of wood ash and its use in concrete manufacturing [2.61]. The properties of wood ashes differed from source to source, within the range of table 2.5. Specific gravity varies between 2260 and 2600 kg/m^3. pH values were reported between 9 and 13.5 and loss on ignition 5-30%.

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[8] Wood from pine, aspen, poplar, red oak, white oak (bark) and Douglas-fir bark were investigated.

Tkaszewska et al assessed the potential of the use of fly ash for production of Portland fly ash cement (CEM II/A-V 42.5 R) [2.62]. The fly ash originated from bituminous coal with 10% co-combusted woody biomass (m/m, fuel based). Unfortunately they give no further information about the fuel, so the chemical/mineralogical influence on the fly ash could not be assessed. The fly ash met the chemical requirements of the EN 450. The measured effects on the produced CEM II could not be related to effects of co-combustion as there are no reference data. Several authors published the use of wood ash as partial cement replacement. Cheah and Ramli investigated a high calcium wood fly ash [2.49], with 39% CaO, obtained from a (Bio-turbomax) boiler with a design temperature of 950˚ C for use in a mortar, whereby part of the Portland cement was replaced (up to 25 %). Workability (slump) decreased with increasing replacement ratio. Compressive strength decreased up to 28 days of hardening. At 90 days the compressive strength with 15% replacement was comparable to the control mix. The activity index, which is derived from the compressive strength of the control mix and of the mix with 25% replacement, was 87% and 91% after 28 and 91 days, respectively. The contribution to the strength was attributed to pozzolanic amorphous silica in the wood ash. Abdullahi reported also a decrease of workability of mortar and concrete with increasing replacement of cement by wood ash (no information about the type of furnace) [2.63]. The influence of cement replacement by wood ash on compressive strength of concrete differed from study to study. Abdullahi reported a decrease of strength (test periods: 90 and 60 days respectively; replacement 0-30% and 0-40%), while Naik et al reported hardly any influence (test period 365 days; replacement 0-12%) [2.64]. Water absorption capacity of concrete increased with increasing wood ash content.

Wang et al investigated the properties of concrete with fly ash from co-combustion with herbaceous biomass (switch grass) from a pilot-scale boiler, wood ash and coal fly ash blended with 20% wood ash [2.65-2.67]. The two investigated fly ashes with herbaceous biomass were rich in K_2O (4.0 % and 2-1%) and P_2O_5 (1.0 and 1.1 %). The LOI of the fly ashes was 3.06 and 3.85 % respectively.
The wood ash was a low calcium ash (14% CaO). Further information about mineralogy of the fly ash and the combustion process was not given. A concrete mixture was prepared with fly ash: cement = 1:3, water binder ratio of 0.50 and air entraining agent (AEA) for 4-6 % air. Water demand of concrete with co-combustion fly ashes seemed to be higher than that of the coal fly ash. Fly ash from pure wood exhibits significantly higher water demand, probably caused by the irregular shape and porosity of the particles and the higher LOI. All co-combustion fly ashes need higher addition of air entraining agents to obtain the same slump and entrained air contents. Setting time was measured with the penetration test according to ASTM C 403/C 403 M-99. Setting behaviour of concrete with co-combustion fly ashes lie within the range of coal fly ashes. Strength development was measured over a period of 365 days. Strength development of the co-combustion fly ashes lie also in the range of coal fly ashes. Concrete with fly ash from wood firing shows lower strength than the other fly ashes, especially at 28 days and further. Resistance to freezing and thawing was tested according to ASTM C666. Weight loss of the pure cement concrete was about 0.4 % m/m after 300 cycles. Concrete with coal fly ash, wood fly ash and fly ash blended with wood ash has a weight loss between 0.6-1% m/m. Concrete with coal fly ash from co-combustion with switch grass has a negative weight loss of about 0.3-1.3 % m/m. This might be attributed to the curing conditions (26 days in air, followed by 2 days in a fog room). Rapid chloride permeability was measured according to ASTM C 1202-91. Concrete with wood fly ash and the blended wood fly ashes showed higher chloride permeability which was thought to be attributed to the coarser particle size of the wood ash particles.

In the Netherlands several co-combustion tests have been performed with wood up to 50% m/m fuel based to generate fly ash for testing for use in concrete [2.68-2.71]. The results of these tests are presented in table 2.6. There is no information available about the coal that was fired during the co-combustion tests. Therefore, it is not possible to identify the influence of co-combustion. Remarkable is the high free lime and MgO content of fly ash from the test in power plant E, which is above the range of Dutch coal fly ash (see table 2.1). Also the Na_2O_{eq} of both fly ash from 50% co-combustion is above this range. The X-ray diffraction analyses of these fly ashes did not show other minerals than normally present in coal fly ash. The fly ashes met the limit values of the European standard EN 450 for use in concrete.

Table 2.6: Chemical analyses of fly ash from co-combustion of wood [% m/m] [2.55-2.58]

power plant*	Unit	D	D	D	E
Co-combustion fuel based	% m/m	33	37	50	50
Co-combustion ash based	% m/m	1.0	1.9	5.3	?
LOI	% m/m	3.6	1.6	3.01	3.04
Reactive SiO_2	% m/m	37.7	35	40.4	40.4
Free CaO	% m/m	1.19	0.87	0.28	1.42
Al_2O_3	% m/m	28.9	32.1	24.3	20.2
CaO	% m/m	6.9	6.3	4.7	5.6
Fe_2O_3	% m/m	7.67	3.5	6.75	7.5
MgO	% m/m	1.13	2.00	1.88	2.7
P_2O_5	% m/m	1.18	0.8	0.76	0.45
Soluble P_2O_5	% m/m	0.001	0.003	0.008	-
SO_3	% m/m	0.89	0.72	0.91	0.86
SiO_2	% m/m	53.1	52.1	56.8	55.5
Na_2O_{eq}	% m/m	1.38	0.76	2.48	3.5
Chloride	% m/m	<0.01	<0.01		<0.01
Fraction > 45um	% m/m	21	14	22.2	12.5
Activity index 28 days	%	85	82	83	86
Activity index 91 days	%	91	97	105	97
Initial setting ref	min.	152	185	167	199
Initial setting fly ash	min.	173	220	211	253
Soundness	mm	2	n.d.	n.d.	2

* The names of these (Dutch) power plants are anonymized for competition reasons

In the Avedøre power plant unit 2 (Denmark) wood is fired together with coal ash. Coal ash is added to avoid slagging and fouling in the system, first as a trial but since some years on a regular base [2.72; 2.73]. The trials consisted of the addition of about 1.6 kg/s of coal fly ash. The coal ash to wood ash ratio was 4.1-7.4.The amount of ash forming matter in the wood was 0.99% m/m. The generated wood ash was leached with L/S=50 and the eluate was analysed to get more insight in the solubilized potassium salts. The concentration of K in the wood ash was 6.3 % m/m, whereby 4.4 % was leached.

The chloride in the wood ash is totally water soluble. Also most of the sulphur was leached. Calculations made clear that about 50% of the amount of K may exist as KCl and K_2SO_4. The other 50% may be present as KOH and K_2CO_3.The pH-value of this ash was 12.04. XRD analyses showed indeed these phases with calcite, periclase and Quartz. The addition of coal ash leads to a decrease of water soluble K, Cl and S, which goes further than the dilution effect according to their conclusion. It is suggested that potassium is mainly present in K-silicates and K-alumino silicates and chloride and sulphur outside the fly ash in gaseous HCl and SO_2 respectively. This effect has also been investigated in the case of co-firing with straw (See further under herbaceous biomass).

2.3.3 Agricultural by-products

Agricultural by-products are residues from the food processing industry. Examples are shells from different nuts like cacao, hazelnut, and pits from cherries, olives and peach, rice husks, coffee grounds and peels from fruits etc. These residues are mostly characterized by relatively high amounts of ash forming matter and high concentrations of K and Ca and to a less extent P and Mg; elements which are essential for the first growth of a plant. See also table 2.9. The concentration of K is even higher than the concentration of Ca. The content of Mg and P (mean values) are relatively higher than in wood (see table 2.5). The amount of ash forming matter is also higher than in wood. Therefore, the impact of co-combustion of agricultural residues on the properties of fly ash will be higher than that of wood co-combustion.

Zygarlicke and Folkedahl investigated wood chips and sunflower hulls as secondary fuels for a stoker-fired facility [2.74]. The inorganic fraction of wood-chips consists of quartz (2 % m/m), mixed clays (12 %), iron oxide (2 %), pyrite (2 %), gypsum (35 %) and ‘unclassifiable’ (43 %). The only identified mineral in the sunflower hulls was iron oxide (2 % m/m). Chemical fractionation indicated that nearly all of the alkali and earth-alkali elements in the biomass fuels are organically associated (see also figure 2.3). ECN studied the combustion behaviour of biomass (wood and cacao) when co-fired in a laboratory scale pulverised coal boiler [2.75]. Fuels and ashes were characterised with CCSEM. The substitution by cacao (7% ash base) resulted in an increase of the illite-associated phase in the fly ash, which is probably due to the increase of K, and of kaolinite, dolomite and Fe-Al-silicate associated phases. Ashes from an incinerator for oil-palm waste were investigated by Tay and Show [2.76]. These ashes were characterized by high LOI and high concentrations of K, Al, Si and Ca. They showed that these ashes did not contributed to the strength development of concrete when combined with Portland cement, except for 10% replacement, and decreased the workability.

Table 2.7: Properties of agricultural by-products (husks, shells and pits) and herbaceous biomass (grass and plants) [2.57]

		agricultural by-products				herbaceous biomass			
property	Unit	median	mean	st.dev.	n	median	mean	st.dev.	n
Moisture cont.	wt% (AR)	8.76	10.1	6.36	69	14.5	30.3	27.4	171
AFM	wt% (dry)	3.1	3.89	3.26	120	6	7.25	6.09	334
AFM at 550°C	wt% (dry)	11.7	11.7	0	1	3.9	5.32	3.22	54
AFM at 815°C	wt% (dry)	7.13	7.45	3.74	10	7.6	7.57	2.97	11
LHV	MJ/kg (DAF)	0.1	0.15	0.17	102	18.4	18.3	0.93	208
Al	mg/kg (dry)	1 030	1 170	953	12	170	273	312	62
Ca	mg/kg (dry)	4 000	5 740	4 230	13	3 820	6 760	8 080	81
Fe	mg/kg (dry)	1 210	1 450	1 190	11	133	456	1 430	63
K	mg/kg (dry)	7 090	13 400	10 400	15	9 810	11 700	9 740	92
Mg	mg/kg (dry)	2 850	3 010	1 840	13	858	1 430	2 640	70
Na	mg/kg (dry)	225	444	480	14	500	865	941	78
P	mg/kg (dry)	2 520	3 230	2 510	13	1 400	2 340	2 880	58
Si	mg/kg (dry)	5 670	10 800	17 700	13	9 060	25 600	76 700	72
Ti	mg/kg (dry)	56.1	124	174	11	11	31	79.6	39
S	wt% (DAF)	2.28	6	7.85	3	0.11	0.17	0.25	230
Cl	mg/kg (DAF)	610	986	1 010	49	2 840	4 260	5 060	176

Key: AFM = amount of ash forming matter; AR= as received; DAF= dry base and ash free

2.3.4 Herbaceous biomass

Many research studies have been performed to ashes from rice husks. The ash forming matter of rice husk is about 20% [2.77], which is relatively high for agricultural by-products. It is estimated that the world-wide production of rice husk is about 115 Mton/year, which makes this biomass an interesting fuel. The ash forming matter in rice husk consists mainly of SiO_2 and to a less extent of potassium and phosphorus [2.77, 2.78]. Depending on the combustion process the silica will be present as crystalline or amorphous silica. Combustion at higher temperature than about 700 °C leads to formation of crystalline silica. Several researchers identified crystoballite and tridymite [2.77-2.79]. Rice husk ash is well known for its pozzolanic properties as shown by many studies like Sata et al [2.80].

Fernandez Llorente and Carrasco Garcia investigated the concentrations of several elements as a function of combustion temperature of wheat straw, thistle (*Cynara Cardunculus*), pine chips and poplar chips [2.81]. The thistle contained the whole plant, while the pine and poplar chips consisted of branches and leaves from tree pruning. The concentration of elements was analysed in the original biomass and in the fuel ash, obtained by incineration at temperatures from 400 to 800˚C. The concentrations in the ashes were calculated to the original biomass. Between 600-800˚C about 40-50% of the present K is volatilised, with exception of pine chips. Si, Al, Ca, Mg, P and also the trace elements Ba, Mn and Sr did not show weight loss, indicating that no volatilisation occurs. Based on comparison of the weight loss of K and Na with the weight loss of Cl it was suggested that other volatilisation mechanisms play a role than simple formation and volatilisation of KCl and NaCl (with exception of thistle).

Zheng et al performed experiments in an entrained flow reactor and combined this with thermodynamic equilibrium calculations on ash formation during co-firing straw with bituminous coal (atmospheric pressure; temperature range 500-1300°C) [2.82]. There is a complex of reactions whereby potassium is involved according to the results of thermodynamic equilibrium calculations (Fact Sage). In the case of pure straw firing, at 1100°C, a significant part of potassium is present as KCl (g)[9], followed by $K_2Si_2O_5$ (l) and $K_2Si_4O_9$ (l) and to small extent K_2SO_4 (g) and KOH (g). If more silicon is present in the system the major amount is $K_2Si_4O_9$ (l) and KCl (g). If alumina and silicon are present practically only $KAlSi_2O_6$ (l) is present. The experiments in the entrained flow reactor showed the dependency of water soluble potassium (like KCl and K_2SO_4) and the presence of silicon, added with coal.

Thy et al investigated the ash formation and especially the volatilization of potassium during combustion of wood, mixed with certain amounts of rice straw [2.83]. The wood ash consisted mainly of CaO (48% m/m), K_2O (16%) and SiO_2 (14%), while the rice ash consisted mainly of SiO_2 (82%) and K_2O (13%). Both fuels were first combusted at 525 °C. Mixtures of these ashes were prepared and heated to different high temperatures and residence times. The resulting ash was analysed. It was shown that depending on heating temperature and wood ash/rice ash ratio the loss of K_2O could vary strongly. In the case of pure wood ash almost all K_2O is lost. When rice straw is added loss of K_2O decreases. Besides the amorphous phase, leucite was found as the only K bearing phase. Other phases found in these mixtures are larnite, periclase, Åkermanite, wollastonite, diopside and quartz (polymorph), depending on the temperature and the wood ash/rice straw ash ratio.

Doshi et al [2.84] proposed that the mechanisms that are involved in ash formation as part of the biomass combustion process are mainly vaporization, condensation and coagulation/agglomeration. These mechanisms also occur during coal combustion but have less significance therein. The alkalis in the biomass are vaporized into mainly KCl, KOH and K_2SO_4 [2.84, 2.85]. It was observed that the increase of Si and Al from coal decreased the amount of volatile potassium. The alkalis condensate during cooling of the flue gases which can occur homogeneously and heterogeneously, depending on the cooling rate of the flue gases, the number of sites for nucleation and the concentration in the flue gas. Particles resulting from homogeneous condensation are in sub-micron size and may act as nucleation sites. The condensation process for alkali chlorides starts below 900 °C, whilst for alkali sulphates this process starts at about 1200 °C [2.84, 2.86]. Heterogeneous condensation occurs when saturation is just above one. Particles from low volatile components as species from Ca and Mg and non-volatilized minerals will act as nucleation seeds. Investigations of fly ash from co-combustion of straw on both real and laboratory scale showed that significant amounts of K are bound in alumina silicates (70-80%), while the remaining K is mainly present as sulphate [2.84, 2.82, 2.87]. The ratio soluble/insoluble potassium in the experiments are similar as the findings of Hansen [2.87, 2.88].

2.4 Fly ash from co-combustion of biomass from animal origin

Organic residues from animals are also used for energy production. Examples are meat and bone meal, litter, feathers and fats. In the Netherlands, meat and bone meal and poultry litter are used for power generation. Therefore, these fuels will be described in this section.

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[9] (g)= gas; (l)=liquid

2.4.1 Meat and bone meal

Meat and bone meal is derived from processing of cadavers and by-products from slaughter houses. The collected material is crushed (pieces to maximum size 50 mm), pasteurized and sterilized at 133 ºC and 3 bars for at least 20 minutes. The fats and meat are then removed by evaporation, separation and pressing. The residue, meat and bone meal, consists of muscular tissue, bone, cartilage, dried blood and sometimes parts of hoofs, horn and hair [2.89]. From medical literature it is clear that bone and teeth consists of 'apatite closely related to hydroxi-apatite' [2.90]. Approximately 10% of phosphate in meat and bone meal is organically bound. The ash-forming matter consists mainly of Ca and P (see table 2.10). The content of Al and Si are very low.

Co-combustion of meat and bone meal was investigated by several authors. However, no concrete information about the properties of the generated fly ash is given [2.91-2.96]. Deydier et al investigated the thermal behaviour of meat and bone meal using TG-DTA [2.97]. At 550 °C thermal decomposition of the organic part of meat and bone meal is completed. XRD-analysis of the resulting ash showed the presence of halite, sylvine, hydroxi-apatite, β tricalcium-phosphate and some amorphous material. Further, the presence of cristobalite, quartz and augite are proposed. Between 550-1000 °C the XRD-peaks of halite and sylvine completely disappear (>700 °C), but chemical analyses showed that K, Na and Cl are still present and not evaporated. When heated up to 1000°C only chloro-apatite and β tricalcium phosphate are identified. It has been shown that different calcium phosphates are able to react with water and calcium hydroxide to form insoluble, stable products. In fact this is analogue to the well-known pozzolanic reaction mechanisms. $\alpha Ca_3(PO_4)_2$ is a reactive mineral, that is used in some bone cements. It reacts with water to form hydroxi-apatite [2.98], according:

$$3\alpha\ Ca_3(PO_4)_2 + H_2O \rightarrow Ca_9(HPO_4)(PO_4)_5OH.$$

However the pore liquid of concrete has a high pH and portlandite is present as reaction product of the cement. In that case the following reaction may take place [2.99]:

$$3\alpha\ Ca_3(PO_4)_2 + Ca(OH)_2 \rightarrow 2Ca_{10}(PO_4)_6OH_2$$

The reaction product hydroxy apatite is a low soluble phosphate. The solubility product is reported to vary between $1*10^{-56}$ and $1*10^{-88}$ for temperatures between 20 and 30 °C [2.100].

Besides the presence in calcium phosphate, phosphorus may also be present as part of a glass phase or even as alkali-phosphate. Hu et al studied hydration phases in the system $CaO\text{-}SiO_2\text{-}P_2O_5\text{-}H_2O$ at low temperatures [2.101, 2.102]. They produced a dried, ground $CaO\text{-}SiO_2\text{-}P_2O_5$ gel or glass, depending on the composition. The powders were mixed with water, using L/S=4 and stored at different curing conditions, namely laboratory conditions, 90°C/1 atm/100% RH and hydrothermal conditions for several periods up to 150 days. The reaction products were investigated using XRD and SEM/EDX. The main phases found in most of the samples from the gel powders after hydration under several conditions and time were portlandite, hydroxy-apatite and crystalline phases of C-S-H and C-S-P-H. Hydroxi-apatite was identified in all samples based on the gel powders independent of the curing conditions and the P_2O_5 content. The CH content of the composition cured at room temperature increased with increasing CaO content of the composition. XRD analyses of the hydrated glass powders show only the presence of an amorphous phase, $CaHPO_4$ and $Ca(H_2PO_4)_2.H_2O$. SEM/EDX observations indicated that C-S-H-P gel is also present in these samples.

Alkali phosphates may act as retarder. In cement chemistry, it is well known that soluble phosphates are able to act as cement hydration retardants [2.103; 2.104]. Retardation is probably caused by the reaction of phosphates with Ca that is liberated during hydration of the clinker grains. Calcium phosphate precipitates on the grains, leading to the formation of a layer around each grain. This layer prevents the grain from further reaction with the surrounding mixing water.

Table 2.8: Properties meat and bone meal and poultry litter [2.57]

property	unit	Meat and bone meal				Poultry litter			
		median	mean	st.dev	n	median	mean	st.dev	n
Moisture	wt% (AR)	2.89	3.55	1.53	9	36.3	40.8	29.4	46
AFM	wt% (dry)	20.0	20.5	4.13	6	26.2	28.5	15.19	30
LHV	MJ/kg (DAF)	21.9	21.3	2.75	8	18.9	19.0	2.07	25
Al	mg/kg (dry)	127	129.4	69.5	3	750	1020	931	10
Ca	mg/kg (dry)	50000	48000	21290	4	48300	45400	29500	18
Fe	mg/kg (dry)	861	967	836	4	1 227	1 660	1100	11
K	mg/kg (dry)	5840	5640	1070	4	24300	28200	24600	27
Mg	mg/kg (dry)	1861	1 860	124	4	7 010	7 290	3040	18
Na	mg/kg (dry)	10940	10600	1840	4	4680	7 620	10900	16
P	mg/kg (dry)	31200	35800	19900	4	17000	15710	8 780	25
Si	mg/kg (dry)	1390	1390	692	2	4 810	5 570	3210	10
Ti	mg/kg (dry)	15.7	15.7	4.7	2	35.1	46.4	35.6	9
S	wt% (DAF)	0.64	0.66	0.37	7	0.82	0.87	0.48	24
Cl	mg/kg (DAF)	8 97	8390	2860	6	8820	10680	7180	18

Key: AFM = amount of ash forming matter; AR = as received; DAF=dry base and ash free

2.4.2 Poultry litter

Compared to coal, poultry litter contains relatively high concentrations of calcium, potassium, and phosphorus (see also table 2.10). The mode of occurrence of P in manure is both organic and inorganic. Barnett [2.105, 2.106] analysed the mode of occurrence in poultry litter (laying-hen). The most important form is inorganic P (40-70%), followed by acid-soluble organic P (25-44%). The actual amount depends on the state of the animal, feed source, age etc. Cooperband and Good investigated the presence of inorganic phosphates in poultry manure (broiler) with SEM/EDX [2.107]. The major part of the investigated particles consisted primarily of Ca, Mg and P. The Ca:Mg:P ratios of these particles could not simply be related to well-defined phosphate minerals. The (Ca+Mg):P ratios of the EDS spectra were consistent with calcium phosphates like $CaHPO_4$ (Ca/P=1) $Ca_4H(PO_4)3.H_2O$ (Ca/P=1.3), amorphous calcium phosphate (Ca/P=1.5) and further whitlockite ((Ca+Mg)/P=1.5) and carbonate apatite (Ca/P<1.67). Co-combustion of litter from cattle is reported by Annamalai et al [2.108] and Sweeten et al [2.109], but no concrete information about the properties of the generated fly ash is given.

2.5 Fly ash from co-combustion of biomass from industrial origin

2.5.1 Municipal sewage sludge

Municipal Sewage Sludge is the residue of the cleaning of municipal waste water. One of these cleaning steps is phosphate removal. This can be performed by precipitation with ferro salts (like $FeSO_4$, and $FeCl_3$) and alumina salts (like $Al_2(SO_4)_3.nH_2O$ and alumina chlorides). 84% (capacity) of the Dutch sewage plants use processes for phosphate removal. Thereby chemical processes are widely used [2.110]. Phosphates are precipitated using Fe and/or Al-salts (mainly chlorides, sulphates). The ash forming matter of municipal sewage sludge is not constant and differs depending on the period of the year, process and location. The location is important because of the influence of climatological and geographical circumstances and human activities in the service area. Material from soil and roads is brought into the sewage system by rain. Sand and clay-like materials are, therefore, present in municipal sewage sludge, together with precipitated components like Al and Fe phosphates. Data about the composition are presented in table 2.11. The data show that the ash forming matter mainly consists of Si, Fe, P, Ca and Al.

Co-combustion experiments with sewages sludge (17-24% m/m P_2O_5, ash based) were reported by Ninomiya and Zhang [2.111, 2.112]. The mineralogical composition of the sludge was investigated with SEM. Most of the ash-forming matter, consisted of Al, Si, Ca, Fe, or P, which could not be related to specific minerals. Phosphorus is found to be present as unknown ‘Ca-P’, as ’unknown P’ and some apatite. Further, kaolinite, calcite, montmorillonite, quartz, mixed Al-Si, Ca Al-Si, ‘unknown Ca’, Si-rich and alumina were identified as other phases. Both the included and the excluded inorganic phases have mean sizes of about 2.0 µm. Combustion tests with two types of pre-dried municipal sewage sludge were performed in a laboratory-scaled drop tube furnace by Zhang et al. Most of the phosphate in the ash from the combusted sewage sludge is present as (Ca, Fe)PO_4 with or without alumino silicate. Ninomiya et al. [2.112] investigated co-combustion of two municipal sewage sludges with three different coals in a drop tube furnace. Several phosphorus bearing phases were identified with SEM, whereby the most important one is a phase consisting of Ca+P+Al+Si.

Several authors investigated the use of sewage sludge ash for use in asphalt and concrete. Normally incinerators used for sewage sludge are operating at lower temperatures than in power coal fired boilers. The presence of quartz, feldspars, mica, rutile, whitlockite, calcium sulphate, magnetite and amorphous phases is quite common in municipal sewage sludge ash from fluidized bed combustors in different European countries [2.113]. Small percentages of municipal sludge are co-fired on a regular base in several power stations [2.114, 2.115]. The generated fly ash is able to meet the limit values of NEN EN 450 up to 5 % m/m co-combustion (coal base).

Fly ash from 10% m/m (fuel-based) co-combustion of municipal sewage sludge in a Dutch power plant was investigated by analysing its properties and its performance in concrete [2.116]. The P_2O_5 content increased from 0.4 to 3.60 % m/m and the particle density increased slightly. The strength development and the resistance to chloride ingress of the concrete with this fly ash was comparable to that of concrete with coal fly ash[10].

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[10] Concrete composition: 320 kg/m^3 binder consisting of 80% CEM I/32,5 R and 20% fly ash; WBF=0.48-0.50.

2.5.2 Paper sludge

Paper sludge (PS) is a by-product of paper manufacture and especially paper recycling (at the de-inking plant and the effluent treatment plant) [2.117]. It consists of short cellulose fibres, water, ink and minerals. These minerals are present due to the use of mineral fillers in paper. Paper sludge has typically a high amount of ash forming matter, in combination with a low heat value of 2.5-6.0 MJ/kg. The possibility of paper sludge co-firing was assessed by Vamvuka et al [2.118]. Combustion experiments with paper mill sludge were performed in bubbling fluidized bed and circulating fluidized bed in combination with bark and wood waste respectively [2.119]. There is no further information about the influence on fly ash quality for use in concrete. Clay (kaolinite) and calcite are the most abundant fillers in paper [2.120]. Minor components are titanium dioxide, sodium components (from paper making and de-inking) and iron e.g. from staples in recycled paper [2.118]. See further table 2.11 for the composition of paper sludge. The ash forming matter mainly consists of Al, Ca and Si, while the other components, like Fe, P and K are present in much lower concentrations. Combustion experiments with paper mill sludge were performed in fluidized bed boilers in combination with bark and wood waste, respectively. The ash-forming matter of this paper mill sludge consisted mainly of kaolinite, calcite and talc. Thermogravimetric analyses showed that one sludge sintering was initiated at about 1050 °C, while another sludge was softened at 1150 °C and the fluid temperature was 1290 °C. The bed temperature of both boilers is 820 °C and 765 °C respectively. XRD-analyses of the fly ash from both boilers indicated the presence of $Ca_2Al_2SiO_7$ as a reaction product of decarbonated limestone with kaolinite. Other identified minerals in the fly ashes were talc, metakaolinite, calcite, lime, quartz (bed material) and rutile. No melted phases were found with SEM, but agglomerates of typically 10-100 um occurs. The sludge contained inorganic particles, size 0.5- 2um, which is typical for paper fillers, and also larger particles, indicating contaminants like sand and dirt.

Table 2.9: Properties municipal sewage sludge and paper sludge [2.57]

		Municipal sewage sludge				Paper sludge			
properties		median	mean	st.dev.	n	median	mean	st.dev.	n
Moisture cont.	wt% (AR)	8.06	24.0	30.1	56	57.1	42.3	29.0	14
AFM	wt% (dry)	38.8	39.4	9.93	54	30.8	32.7	14.1	16
Volatile matter	wt% (DAF)	86.6	86.7	7.31	40	90.0	89.9	5.3	5
LHV	MJ/kg (DAF)	21.6	21.0	3.01	49	16.6	16.8	4.17	12
Al	mg/kg (dry)	16000	20 700	17600	20	54 000	50 800	29 900	4
Ca	mg/kg (dry)	47400	58 500	37 200	18	95 000	77 800	51 000	7
Fe	mg/kg (dry)	32500	37 300	25 200	21	1 900	2 490	1 140	5
K	mg/kg (dry)	4 170	5 170	4830	21	2 200	2 340	1 400	7
Mg	mg/kg (dry)	5 580	5 780	2 820	18	2 600	3 020	1 440	7
Na	mg/kg (dry)	1 430	2 620	4180	21	1 700	1 730	1 250	6
P	mg/kg (dry)	31000	35 500	23 600	15	1 460	1 900	1 270	6
Si	mg/kg (dry)	31 100	34 900	26 000	11	56 400	55 400	8 940	3
Ti	mg/kg (dry)	738	1 460	1 510	11	1 400	1 870	896	3
S	wt% (DAF)	2	2.1	0.83	54	0.35	0.63	0.60	12
Cl	mg/kg (DAF)	1 510	4 500	13100	42	1 110	2 660	3 620	7

Key: AFM = amount of ash forming matter; AR = as received; DAF=dry base and ash free

Fly ash was obtained from co-combustion experiment with 10% paper sludge in a Dutch coal-fired power plant [2.116]. The fly ash from co-combustion has a higher free lime content and lower glass content compared to the reference fly ash (respectively 0.52 instead of 0.07% m/m and 48 instead of 62% m/m). The activity index increased from 85 to 91 % at 28 days.

2.5.3 Demolition wood

Demolition wood originates from demolition of buildings and from construction wastes. The average amount of ash forming matter of demolition wood in the Netherlands is 6.2% m/m. The ash forming matter of uncontaminated wood is not higher than 0.5-1% m/m. This means that the main part of the ash from demolition wood originates from contamination during demolition and/or handling. This may consist of building materials (gypsum, cement mortar), soil (quartz clay) and paint (fillers and pigments). Demolition wood has high contents of Pb and Zn (see table 2.12) [2.57]. Analyses of ashes from waste wood combustion in two fluidized bed boilers by Florea confirmed high concentrations[11] of Cu (210-890 mg/kg) and Zn (1100-10,000 mg/kg) [2.121]. She found also high contents of chlorides and sulphates in the fly ashes. Several minerals were identified, especially several calcium bearing phases (calcite, anhydrite, lime and Portlandite) and further titanium bearing phases and halite in one fly ash.

2.5.4 Solid Recovered Fuels (SRF)

For several reasons it is interesting to separate the high caloric fraction from municipal solid waste and to combust it in dedicated boilers. This fuel mainly consists of paper and plastics, but also wood, textile etc. The composition highly depends on the composition of the waste and the recovery process. It is known as solid Recovered Fuel (SRF) or refused derived fuel (RDF). In this study the name SRF is used. The inorganic matter in SRF originates from different mineral matter, like ceramic, soil, metal but also from fillers in paper and plastics, which are the main components in SRF. Most widely used fillers for thermoplastics are calcium carbonate, kaolinite, chalk and silicates like quartz, feldspar and mica [2.122]. Kaolinite and (precipitated) calcite are most used mineral fillers in paper [2.120]. Another relevant aspect is the relatively high concentration of several (heavy) metals, like Cu, Pb and Zn [2.57, 2.123]. These metals are potential retarders for cement hydration depending on the speciation.

Co-combustion experiments with SRF were performed at Merrimack power station [2.124]. This unit uses a cyclone fired boiler. The coal was bituminous coal from West-Virginia. Tests were performed whereby 5 and 10% of the coal was replaced by SRF (6 and 13 % m/m ash base respectively). The SiO_2 content decreased due to co-combustion while the CaO and Al_2O_3 content remains about the same. The SO_3 content increased with higher co-combustion percentages. The fineness decreased with increasing co-combustion percentage, namely from 4.0% retained #325 mesh sieve to 7.7% for respectively 0% and 13% co-combustion. The pozzolanic behaviour was tested against ASTM C 311-77. The pozzolanic activity was 88% for the coal fly ash and 102 and 94% for fly ash from respectively 6% and 13% co-combustion.

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[11] Pb was not analysed

SRF co-combustion trials were also performed in a lignite fired power station in Weisweiler, Germany [2.125]. The co-firing experiments with lignite were limited to 4% of SRF. This makes it difficult to identify effects of co-combustion of SRF. The concentration of Cu, Pb and Zn increases. The main components show differences especially Ca, but these are more related to differences in lignite composition than to co-firing of SRF.

Table 2.10: Properties demolition wood and Solid Recovered Fuels (SRF) [2.43]

Property	unit	Demolition wood				Solid Recovered Fuel			
		median	mean	st.dev.	n	median	mean	st.dev.	n
Moisture cont.	wt% (AR)	11.6	14.9	9.23	21	5.89	10.1	9.7	24
AFM	wt% (dry)	3.48	6.27	6.61	22	15.5	17.0	8.02	28
LHV	MJ/kg (DAF)	18.8	18.9	0.73	23	22.2	22.7	3.17	30
Al	mg/kg (dry)	520	842	879	12	7000	14700	19100	4
Ca	mg/kg (dry)	3 760	4 650	2 990	12	25900	36200	21400	3
Fe	mg/kg (dry)	640	1 460	2 010	12	3330	5300	5900	4
K	mg/kg (dry)	807	967	467	12	1820	2460	1520	3
Mg	mg/kg (dry)	495	538	281	12	1970	3060	2390	3
Na	mg/kg (dry)	603	788	463	12	2590	2320	810	3
P	mg/kg (dry)	128	180	137	12	480	3280	5040	3
Si	mg/kg (dry)	3 000	4 900	4 050	11	26900	30500	22800	3
Ti	mg/kg (dry)	198	409	445	10	1650	1610	520	3
S	wt% (DAF)	0.08	0.11	0.13	22	0.4	0.43	0.29	25
Cl	mg/kg (DAF)	727	1 250	2 220	19	5700	6690	3760	23
Cr	mg/kg (dry)	33.0	43.8	27.2	14	70	130	169	5
Cu	mg/kg (dry)	25.0	62.7	106	13	253	332	230	5
Pb	mg/kg (dry)	273	441	490	14	93.3	164	134	5
Zn	mg/kg (dry)	390	577	590	14	393	326	171	5

Key: AFM = amount of ash forming matter; AR = as received; DAF=dry base and ash free

2.6 Evaluation

2.6.1 Coal fly ash

Coal fly ash is used as raw material for concrete since many decades. Fly ash is used as cement replacement and as filler. Fly ash has a specific combination of properties:

- The fineness and morphology of the fly ash particles (smooth and spherical).
- The chemical and mineralogical composition, especially the presence of the alumino-silicate glass phase. The glassy phase is responsible for the pozzolanic properties of fly ash. Due to this fly ash is able to contribute to the strength of concrete.

The pozzolanic behaviour of fly ash has also a positive influence on durability of concrete made with this fly ash if properly designed, placed and cured. The precondition is that other components as alkalis, free lime and sulphates are present in low concentrations. The use of fly ash in concrete mitigates the risk on destructive ASR. Also, the resistance to sulphate attack is increased due to the decreased content of $Ca(OH)_2$ and C_3A. The effect on carbonation is twofold. On one hand the permeability is reduced due to the pozzolanic reaction; on the other hand the amount of $Ca(OH)_2$ is lower than in plain Portland cement concrete, which implies a smaller buffer capacity to maintain the pH of the pore water at a sufficiently high level to avoid corrosion. It is shown that at the same strength level carbonation resistance is comparable to that of plain Portland cement concrete. Fly ash concrete shows also a good resistance to chloride penetration if the concrete has been cured well.

The EN 450 is the European standard for the quality assessment of coal fly ash for use in concrete as a so-called Type II addition. These are additions with pozzolanic or latent hydraulic properties. This standard prescribes requirements, which have to be fulfilled by the coal fly ash on both material level and performance level. The set of requirements consists of maximum levels for certain components in the fly ash to avoid destructive reactions and minimum levels to guarantee the fly ash to be effective. The performance based requirements are soundness, setting time and activity index. There is only a qualitative requirement regarding the morphology of the particles, namely that fly ash consists of mainly spherical particles.

2.6.2 Fly ash from co-combustion of vegetable origin

The influence of co-combustion on the properties of fly ash depends on several factors, especially the amount and composition of ash forming matter of the fuel, and the reactions during the combustion process.

The literature study shows that the ash forming matter of secondary fuels can be very different from that of hard coal. The average amount of ash forming matter of coal used in Dutch power plants is about 12 % m/m. The amount of ash forming matter of woody biomass is relatively low (around 1% m/m) and depends on several parameters like the way of harvesting and contamination with soil. Agricultural by-products and herbaceous biomass have higher amounts of ash forming matter. In figure 2.9 the contribution of the co-fired biomass to the amount of ash in the generated fly ash is presented. The calculation is based on average ash forming matter in the fuels and assuming that the distribution of elements (RE factor) does not change significantly (see also chapter 6).

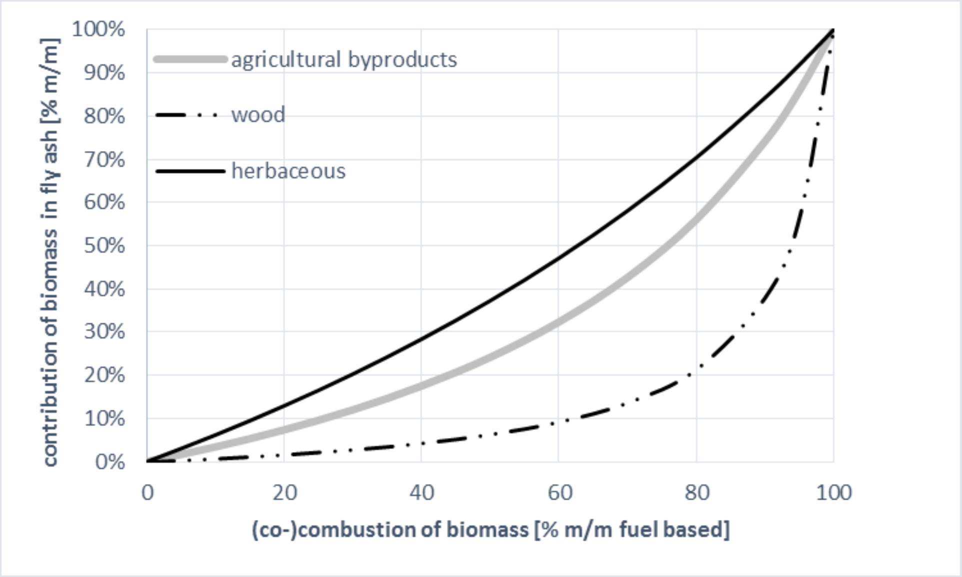

Figure 2:9: The relation between co-combustion percentage fuel based and the contribution of biomass in the fly ash for different type of biomass from vegetable origin.

The ash forming matter of wood and woody biomass consist mainly of Ca, Si, K and to a less extent P and Mg. The content and the composition of the ash forming matter depend on several factors, whereby the variation can be very big. Calcium in the biomass itself is mainly present as calcium oxalate, carbonate or silicate. Silicon will also be present as silicic acid and quartz due to contamination with soil. In that way also other minerals may be present like feldspars and clays. Heating experiments with several types of biomass show that at high temperatures all K will be volatilized, while other elements will hardly or not be volatilized. Also heating experiments with herbaceous biomass showed volatilization of potassium. The minerals found in the residual ash are calcium and potassium minerals, like lime, periclase, and arcanite and several silicates and phosphates.

The addition of coal fly ash to wood before combustion prevents the reaction of potassium with chloride and sulphur due to the binding of potassium by the molten phase of coal fly ash (alumino silicates). If no coal fly ash is added, several potassium bearing components are formed, mainly KCl, K_2SO_4 KOH and K_2CO_3. Laboratory experiments with combined combustion of wood with rice straw showed comparable reaction mechanisms.

It can be derived from the test results on fly ash from co-combustion up to 50% m/m wood (fuel based) that the limit values of the European standard EN 450 can be met. It can be concluded that with 50% co-firing of wood the composition of the generated coal fly ash seems to be slightly influenced. The concentration of some compounds falls outside the range of Dutch coal fly ash like free lime and Na_2O_{eq} in the co-combustion fly ash from power plant E. However, no combustion experiment with just coal was performed to allow better comparisons. The activity index falls within the range of Dutch coal fly ash or above.

Above 50% combustion of wood (combined combustion of wood and coal), the composition of the generated fly ash will be more influenced (see figure 2.9). The behaviour of potassium is of special interest because of the binding of chloride and sulphur and thereby the concentration of these elements in the fly ash. The content of alumino silicates will decrease, while the concentration of other, non-pozzolanic components will increase. This does not mean that these components are inert as most of these consist of Ca, Mg and K. According to EN 206, Type II additions are defined as pozzolanic or latent-hydraulic addition. Above 50% m/m wood combustion, the pozzolanic properties will decrease with increasing wood combustion. However this fly ash will not become more and more inert (Type I addition: inert filler) as the content of reactive components will increase. The fly ash will contain several components that may be suitable as activator in hydraulic binder. Ground granulated blast furnace slag can be activated with calcium sulphates [2.126, 2.127] and other calcium components [2.128] or alkalis [2.129] as shown in practice and by several published research articles. See further section 6.1.

Most authors conclude that the workability of the fresh concrete and mortar is negatively influenced by the use of wood fly ash (100% wood combustion) [2.61-2.65]. The effect on strength development of mortar is comparable or lower than that of mixtures with coal fly ash (25% replacement). The durability (freeze thaw resistance and chloride penetration) decreases due to the use of wood fly ash [2.65-2.67]. Also in these literature limited information is available about fuel and the combustion process. In such cases the combustion temperature and residence time may be different, which may have influenced the ash formation. No information has been found in literature about the properties of fly ash from combined firing of wood and coal with exception of the research about the addition of coal fly ash to wood before combustion. This has to be derived from data about coal fly ash and wood fly ash and from knowledge about reaction mechanisms during combustion of wood and coal (see further chapter 6).

Agricultural by-products have often higher amounts of ash forming matter than wood and woody biomass. Most agricultural residues consist of reproductive parts of the plants and have, therefore, very high percentages of K, Ca, P and Mg. It seems that potassium is mainly organically associated. Potassium will be volatilized during the combustion process as for wood. Several researchers studied combustion of agricultural residues but no information is available about the properties of the generated fly ash and its effect on the properties of concrete. Especially the presence of phosphorus in the fly ash is of interest as it is a potential retarder of cement hydration. It is unknown how the organically bound phosphorus ends up in the fly ash and behaves in concrete. If alkali phosphates are being formed (like $NaHPO_4$ or Na_2PO_4), retardation of cement hydration may occur.

2.6.3 Fly ash from co-combustion of biomass from animal origin

The most relevant fuels from animal origin are meat and bone meal and manures. *Meat and bone meal* consists mainly of Ca, P, Na and to a less extent K. The most important mineral in meat and bone meal is apatite ($Ca_5(PO_4)OH$). A small part of the phosphorus is organically bound. Thermal treatment at high temperatures (1000 °C) may lead to the formation of β-tri calcium phosphate and to a less extent chloro-apatite. The literature shows that α tricalcium phosphate is able to react with water and $Ca(OH)_2$ analogue to pozzolanic reactions. Phosphorus as part of glass phases is able to react to calcium silicate hydrate with incorporated phosphate (C-S-P-H[12]). Via these two path ways, phosphorus is able to contribute to the pozzolanic reactions in concrete. It is unknown how the organically bound phosphorus ends up in the fly ash. No information is known about the properties of co-combustion fly ash and the properties of concrete made with this fly ash.

Manure contains also high contents of P, Ca, K and to a less extent Na. Phosphorus seems to be present in more different compounds than in meat and bone meal. There is hardly any relevant information about properties of fly ash from (co-)combustion of litter.

2.6.4 Fly ash from co-combustion of biomass from industrial origin

The ash forming matter of the group of biomass from industrial origin is very different (amount and composition) from type to type and even from source to source. Figure 2.10 presents the relation between co-combustion percentage (fuel based) and the contribution in the fly ash for different type of biomass from industrial origin

The composition of *municipal sewage sludge* depends on several factors especially the composition of the waste water and the waste water cleaning process. The ash forming matter may consist mainly of Al, Si, Ca, Fe and P. The minerals present in municipal sewage sludge may be quartz, clay minerals, calcite and phosphorus bearing compounds. The latter depends mainly the phosphate removal method as part of the sewage water cleaning process. The combustion process of municipal sewage

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[12] Cement notation: C=CaO, S=SiO_2, P=P_2O_5, H=H_2O.

sludge has been studied on laboratory scale. Also, research has been performed on sewage sludge incinerators, but these incinerators are operating at lower temperatures than pulverized coal boilers. Phosphorus may be present as calcium iron phosphates, iron or alumina phosphates or react with alumino silicates, depending on the process that is used for the removal of phosphate.

Paper sludge has been studied for combustion in mainly fluidized bed boilers. The ash forming matter consists mainly of Ca, Si and Al. These components are mainly present in the minerals calcite and kaolinite. Calcite will be converted to free lime, which may reduce the soundness of fly ash. Kaolinite is a main constituent of coal. It may contribute to the formation of the glass phase in the fly ash. As the physical distribution of the minerals in paper sludge may be different from that of coal, it is not known to what extent calcite and kaolinite will react with each other during combustion in a pulverized coal boiler. This will be an important factor for the free lime content of the fly ash.

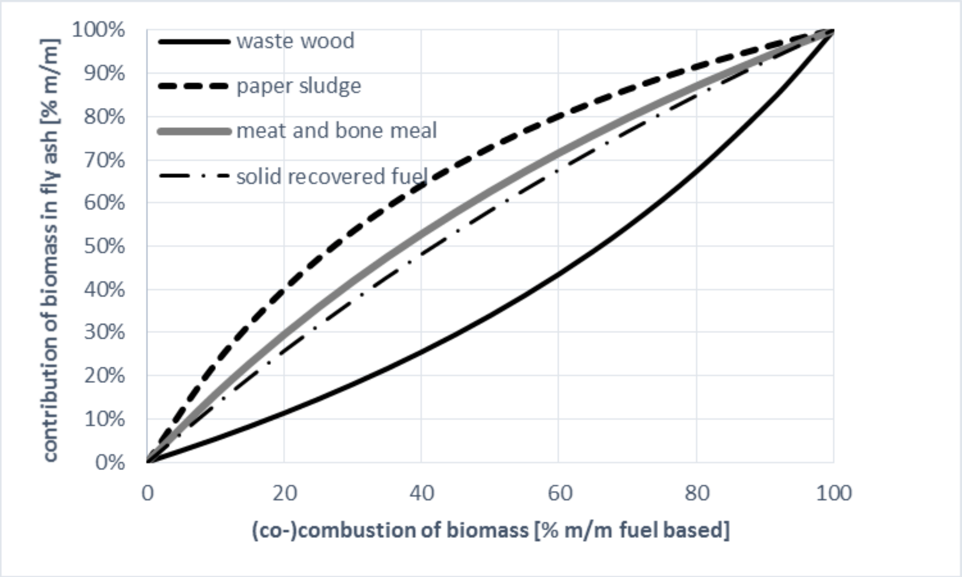

Figure 2:10: The relation between co-combustion percentage fuel based and the contribution of biomass in the fly ash for different type of biomass from animal and industrial origin

The ash composition of *demolition wood* is characterized by high contents of Ca and Si, which is probably caused by the presence of relicts of building materials like mortars and gypsum. Further it contains high contents of Pb and Zn, probably originating from paints. There is no information about the influence of co-combustion of demolition wood on the properties of fly ash.

Solid Recovered Fuels (SRF) covers a wide range of compositions due to the different sources. The ash forming matter may be derived from the wood, paper, textile, plastics etc. Paper and plastic contain fillers, which will contribute to the ash forming matter. In literature, only test results of a fly ash generated in a cyclone fired boiler where SRF is co-fired, have been found. It has been reported that a small change in main components took place and that the pozzolanic activity was even higher than that of the reference.

2.6.5 Overview influence biomass on properties concrete with co-combustion fly ash

This literature study showed that the composition of biomass differs from coal regarding the amount and the composition of ash forming matter (AFM). The coal that is fired in Dutch coal-fired power plants consists mainly of Si, Al, Fe and to a less extent of Ca. Co-combustion of biomass implies that the composition of the generated fly ash will be influenced. Table 2.11 provides an overview of the main components in the different biomasses and their potential influence on the properties of concrete with fly ash from co-combustion with this biomass.

Sulphur and chloride behaves as very volatile elements during combustion and most of it does not end up in the fly ash (see also chapter 6). Therefore these elements are not considered in this overview.

Table 2.11: Overview of main components in ash forming matter (AFM) of biomass and their potential effects on properties of concrete with fly ash from co-combustion with the specific biomass

Biomass	AFM	Potential effect on properties of concrete
Vegetable Origin		
-Wood(y) biomass	Ca	May cause unsoundness (free lime)
		May contribute to strength[2]
	Si	May contribute to strength and durability[2]
	K	May promote ASR, if reactive aggregate is present
-Agricultural residues	K	May promote ASR, if reactive aggregate is present
	Si	May contribute to strength and durability[2]
	Ca	May cause unsoundness (free lime)
Animal origin		
-Meat and bone meal	Ca+P	May contribute to strength[2]
	P[1]	May cause retardation of cement hydration
	Na	May promote ASR, if reactive aggregate is present
-Poultry litter	Ca	May cause unsoundness (free lime)
	P	May cause retardation of cement hydration
	K	May promote ASR, if reactive aggregate is present
Industrial origin		
-Municipal sewage sludge	Ca	May cause unsoundness (free lime)
	Fe	Unknown
	P	May cause retardation of cement hydration
-Paper sludge	Ca	May cause unsoundness (free lime)
	Al+Si	May contribute to strength and durability[2]
-Demolition wood	Ca	May cause unsoundness (free lime)
		May contribute to strength[2]
	Si	May contribute to strength and durability[2]
	Heavy metals	May cause retardation of cement hydration
-Solid Recovered Fuel	Ca	May cause unsoundness (free lime)
	Al+Si	May contribute to strength and durability[2]
	Heavy metals	May cause retardation of cement hydration

[1]) Part of phosphorus is bound organically in the biomass and may be available for formation of alkali phosphates during combustion process.

[2]) If it is present in a reactive form (glass phase, calcium silicate)

2.7 References

[2.1] CBS, 2014. StatLine Database CBS (Centraal Bureau voor de Statistiek), http://statline.cbs.nl/statweb.

[2.2] National Government and power sector, 2002. “Convenant kolencentrales en CO2-reductie”.

[2.3] www.Energieakkoord.nl January 9th 2015.

[2.4 Raask E., 1985.Mineral impurities in coal combustion. Behaviour, problems and remedial measures. Hemisphere Publishing Corporation.

[2.5] Yan et al, 2002. A mathematical model of ash formation during pulverized coal combustion, In: Fuel, vol 81 nr 3, pp 337-344.

[2.6] DNV GL, 2014. Memo Furnace temperatures in coal-fired boilers. Arnhem. 29-1-2014.

[2.7] Baxter L.L., 1993. Ash deposition during biomass and coal combustion: a mechanistic approach; Biomass and Bioenergy, Vol. 4, No 2, pp 85-102.

[2.8] CEN/TC 104WG4, 2010. Backgrounds to the revision of EN 450-1:2005/A1:2007 and EN 450-2:2005 “Fly ash for concrete”.

[2.9] Ward, C.R., 2002. Analysis and significance of mineral matter in coal seams. In: IJCG 50, pp 135-168.

[2.10] IEA Clean Coal centre, 2006. Ash management in coal-fired power plants.

[2.11] Hansen P.F.B. et al, 1998. Co-firing straw and coal in a 150 MWe utility boiler: in situ measurements. In: FPT 54, pp 207-225.

[2.12] KEMA, 2009. Database Trace elements. Report 9. Coals and ashes. Actualized up to and including coal from 2008. KEMA report 50931179-TOS/ECC 09-5285.

