

MASTER

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

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EINDHOVEN UNIVERSITY OF TECHNOLOGY

Paper sludge fly ash

From industrial wastes to new cementitious
mixes

ing. Guillaume Doudart de la Grée

27/6/2012

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Summary

In this study, utilization options are investigated for paper-sludge fly ash. This is because of expansive landfill costs when the material is not utilized and the use of paper sludge fly ash in the concrete industry is minimal. Problems are the increased water demand and content of free lime, which reduce the properties of concrete.

First, the physical and chemical properties of paper sludge fly ash are investigated leading to the suggestion of two possible options to increase the utilization of paper sludge fly ash:

1. Decrease the high water demand by lowering the free lime content of paper sludge fly ash;
2. Use paper sludge fly ash as activator for coal combustion or other types of fly ashes.

After investigation, several attempts to decrease the free lime content or use it sufficiently did not have positive effects on the strength results compared to untreated paper sludge fly ash. However, it is found that paper sludge fly ash has a positive effect on coal combustion fly ash and can by this increase its own utilization.

Further research could examine the potential of larger replacement or even increase the use of coal combustion fly ash.

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1. Introduction

1.1 Problem statement paper sludge fly ash (Topcrete®)

Paper sludge is a residue from the paper recycling process. In the past it consisted of unusable ingredients that needed to go to landfill sites or incineration plants. Nowadays, using an adjusted burning process with low emissions, fly ashes with good pozzolanic properties and absence of any hazardous contaminants are created. Application options are already in place, such as a 10% replacement of cement or substitute in soil stabilization, although on a larger scale there is still no application available.

1.2 Problem definition

Within the Netherlands, there is the need to increase the knowledge about the utilization of paper-sludge fly ashes because of expensive landfill costs. So far the reuse of these materials in the concrete industry is minimal because of the increased water demand and content of free lime, which can reduce the properties of concrete.

1.3 Objectives and research questions

The aim of this research is to find new utilization applications for paper sludge fly ash from a paper-residue burning factories. The role of these materials in a concrete mixture as a binder (partly or totally replacing cement) or filler will be investigated. The scope is to develop a more sustainable and cost-efficient concrete that gives by-products a second life and with that, reduces the CO₂ emissions of the cement production industry. In order to do so, paper-sludge fly ash needs to be chemically optimized to increase its utilization in the concrete industry.

While examining the physical and chemical properties of paper sludge fly ash as described in Chapter 3, two possible options to increase the utilization of paper sludge fly ash have been suggested:

1. Reduce the high water demand by lowering the free lime content of paper sludge fly ash;
2. Use paper sludge fly ash as activator for coal combustion or other types of fly ashes.

1.4 Structure of the report

This report can be divided into two parts. The first part (Chapter 1-3) comprises the theory that describes the origin of paper sludge fly ashes and chemical and physical properties. The second part (Chapter 4-6) described the treatment method to upgrade paper sludge fly ash, performed tests, results and ends with a discussion, conclusions and recommendations.

2. Paper sludge fly ash origin

Paper sludge fly ash is currently used as replacement for cement / lime and as substitute in soil stabilization. The problems however with paper sludge fly ash are the moderate rheological properties of its water-based mixture and low density. To gain more insight about paper sludge fly ash, background information about the origin of the material and production is very important. In this chapter the background information of paper sludge ashes is provided.

2.1 History

The paper recycling industry produces wastes, out of which 10% paper sludge that cannot be reused anymore because of too short fibres (paper cannot bind anymore), inorganic materials and ink. However, with suitable land scarcity in the densely populated Netherlands, and an ever present risk of long term soil and groundwater contamination, the Dutch Government (through the introduction of both legislation and landfill taxes) began pressuring its domestic paper recycling industry to find an alternative to landfill. While conventional industrial incineration offered a possible solution, concern about dioxin emissions, and widespread protests from local communities made this option both financial and politically unacceptable (CDEM, 2011).