[2.13] Swaine D.J., 1990. Trace elements in coal. Published by Butterworth & Co Ltd, Great Britain.

[2.14] Bouska V.,1981. Geochemistry of coal. Published by Elsevier scientific publishing company. Amsterdam.

[2.15] Vassilev S.V. and Vassileva C.G., 1996. Occurrence, abundance and origin of minerals in coals and coal ashes. In: FPT 48, pp 85-106.

[2.16] Wigley F. and Williamson J. (Imperial college of science), 2005. Coal mineral transformations – effects on ash behaviour. Report COAL R278 DTI/Pub URN 05/659.

[2.17] Finkelman R.B. 1981. Mode of occurrence of trace elements in coal.

[2.18] Spears D.A. and Y. Zheng Y.,1999. Geochemistry and origin of elements in some UK coals, In: International Journal of Coal Geology 38 (1999), 161-179.

[2.19] Valkovic V., 1983. Trace elements in coal. Published by CRC Press. United States.

[2.20] IEA Clean Coal Center (Zhangfa Wu), 2006.Fundamentals of pulverized coal combustion

[2.21] Deer W.A. et al, 1975. An introduction to the rock forming minerals. Longman Group Limited, London.

[2.22] Reifenstein et al, 1999. Behaviour of selected minerals in an improved ash fusion test: quartz, potassium feldspar, sodium feldspar, kaolinite, illite, calcite, dolomite, siderite, pyrite and apatite. In: Fuel, vol. 78, pp. 1449-1461.

[2.23] Srinivasachar S. et al, 1990. Mineral behaviour during coal combustion 2: illite transformation. In: Prog. Energy Comb. Sci., vol 16, pp 292-302. Pergamon Press.

[2.24] Vassileva D.G. and Vassilev S.V., 2006. Behaviour of inorganic matter during heating of Bulgarian coals 2. Subbituminous and bituminous coals. In: FPT, pp. 1095-1116. Elsevier.

[2.25] Duval D.J. et al, 2008. In: Ceramic and Glass materials pp 33.Editors: J.F. Shackelford and R.H. Doremus

[2.26] Schiele E. and Berens L., 1972, Kalk Herstellung-Eigenschaften-Verwenlitter. Verlag Stahleisen M.B.H. Düsseldorf.
[2.27] Boynton R.S., 1980. Chemistry and Technology of lime and limestone. John Wiley & Sons.
[2.28] Oates J.A.H., 1998. Lime and limestone. Chemistry and Technology, Production an d Uses. Wiley-VCH, Weinheim Germany.
[2.29] Bauer and Natusch, 1981. Identification of carbonate compounds in coal fly ash. In: ES&T Research, volume 15, number 7, july 1981, pp 783-788.
[2.30] Mitchell, R.S. and Gluskoter, H.J. 1976 Mineralogy of ash of some American coals: variations with temperature and source. In: Fuel, vol. 55, pp.90-96.
[2.31] Meij R. et al,1983. The emission of fly ash and trace species from pulverized coal fired utility boilers. In: Proceedings of the 6th World Clean Air Congress, held in Paris, May 1983, part IV, pp. 317-324.
[2.32] Lutze, D. and Vom Berg, W., 2003. Handbook on fly ash in concrete, p 15. Verlag Bau+Technik. Düsseldorf, Germany.
[2.33] Vliegasunie. 2017. Database Quality control coal fly ash (incl. verification analyses of KOMO certificate EN 450 coal fly ash)
[2.34] CUR, 2007. Use of coal fly ash in mortar, concrete and grouts (in Dutch). CUR-recommendation 94. 3rd revised edition. Page 6.
[2.35] CUR, 1992. CUR-report 144. Fly ash as filler in concrete (in Dutch), page 32-34.
[2.36] Vliegasunie, 2015. Activity index tests non-published data
[2.37] Taylor H.F.W., 1997. Cement Chemistry. Page 275. Telford Publishers
[2.38] Fraay A., 1990. Fly ash a pozzolan in concrete. PhD dissertation Delft University of Technology, pp 7.1-7.18.
[2.39] Thomas M.D.A., 1996; Rieview of the effect of fly ash and slag on alkali-aggregate reaction in concrete. Building Research Establishment, Watford Great Britain.
[2.40] Fournier B. et al, 1999. Proposed guidelines for the prevention of alkali-silica reaction in new concrete structures. Reprinted from Transportation Research Record 1668. Nationa Research co uncil. Washington D.C..
[2.41] Heinz D. et al, 2011. Wirkung von Flugaschen zur Vermeilitter einer Schädigenden Alkali-Kieselsaüre-Reaktion im Beton.
[2.42] Thomas, M. et al, 2011. Effect of fly ash on expansionof concrete due to alali-silica reaction – exposure site studies. In: Cement & Concrete Composites 33 (2011), pp 359-367.
[2.43] Day, R. 1992. The effect of secondary Ettringite formation on the durability of concrete. A literature analysis. By order of the Portland Cement Association.
[2.44] Heinz D. et al, 1989. Delayed Ettringite formation and heat treatment of mortar and concrete. In: Concrete Precast Plant and Technology, 11 1989 pp 56-61
[2.45] Rozière E. et al, 2009. Durability of concrete exposed to leaching and external sulphate attacks. In: Cement and Concrete Research 39 (2009), pp 1188-1198.
[2.46] Heinz D. and Schiessl, P., 2005. Sulfatwiderstand flugaschehaltiger Betone. BVK/VGB Fachtagung. Flugasche im Beton. March 3rd Frankfurt. Page 1/8-8/8.
[2.47] Chindaprasirt P. et al, 2007. Sulfate resistance of blended cements containing fly ash and rice husk ash. In: Construction and Building Materials 21 2007, pp 1356-1361.
[2.48] Härdtl R., 1995. Veränderung des Betongefüges durch die Wirkung von Steinkohlenflugasche und ihr Einfluß auf die Betoneigenschaften. Deutscher Ausschuss für Stahlbeton. Heft 448, pp 65-75.

[2.49] Wegen van der G.J.L., 2014. Ageing coefficient of fly ash concrete and its impact on durability. Proceedings of the International Conference on Ageing of Materials & Structures. Delft 26 – 28 May 2014, the Netherlands. Paper No. 227629.

[2.50] Brameshuber W. et al, 2008. Freeze-thaw resistance with de-icing salt of fly ash concrete in laboratory and practice (in German). BVK/VGB Fachtagug, April 10th 2008. Frankfurt Germany, pp 1/11-11/11.

[2.51] NEN, 2012. EN 450-1 Fly ash for concrete

[2.52] Alley M.M. and VanLauwe, B., 2009 The role of fertilizers in integrated plant nutrient management, International Fertilizer Industry Association. pp 12.

[2.53] Johnston A.E. , 2000. Soil and Plant phosphate. International Fertilizer Industry association, Paris. pp1-2.

[2.54] Fengel D. and Wegener G., 1984. Wood, chemistry, ultrastructure, reactions. Published by De Gruyter, Berlin/New York.

[2.55] Werkelin J. et al, 2005. Ash-forming elements in four Scandinavian wood-species. Part 1: Summer harvest. In: Biomass and Bioenergy 29 (2005), pp 451-456.

[2.56] Vassilev S.V. et al, 2010. An overview of the chemical composition of biomass. In: Fuel 89 (2010), pp 913-933.

[2.57] ECN. 2015. Phyllis database. www.ecn.nl. February 6th 2015..

[2.58] Misra M.K. et al, 1993. Wood ash composition as a function of furnace temperature. In: Biomass and Bioenergy, vol 4, no 2, pp 103-116.

[2.59] Werkelin J. et al, 2011. Ash-forming elements in four Scandinavian wood species. Part 3: combustion of five spruce samples. In: Biomss and Bioenergy 35 (2011), pp 725-733.

[2.60] Oleander B. and Steenari, B., 1995. Characterization of ashes from wood and straw. In: Biomass and Bioenergy vol. 8, No. 2, pp 105-115.

[2.61] Siddique, R. Utilization of wood ash in concrete manufacturing. In: Resouces, Conservation and Recycling 67 (2012) p 27-33.

[2.62] Tkaczewska E. et al, 2012. Coal-biomass fly ashes for cement production of CEM II/A-V 42.5R. In: Construction and Building Materials 28 (2012), pp 633-639.

[2.63] Cheah C.B. and Ramli, M., 2012. Mechanical strength, durability and drying shrinkage of structural mortar containing HCWA as partial replacement of cement. In: Construction and building materials 30 (2012), pp 320-329.

[2.64] Abdullahi, M., 2003?. Characteristics of wood ash/OPC concrete. Available at www.lejpt.academicdirect.org

[2.51] Kraus R.N. et al, 2007?. Use of industrial by-products in sustainable construction practices. Available at www.claisse.info

[2.65] Wang S. et al, 2008. Biomass fly ash in concrete: Mixture proportioning and mechanical properties. In: Fuel 87 (2008), pp 365-371.

[2.66] Wang S. et al, 2008. Biomass fly ash in concrete: Freezing and thawing and rapid chloride migration tests. In: Fuel 87 (2008), pp 359-364.

[2.67] Wang S. et al, 2008. Biomass fly ash in concrete: SEM, EDX and ESEM analysis. In: Fuel 87 (2008), pp 372-379.

[2.68] KEMA, 2003. Confirmity tests coal fly from co-combustion of wood pellets 02-07-22. According to CUR recommendation 94. KEMA report 50331031-KPS/MEC 03-6088. (In Dutch)

[2.69] KEMA, 2005. Confirmity tests coal fly from co-combustion of wood pellets 09-01-2005, conform BRL 2505. KEMA report 5041159-KPS/MEC 05-9361. (In Dutch)

[2.70] KEMA, 2010. Confirmity tests coal fly from co-combustion of wood pellets 01-05-2010, conform BRL 2505. KEMA report 55106218-TOS/HSM 10-4872. (In Dutch)

[2.71] KEMA, 2010. Confirmity tests coal fly from co-combustion of wood pellets 05-09-2010, conform BRL 2505. KEMA report 55106346-PGR/HSM 11-4021. (In Dutch)

[2.72] Wu H. et al, 2012. Full-scale deposition measurements at Avedøre power plant unit 2 during suspension-firing wood with and without coal ash addition. Technical University of Denmark, Department of Chemical Engineering.

[2.73] Ramboll, 2015. Environ. Application of CFA when firing wood pellets. Presented at: IEA workshop on Co-firing Biomass. Drax, UK. 16-17 september 2015.

[2.74] Zygarlycke C.J. and Folkedahl, B.C., 2003. Effects of biomass blending on combustion ash. In: Preprints of papers division of fuel chemistry, vol. 48, pp 641-642. American Chemical Society.

[2.75] Korbee R. et al, 2003. Fuel characteristics and Test methods for biomass co-firing. ECN-report 03-057.

[2.76] Tay J-H. and Show, K-Y,1996. Utilization of ashes from oil-palm wastes as a cement replacement material. In: Water Science Technology Vol. 34, No 11, pp 185-192.

[2.77] Xu W. et al, 2012. Microstructure and reactivity of rice husk ash. In: Construction and building materials 29 (2012), pp 541-547.

[2.78] Zain M.F.M. et al, 2011. Production of rice husk for use in concrete as a supplementary cementitious material. In: Construction and building materials 25 (2011), pp 798-805.

[2.79] Fernandes I.J. et al, 2016. Characterization of rice husk ash produced using different biomass combustion techniques for energy. In; Fuel 165 (2016), pp 351-359.

[2.80] Sata V. et al, 2012. Effect of W/B ratio on pozzolanic reaction of biomass ashes in Portland cement ratio. In: Cement and Concrete composites 34, pp 94-100.

[2.81] Fernandez Lorente, M.J. and Cassarco Garcia, J.E., 2005. Comparing methods for predicting the sintering of biomass in combustion. In: Fuel 84, pp 1893-1900.

[2.82] Zheng Y. et al, 2007. Ash transformation during co-firing coal and straw. In: Fuel 86 (2007), pp 1008-1020.

[2.83] Thy P. et al, 2006. Compositional constraints on slag formation and potassium volatilization from rice straw blended wood fuel. In: Processing fuel Technology, 87, pp 383-408.

[2.84] Doshi V. et al, 2009. Development of a modeling approach to predict ash formation during co-firing of coal and biomass. In: FPT 90 (2009), pp 1148-1156.

[2.85] Nordgre, D. et al, 2011. Ash transformations in pulverised fuel co-combustion of straw and woody biomass.

[2.86] Nutalapati D. et al, 2007. Assessing slagging and fouling during biomass combustion: A thermodynamic approach allowing for alkali/ash reactions. In: FPT 88 (2007), pp 1044-1052.

[2.87] Hansen P.F.B. et al, 1998. Co-firing straw and coal in a !%) MWe utility boiler: in situ measurements. In: FPT 54, pp 207-225.

[2.88] Hansen L. A. ET AL, 1999. Characterization of ashes and deposits from high-temperatur coal-straw co-firing. In: Energy & Fuels vol. 12,pp. 803-816.

[2.89] RIVM, 2002. Beoordeling van het gezondheidsrisico door blootstelling aan BSE ineffectiviteit van het destructiebedrijf Renda Bergum. RIVM report 244920003/2002. Bilthoven, the Netherlands. In Dutch.

[2.90] Eliott J.C.,1994 Structure and chemistry of the apatities and other Calcium orthophosphates. Studies in inorganic chemistry 18. Elsevier. AMSEerdam.

[2.91] Gulyurtlu, I. et al, 2005. Co-combustion of coal and meat and bone meal. In: Fuel 84, pp 2137-2148.

[2.92] Fryda, L. et al, 2006. Experimental investigation of fluidised bed co-combustion of meat and bone meal with coals and olive bagasse.. In: Fuel, 85, pp 1685-1699.

[2.93] Beck, J. et al., 2005. The behaviour of phosphor in flue gasses from coal and secondary fuel co-combustion. In; Fuel 84, pp 1911-1919.

[2.94] Waltl J. et al, 2003. Mitverbrennung biogener Brennstoff in den Kohlekraftwerken der energie AG Oberösterreich. In: VGB PowerTech 9/2003, pp 114-119.

[2.95] Annamalai K. et al., 2003. Co-firing of coal and cattle feedlot biomass (FB) fuels, Part III: fouling results from a 500,000 BTU/h pilot plant. In: Fuel 82, pp 1195-1200.

[2.96] Öhman M. et al, 2003. Ash transformations during combustion of meat-, bonemeal, and RDF in a (bench-scale) fluidized bed combustor. In: Energy & Fuels, 17, pp 1153-1159.

[2.97] Deydier et al, 2005. Physical and chemical characterisation of crude meat and bone meal combustion residue: “waste or raw material”? In: Journal of Hazardous Materials B121, pp. 141-148.

[2.98] Brown P.W., 1999. Hydration behavior of calcium phosphates is analogue to hydration behavior of calcium silicates. In: CCR 29, pp 1167-1171.

[2.99] Takagi S. et al, Formation of hydroxyapatite in new calcium phosphate cements, Biomaterials 19 (1998), 1593-1599.

[2.100] Rakovan J. 2002. growth and surface properties of apatite. In: Phosphates. Geochemical, geobiological, and materials importance. Editors: Kohn, M.J. et al. Mineral Society of America. 2002.

[2.101] Hu, J.W. et al, 1988. Investigation of hydration phases in the system CaO-SiO2-P2O5-H2O. In: J. Mater. Rs. 4, pp 772-780.

[2.102] Hu, J.W. et al, 1988. Studies of strength mechanism in newly developed chemically bonded ceramics in the system CaO-SiO2-P2O5-H2O. In: CCR 18, pp 103-108.

[2.103] Taylor, H.F.W., 1997. Cement chemistry. Thomas Telford Publishers. P 338.

[2.104] Lieber, W., 1974. The influence of phosphates on the hydration of cement. Proceedings of the VI International congress on the chemistry of cement, Moscow, september 1974.

[2.105] Barnett, G.M. Litter P fractionation, Bioresource Technology 49 (1994), 149-155.

[2.106] Barnett, G.M. Phosphor forms in animal manure, Bioresource Technology 49 (1994), 139-147.

[2.107] Cooperband, J.R. and L.W. Good. Biogenic phosphate minerals in litter: implications for phosphor loss to surface waters. In: Environmental Science Technology, 36 (2002), 5075-5082.

[2.108] Annamalai, K. et al, Co-firing of coal and cattle feedlot biomass (FB) fuels, Part III: fouling results from a 500,000 BTU/h pilot plant, Fuel 82 (2003), 1195-1200.

[2.109] Sweeten J.M. et al, Co-firing of coal and cattle feedlot biomass (FB). Part 1: feedlot biomass (cattle manure) fuel quality and characteristics, Fuel, 82 (2003) 1167-1182.

[2.110] CBS (Kees Baas et al), 2005. Verwijdering van fosfaat en stikstof op rioolwaterzuiveringsinstallaties, 2003.

[2.111] Ninomiya Y. et al, 2004. Transformation of mineral and emission of particulate matters during co-combustion of coal with sewage sludge. In: Fuel 83. Pp 751-764.

[2.112] Zhang L. et al, 2004. Combustibility of dried sewage sludge and its mineral transformation at different oxygen content in drop tube furnace. In: Fuel Processing Technology, pp 983-1011.

[2.113] Cheeseman C.R. et al., 2003. Properties, microsturcture and leaching of sintered sewage sludge ash. In: Resources, Conservation and Recycling, 40, pp 13-25.

[2.114] Buck P., 2003. Mitverbrennung von Klärschlammen in Kohlekraftwerken. In: WLB Wasser, Luft und boden 3/2003, pp 52-54.

[2.115] Anonymous, 2000. Kohlersatz aus dem Klärwerk. In: Energie Spektrum 4/2000, pp 58-60.

[2.116] CUR, 1999. Concrete and mortar with coal fly ash from co-combustion. CUR-report 99-1.

[2.117] WRAP and Environment Agency, 2008. Paper sludge ash. A technical report on the production and use of paper sludge ash. Banbury, Oxon, UK.

[2.118] Vamvuka D. et al, 2009. Possibility of using Paper sludge in co-firing applications. In: Fuel 88 (2009) pp 637-643.

[2.119] Latva-Somppi J., et al 1998. The ash formation during co-combustion of wood and sludge in industrial fluidised bed boilers. In: FPT, 54, pp. 79-94.

[2.120] Bos J.H. et al, The Paper Book (in Dutch). VAPA opleidingsinstituut voor de papier- karton en golfkartonindustrie. Apeldoorn, the Netherlands, 1995.

[2.121] Florea M.V.A., 2014. Secondary materials in cement-based products. Treatment, modelling and environmental interaction. PhD dissertation Eindhoven University of Technology.

[2.122] Mark H.K. et al, Encyclopedia of polymers science and engineering, 2nd edition, John Widely and Sons, New York, 1987.

[2.123] Wu H. et al, Trace elements in co-combustion of solid recovered fuel and coal, Fuel Processing Technology 2011. Article in press.

[2.124] Mohamed A.B. et al, The physical and environmental properties of coal-SRF fly ash. In: Proceedings International conference on municipal waste, Hollywood USA, 11-14 april 1989.

[2.125] Hilber Th. et al, Advantages and possibilities of Solid Recovered Fuel co-combustion in the European Energy Sector, Journal of the Air & Waste Management Association, 57 (2007), 1178-1189.

[2.126] Bijen J. and Niël, E., 1981. Supersulphated cement from blast furnace slag and chemical gypsum available in the Netherlands and neighbouring countries. In: Cement and concrete Research. Vol. 11, pp 307-322. Pergamon Press.

[2.127] Taylor H.F.W. Cement Chemistry, pp 262-263 and 1264. Thomas Telford Publishers.

[2.128] Belmann, F. and stark, J., 2009. Activation of blast furnace slag by a new method. In: Cement and Concrete Research 39, pp 644–650.

[2.129] Jünger M.C.G. et al, 2011. Advances in alternative cementitious binders. In: Cement and Concrete Research 41, pp 1232-1243.

3 FLY ASH FROM PILOT-SCALE CO-COMBUSTION TESTS

3.1 Introduction

The goal of this experimental research is to investigate the effects of high percentages of co-combustion biomass from different origins (animal and industrial origin) on the properties of the generated fly ash and the properties of mortar and concrete made with this fly ash. The pilot-scale experiments were performed with three different secondary fuels from different origin to generate a wide spectrum of fuels. Demolition wood (DW), Solid Recovered Fuel (SRF) and poultry litter (PD) were selected. The selection of the coal was limited by the practical availability of pre-milled coal in the region.

These pilot-scale trials consisted of four steps, namely:
- Characterization of coal and secondary fuels.
- Performance of co-combustion experiments to generate fly ashes.
- Characterisation of generated fly ashes.
- Properties of mortar and cement paste with fly ash.

The coal and the secondary fuels were characterised by chemical and mineralogical methods. Not only main elements were analysed but also trace elements. The fuels were analysed in order to explain how they influence fly ash characteristics. A set of 10 co-combustion trials were performed with the test boiler of KEMA with a capacity of 1 MW_{th} to generate fly ashes. One reference experiment was performed to generate fly ash obtained from 100% coal. This fly ash was also used to assess the representativeness of the co-combustion experiments.

The fly ashes were physically, chemically and mineralogically characterised, to be able to explain the properties of mortar and cement paste with fly ash. The trace elements are of interest in view of their potential influence on hydration behaviour of the cement. The mineralogical characteristics provide information on how main elements are present in the fly ash and explain the performance of the fly ash. Especially the glass phase (content and composition) is very important for the pozzolanic properties of the fly ash. The mineralogical characteristics of the fly ash were obtained by X-ray diffraction and sequential dissolution. Sequential dissolution provides information about the glass content and glass composition of the fly ash.

The performance of the fly ash when used in concrete was analysed according to test methods and limit values of the EN 450-1 [3.1]. This is the European harmonised standard for use of fly ash in concrete. The setting time, pozzolanity (activity index) and soundness[13] of fly ash cement paste were tested.

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[13] Soundness or volume stability. The European standard for coal fly ash in concrete uses the term soundness. The soundness is measured with the LeChatelier test.

3.2 Materials and methods

3.2.1 Coal and secondary fuels

Demolition wood was supplied by Electrabel Nederland from power plant ‘Centrale Gelderland’ (Nijmegen, the Netherlands). The fuel was sampled after the pre-treatment with hammer mills and micro mills. However, it was still too coarse for direct combustion. Therefore, the material was treated by a so-called Ultrarotor (Jäckering Germany) to obtain further size reduction. Poultry litter from layers was derived from a poultry farm (Mr Wisse's poultry farm, Colijnsplaat, the Netherlands). The sample was taken from the transport belt leading from the shed. The moisture content of this poultry litter is reduced by drying it with warm air from the stable, which makes it more suitable for combustion processes. The grain size of the poultry litter was reduced with a hammer mill (type Hamex, 30 kW). A sample of SRF was supplied by Eco Energy Europe (Born, the Netherlands). The fuel was sampled after shredding and pelletizing (pellet diameter 10 mm). Because of the low pellet strength, the material was again pelletized and then treated by the ultrarotor (Jäckering Germany) to obtain sufficient size reduction. The coal was from Venezuelan source (Paso Diablo). It was milled and dried by IKO (Germany).

3.2.2 Combustion experiments

The combustion experiments were performed in the 1 MW_{th} test boiler of KEMA. The experimental boiler installation basically consists of (see figure 3.1):

- A pulverised coal silo and transport system.
- A pulverised secondary fuel silo and transport system.
- A pulverised coal burner and combustion chamber.
- A flue gas cooler.
- A fabric filter with an ash disposal system.
- A low and high-pressure water-cooling system.

The pulverised coal is supplied in bulk cars in a nitrogen atmosphere (see also table 3.1). The pulverised coal is transported by means of nitrogen to one of the two storage silos, which can contain 45 m^3 each. Coming from the silos, the pulverised coal is weighed and transported in dosed quantities to the burner of the vertically built combustion chamber. Transportation is performed by means of air (primary air) at about 60 to 65 °C. The burner, having a capacity of 1 MW thermal, has ample adjustment facilities and is suitable for several kinds of pulverised coal. The capacity can range from 100 to 40%. The combustion air is preheated in an air heater, which is placed in the second part of the flue gas cooler. The combustion air is supplied as so-called secondary combustion air to the burner and partly (15%) as tertiary combustion air into the combustion chamber. In the co-firing experiments, the secondary fuels are introduced by means of a special dosing installation. Coal and secondary fuel were introduced into the boiler by means of a special burner for co-combustion. In this burner, the secondary fuel (and transport air) is transported through the centre and the coal (and transport air) through an annular ring around the centre of the burner.

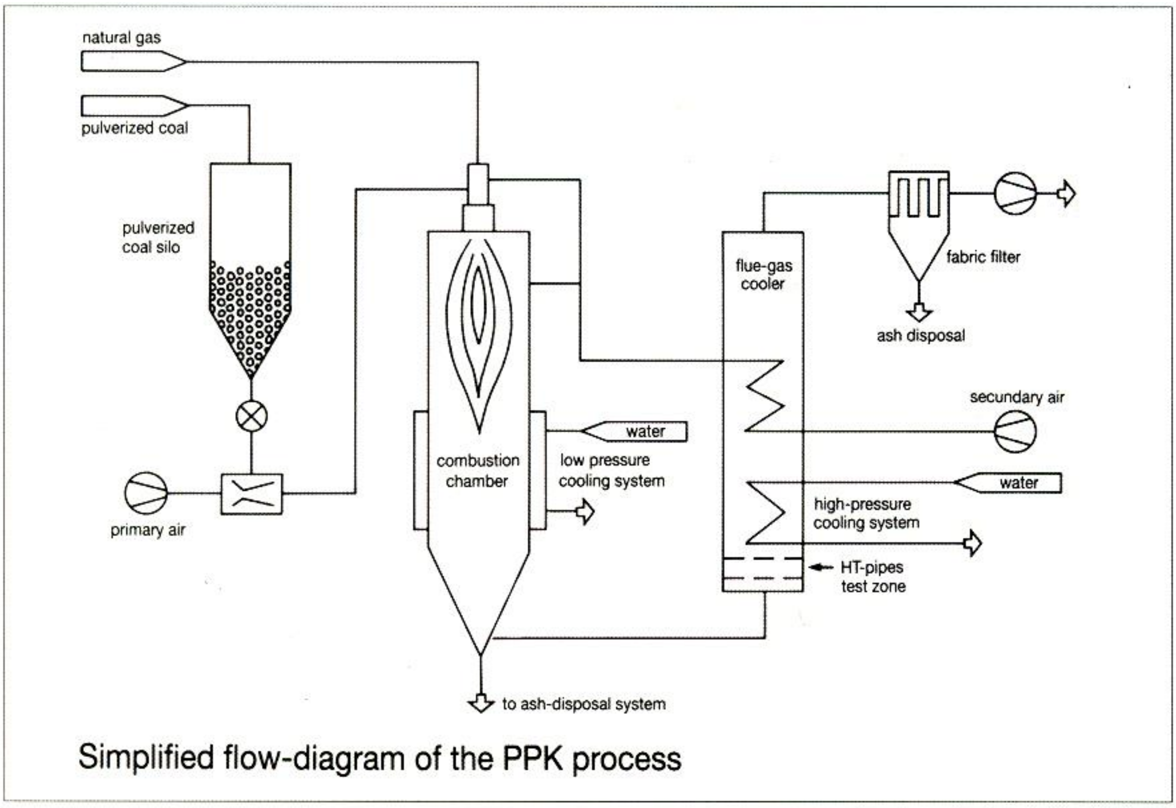

Figure 3:1: Flow diagram of KEMA Test boiler. Coal and secondary fuels are introduced in the combustion chamber by a special burner for co-combustion.
The generated fly ash is separated from the flue gas with a fabric filter.

The combustion chamber is composed of a number of detachable, cooled ring sections (15 rings of 30 cm high each), which means that the chamber can be varied in height. These ring sections are provided with entry ports for observation and sampling. On the fourth ring, the tertiary combustion air is supplied to the combustion chamber. Natural gas is used for starting up and preheating the installation, after which pulverised coal can be fired. The flue gases leave the combustion chamber at a temperature of about 1150 °C and are cooled down in the flue gas cooler by means of water-cooled pipes and the previously mentioned combustion air pre-heater. Filtering of the flue gas is performed with a fabric filter, which is installed behind the flue gas cooler. After removal of the fly ash, the flue gases are transported to the chimney by means of a ventilator.

The temperature of the flame was measured with a suction pyrometer. This pyrometer consists of a cooled tube that is put in the centre of the flame. An amount of gas is extracted from the flame and brought to a thermocouple, which serves to measure the temperature.

Each secondary fuel was co-fired in three percentages ranging from 10 to 33 %. A reference fly ash (REF) was produced from 100 % coal only. The ashes are coded using the co-combustion percentage, for example DW10 is the ash from co-combusting 10% (e/e) Demolition Wood.

Table 3.1: Selected design data for the KEMA Test Boiler

Design data	Value	Unit
Thermal capacity (vaporiser)	1.0	MW
High-pressure cooling system	27	bar
Low-pressure cooling system	5.6	bar
Maximum flue gas capacity	1905	kg/h
Residence time	1.7	s
Temperature of flue gases at boiler exhaust	900 - 1150	°C
Intake temperature of fabric filter	170	°C
Maximum velocity of flue gases	10	m/s
Excess air	5 - 40	%
Pulverised coal primary air	161	kg/h

3.2.3 Chemical characterization of (secondary) fuels and fly ashes

The chemical composition of the mineral matter of the fuels and fly ashes was analysed after total digestion in line with EN 15290 [3.2] and EN 15410 [3.3]. Digestion of the fuels was performed after incineration of the organic components at low-temperature conditions. The fly ash and the mineral matter from the incinerated fuel were each melted together with lithium tetra borate to produce a glass. This glass was digested by the following procedure: a mixture of 500 g 65% $HN0_3$, 50 g 70% $HClO_4$ and 450 g 38% HF was made in 1 l PE bottle. 100-500 mg of the sample was mixed with 10 g of the acid mixture to digest the sample by heating in a bomb[14] overnight at 190 °C. The elements Al, Fe, K, Mg, Na, P and Si were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Free lime was analysed in accordance with EN 450. Cl, F and Br in coal were analysed after pyro hydrolysis. Mercury was analysed after digestion with O_2 bomb.

The amount of inorganic phosphorus and organic phosphorus which is soluble in acid was analysed by ICP after extraction, according to the method of Salomons and Gerrtisen [3.4] and Barnett [3.5]. This was only performed for poultry litter because of its high phosphorus contents.

3.2.4 Characterization of mineralogy of secondary fuels and fly ash

The mineralogical characteristics were determined using two different methods, namely X-ray diffraction (XRD) and sequential dissolution. The scan range of the XRD was 5-75 2θ and 6-130 θ

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[14] Materials which are not fully dissolved by acid-digestion at atmospheric pressure may require a more vigorous treatment in pressure vessels lined with polytetrafluoroethylene (PTFE) glass, silica or vitreous (glassy) carbon or in sealed silica tubes; this treatment is called bomb-digestion. The test sample and acids are heated in such a closed vessel, so that the digestion is carried out at higher temperature and pressure. Source: PAC, 1988, 60, 1461 (Nomenclature, symbols, units and their usage in spectrochemical analysis-X. Preparation of materials for analytical atomic spectroscopy and other related techniques (Recommendations 1988)) on page 1469.

respectively. The count time was 1-2 s. The XRD analyses were performed with a Philips diffractometer PW1820 (Co X-ray tube) or a Bruker D4 Endeavor (Cu X-ray tube). If the XRD was meant to quantify the concentration of the minerals, an internal standard was added (metallic Si) before the XRD analysis was performed. These XRD analyses were performed with the Bruker D4 Endeavor. The identified minerals were quantified using the Rietveld method and adjusted to the known mass percentage of the added standard. The percentage amorphous material is assumed to be 100% minus the sum of the mass percentages of the identified minerals. The X-ray diffraction measurements (XRD) were carried out by Wageningen University/TCKI and CORUS.

The glass composition was determined based on the determination method of reactive silicon [3.6]. This was combined with so-called sequential dissolution. A key feature of the analysis is the cascade approach, which involves removing in turn the fraction that is soluble in acid and the fraction that is soluble in potassium hydroxide, and analysing each separately. The dissolved fraction from these steps is analysed with ICP-AES for Al, Ca, Fe, K, Mg, Na, S, Si and Ti.

3.2.5 Scanning electron Microscopy (SEM)

The morphology of the fly ashes were investigated using a scanning electron microscope (SEM). The SEM was a JEOL 6300. The pictures were taken in the SE-mode (secondary electrons) with an acceleration voltage of 15 kV. The samples were sputtered with gold.

3.2.6 Grain size distribution of fuels and fly ashes

Grain size distribution of fly ashes and pre-milled coal was analysed with laser granulometry (Malvern). The other fuels were analysed with a combination of mechanical sieving (coarse fraction) and laser granulometry (fine fraction).

3.2.7 Properties of cement paste and mortar with fly ash

The following characteristics were used to assess the performance of fly ash:

- Setting time was tested in accordance with EN 450. This test is based on the penetration behaviour of a standard needle in a cement paste or cement fly ash paste. This cement fly ash paste consists of 75% cement and 25% fly ash. The amount of mixing water is adjusted to obtain a standard consistency. See figure 3.2.
- Pozzolanic behaviour was tested in accordance with EN 450. The pozzolanic behaviour is expressed as the Activity Index (see Box 1 in 2.2.4).
- The soundness of cement fly ash paste was tested in accordance with EN 450 using the LeChatelier test. This cement fly ash paste consists of 50% cement and 50% fly ash. The amount of mixing water is adjusted to obtain a standard consistency. This fresh cement paste is to fill a ring with two needles (see figure 3.3). After 24 hours of hardening, the distance between the tips of the needles is determined with a calliper. After that, the hardened cement paste together with the ring is stored in boiling water for a quarter of an hour. After that the distance between the tips of the needles is measured again. The increase of the distance before and after boiling is a measure for the unsoundness.

Figure 3:2: Vicat apparatus for determination of setting time, which is measured as the penetration behaviour of a standard needle in a cement (fly ash) paste.

Figure 3:3: LeChatelier test ring, filled with cement (fly ash) paste for determination of soundness. This is measured as the increase in distance between the tips of the needles before and after boiling the sample in water.

3.3 Experimental results: properties of fuels and fly ashes

3.3.1 Chemical characteristics of fuels

The chemical and physical characteristics of the fuel are represented in table 3.2 and 3.3. The coal used in this research has a relatively low amount of ash forming matter (8.5% m/m) compared to the coal that is used in Dutch power stations (average about 12.4 % m/m over the past ten years), while the heating value is relatively high. Further, this coal has a relatively low content of Al_2O_3 and Fe_2O_3, accompanied with a high SiO_2 content. The ash content derived from the element composition, expressed as oxides, fits very well with the ash content based on gravimetry (8.36 versus 8.50% m/m). The XRD analyses showed the presence of the well-known coal minerals like illite; kaolinite, pyrite etc. (see table 3.5).

The poultry litter did not contain any straw or other such materials, but broken eggs and feather were occasionally present. Poultry litter contains hardly any Al_2O_3, but very high contents of CaO, K_2O and P_2O_5. Further, the content of SiO_2 is considerably lower than that of coal, normally used in Dutch coal-fired power stations [3.7]. The concentrations of Mn and Zn in poultry litter are significantly higher than in the coal (see table 3.4). A reliable comparison between the ash content derived from the elemental composition, expressed as oxides and the ash content based on gravimetry (14.2 versus 19.1% m/m) cannot be made as Ca is present in combination with phosphates and carbon dioxide. The very low content of Al_2O_3 stipulates to the minor presence (or even absence) of glass-forming minerals like clay minerals and feldspars. XRD analyses were performed on two samples of poultry litter that were ignited at 550º and then separated in a coarse and a fine fraction. Calcite, quartz, sylvine and apatite were identified in both fractions. Dolomite may also be present. The presence of these minerals fits well with the chemical analyses. No sulphur bearing minerals were identified, which stipulates to an organically associated form.

Table 3.2: Ash composition of coal and secondary fuels

Fuel	Coal	Demolition wood	Poultry litter	Solid Recovered Fuel
Element	% m/m	% m/m	% m/m	% m/m
Al_2O_3	1.72	0.42	0.11	1.15
CaO	0.28	1.09	8.22	1.90
Fe_2O_3	0.59	0.24	0.13	1.14
K_2O	0.16	0.11	1.72	0.18
MgO	0.22	0.12	0.63	0.22
Na_2O	0.07	0.16	0.19	0.16
P_2O_5	0.02	0.02	1.60	0.09
SiO_2	5.25	2.49	1.54	4.46
TiO_2	0.07	0.13	0.00	0.53
Cl	0.02	0.14	0.58	0.89

N.B. all characteristics are “dry base"

Table 3.3: Ultimate and proximate analyses of coal and secondary fuels

Fuel		Coal	Demolition wood	Poultry litter	Solid Recovered Fuel
Element	Unit				
Dry matter	% m/m	98.4	91.2	86.0	98.3
AFM	% m/m	8.50	5.65	19.06	10.68
Heating value	MJ/kg	30.3	18.0	12.5	28.4
C	% m/m	78.2	47.76	35.9	64.3
H	% m/m	5.17	5.88	4.66	9.5
N	% m/m	1.45	0.97	5.29	0.36
S	% m/m	0.76	0.164	0.516	0.203

Key: AFM = amount of ash forming matter

The percentage of soluble organic P was about 0.6% m/m, which is about 83% of total amount of P. Results from literature, based on analyses, showed values of 40-70% (average 49) inorganic P of the total amount of P present in the litter and acid-soluble organic P 25-44% (average 33%) [3.8]. The XRD-analyses showed the presence of apatite as phosphate bearing phase. In coal, much of the phosphorus is present as apatite [3.9], usually Fluor apatite [3.10]. Alumina phosphate minerals have been found in a number of Australian and British coals [3.10, 3.11].

The SRF sample consisted of different fractions, namely 13% paper, 56% plastics, 7% textile and 24% other materials including wood, metals and non-identifiable materials. The content of CaO, TiO_2 and Fe_2O_3 are higher than that of the coal, accompanied with lower contents of Al_2O_3 and SiO_2. The concentrations of Br, Cr, Cu, Pb, Sb and Zn in SRF are significantly higher than in the coal. Qualitative and quantitative XRD analyses were performed on the above mentioned SRF fractions. A lot of minerals were identified, viz. $CaSO_4$ (anhydrite), calcite, hematite, vermiculite, chalk, illite, kaolinite, mica, rutile, plagioclase and possibly alkali feldspar. A significant amount of SiO_2 is present as quartz, but a significant part is also present in illite and kaolinite.

The demolition wood sample was contaminated with small parts of stony material. The fuel was analysed by XRD using Rietveld's method for phase quantification. This fuel consisted of quartz (41%, ash base), calcite (12%), rutile (4%) and X-ray amorphous/non-identifiable phase (43%). The concentrations of Cu, Cr, Pb, Sb and Zn in demolition wood are also significantly higher than in the coal.

Table 3.4: Concentration of trace elements in coal and secondary fuels

Fuel	Coal	Poultry litter	Demolition wood	Solid Recovered Fuel
Element	mg/kg	mg/kg	mg/kg	mg/kg
As	1.3	0.9	6.0	2.1
B	53	34	18	41
Br	1.4	8.8	.3.8	69.1
Cd	0.1	0.3	1.9	3.4
Co	1.9	0.7	1.7	4.2
Cr	12	6	42	122
Cu	4	60	126	553
F	50	65	25	140
Hg	0.04	< 0.04	0.12	0.11
Mn	53	392	98	107
Mo	1.8	5.4	< 0.8	5.4
Ni	9.4	4.4	4.7	22.3
Pb	3.4	5.2	756	271
Sb	0.41	0.12	20	321
Se	5.9	0.5	<1	<1
Sn	< 4	< 4	.6	.25
Sr	< 75	152	< 75	< 75
V	20.3	4.1	1.6	4.2
W	0.36	< 0.3	< 0.3	1.45
Zn	20	349	681	640

Table 3.5: Some mineralogical characteristics of coal and secondary fuels

Fuel	Coal		Poultry litter	Demolition wood		Solid Recovered Fuel		
(Q)XRD?	XRD	XRD	XRD	XRD	QXRD[3]	XRD	XRD	QXRD[3]
preparation	550°	Plasma	550°	550°	550°	550°	Plasma	550°
Al (metal)	-	-	-	-	-	-	-	(1)
Amorphous	-	-	-	-	37	yes	-	53
$CaSO_4$	Yes[1]	yes[2]	-	yes	-	yes	-	2
Apatite	-	-	yes	-	-	-	-	-
Calcite	possibly	-	yes	yes	13	-	Yes	8
Dolomite	possibly	possibly	possibly	-	-	-	-	-
Feldspar	possibly	possibly	-	-	-	-	Yes	-
Halite	-	-	-	-	-	-	-	3
Hematite	yes	-	-	-	-	yes	-	1
Illite	-	yes	-	-	-	-	Yes	-
Kaolinite	-	yes	-	-	-	-	Yes	-
Magnetite	-	-	-	-	-	-	-	1
Mica	yes	-	-	-	-	yes	-	-
Pyrite	-	yes	-	-	-	-	-	-
Quartz	yes	yes	yes	yes	46	yes	Yes	30
Rutile	-	-	-	yes	4	-	-	2
Sylvine	-	-	yes	-	-	-	-	-

1) Identified as anhydrite

2) Identified as hemi hydrate

3) [% m/m]

3.3.2 Co-combustion experiments

An overview of the experiments is presented in table 3.6. The co-combustion percentage is calculated on the fuel, energy based [e/e] and on the fly ash, mass based [% m/m]. A reference fly ash (REF) was produced from 100 % coal only. The ashes are coded using the co-combustion percentage, for example DW10 is the ash from co-combusting 10% (e/e) demolition wood. During the co-combustion experiments, the flame temperature was analysed with a suction pyrometer. The temperatures are within the range of measurements from combustion experiments with 100% coal firing at full load, but are lower than on a real scale[15]. The fly ash was sampled when the combustion process was in equilibrium, mostly two hours after the start of the experiment.

The loss on ignition (LOI) of the generated fly ashes is considerably higher than in fly ashes from real scale power plants due to the lower burn-out, which is mainly caused by the shorter residence time of the fuel particles. The loss on ignition (LOI) of fly ash depends on several factors besides the properties of the fuel, i.e. mainly the milling process (fines of the coal) and the performance of the boiler.

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[15] No temperature measurements were performed during the experiments with SRF due to failure of the pyrometer.

As higher LOI (>> 5% m/m) may reduce workability of fresh cement paste and mortar (see further 4.5.4), it was decided that fly ash samples were subjected to heat treatment (at 550 ºC) to remove unburned carbon by glowing, before preparing mortars for activity index and flow test of mortar. This temperature is much lower than sintering temperatures of fly ash (1000-1200 °C). The LOI of the treated fly ash was 1 - 2% m/m. When a fly ash sample was tested which was subjected to heat treatment it is mentioned in the text.

Table 3.6: Survey of co-combustion experiments: LOI, co-combustion percentages (CC), O_2 surplus, combustion efficiency and flame temperatures

Parameter	% CC	%CC	LOI	LOI after treatment	O_2 surplus	Burn-out	Flame Temperature
Unit	% e/e	% m/m^1	% m/m	% m/m	%	% m/m	° C
Fly ash							
REF$^{2)}$	0	0	36.9	1.5	-	95.1	1240
DW10	10	11	39.5	1.6	3.9	94.7	1230
DW20	20	22	33.2	1.5	3.7	96.0	1180
DW30	30	32	25.5	1.4	3.7	97.3	1160
PD11	11	40	15.2	-	5.0	97.8	1170
PD16	16	50	11.7	-	4.3	98.2	1130
PD19	19	56	11.9	-	4.4	98.1	1090
SRF14	14	18	29.9	1.3	4.0	96.4	-
SRF27	27	33	24.4	1.1	4.0	96.5	-
SRF33	33	39	25.6	1.2	3.8	96.5	-

1) Ash based

2) Explanation fly ash codes is given in table 3.4

3.3.3 Physical characteristics of generated fly ash

The morphology of the fly ashes was assessed using SEM. A SEM photograph of the reference fly ash (REF) is presented in Figure 3.4 and 3.5. The morphology of the co-combustion fly ashes were quite similar. The particles of all fly ashes were less spherical than fly ash generated in Dutch power plants. The grain size distribution (see table 3.7), expressed as D_{10}, D_{50} and D_{90} of the fly ashes from 100% coal and from co-combustion of demolition wood and SRF were comparable, having D_{10}, D_{50} and D_{90} values of about 4, 14 and 69 µm respectively. The fly ash from co-combustion of poultry litter was somewhat coarser than these fly ashes. The particle density of the generated fly ashes is higher than that of fly ashes generated in Dutch power plants (about 2275 kg/m^3) [3.13]. See further 3.4.2 for an explanation for the high particle density.

Table 3.7: Grain size [μm] and volume weight [kg/m³] of the generated fly ashes

Fly ash	REF[1]	PD19	DW30[1]	SRF33[1]
parameter				
D10	3	5	3	3
D50	15	22	14	14
D90	70	87	68	68
Particle density	2428	2508	2538	2558

1) LOI has been reduced by treatment; see subsection 3.3.2

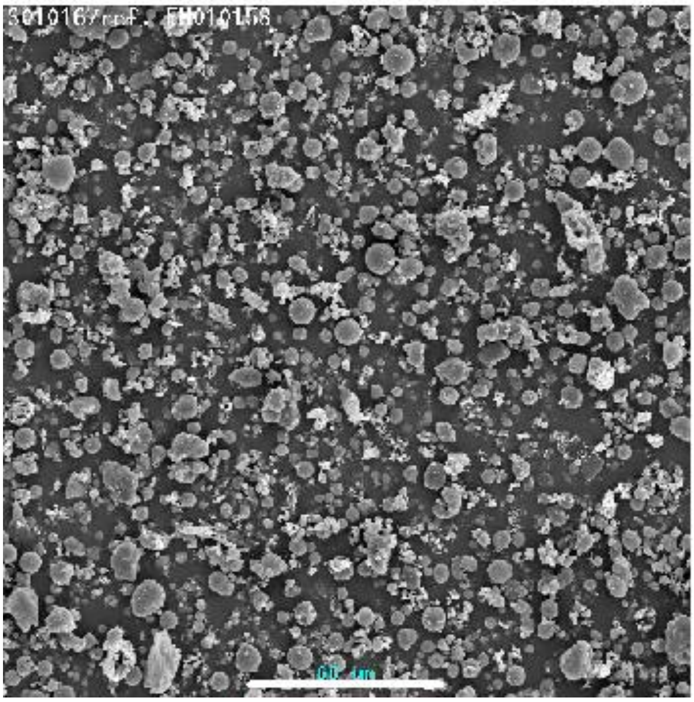

Figure 3:4: SEM photograph of reference fly ash (REF. The particles in the fly ash are less spherical than in fly ash generated in coal-fired power plants (1 scale unit = 60 µm)

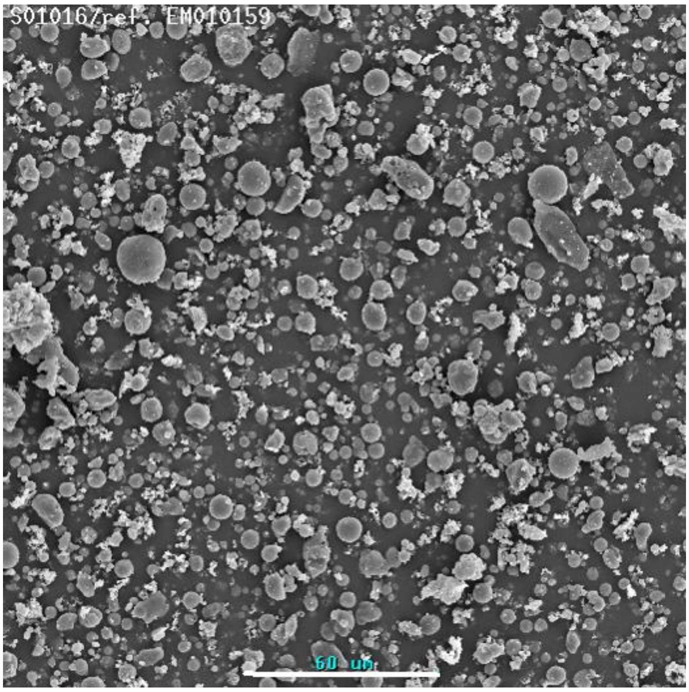

Figure 3:5: SEM photograph reference fly ash (REF). The particles in the fly ash are less spherical than in fly ash generated in coal-fired (1 scale unit = 60 µm)

3.3.4 Chemical characteristics of generated fly ashes

The influence of co-combustion on the chemical composition of the produced fly ash differs from fuel to fuel (see table 3.8 and 3.9). Co-combustion of demolition wood and Solid Recovered Fuel results in an increase of amount of CaO. It should be noted that the coal has a relatively low CaO content. The Al_2O_3 and SiO_2 content are reduced to a limited extent. The influence on the content of MgO, P_2O_5, Fe_2O_3 and Na_2O is of minor importance (however small concentrations of soluble phosphate are able to cause retardation of cement hydration). Several (heavy) metals are also increased, especially Cu, and Zn in all fly ashes from co-combustion and Cr, Pb and Sb in fly ashes from co-combustion of Solid Recovered Fuel and demolition wood.

The influence of co-combustion of poultry litter on the chemical composition of the generated fly ash exceeds the influence of the other secondary fuels due to its high amount of ash forming matter and its very different composition compared to coal. The content of CaO, K_2O, P_2O_5 and SO_3 is strongly increased. The latter is increased due to the reaction of SO_2 with CaO and K_2O. Also the content of Mn and Zn is increased, but to a lower extent than if demolition wood or SRF is being co-fired.

Table 3.8: Concentration of main components [% m/m] of the generated fly ashes

Fly ash	REF	PD11*	PD16*	PD19*	DW10	DW20	DW30	SRF14	SRF27	SRF33
Compound										
Al_2O_3	19.7	11.3	11.1	10.6	19	19.4	17.2	18.1	17.6	16.9
CaO	3.6	19	20	23	-	-	8.1	6.1	7.2	8.1
Fe_2O_3	6.8	-	-	4.1	-	-	6.3	-	-	7.6
K_2O	1.8	4.9	6.1	7.1	-	- .	2.3	..	-	2.1
MgO	2.7	-	-	3.3	-	-	2.8	-	-	2.5
Na_2O	0.7	-	-	1.1	-	-	1.4	-	-	1.2
P_2O_5	0.2	4.9	5.1	5.9	-	-	0.4	-	-	0.5
SiO_2	59	38.4	37.5	34.7	55.2	53.7	53.5	54.4	54.2	53.3
SO_3	1.8	6	6.5	7.2	2.5	2.4	3.1	2.2	2.3	2.4
Cl	0.0	0.35	0.57	0.92	0.06	0.06	0.0	0.06	0.06	0.11
Free CaO	0.2	7	7.8	9.8	-	0.4	1.3	-	-	0.5
Glass	48	-	-	19	-	-	44	-	-	40
LOI	35.6	15.2	11.7	11.9	38	32.5	25.5	27.9	24.6	25.1
Na_2O eq.	1.8	2.77	3.56	5.0*	-	-	2.9	-	-	2.59

Table 3.9: Concentration of trace elements in the generated fly ashes (mg/kg)

Fly ash	REF	PD11	PD16	PD19	SRF14	SRF27	SRF33	DW10	DW20	DW30
Element										
As	21	10	11	10	16	13	10	35	42	54
B	410	-	-	428	-	-	441	-	-	458
Br	21	23	28	33	88	95	157	40	41	50
Cd	1.3	-	-	1.0	-	-	6.7	-	-	9.2
Co	22	13	14	13	23	24	26	25	24	26
Cr	131	98	102	97	271	305	396	195	214	267
Cu	62	-	-	151	-	-	1040	-	-	212
F	222	-	-	474	-	-	423	-	-	308
Hg	0.5	-	-	0.33	-	-	0.58	-	-	1.31
Mn	624	1050	1070	1120	662	712		741	892	1010
Mo	24	22	24	23	25	29	33	25	22	22
Ni	53	-	-	60	-	-	90	-	-	66
Pb	188	-	-	34	-	-	388	-	-	3870
Sb	15	3	3	3	684	864	1318	98	77	84
Se	83	42	42	41	56	52	48	71	61	58
Sn	< 6	-	-	< 6	-	-	58	-	-	25
Sr	310	-	690	717	850	729	657	1008	961	-
V	231	140	153	130	187	187	-	227	220	199
W	4.4	2.4	2.1	1.6	4.7	-	-	6.2	7.2	23.3
Zn	262	509	714	900	1070	1230	1450	1760	1710	3600

3.3.5 Characteristics of mineralogy of generated fly ashes

The mineralogical characteristics of the fly ashes were analysed by XRD (see figure 3.6 and table 3.10). Samples were used without heat treatment. Quartz, mullite, hematite, anhydrite and free lime were identified in all fly ashes. These minerals are usually present in class F fly ashes. In the fly ash from co-combustion of poultry litter, several peaks were present that could not be related to specific XRD-patterns of minerals. The presence of the background in the diffraction pattern points to amorphous phases. The position of the background is influenced by the composition of the amorphous phase as shown by Diamond [3.14]. The positions of the REF and the DW30 fly ash are comparable (maximum reflection at 28° 2θ).

However, the backgrounds of the SRF33 and PD19 fly ash are shifted compared to the REF. The maximum peaks lies at 30° 2θ and 30 - 34° 2θ, respectively. The height of the background differs from ash to ash. The ranking is: REF>DW30>SRF33>PD19. This ranking is similar to that of the chemically analysed glass contents (see table 3.10).

The generated fly ashes were also analysed with QXRD. Elementary silicon (10%) was added to all samples as internal standard, with exception of PD19. After the peaks of the XRD-analyses were quantified with Rietveld's method, the concentrations were normalised to 10% of silicon. The remaining part consists of unburned matter (LOI), glassy[16] and non-identified minerals. In the case of PD19 the concentrations were normalised to the concentration of free lime, which was also chemically analysed. After this, all concentrations were normalised to 5% LOI for reasons of comparison. The QXRD results of the major phases fit well with the XRD results. Main differences are the identified minor phases. Free lime is only detected in PD19, but not detected in REF, DW30 and SRF33 with QXRD. Rutile and possibly diopside were identified with QXRD, but not with XRD. It was possible to identify some peaks in the diagram of PD19 with QXRD as sulphate bearing minerals (K_2SO_4 and langbeinite). Important is that both with XRD and QXRD no phosphate bearing minerals were identified in PD19, while the P_2O_5 content is 5.9% m/m.

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[16] Including other phases which are X-ray amorphous.

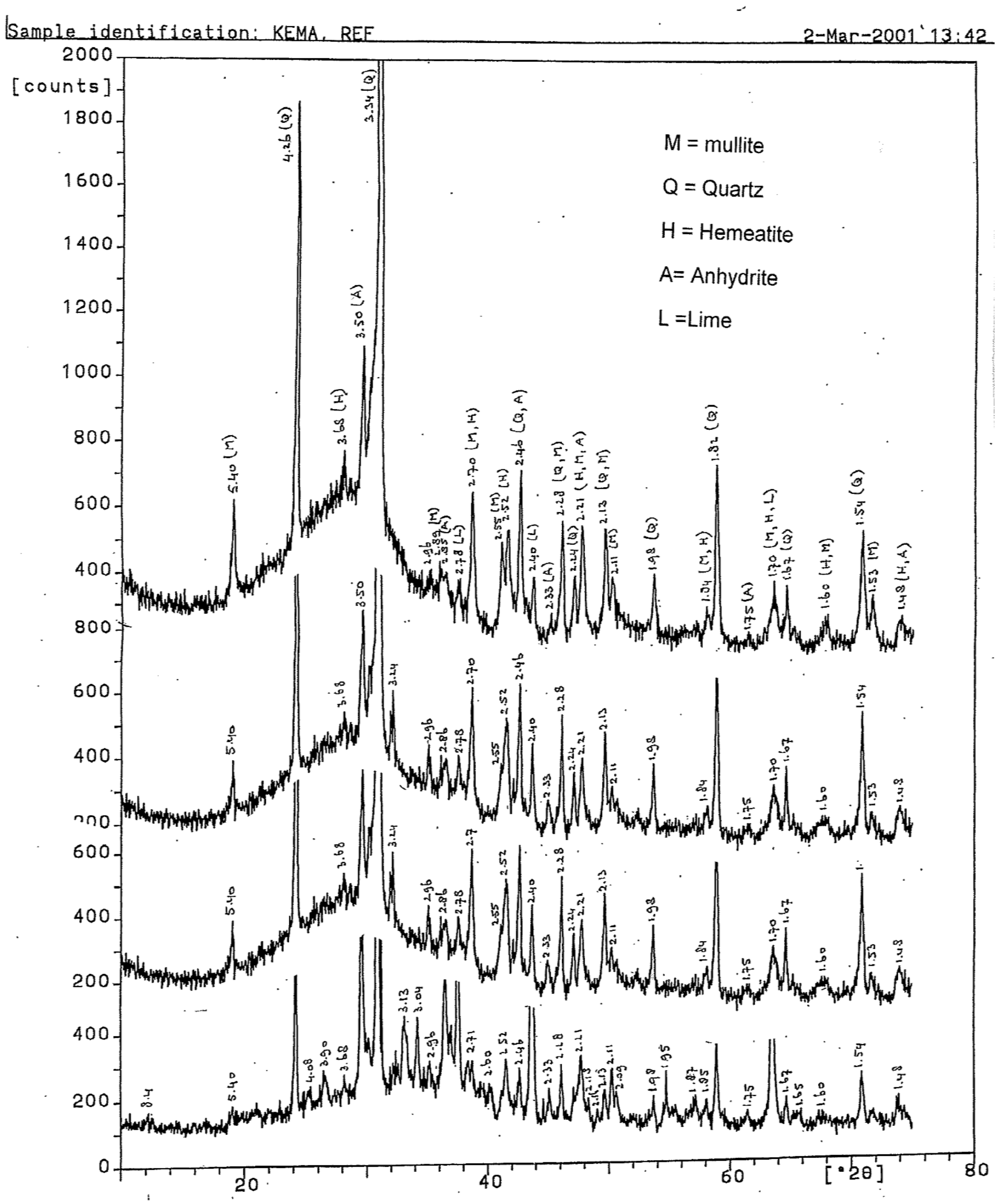

Figure 3:6: X-ray diffraction patterns of generated fly ashes (from above: REF, DW30, SRF33 and PD19).

Table 3.10: Identified and quantified (%) minerals in fly ash (all results are normalised to 5% m/m LOI)

Fly ash	REF	REF	PD19	PD19	DW30	DW30	SRF33	SRF33
method	XRD	QXRD	XRD	QXRD	XRD	QXRD	XRD	QXRD
Mineral								
Amorphous	yes	46	yes	34	yes	42	yes	45
Unburnt matter	yes	5	yes	5	yes	5	yes	5
Anhydrite	yes	3±1	yes	11±3	yes	1±1	yes	4±1
Free CaO	yes	-	yes	10	yes	-	yes	-
Quartz	yes	24±1	yes	22±1	yes	25±1	yes	32±1
Hematite	yes	2±1	yes	2±1	yes	1±1	yes	1±0.5
Mullite	yes	20±1	yes	12±1	yes	24±1	yes	12±1
Rutile	-	-	-	-	-	-	-	1±0.5
Arcanite (K_2SO_4)	-	-	?[1]	2±1	-	-	-	-
Diopside	-	1±1?	-	-	-	-	-	-
Langbeinite	-	-	?[1]	2±1	-	-	-	-

[1] Some unidentified peaks were present in the XRD-pattern, these are marked with '?'

Sequential dissolution was performed to obtain more information about the mineralogical composition of the fly ashes. The acid-soluble phase increases due to co-combustion (see table 3.11), especially if poultry litter is co-combusted. CaO is the most important component in the acid-soluble phase of fly ash PD19, followed by SiO_2, SO_3, K_2O and P_2O_5. The acid solubilised CaO, consists of different CaO bearing phases particularly free lime and anhydrite. However, after correction for these phases, 5.6% CaO remains, which is present in other phases. The combination with phosphate seems reasonable as apatite is present in the original fuel. The ratio CaO/P_2O_5 in the acid-soluble is 1.2. This ratio is of the same order of magnitude as for tricalcium phosphate (1:1.8), as found in the study of Cooperband and Good [3.15].

Table 3.11: Quantity and composition of acid soluble fraction [% m/m] in fly ash, normalised to 5% m/m LOI

Fly ash	REF	PD19	DW30	SRF33
compound	% m/m	% m/m	% m/m	% m/m
Al_2O_3	0.5	3.8	1.4	2.9
CaO	3.2	20.1	5.9	6.8
Fe_2O_3	0.3	0.7	0.5	1.3
K_2O	0.1	5.2	0.3	0.3
MgO	1.1	2.4	1.2	1.2
Na_2O	0.1	0.7	0.3	0.2
P_2O_5	0.1	4.6	0.3	0.4
SO_3	2.1	6.2	2.6	2.0
SiO_2	0.6	6.2	1.7	3.1
Total	8.3	49.8	14.1	18.1

The glass contents were analysed by solubilising the amorphous phase in KOH, after the treatment with hydrochloric acid. The glass content of REF, DW30 and SRF33 determined with QXRD fits well with the results of the chemical analyses (see table 3.12). In contrary to these glass contents PD19 does not fit well, which can be explained by the lack of XRD identified phosphorus bearing phases and to a smaller extent chloride bearing phases, which are attributed to the amorphous phases by the Rietvelds method.

Table 3.12: Glass content in fly ash, based on chemical and mineralogical analyses (QXRD) [% m/m]

determination	QXRD	chemically	difference
Fly ash	% m/m	% m/m	% m/m
REF	46	48	-2
PD19	34	19	+15
DW30	42	44	-2
SRF33	45	40	+5

The composition of glass phase of fly ash was derived from the composition of the fraction that was dissolved in the KOH solution. The amount of modifiers is increased to a small extent due to co-combustion (see table 3.13). Depending on the fuel, CaO (DW), K_2O (DW and PD) or Na_2O (DW) are increased. In all experiments, the glass phase remains an alumina-silicate glass despite the high co-combustion percentages and the different chemistry of the secondary fuels.

Table 3.13: Chemical composition of the fraction of fly ash, which is soluble in KOH [% m/m]

Fly ash	DW30	PD19	SRF33	REF
Component	% m/m	% m/m	% m/m	% m/m
Al_2O_3	20.1	16.4	20.1	20.6
CaO	1.2	1.2	2.5	0.9
Fe_2O_3	3.3	3.9	4.0	3.2
K_2O	2.1	3.4	1.8	1.3
MgO	1.7	1.8	2.0	1.9
Na_2O	1.2	0.7	0.9	0.5
P_2O_5	0.1	0.2	0.2	0.2
SO_3	1.3	0.5	0.6	1.6
SiO_2	69.1	71.8	67.8	69.9
Total	100.0	100.0	100.0	100.0
Sum of Al_2O_3+SiO_2	89.2	88.2	88.0	90.5

3.4 Experimental results: properties of cement paste and mortar

Table 3.14 and figure 3.7 and 3.8 presents the results of the tests performed on cement paste Setting time) and mortar, prepared with the generated fly ashes (see further 3.2.7 for the mix composition and preparation). The initial and final setting is retarded when fly ash from high percentages of co-combustion of SRF is used. Cement paste with fly ash DW30 shows also retardation of initial setting, but less than that with fly ash SRF33. The initial setting of PD19 fly ash cement pastes is comparable with that of the reference coal fly ash. The samples used for these tests were not treated to reduce the LOI to avoid changes in the availability of potential retarding components.

Table 3.14: Pozzolanic behaviour (measured as activity index, AI) and flow of mortars and setting time of cement pastes in which 25% m/m of the cement is replaced by the generated fly ashes. Fly ashes are derived from co-combustion of demolition wood (DW), poultry litter (PD) or solid Recovered Fuels (SRF). Further details of mix composition of mortar are given in 3.2.7 and Box 1.1 in 2.2.4.

Parameter	Flow	AI 28 d	AI 91 d	Water binder ratio	Initial setting	Final setting
Fly ash	[mm]	[%]	[%]	[-/-]	[min.]	[min.]
REF	176	88	93	0.30	271	388
PD19	162	87	99	0.29	283	396
PD16	162	89	96	-	-	-
PD11	139	87	93	-	-	-
DW30	181	84	93	0.33	290	459
DW20	179	84	93	-	-	-
DW10	178	85	91	-	-	-
SRF33	182	70	77	0.32	405	557
SRF27	182	76	85	-	-	-
SRF14	179	82	90	0.34	297	477

The pozzolanic behaviour was tested by determining the Activity Index (AI). The AI of fly ash from coal (REF) after 28 and 91 days was 88% and 93%, respectively, thus meeting the requirements of EN 450 (>75% and >85%). These values are also within the 95% range of the statistics from the Dutch certification tests. In figure 3.7, the AI is presented as a function of co-combustion percentage and of co-fired fuel. The AI of the fly ashes from co-combustion of Solid Recovered Fuel (SRF) is reduced by co-combustion. The AI trends at 28 and 91 days are very similar for co-combustion of SRF and demolition wood. Co-combustion of poultry litter (PD) has more or less the opposite effect. However, this is not only related to pozzolanic behaviour, but also to the presence of high percentages of free lime, sulphate (formation of ettringite) and probably calcium phosphates. Co-combustion of demolition wood has only small effects on the AI.

The fly ash samples from 100 % coal (REF) and from co-combustion of Solid Recovered Fuel (SRF) and poultry litter (PD) were first subject to heat treatment to reduce the LOI before testing the activity index.

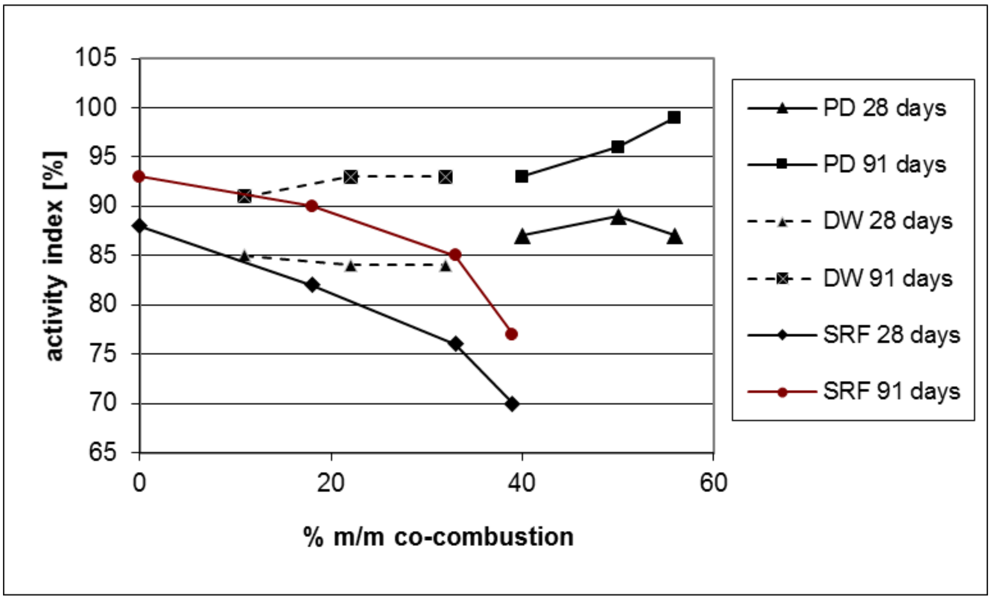

Figure 3:7: Pozzolanic behaviour (measured as Activity Index) at 28 and 91 days as a function of co-combustion percentage and co-fired fuel for demolition wood (DW), Solid Recovered Fuel (SRF) or poultry litter (PD)

The soundness of cement paste with fly ash from co-combustion of poultry litter (PD11) and demolition wood (DW30) was tested using the Le Chatelier test. The expansion of the hardened cement paste is 1-2 mm, which is far below the limit value of 10 mm, which is used as a criterion.

3.5 Evaluation and discussion

The goal of this experimental research is to investigate the effects of high percentages of co-combustion biomass from different origins (animal and industrial origin) on the properties of the generated fly ash and the properties of mortar and concrete with this fly ash. The following questions should be answered in the research:

1. Which is the effect of co-combustion of these biomass on the properties of fly ash?
2. Can these properties be explained by the composition of the fuel and the combustion process?
3. Which the effect of co-combustion of these biomass on the performance of concrete made with this fly ash. Can this be explained by the properties of the fly ash?

The discussion opens with the representativeness of the combustion experiments for real-scale combustion regarding the generated fly ash, as this is decisive for the validity of the research. This is followed by the discussion of the characteristics of the co-combustion fly ashes and the properties of cement paste and mortar with these fly ashes.

3.5.1 Combustion process and representativeness

The flame temperature of the test boiler is about 1090-1230 ºC, which is lower than in real scale pulverised coal boilers. The estimated residence time in the test boiler is 1.7s, which is related to the dimensions of the test boiler and the burner configuration, which is considerably shorter than in practice, namely about 4-5 s. This causes also a lower burnout of the fuel particles (95.1-98.2%), while in practice, the burnout is 99% and higher. The ash particles in the test boiler were removed from the flue gases by a fabric filter. In real-scale power plants, removal of ash particles is realised by using electrostatic precipitation (ESP), in so-called ESP-filters. This will cause only minor differences for fly ash properties as the difference between the removal efficiency of the ESP filter and the bag filter is very small.

An indication of the representativeness of the results can be obtained from a comparison of the properties of the 100% coal fly ash (REF) with fly ashes from power plants. A very important aspect is the presence of glass phases in fly ash, because these are the origin of pozzolanic behaviour. The glass content of REF is 48% m/m. This value is lower than the average glass content of Dutch fly ash (average 56% deviation 4%), but it is still within this range. Mullite is present in the REF fly ash. Mullite is considered to be a secondarily formed mineral. Also, the other crystalline components, like quartz and hematite, are normally present in class F fly ash. The amount of SO_3 (mainly present as anhydrite) in REF is higher than normally found in Dutch fly ashes. An explanation may be that the temperature conditions in and after the test boiler favour binding of SO_3 by CaO, forming anhydrite.
The morphology of the particle in the REF fly ash differs from the well-known spherical particles that are typically found in practice. This can be explained by the shorter residence time (less time for formation of spherical particles and fusion) and the lower temperature of the flame (higher viscosity) compared with combustion conditions in practice. The grain size distribution is somewhat finer than the average of Dutch fly ash ($D_{50} = 21 \pm 7$ μm).

It is concluded that the most important ash formation processes have taken place during the combustion process. However, morphology of the fly ash (less spherical particles) and sulphate content differs from fly ash from real-scale combustion. The former may result in an underestimation of the workability of mortar with fly ash as in practice more spherical particles may be formed due to the higher combustion temperatures (lower viscosity of the molten alumina silicates will facilitate formation of more spherical particles).

3.5.2 Properties of fly ashes from co-combustion

The ash forming matter in both Solid Recovered Fuels and demolition wood has higher ratios $CaO/(SiO_2+Al_2O_3)$ and $(Na_2O+K_2O)/(SiO_2+Al_2O_3)$ than the coal. The ash forming matter in the poultry litter differs strongly from the coal and the other secondary fuels. The ratios $CaO/(SiO_2+Al_2O_3)$, $(Na_2O+K_2O)/(SiO_2+Al_2O_3)$ and $P_2O_5/(SiO_2+Al_2O_3)$ are much higher than those of coal. If demolition wood or SRF is co-combusted, the influence on the concentration of main elements is limited, but the concentrations of several trace elements, like Cu, Pb and Zn are raised.

The glass content is strongly reduced if poultry litter is co-combusted. Contrary to this, demolition wood and SRF contain some glass forming matter as the ash contribution of the secondary fuel is higher than the decrease of the glass content. This can be explained by the presence of potential glass forming matter (illite and kaolinite) in SRF. The presence of an amorphous phase in demolition wood, which contains the alumina bearing phase(s), also points to glass forming matter. Important for the pozzolanic behaviour is also the glass composition, besides the glass content and the specific surface of the glass phase. As shown by sequential dissolution, the influence of co-combustion on this glass composition is very limited. Al_2O_3 and SiO_2 are hardly influenced by co-combustion, but the total content of modifiers increases slightly. Remarkable is the relatively small influence of poultry litter on the glass composition. Apparently mineral matter from poultry litter and coal does hardly interact during combustion.

The identified crystalline components in the co-combustion fly ashes are mostly the same as normally found in Dutch fly ashes (class F). Fly ash from co-combustion of poultry litter, however, contains other additional components like K_2SO_4 and langbeinite and the amount of free lime and anhydrite increases strongly. Remarkably no phosphate bearing minerals were identified with XRD. Based on sequential dissolution, the presence of calcium phosphates is likely.

The particle density of the generated fly ashes (2430-2560 kg/m^3) is higher than that of fly ashes from Dutch power plants [3.13] (about 2275 kg/m^3). This may be due to less inclusion of gasses within fly ash particles formed in these experiments (more solid particles).

3.5.3 Properties of cement paste and mortar with fly ash from co-combustion

Table 3.14 presents an overview of parameters that describe the properties of fly ash and its behaviour in cement paste and mortar. Requirements for these parameters are given in the European standard for fly ash in concrete (EN 450; see also table 2.3).

The setting time of cement paste with fly ash from co-combustion of SRF is retarded; probably due to presence of potential retarders, like F and Zn. However, demolition wood fly ash cement paste is not retarded, while the concentrations of Pb and Zn are even higher than in fly ash from SRF co-combustion. Co-combustion of poultry litter does not seem to influence setting time. The presence of free lime and anhydrite does not cause false or rapid setting, nor is retardation caused by the phosphorus present in fly ash from co-combustion of poultry litter. Phosphorus is probably present in the fuel as apatite and in the fly ash as a calcium phosphate. As described in subsection 2.3.1, it is well known in cement chemistry that soluble phosphates can act as cement hydration retardants, while some calcium phosphates like $\alpha Ca_3(PO_4)_2$ are able to react with water to form insoluble reaction products. The maximum concentration of trace elements, whereby no significant retardation of the hydration in terms of setting time and early strength occurs, depends on the type of element and its mineralogical presence. Schmidt concluded that the addition of about 0.3% ZnO or PbO to Portland cement resulted in strong retardation of initial setting (from about 3 hours to 5-6 hours) [3.17].

Table 3.15: Overview of chemical, mineralogical and physical properties of coal fly ash and fly ash from co-combustion of 56% m/m poultry litter, 32% m/m demolition wood or 39% m/m Solid Recovered Fuels (SRF) (all ash based)

Fly ash		Poultry litter	Demolition wood	SRF	Coal	
Parameter	Unit					EN 450 Requirement
Al_2O_3+Fe_2O_3+SiO_2	% m/m	48	77	78	84	≥70
Reactive SiO_2	% m/m	15	30	27	34	≥25
CaO	% m/m	23	8.1	8.1	3.6	≤10
Cl	% m/m	0.92	0.04	0.11	0.01	≤0.10
CaO free	% m/m	9.8	1.3	0.11	0.2	≤1.5
MgO	% m/m	3.3	2.8	2.5	2.7	≤4.0
P_2O_5	% m/m	5.9	0.4	0.5	0.2	≤5.0
SO_3	% m/m	7.2	3.1	2.4	1.8	≤3.0
Na_2O_{eq}	% m/m	5.0	2.9	2.6	1.8	≤5.0
Morphology	-		Partly spherical			Mainly spherical
Flow	mm	162	181	182	176	-
Initial setting	min.	283	290	405	271	1)
Final setting	min.	396	459	557	388	-
28 days activity index	%	87	84	70	88	>75
91 days activity index	%	99	93	77	93	>85
Soundness	mm	1	1	-	1	≤10

1) Initial setting of fly ash cement paste shall not be more than twice as long as the initial setting time of the test cement alone.

The flow of mortar with fly ash from co-combustion of poultry litter is lower than the flow of mortar with the other fly ashes. An explanation is that less free water is available due to absorption by unburnt particles and chemical reaction with free lime and arcanite.

In figure 3.8 the relation between the glass content of fly ash and the pozzolanic behaviour (measured as activity index) is visualised. It can be seen that there is quite a good relation between the glass content and the activity index after 28 days. Note: The glass content of co-combustion fly ashes was only measured at the highest co-combustion percentage. In the other cases, the glass content is calculated based on the co-combustion percentage of the fly ash and assuming that the influence of co-combustion on the glass content is linear with the ash-based co-combustion percentage.

The pozzolanic behaviour of fly ashes from the co-combustion of SRF is negatively influenced, but relatively high percentages are possible before a point is reached where the requirements are no longer met. This influence can be attributed to the reduction in glass content from 48% to 40%. See also figure 3.8. The pozzolanic behaviour is hardly influenced by the co-combustion of demolition wood, which may be due to the small effect of co-combustion of demolition wood on the glass content.

The positive influence of co-combustion of poultry litter on the pozzolanic behaviour seems contrary to the lower glass content. However, due to the presence of high amounts of free lime, anhydrite and possibly calcium phosphates, other reaction mechanisms take place besides the pozzolanic reaction mechanism, like formation of ettringite.

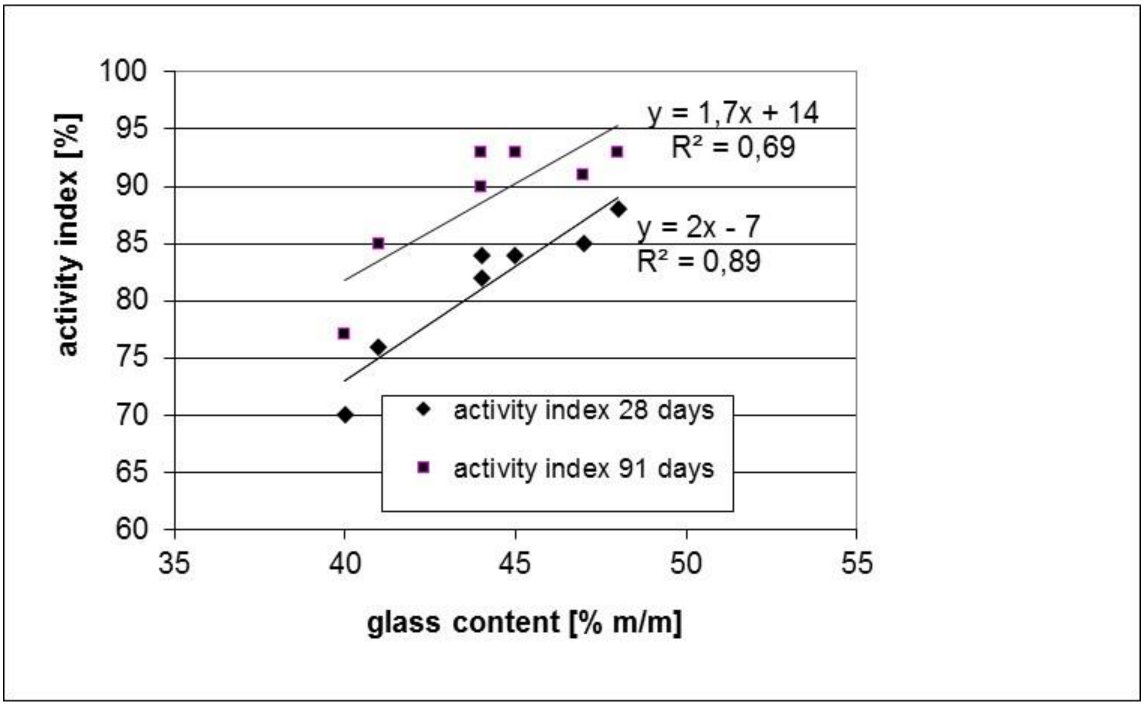

Figure 3:8: Relation between the glass content of fly ashes from co-combustion and the pozzolanic behaviour, expressed as activity index after 28 and 91 days (see Box 1 in 2.1.7),

The presence of high amounts of free lime and sulphate in fly ash from co-combustion of poultry litter may lead to unsoundness of mortar and concrete. However, the requirement of the LeChatelier test, which has been developed for testing soundness in relation to free lime, is passed despite the high amount of free lime. This can be explained by the reactivity of the free lime grains (due to specific surface of the particles). No expansion will be generated if the free lime reacts during the plastic phase of the cement fly ash paste. Further, smaller free lime particles may generate less expansion in hardened cement paste (see also 5.5) .The presence of high amount of sulphate may lead to the formation of secondary ettringite in mortar and concrete, which may cause unsoundness on the long term (expansion and crack formation) [3.18].

Table 3.16 provides an overview regarding the effects of co-combustion of poultry litter, demolition wood or Solid Recovered Fuel on concrete made with fly ash, as identified (chapter 2) and based on the pilot-scale experiments.

Table 3.16: Overview of the effects of co-combustion of poultry litter, demolition wood or Solid Recovered Fuel on concrete made with fly ash as identified in the literature study (chapter 2) and based on the research with fly ashes from the pilot-scale experiments.

Biomass	Potential effect according to literature study	Conclusion based on experimental research with fly ash from pilot-scale co-combustion tests
Poultry litter	Unsoundness (free lime)	Unsoundness in relation to free lime was not observed despite the high content of free lime.
	Retardation of cement hydration (P)	No significant retardation was observed despite the presence of phosphate
	Promotes ASR if reactive aggregate is present (K)	The Na_2O_{eq} increases, which may promote ASR. Also the amount of reactive SiO_2 (glass phase) in the fly ash decreases.
		Unsoundness by formation of secondary ettringite may occur
Demolition wood	Unsoundness (free lime)	The content of free lime increased, but the soundness test was passed.
	Contribution to strength and durability (Si)	The strength development was not influenced
	Retardation of cement hydration (Pb, Zn)	No retardation occurred despite the presence of heavy metals.
Solid Recovered Fuel	Unsoundness (free lime)	The amount of free lime did not increase. The soundness test was passed.
	Contribution to strength and durability (Al+Si)	The strength at 28 and 91 days decreased, which was explained by the lower glass content in the fly ash.
	Retardation of cement hydration (Cu, Pb, Zn)	Retardation was observed.

3.6 Conclusions

A set of pilot-scale co-combustion experiments was performed to generate co-combustion fly ashes for further research to investigate the relation between co-combustion and the properties of fly ash and of cement paste and mortar made with these fly ashes. The co-combustion percentages were 0 to 33 % m/m (ash based).

Co-combustion of demolition wood results in an increase of the content of CaO and free lime in the generated fly ash. Further the Na_2O equivalent increased. The amount of heavy metals increased especially Cr, Cu, Pb and Zn. Initial setting of cement paste was not significantly influenced but final setting was retarded. The pozzolanic behaviour (measured as activity index) at 28 and 91 days was hardly influenced, which is explained by the glass content which is also hardly influenced.

Co-combustion of Solid Recovered Fuels (SRF) results also in in an increase of CaO, but the free lime content did not increase. This difference with co-combustion of demolition wood is due to the lower presence of calcium (calcite) in the SRF fuel. Initial setting of cement paste was retarded due to co-combustion of SRF. The pozzolanic behaviour was negatively influenced, which is explained by the reduced glass content, resulting in a lower strength at 28 and 91 days. Co-combustion of poultry litter results in stronger influence on the chemical composition of the generated fly ash compared to co-combustion of demolition wood and SRF. Especially, the content of CaO, P_2O_5 and K_2O increases.

This has also consequences for the mineralogical composition (like the presence of more free lime and arcanite). The activity index after 28 days is hardly influenced, but it is increased after 91 days. However, this is not only due to pozzolanic behaviour but also to the presence of other phases like anhydrite and free lime. The composition of the glass phase in the fly ash is influenced to a small extent by co-combustion, which is explained by the obviously limited interaction between the ash forming from coal and from the co-fired biomass.

3.7 References

[3.1] NEN, 2005. EN 450-1 Fly ash for concrete – Part 1: Definition, specifications and conformity criteria (European standard), Delft, the Netherlands.

[3.2] NEN, EN 15290. Solid biofuels - Determination of major elements - Al, Ca, Fe, Mg, P, K, Si, Na and Ti. European standard.

[3.3] NEN, EN 15410. Solid Recovered Fuels - Methods for the determination of the content of major elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti). European standard.

[3.4] Salomons W. and Gerritse, R.G., 1981. Some observations on the occurrence of phosphor in recent sediments from western Europe, The science of the total environment, 17 (1981), 37-49.

[3.5] Barnett G.M., 1994. Litter P fractionation, Bioresource Technology 49, pp 149-155.

[3.6] NEN, 1994. EN 196-2; Methods for testing cement; Chemical analysis of cement (European standard), Delft, the Netherlands.

[3.7] KEMA, 2009. Database Trace elements. Report 9. Coals and ashes. Actualized up to and including coal from 2008. KEMA report 50931179-TOS/ECC 09-5285.

[3.8] Barnett G.M., 1994. Phosphor forms in animal manure, Bioresource Technology 49, pp 139-147.

[3.9] Raask E., 1985. Mineral impurities in coal combustion. Behaviour, problems and remedial measures. Published by Hemisphere Publishing Corporation. Washington, 1985.

[3.10] Spears D.A. and Zheng Y., 1999. Geochemistry and origin of elements in some UK coals, International Journal of Coal Geology 38, pp 161-179.

[3.11] Ward C.R. et al, 1996. Occurrence of phosphor minerals in Australian coal seams, International Journal of Coal Geology 30, pp 185-210.

[3.12] Bijen J. and E. Onstenk, 1985. Physical characterization of Dutch fly ashes from coal fired power plants. Intron report 85275, In Dutch.

[3.13] Vliegasunie, 2011. Databases quality control coal-fired power plants.

[3.14] Diamond S. 1982. On the present in low-calcium and in high-calcium fly ashes. Cement and Concrete Research, 13, pp 459-464.

[3.15] Cooperband J.R. and Good, L.W., 2002. Biogenic phosphate minerals in manure: implications for phosphor loss to surface waters. In: Environmental Science Technology, 36, pp 5075-5082.

[3.16] KEMA (R. Meij and B.H. te Winkel), 2001. Composition and leaching of ashes generated during high percentages of co-combustion of poultry litter, RDF and waste wood. KEMA report 50131024-KPS/MEC 01-6154 (in Dutch).

[3.17] Schmid O., 1980. Einfluss von ZnO und PbO auf die Eigenschaften von Portlandklinker und Portlandzement. PhD disseration Technischen Univetrsität Clausthal, Germany.

[3.18] Day, R. 1992. The effect of secondary Ettringite formation on the durability of concrete. A literature analysis. By order of the Portland Cement Association.

4 FLY ASH FROM REAL SCALE CO-COMBUSTION TESTS

4.1 Introduction

The previous chapter showed the results of research on the properties of fly ash from co-combustion of biomass from animal (poultry litter) or industrial origin (demolition wood, Solid Recovered Fuel) on the properties of cement paste and mortar with this fly ash. These ashes were generated in a pilot scale test boiler. It was shown that also fly ashes from high co-combustion percentages are able to act as a pozzolanic filler for concrete.

As a follow-up the research was continued with fly ashes generated in real-scale co-combustion tests. These tests were performed in several Dutch coal-fired power plants with different types of biomass:

- from vegetable origin, namely palm kernels, cacao residues and wheat pollard pellets;
- from animal origin, namely meat and bone meal;
- from industrial origin, namely sewage sludge and paper sludge.

The investigation in fly ashes from full-scale trials consisted of three steps, namely:

- performance of co-combustion experiments and collection of fly ash samples;
- chemical, mineralogical and physical characterisation of generated fly ashes;
- assessment of the properties of mortar and concrete with co-combustion fly ashes. The workability, strength development, E-modulus and freeze thaw resistance with de-icing salts of two concrete compositions with (co-combustion) fly ash were determined.

4.2 Materials and methods

4.2.1 Co-combustion experiments

Co-combustion experiments were performed at three Dutch coal-fired power plants (pulverized fuel) with a capacity of 403-600 MW_e, which are coded as A, B and C (see table 4.1) The boilers are all tangentially fired. Power plant C is equipped with low NOx burners and over-fire air supply. Fly ash was removed from the flue gas with an electrostatic precipitator. During these trials, fly ashes were obtained from the electrostatic precipitator when the combustion process was reasonably stable, which was normally several hours after starting. An overview of the co-combustion experiments is given in table 4.1.

The secondary fuels were fed into the boiler using different ways (see appendix A, route 1, 2 and 3) to obtain a good combustion process to maintain the efficiency of the boiler. The choice depends on the co-combustion percentage and the properties of the secondary fuel in relation to combustion and size reduction. The most straight forward approach is to add the secondary fuel to the coal before the coal mill (see also appendix A, route 1). In a more advanced approach the fuels are milled in a dedicated device (like hammer mills) to obtain size reduction (route 2). In the most advanced approach the biomass is also burned in dedicated burners (route 3).
The particle size of powdered coal is 100% <100 µm, and 75-95% <75 µm. The particle size of the prepared biomass is 100% <3 mm and 90% <1 mm.

Table 4.1: Overview of full scale co-combustion experiments which generated fly ashes. Co-combustion percentages are based on process data [% m/m, fuel based]

Co-combustion test code	*CRE*	*MBME*	*PKE*	*PSE*	*MSE*	*MSE+*	*WPPE*
Power plant	*B*	*A*	*C*	*B*	*B*	*B*	*C*
Secondary fuels							
Palm kernels (PK)	*10*	*-*	*20*	*-*	*-*	*-*	*-*
Cacao residues (CR)	*11*	*-*	*-*	*-*	*-*	*-*	*-*
wheat pollard pellets (WPP)	*-*	*-*	*-*	*-*	*-*	*-*	*14*
Wood (WD)	*-*	*-*	*-*	*3*	*-*	*-*	*3*
Meat and bone meal (MBM)	*-*	*10*	*-*	*-*	*-*	*-*	*-*
Biomass pellets (BMP)	*-*	*4*	*-*	*-*	*-*	*-*	*-*
Poultry litter (PD)	*-*	*1*	*-*	*-*	*-*	*-*	*-*
Cattle feed (CF)	*-*	*1*	*-*	*-*	*-*	*-*	*-*
Paper sludge (PS)	*-*	*-*	*-*	*6*	*-*	*-*	*-*
Municipal sewage sludge (MS)	*-*	*0.1*	*-*	*-*	*5*	*9*	*-*
Soot paste (SP)	*-*	*0.3*	*-*	*-*	*-*	*-*	*-*
total	*21*	*16*	*20*	*9*	*5*	*9*	*17*
Reference test	*yes*	*None*	*none*	*yes*	*yes*	*yes*	*none*

4.2.2 Coal and secondary fuels

The coals that were fired by the power plants, also during the co-combustion experiments, were blends from typically ‘world traded’ coal. Three co-combustion experiments were accompanied by a reference combustion test, notably experiments CREref, PSEref and MSEref. Cacao residues, wheat pollard pellets and palm kernels were tested as examples for agricultural by-products (biomass from vegetable origin). Meat and bone meal was co-fired as example for biomass from animal origin. Municipal sewage sludge, biomass pellets and paper sludge were tested as examples of biomass from industrial origin. Some of the co-combustion experiments were performed with small percentages of wood or poultry litter. The municipal sewage sludge was pre-dried obtained from Slibdroog Installatie Beverwijk. This sewage sludge originated from different sewage treatment plants, whereby, at that time, phosphate was mainly precipitated with ferro sulphate and -chloride.

4.2.3 Chemical characterization of (secondary) fuels and fly ashes

The concentration of the main components Al, Ca, Fe, K, Mg, Na, P, Si and Ti in fly ashes was analysed with X-ray fluorescence. This is the standard analysis method used in quality control of fly ash in the Netherlands. The concentration of the main components - with exception of S - in the fuels was determined by analysing the residue after glowing with X-ray fluorescence or after total digestion with Inductively Coupled Plasma (ICP). Two fly ashes were analysed with ICP after total digestion, namely the fly ash from co-combustion of municipal sewage sludge (MSE+) and its reference (MSEref).

The concentration of free lime (CaO) in fly ash was determined in accordance with NEN-EN 451-1 [4.1]. The loss of ignition in fly ash was analysed in accordance with ISO 10694 by glowing at 975° C for 1 hour.

4.2.4 Characterization of mineralogy of fly ashes

The mineralogical characteristics were determined using three different methods, namely X-ray diffraction (2 different analyses), sequential dissolution and Scanning Electron Microscopy (SEM). The scan range was 5-75 2θ and 6-130 θ, respectively. The count time was 1-2 s. The XRD analyses were performed with a Philips diffractometer PW1820 (Co X-ray tube) or a Bruker D4 Endeavor (Cu X-ray tube). If the XRD was meant to quantify the concentration of the minerals, an internal standard was added (metallic Si) before the XRD analysis was performed. These XRD analyses were performed with the Bruker D4 Endeavor. The identified minerals were quantified using the Rietveld method and adjusted to the known mass percentage of the added standard. The percentage amorphous material is assumed to be 100% minus the sum of the mass percentages of the identified minerals.

The glass composition was determined based on the determination method of reactive silicon [4.2]. This was combined with sequential dissolution. A key feature of the analysis is the cascade approach, which involves removing in turn the fraction that is soluble in acid and then the fraction that is soluble in potassium hydroxide, and analysing the removed fraction each separately. The dissolved fraction from these steps is analysed with ICP-AES for Al, Ca, Fe, K, Mg, Na, S, Si and Ti.

Fly ashes were further investigated with SEM. The fly ash samples were prepared by embedding them in Caldofix epoxy resin (Struers). After hardening of the epoxy, the samples were ground with gradual finer sizes of Silicon carbide paper and polished water free with diamond pastes up to a size of 0.25 µm. The samples were analysed with a JEOL 6300 SEM that is coupled with a Noran Voyager M3200 Energy Dispersive X-ray Spectroscopy micro-analysis system (EDX). The elemental composition of each area of about 1 µm^2 (= 1 pixel) is analysed (in the EDX mode). A magnification of about 250x is used, which implies that the analysed field is 400x400 µm. The data are further processed using Noran System Six (NSS), whereby deconvolution is used to separate peak intensities in the EDX spectra for the elements that are present. The output is a series of element mappings in netto-counts, atom or weight percentages. The generated output is used as input for the software program KEMPHASE®. This software program has been developed by KEMA for relating the composition of each pixel to the composition of components/phases and for visual and statistical manipulation of these data. The composition of the components is described by several conditions concerning the concentration of the main elements of that component. These conditions or identification rules are given in table 4.2 (for the identified components).The natural impurity of the minerals and the variation of the analysis is taken into account (15%) in these rules. As the type of crystal lattice cannot be analysed with EDS, this method cannot distinguish between for example kaolinite or glass with a kaolinitic composition. The output of KEMPHASE is in surface percentages. This is corrected for the density of the phases afterwards. No correction has been made for surface to volume. It can be seen as a semi-quantitative method.

Table 4.2: SEM phase classification and identification rules [atom%]

Element Phase	Al	Ca	Fe	K	Mg	Na	O	P	Si	other
Fe rich unclassified	≤10	≤10	≥10	≤10	≤10	≤10	-	-	≤10	-
Ca rich unclassified	≤10	≥10	≤10	≤10	≤10	≤10	-	-	≤10	-
Mg rich unclassified	≤10	≤10	≤10	≤10	≥10	≤10	-	-	≤10	-
K rich unclassified	≤10	≤10	≤10	≥10	≤10	≤10	-	-	≤10	-
Si rich unclassified	≤10	≤10	≤10	≤10	≤10	≤10	-	-	≥10	-
Al rich unclassified	≥10	≤10	≤10	≤10	≤10	≤10	-	-	≤10	-
Alumina silicate unclassified	≥5	-	-	-	-	-	-	-	≥5	20≤(Al+S)
Fe alumina silicate	≥6	≤2	≥3	≤2	≤2	-	-	-	≥10	30≤(Al+Si+Fe); (K+Na)≤3;a)
Ca alumina silicate	≥6	≥3	≤2	≤2	≤2	≤2	-	-	≥10	30≤(Al+Si+Ca); 3≤(K+Na)≤15
Mg alumina silicate	≥6	≤2	≤2	≤2	3	≤2	-	-	≥10	30≤(Al+Si+Mg); 3≤(K+Na)≤15
K alumina silicate	≥6	≤2	-	≥3	≤2	≤2	-	-	≥10	30≤(Al+Si+K); 3≤(Ca+Mg)≤15
(Ca, Mg) alumina silicate	≥6	≥2	≤2	-	≥2	≤2	-	-	≥10	30≤(Al+Si+Ca+Mg);
$CaAl_2Si_2O_8$ (anorthite)	13-17	6-8	-	≤2	≤2	≤2	-	-	13-17	3≤(K+Na)≤15
Al4(Si4O10) (kaolinite)	14-20	≤2	-	≤2	≤2	≤2	-	-	14-20	-
Al_2O_3 (corundum)	≥32	≤2	≤2	≤2	≤2	≤2	≥48	-	≤2	-
Fe oxides (hematite, magnetite)	-	-	≥32	-	-	-	≥38	-	-	-
SiO_2 (quartz etc.)	≤3	≤3	-	≤3	≤3	≤3	≥55	-	≥28	-
K silicate	-	-	-	5-	-	-	-	-	≥3	-
MgO, CaO	-	4-	-	40	4-	-	≥40	-	-	35≤(K+Si);
(Mg,Ca, Fe) oxide	-	40	≥10	-	40	-	-	-	-	40≤(Ca+Mg);
Phosphates unclassified	-	4-	-	-	4-	-	-	≥5	≥5	30≤(Ca+Mg);
Fe phosphate	-	40	≥6	-	40	-	-	≥6	≥6	-
$FePO_4$ (heterosite,rodolicoite)	≤3	-	≥13	-	-	≤3	-	≥13	≥13	-
$Mg_3(PO_4)_2$ (farringtonite)	≤3	-	≤3	≤3	-	≤3	-	-	≥14	-
$(Fe,Mg)_3(PO_4)_2$ (sarkopsite)	≤3	≤3	≥ 2	≤3	≤3	≤3	-	≥14	≥14	-
$(Fe,Ca)_3(PO_4)_2$ (graftonite)	≤3	≤3	≥ 2	≤3	9-	≤3	-	-	≥14	9≤(Mg+Fe)
		≤3		≤3	40					9≤(Ca+Fe);
		≥ 2			≥ 2					
					≤3					

[a] Further 3≤(Ca+Mg)≤15

The fly ash samples from co-combustion of meat and bone meal (MBME), paper sludge (PSE) and its reference (PSEref) were first sieved to remove the coarse fraction (ca 10%) as these contained much organic matter and irregular particles. These particles were investigated separately with SEM (qualitatively), see section 3.5.

4.2.5 Physical characterization of generated fly ashes

The particle size distribution was analysed by laser granulometry in an ethanol suspension. The volume weight was determined in accordance with NEN-EN 196-6 [4.3]. This method is based on the use of a pycnometer, whereby toluene is used as fluid. The morphology was assessed by SEM. The pictures were taken in the secondary electron image mode (SEI mode) at an acceleration voltage of 15 kV. Gold was sputtered on the surfaces of the samples to overcome charging of the sample during SEM investigation.

4.2.6 Properties of cement paste and mortar

The assessment of the properties of cement paste and mortar with fly ash consisted of measuring setting time and soundness of cement paste and the pozzolanic behaviour and workability of mortar. See also subsection 3.2.7 for a description of these methods.

Remark: For tests concerning properties of mortar and concrete, fly ash sample from co-combustion of meat and bone meal (MBME) was subjected to heat treatment at 550 ºC to remove unburned carbon by glowing. This temperature is much lower than sintering temperatures of fly ash (1000-1200 °C). The procedure was as follows:

- Part of the sample of the fly ash was smouldered at circa 550 °C for four hours.
- This part of the sample was mixed with non-smouldered fly ash in a ratio sufficient to give a final LOI of just 5.0%. The original LOI of this fly ash was 7.3%. After pre-treatment, it was 4.6%.

4.2.7 Properties of concrete

Different compositions of concrete were used to verify the quality of the fly ash and the findings with the standard mortar. Three different concrete compositions were chosen; one ordinary concrete, one according to the so-called Equivalent Performance Concept (EPC) and one High Performance Concrete (HPC). The compositions are given in table 4.3.

The workability of the equivalent performance concrete (EPC) and an ordinary concrete (OC) was assessed using the slump test [4.4] and the flow table test [4.5]. The workability of the high performance concrete (HPC) was assessed using the flow test [4.6]. The bleeding was assessed visually.

The compressive strength was tested in accordance with [4.7], using cubes. The splitting tensile strength was measured in accordance with [4.8]. The modulus of elasticity (E-modulus) was tested on concrete prisms in accordance with CUR report 94-12 [4.9].

The durability of concrete was tested for freeze-thaw salt resistance with the CDF test method [4.10]. The freeze-thaw salt resistance is determined as the weight loss by scaled material [kg/m^2] of the sample after 14 freeze-thaw cycles. The concrete specimen for this test were demoulded after 24 hours of hardening, airtight sealed with plastic foil and stored in a room with temperature 20±4 °C. After this period, the foil was removed and the specimen were stored for 21 days with temperature 20±4 °C and a relative humidity 65±5 %. After this, the specimen were ready for preparation for the CDF test.

Table 4.3: Concrete mixtures (in kg/m^3 unless indicated otherwise)

Concrete mixture	OC	EPC	HPC
Component			
Cement CEM I 32.5 R	272	-	-
Cement CEM I 42.5 R	-	210	350
Fly ash	68	100	150
Water [l/m^3]	164	165	170
Sand	723	713	639
Gravel	1180	1163	1045
Grading	A-B	A-B	-
D_{max} [mm]	31.5	31.5	16
Water-binder ratio[1] [-]	0.48	0.53	0.34
Type of admixture (% m/m in cement)	no	no	Glennium, 0.34
Amount of fines [l/m^3]	153	146	208

Key: EPC = equivalent performance concrete
OC = ordinary concrete
HPC = high performance concrete

[1]) The waterbinder ratio was calculated as the weight ratio water/(cement+fly ash).

4.3 Experimental results: properties of fuels and fly ashes

4.3.1 Co-combustion experiments

The chemical compositions of the fired coals and co-fired secondary fuel are presented in table 4.4 and 4.5. Some secondary fuels were analysed with XRD to assess the mineralogical composition. Apatite, calcite and quartz were identified in meat and bone meal. Calcite and quartz were also found in the paper sludge/wood mix (PS/WD) together with chalk, kaolinite, rutile and possibly serpentine.

Table 4.4: Amount of ash forming matter (AFM) and its composition of coals, fired during co-combustion tests

Co-combustion test	CRE	MBME	PKE	PSE	MSE	WPPE
AFM (ar)	10.7	12.8	11.0	10.7	17.1	10.1
Al_2O_3	31.8	30.5	31.8	26.0	26.7	24.8
CaO	5.1	5.4	4.9	2.61	4.23	3.9
Fe_2O_3	5.33	4.96	4.73	8.91	7.49	6.88
K_2O	1.64	0.91	0.69	1.93	3.04	1.48
MgO	1.01	1.65	1.54	1.66	3.19	2.26
Na_2O	0.38	0.72	0.25	0.49	0.90	0.63
P_2O_5	1.1	1.2	0.7	0.58	0.46	0.7
SiO_2	51.1	53.2	53.5	56.4	52.9	58.2
TiO_2	2.46	1.52	1.89	1.38	1.11	1.19
Total	100	100	100	100	100	100

Table 4.5: Amount of ash forming matter (AFM) and ash composition of secondary fuels, co-fired during co-combustion tests

Co-combustion test	CRE		MBME				PKE	PSE	MSE MSE+	WPPE	
Fuel	CR	PK	MB	BMP	PD	CF	PK^1	PS/ WD	SS	WPP	WD^1
AFM (ar)	9.2	4.1	20.4	18.7	12.5	6.8	4.91	40.0	32.4	4.77	2.0
Compound											
Al_2O_3	1.79	3.04	0.31	16.0	1.37	1.41	3.24	14.8	13.1	0.35	7.47
CaO	13.0	9.5	40.0	34.9	40.1	25.6	13.4	43.5	14.5	2.7	19.8
Fe_2O_3	5.29	6.95	0.53	6.11	1.04	1.16	6.91	1.95	16.0	0.56	4.11
K_2O	56.4	22.3	4.56	1.14	16.0	20.4	18.9	0.72	1.9	30.20	8.96
MgO	5.89	11.10	1.67	2.30	12.5	7.44	10.9	4.97	2.6	12.91	5.34
Na_2O	0.21	0.16	5.57	0.45	3.18	4.23	0.23	0.77	0.8	0.55	2.67
P_2O_5	10.3	35.0	44.9	10.7	16.4	29.5	31.4	0.36	21.7	49.0	2.1
SiO_2	6.72	11.9	2.40	27.8	9.32	10.3	14.9	32.4	28.7	3.73	49.0
TiO_2	0.38	0.09	0.03	0.65	0.11	0.11	0.11	0.54	0.7	0.00	0.53
Total	100	100	100	100	100	100	100	100	100	100	100

Key: AFM = amount of ash forming matter

[1]) No lot samples were available. Instead of that, analyses were used from samples taken from the same origin.

The realized co-combustion percentages during the real-scale co-combustion experiments are presented in table 4.6. These figures are based on the process data of the power plant (like tons/day) and the amount of ash forming matter of the fuels. Each co-combustion percentage was also derived from the measured fly ash composition. The fly ash composition was calculated from the composition (Ca, Mg, P, K) of the coals and the secondary fuels using the KEMA trace model, assuming a certain co-combustion percentage (see chapter 6 for a description). The calculated fly ash composition was fit by varying the co-combustion percentage to one or two characteristic components to obtain the smallest deviation between the measured and the calculated concentration in the co-combustion fly ash.

In the case of a co-combustion experiment with a combination of secondary fuels, it is assumed that the ratio between the secondary fuels is the same as based on the registered quantity in the power plant. It can be derived that the range between the estimated co-combustion percentages, ash based is significant, with exception of the experiments with co-firing palm kernels (PKE) and municipal sewage sludge (MSE+). In most cases the calculated co-combustion percentage was lower than that based on process data.

Note that during the co-combustion experiment with wheat pollard pellets (WPPE), slagging occurred in very short time and the experiment had to be stopped due to this.

Table 4.6: Overview of ash-based co-combustion percentages [% m/m], based on process data and derived from the chemical composition of the generated fly ash

Co-combustion test	CRE	MBME	PKE	PSE	MSE	MSE+	WPPE
Power plant	B	A	C	B	B	B	C
Total based on process data	14	17	10	24	10	17	9
Secondary fuels							
Palm kernels (PK)	2.0-2.5	-	7.0-8.5	-	-	-	-
Cacao residues (CR)	4.9-6.1	-	-	-	-	-	-
wheat pollard pellets (WPP)	-	-	-	-	-	-	8.3-13
Wood	-	-	-	0.4-0.6	-	-	0.7-1.1
Meat and bone meal (MBM)	-	6.1-8.2	-	-	-	-	-
Biomass pellets (BMP)	-	3.1-4.2	-	-	-	-	-
Poultry litter (PD)	-	0.5-0.7	-	-	-	-	-
Cattle feed (CF)	-	0.3-0.4	-	-	-	-	-
Paper sludge (PS)	-	-	-	13-19	-	-	-
Municipal sewage sludge (SS)	-	0.1	-	-	6.7-7.3	15-18	-
Soot paste (SP)	-	0.0	-	-	-	-	-
Total derived from composition	6.9-8.6	10-14	7.0-8.5	13-20	6.7-7.3	15-18	9.0-14
Fit to	P_2O_5 K_2O	P_2O_5, CaO Al_2O_3	P_2O_5, K_2O Al_2O_3	CaO Fe_2O_3	P_2O_5 Fe_2O_3	P_2O_5 Fe_2O_3	P_2O_5 K_2O Al_2O_3

4.3.2 Characterization of coal, secondary fuels and fly ashes

The results of the chemical analyses are presented in table 4.7 (Please note all concentrations are normalized to 5% LOI to make the results more comparable). The amount of SiO_2 + Al_2O_3 + Fe_2O_3 is about 74 - 83% m/m. The range for Dutch coal fly ashes is 88±2 % m/m (reference values from table 2.3). In many cases the Al_2O_3-content decreases due to co-combustion as the secondary fuels do not contain much of this component. The range of Al_2O_3 concentration in coal fly ashes generated in Dutch power plants without co-combustion is 27±2.6 % m/m[17] (see further table 2.3).
Specific elements in fly ash do significantly increase due to co-combustion, namely:

- CaOtotal, due to co-combustion of paper sludge and meat and bone meal (range coal fly ash is 4.5±1.7 % m/m). However the increase of CaOtotal does not mean that also CaOfree increases.
- K_2O, due to co-combustion of cacao residues and wheat pollard pellets (range coal fly ash is 1.6±0.5) % m/m.
- P_2O_5, due to co-combustion of meat and bone meal, palm kernels, cacao residues, wheat pollard pellets and municipal sewage sludge (range coal fly ash is 0.8±0.4 % m/m).
- MgO, due to co-combustion of cacao resides and wheat pollard pellets. Reference value is 1.8±0.3 % m/m.

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[17] Average ± standard deviation

Table 4.7: Chemical composition (main components; normalized to 5% LOI) of generated fly ashes

Fly ash from:	CRref-T	CRE	MBME	PKE	PSEref	PSE	MSEref	MSE+	WPPE
Compound									
Al_2O_3	30.2	28.3	25.1	27.9	23.7	21.7	24.7	23.4	20.2
CaO	4.9	4.5	9.1	4.7	2.2	7.5	4.2	4.9	4.8
Fe_2O_3	5.1	5.1	4.5	5.2	9.0	7.5	7.8	8.7	5.4
K_2O	1.6	4.9	1.6	1.8	2.0	2.2	2.3	2.4	3.7
MgO	1.0	1.3	1.3	1.7	1.4	1.6	2.6	2.7	4.5
Na_2O	0.4	0.3	0.8	0.4	0.3	0.3	0.9	1.1	0.7
P_2O_5	1.1	2.3	4.0	2.8	0.6	0.8	0.6	3.4	5.2
SiO_2	48.6	46.2	47.1	48.3	54.4	52.0	50.5	47.1	48.7
SO_3	0.0	0.0	0.3	0.6	0.3	0.4	0.5	0.4	0.7
TiO_2	2.3	2.2	1.3	1.7	1.1	0.9	0.9	1.1	1.0
LOI	3.1	3.9	7.3	2.7	5.3	4.0	2.1	2.1	4.0
Na_2O-eq	1.4	3.7	1.9	1.6	1.7	1.7	2.4	2.6	3.1
Cl	-	<0.01	0.0	0.01	< 0,08#	< 0,08#	0.01	0.01	<0,01
CaO_{free}	0.80	0.61	1.02	0.68	<0.05	<0,05	0.03	<0,02	0.43
Reactive SiO_2	-	30.0	33.6	38.1	-	28.4	-	-	32.0
Al_2O_3/SiO_2	0.53	0.53	0.53	0.58	0.44	0.42	0.49	0.50	0.42
$\sum Al_2O_3\ Fe_2O_3\ SiO_2$	83.9	79.6	76.6	81.3	87.1	81.2	83.0	79.2	74.4

* Analyses according the modified method (pH=8.5) # analysed with Instrumental Neutron Activation Analysis

The fraction of the co-combustion fly ash that is soluble in acid varies between 10 and 25% m/m (see table 4.8). This is significantly higher than that of fly ashes from 100% coal (6-8 % m/m). Substantial proportions of Ca, P, Mg and K are dissolved. The dissolution of small amounts of Si and Al is noteworthy. These amounts seem to be higher in the case of co-combustion. The distribution between acid soluble and acid insoluble of K_2O, CaO, MgO and P_2O_5 is visualized in figures 4.1-4.3. K_2O, is mainly present as acid insoluble fraction. Only in the case of co-combustion of cacao residues (CRE) and wheat pollard pellets (WPPE) significant amounts of K_2O are acid soluble. CaO is mainly acid soluble (like free lime, tri calcium phosphate and anhydrite). A glass phase is present in the fly ash from co-combustion of paper sludge (PS) which is very CaO rich. The fly ash from co-combustion of meat and bone meal (MBME) contains high amounts of acid soluble P_2O_5. According to the calculation it should be more than the total concentration. Inhomogeneities in the fly ash are possibly responsible for these differences. In the other fly ashes about 1/2-1/3 of the present P_2O_5 is acid soluble.

Table 4.8: Composition of acid soluble fraction (elements expressed as oxides [% m/m]

Fly ash from:	CRref T	CRE	MBME	PKE	PSEref	PSE	MSEref	MSE+	WPPE
Al_2O_3[a]	1.07	2.79	3.52	1.74	2.89	3.33	0.76	1.56	1.50
CaO	2.67	2.69	8.83	3.79	1.75	6.07	2.74	3.16	2.95
Fe_2O_3	0.24	0.53	0.83	0.51	0.94	0.70	0.62	0.90	0.41
K_2O	0.12	1.11	0.15	0.26	0.14	0.12	0.03	0.09	0.94
MgO	0.49	1.07	1.00	1.20	0.56	0.92	1.20	1.18	2.86
Na_2O	0.03	0.06	0.17	0.08	0.06	0.06	0.05	0.10	0.11
P_2O_5	0.54	1.53	4.34	1.92	0.29	0.48	0.44	1.90	3.66
SO_3	0.32	0.35	0.22	0.40	0.23	0.32	0.41	0.35	0.34
SiO_2	1.07	2.36	4.28	3.16	1.42	5.09	0.97	1.66	2.11
TiO_2	0.08	0.17	0.17	0.11	0.10	0.12	0.04	0.07	0.07
Total main components	6.63	12.66	23.51	13.17	8.38	17.21	7.25	10.98	14.94
Total gravimetric analysed	8.1	15.6	25.3	13.31	9.5	18.6	9.2	9.6	15.8
Difference [rel %][b]	20	21	7	1	12	8	23	14	6

[a] The components are measured as elements and expressed as oxides

[b] The difference is calculated as (total components-gravimetric analysed) divided by the average of both

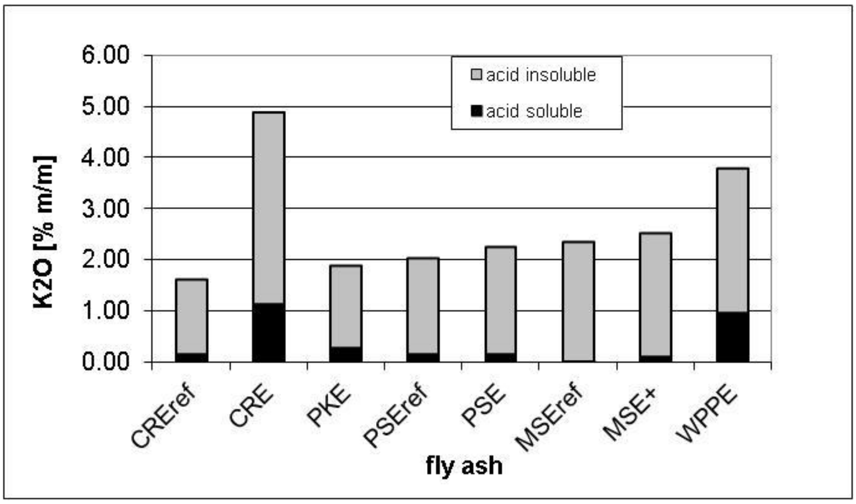

Figure 4:1: Content of acid soluble and insoluble potassium (as K_2O) in fly ashes

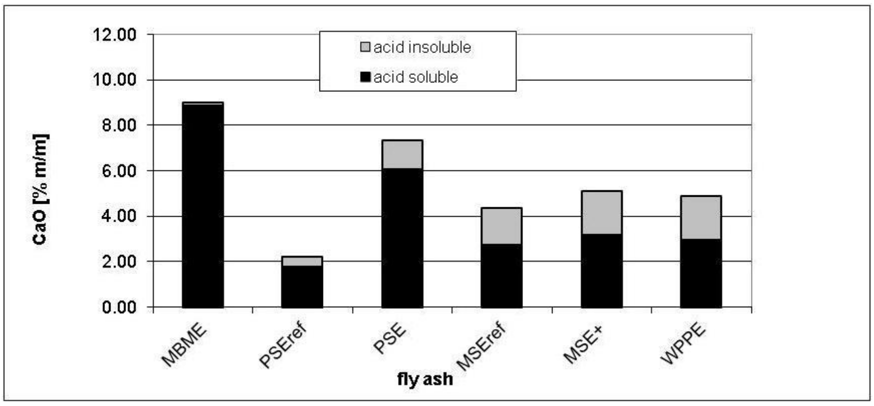

Figure 4:2: Content of acid soluble and insoluble calcium (as CaO) in fly ashes

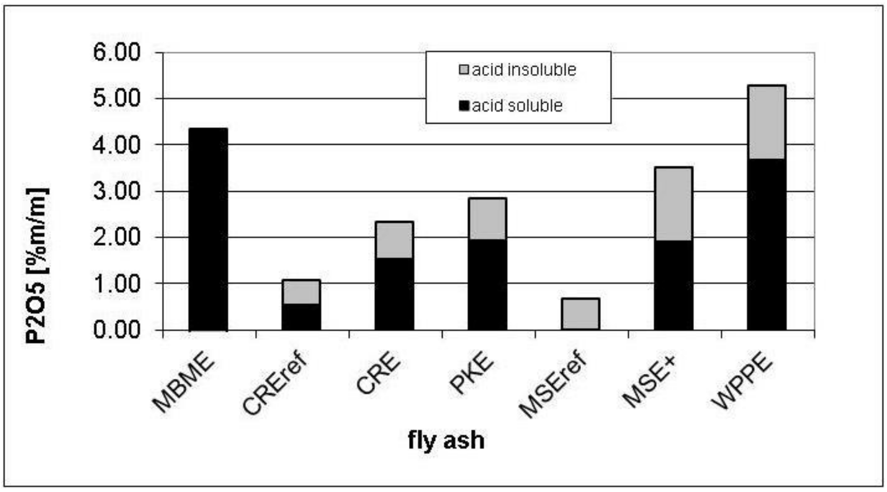

Figure 4:3: Content of acid soluble and insoluble phosphorus (as P_2O_5) in fly ashes

Table 4.9 shows the results of the analyses of the determination of the fraction soluble in potassium hydroxide. No reliable data could be obtained from the analyses of fly ashes CRE and CREref. The results show that in all cases this fraction, which is often seen as the glass phase, is an alumino silicate glass with a limited content of network modifiers (see also box 4.1, section 4.5).

Table 4.9: Composition of fraction, soluble in potassium hydroxide (elements expressed as oxides)

Fly ash		MBME	PKE	PSEref	PSE	MSEref	MSE	WPPE
Compound	Unit							
Al_2O_3	% m/m	22,2	16,1	29,1	22,9	26,2	16,1	9,1
CaO	% m/m	4,7	2,1	0,0	5,1	2,0	2,1	2,2
Fe_2O_3	% m/m	3,2	2,4	0,7	4,3	4,4	2,7	1,7
K_2O	% m/m	2,5	1,9	2,5	3,2	1,1	0,0	3,3
MgO	% m/m	1,4	1,0	0,0	2,0	2,0	1,2	1,2
Na_2O	% m/m	1,1	0,4	0,4	0,4	0,4	0,0	0,7
P_2O_5	% m/m	1,4	0,8	0,4	0,4	0,3	0,6	2,8
SO_3	% m/m	0,0	0,0	0,1	0,1	0,0	0,0	0,4
SiO_2	% m/m	64,7	75,0	66,6	64,0	63,0	76,0	62,4
TiO_2	% m/m	0,7	1,4	0,1	0,8	0,6	1,2	0,4
Intermediaries	mol %	16	11	20	17	20	12	8
Network modifiers	mol %	11	7	2	12	7	4	9
Network formers	mol %	73	83	78	71	73	84	83

4.3.3 Characterization of mineralogy of generated fly ashes

The results of the XRD-analyses are presented in tables 4.10-4.12. In general, there is a good match between the minerals identified with quantitative XRD and qualitative XRD (QXRD). All fly ashes consist mainly of amorphous matter (60-81%), while a large share is mullite (11-31%) and a smaller share is quartz (5-12%). These three phases sum up to 93-98%. Quartz is identified in all fly ashes, with both XRD and QXRD. In all fly ashes hematite and/or magnetite are present as the only iron bearing minerals. Free lime was found in a few fly ashes. It is possible that feldspar is present in fly ash from co-combustion of cacao residues (CRE). In fly ash from co-combustion of meat and bone meal (MBME) the modification of tricalcium phosphate was found.

Table 4.10: Mineralogical composition of fly ashes [% m/m], analysed with XRD and QXRD

Fly ash	CREref		CRE		MBME	
XRD?	XRD	QXRD	XRD	QXRD	XRD	QXRD
Mineral						
Amorphous	yes	60	yes	67	yes	68
Unburnt matter[a]	yes	-	yes	-	yes	-
Free CaO[a]	-	<0.5	yes	<0.5	-	-
Quartz	yes	7	yes	7	yes	10
Hematite	possible	1	-	1	yes	1
Mullite	yes	31	yes	23	yes	15
Magnetite	yes	2	yes	2	-	1
Corundum	-	-	-	-	-	-
Feldspar	-	-	possible	-	-	-
α tricalcium phosphate	-	-	-	-	-	6

a) Analysed with methods according to EN 450.

Table 4.11: Mineralogical composition of fly ashes [% m/m], analysed with XRD and QXRD

Fly ash	PSEref		PSE		WPPE	
XRD?	XRD	QXRD	XRD	QXRD	XRD	QXRD
Mineral						
Amorphous	yes	74	yes	76	yes	73
Unburnt matter^a	yes	-	yes	-	yes	-
Free CaO^a	-	-	-	-	-	-
Quartz	yes	11	yes	12	yes	11
Hematite	possible	1	probably	1	yes	1
Mullite	yes	13	yes	11	yes	13
Magnetite	probably	1	probably	1	-	2
Corundum	-	-	-	-	-	-
Feldspar	-	-	-	-	-	-
α tricalcium phosphate	-	-	-	-	-	-

a) Analysed with methods according to EN 450.

Table 4.12: Mineralogical composition of fly ashes [% m/m], analysed with XRD and QXRD

	MSEref		MSE	MSE+		PKE	
XRD?	XRD	QXRD	XRD	XRD	QXRD	XRD	QXRD
Mineral							
Amorphous^a	yes	79	yes	yes	80	yes	63
Unburnt matter^a	yes	-	yes	yes	-	yes	-
Free CaO^a	-	<0.5	-	-	<0.5	yes	<0.5
Quartz	yes	5	yes	yes	5	yes	7
Hematite	possible	2	possible	possible	2	possible	1
Mullite	yes	11	yes	yes	10	yes	27
Magnetite	yes	3	yes	yes	3	possible	2
Feldspar	-	-	-	-	-	-	-
α tricalcium phosphate	-	-	-	-	-	-	-

a) Analysed with methods according to EN 450.

4.3.4 SEM analyses

The main phase in all fly ashes is 'alumina silicate unclassified' (30-65% m/m), which is in fact part of the glass phase and mullite (see table 4.13). The identified phases are normalized to 95% as with the chemical composition; so the other 5% is organic. The presence of mullite could not be identified due to the small crystal size in relation to the resolution of the SEM and is, therefore, recognized as 'alumina silicate unclassified'. The reference coal fly ash sample from co-combustion of paper sludge has the highest content of this alumina silicate phase (65%), while its co-combusting counterpart (PSE) consists of only 45% of this phase, although it contains more ”Ca alumina silicate” and "(Ca, Mg) alumina silicate”, which has its origin in the mineral fraction of the paper sludge. All samples contain a significant amount of a phase with a kaolinite-like composition (2-11% m/m). Kaolinite is a common mineral in coal, but will be converted into glass and mullite during the combustion process. Other alumina silicates enriched in Fe, Ca and K were identified. SiO_2 is found in all samples in the range 2-12% m/m. The match with the QXRD results of quartz is very good in the case of fly ash from co-combustion of sewage sludge (MSE) and from co-combustion of palm kernels (PKE), but not so good for fly ashes from co-combustion of paper sludge ant its reference (PSE and PSEref). However, these ashes were separated in a coarse and bulk fraction (together with MBME). The SiO_2-phase is 96-98% pure. Fe-rich unclassified and/or Fe-oxides were identified in all samples. In general it can be stated that P is present in discrete phases; the occurrence of P seems to be associated with Ca and Mg. K seems to be distributed over all particles. Phosphate containing phases were found back in all fly ashes from co-combustion of phosphorus containing fuels. The main phase is ‘phosphate unclassified’. The average composition of this phase differs per fly ash and is given in table 4.14 It can be inferred from these results that fly ash from co-combustion of municipal sewage sludge (MSE+), has a relatively high concentration of Fe within this phase (36% m/m). This is coupled with the presence of Fe-phosphate (4% m/m). Traces of phases with a composition corresponding with farringtonite and graftonite were identified in several fly ash samples. In a few fly ashes “Ti-rich unclassified’’ (traces) and Al_2O_3 (corundum) were found. ‘Sulphates unclassified’ is found in only one fly ash sample. K seems to be distributed over all particles.

Table 4.13: Identified phases with KEMPHASE in fly ashes (normalized to 95%)

Fly ash	MSE+	CRE	PKE	MBME	PSE	PSEref
Phase	%[1]	%[1]	%[1]	%[1]	%[1]	%[1]
Fe rich unclassified	3	1	1	1	2	1
Ca rich unclassified	2	1	1	5	5	0[2]
Mg rich unclassified	0	3	-	-	-	-
K rich unclassified	-	0	-	-	-	-
Al rich unclassified	-	0	0	0	-	-
Si rich unclassified	13	11	9	19	11	10
Ti rich unclassified	-	-	0	0	-	-
alumina silicate unclassified	56	30	33	35	45	65
Fe alumina silicate	1	1	1	0	0	5
Ca alumina silicate	1	1	3	4	8	1
Mg alumina silicate	-	0	-	-	-	-
K alumina silicate	0	8	1	-	1	1
(Na, K) alumina silicate	-	-	0	-	-	-
(Ca, Mg) alumina silicate	1	2	2	1	14	0
$CaAl_2Si_2O_8$ (anorthite)	-	0	-	-	-	-
$Al_4(Si_4O_{10})$ (kaolinite)	2	7	11	6	3	4
Al_2O_3 (corundum)	-	1	-	-	-	-
Fe oxides (hematite, magnetite)	2	1	2	-	2	0
SiO_2 (quartz, cristobalite, tridymite)	5	12	6	8	2	6
Ca silicate	0	0	0	-	-	-
Fe silicate	0	0	0	-	0	0
K silicate	-	0	-	-	1	1
MgO, CaO	0	1	-	-	-	-
(Mg,Ca,Fe) oxide	0	-	-	-	-	-
sulphates unclassified	-	-	0	-	-	-
phosphates unclassified	4	12	24	15	-	0
Fe phosphate	4	1	0	-	-	-
$FePO_4$ (heterosite, rodolicoite)	0	-	-	-	-	-
$(Fe,Mg)_3(PO_4)_2$	0	-	-	-	-	-

[1] The output of KEMPHASE is in surface percents.

[2] <0.5;

Table 4.14: Average composition of 'phosphate unclassified' phase (normalized to 100 atom %)

Fly ash	PKE	CRE	MSE+	MBME
Compound	atom %	atom %	atom %	atom %
Al_2O_3	4.1	6.3	8.4	4.4
CaO	39.5	13.7	13.3	48.1
Cl	0.0	0.0	0.0	0.0
Fe_2O_3	4.0	7.3	36.2	1.8
K_2O	0.5	6.5	0.3	0.1
MgO	8.6	24.6	3.5	1.3
Na_2O	0.2	0.1	0.9	0.2
P_2O_5	33.2	24.4	22.8	33.5
SO_3	0.3	0.2	0.1	0.2
SiO_2	9.2	16.3	14.0	9.9
TiO_2	0.3	0.5	0.3	0.3

Figure 4.4 and 4.5 give a graph of the distribution of phases in fly ash from co-combustion of wheat pollard pellets (WPPE). The phases *K alumino silicate* and *phosphates unclassified* are mainly found in the fine fraction of the fly ash. The latter is also found as part of the agglomerates. Quartz is present in angular particles, discrete or as part of the agglomerates. Figure 4.6 shows that the phosphate bearing phases (like Fe phosphate) in fly ash from co-combustion of sewage sludge (MSSE) are mainly present as discrete particles. The same goes for fly ash from co-combustion of meat and bone meal (MBME) (see figure 4.7 and 4.8). The coarse fraction of fly ash from co-combustion of paper sludge (PSE) contains more spherical particles (see figure 4.9 and 4.10) than its reference fly ash (PSEref). The coarse fraction of the latter contains mainly organic and irregular particles (see figure 4.11). The spherical particles in fly ash from co-combustion of paper sludge consists of mainly Si/Al/O/Ca and Si/Al/O/Mg/Ca. The spherical particle morphology points to the occurrence of a molten phase during combustion, which is 'frozen' by cooling during transport of the particles by the flue gases.

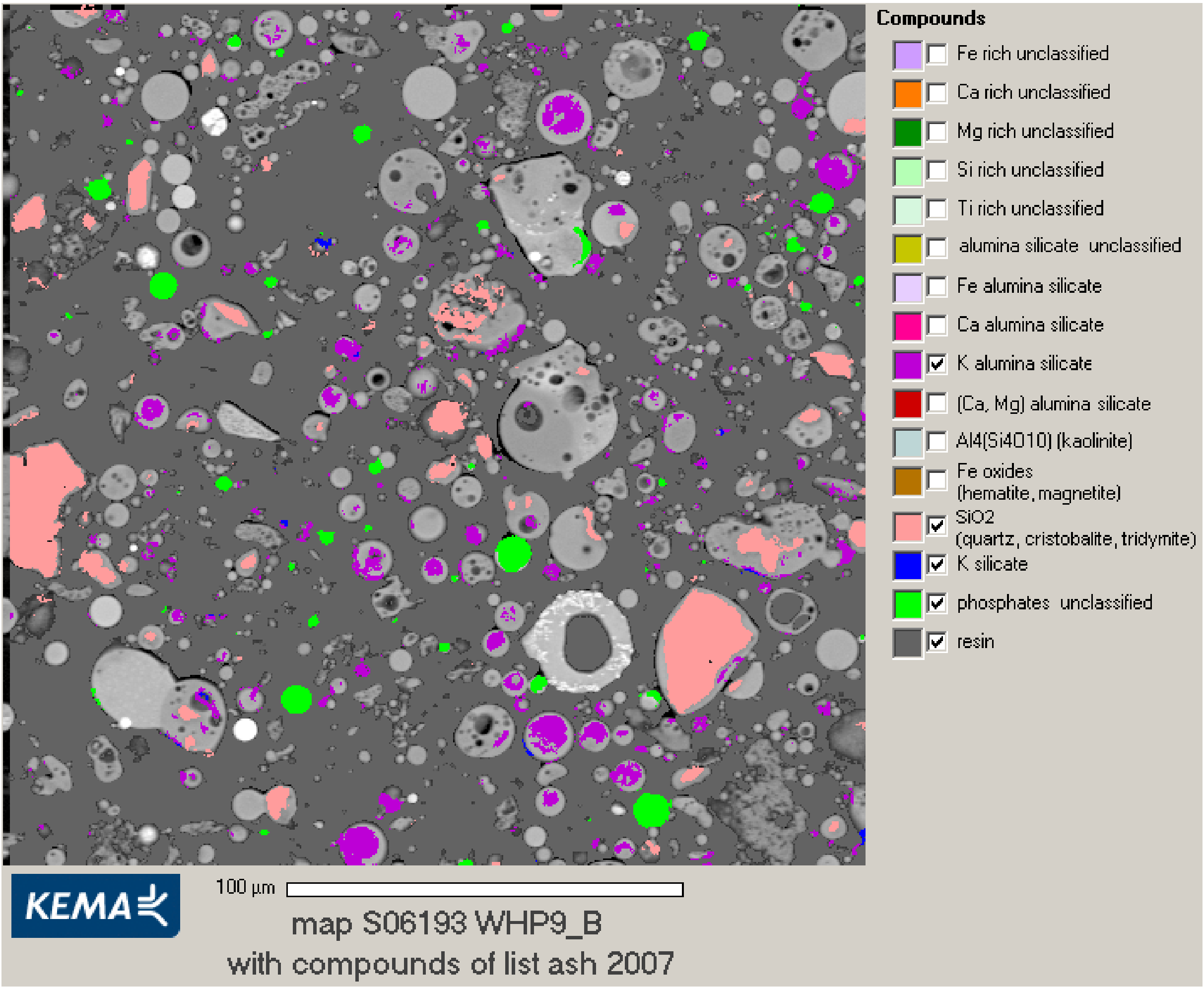

Figure 4:4: Graphical representation of KEMPHASE analysis of fly ash from co-combustion of wheat pollard pellets (WPPE) (fine fraction), showing the presence of several identified phases. ‘SiO_2; probably quartz’: present in some particles. ‘Phosphate unclassified’ present in small spherical particles. ‘K alumina silicate’ also present in small spherical particles (courtesy: KEMA).

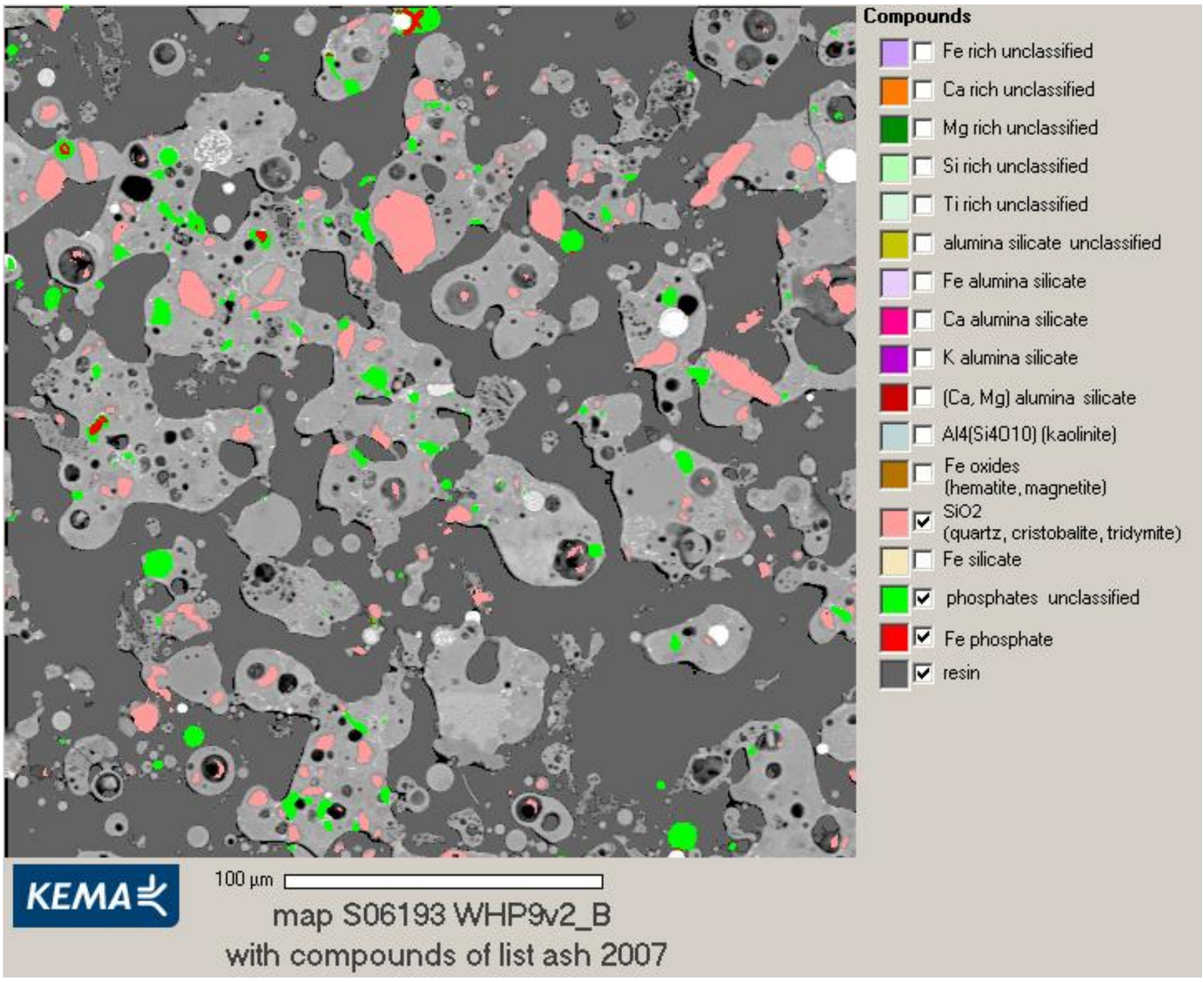

Figure 4:5: Graphical representation of KEMPHASE analysis of fly ash from co-combustion of WPPE (coarse fraction), consisting of non-typical morphologies (agglomerates), showing the presence of several identified phases. ‘SiO_2; probably quartz’: present in some particles. ‘Phosphate unclassified’ present in small parts of bigger agglomerates (courtesy: KEMA).

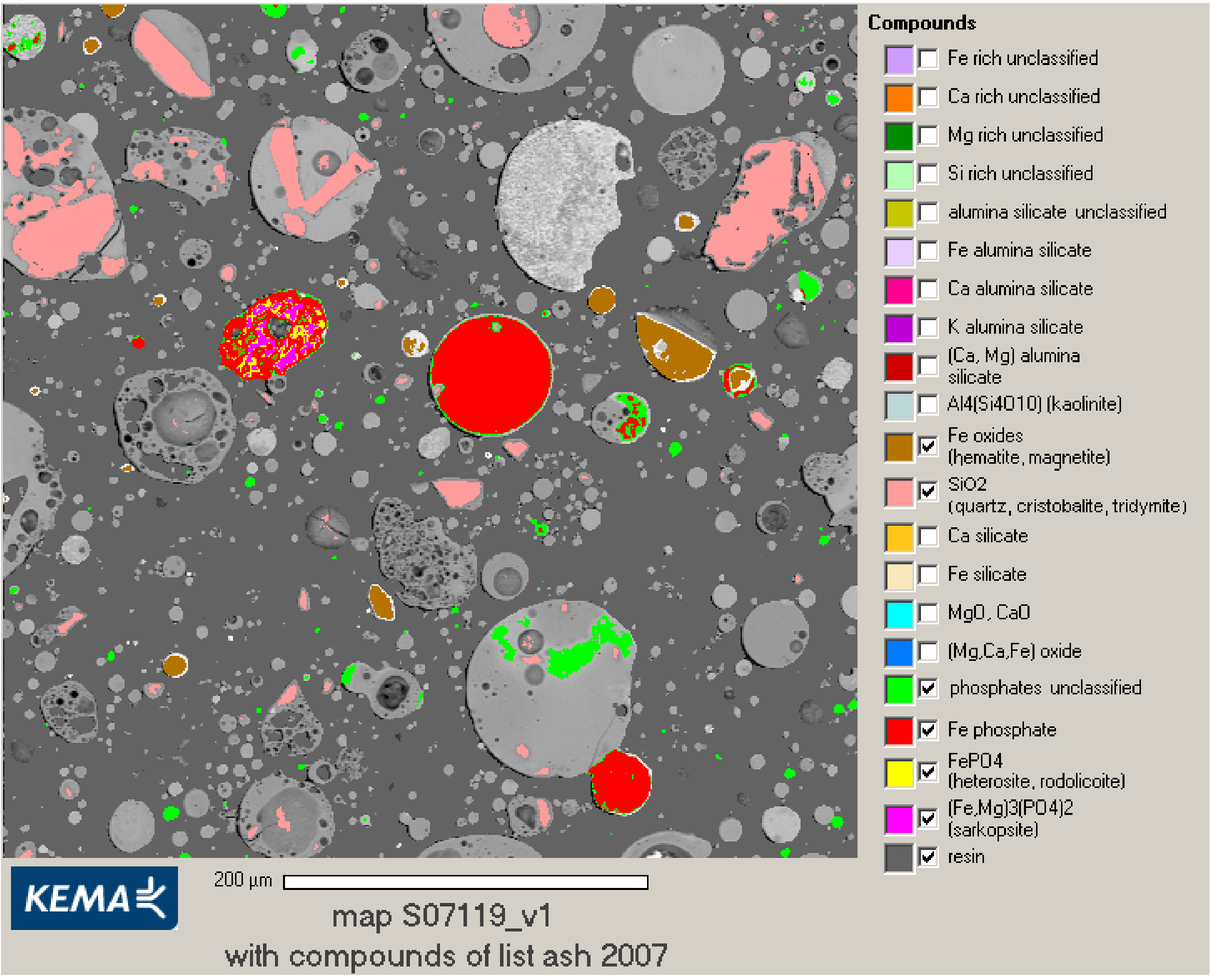

Figure 4:6: Graphical representation of KEMPHASE analysis of fly ash from co-combustion of municipal sewage sludge (MSE) showing the presence of several identified phases. 'SiO$_2$; probably quartz': present. 'Fe phosphate unclassified' and 'FePO4' present in spherical particles, pointing to the existence of a molten phase during the combustion process. The light coloured zone around these particles is an artefact (courtesy: KEMA).

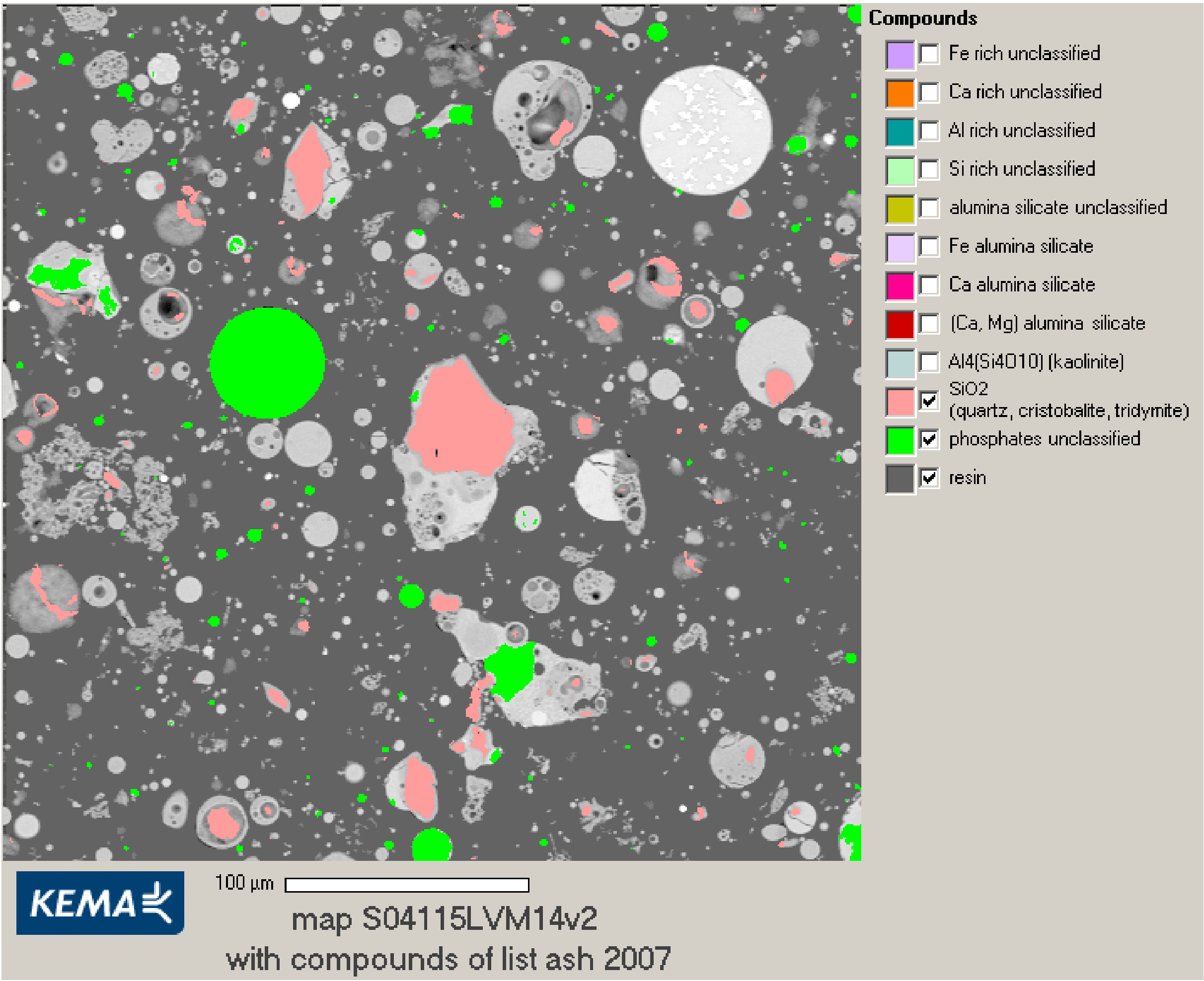

Figure 4:7: Graphical representation of KEMPHASE analysis of fly ash from co-combustion of mainly meat and bone meal (MBME) showing the presence of several identified phases.
‘SiO_2; probably quartz’: present in several non-spherical parts,
‘phosphate unclassified’ present in spherical particles, pointing to the existence of a molten phase during the combustion process
(courtesy: KEMA)

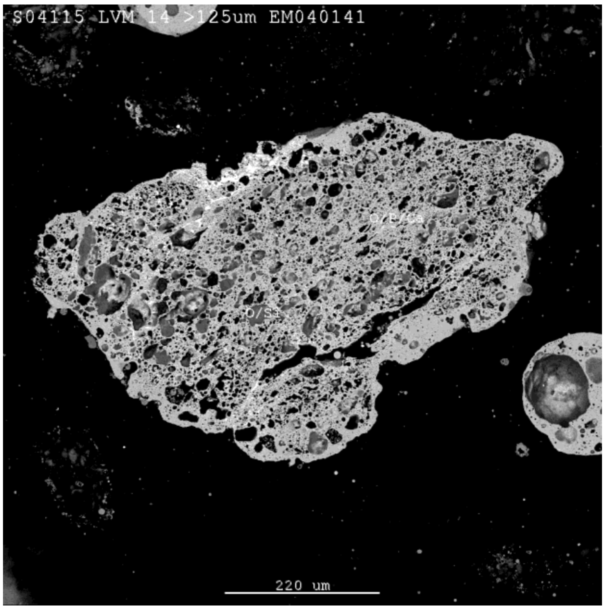

Figure 4:8: SEM photograph of inorganic coarse particles in fly ash from co-combustion of mainly meat and bone meal (MBME), which consist mainly of O+P+Ca. (back-scattered plot). The porous structure shows resemblance to the structure of bone. The angular morphology points to the absence of a molten phase during combustion

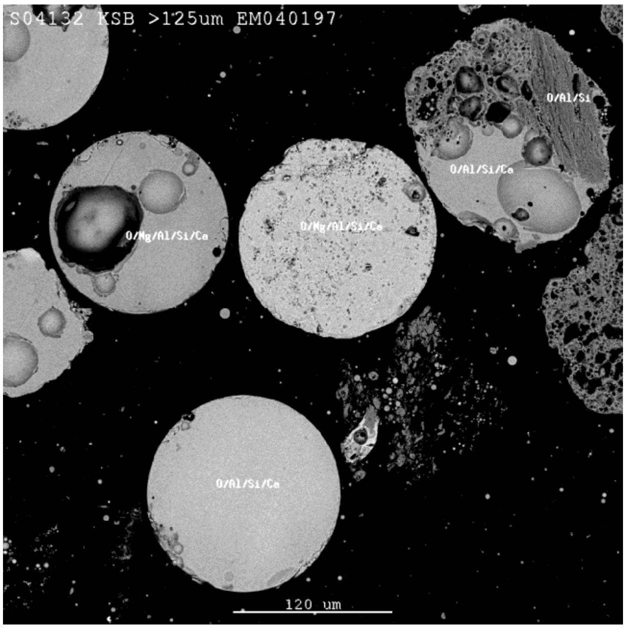

Figure 4:9: SEM photograph of coarse particles in fly ash from co-combustion of paper sludge (PSE)(back-scattered plot). These coarse, spherical particles consist mainly of O+Al+Si+Ca and O+Al+Si+Mg+Ca, originating from the mineral matter of paper sludge.

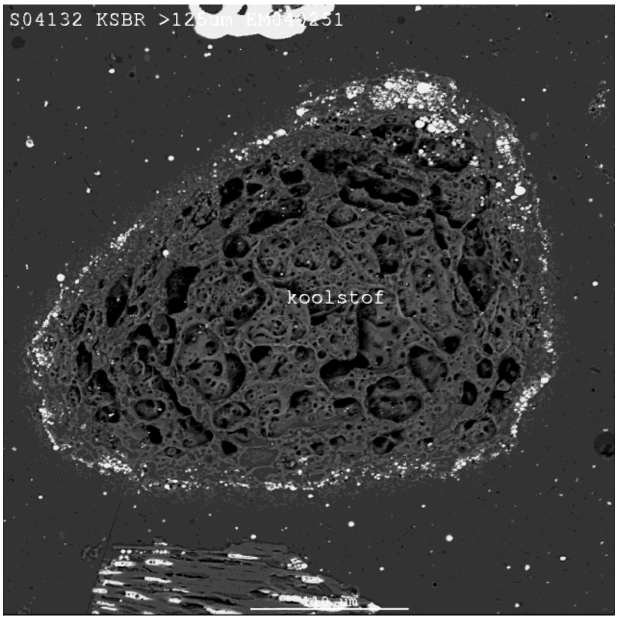

Figure 4:10: SEM photograph of organic coarse particle in coal fly ash, reference of co-combustion of paper sludge (PSE) (back-scattered plot). Particle consisting of char with spherical sub particles mainly at the surface. Incomplete char burn-out whereby the included minerals were melted during combustion and formed a kind of a layer on the surface.

Figure 4:11: SEM photograph of inorganic coarse particles in coal fly ash reference of co-combustion of paper sludge (PSEref), which consists of quartz with alumina-silicate (back-scattered plot).

4.3.5 Physical characterization of generated fly ashes

The results of the physical analyses are presented in table 4.15. The particle size distribution is expressed as D_{10}-, D_{50}- and D_{90}-values, which is very similar for coal and co-combustion fly ashes. The D_{50}-value of the co-combustion ashes varies between 19 and 25 µm, with exception of the fly ash from co-combustion of municipal sewage sludge (MSE+), which is considerably lower (8.3 µm). The D_{90} of fly ash from co-combustion of paper sludge is considerably higher than of the reference fly ash. This confirms the identification of bigger particles during the SEM microscopy. The particle density is in the range of Dutch coal fly ash (2290±60 kg/m^3). The fly ashes from co-combustion of paper sludge and sewage sludge show an increase of particles density

Table 4.15: Grain size distribution [µm], finesses expressed as fraction passing sieve 45 µm [% m/m] and particle density [kg/m^3] of generated fly ashes

Fly ash from:	CRref	CRE	MBME	PKE	PSEref	PSE	MSEref	MSE+	WPPE
Parameter									
D10 [µm]	2.8	6.0	4	3	4	4	2	1.2	3
D50 [µm]	25	24	21	20	19	23	22	8.3	20
D90 [µm]	59	59	82	66	66	118	65	31	65
Pass. sieve 45 µm	69	64	66	73	83	70	72	73	65
Particle density	-	-	2190	2263	2095	2225	2134	2261	2197

Most fly ashes consist of more or less spherical particles (see figure 4.12), with exception of fly ash from co-firing wheat pollard pellets (WPPE). The morphology of this fly ash (figure 4.5) is different from ‘standard’ more or less spherical particles of coal fly ashes. This fly ash contains a considerable amount of agglomerates.

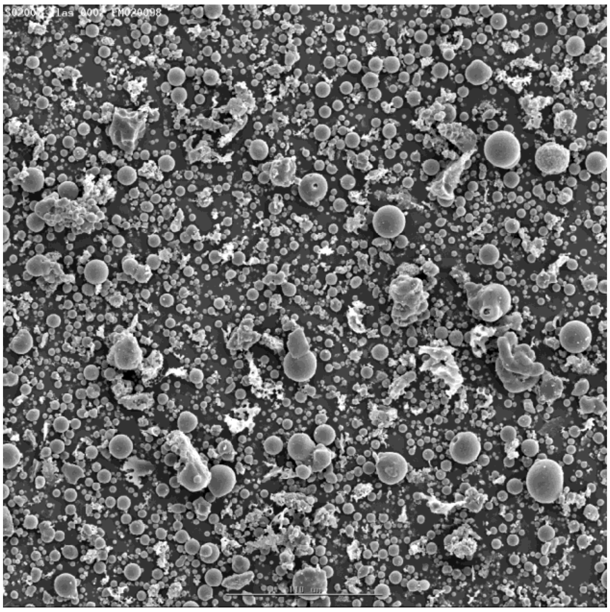

Figure 4:12: SEM photograph of fly ash from co-combustion of meat and bone meal (MBME), secondary electron image. The fly ash mainly consists of spherical particles

4.4 Experimental results: properties of cement paste, mortar and concrete

Properties of cement paste with fly ash from co-combustion

Cement paste was prepared for determination of setting time and soundness (measured with Le Chatelier test) to investigate the effects of co-combustion. The cement/fly ash ratio was 75/25 m/m and 50/50 m/m, respectively. The water-binder ratio was adjusted to obtain standard consistency (see further subsection 3.2.7). The results of the cement paste and mortar experiments are presented in table 4.15. The initial setting of all cement fly ash pastes is within the range of cement paste with coal fly ashes (REF). The initial setting of the fly ash cement pastes is retarded compared to that of the reference cement paste, but this is a normal consequence due that fly ash behaves inert in the first phase of hydration and so less reactive material is present in the fresh cement paste. The retardation of the initial setting of cement paste with co-combustion fly ash is 25 – 51 minutes, which meets the maximum limit value of the standard EN 450. The initial setting time of cement paste with fly ash co-combustion of cacao residues is later than the other samples. However, this is not an effect of co-combustion as the initial setting time of the cement paste with the reference coal fly ash (CRref) was also later. The measured expansion with the LeChatelier test was maximum 1.0 mm. According to the standard EN 450 (criterion: ≤ 10 mm) these fly ashes will not cause unsoundness when used in mortar and concrete.

Properties of mortar with fly ash from co-combustion

Mortars with fly ash were prepared for the determination of the impact of co-combustion on the pozzolanic behaviour and workability of fresh mortar. The binder consists of Portland cement (CEM I) (reference mortar) or Portland cement (CEM I) with 25% m/m replacement with fly ash. The water binder ratio was 0.50 for all mortars. The flow of the fly ash cement mortars is in most cases a bit higher than that of the reference cement mortar. Mortar with fly ash from co-firing cacao residues (CRE), and also with the reference coal fly ash has a lower flow compared to that of the reference cement mortar. Therefore, this effect is not caused by co-combustion. Obviously, the combination of fly ash and this cement together requires more water than the cement alone. Note that the flow of the reference cement mortar belonging to these tests is higher than the others (185 mm versus 142-178 mm).

The development of the compressive strength in time has a normal progress (see table 4.16, 4.17 and figure 4.13). The activity indices (measure for pozzolanic behaviour) at 28 days vary between 77 and 84% and increase up to 90 - 98% after 91 days. These values meet the EN 450 criteria (minimums of 75% and 85%, respectively). The activity indices of the mortars with fly ashes from co-combustion are very similar to the indices of mortar with the reference coal fly ashes.

Table 4.16: *Properties of (fly ash) cement paste (soundness and setting time). Mix composition: see subsection 3.2.7*

Fly ash		CRE ref	CRE	MBME	PKE	PSE	PSE ref	MSE ref	MSE	MSE+	WPPE
Property	unit										
Soundness	mm	-	-	1.0	1.0	1.0	0.5	0.9	0.6	0.2	-
WBR ref.[1]	-/-	0.30	0.30	0.28	0.28	0.28	0.28	0.24	0.24	0.24	0.30
Initial set ref.	hr:min	2:38	2:38	3:15	3:44	2:32	2:32	3:10	3:10	3:10	3:03
Final set ref.	hr:min	4:44	4:44	4:19	5:32	3:30	3:30	4:10	4:10	4:10	4:34
WBR	-/-	0.32	0.32	0.27	0.34	0.27	0.28	0.25	0.25	0.24	0.33
Initial set	hr:min	4:15	4:40	3:40	4:35	3:03	3:10	3:50	3:50	3:40	3:30
Final set	hr:min	7:00	7:19	5:00	7:00	4:35	4:25	5:10	5:00	4:50	5:25
Retardation	hr:min	1:37	2:02	0:25	0:51	0:31	0:38	0:40	0:40	0:30	0:27

[1] Ref.= reference: paste or mortar without replacement of cement with fly ash

Table 4.17: *Properties of (fly ash) cement mortars (flow and activity index). Mix composition: see subsection 3.2.7*

Fly ash		CRE ref	CRE	MBME	PKE	PSE	PSE ref	MSE ref	MSE	MSE+	WPPE
Property	unit										
Flow ref.	mm	185	185	170	-	178	178	142	142	142	176
Flow	mm	175	177	170	-	178	189	143	151	158	175
28d strength ref.	MPa	59.4	59.4	58.8	60.4	59.4	59.4	54.4	54.4	54.4	60.2
91d strength ref.	MPa	-	-	65.8	66.3	67.1	67.1	57.0	57	57.0	70.7
28d strength	MPa	48.3	49.5	46.7	46.4	48.5	48.4	44.0	42.8	45.6	48.1
91d strength	MPa	-	-	62.1	59.8	64.4	63.9	51.8	52.6	55.0	63.9
Activity index 28d	%	83	84	79	77	82	81	81	79	84	80
Activity index 91d	%	-	-	94	90	96	95	91	92	96	90

[1] Ref.= reference: paste or mortar without replacement of cement with fly ash

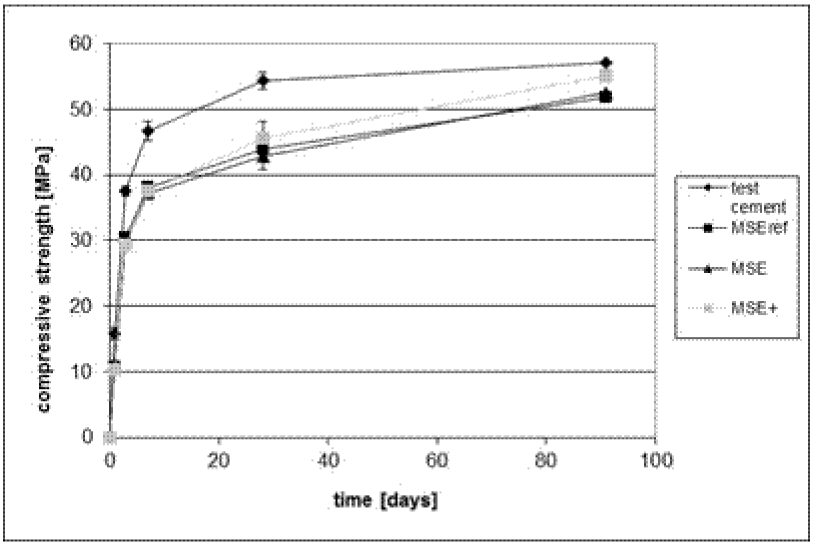

Figure 4:13: Development of compressive strength of standard mortar prisms with fly ash with and without co-combustion of municipal sewage sludge 0-18%.
Mix composition: see 3.2.7.

Properties of concrete with fly ash from co-combustion

The effect of co-combustion on the properties of fly ash concrete was investigated using three different mix compositions, one ordinary concrete (OC), one so-called equivalent performance concrete (EPC) and one High Performance Concrete (HPC). Workability of fresh concrete, mechanical properties and freeze thaw salt resistance of hardened concrete were assessed. The results are presented in table 4.18. The HPC mixtures showed no bleeding or segregation. After demoulding, the concrete cubes were visually inspected. No peculiarities or aberrations were observed.

The results of the experiments with ordinary fly ash concrete (OC) showed that with increasing co-combustion of municipal sewage (MS) workability in terms of flow and slump decreased. The workability of all tested concrete mixtures is characterized as *half-plastic* (S2, F2) according to the EN 206. The compressive strength at 28 days is about 43-44 MPa. The compressive strength is not influenced by co-combustion of sewage sludge. Neither freeze-thaw salt resistance is influenced as the difference in mass loss of concrete at the end of the CDF test is not substantial, since only minor effects were observed.

The influence of co-combustion of meat and bone meal (MBME) and paper sludge (PS) on concrete properties was investigated for equivalent performance concrete (EPC) and for high performance concrete (HPC). According to the EN 206, the workability of these concrete mixtures is characterized as *plastic* (S3, F3) and very *flowable* (F6) respectively. There are some small differences between the measured values of concrete with fly ash MBME and with coal fly ash (PSEref), but there is no univocal influence. This may also be an effect of the coal, as the blends are not the same. The influence of co-combustion of paper sludge on workability of both concrete mixtures is not substantial since only minor effects were observed.

The initial compressive strength (after 1 day) of concrete with fly ash from co-combustion of meat and bone meal or paper sludge is comparable to the one with coal fly ash. There are only very small differences between the mechanical properties (compressive strength and the E-modulus) of concrete with and without co-combustion of paper sludge. The effect of co-combustion of meat and bone meal on the mechanical properties of concrete is not univocal. The compressive strength at 28 and 91 days is lower than that of concrete with coal fly ash, but, contrary to this, the E-moduli of both concrete mixtures are higher.

Table 4.18: Properties of different concrete mixtures, made with generated fly ashes

Concrete mixture		HPC			EPC			OC		
Fly ash		PSEref	PSE	MBME	PSEref	PSE	MBME	MSEref	MSE	MSE +
property	Unit									
Slump	mm	-	-	-	145	150	125	75	60	70
Flow	mm	678	745	700	-	-	-	-	-	-
Flow table	mm	-	-	-	460	460	435	380	350	370
Strength										
1d	MPa	28.4	30.8	32.7	10.5	11.0	10.2	-	-	-
3d	MPa	43.0	43.1	44.9	19.8	19.8	19.4	-	-	-
7d	MPa	51.3	51.1	52.9	26.2	26.1	25.3	32.6	30.8	32.7
28d	MPa	66.8	65.6	65.8	38.1	37.2	35.1	43.0	44.1	43.7
91d	MPa	86.5	84.7	74.8	48.7	50.0	45.1	-	-	-
E-modulus										
28 d	MPa	36500	36000	39500	25700	28700	32700	-	-	-
91d	MPa	38000	38900	41000	33100	32800	37200	-	-	-
CDF test	kg/m^2	-	1.64	0.07	-	3.75	7.24	0.13	0.22	0.18

Key: EPC= equivalent performance concrete
OC = ordinary concrete
HPC=high performance concrete

The results of the CDF test on concrete with fly ash from co-combustion of paper sludge and bone meal are also not univocal if the results of both mix compositions are compared. This may be caused by other factors like different curing conditions of the samples. It is also known from practice that the test results of the CDF test gives high variations.

4.5 Evaluation and discussion

4.5.1 Co-combustion of biomass from vegetable origin

The biomasses which are co-fired during the tests have all high contents of K and P and in several cases also Ca, Mg and Si (see table 4.7), which is reflected in the generated fly ashes. Especially K, P, Ca and Mg will be mainly organically associated. It is unknown whether silicon in palm kernels is due to contamination with soil or inherent to the palm kernel. The presence of significant shares of acid insoluble potassium shows that much of the potassium will be present in glassy phases of the fly ash instead of salts from phosphates, sulphates or carbonates. Also, the XRD results did not show crystalline potassium bearing components in significant amounts. The SEM results indicate also the presence of a K alumina silicate phase in fly ash from co-combustion of cacao residues (CRE) and palm kernels (PKE). Interesting to note is that the free lime content in the fly ashes does not increase significantly despite the presence of more organic associated calcium. The combination of K with Al indicates that during the combustion process interaction occurs between the ash forming matter of the biomass and the coal. Investigations of fly ash from co-combustion of straw on both real and laboratory scale showed also that significant amounts of K are bound in alumina silicates (70-80%), while the remaining K is mainly present as sulphate (see subsection 2.2.4).

The properties of mortar with fly ashes from co-combustion with cacao residue, palm kernels and wheat pollard pellets is similar to that of coal fly ash. In the EN 450 the amount of Na and K is limited to 5.0% m/m (expressed as Na_2O equivalent in fly ash). In several countries the preventive effect of fly ash regarding Alkali Silica Reaction (ASR) is coupled to a more stringent limitation the Na_2O equivalent of the fly ash. For example in the Netherlands the Na_2O equivalent is maximum 3.0% m/m and 3.0-4.5% m/m for ≥25% and ≥30% cement substitution, respectively.

In general, an increase of the amount of alkalis in the glass phase means that the amount of network modifiers increases (see further box 4.1, par. 4.5.4).
No phosphate bearing minerals were identified with XRD. This means that phosphate is present as X-ray amorphous phase and/or as crystalline phases in contents below the detection limit of XRD. SEM examination showed in one case a ‘Fe phosphate’ phase and a ‘phosphate unclassified’. This (glassy) phase of fly ash from co-combustion of palm kernels and cacao residues consists mainly of CaO, SiO_2, P_2O_5, and MgO. Phosphorus containing glasses are able to hydrate and to develop strength with time (see further 2.3.1).

4.5.2 Co-combustion of biomass from animal origin

Meat and bone meal consists mainly of an apatite (see 2.3.1). This mineral is only present in small amounts in coal and, therefore, it is not extensively studied for coal fly ash. However, during the combustion process this mineral converts to $\alpha Ca_3(PO_4)_2$ as shown by the XRD analysis of the generated fly ash. This is confirmed by the composition of the fraction soluble in hydrochloric acid, which consists of relatively high shares of calcium and phosphorus. The SEM results show the presence of a ‘phosphate unclassified’ phase, which have a Ca/P ratio practically equal to that of $Ca_3(PO_4)_2$. A small part of this phase may origin from the biomass pellets. There is no proof of significant interaction between the mineral matter of the coal and that of the meat and bone meal. In general, only minerals have been found which are normally present in coal fly ashes together with calcium phosphate. The presence of low soluble phosphates explains the absence of retardation of setting time of the mortar made with this fly ash. Different calcium phosphates are able to react with water and calcium hydroxide to form stable insoluble products. It implies that in principle the reaction product of co-fired meat and bone meal is able to participate in pozzolanic reaction mechanism.

4.5.3 Co-combustion of biomass from industrial origin

The free lime content in both the fly ash from co-combustion with paper sludge and its reference (PS ref) is very low. This can be attributed to the low calcium content of the coal itself, but in the co-combustion situation it implies that calcium (probably present in calcite) has reacted with other components, especially mineral filler as kaolinite. The SEM identification indicates also an increase of Ca-rich unclassified, Ca alumina silicate and (Ca, Mg) alumina silicate, accompanied with a decrease of SiO_2 and 'alumina silicate unclassified'. Obviously, the fine filler particles (see 2.4.2) within the paper sludge particles are able to react with each other during the combustion process. This process lead also to formation of bigger particles than with pure coal as shown by the SEM observations. The spherical shape of these particles indicates melting during the combustion process with a high Ca and Mg content in combination with O+Al+Si.

The reactions between lime and alumina silicates prevent the decarbonated calcite to remain as free lime in the fly ash, and potentially influencing the soundness of the concrete. Another consequence is the increase of the amount of modifiers (Ca+Mg) in the glassy structure (see further box.4.1).

The fly ash from co-combustion of sewage sludge in our study contains no clear crystalline phosphorus bearing components, although the presence of ferro phosphates is very likely. This component was found in the fly ash with SEM, together with 'phosphate unclassified'. The average composition of this phase is rich in Fe, compared to the other phosphorus bearing ashes. The presence of the phosphate rich phase did not significantly influence the strength development (see figure 4.13).

4.5.4 Summary of effects of co-combustion on properties of fly ash and concrete

Properties of fly ash

Table 4.19 presents an overview of the properties of co-combustion fly ashes and the properties of cement paste and mortar made with these fly ashes. The criteria of the European standard for fly ash in concrete (EN 450) are given in the last column of the table. The requirements consider LOI, Cl, SO_3, Na_2O-equivalent, the sum of Al_2O_3+SiO_2+Fe_2O_3, total CaO, total P_2O_5, free CaO, and reactive silicon acid. The content of CaO, K_2O, P_2O_5 and in some cases MgO increased, while the content of other main elements (SiO_2, Al_2O_3, Fe_2O_3, Na_2O and TiO_2) reduced. The criteria of EN 450 regarding the chemical properties were met, with exception of P_2O_5 of fly ash from co-combustion of wheat pollard pellets (WPPE). However, this fly ash cannot be regularly generated due to excessive slagging in the boiler.

The loss on ignition (LOI) of almost all tested fly ashes meets the criteria for category A (≤5% m/m). One fly ash exceeds this limit but meets the criterion for category C (≤9% m/m). Effects of a higher LOI are:

- Reduced workability of mortar and concrete due to absorption of water [4.11]. However, there is no simple relation between both, as its depends also on parameters as morphology and internal structure of the pyrolised fuel particles.
- Reduced efficiency of organic admixtures, especially air entraining agents [4.12], due to adsorption of the molecules of the agents on the (internal) surface of the pyrolised fuel particles.

This depends not only on the LOI as such, but also on other factors especially specific surface, pore structure and the polarity of the surface of the pyrolised fuel particles.

- Esthetical aspects of the surface of concrete. This depends also on other factors than the LOI as such, especially grain size of the pyrolised fuel particles (own observations), but also on mix composition and workability of the concrete.

Tests on concrete with fly ash with LOI between 5 and 9% m/m showed no effect on durability and compressive strength (cement replacement: 0, 15, 25 and 30% m/m respectively) [4.13].

Table 4.19: Overview of chemical, mineralogical and physical properties of coal fly ash and fly ash from co-combustion of mainly cacao residues (CRE), meat and bone meal (MBME), palm kernels (PKE), municipal sewage sludge (MSE) or wheat pollard pellets (WPPE)

Component	Unit	CRE	MBME	PKE	PSE	MSE+	WPPE	Coal	EN 450 criteria
Loss on ignition	% m/m	3,9	7,3	2,7	4,0	2,1	4,0	3,64±1,8	≤5,0[1]
Al_2O_3+Fe_2O_3+SiO_2	% m/m	79,6	76,6	81,3	81,2	79,2	74,4	87,9±2,3	≥70
Reactive SiO_2	% m/m	30,0	33,6	38,1	28,4	-	32,0	-	≥25
CaO	% m/m	4,9	9,1	4,7	7,5	4,9	4,8	4,20±1,2	≤10
Cl	% m/m	<0,01	0,01	0,01	<0,08	0,01	<0,01	<0,01	≤0.10
CaO free	% m/m	0,61	1,02	0,68	<0,05	<0,02	0,43	0,2±0,3	≤2,5
MgO	% m/m	1,3	1,3	1,7	1,6	2,7	4,5	1,83±0,34	≤4,0
P_2O_5	% m/m	2,3	4,0	2,8	0,8	3,4	5,2	0,58±0,31	5.0
SO_3	% m/m	0,4	0,3	0,6	0,4	0,4	0,7	0,68	≤3.0
Na_2O_{eq}	% m/m	3,7	1,9	1,6	1,7	2,6	3,1	1,5±0,5	≤5.0
Morphology	-							Mainly spherical	Mainly spherical
Flow[2]	mm	177	170	-	178	158	175	180±8	-
Initial setting[3]	hr:min.	2:02	0:25	0:51	0:31	0:40	0:27		
28 days AI[2]	%	84	79	77	82	79	84	80±5.6	>75
91 days AI[2]	%	-	94	90	96	92	96	93±6.5	>85
Soundness[3]	mm	-	1	1	1	1	1	1,3±0,7	≤10

1) Requirement for category A.
2) Standard test on mortar.
3) Standard test on paste.

Important for understanding the effects of co-combustion on the properties of concrete with fly ash are the effects on the mineralogical composition. Crystalline minerals were identified with XRD that are normally present in fly ash namely quartz, mullite, magnetite, free lime, hematite and possibly feldspar. Cristoballite and trydimite were not found with XRD in contrary to quartz, which is very common in coal and fly ash. In one case, with co-firing of (mainly) meat and bone meal and biomass pellets, α-tricalcium phosphate was identified, which can be related to and explained by the presence of apatite in the fuel. It is shown that in co-combustion fly ash with herbaceous biomass, P_2O_5 is mainly present in combination with Al_2O_3, SiO_2, CaO and MgO in amorphous phases. The phosphates will participate in the pozzolanic reactions of these phases by forming apatite and/or phosphate containing calcium silicate hydrate gel as reaction products. If sewage sludge is co-fired also phosphate in combination with Fe is present, due to the use of Fe for precipitation of phosphates during the sewage water cleaning process.

Most calcium which is present in biomass is not present as free lime in the generated fly ash, but present as part of the amorphous alumina silicate phases. The same holds for magnesium and potassium. This glassy phase is important for the pozzolanic behaviour of fly ashes. The amount of network formers, network modifiers and intermediaries, according to the network theory of Zachariasen-Warren,(see 4.14 and Box 4.1) are used to describe the chemical composition and the properties of glass. Figure 4.15 shows a ternary diagram with the composition of the glass phase of reference coal fly ash (see appendix C) and the composition of the investigated co-combustion fly ashes. The conclusion from the assessment of the glass phase is that, despite co-combustion, the glassy phase is a silica-alumina glass, as in fly ash from 100% anthracite or bituminous coal (siliceous) and natural pozzolans (such as trass).

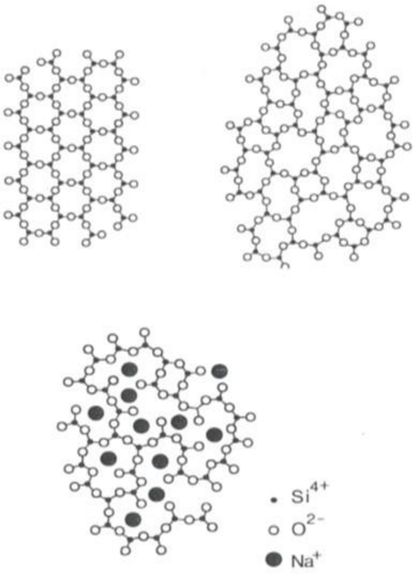

Figure 4:14: Regular ordered SiO_2 tetrahedrons in Quartz (left above), disordered SiO_2 tetrahedrons in pure silicate glass (right above) and a sodium silicate glass, with a disordered connection of SiO_2 tetrahedrons with broken oxygen bridges due to the presence of Na cations (source: TPD-TNO, 1994. NCNG Glascursus).

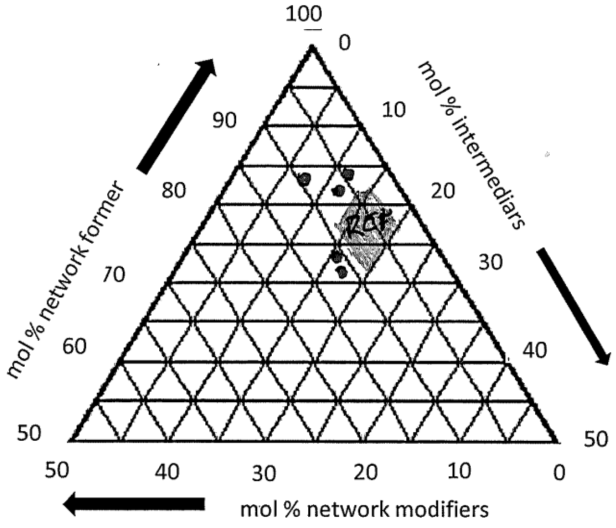

Figure 4:15: Ternary diagram with the composition of the glass phase of reference fly ashes (grey area with REF) and investigated fly ashes from co-combustion (black dots)

Box 4.1: Network theory of Zachariasen-Warren

The network theory of Zachariasen-Warren proposes conditions under which an oxide (like SiO_2) is able to form a glass and the role of different anions and cations. They proposed that an oxide tends to form a glass if it easily forms polyhedron groups as smallest building units. Further

- The polyhedrons should not share more than one corner (bridge).
- The anions should not bind more than two central atoms of a polyhedron (like the oxygen bridge).
- At least three corners of the polyhedron must be connected with their neighbour polyhedrons.
- The numbers of corners of a polyhedron must be <6.

Zachariasen classified the cations in a glass in three groups:

- Network formers, such as Si, P and B. These cations have a coordination number of generally 3 or 4
- Network modifiers, such as K, Na, Ca and Mg. these cations have a coordination number generally ≥6
- Intermediates. These cations may either reinforce polymerization (coordination number 4) or disrupt the network (coordination number 6-8)

Reference: Vogel, W. Chemistry of glass, VEB Deutscher Verlag für Grundstoffindustrie, pp 33-36 Leipzig GDR, 1979.

Properties of concrete

No relation was found between phosphorus content of the fly ash and retardation of initial setting of cement with fly ash (see figure 4.16). The conclusions of Tkaczewska et al (see 2.2.2) that biomass co-combustion retards the setting time and enhances strength development, are not confirmed by the findings presented in this thesis. The tests with concrete confirmed the findings with mortar and paste that there was no significant influence of co-combustion on the properties of concrete.

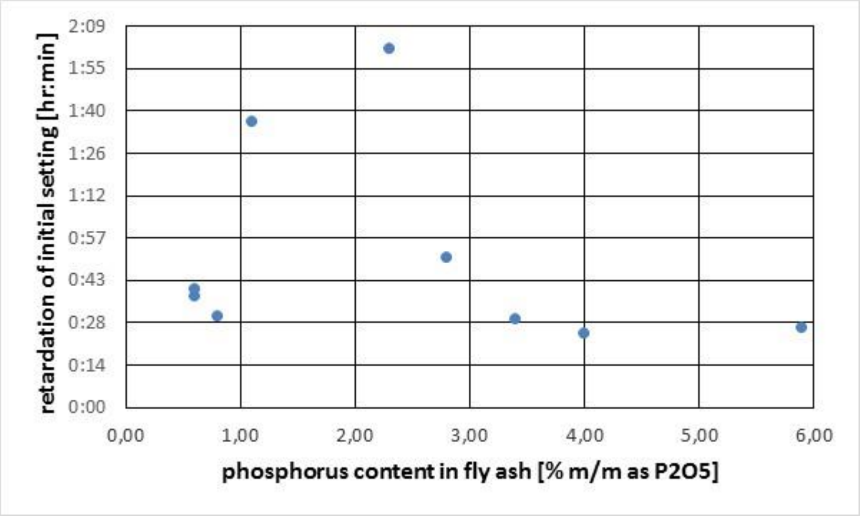

Figure 4:16: Retardation of initial setting of cement fly ash paste related to the *phosphorus content of the fly ash*

Table 4.20 provides an overview regarding the effects of co-combustion of agricultural residues, meat and bone meal, municipal sewage sludge and paper sludge on concrete made with fly ash, as identified (chapter 2) and based on the pilot-scale experiments.

Table 4.20: Overview of the effects of co-combustion of agricultural residues, meat and bone meal, paper sludge and municipal sewage sludge on concrete made with fly ash, as identified in the literature study (chapter 2) and based on the research with fly ashes from the real-scale experiments.

Biomass	Potential effect according to literature study	Conclusion based on experimental research with fly ash from pilot-scale co-combustion tests
Agricultural residues	Promotes ASR if reactive aggregate is present (K)	The Na_2O_{eq} (K) increases, which may promote ASR.
	Contributes to strength and durability (Si)	The strength development was not influenced
	Unsoundness (free lime)	Unsoundness in relation to free lime was not observed. No significant retardation was observed despite the presence of phosphorus
Meat and bone meal	Contribution to strength and durability (Ca+P)	The strength development did not changed despite 10-14% co-combustion (ash based)
	Retardation of cement hydration (P)	No retardation occurred despite the presence of phosphorus
	Promotes ASR if reactive aggregate is present (Na)	The Na_2O_{eq} was hardly influenced. Not confirmed
Municipal sewage sludge	Unsoundness (free lime)	No increase of free lime content measured. Soundness test was passed
	Fe (unknown)	No specific behaviour was observed. Strength development and freeze-thaw salt resistance were not influenced
	Retardation of cement hydration (P)	No significant retardation was observed despite the presence of phosphorus
Paper sludge	Unsoundness (free lime)	The amount of free lime did not increase. The soundness test was passed.
	Contribution to strength and durability (Al+Si)	The strength at 28 and 91 days did not changed despite 13-20% co-combustion (ash based).

4.6 Conclusions

A series of co-combustion experiments has been performed in Dutch coal-fired power plants to generate co-combustion fly ashes for further research to the effect of co-combustion on the properties of fly ash and on the properties of concrete made with this fly ash. Biomass from different origins were co-fired whereby the co-combustion percentages were 7 to about 18 % m/m (ash based).

Based on the test results the following conclusions can be drawn:

1. The main influence of co-combustion of biomass from agricultural and animal origin on the chemical composition of the fly ash is that the content of P_2O_5, CaO, MgO and/or K_2O is increased and that thereby the content of other main elements decreased. Co-combustion of biomass which is contaminated with mineral matter from industrial origin lead to different effects; for instance the co-combustion of sewage sludge and paper sludge leads to fly ashes with a relatively high content of Al, Si and some other minor elements like Ti and Zn.
2. The occurrence of crystalline phases in co-combustion fly ashes does not differ from the occurrence of these phases in coal fly ash (based on X-ray diffraction analyses). An exception

is formed by fly ashes resulting from co-combustion of meat and bone meal, where tri-calcium phosphate is present, as a result of decomposition of apatite, which is the main ash forming matter in meat and bone meal. In the cases of other phosphorus containing secondary fuels the increase of phosphate leads to the presence of amorphous alumina silicate phases containing phosphate. The phosphates will participate in the pozzolanic reaction by formation of less soluble calcium phosphates and C-S-P-H gel. The increase of content of cations (like calcium, potassium and magnesium) in the biomass results in an increase of these compounds in the glass phase of the fly ash.

3 Fly ashes from high co-combustion percentages are able to meet the criteria for use as pozzolanic filler in mortar and concrete, as defined in the standard NEN-EN 450. The properties of concrete concerning workability, strength development and E-modulus confirmed this.

4 The performance of these co-combustion fly ashes can be explained by their mineralogical composition. The latter on its turn can be explained by the composition of the secondary fuels and the combustion behaviour in the boiler.

4.7 References

[4.1] NEN, 1994. NEN 451-1. Method for testing fly ash. Part 1: Determination of free calcium oxide content.

[4.2] NEN, 1994. NEN-EN 196-2:2005 Methods of testing cement. Part 2: Chemical analysis of cement).

[4.3] NEN, 1993. NEN-EN 196-6. Methods of testing cement. Part 2: determination of fineness.

[4.4] NEN, 1988. NEN 5956.Concrete. Determination of consistency of fresh concrete. Slump test

[4.5] NEN, 1988. NEN 5957. Concrete. Determination of consistency of fresh concrete. Flow test

[4.6] CUR, 2002. Self-compacting concrete. Back-ground report for CUR-recommendation 93. CUR-report 2002-4. Gouda the Netherlands.

[4.7] NEN, 1999. NEN 5968. Concrete and mortar. Determination of compressive strength of test specimen

[4.8] NEN, 1999. NEN 5969. Concrete and mortar. Determination of splitting tile strength of test specimen

[4.9] CUR. Assessment of alternative aggregates for concrete. CUR-report 94-12. Gouda, the Netherlands. In Dutch.

[4.10] RILEM, 1996. CDF-test Test method for the freeze thaw resistance of concrete – tests with sodium chloride solution (CDF). In: Materials and Structures/Matériaux et constructions, Vo 29. November 1996, pp. 523-528.

[4.11] Bijen, J. and E. Onstenk, 1985. Physical characterization of Dutch fly ashes from coal fired power plants. Intron report 85275, In Dutch.

[4.12] Brameshuber, W. et al (IBAC), 2003. Einfluss von Flugasche auf die Bildung und Stabilität künstlich eingeführte Luftporen im Beton. Abschlussbericht F806. Auftraggeber VGB.

[4.13] Play, A.(EDF), 1998. Fly ash in concrete - unburned carbon. Prepared for ECSC-workshop (European Coal and Steel community), Vienna, October 1998, pp 93-111.

5 EXPERIMENTAL RESEARCH OF WOOD FLY ASH

5.1 Introduction

In the previous chapter the partial replacement of coal with biomass up to about 20% has been investigated. A further development in the co-combustion of biomass is that more biomass than coal is fired. As already mentioned in the introduction of this thesis, wood will be the only option for several reasons. Combustion of just wood in a pulverized coal boiler is the final stage of co-combustion of wood. In this chapter, several fly ashes from 100% wood combustion in a modified pulverized coal boiler are characterized by chemical and physical methods. Also some additional tests on the solubility of potassium of fly ash from 50% wood co-combustion have been performed to understand the behaviour of potassium during combustion.

Furthermore, the use as reactive filler in concrete was assessed especially as (pozzolanic) filler and as an activator for ground granulated blast furnace slag. The latter has been performed because with increasing ratio wood/coal the generated fly ash contains more components which may act as activator for granulated blast furnace slag, especially sulphates and lime. Activation of slags using sulphates is well-known from super sulphated cements [5.1, 5.2, 5.3], but also calcium hydroxide with other more soluble calcium salts can be used [5.4].

5.2 Materials and methods

5.2.1 Materials

Three samples of wood fly ash were taken at different times at a real-scale wood-fired power plant (coded as F), which is equipped with a modified pulverized coal boiler. Unfortunately it is impossible to relate the wood fly ash to the fired wood pellets, as the wood pellets are taken random from several lots present in the storage. Wood pellets are mainly imported from United States and Canada (all from logging). The samples of wood fly ash were taken at different times:

- February 25th 2014 (WD100-1), from a loaded silo truck
- March 4th 2016 (WD100-2), during production
- March 23rd 2016 (WD100-3) during production.

Wood fly ash WD100-1 was tested unground as well as ground in a laboratory ball mill.

Additionally, fly ashes from two real-scale co-combustion tests with wood pellets were considered in this research. These fly ashes are already analysed and tested, as described in subsection 2.3.2 and in table 2.6, but some additional tests were performed to provide information for modelling of the composition of fly ash from combined combustion of wood and coal (see chapter 6). Table 5.1 presents an overview of the samples.

Table 5.1: Overview of fly ash samples from 100% and 50% wood firing (fuel based). Co-combustion percentages are based on process data [% m/m, fuel based]

Co-combustion test	*WD100-1*	*WD100-2*	*WD100-3*	*WD50-1*	*WD50-2*
Power plant	*F*	*F*	*F*	*D*	*E*
Wood (WD)	*100*	*100*	*100*	*50*	*50*
total	*100*	*100*	*100*	*50*	*50*
Reference test	*none*	*none*	*none*	*none*	*none*

5.2.2 Characterization of ashes

Chemical characterization

Loss on ignition, free lime, main and trace elements have been analysed. See 4.2.3 for further details. Chloride was analysed with ion chromatography, after total destruction. Sulphur was analysed after total destruction with ICP-MS. Carbonate was analysed as CO_2 gas (volumetric) after destruction with phosphoric acid.

The pH development of fly ash in water was measured by bringing 10 grams of fly ash into demineralized water with liquid/solid=10 with continuous stirring. pH was measured after 1/4, ½, 1 and 2 hours.

Mineralogical characterization

The mineralogical characteristics were determined using X-ray diffraction (XRD). The details of the XRD are described in 4.2.4. The XRD analyses were performed by TCKI and Qmineral. Details of the XRD analyses by TCKI are given in 3.2.4. The X-ray diffraction analyses of QMineral were performed with a Bruker diffractometer D5000 (Cu X-ray tube). Rietvelds' method was used to quantify the minerals.

The amount of reactive silicon oxide was determined in accordance with EN 196-2 [5.5]. The first step of this method is to remove the fraction that is soluble in acid. This was combined to the so-called cascade method. A key feature of the analysis is the cascade approach, which involves removing in turn the fraction that is soluble in acid and the fraction that is soluble in potassium hydroxide, and analysing each separately. The dissolved fraction from these steps is analysed with ICP-AES for Al, Ca, Fe, K, Mg, Na, S, Si and Ti.

Physical characterization

Particle density and grain size distribution have been analysed. See 4.2.5 for further details.

Scanning Electron Microscopy

The morphology was assessed by SEM. See also section 3.2 for further details. The pictures were taken in the secondary electron image mode (SEI mode) at an acceleration voltage of 15 kV. Gold was sputtered on the surfaces of the samples to overcome charging of the sample during SEM investigation.

5.2.3 Properties of cement paste and mortar with wood fly ash

The following properties of cement paste and mortar with wood fly ash were investigated (see also 3.2.7 for a more detailed description):

- Setting time of cement paste in accordance with EN 196-3.
- X-ray diffraction was performed to identify reaction products, which could explain false set phenomena observed during setting time measurements.
- Soundness of cement paste in accordance with EN 196-3.
- The pozzolanic behaviour was determined with the activity index in accordance with EN 450 (see Box 1, 2.2.4).
- The compressive strength of mortar with different combinations of ground granulated blast furnace slag (GGBS) and wood fly ash (as activator). The optimum ratio slag/fly ash and the effects of grinding, pre-hydration of wood fly ash and the use of other additives on compressive strength were investigated. SEM microscopy was used to assess the formation of reaction products.

The GGBS sample was from a commercial production for concrete industry. The specific surface (Blaine) was 4000-4300 cm^2/g according to the specifications of the producer.

5.3 Experimental results properties of fly ashes

5.3.1 Chemical characterization of wood fly ashes

The results of the chemical characterization are presented in table 5.2 (main components) and table 5.3 (trace elements). All investigated wood fly ashes have high contents of calcium and potassium compared to coal fly ash. This is well-known for the mineral matter in wood (see also subsection 2.2.2). These high contents are combined with low alumina content, which indicates to limited contamination with clays, feldspar etc. from soil. The amount of silicon is also lower. Carbonate, sulphur and chloride contents are significantly higher than in coal fly ash. About 50% of the loss on ignition can be explained by decomposition of calcium carbonate during heating of the fly ash sample. The other 50% will be mainly from combustion of residual carbon. The trace elements show higher contents of Mn and Zn, compared to coal fly ash. These elements are taken up by plants as micro-nutrients. Also Ba and Sr are present in relatively high concentrations. However these are not considered nutrients (see further subsection 2.2.1). It is known from literature that Ba and Sr are taken up by plants [5.6, 5.7]. Strontium is taken up via the normal pathway of calcium. Both elements are in the same group as calcium (alkaline earth elements).

The ratio of the content of main non-volatile[18] elements in the investigated wood fly ashes can be compared with the ratio in the wood, co-fired during real-scale experiments (see table 4.5). The Al_2O_3/CaO and SiO_2/CaO ratio in the wood fly ashes are lower than in the co-fired wood. This can be explained by less contamination of the wood fuel with soil from the forest during harvesting.

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[18] RE factor =1; see chapter 6.

Table 5.2: Concentration of components [% m/m] in fly ash from wood combustion

Fly ash	WD100-1	WD100-2	WD100-3
Component			
Al_2O_3	4.76	2.47	2.59
CaO	29.7	32.6	29.9
Cl	0.42	0.21	0.16
Fe_2O_3	2.45	1.30	1.66
K_2O	12.3	11.7	10.7
MgO	5.65	5.67	4.79
Na_2O	1.19	0.92	0.69
P_2O_5	2.86	2.93	2.54
SO_3	5.78	4.20	3.55
SiO_2	29.7	23.7	27.9
TiO_2	0.32	0.20	0.22
LOI	10.3	11.2	10.9
Total	105.4	97.2	95.6
Carbonate (CO_2)	6.29	5.74	-
CaO free	6.1	10.3	7.8

Table 5.3: Concentration [mg/kg] of trace elements in fly ash from wood combustion

Fly ash	WD100-1	WD100-2	WD100-3
Element			
As	6.48	4.05	3.91
B	301	273	271
Ba	2860	3220	2920
Cd	8.80	7.45	7.27
Co	14.5	14.1	12.3
Cr	108	80.0	80.7
Cu	143	170	176
F	61.6	33.2	33.9
Hg	<0.05	<0.020	<0.020
Mn	11000	8940	9460
Mo	5.9	7.7	8.7
Ni	15.6	36.8	38.1
Pb	22.3	48.5	50.6
Sb	9.7	6.1	4.3
Se	2.39	3.67	3.40
Sn	29.2	-	-
Sr	1430	1060	1250
V	40.8	20.8	22.0
W	17.0	28.0	30.0
Zn	1043	880	818

Table 5.4 presents the composition of the acid soluble fraction of the five fly ash samples[19]. The fly ash from 100% wood combustion has very high percentages of matter that is soluble in acid. They mainly consist of Ca, K and Si. Both fly ashes from 50% wood co-combustion consist mainly of Ca, Si and S. The major part of the potassium present in wood fly ash is acid-soluble, while in fly ash from co-combustion of wood almost no potassium is acid-soluble. See also figure 5.1 and 5.2.

Table 5.4: Chemical composition of acid soluble fraction (elements expressed as oxides) in fly ash from 100% wood combustion and 50% wood + 50% coal; calculated to the original sample [% m/m]

Fly ash	WD100-1	WD100-2	WD100-3	WD50-1	WD50-2
Component					
Al_2O_3	1.9	1.34	1.33	0.23	0.18
CaO	23.5	26.5	25.2	1.42	1.56
Fe_2O_3	0.78	0.81	0.63	0.04	0.06
K_2O	9.52	11.3	9.1	0.01	0.01
MgO	3.03	3.48	2.85	0.18	0.27
Na_2O	0.95	0.78	0.56	0.01	0.01
P_2O_5	1.04	1.09	1.02	0.18	0.27
SO_3	1.29	1.31	1.12	0.2	0.36
SiO_2	9.86	7.41	0.15	0.54	0.46
TiO_2	0.08	0.05	0.06	0.01	0.01
Mn	0.41	0.31	0.38	0.01	0.01
total	52.4	54.4	42.4	2.85	3.22

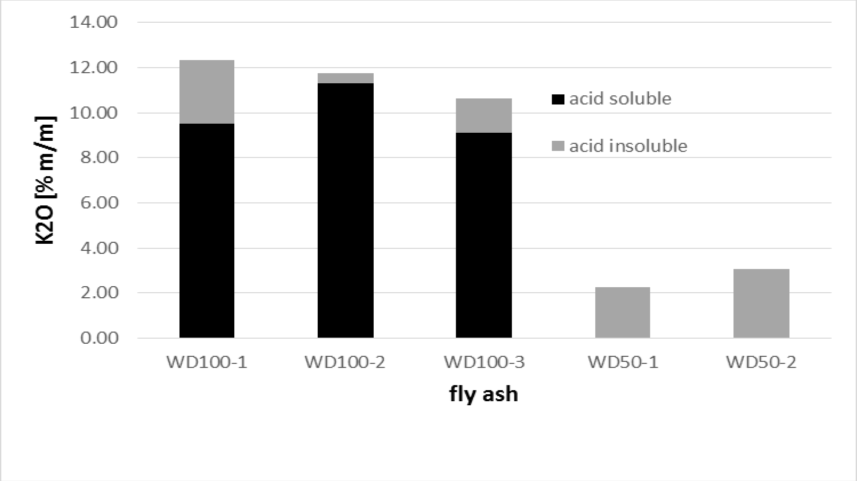

Figure 5:1: Content of acid soluble and insoluble potassium (as K_2O) in fly ash from wood and coal+wood combustion [% m/m]

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[19] The acid soluble fraction contains also anions like chlorides, sulfates and carbonates

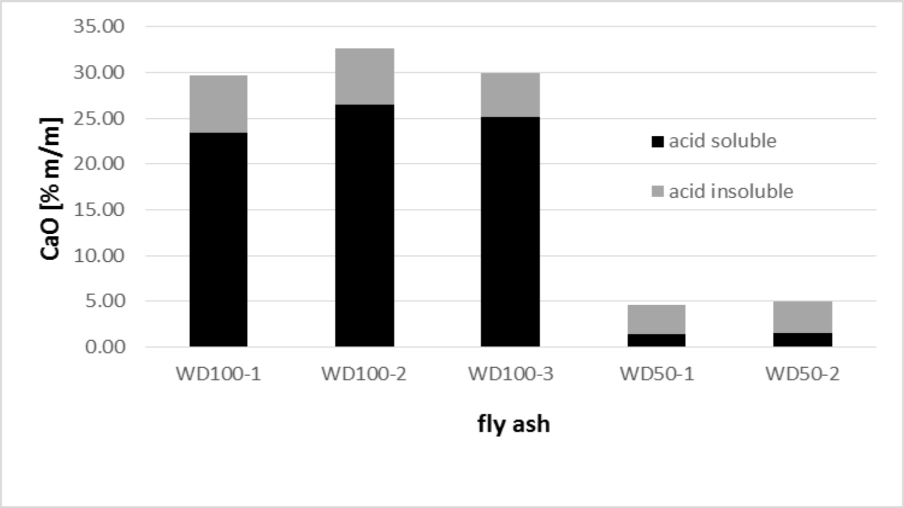

Figure 5:2: Content of acid soluble and insoluble calcium (as CaO) in fly ash from wood and coal+wood combustion [% m/m]

The pH development of wood fly ash WD100-1 (ground and unground) is presented in figure 5.3. The results show that wood fly ash has a high pH value. Wood fly ash WD100-2 and WD100-3 has a pH after ten minutes of 12.5 and 12.2 respectively. Interesting is the difference between ground and non-ground fly ash. The former shows a decrease of pH, while the ground fly ash show a higher and constant pH. Obviously, there is no equilibrium in the mix of water with the non-ground wood fly ash during the test period. This may be due to the lower specific surface compared to the ground fly ash.

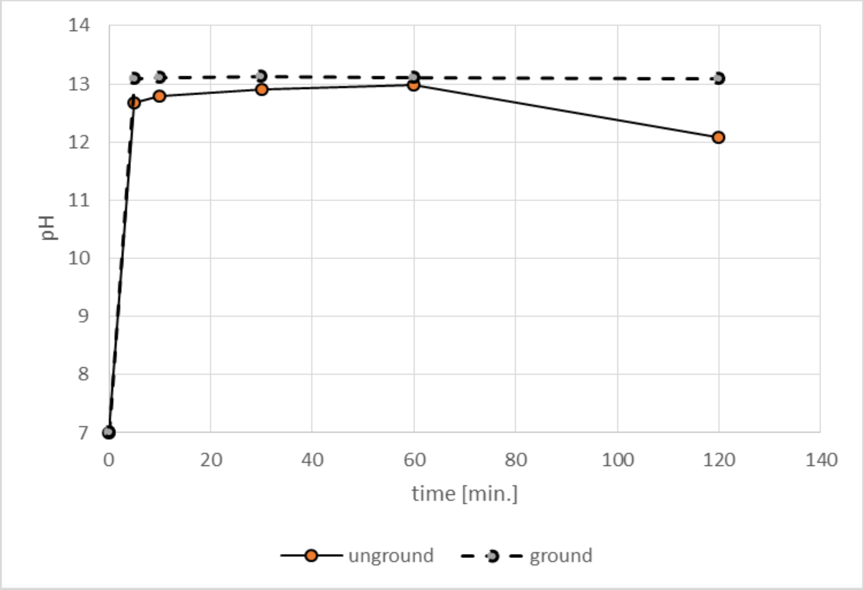

Figure 5:3: Development of pH of water after addition of ground or unground wood fly ash WD100-1 (10 grams of fly ash in 100 ml demineralized water)

5.3.2 Mineralogical characterization of wood fly ashes

The results of the mineralogical analyses of the wood fly ashes are presented in table 5.5. Silicon is present in several phases. Quartz and dicalcium silicate are the main crystalline silicate phases in all wood fly ashes. Di-calcium silicate is the result of the combustion process as this mineral does not occur in nature. Also part of silicon is present in the X-ray-amorphous phase. Calcium is mainly present as lime and calcite. There is quite a good match between the content analysed with XRD and with the results of the chemical analyses of the contents of lime and carbonate. Potassium is present in four different crystalline phases, but arcanite is the most important one, followed by sylvine. Arcanite is also the most important sulphur bearing phase in the analysed wood fly ashes. A majority of magnesium is present as periclase. Most identified minerals are in line with the literature about wood firing (see 2.2.2).

Table 5.5: Results of mineralogical characterization of wood fly ashes

Mineral	Formulae	WD100-1		WD100-2		WD100-3	
		QXRD	XRD	QXRD	XRD	QXRD	XRD
Quartz	SiO_2	4.3	yes	3.8	yes	6.1	Yes
Tridymite	SiO_2	0.3	-	0.2	-	-	-
Dicalcium silicate α-C2S	Ca_2SiO_4	6.0	-	4.0	-	4.7	-
Calcite	$CaCO_3$	6.4	yes	7.0	Yes	6.6	Yes
Lime	CaO	6.1	yes	11.0	Yes	8.9	Yes
Periclase	MgO	3.5	yes?	4.1	-	3.1	-
Srebrodolskite	$Ca_2Fe_2O_5$	3.4	-	3.0	-	2.3	-
Tricalcium aluminate	$Ca_3Al_2O_6$	3.2	-	0.8	-	0.7	-
Portlandite	$Ca(OH)_2$	1.3	yes	2.1	-	0.9	-
Anhydrite	$CaSO_4$	0.4	-	0.4	-	0.5	-
Alunite	$KAl_3(OH)_6(SO4)_2$	0.6	-	0.5	-	0.3	-
Arcanite	K_2SO_4	7.1	yes	7.2	Yes	6.3	Yes
Langbeinite	$K_2Mg_2(SO_4)_3$	1.0	-	0.6	-	0.7	-
Sylvine	KCl	1.7	yes	0.8	-	1.4	-
Merwinite	$Ca_3Mg(SiO_4)_2$	-	-	6.4	-	5.5	-
Anatase	TiO_2	-	-	0.2	-	0.3	-
Amorphous		54.7	-	47.9	-	51.2	-

5.3.3 Physical characterization of ashes

The results of the physical characterization are given in table 5.6. The particle density of wood fly ash is higher than of coal fly ash (normally about 2190 kg/m^3). This may can be explained by the different mineralogical composition. The average grain size (D 50) of the wood fly ashes is comparable to that of coal fly ash (15-27 µm).

Table 5.6: Results physical characterization of wood fly ashes

		WD100-1 unground	WD100-1 ground	WD100-2	WD100-3
Particle density	kg/m^3	2790	-	2790	2830
Particle size D 10	µm	5	1.6	4	3
Particle size D 50	µm	33	15	20	24
Particle size D 90	µm	140	69	58	83

5.3.4 Microscopic observations

The wood fly ash (WD100-1) contains particles with a particle size of 50-100 µm (see figure 5.4), which are considerably coarser than most of the particles. The morphology of these particles is different: some are well rounded particles, but also sub-rounded and angular particles. The spherical particles point to the formation of a melt during combustion. The smaller particles (see figure 5.5) consist of agglomerates. These may be formed by vaporization and condensation of organically bound elements (see 2.2.4). Small, solid well-rounded particles can be recognized in these agglomerates. EDX-analyses show that silicon and iron are mainly present in the massive particles. Agglomerates with relatively high content of sulphur (1.7-2.5%) is accompanied with higher content of potassium (8-12%). This points to the presence of phases consisting of potassium and sulphur, like arcanite (see table 5.5). There are a few analyses with relatively more phosphorus (ca 1.5%). These are accompanied with higher content of calcium which points to the presence of calcium phosphates.

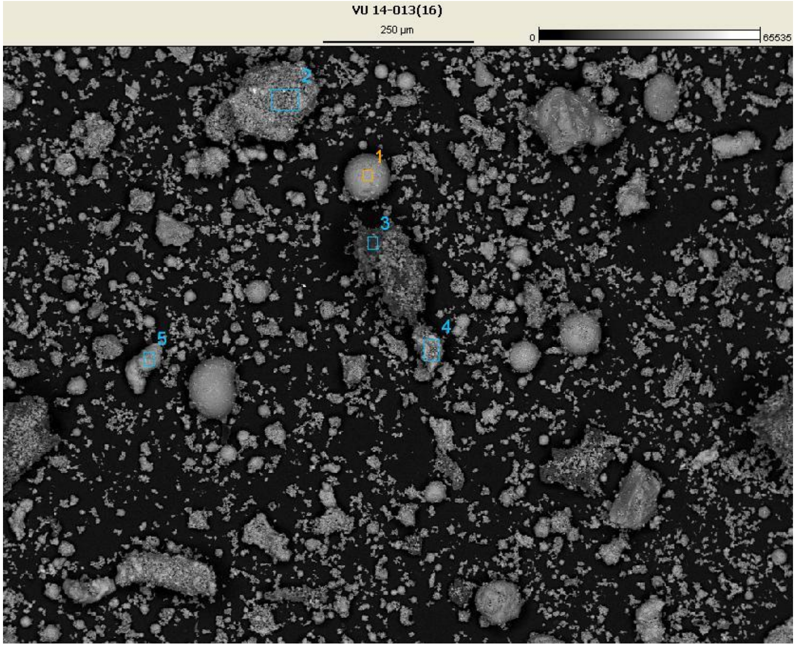

Figure 5:4: SEM photograph of wood fly ash WD100-1 (BE image). Particles with a particle size of 50-100 µm can be distinguished. The morphology of these particles is different: some are well rounded particles, but also sub-rounded and angular particles.

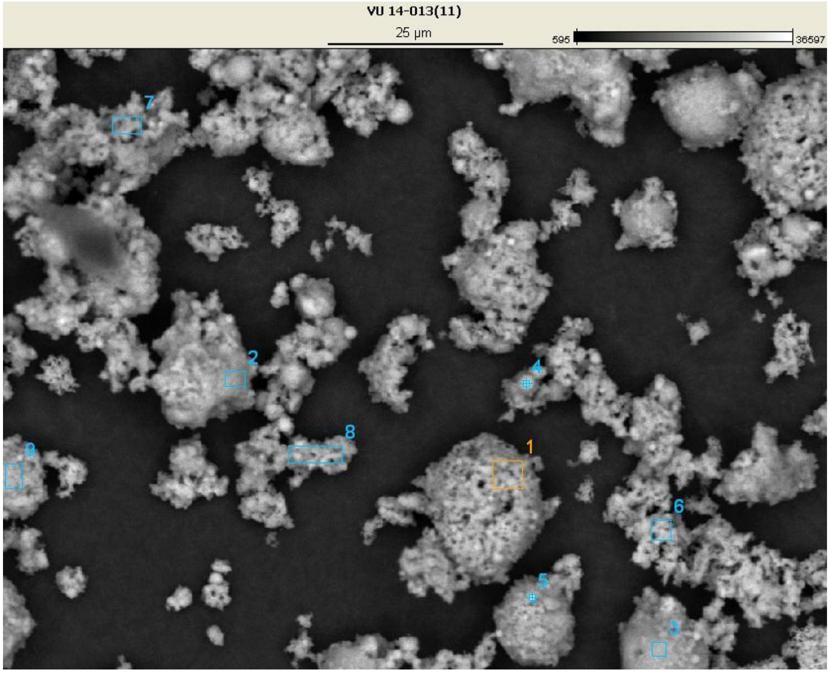

Figure 5:5: SEM photograph of wood fly ash WD100-1.
Particles consisting of agglomerates. Small, solid well-rounded
particles can be recognized in these agglomerates.

5.4 Experimental results: properties of cement paste and mortar

5.4.1 Properties of mortar with combination of Portland cement and wood fly ash

Properties of fresh cement paste and mortar

Table 5.7 presents several properties of cement paste and mortar, made with Portland cement and wood fly ash as pozzolanic filler. The Portland cement was a CEM I 52,5 R (Milke). Substitution of cement by wood fly ash leads to very rapid setting compared to the reference cement paste. Also, the water-binder ratio to obtain standard consistency increases. Grinding of the wood fly ash results in a decrease of the water binder ratio for standard consistency. The flow of the mortar with wood fly ash is significantly lower than that of the reference mortar, which can be attributed to the less spherical morphology of the particles and to false set phenomena (see further 5.4.2).

Properties of hardened cement paste and mortar

The strength development of mortar with wood fly ash at both 28 and 91 days is considerably lower than that of standard mortar with coal fly ash and even lower than with limestone filler.

Table 5.7: Properties of the (fly ash) cement paste (soundness and setting time) and properties of (fly ash) cement mortars (flow and activity index) and requirements of EN 450

Fly ash		WD100-1	WD100-1 ground	WD100-2	WD100-3	
Parameter	Unit					EN 450
Soundness	mm	31	9	74	77	≤ 10
Initial set ref	min.	140	140	150	150	-
Final set ref.	min.	195	195	195	195	-
Initial set	min.	10	10	10	5	1)
Final set	min.	15	15	15	-	-
WBR ref	-/-	0.34	0.34	0.30	0.30	-
WBR	-/-	0.37	0.31	0.35	0.31	-
Flow ref	mm	196	196	186	186	-
Flow	mm	126	106	147	139	-
28 days strength ref	N/mm^2	71.2	71.2	74.3	74.3	-
91 days strength ref	N/mm^2	76.4	76.4	76.4	76.4	-
28 days strength	N/mm^2	43.3	43.1	40.0	41.9	-
91 days strength	N/mm^2	50.7	-	47.1	48.3	-
28 days activity index	%	61	61	54	56	75
91 days activity index	%	68	-	62	63	85

1) The initial setting time shall be determined on a 25 % fly ash plus 75 % test cement paste in accordance with EN 196-3 and shall not be more than twice as long as the initial setting time of a 100 % (by mass) test cement paste.

An additional series of experiments was performed to investigate the effect of lower additions of wood ash (WD100-2) on strength development and setting time. Figure 5.6 shows the results of the 28 days compressive strength as function of replacement level and type of fly ash (wood fly ash or standard coal fly ash). Further, coal fly ash was combined with K_2SO_4, whereby the concentration was adjusted to the concentration introduced by wood fly ash at the same replacement level. It shows that even at low replacement level wood fly ash reduces compressive strength, which cannot be attributed to the effect of K_2SO_4 alone. More research will be necessary to find an acceptable explanation for this phenomenon. At a replacement level of 9-12% m/m, initial setting of cement fly ash paste (10-15 minutes) was comparable to the 25% replacement level (10 minutes).

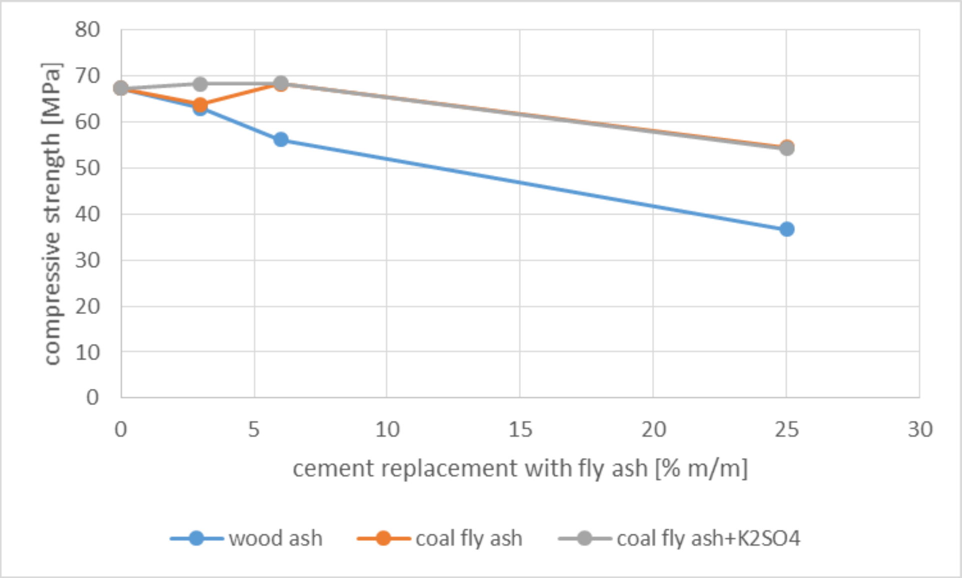

Figure 5:6: Effect of cement (CEM I) replacement by wood fly ash, coal fly ash or coal fly ash with K_2SO_4 on 28 days compressive strength of standard mortar

5.4.2 Properties of mortar with combinations of blast furnace slag and wood fly ash

Properties of fresh cement paste and mortar

In table 5.9 the results are presented the properties of mortars prepared with a binder consisting of blast furnace slag and wood fly ash as activator. Wood fly ash WD100-1 was tested ground and unground. Mortar with only blast furnace slag as binder was used as a reference.

During preparation it was observed that the workability of fresh mortars with combinations of wood fly ash and blast furnace slag reduced very quickly. Extra mixing of the fresh mortar recovered the workability to the original level. This is a typical false set phenomenon. The original dry fly ash WD100-1 contains arcanite and some anhydrite. XRD analyses on fly ash itself and after one hour contact with water showed the presence of gypsum after contact, but no ettringite (see figure 5.7). Probably part of the arcanite has reacted with calcium components to form gypsum as known from cement chemistry, according to the reaction:

$$2K^{+}_{aq} + SO_4{}^{2-}{}_{aq} + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O\downarrow + 2K^{+}_{aq} + OH^{-}_{aq}$$

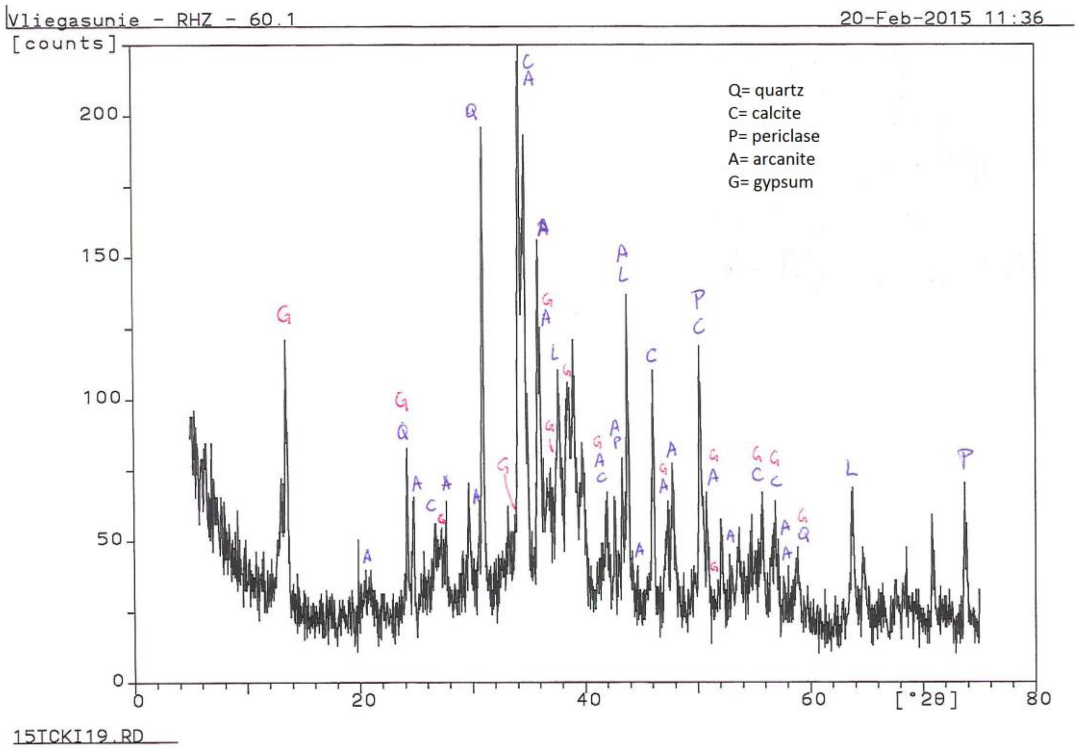

Figure 5:7: XRD patterns of fly ash WD2 after one hour of contact with water.

Properties of hardened cement paste and mortar

The strength development of the mortar with just blast furnace slag as binder (nr 1 in table 5.8a) is very slow compared to that of current cements in the ready-mixed concrete industry (using standard mortar: ratio sand/binder=3/1 and water-binder ratio=0.50). The compressive strength after 28 days is 12.8 N/mm^2. The partial replacement of blast furnace slag (15-20%) with wood fly ash results in a similar strength at 7 days. At 28 days the maximum strength was about 22 N/mm^2 (see figure 5.8). Using 15% wood fly ash as activator means that the sulphate content in the binder is 5.8*15/100=0.87% m/m (as SO_3), which is very low compared to super sulphated cements. Therefore, in a second series the wood fly ash content was increased, without decreasing the content of blast furnace slag. The amount of sand was decreased proportional with the increase of wood fly ash. This leads to a mortar which could not be moulded due to the low workability. Therefore, it was decided to prehydrate the wood fly ash for 1.5 hrs by premixing the wood fly ash with the water. This resulted in a better workability, but the strength at 28 days was not increased (see table 5.9). Also several additions[20] were used to increase the concentration of calcium in solution. The addition of higher percentages of calcium formiate decreased the strength after 7 days but increased the strength after 28 days. The addition of $CaSO_4$ (anhydrite) increased the strength after 7 days. However, the total effect of use of wood fly ash and anhydrite is less than the effect of just anhydrite as activator.

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[20] These additions were mixed with the wood ash before the standard mixing procedure for the mortars was started

Table 5.8: Flow and compressive strength of mortars with combinations of blast furnace slag and wood fly ash as binder

Nr	binder			Compressive strength		
	Wood fly ash	Blast furnace slag	Sample wood fly ash	2 days	7 days	28 days
	%	%	-	N/mm²	N/mm²	N/mm²
1	0	100	-	<0.5	0.8	12.8
2	5	95	WD100-1	<0.5	5.6	15.3
3	10	90	WD100-1	<0.5	9.5	20.1
4	15	85	WD100-1	<0.5	12.1	22.4
5	20	80	WD100-1	<0.5	12.5	21.3
6	30	70	WD100-1	<0.5	-	16.1
7	100	0	WD100-1	<0.5	<0.5	2.2
8	5	95	WD100-1 ground	0.5	5.0	14.7
9	10	90	WD100-1 ground	4.6	11.2	19.7
10	15	85	WD100-1 ground	5.9	12.5	17.9
11	20	80	WD100-1 ground	5.1	11.1	15.7
12	25	75	WD100-1 ground	<0.5	9.2	13.6
13	30	70	WD100-1 ground	<0.5	7.8	11.6
14	100	0	WD100-1 ground	<0.5	2.2	4.4
15	15	85	WD100-2	-	-	11.8
16	15	85	WD100-3	-	-	12.2

1) The flow of the fresh mortar could not be measured and compaction could not be performed

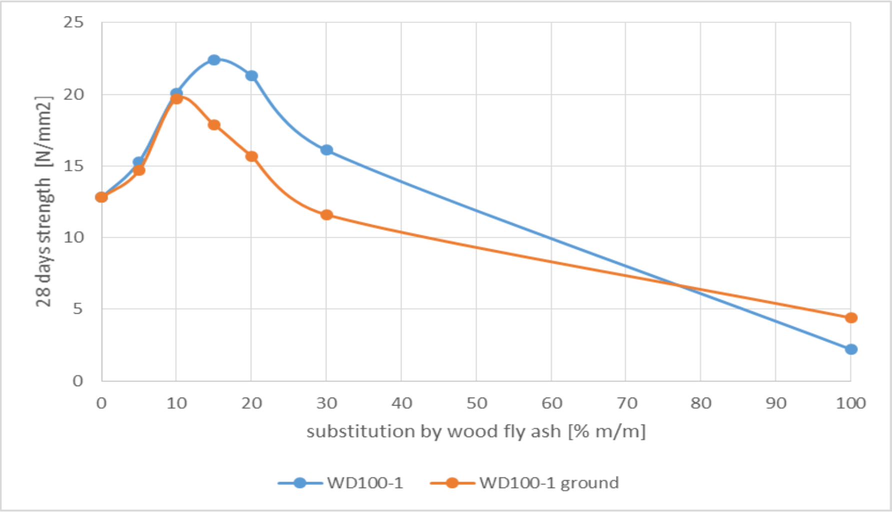

Figure 5:8: Effect of wood fly ash share on 28 days compressive strength of standard mortar with ground granulated blast furnace slag and wood fly ash as binder

Table 5.9: Compressive strength of mortars with combinations of blast furnace slag and ground wood fly ash as binder

Wood Fly ash	Granulated blast furnace slag	Additive/ pre-treatment	7 days	28 days
%	%		N/mm^2	N/mm^2
15+15*	85	Pre-hydration	12.1	18.9
15+7*	85	Pre-hydration	12.2	19.4
15+4*	85	Pre-hydration	12.2	19.7
15	85	2% $CaCl_2$	12.5	22.5
15	85	1% calciumformiate	10.6	22.4
15	85	2% calciumformiate	8.5	30.5
15	85	3% calciumformiate	4.2	30.4
15	85	1% $CaSO_4$	22.6	22.8
15	85	2% $CaSO_4$	21.4	20.6
15	85	5% $CaSO_4$	16.4	15.1
15	85	10% $CaSO_4$	19.0	18.5
0	100	1% $CaSO_4$	4.4	10.4
0	100	2% $CaSO_4$	8.5	26.7
0	100	5% $CaSO_4$	19.1	43.2
0	100	10% $CaSO_4$	24.9	55.3

* Wood ash was pre-hydrated to avoid false set. Extra hydrated wood ash was added to the mix to increase the amount of activator (the addition of sand was reduced with the same amount)

Mortars with 100% ground granulated blast furnace slag (GGBS) and with 15% wood fly ash (WD100-1) and 85% GGBS as binder were investigated with SEM microscopy to assess to formation of reaction products. Figure 5.9-5.12 show SEM photographs of the cement paste in the mortar after 28 days of hardening. The angular blast furnace slag particles can easily be recognized in the cement paste with just GGBS (figure 5.9-5.10). It can be seen that at higher magnification the blast furnace slag particles are covered with needle like reaction products. Reaction products with a size of about 1 µm and a hexagonal-like structure can be recognized in the cement paste. The chemical composition of these reaction products were analysed with EDX (see numbered spots in figure 5.10). EDX-analyses showed that these reaction products consist mainly of Ca, Si, O and to a less extent Mg and Al. The atomic ratio Ca/Si/Al is about 17/3/1. No clear difference could be found between the composition of the surface with needles and the hexagonal reaction products. Also in the mortars with 15% wood fly ash and 85% GGBS the angular particles can be recognized (see figure 5.11-5.12). However it seems that more reaction products have been formed than in the mortars with only GGBS as binder. Also in this mortar reaction products with a size of about 1 µm and partly a hexagonal-like structure can be recognized. There is also an amorphous mass as reaction product present in the hardened cement paste. The atomic ratio Ca/Si/Al of the former and latter reaction products is about 8/3/1 and about 4/3/1. No other reaction products (like ettringite) were found in this hardened cement paste.

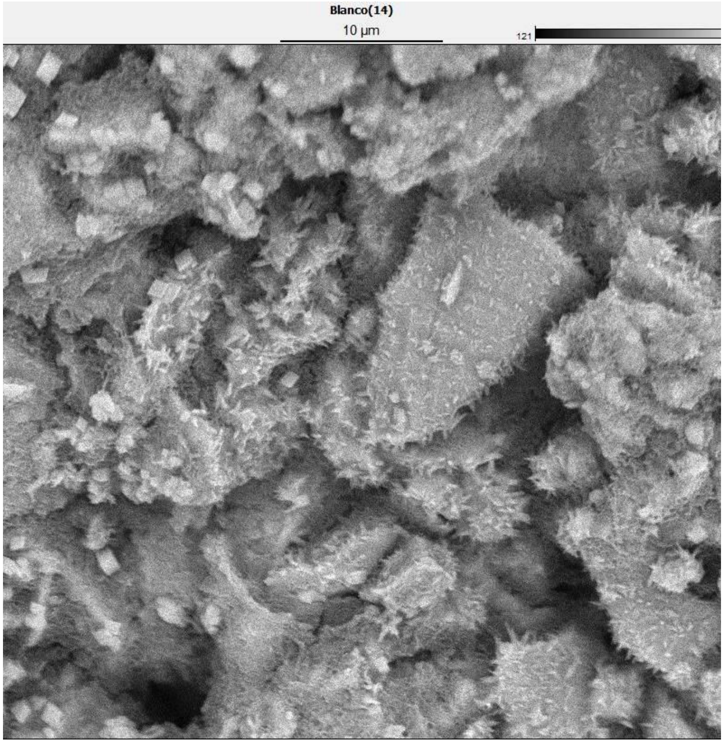

Figure 5:9: SEM photograph of reaction products in standard mortar with binder consisting of 100% GGBS after 28 days hardening

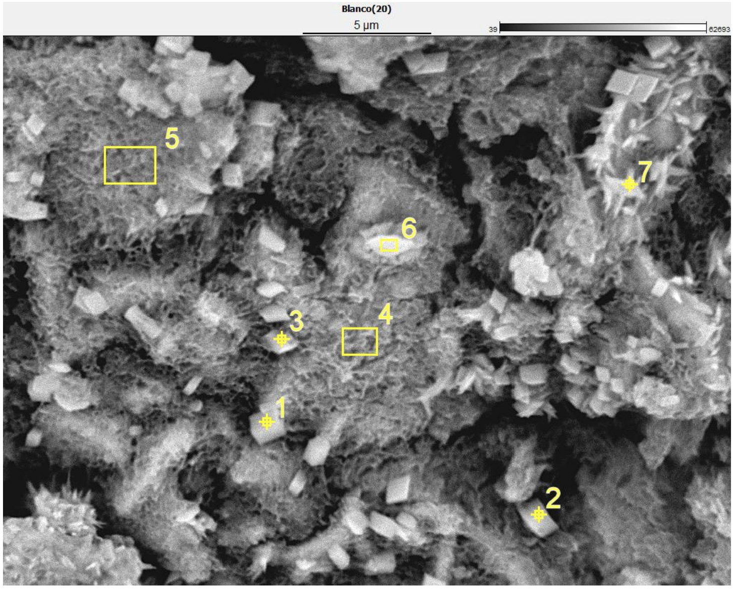

Figure 5:10: SEM photograph of reaction products in standard mortar with binder consisting of 100% GGBS after 28 days hardening.

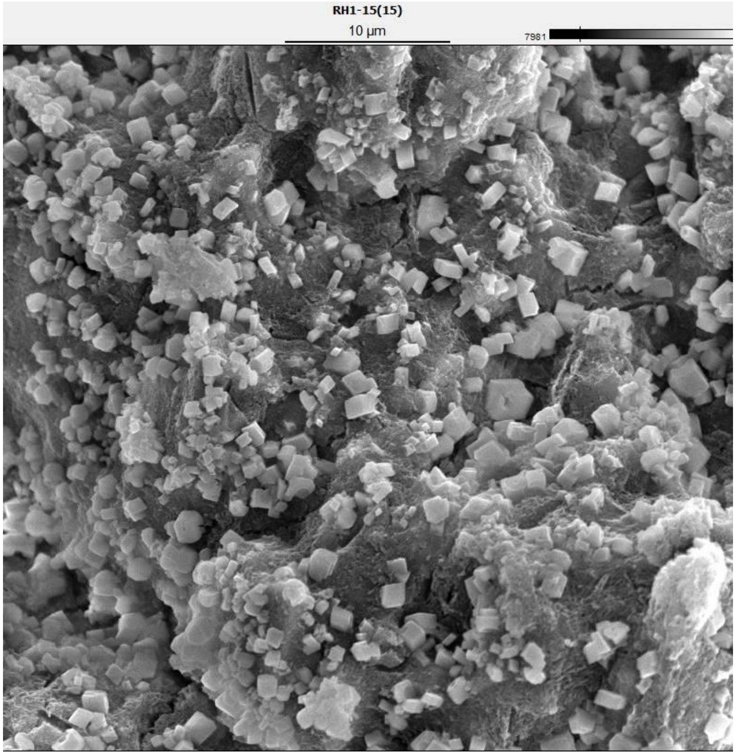

Figure 5:11: SEM photograph of reaction products in standard mortar with binder consisting of 85% GGBS and 15% wood fly ash after 28 days hardening.

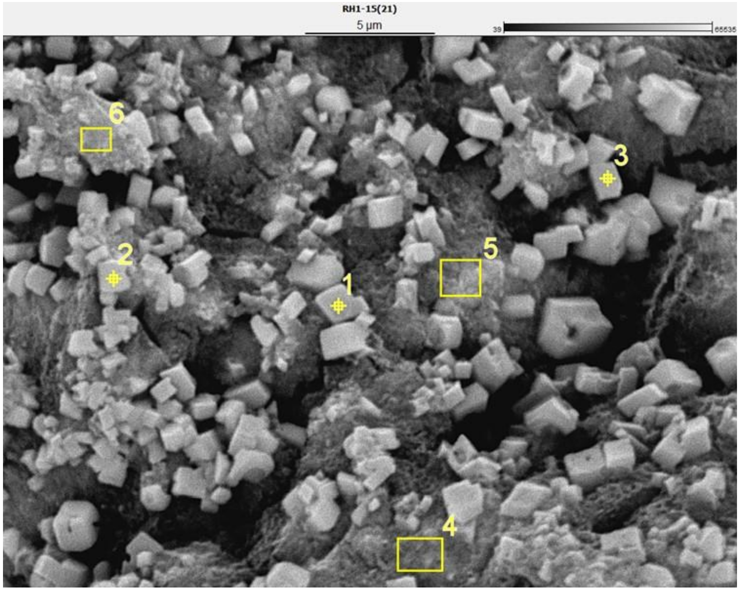

Figure 5:12: SEM photograph of reaction products in standard mortar with binder consisting of 85% GGBS and 15% wood fly ash after 28 days hardening

5.5 Evaluation and discussion

Properties of wood fly ash

The composition of wood, as used for large-scale wood-fired energy production is different from that of coal. The composition of the wood fly ashes reflects this. CaO and K_2O are main compounds in wood fly ash, while SiO_2 and Al_2O_3 are the main compounds in coal fly ash. SiO_2 is also a main compound in wood fly ash, but its content is about half of that in coal fly ash. Also the content of several heavy metals is higher in wood fly ash than in coal fly ash, especially Ba, Mn and Zn (see table 5.2).

Calcium in woody biomass is mainly present as calcite, calcium oxalate and calcium silicate. Calcite decompose at maximum 900°C to lime (depending on the CO_2 partial pressure) [5.8] and also calcium oxalate decomposes in steps at higher temperatures (800-900 °C) to CaO, CO_2 and H_2O [5.9]. The presence of calcite and portlandite in the fly ash will be the result of the reaction of CaO with CO_2 and H_2O in the flue gasses after the boiler before the electrostatic precipitator (ESP) or during handling (pneumatic transport) of the fly ash. The presence of α $2CaO.SiO_2$ and merwinite ($Ca_3Mg(SiO_4)_2$) will be the result of reaction between calcium and silicon compounds. Silicon is further present as quartz and tridymite, which can be explained by crystallization of amorphous silica or by the presence of quartz from soil and dust in the wood (especially in bark). Potassium is mainly present in arcanite (K_2SO_4). Wu et al identified also KOH and K_2CO_3 in wood fly ash, but these compounds were not found in the three analysed wood fly ashes. Several studies describe the formation of arcanite during combustion of wood [5.10] and straw [5.11]. If coal ash is added to wood before combustion less arcanite is present and more potassium is taken up in the alumino silicates of the fly ash. According to the X-ray diffraction analyses, magnesium is mainly present as periclase and only a smaller part is present in langbeinite (see table 5.5). Obviously, during the combustion of chlorophyll and afterwards there is limited reaction of magnesium with other compounds. Magnesium will originate mainly from the chlorophyll in the trees (leaves and needles). Phosphorus and potassium are mainly present in the living parts of the trees.

Wood fly ash mainly consists of agglomerates in contrast to coal fly ash, which consists of solid spherical particles. These agglomerates have higher sulphur and potassium concentrations than the solids. These agglomerates will originate from condensation of potassium sulphate, probably on particles with different composition (heterogeneous condensation) as described by Doshi et al [5.12].

Properties of cement paste and mortar with Portland cement and wood fly ash

The replacement of Portland cement with wood fly ash, also at low levels, results in a lower compressive strength at 28 days, even lower than that of coal fly ash and limestone filler at the same replacement level. This cannot be attributed to the effect of K_2SO_4 as such. More research will be necessary to find an acceptable explanation for this phenomenon.

The results show that substitution of more than a few percent leads to a decrease of 28 days compressive strength compared to mixtures with the same amount of coal fly ash. The wood fly ash contains some mineral phases, especially $\alpha CaO.SiO_2$ and tri calcium aluminate that are able to contribute to the strength development, but the amount of amorphous silicon and alumina, derived from the XRD analyses, is considerably lower than in coal fly ash. This means that less material is present in wood fly ash for a pozzolanic reaction.

The soundness of cement paste with wood fly ash does not meet the criterion of EN 450 (31-77 mm expansion). An expansion of maximum 10 mm is regarded for coal fly ash to be safe for use in concrete. Often, the volume change during the reaction of lime with water is seen as the cause for expansion. However, the volume of lime and water needed for the reaction is more than the volume of the hydrated lime. It is suggested that local formation of Portlandite crystals causes local stress [5.13, 5.14]. If the stress exceeds the maximum stress of the material, crack formation occurs. This hypothesis explains the reduction of expansion if the fly ash has been milled before. The smaller lime particles will generate less local tensile stress than bigger particles.

Table 5.10 presents a summary of the properties of wood fly ash for use in concrete in combination with Portland cement. The reduction of workability of mortar and concrete with wood fly ash as mentioned in the literature (see subsection 2.2.2) is confirmed in this thesis. Wood fly ash contains also high concentrations of compounds which are limited in coal fly ash to avoid destructive reactions, especially Cl, K (Na_2O_{eq}) and S.

Table 5.10: Overview of chemical, mineralogical and physical properties of fly ash from wood combustion and range for coal fly ash

Component	Unit	Wood fly ash	Coal fly ash	EN 450 Criteria
Parameter				
CaO	% m/m	30-33	4.2±1.2	≤10.0
Cl	% m/m	0.16-0.42	<0.01	≤0.10
CaO free	% m/m	6.1-10.3	0.2±0.3	≤1.5[1]
P_2O_5	% m/m	2.5-2.9	0.58±0.31	5.0
SO_3	% m/m	3.6-5.8	0.68±0.18	≤3.0
Na_2O_{eq}	% m/m	7.6-9.3	1.5±0.5	≤5.0
$Al_2O_3+Fe_2O_3+SiO_2$	% m/m	28-36	88±2	≥70
Ba	mg/kg	2857-3224	1695±365	-
Mn	mg/kg	8935-10980	633±288	-
Zn	mg/kg	818-1043	190±122	-
Morphology		agglomerates	Mainly spherical	Mainly spherical
Flow	mm	106-147	180±8	-
28 days activity index	%	54-56	84±3	>75
91 days activity index	%	62-63	98±4	>85
Soundness	mm	31-77	1.3±0.7	≤10

1) If the content of free lime is greater than 1.5 % by mass, the fly ash must be tested for conformity to the requirement for soundness. Soundness or volume stability. The European standard for coal fly ash in concrete uses the term soundness. The soundness is measured with the LeChatelier test.

Properties of cement paste and mortar with combinations of blast furnace slag and wood fly ash

Activation of slags using sulphates is well-known from super sulphated cements. These cements consist of 80-85% of granulated blast furnace slag, 10-15% of calcium sulphate and about 5% of an activator, which is usually Portland clinker [5.1]. The reaction products consist mainly of ettringite and CSH. The basis of super sulphated cement is granulated blast furnace slag and especially its glass phases. The glass phase has to be dissolved in a highly alkaline conditions.

As already mentioned the activator is mostly Portland clinker, but also calcium hydroxide, potassium hydroxide and sodium carbonate are used. Also, too high a content of alkaline activators causes strength loss [5.2]. Calcium sulphate is mainly added as gypsum, but also anhydrite and hemihydrates are mentioned in research [5.3].

The activation of slag with calcium hydroxide in combination with other more soluble calcium salts was investigated by Belmann and Stark [5.4]. They showed that also at a lower pH (12.0-12.8) than in Portland cement a good strength could be developed if the calcium concentration remains at a high level. In some mixtures, soluble calcium salts, as calcium chloride, - bromide, - nitrate, - acetates and – formiate were used to have a high calcium ion concentration in solution.

The results of the experiments in this thesis with wood fly ash as an activator for blast furnace slag showed that at 28 days a compressive strength could be obtained of about 20 MPa or with addition of calcium formiate 30 MPa. However, the early strength at 2-7 days was very low. The microscopic observations showed that the addition of wood fly ash leads to formation of more reaction products at 28 days than with blast furnace slag alone and to a shift in the chemical composition of the reaction products as the Ca/Si/Al ratio of the reaction products decreases from 17/3/1 to 8/3/1 – 4/3/1.

5.6 Conclusions

The purpose of this chapter was to obtain a better understanding of the characteristics of wood fly ash, from modified pulverized coal boiler, the properties of cement paste and mortar with Portland cement and this fly ash as partial cement replacement and the properties of mortar prepared with ground granulated blast furnace slag and wood fly ash as binder.

Wood fly ash has fundamentally different chemical, mineralogical and physical properties compared to coal fly ash. The content of CaO, Cl, K_2O and SO_3 are much higher than in coal fly ash. This leads also to a different mineralogical composition especially by the presence of arcanite, and more lime, calcite and periclase than in coal fly ash. Due to the ash forming process in the boiler, most wood fly ash particles consist of agglomerates.

The partial replacement (25%) of Portland cement with wood fly ash reduces the workability of mortar and also the compressive strength at 28 and 91 days. The activity index was lower than that of coal fly ash and of limestone filler. Furthermore compounds are introduced, that have a negative impact on durability of concrete regarding corrosion of reinforcement and alkali silica reaction (chlorides, alkalis). False set phenomena occur probably due to the presence of arcanite.

An alternative use in concrete would be as an activator for ground granulated blast furnace slag like in super sulphated cements. The results show that wood fly ash has a positive effect in accelerating the strength development of ground granulated blast furnace slag. However, the effect is considerably less than the use of anhydrite as activator. From this point of view the use of wood fly ash is not very effective.

5.7 References

[5.1] Taylor. Cement Chemistry, pp 262-263 and 1264

[5.2] Jünger, M.C.G. et al, 2011. Advances in alternative cementitious binders. In: Cement and Concrete Research 41, pp 1232-1243.

[5.3] Bijen J. and Niël E., 1981. Supersulphated cement from blast furnace slag and chemical gypsum available in the Netherlands and neighbouring countries. In: Cement and concrete Research. Vol. 11, pp 307-322. Pergamon Press.

[5.4] Belmann F. and Stark J., 2009. Activation of blast furnace slag by a new method. In: Cement and Concrete Research 39, pp 644–650.

[5.5] NEN, 1994. EN 196-2. Methods for testing cement, Chemical analysis of cement (European standard), Delft, the Netherlands.

[5.6] WHO, 2001. Concise International Chemical Assessment Document 33. Barium and barium compounds. Page 8.

[5.7] WHO, 2010. Concise International Chemical Assessment Document 77. Strontium and strontium compounds. Page 10.

[5.8] Boyton S., 1980. Chemistry and Technology of limestone.

[5.9] Ebatco, 2016. Thermogravimetric analysis of Calcium oxalate www.ebatco,com downloaded September 2016.

[5.10] Wu H. et al, 2013. Impact of coal fly ash addition on ash transformation and deposition in a full-scale wood suspension-firing boiler. In: Fuel (113), pp 632-643.

[5.11] Zheng Y. et al, 2007. Ash transformation during co-firing coal and straw. In: Fuel 86 (2007), pp 1008-1020.

[5.12] Doshi,V. et al, 2009. Development of a modelling approach to predict ash formation during co-firing of coal and biomass. In: Fuel Processing Technology 90 (2009), pp 1148-1156.

[5.13] Chatterji, S. et al, 1966. The volume expansion of hardened cement paste due to the presence of ‘dead-burnt’ CaO. In: Magazine of concrete research, vol. 18, no 55. pp 65-68.

[5.14] Min, D. et al, 1995. Mechanism of expansion in hardened cement paste with hard-burnt free lime. In: Cement and Concrete Research, vol. 25, no. 2, pp 440-448.

6 PREDICTING COMPOSITION OF FLY ASH FROM COMBINED COMBUSTION OF WOOD AND COAL

6.1 Introduction

The goal of this modelling work is to predict the composition of fly ash from combined combustion of wood and coal. This prediction is based on the KEMA Trace model. The KEMA Trace model® is an empirical statistical model for the prediction of the composition of the emissions and of the ashes of coal-fired power stations [6.1, 6.2]. The composition is predicted using a so-called relative enrichment factor (RE) for each element. The concept of relative enrichment factors has been developed by Meij in the eighties of the last century to characterize the behaviour of a specific element during combustion in a power station [6.3] and more specific during combustion in the boiler, during the route of the flue gases to the ESP and in the ESP (electro static precipitator).

The concentration of a specific element in a fly ash (C_{ash}) can be calculated if the concentration in the fuel (C_{coal}), the amount of ash forming matter of the fuel (AFM) and the RE are known.

$$C_{ash}=RE*[C_{fuel}/AFM]*100 \qquad (6.1)$$

or

$$RE= [C_{ash}/C_{fuel}*AFM]/100 \qquad (6.2)$$

Where:

RE = relative enrichment factor of a specific element

C_{ash} = concentration of a specific element in the fly ash

C_{fuel} = concentration of a specific element in the fuel

AFM = amount of ash forming matter of the fuel [% m/m]

The amount of ash forming matter of the fuel and the concentration of a specific element in the fuel and the fly ash (and bottom ash) can be measured during a mass balance on a power station (see figure 6.1). The RE-factor for each element can be derived using the formulae above,

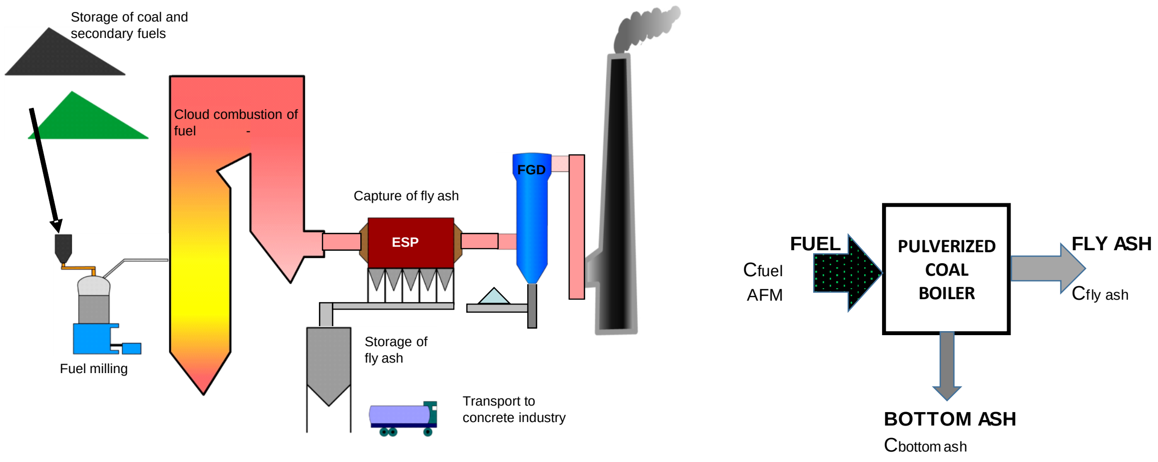

Figure 6:1: Principle of coal fired power plant (left) and simplified mass balance (right). Amount of ash forming matter (AFM) in fuel and concentrations of each element in all input and output streams are measured. The RE factors can be derived from these values.

A high RE-factor of a specific element for fly ash means that most of this element ends up in the fly ash, while a low RE factor means that most of the element ends up elsewhere (bottom ash, flue gas desulphurization gypsum or flue gas). The relative enrichment in the ash depends on the type of ash (bottom ash, fly ash), the particular element and boiler type. Based on the RE factor, elements can be grouped into three classes:

- Class I elements. These elements do not vaporize during combustion. Their concentration is about the same in fly ash and bottom ash (see table 6.1). In this case, the RE factor is about one.
- Class II elements. These elements are vaporized in the boiler, which leads to redistribution among fly ash and bottom ash. During the route of the flue gases through the boiler and to the ESP, the temperature decreases from about 1600° C to about 120° C. Depending on the chemical component, the dew point will be passed somewhere on this route and condensation will start. Condensation occurs at the surface of the fly ash particles and surface reactions will then take place. Fly ash particles can also be formed through nucleation of vaporized material and growth through coagulation and heterogeneous condensation. The smallest particles have the largest specific surfaces. Therefore, on a weight basis, the condensing elements have been found in greatest concentrations on the smallest particles. All elements that condense within the installation are grouped in class II. This class is subdivided into three subclasses. The RE factor of the bottom ash is less than 0.7 because elements originally present in the vapour phase have no chance to condense on the bottom ash particles.
- Class III elements. These elements are found in components with a low dew point condense only partly within the installation and, in the absence of flue gas desulphurization, are totally or partly emitted in the vapour phase. They are grouped as class III. Their RE factor is very small (<< 1), especially in the bottom ash.

Table 6.1: Classification of elements based on their behaviour during combustion in boiler and ducts (see also figure 2.2) with their Relative Enrichment factor (RE)

Class	RE Bottom ash	RE Fly ash	classified elements
I	~1	~1	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th and Ti
II	<0.7	~1	Ba, Cr, Mn, Na and Rb, Be, Co, Cu, Ni, P, U, V and W, As, Cd, Ge, Mo, Pb, Sb, Tl and Zn
III	<<1	<<1	B, Br, C, Cl, F, Hg, I, N, S and Se

It is assumed in the original model that the RE factor is not influenced by the type of coal and secondary fuel. The RE-factors were derived from mass balances performed on Dutch coal-fired power plants, whereby mass flows and concentrations of all input and output streams were measured (see scheme of figure 6.1). The values for the RE-factors were validated for co-combustion up to 30% wood co-combustion.

6.2 Derivation of RE factors for >30% biomass firing

Relative Enrichment (RE) factors were also derived from the pilot-scale co-combustion experiments by comparison of the composition of the generated fly ashes (see chapter 3) and the composition of the fuel mix (coal with or without co-combustion of demolition wood, poultry litter or Solid Recovered Fuel). It was concluded that the elements behaved in the same way during the co-firing of high secondary fuel percentages as during firing the coal itself [6.1]. These conclusions were valid for the main elements Al, Ca, Fe, K, Mg, Na, P, Si and Ti, and the trace elements (like As, Cr, Pb and Zn). The elements whose RE factors in the co-firing trials did differ from those normally associated with the combustion of coal in power stations were all class III (elements that partially leave the electrostatic precipitator (ESP) in the gas phase), especially Cl, S, B, Br, F, Hg and Se. It should be remarked that the RE factors for these elements were also higher than normal during the coal reference test. The behaviour of these elements is known to be influenced by variations in temperature and residence time (cooling regime of the flue gases). Nevertheless, it is clear that the co-firing of poultry litter resulted in higher RE factors for Cl, S and F than those associated with the combustion of coal on its own. It was also concluded that there is a positive correlation between the percentage of secondary fuel used and the RE factors for these elements. The RE factors for coal firing and derived from the co-combustion tests on pilot-scale are presented in table 6.2.

Table 6.2: Relative enrichment (RE) factors for fly ash from coal combustion as determined by Meij [6.3], derived from the pilot-scale co-combustion tests [6.1] and derived from the laboratory experiments of Misra et al [6.4] and Wu et al [6.5]

Source	Meij [6.3]	Meij and Te Winkel [6.1]	Misra et al [6.4]	Wu et al [6.5]
Fuel	coal	Coal + biomass	wood	wood
Element	Real-scale	Pilot-scale	laboratory	Real-scale
Al	1.0	0.9-1.2	1.0	≈1.0
Ca	1.0	0.8-1.1	1.0	1.0
Cl	0.01	0.04-0.35	-	<1.0
Fe	1.0	0.9-1.2	1.0	≈1.0
K	1.0	1.1-1.2	≤1.0	0,68
Mg	1.0	1.0-1.3	1.0	≈1.0
Na	1.0	1.0-1.3	-	0,63
P	1.0	0.8-1.2*	1.0	≈1.0
S	0.02	0.08-0.53	≤1.0	<1.0
Si	1.0	0.9-1.1	1.0	1.0
Ti	1.0	0.8-1.2	-	-
Mn	1.0	0.8-1.0	1.0	-
Sr	1.0	-	-	-
Zn	1.0	0.6-1.1	≤1.0	-

The literature provides no direct information about RE-factors for more than 30% wood firing, but combustion experiments, whereby the composition of fuel and fly ash are given, can be used to derive the behaviour of elements during combustion and thereby the RE-factors. Misra et al investigated the composition of wood ash as a function of furnace temperature up to 1300-1400 °C [6.4]. Wood samples from different species were tested (see also subsection 2.2.2). The combustion or heating process in a laboratory furnace is not completely the same as a boiler, because in the laboratory furnace elements can evaporate without condensation. This is in contrast to combustion in a boiler where during cooling of the flue gas, elements can condensate before the electrostatic precipitator and therefore remain in the fly ash. So, when the element content in the ash remains constant with increasing temperature, the RE-factor is 1 (see figure 6.2). In the case that during combustion in the laboratory furnace the content of an elements is decreased, the only conclusion is that the element behaves as a class II or class III element (the condensation mechanism does not occur during the laboratory experiments, like in full-scale boilers).

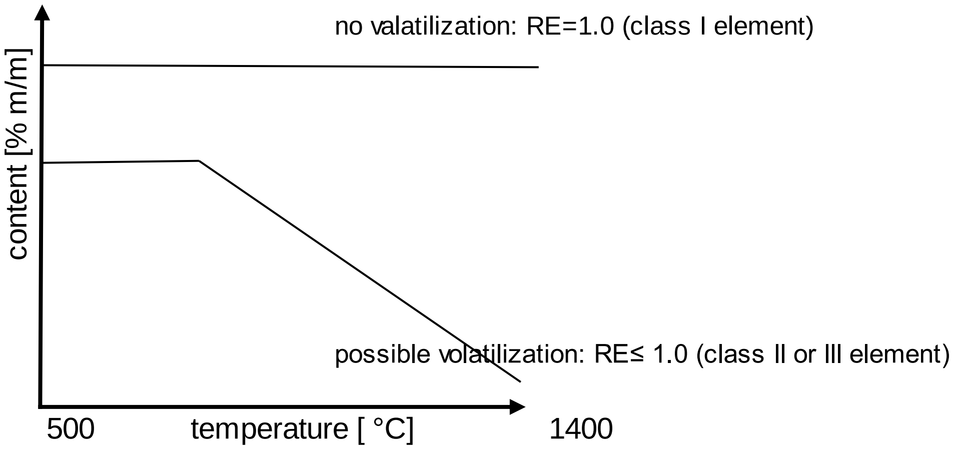

Figure 6:2: Basic approach to derive RE-factors from the results of the heating experiments of wood performed by Misra et al [6.4]. The RE factor is 1.0 if the content of an element remains at the same level with increasing furnace temperature. The RE-factor is ≤1.0 if the content of an element reduces with increasing furnace temperature.

The derived RE factors from the heating experiments of Misra are given in the fourth column. The heating experiments show that potassium is evaporated during the experiments. Wu et al compared the composition of the fuel ash and the fly ash in the case of wood combustion [6.4] (see table 6.3). The concentration of potassium was lower in the fly ash than in the fuel ash. They suggested that this could partly be due to deposition in the boiler, but also to possible variation in fuel properties.

The concentration of potassium in fly ash and in fuel ash is also compared for straw co-firing [6.6], whereby considerably more data are used. There was a very good relation between the content of potassium in fuel ash and fly ash. This confirms that the RE-factor is 1.0. It can be expected that the behaviour of Na will not be different from that of K, in other words the RE-factor of Na will also be 1.0.

This means that potassium from biomass combustion in a pulverized boiler may evaporate, but the major part will condense before fly ash is precipitated. In other words: potassium, which is present in biomass is a class II element in contrary to coal where potassium is a class I element.

The relative enrichment factor for sulphur is about 0.02 (class III element) in coal combustion. Several investigations on co-firing of straw and wood show that the presence of sulphur in fly ash has to be seen in relation to potassium. Also, the mineralogical analyses of wood fly ash (see section 5.3) show the presence of compounds like arcanite, alunite and langbeinite. The most straight forward approach is to derive a direct statistical relation between the potassium content and the sulphur content in the fly ash. The dataset that is used for this analyses is given in table 6.3. The statistical relation between both is presented in figure 6.3.

Table 6.3: Dataset used for statistical analysis relation between content of K_2O and SO_3 in fly ash from coal, wood or combined firing [% m/m]

Sample	K_2O	SO_3	Data origin
REF^1	1.52	0.42	See appendix C:
WHP	3.8	0.70	See subsection 3.3.4
CR	4.6	0.35	See subsection 3.3.4
PK	1.9	0.60	See subsection 3.3.4
WD50-1	2.2	0.91	See table 2.8
WD50-2	3.1	0.86	See table 2.8
WD100-A	7.57	2.70	Wu et al [6.5]
WD30-B	0.99^2	0.23^2	Wu et al [6.5]
WD100-C	6.90	2.08	[6.7]
WD100-D	16.5	3.35	[6.8]
WD100-1	12.58	5.78	See section 5.3
WD100-2	13.61	4.20	See section 5.3
WD100-3	11.89	3.55	See section 5.3

1) Average of 10 coal fly ashes

2) Concentrations calculated from test data

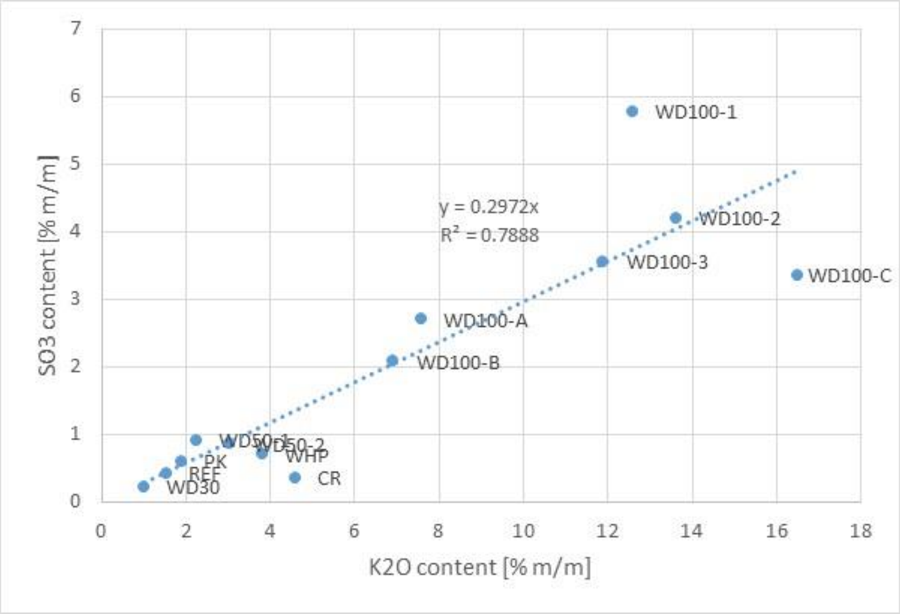

Figure 6:3: Relation between sulphur content and the potassium content in the fly ash from coal, with or without co-combustion of biomass (wood)

The restriction in this approach is that the database contains fly ash from 100% wood combustion, 100% coal combustion and fly ash from co-combustion with limited potassium contents but no fly ash from combined combustion of wood and coal with potassium contents above 5% m/m. The effect of uptake of potassium by alumina silicates in coal fly ash is not taken into account (see subsection 2.2.2). Therefore, the relation can be used for a rough prediction of the maximum sulphur content in the fly ash if the potassium content is known using the formulae.

$$SO_3 \leq 0.30^* K_2O \qquad (6.3)$$

Where:
K_2O = K_2O content in the fly ash [% m/m]
SO_3 = SO_3 content in fly ash [% m/m]

In the past, attempts has been made to predict the free lime content in coal fly ash from the CaO content of the fly ash and from the calcium content of the coal [6.10]. This attempt has been repeated, using the data of several Dutch power plants over the period 2013-2016. It was concluded that no correlation could be identified. The dataset for free lime in wood fly ash is too limited to perform a statistical analysis. The ratio CaO_{free}/CaO_{total} of the three analysed wood fly ashes is 0.21-0.32. If the amount of CaO present as portlandite and calcite in wood fly ash is taken also into account, the ratio is 0.36-0.48.

The RE-factor of chloride is about 0.01 for coal firing (class III element), which means that most chlorides do not end up in the fly ash but elsewhere (mainly emitted with the flue gasses of the power plant). The chloride content in coal fly ash is relatively low (<0.01% m/m; see table 4.7) while it is much higher in wood fly ash (0.16-0.42 % m/m; see table 5.2). The mineralogical analyses of wood fly ashes (see section 5.3) show the presence of sylvine, which indicates that it is related to the presence of potassium that reacts during the combustion process with chloride. It was not possible to identify a reliable correlation between the chloride content in the fly ash and the composition of the fuels.

6.3 Evaluation and discussion

The modelling of fly ash from combined combustion of wood and coal is based on the approach of the KEMA TRACE® model. This approach consists of the concept of the RE-factor to characterize the behaviour of elements. Up to now the model assumes that the relative enrichment factor is independent from type of fuel (coal and/or biomass) and biomass/coal ratio. In this chapter an attempt has been made to extend this approach for firing of wood with or without coal.

The results (see table 6.3) show that relative enrichment factors remains 1.0 for the elements Al, Ca, Fe, K, Mg, P, Si and Mn in the case of 100% wood firing. The uncertainty is that the experiments have been performed to a temperature up to 1300-1400 °C [6.5, 6.6] and in the test boiler up to 1090-1240 °C [6.1] while the temperature in the flame of the boiler of a power plant may be higher up to 1700 °C.

The behaviour of sulphur cannot be described by a constant relative enrichment factor, but depends on the presence of potassium in the wood. A simple relation has been derived to predict the maximum content of sulphur (as SO_3) in fly ash for combined wood coal combustion.

Figure 6.4 and 6.5 give a prediction of the concentration of relevant elements for use of fly ash in concrete. As already stipulated the SO_3 content may be a maximum value. This prediction has been performed using the derived RE factors. The used coal composition is the Dutch Average Coal

Composition 2014 (NNG 2014) [6.9], whereby the amount of ash forming matter is 12.2% m/m. The used wood composition is the mean composition for untreated wood from the Phyllis database (see also table 2.5), whereby the Ca content in the wood has been decreased from 0.57 into 0.15 % m/m, because this corresponds better with data from regular co-combustion in Dutch power plants. The amount of ash forming matter of the wood was 0.83% m/m.

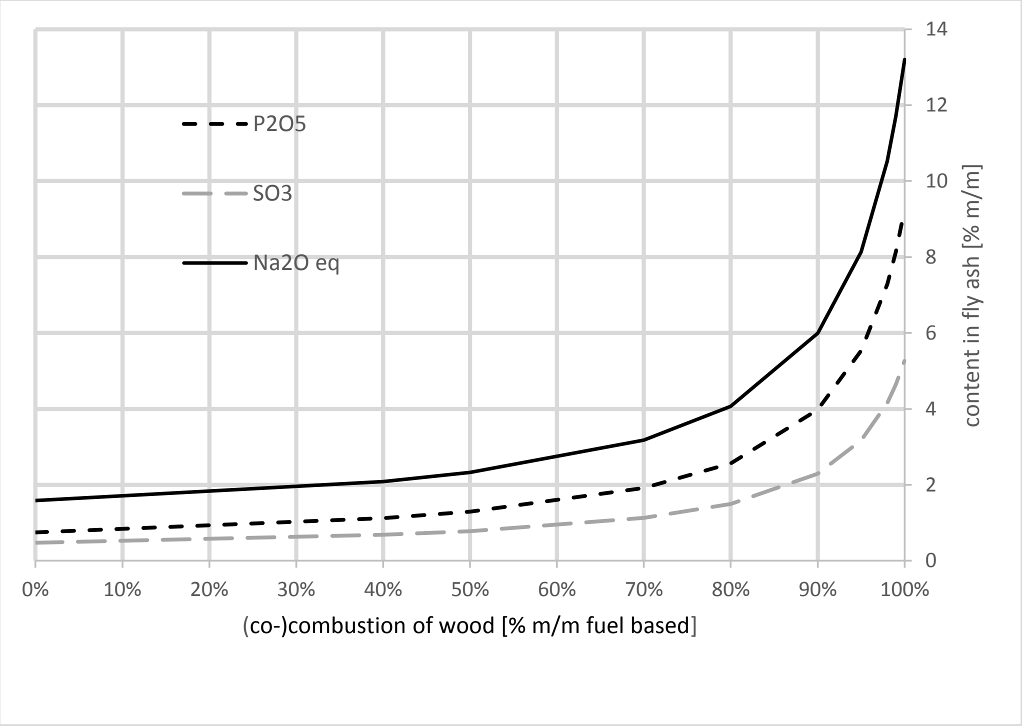

Figure 6:4: Calculated concentration of P_2O_5, SO_3 and Na_2O equivalent in fly ash as function of the share of wood in the fuel.

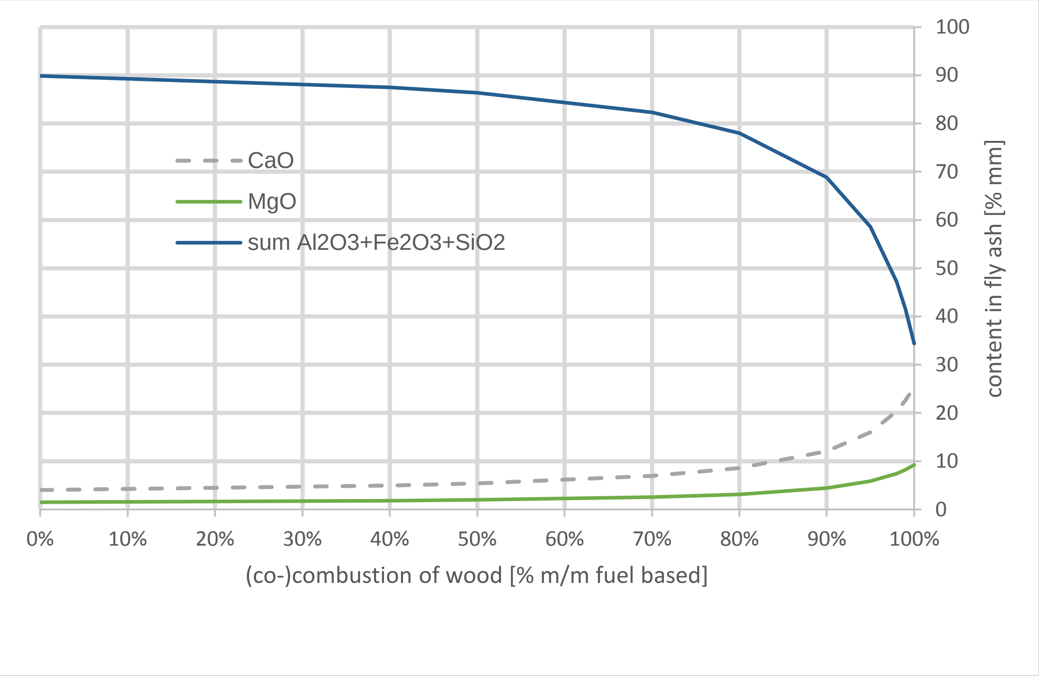

Figure 6:5: Calculated concentration of CaO, MgO and sum of, Al_2O_3, SiO_2 and Fe_2O_3 equivalent in fly ash as function of the share of wood in the fuel.

Note that the calculations are based on average values for the composition of coal and wood. The composition will vary in practice.

6.4 Conclusions

The chemical composition of fly ash from combined combustion of wood and coal is of importance for the use in concrete. A reliable prediction of this composition is thereby helpful. The concept of the RE factors is extended for wood firing with or without coal. Most important difference with coal firing is the behaviour of potassium. Potassium is a class I element for coal firing, but a class II element for biomass firing. Due to this the RE factor of sulphur and chloride changes as result of the enhanced formation of potassium sulphates and sylvine (KCl). When a significant amount of biomass is co-fired, the sulphur content can be predicted by using the derived relation with the potassium content in the fly ash (see formulae 6.3) instead of the concept of the RE factor.

The concept of the (modified) RE factors and the formulae 6.1 was used to predict the composition of fly ash from combined combustion of wood and coal. The influence of wood combustion on the content of elements is limited in the range 0-50 % m/m. These fly ashes will meet the criteria of the standard EN 450 regarding the content of compounds. The influence is moderate in the range 50-80% m/m wood combustion. The requirements regarding MgO, CaO, P_2O_5, SO_3, Na_2O_{eq} and sum of Al_2O_3 + SiO_2 and Fe_2O_3 will be met for an average composition of wood and coal. The other requirements (LOI, chloride, reactive SiO_2 and fineness) have to be assessed by testing fly ash from real-scale co-combustion experiments. Fly ash from this range of wood combustion can be regarded as suitable for use in concrete. Although the capacity of fly ash to suppress ASR, if reactive aggregate is present in concrete, will be reduced due to the increase of the content of potassium (Na_2O_{eq}) and the decrease of the content of amorphous alumina silicates (reactive SiO_2).

There is a strong influence of wood combustion in the range 80-100% wood combustion on the chemical and mineralogical composition of the fly ash. The concentration of components which are able to cause degradation of concrete due to corrosion of reinforcement (chlorides) and due to expansion by reaction of free lime, periclase and sulphates will increase. At the same time, the contribution to strength development of concrete with this fly ash will decrease.

6.5 References

[6.1] Meij R. and Te Winkel B.H. (KEMA), 2001. Composition and leaching of ashes generated during high percentages of co-combustion of poultry litter, RDF and waste wood. KEMA report 50131024-KPS/MEC 01-6154 (in Dutch).

[6.2] 2013. Helpfile bi KTM bv7.0-2013. Beschrijving, achtergrond en handleiding KEMA Trace Model v7.0 2013.

[6.3] Meij R., 1994 Trace element behaviour in coal-fired power plants. In: Fuel Processing Technology 39 (1994), pp 199-217.

[6.4] Misra M.K. et al, 1993. Wood ash composition as a function of furnace temperature. In: Biomass and Bioenergy, vol 4, no 2, pp 103-116.

[6.5] Wu H. et al (Technical University of Denmark), 2012. Full scale ash deposition measurements at Avedore power plant unit 2 during suspension-firing of wood with and without coal ash addition.

[6.6] Zheng Y. et al, 2007. Ash transformation during co-firing of coal and straw. In: Fuel 86 (2007), pp 1008-1020.

[6.7] TLR laboratories, 2012. Elemental analyses of wood fly ash from power plant Rodenhuize Report number 322768

[6.8] TLR laboratories, 2013. Elemental analyses of wood fly ash from power plant Rodenhuize Report number 388465.

[6.9] Saraber, A.J. and Loenen-Imming, D.C. (KEMA), 1997. Coal fly ash in cement and concrete: free lime. KEMA report 58163-KST/MAT 97-6572.

7 CIRCULARITY OF USE OF FLY ASH FROM CO-COMBUSTION OF BIOMASS

7.1 Introduction

The most popular definition of sustainability originates from the Brundtland Report of 1987, which states that: sustainable development is *development that meets the needs of the present without compromising the ability of the future generations to meet their own needs*. This encompasses both environmental, social and economic aspects. In this chapter, the focus will be on the environmental aspects, especially circularity. In the national and in the EU policy circularity is one of the ways to create a more sustainable society [7.1, 7.2]. In the concept of a circular economy the value of products and materials is maintained as long as possible. In fact waste generation and down cycling[21] have to be avoided as much as possible. If this cannot be avoided a cascade approach has to be followed. The concept of a circular economy distinguishes two basic cycles, namely the biological and the technological cycle [7.3]. The technological cycle involves the management of finite stock materials like iron, alumina, granite etc. The biological cycle involves basically renewable materials like wood and grass and includes the return of elements to the biosphere.

Figure 7.1 visualizes the circularity approach applied on buildings. It starts with material and construction design as part of the building process. During its use, maintenance and repair is standard part of the life cycle of the building to ensure or to extend its lifetime. After time, renovation, upgrading and retrofitting may be required to meet new requirements of potential users and extending the functional lifetime. When this is not possible or feasible anymore the construction will be dismounted or demolished. Prefab parts (like roofing tiles, doors, etc.) will be used directly for new buildings while other parts of the building will be recycled by using it as raw material. Separation and recycling processes may be necessary to upgrade the material before use in new building materials. Disposal and landfill do not fit within the concept of circularity and have to be avoided. The input of energy in the cycle will be needed to perform the several steps of the building cycle, but has to be from renewable sources. Also, the input of new materials in the cycle has to be from renewable sources.

It has been shown in the previous chapters that the composition of fly ash will change with increasing co-combustion of biomass. Especially the content of K_2O, CaO and to a less extent P_2O_5 and MgO will increase. When co-combustion fly ash is used in concrete, these compounds will also be introduced in the concrete cycle. A question to be answered is how this affects the circularity of the concrete cycle. Another question is the effect of co-combustion on the nutrient cycle as part of the biological cycle. In this chapter attempts will be made to give answers to these questions.

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[21] Definition: process of recycling whereby the second utilization has less quality than its first utilization.

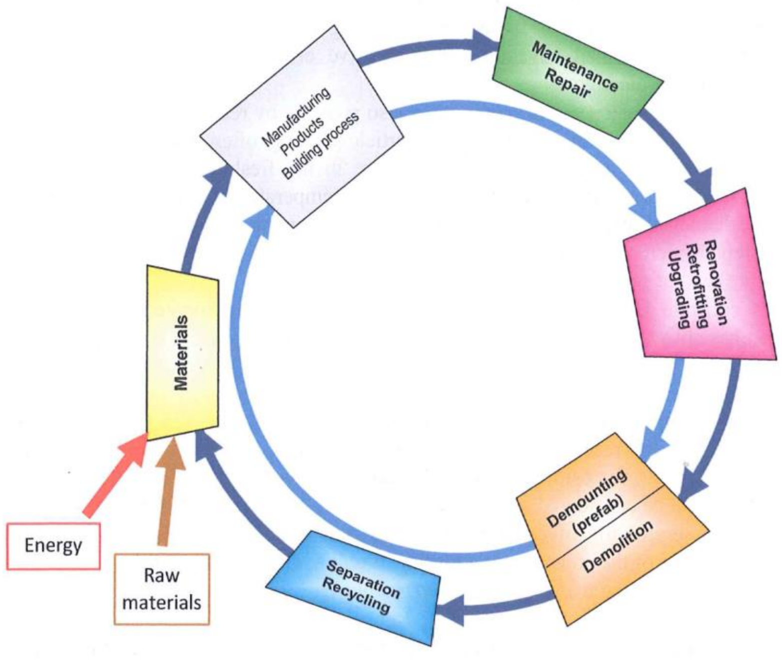

Figure 7:1: Circularity approach for building: the building cycle [7.4]

7.2 Effect on the concrete cycle

7.2.1 The concrete cycle and ash recycling

The concrete cycle can be distinguished into four basic stages, namely based on:

- Prolonged use of concrete (with or without maintenance).
- Reuse/redistribution of concrete construction and products.
- Remanufacture of concrete.
- Recycling of the raw materials.

Figure 7.2 presents a flow scheme of the concrete cycle with input of fly ash.

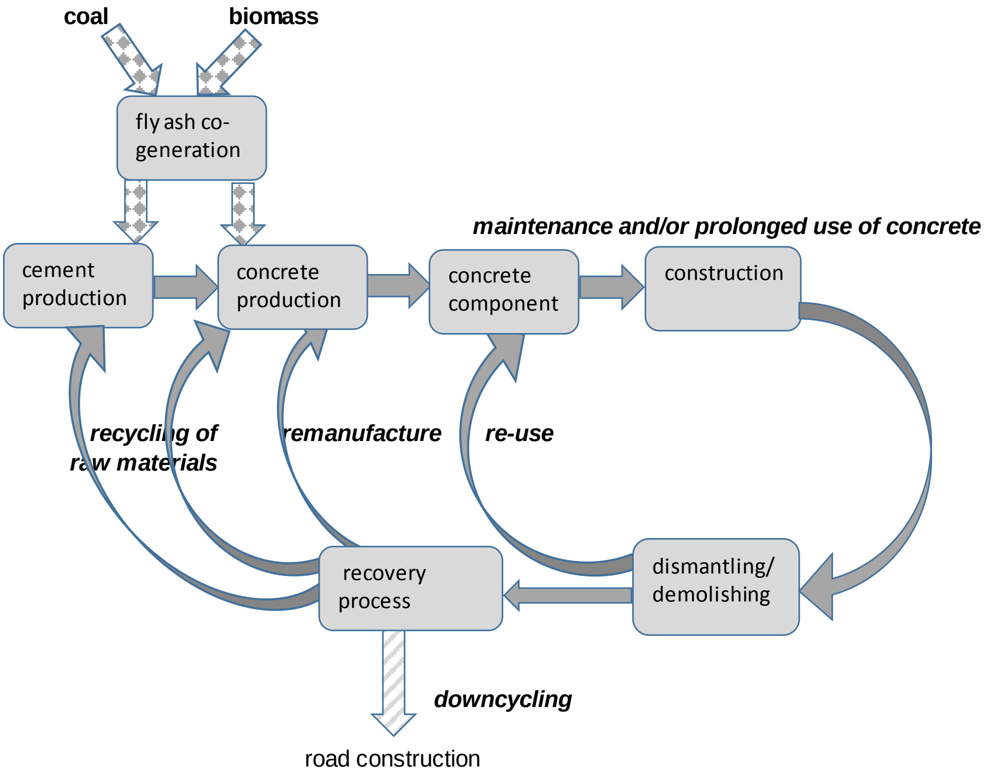

Figure 7:2: the concrete cycle with input of fly ash and different levels of recycling; based on [7.5]

7.2.2 Prolonged use of concrete

In general, concrete structures have a long technical lifetime (average 35-70 years, for infrastructure often more than 100 years is required) if properly designed, produced and placed [7.6]. In many cases the technical lifetime of concrete structures will be longer than the economic and functional lifetime.

<u>Effect of coal fly ash on prolonged use of concrete</u>
The use of coal fly ash in concrete has, in general, a positive influence on the performance of concrete under many conditions (as already discussed in 2.1.7) due to the pozzolanic reaction of the fly ash. On the other hand, the content of compounds with a potential negative effect on durability has to remain at a low level, especially free lime, sulphates, magnesium oxide and alkali content. Therefore, criteria for maximum levels for the concentrations of these compounds (see table 2.3) have been formulated in the standards, e.g. the EN 450 (see also table 2.3). The ranges for Dutch coal fly ash are normally below these maximum limit values.

<u>Effect of co-combustion on prolonged use of concrete</u>
The experiments with the fly ashes from co-combustion trials in power plants as described in chapter 4, show that the pozzolanic behaviour was not significantly influenced by co-combustion. This implies also that the positive influence on durability related to this pozzolanic behaviour does not differ from that of coal fly ash. It is generally acknowledged that the use of fly ash is able to prevent deleterious

alkali silica reaction (ASR) in concrete. The increase of CaO and Na_2O-equivalent (Na_2O_{eq}) due to co-combustion are of concern for the potential of co-combustion fly ash to suppress ASR. The literature does not give a univocal approach how to relate both to suppress ASR in combination with the minimum dosage to the concrete. Attempts has been made using the accelerated mortar bar test and the concrete prism test [7.7, 7.8], but up to now the approach is not based on experience in practice or long-term field tests. Thomas et al [7.9] reported about ASR in concrete made from reactive aggregate with Portland cement (Na_2O_{eq} = 1.15 %) and two coal fly ashes (Na_2O_{eq} =3.5-3.7 %, after outside exposure for 16-18 years. Replacement levels of 25-40% were effective in significantly reducing expansion and cracking. Heinz and Urbonas concluded that 25% replacement of Portland cement (Na_2O_{eq} = 0.65-1.21 %) with coal fly ash (Na_2O_{eq}=3.2-3.8 %) in concrete with reactive aggregate was sufficient to suppress expansion over 5 year storage in water [7.10]. In both studies fly ashes were used with less than 5% CaO. Shehata and Thomas investigated the effect of a wide range of fly ash compositions on the expansion of concrete [7.7]. The results show that in the range up to 20% m/m CaO in combination with limited Na_2O_{eq} (<4% m/m) expansion at 2 years does not exceed the expansion limit (0.05%), that was used in the study.

Co-combustion of vegetable biomass will lead to an increase of both calcium and potassium content in fly ash. Figure 6.4 and 6.5 show the relation between co-combustion percentage of wood and the Na_2O_{eq} and CaO content of fly ash. It shows that up to about 80% wood combustion, the content of these in the fly ash are below 20% m/m and 4% m/m respectively as mentioned by Shehata and Thomas, if replacement of cement is at a sufficient level.

7.2.3 Reuse/redistribution of concrete structures and products

Re-use of concrete products is possible for e.g. concrete roofing tiles, pavement blocks and floor sections. If this is not feasible, then remanufacture of concrete is favourable. Also concrete structures can be re-used (see figure 7.3). The effect of fly ash on reuse/redistribution of concrete structures and products is similar to that of prolonged use of concrete.

Figure 7:3: Example of re-use of concrete structure: former cooling tower of nuclear power station Kalkar (Germany): nowadays a climbing wall as part of the amusement park (source: www.Wikipedia.org)

7.2.4 Remanufacture of concrete

Concrete demolition waste can be processed and upgraded for utilization as recycled aggregate in concrete. At present, almost all construction and demolition waste in the Netherlands is used in road construction, whereas the use in concrete is limited [7.11]. The use of recycled aggregate in road construction can be seen as down cycling. At present, remanufacture of concrete is performed, whereby the aggregate and the hardened cement paste are not separated but reused as one secondary product. On the long term, concrete with fly ash develops even higher strength and lower permeability then concrete without fly ash (if properly cured and mix design based on the same 28 days strength). As concrete is mostly recycled after several decades, there is sufficient time to develop higher strength and lower permeability. Therefore, it can be expected that in general the influence of fly ash on the properties of recycled aggregate will be neutral or positive compared to Portland cement based concrete.

Effect of fly ash with or without co-combustion on remanufacture of concrete

Literature does not provide much information about the effect of the use of fly ash on the concrete material cycle. KEMA studied the properties of second generation concrete[22], using recycled aggregate (coarse fraction) from first generation concrete, which was produced with fly ash as partial cement replacement. The properties of the second generation concrete were compared with the properties of first generation concrete without fly ash, made with river dredged gravel as coarse aggregate [7.12]. The study showed that the compressive strength of the second generation concrete improved slightly compared to the first generation concrete (without fly ash) with gravel. The resistance against chloride penetration and freeze-thaw resistance did not differ significantly. Due to the lay-out of the study the effect of fly ash as such could not be derived.

7.2.5 Recycling of the raw materials.

A more sophisticated approach of remanufacture of concrete is to separate hardened cement paste from the aggregate and re-use these separately, as aggregate and the hardened cement paste for direct cement replacement or as raw material for the production of cement. In this way the *embodied energy*[23] of the hardened cement paste can be beneficiated more efficiently than recycling of the aggregate and hardened cement paste together.

Several technologies are being developed to separate hardened cement paste from the aggregate of demolished concrete. Examples are the Smart Crusher technology, Advanced Dry Recovery technology and Electric Pulse Technology [7.13, 7.14]. Recycled hardened cement paste can be used in the remanufacture of concrete via two ways:

- Re-use as filler in new concrete, replacing part of the cement. Thereby, the reactivity of the non-hydrated cement particles is exploited.

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[22] The cement content of the second generation concrete was 310 kg/m^3 CEM III/B 42.5 R with a water cement ratio of 0.54.

[23] The sum of the energy requirements associated, directly or indirectly, with the delivery of a good or service. See https://www.ice.org.uk/knowledge-and-resources/briefing-sheet/embodied-energy-and-carbon for further information

- Re-use as raw material for the production of Portland clinker. In this way primary raw materials like limestone and clay are substituted and less energy is needed for production.

Effect of coal fly ash

When fly ash is used in concrete the amount of cement is mostly reduced to some extent. This means that hardened cement paste with fly ash has less non-hydrated cement particles than a similar concrete without fly ash. Basically, fillers[24] from hardened cement paste with fly ash are, therefore, less hydraulic due to this dilution effect. On the other hand, a part of the amorphous phases (pozzolanic) of the fly ash may still be present as unreacted material.

As pure hardened cement paste has a chemical composition comparable to that of the original cement (with exception of bound water and carbonated compounds), the re-use of hardened cement paste for clinker production is of interest to save primary materials and energy. Hardened cement paste with fly ash (but also blast furnace slag) has a higher content of Al_2O_3 and SiO_2 and a lower content of CaO due to the different composition of fly ash (and slag). Replacement of raw meal[25] for clinker production with recycled hardened cement paste with fly ash is, therefore, only possible with adjustment of the chemical composition (ratio between CaO, SiO_2, Al_2O_3 and Fe_2O_3). The chemical composition of recycled hardened cement paste is also influenced by the presence of fine material from the aggregate (mostly quartz) even if advanced separation technologies are used, as shown by Schoon et al and others [7.13-7.15], This implies that in any case raw material has to be added to recycled hardened cement paste to get a raw meal with the same chemical composition as the original clinker.

Effect of co-combustion

In general, raw meal for clinker production contains about 0.2% m/m phosphorus as P_2O_5 [7.16]. Higher contents than 0.2% P_2O_5 in the raw meal affect the formation of alite ($3CaO{,}SiO_2$) in clinker production as shown by several studies [7.17]. It has been stated that the amount of phosphorus that can be taken up in the alite phase is 0.5-1.0%. Any further increase in phosphorus causes a decrease in the alite content, favouring the belite and free lime contents. Also other modifications of belite will be formed, namely a so-called α and α' form (crystal structure). This shift in the mineralogical composition of the clinker affects the strength development. The strength development of Portland cement made with this clinker was not significantly influenced up to about 0.7 % P_2O_5 (see figure 7.4). When the P_2O_5 content increased further, the strength at 1-7 days[26] was reduced, [7.17], but at 28 days the effect on strength was nihil or positive to a small extent.

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[24] Fillers can be added to cement (blended cements) and directly in the mixer of the concrete production plant.

[25] Raw meal is defined as the mix of specially selected raw materials, ready to be thermally processed in the cement kiln for the production of portlandcement clinker.

[26] Measured on standard mortar prism 15x15x60 mm.

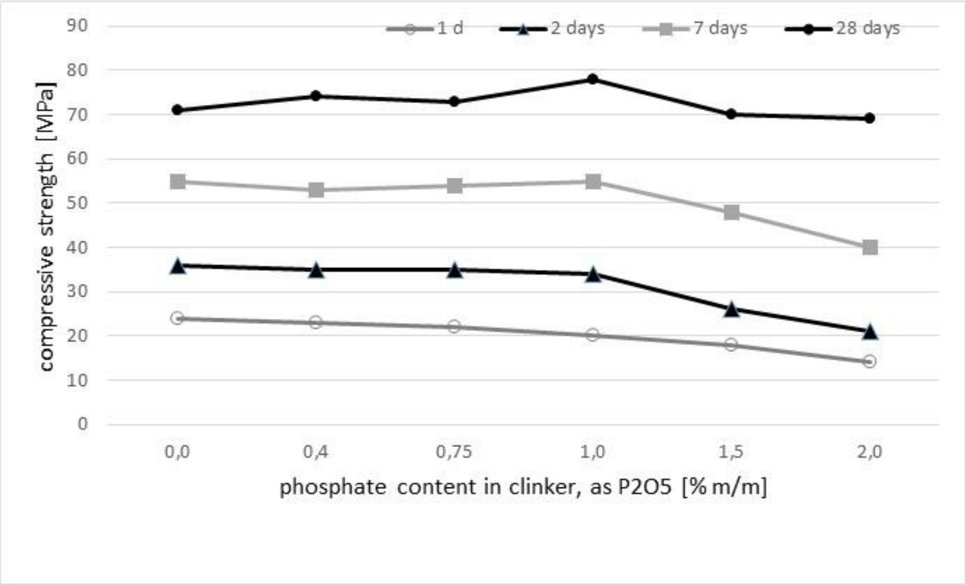

Figure 7:4: Relation between phosphor content in clinker and the compressive strength of mortar with Portland cement prepared with this clinker (mortar composition: EN 196; 1,5x1,5x6 cm prisms; curing at 20° C) [7.17].

An estimation of the potential increase of phosphorus of hardened cement paste with (co-combustion) fly ash can be made assuming that it consists of 70% Portland cement and 30% fly ash, which is a common ratio for Dutch ready mixed concrete. The calculated phosphorus contents in the hardened cement pastes are presented in table 7.1. If this hardened cement paste is recycled without any contamination of fines etc. as raw material for the same type of Portland clinker, the composition of the new raw meal (second generation) has to be adjusted with e.g. quartz sand and limestone. In this way, the phosphorus content in the 'new' raw meal will be reduced due to the addition of CaO and SiO_2 bearing raw materials. The calculated concentrations in the 2nd generation raw meal are given in the fifth column of table 7.1. The calculated P_2O_5 content 0.75-0.95 % m/m in the raw meal may influence the strength development (after one day) of the Portland cement made with this second generation raw meal.

Table 7.1: Phosphorus content (as P_2O_5) second generation raw meal (water free), made from of hardened cement paste with different fly ashes and with addition of quartz sand and limestone to adjust the chemical composition

Addition	Phosphorus content [%m/m]			
	Portland Cement[1)]	Fly ash[2]	Hardened Cement paste	Raw meal 2nd generation
Coal fly ash	0.2	0.6	0.3	0.25
Fly ash co-combustion	0.2	4.0	1.3	0.75
Fly ash co-combustion	0.2	5.2	1.7	0.95

[1)] Average phosphorus content of clinker according [7.16]

[2)] Coal fly ash: see table 2.1; fly ash co-combustion: table 4.7

The Na_2O and K_2O content of modern Portland clinkers are about 0.3 and 1.0, respectively [7.16]. Both compounds are volatile in the kiln environment and may give rise to problems in the production process of clinker (deposits in the system and internal recirculation) [7.18]. The influence of an increase of the alkali content in clinker depends on the clinker composition and the way alkalis are present (hydroxides, sulphates). A small increase is in some cases positive for early strength of the cement. The influence on the 28-days strength is always negative [7.19].

7.2.6 Evaluation and conclusions

Coal fly ash in concrete is able to improve the durability of concrete under many conditions, if the concrete is properly designed, placed and cured. The improvement of durability enables to prolong the use of the concrete product, which fits within the concept of a circular economy. The increase of alkalis, phosphorus and calcium due to co-combustion is an important aspect in the assessment of the impact of co-combustion on the concrete cycle. Up to about 80% co-combustion of wood will result in a limited increase of the Na_2O equivalent (ca. 4% m/m) and CaO content (ca. 9 % m/m). Fly ash with these contents of both components are able to suppress ASR if it is used at a sufficient high level (calculated for average coal and wood compositions). On the other hand, the glass content of the fly ash will be decreased, which implies that the pozzolanic properties will be reduced.

If concrete with co-combustion fly ash is recycled whereby the hardened cement paste is used for the production of new clinker, the increase of phosphorus content is relevant. The phosphorus content in the investigated fly ashes from co-combustion is maximum 4-5.2% m/m as P_2O_5. If hardened cement paste with such co-combustion fly ash is recycled for production of new clinker, the addition of other raw material, like quartz sand and calcite is necessary to obtain the same ratio of the main components CaO-SiO_2-Al_2O_3-Fe_2O_3. This will reduce the phosphorus content in the second generation raw meal (if the same primary raw materials are used as for the first generation raw meal). Also, contamination with fines from the aggregates, even if advanced separation technologies are used, will require extra adjustment with raw materials which will further reduce the phosphorus content in the raw meal.

7.3 Effects on the biological cycle

7.3.1 The biological cycle and ash recycling

The extraction of nutrients, together with wood and other biomass, from ecosystems is of concern for the biological cycle. In a natural situation most of the biomass (leaves, needles, branches and finally the stem) will fall on the ground near the tree or plant. In this way the nutrients are kept within the ecosystem. The nutrient balance of an ecosystem is influenced by several factors especially by wash-off of compounds and soil erosion (weathering of minerals) whereby nutrients (like K, Ca, Mg and P) become available for organisms and by deposition from the atmosphere [7.20]. The latter is mainly relevant for nitrogen. Nitrogen can also be bound from the atmosphere by specific plants. Figure 7.5 gives a simplified illustration of the recycling of nutrients and inputs and outputs of a forest ecosystem.

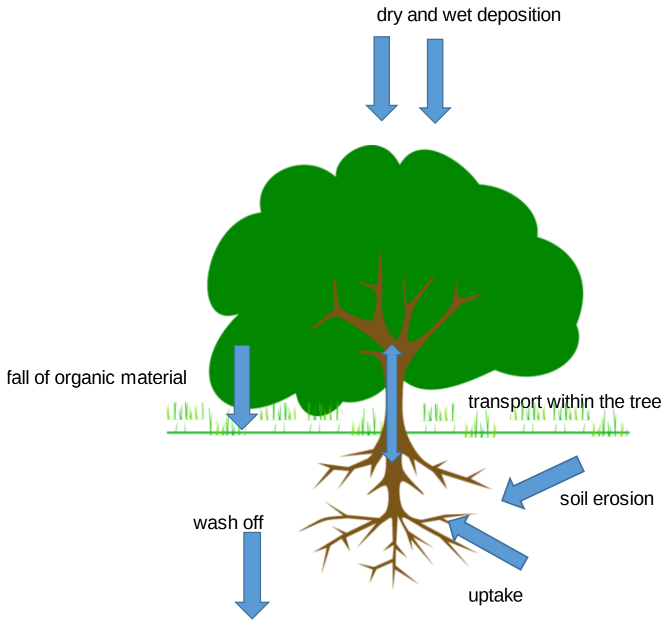

Figure 7:5: Simplified model for nutrient cycling in forest ecosystem [7.20]

When biomass is harvested, the eco system is not closed anymore as nutrients are taken away together with the biomass. In several countries, like Austria, Germany, Finland and Sweden, spreading wood ash in the forests is practiced to recycle nutrients or as liming agent [7.21-7.24]. In this way macro- and micronutrients are recycled, with exception of nitrogen as this compound is not bound in the fly ash during combustion (RE<<1; see also section 6.1).[27]

7.3.2 Effects on the biological cycle in relation to forests

In many countries wood is harvested on a large scale for timber wood, paper production (cellulose) and for energy production. Also, forest tree plantations have been developed to enhance the production of wood per hectare. Table 7.2 gives an indication of the removal of macro-nutrients N, P, K and Ca (data about the other macro-nutrients Mg and S were not given) due to extraction of biomass in several forests in the United States [7.25]. Two types of harvesting were compared, namely conventional harvesting (stem only) and so-called ‘whole tree harvesting’, whereby the complete tree including branches, leaves etc. is removed from the forest. As most nutrients are present in the living parts of the tree, whole tree harvesting leads to considerably higher nutrient loss than conventional harvesting where just the stems are taken away [7.25-7.27].

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[27] The effect of ash recycling on forest ecosystem encompasses many aspects like recycling of heavy metals, contamination of heavy metals and mineral matter in the ash, basicity of the ash and effects of spreading on soil properties in the forest.

Table 7.2: Removal of N, P, K and Ca due to whole tree harvesting and conventional harvesting in forests on poor (P) and rich (R) soils in the USA (harvested after 55 years of growth) [7.25]

	Conventional harvesting					Whole tree harvesting				
Tree	EXT* ton/ha	N kg/ha	P kg/ha	K kg/ha	Ca kg/ha	EXT. ton/ha	N kg/ha	P kg/ha	K kg/ha	Ca kg/ha
Douglass (R)	281	478	56	225	23	318	728	96	326	411
Douglas (P)	134	161	27	121	-	165	325	56	140	-
High alder (R)	137	287	41	151	388	147	347	47	174	426
Low alder (P)	111	311	22	122	-	120	242	27	143	-

*EXT.=extraction of wood

Alterra Wageningen assessed the nutrient balance on the sustainability of different timber harvesting scenarios in the Netherlands in relation to the nutrient balance for Ca, Mg, K and P [7.28]. Nitrogen was excluded in this study as no depletion is expected due to the high level of deposition in the Netherlands. A negative nutrient balance is hardly calculated for richer soil types (loamy and clayey soil types), but for poorer soils (sandy) depletion occurs, especially for Ca and K, for all growth classes. For some situations depletion of these elements was calculated even after one harvesting. It was remarked by the authors that the calculation shows high uncertainties, especially about the relation between uptake of nutrients in parts of the trees and the availability of nutrients and further the impact of deposition and weathering for phosphorus on the phosphorus balance.

7.3.3 Discussion

Every ecosystem with plants and/or trees has a nutrient cycle, whereby nutrients are taken up from the soil by plants and trees and return to the soil when fruits, leaves, branches etc. fall on the soil and decompose. Normally it is not a complete closed nutrient balance due to wash off to the deeper soil, weathering of minerals and deposition from the atmosphere (especially for nitrogen). The system is also not closed if biomass is harvested and taken away, e.g. for food production, energy fuels, paper production etc. Harvesting leads inevitable to nutrient removal and, if no countermeasures are taken, to nutrient depletion of the soil and to exhaustion at the end. The difference between different types of soil, harvested biomass and climate is only the timescale. Due to the concerns about the sustainability and deforestation of wood production, several certification schemes (like FSC, Green Gold label and PEFC) and regulations have been developed to promote a more sustainable forest management for harvesting wood for timber wood, paper and energy. For example, one of the requirements for sustainable forest management to get the Green Gold Label is that *the quality of the soil in the forest management unit shall be maintained and, if necessary, improved* [7.30, 7.31].

In agriculture it is common practice to restore or even to improve the nutrient budget in relation to the crops by adding fertilizers to the soil. Nutrients removal and acidification due to wood harvesting is of concern for sustainable forest management. The number of systematic studies to nutrient depletion due to wood harvesting is very limited up to now. A model study showed that in certain Dutch forests nutrient depletion may already occur after one rotation (very poor soils). Nitrogen deposition is mostly sufficient to compensate the nitrogen loss. However, in other forests on rich soils depletion will hardly occur. On the other hand sometimes diminishment of soils is promoted to enhance bio diversity [7.29].

It is already practiced in several countries, to leave the living parts of the tree in the forests, as these contain most of the nutrients in a tree. A second step can be to bring ash from combusted wood back to the forest where the wood was harvested. However in a co-combustion situation the biomass is combined with coal, which leads to an increase of ash volume to be recycled and to the introduction of a considerable amount of heavy metals (see also appendix E for estimations). In this situation utilization of adequate fertilizers or manure will be a solution to restore the nutrient budgets of these forests.

In a future circular economy at least two scenarios regarding the use of wood for energy conversion can be assumed:

1. use of wood directly as renewable fuel in the region where the biomass originates, and
2. Cascade approach, whereby wood is first used for paper and building materials and after one or more recycling steps used for energy conversion.

In the first scenario, ash will be generated from combustion of wood without other fuels. This ash is suitable to restore the nutrient budget (with exception of nitrogen). The literature describes several effects of using wood ash for restoring the nutrient budget of the forest. The effect of recycling of wood ash to (Northern) forest on tree growth are not univocally positive [7.20, 7.21, 7.32]. Sometimes no significant effect is observed. The absence of the macro nutrient nitrogen in the ash is mainly seen as responsible for this. If there is sufficient nitrogen available in the forest, than tree growth can be positively influenced by bring ash back to the forest. In other situations actions can be taken to compensate the nitrogen loss by fertilization.

In the second scenario wood is first used for other applications (construction, furniture etc.) and at the end of its lifetime the remaining product is combusted for energy production. In most cases the generated ash will be contaminated with mineral matter and undesired components (heavy metals) for the forest ecosystem (see also appendix E). In general it is preferred that wood ash is returned to the forests where it originates from, or at least to the same area to avoid changes in the concentration of heavy meal concentrations in the soil. This is difficult to realize if the wood is first used for other applications before it is combusted.

7.3.4 Evaluation and conclusions

Recycling of ash from non-contaminated wood is able to compensate nutrient loss of forest ecosystems with exception of nitrogen. The use of commercial fertilizers and manure should be considered as a way to compensate nutrient depletion in (production) forests in the case wood ash cannot be recycled and/or nitrogen deposition from the atmosphere is insufficient. Therefore, even in a circular economy nutrient cycles cannot completely be closed by using the ashes.

The presence of contaminants in ash from wood, that is combusted after a series of cascaded applications, is very likely (construction materials, paints etc.). This may imply that the use of ash to compensate nutrient loss is not feasible from an ecological point of view. Also, in that case compensation of nutrient loss by using commercial fertilizers and/or manure has to be considered.

7.4 References

[7.1 European commission, 2015. Closing the loop; Commission adopts ambitious new Circular Economy Package to boost competiveness, create jobs and generate sustainable growth. Press Release December 2nd 2015.

[7.2] Ministry of Economic Affairs, 2015. Letter to the Tweede Kamer regarding Information Request Circular Economy, January 20th 2015.

[7.3] Ellen Macarthur Foundation, 2015. Towards a circular economy: business rationale for an accelerated transition.

[7.4] Breugel,K. van (Delft University of Technology), 2017. Ageing infrastructure and circular economy: challenges and risks. Proceedings of the 2nd World Congress on Civil, Structural and Environmental Engineering (CSEE, 17), Barcelona, Spain. April 2-4 2017.

[7.5] Cement en beton centrum, 2014. Duurzaam beton. Trending topics.

[7.6] SBR, 2011 .Levensduur van bouwproducten. Methode voor referentiewaarden.

[7.7] Shehata M.H. and Thomas, M.D.A., 2000. The effect of fly ash composition on the expansion of concrete due to alkali-silica reaction. In: Cement and Concrete Research 30 (2000), pp 1063-1072.

[7.8] Vaygham A.G. et al, 2016. An extended chemical index model to predict the fly ash dosage necessary for mitigating alkali-silica reaction in concrete. In: Cement and Concrete Research 82 (2016), pp 1-10.

[7.9] Thomas M. et al, 2011. Effect of fly ash on the expansion of concrete due to alkali-silica reaction – Exposure site studies. In: Cement & Concrete Composites 33 (2011), pp 359-367.

[7.10] Heinz D. and Urbonas L. (Technische Universität München), 2010. Abschlussbericht Nr 10-F-0025. AKR- Vermeilitter durch Flugasche-Langzeitlagerung.

[7.11] Leiden University and Delft University of Technology, 2015. Close-loop Economy. Case of concrete in the Netherlands

[7.12] KEMA, 2000. Second recycling of fly ash concrete (in Dutch). KEMA report 50030002.30000-6160.

[7.13] Florea M. and Brouwers J., 2013. Slim breken sluit materiaalkringloop. In; Cement 2013, pp 2-7.

[7.14] Lotfi S., 2016. C2CA Concrete Recycling Process. From Development To Demonstration. PhD thesis Delft University of Technology,

[7.15] Schoon J. et al, 2015. Fines extracted from recycled concrete as alternative raw material for Portland cement clicker production. In: Cement and Concrete Composites, no 56 (2015), pp 70-80.

[7.16] Taylor H.F.W., 1997. Cement Chemistry. Page 87. Thomas Telford Publishers. Second edition.

[7.17] Puntke S. 2004. Auswirkungen des Phosphateintrages in Drehofenanalagen der Zementindustrie auf Klinkermineralogie und Zementeigenschaften. PhD dissertation Technical University of Clausthal.

[7.18] Chinyama, M.P.M., 2011. Alternative Fuels in Cement Manufacture. In: Alternative Fuels. Available at www.intechopen.com

[7.19] Halaweh M., 2006. Effect of alkalis and sulphates on Portland cement systems. PhD thesis University of South Florida. USA.

[7.20] Paré D. and Thiffault, E., 2016. Nutrient budgets in forests under increased biomass harvesting scenarios. In: Curr Forestry Rep (2016) 2:81-91.

[7.21] Eijk van R.J. (Kema) et al, 2012. Options for increased utilization of ash from biomass combustion and co-firing. By order of IEA Bioenergy Task 32: Biomass combustion and co-firing.

[7.22] Ingerslev M. et L, 2014. Effects of wood chip ash fertilization on soil chemistry in a Norway spruce plantation on a nutrient-poor soil. In: Forest Ecology and Management 334 (2014), pp 10-17.

[7.23] Skogsvårdsstyrelsen and RecAsh, 2005. Recirculating wood ash. Theory, practice and recommendations. International teaching material produced within the Life Project RecAsh.

[7.24] Pitman R.M., 2006. Wood ash use in forestry. A review of the environmental impacts. Forestry Advance Access published 1 november 2006.

[7.25] Mann L.K. et al, 1998. Effects of Whole-Tree and Stem-only Clearcutting om postharvest Hydrologic Losses, Nutrient Capital and Regrowth. In: Forest Science, volume 34 Number 2, 1 june 1988 pp 412-418 (17).

[7.26] De Schrijver A. et al, 2012. Koolstof- en nutriëntenkringlopen. In: Bosecologie en Bosbeheer, pp 167-175. Uitgeverij Acco, Leuven.

[7.27] Alterra, Wageningen University, 2011. Effecten van de oogst van takhout op de voedingstoestand en bijgroei van bos.

[7.28] Alterra, Wageningen University, 2015. Houtoogst en bodemvruchtbaarheid. Een modelstudie naar duurzaamheid op Nederlandse bosgroeiplaatsen.

[7.29] Timmermans B. et al (Louis Bolk Instituut), 2010. Evenwichtige verschraling van natuurpercelen. Eindverslag 2007-2009.

[7.30] Green Gold Label, 2016. GGLS5 Forest Management Criteria. Version 2.1 (april 2016).

[7.31] FAO and IEA, 2010. Criteria and indicators for sustainable woodfuels. P 51-53. Available at www.fao.org.

[7.32] Knapp B.A. and Insam, H., 2011. Recycling of biomass Ashes: Current Technologies and Future Research Needs. In: Recycling of biomass ashes, pp1-16. Springer Verlag.

8 DISCUSSION AND EVALUATION

8.1 General

The properties of fly ash from coal combustion and its performance in concrete have been well investigated. These investigations were the basis for the technical regulations to assess the quality for its use in concrete, like the European standard EN 450 and American standard ASTM 618. The introduction of co-combustion in coal-fired power stations means that fly ash is generated which is not only derived from the ash forming matter in coal, but also from different types of biomass. To keep fly ash as a valuable resource for concrete, it is essential to create thorough understanding of the relation between the compositions of biomass, the combustion process, the properties of fly ash and concrete made with this fly ash. Also the impact of (co-)combustion of biomass on the sustainability and circularity aspects of concrete is important in the context of social responsibility. Six research questions have been formulated based on these goals (see also section 1.2), which will be answered in this evaluation:

1. Which is the effect of co-combustion of biomass on the properties of fly ash?
2. Can these properties be explained by the composition of the fuel and the combustion process?
3. Which effects has co-combustion of biomass on the performance of concrete made with this fly ash. Can this be explained by the properties of the fly ash?
4. Which are the properties of fly ash from the combustion of biomass (wood) with or without coal? Can this be explained by the composition of the fuel and the combustion process?
5. Are fly ashes from the combustion of biomass (wood) with or without coal able to act as a pozzolan in concrete? If not can these fly ashes be used in concrete in a different way?
6. To what extent does the use of fly ash from co-combustion of biomass (wood) fit within the concept of circularity?

Five basic preconditions have been formulated for practical reasons. It is not seen as necessary to reformulate these preconditions from a methodological point of view:

- Only (co-)combustion in pulverized coal boilers fired with hard coal or biomass will be investigated. As a consequence, (co-)combustion in lignite fired boilers and other type of boilers like fluidised bed and grate-fired boilers are not considered. Co-combustion is further limited to direct co-combustion (see appendix A)
- Herbaceous and annual growth material will not be considered in this study, because these types are not widely used on a large scale in pulverized coal boilers
- Combustion of >50% of biomass will only be assessed for wood as this is the only biomass with sufficient availability and technical suitability to be fired in the large scale pulverized coal boilers
- The use of fly ash as pozzolan will only be assessed for the combination with Portland cement. Combinations with other cements like blast furnace slag cement and alumina cement are not considered.
- The focus of the dissertation will be on technical and sustainability aspects.

8.2 Effects of co-combustion on the properties of fly ash

Chemical composition of fly ash

The main components of coal fly ash are SiO_2, Al_2O_3, Fe_2O_3 and CaO and to a lower extent Na_2O, K_2O, TiO_2, P_2O_5, MgO and carbon. Besides these components trace elements are also present. The main trace elements are Ba, Mn and Sr, but also to a less extent B, V and Zn. The trace elements are relevant for environmental and health aspects, but not for technical aspects.

Several fly ashes from co-combustion of *biomass from vegetable origin* (co-combustion range: 7-14% [28]) have been investigated, namely three types of agricultural by-products. These biomasses have relatively high contents of K_2O and P_2O_5 and in several cases also CaO, MgO and SiO_2, which is reflected in the generated fly ashes. The K_2O and MgO content of the investigated co-combustion fly ashes was maximum 4,9 % m/m and 4,8% m/m, respectively, which is still in the range that applies for coal fly ash, mentioned in literature (see table 2.1). The P_2O_5 content increased to 5.2% m/m, which is far above the range measured in Dutch coal fly ashes. Analyses of fly ash from co-combustion of wood up to 50% m/m fuel based have been reported in the literature study (co-combustion range 1-5% m/m, ash based). No effects on the properties of the fly ash and mortar made with this fly ash were found, which can be attributed to the low contribution of wood to the generated fly ash volume.

Biomass from animal origin is generated directly and indirectly from animals (most relevant fuels for power generation are meat and bone meal and litter). The amount of ash forming matter of this biomass group is generally higher (mean values 20-28 % m/m) than that of coal (about 12% m/m). The main elements are P_2O_5, CaO and to a lower extent K_2O and SiO_2. It implies that especially the amounts of CaO and P_2O_5 increase.

Biomass from industrial origin is a group with strongly different origins. In this study fly ash from co-combustion of demolition wood (co-combustion range 11-32%), SRF (co-combustion range 18-39%), paper sludge (±17 %) and sewage sludge (co-combustion range 7-18%). The influence on the chemical composition of the fly ash regards a small reduction of the Al_2O_3 and SiO_2 content in favour of CaO and also P_2O_5 in the case of sewage sludge. The concentration of several heavy metals (Cr, Cu, Pb, and/or Zn) increases when these biomasses are co-fired.

The chemical composition of coal fly ash can be predicted from the fuel composition with the KEMA Trace model, using the concept of relative enrichment (RE) factors (see section 6.1). This model has been validated for coal firing and for co-combustion up to 30% (fuel based) of wood. Results of several research projects have been used to assess the classification of elements and their RE-factors for wood firing. The RE-factors of Al, Ca, Fe, K, Mg, P, and Si are not different from that of coal. It can be expected that the behaviour of Na will not be different from that of K, in other words the RE-factor will also be 1.0. In this study a correlation was derived between the potassium content in the fly ash and the sulphur content (R^2=0.78), which can be used to predict the sulphur content in fly ash (as a maximum value). No RE-factor could be derived for chloride.

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[28] All co-combustion percentages are m/m 'ash based', unless indicated differently in this chapter.

Mineralogical composition of fly ash

The elements of coal fly ash are present in different minerals, especially in the glass phase. This glass phase is the basic component in coal fly ash for the pozzolanic reaction. It consists mainly of SiO_2, Al_2O_3 and to a lower extent CaO, MgO and K_2O. According to the network theory of Zachariasen-Warren (see Box 4.1, par. 4.5.4) these are network formers, intermediaries and network modifiers respectively.

In this thesis the glass phase of a set of 10 coal fly ashes has been analysed, using sequential dissolution, to obtain a better understanding of the glass composition than based on the bulk composition. Well-known minerals in coal fly ash are mullite, quartz, hematite and some free lime (see table 2.2 for an overview of minerals based on X-ray diffraction analyses of coal fly ashes).

Co-combustion of *biomass from vegetable origin* (co-combustion range 7-14%) did not result in the identification of other minerals than in coal fly ash, but the acid soluble fraction increased from 7% m/m (average for coal fly ash) to 12-15% m/m. The main compounds found in this fraction were CaO, MgO en SiO_2. Most of the K_2O in the fly ash is present in the glass phase. About 1/3 of the P_2O_5 is also present in this phase.

Co-combustion of *biomass from animal origin* resulted in the presence of phosphorus. αTri-calcium phosphate and a ‘phosphate unclassified’ phase were present if meat and bone meal was co-fired. The latter has a Ca/P ratio about equal to that of tri calcium phosphate, but with some Si and Al. In fly ash from co-combustion of poultry litter (co-combustion range 40-56%) no tri-calcium phosphate was found but the acid-soluble fraction contains calcium and the major part of phosphate. Arcanite and Langbeinite were present in this fly ash, which are normally not found in coal fly ash. The free lime content of this fly ash was much higher than normally observed in coal fly ash.

Co-combustion of sewage sludge (*biomass from industrial origin*) resulted in the presence of iron phosphate and an ‘unclassified’ phase, consisting of Si, P, Ca and Fe (tested up to 15-18% m/m ash based). No other minerals than in coal fly ash were identified in the fly ashes from co-combustion of paper-sludge, demolition wood and Solid Recovered Fuel (co-combustion range 30% and 39 % ash based respectively), but the acid soluble fraction increased, which was mainly composed of CaO, Al_2O_3 and SiO_2.

In general, there is no clear relation between the free lime content of fly ash and co-combustion of biomass. However, at higher co-combustion percentages the probability of higher free lime contents will increase for biomasses where calcium is organically associated (wood) or if it is present in discrete particles consisting of calcite (like poultry litter).

Physical properties of fly ash

Coal fly ash from pulverized fuel boilers consists of mainly spherical glassy particles. The particle density is determined by the chemical and mineralogical composition and by the inclusion of gas pores in the particles. The particle density of coal fly ash is typically lower than Portland cement and blast furnace slag cement (±2290 kg/m^3 to 3150 and 2950 kg/m^3). The particle density was not significantly influenced by co-combustion of biomass, with exception of co-combustion of paper sludge.

The morphology of coal fly ash is characterized by its spherical particle shape. However, the fly ashes from the pilot-scale tests contain less spherical particles. This can at be explained at least partially by the lower flame temperature in the test boiler compared to power plants. The main part of the particles in fly ash from real-scale co-combustion tests has a spherical particle shape. The grain size (as D_{50}) was not influenced by co-combustion, with exception of co-combustion of sewage sludge and poultry litter. If paper sludge is co-fired more coarser particles are present in the fly ash (D_{90} = 118 µm), compared to the reference coal fly ash (D_{90} = 66 µm).

8.3 Effects of co-combustion on the properties of concrete with fly ash

The setting time of cement paste with fly ashes from co-combustion of biomass did not show significant retardation despite the presence of up to 5.2% phosphate. Exception was the retardation of setting time of cement paste with fly ash from co-combustion of 33% m/m Solid Recovered Fuel (ash based). It was not possible to find which compound interfered with the cement hydration.

The workability of concrete with fly ashes from co-combustion has been tested with different concrete mix compositions. Fly ash from co-combustion of meat and bone meal (10-14% m/m), municipal sewage sludge (15-18% m/m) and paper sludge (13-20% m/m) were tested. Relatively small differences in workability occurred, but all mixtures remained in the consistence class, where the mix composition was designed for. There was no reference coal fly ash available for the fly ash from co-combustion of meat and bone meal, so these results had to be compared with the results from the reference coal fly ash from the co-combustion experiment with paper sludge.

The mechanical properties of the concrete with fly ash from co-combustion of municipal sewage sludge and paper sludge were not substantially influenced. There were some non-univocal variations in the mechanical properties and the freeze-thaw salt resistance of concrete with fly ash from co-combustion of meat and bone meal. There was no explanation for this. Possible explanations are inhomogeneity of samples and differences in curing of test samples and the performance of the tests. Freeze-thaw salt resistance tests on concrete with fly ash from co-combustion of municipal sewage sludge and coal fly ash showed that there was no substantial effect of co-combustion.

The results on mortar confirm that the workability and strength development is not significantly influenced by co-combustion. Exception is the effect of co-combustion of Solid Recovered Fuel. The compressive strength at 28 and 91 days of mortars made decreases with increasing co-combustion up to 39% ash-based. This can be explained by the lower glass content in these fly ashes.

The influence of co-combustion does not only depend on the co-combustion percentage, but also on the amount of ash forming matter in the coal and biomass and on the chemical/mineralogical composition of both. The ash forming matter of biomass is different from that of coal (an exception may be paper sludge). Biomass from vegetable origin contains often less amount of network formers and intermediaries (especially SiO_2 and Al_2O_3) compared to coal. The probability of formation of free lime and periclase increases with increasing co-combustion. Both compounds may cause expansion of concrete. Fly ash from wood combustion contains 6-11 % m/m free lime. The soundness of these fly ashes is 31-77 mm, while 10 mm is seen as a safe maximum value for use in mortar and concrete.

The increase of the CaO content and the Na_2O equivalent will reduce the capacity of the fly ash to suppress ASR in concrete.

8.4 Explanation of properties by the composition of the fuel and the combustion process

Co-combustion of biomass from vegetable origin

Especially K, P, Ca and Mg are mainly organically associated in biomass from vegetable origin. Potassium in biomass behaves as a class II element according to the classification by Meij (see section 6.1). This in contrast with coal, where potassium is a class I element (most potassium in coal originates from minerals in the coal). During combustion potassium volatilizes and is able to react with other compounds. In ash from 100% wood combustion most potassium reacts with sulphur whereby Arcanite (K_2SO_4) as main compound is being formed and to a lower extent Alunite ($KAl_3(OH)_6(SO4)_2$), Langbeinite ($K_2Mg(SO_4)_2$) and Sylvine (KCl). If ash forming matter from coal is present, potassium reacts with the alumina silicates from the coal. In that case most potassium reacts with the alumino silicates and becomes part of the glass phase. In this way potassium participates in the pozzolanic reaction. Theoretically, the reactivity of the glass increases as the amount of modifiers (K) increases (less polymerization).

Phosphorus is a class I element (non-volatile) in coal combustion according to the findings of Meij. The results of Misra et al (see section 6.2) indicate that this is the same in biomass combustion from vegetable origin. This means that reactions whereby phosphorus is involved are physically restricted due to its non-vapour state during combustion. No phosphate bearing minerals were identified with XRD in fly ash from co-combustion with agricultural by-products, which means that phosphate is present as X-ray amorphous phase and/or as crystalline phases in contents below the detection limit of XRD. The SEM analyses of fly ashes show that phosphorus is associated with calcium and silicon to a lower extent. About 1/3 of the phosphorus present in the investigated fly ashes is acid insoluble, but soluble in KOH. This share is part of the glass phase. The spherical shape of the particles from co-combustion of wheat pollard pellets (see figure 4.4 and 4.5) indicates also that a molten status has occurred during combustion. This probably amorphous phase will participate in the pozzolanic reaction. The absence of retardation of the setting time can be well explained by the absence of alkali-phosphate in the fly ashes.

Calcium and magnesium are class I elements in both coal and biomass. About 2/3 of the CaO and MgO in the fly ash from co-combustion is acid soluble. Only a part of it is free lime. Periclase was not found with X-ray diffraction. This means that most of the acid soluble fraction have reacted with other compounds during combustion, like phosphate, silicates, carbonate and sulphate.

Co-combustion of biomass from animal origin

The investigated biomass from animal origin contains high concentrations of phosphorus and calcium. The ash forming matter in meat and bone meal consist mainly of apatite. During combustion of meat and bone meal in the boiler, apatite is converted to tri calcium phosphate ($Ca_3(PO_4)_2$). The stable form at high temperature (above 1150°C) is the α-modification (monoclinc crystal structure), but these persist in fly ash at low temperature. Practically all phosphorus is present in the acid-soluble phase, which means that hardly any phosphorus has been taken up in the glass phase of the fly ash. In other words: the interaction between the ash forming matter of coal on one hand and the ash forming matter of meat and bone meal combustion is very small. Otherwise, more phosphorus would be part of the amorphous glass phase of the generated fly ash. Both α tricalcium phosphate and glass phase with phosphate are able to react with portlandite, in this way acting as pozzolanic.

No phosphorus bearing minerals could be detected in the fly ash from co-combustion of poultry litter by X-ray diffraction. Most of the phosphorus was acid soluble (78%), but less than in the case of fly ash from co-firing of meat and bone meal. This can be explained by the fact that part of the phosphorus in poultry litter is organically bound (25-44%), which will lead to a different behaviour during combustion and differences in the formation of fly ash.

Co-combustion of biomass from industrial origin

The ash forming matter of sewage sludge contains relatively high contents of phosphorus due to the phosphorus removal during the cleaning step. At the time of sampling, most phosphate was removed with ferro salts. Examination with Scanning Electron Microscopy (SEM) of the co-combustion fly ash showed a ‘Fe phosphate’ and a ‘phosphate unclassified’ phase. The latter consists mainly of CaO, SiO_2, P_2O_5, and MgO. The former was present in spherical particles,

Phosphorus is able to act as a strong retarder for the hydration of cement when it is added as a phosphate with a higher solubility than calcium phosphates, like alkali phosphates. The absence of retardation despite of the presence of high phosphorus contents in co-combustion fly ash (up to 5.2 % m/m as P_2O_5) can be well explained by the absence of any alkali phosphates. Phosphorus in the glass phase will be released together with the other ions when the glass phase is attacked by the hydroxyl ions. This occurs when the pH of the pore water is sufficiently high. The released phosphorus will react with available calcium to form calcium phosphate and/or CPSH.

Paper sludge has a high content of CaO. Minerals in paper sludge are in general kaolinite, calcite and talc. Paper fillers are very small. During co-combustion these minerals are able to react with each other (different minerals present in one fuel particle) and thereby forming an alumina silicate glass, but with higher CaO and MgO (increase from 0 to 5% m/m and from 0 to 2% m/m respectively). In this way the probability of formation of free lime and periclase during combustion is reduced and thereby unsoundness of concrete.

The effects of co-combustion of biomass on the properties of fly ash and mortar and concrete have been investigated for biomass from different origins. The effects of biomass from vegetable and animal origin on fly ash are already described in the criteria of the standard EN-450 (criteria for properties of fly ash itself and criteria for property of cement paste and mortar made with this fly ash). From this point of view there is no need to extend the criteria in the standard EN 450 regarding the influence of co-combustion on workability and mechanical properties of concrete with fly ash. Based on the chemical and mineralogical composition, it can be expected that the same holds for durability of concrete. The same holds for paper sludge and municipal sewage sludge. However, the conclusion is not valid for Solid Recovered Fuel as it leads to effects on setting time which are not understood.

8.5 Properties of fly ash from the combustion of wood with or without coal

The main components in the ash forming matter of wood are CaO, SiO_2 and K_2O. The influence of co-combustion on the properties of fly ash (and so also the concrete made with it) are not significant up to 50% co-combustion fuel based, which is mainly caused by the low amount of ash forming matter. Generally, the amount of ash forming matter of wood is relative low compared to other types of biomass like palm kernels and wheat pollard pellets etc.

With increasing ratio wood/coal, the influence of wood on the properties of the ash increases. In this study, fly ash generated from 100% wood combustion has been investigated. The chemical composition shifts whereby the content of CaO, K_2O, SO_3 and P_2O_5 increase while SiO_2 and especially Al_2O_3 decreases. Wood fly ash shows a wide spectrum of minerals compared to coal fly ash. Minerals in considerable amounts present in wood fly ash and not in coal fly ash are arcanite, langbeinite, merwinite, periclase, lime and calcite. This leads to a different behaviour of cement paste and mortar made with this fly ash (unsoundness, different setting time). From a morphological point of view, wood fly ash is characterized by agglomerates while coal fly ash is characterized by smooth spherical particles. These agglomerates are the result of the ash-forming process in the boiler and especially the role of potassium.

8.6 Use of fly ash from combustion of wood with or without coal in concrete

The replacement of cement by wood fly ash results in a decrease of compressive strength of mortars, which is almost linear with the replacement level. At replacement level of 25%, the activity index at 28 and 91 days (see Box 1, subsection 2.2.4) is far below the range for coal fly ash and even below that of limestone filler, which means that it cannot be seen as a pozzolan.

False set occurs in cement paste with wood fly ash, which is most probably due to the reaction of the formation of gypsum out of arcanite with lime. Further, the soundness (measured with LeChatelier test) fails for standard fly ash cement pastes, which means that the binder is suspicious for use in concrete. This unsoundness is attributed to the presence of free lime in the fly ash. The unsoundness can be counteracted by grinding the fly ash to generate smaller particles that generate less tensile stress.

An alternative way of using wood fly ash as binder in mortar and concrete is to combine it with granulated blast furnace slag to act as an activator for the slag. Mortars have been prepared with different ratios fly ash/blast furnace slag (standard mortars; see Box 1.1, subsection 2.2.4). Fly ash was tested ground/unground, dry/prehydrated and with or without other additions. At replacement level 10-15% m/m the compressive strength at 28 days was maximum. It resulted in higher compressive strength at 2, 7 and 28 days compared to granulated blast furnace slag only. However, the effect was never comparable to the addition of 5-10% calcium sulphate.

8.7 Use of fly ash from co-combustion of biomass and the concept of circularity

Coal fly ash in concrete is able to improve the durability of concrete under many conditions, if the concrete is properly designed, placed and cured. A longer lifetime fits within the concept of a circular economy. An increase of alkalis and calcium is an important aspect of the impact of co-combustion on the concrete cycle. Up to about 80% co-combustion of green wood will result in a limited increase of the Na_2O equivalent and CaO content. The generated fly ash is still able to suppress ASR in concrete if replacement of cement is at a sufficient high level (calculated for average coal and wood compositions). If concrete with co-combustion fly ash is recycled whereby the hardened cement paste is used for the production of new clinker, the increase of phosphorus content is relevant as the phosphorus content of the raw meal may affect the early strength of concrete made with it. However, new raw materials have to be added to adjust the ratio of the main components CaO-SiO_2-Al_2O_3-Fe_2O_3 to produce the same clinker also, because the hardened cement paste will also be contaminated with fines from the aggregate even if new separation technologies are used. In this way the effect of phosphorus in co-combustion fly ash on the properties of the new clinker will be negligible in practice.

Harvesting of biomass leads inevitably to nutrient removal and, if no countermeasures are taken, to nutrient depletion of the soil and to depletion of nutrients at the end. It is already practiced, to leave the living parts of the tree in the forest, as these contain most of the nutrients in a tree, to restore the nutrient cycle as far as possible. A second step can be to bring the ash from the combusted wood back to the forest. Thereby all nutrients are recycled with exception of nitrogen. However, in a co-combustion situation the biomass is combined with coal, which leads to an increase of ash volume to be transported and spread and to the introduction of a considerable amount of heavy metals. It can be doubted whether this is efficient or effective. As an alternative, the use of fertilizers should be considered to restore the nutrient budgets of these forests. Also when atmospheric deposition of nitrogen is sufficient to compensate the loss by harvesting of wood.

In a future circular economy wood will be used in a cascade approach. At the end, after one or more recycling steps, it will be used for energy conversion. In most cases, the generated ash will be contaminated with mineral matter and undesired components (heavy metals) for the forest ecosystem. A chain approach will be necessary to avoid contamination in the wood fuel and thereby in generated wood ash. Further, it is preferred that wood ash is recycled to the forests where it originates from to avoid changes in heavy metal concentrations, which is complicated to realize.

For the realization of a circular economy regarding use of wood as renewable material and fuel it is necessary that more knowledge will be developed about the effects of long-term extraction of biomass on the nutrient budget of forest ecosystems and how ash from used wood can be utilized for restoration of the nutrient budget.

An important issue connected to the use of fly ash is the release of hazardous components to the environment. Leaching is seen as one of the relevant mechanism for release of hazardous components. This mechanism has been investigated in the Netherlands since several decades, this has resulted in specific regulation, namely the Dutch Besluit Bodemkwaliteit (Soil Quality Decree) [8.1]. This decree is the legal framework for the environmental assessment of building materials. The requirements in the original Bouwstoffenbesluit (Building materials Decree) were based on the concept of ‘Marginal Soil Burden’, which was seen as a maximum increase of the concentration of each of 19 defined inorganic components with 1% over 100 years in the upper layer of 1 m. In the Decree Soil Quality, which is a modification of the Building Materials Decree, the levels for each of these components are based on an eco-toxicological risk assessment, whereby 95% of the ecosystem does not indicate any demonstrable negative effects of the emissions from the building material. Concrete made with different fly ashes from co-combustion has been tested over years and never exceeded limits of the Decree Soil Quality [8.2].

In the last twenty years, KEMA has made extensive assessments of health and safety aspects of fly ash on request of the Dutch power sector. The results were validated by third parties and communicated to the society and the industry. If the standard safety precautions are taken, inhalation (by workers) is the most relevant path way for exposure of human beings to fly ash. Inhalation is more probable to occur than skin contact and oral uptake. Information about safe handling and use of fly ash is provided to transporters and concrete and cement industry. In this way they can take adequate protection measures [8.3] to reduce health and safety risks. This safety information is based on many studies of KEMA from 1997 up to now.

8.8 References

[8.1] Dutch Ministry of Infrastructure and Environment, 2007. Besluit Bodemkwaliteit (Soil Quality Decree)

[8.2] KEMA, 2007. Summary of leaching tests of concrete with fly ash from co-combustion tests 1995-2006. KEMA-report 50762822 TOS/MEC 07-9107.

[8.3] Vliegasunie, 2016. Safety Information Sheet Fly ash. Available at www.vliegasunie.nl.

9 CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

The goals in this PhD thesis are to create thorough understanding of the relation between the fuel, being biomass with or without coal, the combustion process, the properties of the generated fly ash and the technical performance of concrete made with this fly ash and the impact of (co)combustion of biomass on the sustainability and circularity aspects of the use of this fly ash in concrete. After a literature study, an experimental program was performed. This experimental program consisted of several steps: the generation of fly ashes from defined co-combustion experiments (pilot and full scale) and, second, investigation of the properties of these ashes and the properties of cement paste, mortar and concrete made with these fly ashes. Further, fly ashes from wood combustion in a pulverised coal boiler were investigated. Also the properties of cement paste and mortar using these ashes as addition and activator for ground granulated blast furnace slag were investigated. As last step the sustainability and circularity aspects of co-combustion ashes was evaluated.

Based on this research, the following conclusions are drawn:

- Co-combustion of biomass from vegetable and animal origin results in an increase of the content of CaO, P_2O_5, MgO and K_2O, whereby the content of other macro components, especially Al_2O_3, are decreased. The concentration of main components in fly ash from co-combustion of biomass of vegetable origin can be predicted using the concept of RE-factors if the concentration of these compounds in the fuels are known. The restriction is that the predicted amount of sulphur is a maximum and that the RE-factors are partly derived from heating experiments up to 1300ºC, while the temperature in the flame of the boiler may be 1700ºC.
- Calculations of the chemical composition of fly ash (with an average coal and wood composition) made clear that in the range up to about 80% m/m wood combustion (fuel based) the requirements of the standard EN 450 can be fulfilled regarding the components CaO, MgO, P_2O_5 and Na_2O_{eq}.
- The influence of co-combustion of biomass from industrial origin on the properties of fly ash differs from type to type. In the case of biomass consisting of different materials, especially waste or demolition wood and Solid Recovered Fuels, it may even differ from source to source or from lot to lot. In most cases the amount of heavy metals (like Pb, Zn) in the generated fly ash will increase.
- Phosphates in fly ash from co-combustion do not cause retardation of cement hydration due to its presence in low soluble compounds, namely in calcium phosphates and as part of the glass phase of fly ash. In this way phosphate may even contribute to the pozzolanic properties of the fly ash.
- Fly ash from large scale combustion of 100% wood has neither a potential as pozzolan in concrete (type II addition) nor as inert addition to concrete (type I addition). Wood fly ash contains high contents of compounds which are basically not improving the properties of concrete (durability, soundness, compressive strength). An alternative use in concrete would be as an activator of ground granulated blast furnace slag. However, it was shown that it was much less effective as, for instance, the use of anhydrite.

- The circularity of concrete with fly ash is not negatively influenced by co-combustion of biomass from agricultural and animal origin if the fly ash fulfils the limit values for CaO, P_2O_5 and Na_2O_{eq} given in the European standard EN 450.

9.2 Recommendations

The present European standard EN 450 postulates a maximum value for soluble phosphate. This parameter is superfluous as there is already a requirement for setting time and it is shown that all tested co-combustion fly ashes with increased phosphate contents, show no retardation of the hydration process, with exception of Solid Recovered Fuels.

For the realization of a circular economy regarding use of wood as renewable resource (material and fuel) it is needed that more knowledge will be developed about the effects of long-term extraction of biomass on the nutrient budget of forest ecosystems and how ashes from used wood can be utilized for restoration of the nutrient budget.

SUMMARY

Fly ash from coal combustion is widely used in concrete because fly ash is able to contribute to the strength development of concrete due to its pozzolanic properties. Further, the addition to concrete improves the workability, sustainability and durability of the concrete. It is important that the amount of specific components, especially free lime, periclase, sulphates and alkalis is limited, to avoid negative effects on the durability of concrete. Therefore, standards like EN 450 give requirements for the maximum concentrations.

Because of the concern about climate change more and more biomass is co-fired to reduce the CO_2 emissions of coal-fired power plants. This means that the fly ash is not only derived from the ash forming matter in coal, but also from different types of biomass. To keep fly ash as a valuable resource for concrete it is essential to create thorough understanding of the relation between the compositions of biomass, the combustion process, the properties of fly ash and concrete made with this fly ash.

The first step of the PhD-study was a literature study. Thereby, biomass was classified in three groups, based on the origin of the ash forming matter. These three groups are biomass from vegetable, animal and industrial origin, respectively. Biomass from vegetable origin is further subdivided into: wood and woody biomass, agricultural by-product and herbaceous biomass.

The second step consisted of co-combustion tests in a pilot-scale test boiler (1 MW_{th}) to generate co-combustion fly ashes with defined origin from the point of process conditions and fuels. Paso Diablo coal was combined with poultry litter, demolition wood and Solid Recovered Fuels (SRF). Each biomass was co-fired in three different percentages. One reference test was performed. The fly ashes were characterized physically, chemically and mineralogically and properties of cement paste and mortar with these fly ashes were determined.

The next step was an extensive experimental study on co-combustion fly ashes from full-scale co-combustion experiments using biomass from different origins, namely agricultural by-products, meat and bone meal, paper sludge and municipal sewage sludge. Also these fly ashes were characterized physically, chemically and mineralogically and the properties of cement paste, mortar and concrete made with these fly ashes were determined. In some cases a reference coal fly ash was available.

Further, three fly ashes were obtained from a modified pulverized coal-fired power plant, which is completely fired with wood pellets. These ashes were characterized and it was assessed to what extent these ashes can be utilised as a filler in concrete or as activator for ground granulated blast furnace slag. The main components in these fly ashes were CaO, SiO_2 en K_2O, while in coal ash these are SiO_2 en Al_2O_3. CaO is mainly present as free lime, calcite and to a less extent dicalciumsilicate. K_2O is mainly present as arcanite and to a less extent as sylvine. The wood fly ash consists mainly of agglomerates, which are the result of the ash formation in the boiler (role of potassium).

Co-combustion of biomass from vegetable and animal origin results in an increase of the content of CaO, P_2O_5, MgO and K_2O, whereby the content of other macro components, especially Al_2O_3, are decreased. The influence of co-combustion of biomass from industrial origin on the properties of fly ash differs from type to type. In the case of biomass consisting of different materials, especially waste or demolition wood and Solid Recovered Fuels, it may even differ from source to source or from lot to

lot. In most cases the amount of heavy metals (like Pb, Zn) in the generated fly ash will increase. Phosphates in fly ash from co-combustion do not cause retardation of cement hydration due to its presence in low soluble compounds, namely in calcium phosphates and as part of the glass phase of fly ash. In this way phosphate may even contribute to the pozzolanic properties of the fly ash.

The chemical composition of coal fly ash can be predicted using the concept of RE-factors if the concentration of elements, like Si, Ca, and K, in the coal are known. The concept has been extended to wood firing with and without coal using literature data and experimental data of fly ashes from co-combustion and fly ashes from wood combustion. The sulphur content in the fly ash will not be calculated using the RE factor, but based on the content of potassium. The restriction is that the predicted amount of sulphur is a maximum and that the RE-factors are partly derived from heating experiments up to 1300ºC, while the temperature in the flame of the boiler may be 1700ºC. Calculations of the chemical composition have been performed with an average coal and wood composition. This made clear that in the range up to about 80% m/m wood combustion (fuel based) the requirements of the standard EN 450 can be fulfilled regarding the components CaO, MgO, P_2O_5, SO_3 and Na_2O_{eq}.

Further, the application of fly ashes from co-combustion is assessed from the point of view of a circular economy. The effect of co-combustion on the recyclability of concrete with fly ash has been assessed (technical cycle). Also, the biological cycle has been assessed. The side effect of Wood harvesting is that nutrients are withdrawn from the soil of the forest. The nutrients end up in the ashes after combustion, with exception of nitrogen. It depends on several parameters to what extend the forest ecosystem is influenced. The spreading of ashes in the forests where the wood originates from is already practised in several countries to restore the nutrient balance. It is the idea that in the concept of a circular economy, wood will be used in a cascade approach of applications, with at the end energy conversion. The ashes will be contaminated in many cases, which implies that contaminants are introduced in the forest, besides the positive effect of restoration of the nutrient budget.

For the realization of a circular economy regarding use of wood as renewable resource (material and fuel) it is needed that more knowledge will be developed about the effects of long-term extraction of biomass on the nutrient budget of forest ecosystems and how ashes from used wood can be utilized for restoration of this nutrient budget.

SAMENVATTING

Vliegas afkomstig van de verbranding van poederkool (gemalen steenkool) wordt op grote schaal gebruikt in beton omdat het in staat is bij te dragen aan de sterkte-ontwikkeling van beton door zijn puzzolane eigenschappen. Daarnaast kan door de toevoeging van poederkoolvliegas de verwerkbaarheid en duurzaamheid van beton verbeterd worden. Het is daarbij belangrijk dat het aandeel van bepaalde componenten, met name vrije kalk, periklaas, sulfaat en alkaliën beperkt blijft zodat deze geen negatieve effecten op de duurzaamheid van beton kunnen uitoefenen. Er worden daarom in normen, zoals de EN 450, dan ook eisen gesteld aan de maximale concentraties.

Vanuit de zorgen over de klimaatverandering wordt, om de uitstoot van CO_2 te reduceren, meer en meer biomassa meegestookt in kolengestookte elektriciteitscentrales. Dit heeft tot gevolg dat de asvormende bestanddelen niet alleen uit steenkool afkomstig zijn, maar ook uit diverse soorten biomassa. Om er voor te zorgen dat vliegas als waardevolle grondstof voor beton behouden blijft, is het essentieel dat goed inzicht verkregen wordt in de relatie tussen de samenstelling van de biomassa, het verbrandingsproces, de eigenschappen van de vliegas en de eigenschappen van het beton vervaardigd met deze vliegas.

De eerste stap van dit promotieonderzoek bestond uit een literatuurstudie. In deze studie werd de biomassa ingedeeld in drie groepen op grond van de herkomst van de asvormende bestanddelen. Deze drie groepen betreffen: biomassa van plantaardige, dierlijke en industriële herkomst. De biomassa van plantaardige herkomst kan verder verdeeld worden in: hout en houtachtige biomassa, bijproducten uit de landbouw en zogenaamde kruidachtige biomassa.

De tweede stap bestond uit het uitvoeren van meestookproeven in een pilot-scale poederkoolketel (1 MW_{th}) om meestookvliegassen te genereren van gedefinieerde herkomst qua procescondities en brandstoffen. Daarbij werd steenkool (Paso Diablo) gecombineerd met pluimveemest, afvalhout of Solid Recovered Fuel (SRF). Elke biomassa werd in drie verschillende percentages meegestookt. Daarbij werd één referentieproef uitgevoerd. Vervolgens werden de vliegassen fysisch, chemisch en mineralogisch gekarakteriseerd en werden de eigenschappen van cementpasta en mortel met deze vliegassen bepaald.

De daaropvolgende stap bestond uit onderzoek aan vliegas afkomstig van meestookproeven op diverse Nederlandse poederkoolgestookte elektriciteitscentrales. De meegestookte brandstoffen betroffen diverse agroresiduen, diermeel, zuiveringsslib en papierslib. Ook deze vliegassen werden fysisch, chemisch en mineralogisch gekarakteriseerd. Vervolgens werden de eigenschappen bepaald van cementpasta, mortel en beton vervaardigd met deze vliegassen. In sommige gevallen waren referentievliegassen beschikbaar.

Ook werden drie vliegassen onderzocht afkomstig van een gemodificeerde poederkoolgestookte elektriciteitscentrale die volledig op hout gestookt wordt. Deze vliegassen werden niet alleen gekarakteriseerd, maar tevens werd beoordeeld in welke mate deze vliegassen in beton en mortel als vulstof of als activator voor gemalen gegranuleerde hoogovenslak (bindmiddel) toegepast kan worden. De belangrijkste componenten in deze vliegassen zijn CaO, SiO_2 en K_2O, terwijl dit in poederkoolvliegassen SiO_2 en Al_2O_3 zijn. CaO is hoofdzakelijk aanwezig als vrije kalk, calciet en in mindere mate als dicalciumsilicaat. K_2O is hoofdzakelijk aanwezig als arcaniet en in mindere mate als

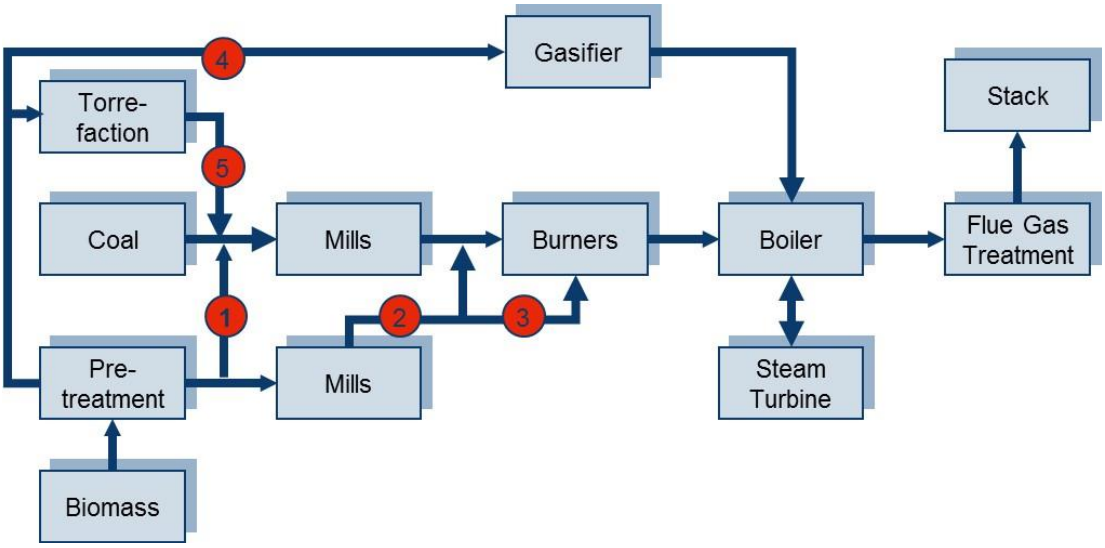
sylvien. Hout vliegas bestaat hoofdzakelijk uit agglomeraten. die het resultaat zijn van de asvorming in de verbrandingsketel (rol van kalium).

Het meestoken van biomassa van plantaardige en dierlijke herkomst resulteert in een toename van de concentratie CaO, P_2O_5, MgO en K_2O, waarbij het aandeel van andere macrocomponenten, met name Al_2O_3 afneemt. De invloed van biomassa van industriële herkomst verschilt van type tot type. In het geval van biomassa die samengesteld is uit verschillende materialen (met name afvalhout en Solid Recovered Fuels), kan het zelfs van bron tot bron of partij tot partij verschillen. In veel gevallen neemt het aandeel zware metalen (zoals Pb en Zn) in de vliegas toe. Fosfaten in vliegas afkomstig van meestoken veroorzaken geen vertraging in de hydratatiereactie omdat deze aanwezig zijn in slecht oplosbare vorm. Fosfaten zijn met name aanwezig als calciumfosfaten en als deel van de glasfase in vliegas. Fosfaten kunnen op deze wijze zelfs bijdragen aan de puzzolane eigenschappen van vliegas.

De chemische samenstelling van poederkoolvliegas kan berekend worden door gebruik te maken van het concept van RE-factoren, wanneer het aandeel asvormende bestanddelen en de concentratie van elementen als Si, Ca en K in de steenkool bekend zijn. Het concept is uitgebreid voor hout stoken met en zonder steenkool, door gebruik te maken van literatuur- en eigen gegevens van vliegassen afkomstig van meestoken en hout stoken. Het gehalte zwavel in de vliegas wordt daarbij niet berekend via de RE factor, maar via de concentratie kalium. De kanttekening daarbij is dat het gehalte zwavel een maximum waarde is en de afleiding deels gebaseerd is op hoge temperatuur experimenten, die zijn uitgevoerd tot maximaal 1300ºC, terwijl de temperatuur van de vlam van de ketel wel 1700ºC kan bedragen. Berekeningen van de chemische samenstelling van vliegas zijn uitgevoerd voor een gemiddelde steenkool- en houtsamenstelling. Daaruit blijkt dat in de range tot circa 80% m/m hout stoken (op brandstofbasis) voldaan kan worden aan de grenzen die in de norm EN 450 gesteld worden aan componenten als CaO, MgO, P_2O_5, SO_3 en het Na_2O_{eq}.

Verder is de toepassing van vliegassen uit meestoken beoordeeld in het licht van het concept van een circulaire economie. Beoordeeld is welke effecten het meestoken heeft op de recyclebaarheid van beton waarin vliegas uit meestoken is toegepast (technische cyclus). Ook de biologische cyclus is daarbij beoordeeld. Het oogsten van hout, voor welke toepassing dan ook, heeft tot nevengevolg dat nutriënten aan de bosbodem worden onttrokken. Na verbranding komen deze nutriënten in de assen terecht, met uitzondering van stikstof. De mate waarin dit het ecosysteem beïnvloedt hangt van diverse factoren af. Het verspreiden van de assen afkomstig van het verbrande geoogste hout wordt in diverse landen gepraktiseerd om de nutriëntenbalans te herstellen. Binnen het concept van de circulaire economie is het idee dat biomassa via een cascade van toepassingen wordt benut met aan het einde energie-conversie. De assen zullen in veel gevallen gecontamineerd zijn, wat tot gevolg heeft dat contaminanten in het bos geïntroduceerd worden, naast het positieve effect van herstel van de nutriëntenbalans. Voor de realisatie van een circulaire economie met betrekking tot het gebruik van hout als hernieuwbare grondstof (materiaal en brandstof) wordt aanbevolen dat meer kennis ontwikkeld wordt over de lange–termijn effecten van het onttrekken van hout op het nutriëntenbudget van ecosysteem van bossen en op welke wijze assen van gebruikt hout gebruikt kunnen worden voor het herstel van het nutriëntenbudget.

APPENDIX A: DIFFERENT TYPES OF CO-COMBUSTION



1. Co-milling of biomass with coal
2. Separate milling, injection in pf-lines, combustion in coal burners
3. Separate milling, combustion in dedicated biomass burners
4. Biomass gasification, syngas combusted in furnace boiler
5. Co-milling of torrefied biomass with coal

Source: Meijer, R. (DNV GL), 2017. Personal communication.

APPENDIX B: CONCENTRATION OF TRACE ELEMENTS IN COAL FLY ASH

Table A.1 Concentration of trace elements [mg/kg] (Source: KEMA Database Trace elements)

Element	Value[1]	Element	Value
As	25±18	Mn	633±288
B	267±84	Mo	14±8
Ba	1700±365	Ni	103±45
Be	9±3	Pb	54±132
Br	5±4	Rb	73±36
Cd	1.2±0.8	Sb	6±5
Ce	107±76	Sc	38±13
Co	45±13	Se	9±7
Cr	148±35	Sm	15±4
Cs	5.8±1.2	Sn	<8
Cu	102±19	Sr	1420±461
Eu	3.2±1.0	Te	<2,5
F	103±67	Th	30±9
Ge	76±51	Tl	<1,6
Hf	12±4	U	8±4
Hg	0.4±0.2	V	246±163
I	1.5±2.0	W	5±2
La	92±27	Zn	190±122

1) average ± standard deviation

APPENDIX C: CHARACTERISATION OF REFERENCE FLY ASHES

General

Ten coal fly ashes from 100% coal fired power generation from several Dutch coal fired power stations have been analyzed X-ray fluorescence or ICP after total digestion. The fraction dissolved in potassium hydroxide has been analysed and also the mineralogical composition. The fly ashes have been selected (see table C-1) based on variation in chemical composition to get a maximum variation in mineralogical composition.

The following analyses were performed (sequential dissolution; see subsection 3.2.4):

- The concentration of main components (already available from quality control at the power plants)
- The content and composition of the fraction dissolved in hydrochloric acid
- The content and composition of the fraction dissolved in potassium hydroxide
- X-ray diffraction analyses of the resulting residue from dissolution steps

Table C-1 Selected reference coal fly ashes

code	fuel
BWH	blend
KSBR	blend
RD1	Indonesian coal
RD2	South-African coal
RD3	Australian coal
RD4	Colombian coal
RD5	American coal
RD6	Polish coal
RD7	blend 1
RD8	blend 2

Chemical composition of the bulk

The composition of the fly ashes is presented in table C-2. The analyses have been performed with X-ray fluorescence or ICP after total digestion. The LOI was analyses according to NEN-EN 450. Coal fly ash has an extreme high content of CaO, which is well-known for coal from South-Africa. Remarkable is the high Fe_2O_3 of fly ash RD5.

Table C-2 Concentration of main components [% m/m]

	BWH	KSBR	RD1	RD2	RD3	RD4	RD5	RD6	RD7	RD8	av.	max	min
method	XRF	XRF	ICP	ICP	ICP	ICP	ICP	XRF	XRF	XRF			
Al2O3	22,3	23,7	24,8	26,6	26,3	20,3	23,0	24,8	26,4	22,1	24,0	26,6	20,3
CaO	5,2	2,2	4,1	10,7	3,2	2,1	2,4	4,2	3,6	3,0	4,1	10,7	2,1
Fe2O3	9,0	9,0	6,8	6,5	6,3	9,6	17,1	7,8	7,7	10,9	9,1	17,1	6,3
K2O	1,0	2,0	1,7	0,8	1,0	2,2	1,8	2,3	1,4	1,7	1,6	2,3	0,8
MgO	1,5	1,4	2,0	2,3	1,0	1,9	0,8	2,6	1,2	1,3	1,6	2,6	0,8
Na2O	0,2	0,3	0,4	0,3	0,3	1,0	0,6	0,9	0,5	0,4	0,5	1,0	0,2
P2O5	0,7	0,6	0,9	2,0	1,1	0,3	0,5	0,7	1,1	0,4	0,8	2,0	0,3
SO3	0,3	0,3	0,3	0,6	0,3	0,5	0,6	0,5	0,3	0,5	0,4	0,6	0,3
SiO2	54,6	54,4	49,5	41,8	53,5	51,7	46,9	50,8	51,3	56,0	51,1	56,0	41,8
TiO2	1,1	1,1	1,1	1,5	1,3	0,8	1,1	0,9	1,5	0,8	1,1	1,5	0,8
LOI	4,0	5,3	8,4	7,0	5,7	9,7	5,2	4,6	4,9	2,6	5,7	9,7	2,6

Chemical composition of the fraction dissolved in potassium hydroxide

The chemical composition of the fraction dissolved in potassium hydroxide has been determined with ICP after lowering the pH. Potassium could not be analysed as the use of KOH reagents. There was also contamination with sodium. The calculation of composition has been performed assuming two extreme situation, namely maximum potassium content in the amorphous phase and zero potassium in the residue and vice versa for the second worst case. The composition of this phase, the glass phase is calculated using the network theory of Zachariasen-Warren. The statistical data are based on the average of each range for D1-D8.

Table C-3a Chemical composition of the fraction dissolved in potassium hydroxide (100% = total dissolved fraction)

Component	KSBR	BWH	RD1	RD2	RD3
Al2O3	29,1	18,7	24,2-25,0	24,7-25,2	18,9-19,4
CaO	0,0	2,6	2,4-2,5	3,9-4,0	1,4-1,4
Fe2O3	0,7	5,2	4,3-4,5	2,9-2,9	3,5-3,6
K2O	2,6	0,7	2,7-0,0	1,4-0,0	1,8-0,0
MgO	0,0	1,0	1,7-1,7	1,1-1,2	0,8-0,8
Na2O	0,3	0,2	0,7-0,0	0,5-0,0	0,5-0,0
P2O5	0,4	0,2	0,5-0,5	0,6-0,6	0,6-0,6
SO3	0,1	0,1	0,0-0,0	0,1-0,1	0,1-0,1
SiO2	66,6	70,4	62,5-64,7	63,2-64,4	71,1-72,7
TiO2	0,1	0,9	0,9-1,0	1,6-1,6	1,3-1,3
sum Al_2O_3 + SiO_2	96	89	87-90	88-90	90-92
Ratio Al_2O_3/SiO_2	0,29	0,18	0,27	0,27	0,21
intermediaries [mol %]	20	13	18-19	18-18	14
Modifiers [mol %]	2,4	5,7	8,6-6,0	8,3-6,8	4,8-3,0
Network formers [mol %]	78	82	73-75	74-75	81-83

Table C-3b Chemical composition of the fraction dissolved in potassium hydroxide (100% = total dissolved fraction)

component	RD4	RD5	RD6	RD7	RD8
Al2O3	21,7-23,0	23,0-24,1	22,6-24,6	19,8-20,7	19,5-20,4
CaO	0,9-1,0	1,6-1,7	2,1-2,3	2,5-2,7	1,7-1,8
Fe2O3	6,4-6,8	7,8-8,2	4,7-5,1	4,8-5,0	5,1-5,4
K2O	3,8-0,0	3,3-0,0	5,8-0,0	3,4-0,0	3,6-0,0
MgO	1,7-1,9	0,9-1,0	1,6-1,7	1,3-1,3	1,5-1,6
Na2O	1,7-0,0	1,1-0,0	2,3-0,0	1,3-0,0	0,9-0,0
P2O5	0,2-0,2	0,5-0,5	0,5-0,5	0,8-0,8	0,2-0,3
SO3	0,0-0,1	0,0-0,0	0,1-0,1	0,1-0,1	0,1-0,1
SiO2	62,6-66,3	60,7-63,5	59,4-64,6	65,0-68,2	66,2-69,4
TiO2	0,8-0,9	1,0-1,1	1,0-1,1	1,1-1,2	1,1-1,2
sum Al_2O_3 + SiO_2	84-89	84-88	82-89	85-89	86-90
Ratio Al_2O_3/SiO_2	0,25-0,27	0,27-0,29	0,25-0,27	0,22-0,23	0,22-0,23
intermediaries [mol %]	18-19	20	18-19	15-16	15-16
Modifiers [mol %]	8,9-4,4	7,4-3,8	12,3-5,9	9,1-5,4	8,2-4,8
Network formers [mol %]	74-77	73-76	70-75	76-79	77-79

Table C-3c Chemical composition of the fraction dissolved in potassium hydroxide (100% = total dissolved fraction)

component	mean	st.dev.	max	min
Al2O3	22,6	3,2	29,1	18,7
CaO	1,9	1,1	3,9	0,0
Fe2O3	4,6	2,0	8,0	0,7
K2O	1,6	0,7	2,9	0,7
MgO	1,2	0,5	1,8	0,0
Na2O	0,5	0,3	1,1	0,2
P2O5	0,4	0,2	0,8	0,2
SO3	0,1	0,0	0,1	0,0
SiO2	65,9	3,4	71,9	62,0
TiO2	1,0	0,4	1,6	0,1
sum Al_2O_3 + SiO_2	89	3,0	96	86
Ratio Al_2O_3/SiO_2	0,25	0,03	0,29	0,18
intermediaries [mol %]	17	2,5	20	13
Modifiers [mol %]	6,2	1,9	9,1	2,4
Network formers [mol %]	77	3,1	82	73

Mineralogical composition of the fraction dissolved in potassium hydroxide

The results of the X-ray diffraction analyses are presented in table C-4.

Table C-4 Mineralogical composition of the fly ashes

	Acid soluble		Soluble in KOH	Insoluble in KOH							
		CaO free		quartz	mullite	hematite	magnetite	Rutile	feldspar	rest	LOI
method	grav.	anal.	grav.	X-ray diffraction							
BWH	8,2		41,8	6,3	14,9	2,1				23,2	3,5
KSBR	9,4		34,4	4,9	11,4	0,2				34,4	5,3
RD1	6,5	0,1	56,1	6,7	12,9	0,2	0,5	0,1	0,0	8,5	8,4
RD2	10,6	0,8	46,7	4,6	18,8	0,4	0,7	0,0	0,0	10,3	7
RD3	2,4	0,1	51,2	9,1	30,2	0,4	0,7	0,0	0,1	0,0	5,7
RD4	3,7	0,3	45,1	9,2	12,3	0,6	1,2	0,0	0,0	18,0	9,7
RD5	4,76	0,14	52,3	4,9	11,7	1,2	1,7	0,0	0,0	18,1	5,2
RD6	9,1	0,03	41,9	7,9	9,3	0,7	0,8	0,0	0,0	25,7	4,6
RD7	6,5	0,3	45,3	7,4	19,5	0,9	0,9	0,1	0,0	14,3	4,9
RD8	6,8	0,1	47,4	10,4	17,0	0,4	0,7	0,1	0,0	14,4	2,6
Average	**6,8**	**0,2**	**46,2**	**7,1**	**15,8**	**0,7**	**0,9**	**0,0**	**0,0**	**16,7**	**5,7**
Deviation	**2,6**	**0,2**	**6,2**	**2,0**	**6,1**	**0,6**	**0,4**	**0,0**	**0,0**	**9,6**	**2,2**
min.	**10,6**	**0,8**	**56,1**	**10,4**	**30,2**	**2,1**	**1,7**	**0,1**	**0,1**	**34,4**	**9,7**
max.	**2,4**	**0,0**	**34,4**	**4,6**	**9,3**	**0,2**	**0,5**	**0,0**	**0,0**	**0,0**	**2,6**

APPENDIX D: EDX ANALYSES OF WOOD FLY ASH PARTICLES

Table D-1 Results of EDX analyses of wood fly ash particles

figure	EDX Analyse	morphology particle	elements									
			C	O	Mg	Al	Si	P	S	K	Cl	Ca
5.5	1	agglomerate	10	64	0.3		0.2	0.1	1.3	5.0	0.3	17.7
5.5	2	agglomerate	9	67	4.3	2.0	0.2	1.0	0.3	1.5	0.1	14.3
5.5	3	solid	10	54	0.3	5.8	15.7		0.3	8.7	0.1	3.8
5.5	4	solid	8	50	1.7	0.6	12.3		0.9	9.0	0.2	15.0
5.5	5	agglomerate	9	56	3.8	0.9	3.2	1.6	1.4	4.9	0.2	17.1
5.5	6	agglomerate	16	58	3.2	0.3	0.5	0.8	2.2	10.1	0.5	7.2
5.5	7	agglomerate	16	62	0.8	0.2	0.5	0.2	1.7	8.2	0.5	8.1
5.5	8	agglomerate	19	53	2.2	0.1	0.4	0.5	2.0	11.3	1.8	7.6
5.5	9	agglomerate	12	61	0.3	0.1	0.2	0.1	1.4	12.4	0.8	10.6
-	1	solid	9	61	3.5	1.0	3.4	1.6	0.8	3.4	0.4	14.8
-	2	solid	8	61	1.9	2.6	1.2	1.5	0.3	1.7	0.1	17.9
-	3	solid	8	56	2.2	2.1	0.7	1.3	0.7	3.7	0.6	21.1
-	4	solid	9	62	0.1		23.3		0.2	3.5		0.4
5.4	1	solid	10	56	3.4	3.1	11.3	0.5	0.6	4.3	0.4	7.2
5.4	2	agglomerate	12	62	1.4	0.4	1.1	0.4	2.4	12.5	1.1	5.3
5.4	3	agglomerate	40	40	1.3	0.4	0.9	0.3	1.5	8.7	0.9	4.2
5.4	4	agglomerate?	11	61	3.0	0.5	1.1	1.0	1.4	6.0	0.7	12.8
5.4	5	solid	8	59	10.4	1.1	3.5	0.7	0.4	1.7	0.1	12.7

APPENDIX E: CALCULATED COMPOSITION OF ASHES FOR NUTRIENT RECYCLING

Table E-1 shows the calculated composition and volumes of ashes from wood or wood with coal. Four scenarios of application of harvested wood and nutrient recycling are distinguished:

- Reference scenario: wood is harvested and directly used as fuel without addition of other fuels or agents. The resulting fly ash and bottom ash is used for nutrient recycling in the forest
- Scenario I-a: as reference scenario but wood is fired together with coal. The wood/coal ratio is 80/20. The resulting fly ash and bottom ash is used for nutrient recycling in the forest
- Scenario I-b: as reference scenario but wood is fired together with coal. The wood/coal ratio is 50/50 The resulting fly ash and bottom ash is used for nutrient recycling in the forest
- Scenario II: wood is harvested in the forest and first used for construction and timber wood. Wood is collected after demolition and used as fuel the generated fly ash and bottom ash is used for nutrient recycling in the forest.

The calculations of the chemical composition of the generated ashes have been performed with the KEMA Trace model with modified approach for the SO_3 content (see section 6.3). Coal composition: Dutch Average Coal Composition 2014 (NNG 2014).Wood composition: table 2.5 and section 6.3. Composition of Demolition wood: fuel used for pilot-scale experiments. See section 3.3.

Table E-1 shows also the concentration of heavy metals in the ash for the different scenarios. The concentration of several heavy metals in co-combustion scenarios is lower than in ash from pure wood (reference scenario). This is a bit misleading as the ash volume increases strongly. The net effect is negative, which means that more heavy metals are introduced in the forest than extracted by the harvested wood. Adjustment of the ash volume to be recycled to the small contribution of coal and contamination in demolition wood to the nutrient balance does not change this.

Table E-1 Comparison of scenarios: increase of ash volume, amount of nutrients and concentration of heavy metals not being micro-nutrients. Composition and volume based on calculations with KEMA TRACE model (see further main text)

Scenario		reference	I-a	I-b	II
First use		fuel	Fuel with 20% coal	Fuel with 50% coal	Construction & Timber wood
Second use		Nutrient recycling	Nutrient recycling	Nutrient recycling	Fuel
Third use		-	-	-	Nutrient Recycling
Increase ash volume	-/-	-	5x	15x	3x
Primary macro nutrients$^{1)}$	% m/m	27	8	4	2
Secondary macro nutrients$^{2)}$	% m/m	40	13	8	22
Cd	mg/kg	24	6.3	2.9	140
Hg	mg/kg	<0,03	0.4	0.5	5
Ni	mg/kg	250	139	122	340
Pb	mg/kg	217	86	61	55100

1) Calculated as sum of $P_2O_5 + K_2O$. The amount of N is negligibly

2) Calculated as sum of $CaO+MgO+SO_3$

APPENDIX F: LIST OF MINERALS

Name	Formulae	Crystal system	Density [kg/m^3]	Hardness Mohs
Akermanite	$Ca_2Mg(Si_2O_7)$	Tetragonal		5-6
Alunite	$KAl_3(OH)_6(SO4)_2$	Romboëdric	2.7-2.8	3.5-4
Anatase	TiO_2	Tetragonal	3.8-3.9	5.5-6
Anhydrite	$CaSO_4$	Orthorhombic	2.9-3.0	3-3.5
Ankerite	$CaFe(CO_3)_2$	Romboedric	3.0-3.1	3.5-4
Anorthite	$Ca(Al_2Si_2O_8)$	Triclin	2.76	6-6.5
Apatite	$Ca_5(PO_4)_3(OH, F Cl)$	Hexagonal	3.16-3.22	5
Aragonite	$CaCO_3$	Orthorhombic	2.95	3.5-4
Arcanite	K_2SO_4	Orthorhombic	2.66	2
Augite	$CaMg(Si_2O_6)$	Monoclinic	3.3-3.5	5.5-6
Barite	$BaSO_4$	Orthorhombic	4.48	3-3.5
Biotite (mica)	$K(Mg,Fe)_3AlSi_3O_{10}(OH,F)_2$	Monoclinic	2.8-3.2	2.5-3
Calcite	$CaCO_3$	Trigonal	2.6-2.8	3
Chalk	$Mg_3Si_4O_{10}(OH)_2$	Monoclinic	2.7-2.8	1
Chlorite group	Fe-Mg silicates	monoclinic	2.5-4.8	2-2.5
Corrundum	Al_2O_3	Trigonal	3.9-4.1	9
Diopside	$CaMgSi_2O_6$	monoclinic	3.22 - 3.38	5.5-6.5
Dolomite	$Ca, Mg(CO_3)_2$	Trigonal	2.85-2.95	3.5-4
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$	trigonal	1.77	2-2.5
Farringtonite	$Mg_3(PO_4)_2$	monoclinic	2.74	
Graftonite	$(Fe, Mn, Ca)_3(PO_4)_2$	monoclinic	3.67	5
Goyazite	$SrAl_3[(OH)_6lPO_4lPO_3OH]$	romboedric	3.2	4.5
Gypsum	$CaSO_4.2H_2O$	Monoclinic	2.3-2.4	1.5-2
Halite	$NaCl$	Cubic	2.1-2.2	2
Hematite	Fe_2O_3	Trigonal	5.2-5.3	6.5
Illite (mica)	$K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$	monoclinic	2.8	1-2
Kaolinite	$Al_2SiO_5(OH)_4$	Triclin	2.6	1
Langbeinite	$K_2Mg_2(SO_4)_3$	isometric	2.83	3.5-4
Larnite (belite)	Ca_2SiO_4	monoclinic	3.3	6
Lime	CaO	isometric		
Leucite	$KAlSi_2O_6$	tetragonal	2.5	5.5-6
Maghemite	Fe_2O_3	isometric		6
Magnetite	Fe_3O_4	Cubic	5.2	5.5
Marcasite	FeS_2	Orthorhombic	4.8-4.9	6-6.5
Merwinite	$Ca_3Mg(SiO_4)_2$	monoclinic	3.15-3.32	6
Mullite	$3Al_2O_3.2SiO_2$ - $2Al_2O_3.SiO_2$	Orthorhombic	3.2	6-7
Muscovite (mica)	$KAl_2(AlSi_3O_{10})(OH)_2$	monoclinic		2.5
Parawollastonite	$CaSiO_3$			
Periclase	MgO	Cubic	3.7-3.9	6

Plagioclase group	$NaAlSi_3O_8$ to $Ca(Al_2Si_2O_8$	Tricline	2.61-2.76	6-6.5
Portlandite	$Ca(OH)_2$	isometric		
Pyrite	FeS_2	Cubic	5.0-5.2	6-6.5
Rutile	TiO_2	tetragonal	4.2-4.3	6-6.5
Quartz	SiO_2	Trigonal	2.65	7
Siderite	$FeCO_3$	tetragonal	3.7-3.9	4-4.5
Sillimanite	Al_2SiO_5	orthorhombic	3.2	6-7
Srebrodolskite	$Ca_2Fe_2O_5$	orthorhombic		5.5
Strontianite	$SrCO_3$	orthorhombic	2.95	3.5
Sylvine	KCl	Cubic	1.99	2
Trydimite	SiO_2	triclinic	2.25-2.28	6.5-7
Vermiculite	$Mg_{0.7}(Mg,Fe,Al)_6(Si,Al)_8O_{20}(OH)_4 \cdot 8H_2O$	Monoclinic	2.3	1.5-2
Wollastonite	$CaSi_3O_3$	Triclinic	2.8-2.9	4

Literature:
Duda, R. and Reijl, L., 1986.De grote encyclopedie der Mineralen. Rebo productions
Pannekoek A.J. and Van Straaten L.M.J.U., 1992. Algemene geologie. Wolters- Noordhoff
www.mindat.org

Curriculum vitae

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Publications (reviewed)

- Sarabèr, A.J., 2003. Effects of co-combustion on the performance properties of coal fly ash. Background report for CUR-recommendation 94. CUR-report 2003-8.
- Sarabèr, A.J. et al, 2011. Ashes from combustion of cacao residues for nutrient recycling. In: Recycling of biomass ashes, pp 107-120. Editors: Heribert Insam and Brigitte A. Knapp. Springer Verlag.
- Sarabèr, A.J., 2012. Co-combustion and its effects on fly ash quality; pilot-scale experiments. In: Fuel Processing Technology 104 (2012) pp 104-114.
- Sarabèr, A.J., 2014. Co-combustion and its effects on fly ash quality; real-scale experiments. In: Fuel Processing Technology 124 (2014) pp 68-82.