In the early nineties, four large Dutch paper producers went into a partnership to solve the paper residue problem. The newly formed company was named CDEM, the initials of their own names: Celtona, Doetinchem, Edet and Mayr Melnhof.

Using a newly developed incineration process, minerals can be recovered and paper recycling waste streams can be used to manufacture paper sludge fly ash. This requires a combustion process under strict conditions to activate the kaolin clay.

2.2 Fuel

Paper sludge is the residue leftover from the paper recycling process. It mainly consists of 50% water, 25% short fibres providing strength to paper and 25% of other minerals like calcium oxide (which gives paper a white colour) and clay to make paper smooth. Before transported to the combustion plant, large amounts of water are removed in order to lower the transport.

2.3 Process

The installation of the combustion of paper sludge is comparable with the fluidized bed installation. The small changes in the installation will be shortly described per stage. The complete process is illustrated in Figure 1.

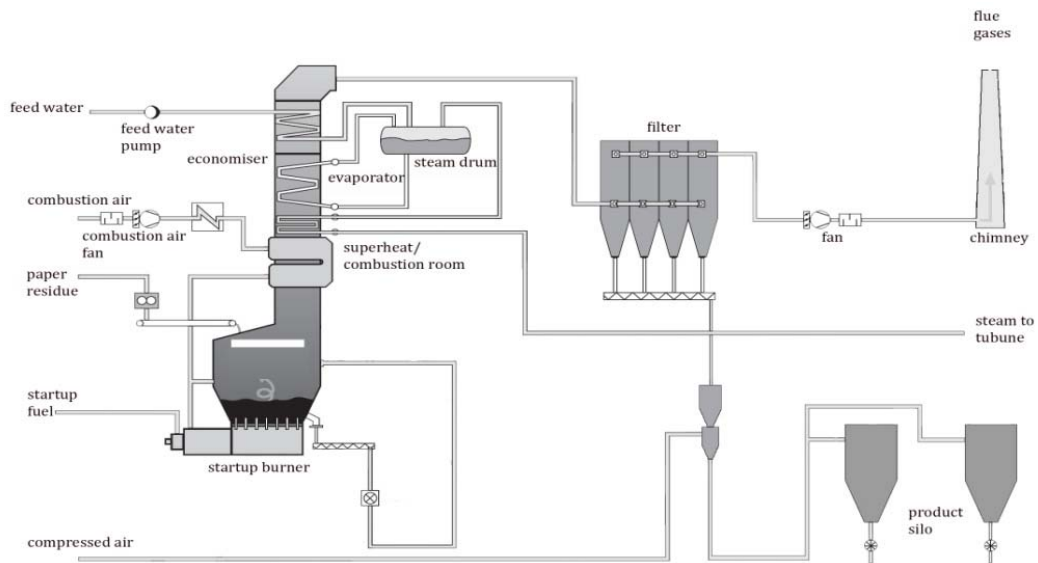


Figure 1: schematic overview paper sludge process (CDEM, 2003)

2.3.1 Paper sludge bunker

Paper sludge coming from paper recycling factories is firstly stored in a big bunker. The storage capacity of this bunker is 500 ton. This is necessary because the pulp supply rate varies because of 20 different suppliers. In the bunker the different paper sludge's are mixed to get a more homogeneous mixture. From that point it is transported with cranes to different inlets of pelletizers. Around 3800 ton of paper sludge is incinerated every week in a 24 hours, 7 days per week manufacturing process; 24% is transformed into paper sludge fly ash depending on the pulp supply. The maximum capacity is 25 ton of paper sludge incinerated per hour.

2.3.2 Pelletizers

The pelletizers make pellets from the paper sludge as illustrated in Figure 2. This method increases the efficiency in the combustion room because of higher contact surface which leads to low emissions and better product manufactory.



Figure 2: illustration of pelletizers installation with pellets coming out

2.3.3 Combustion room

The combustion room consists of two parts, the lower part is the fluidized bed and the upper part is the freeboard which is isolated to decrease the emission. From the pelletizers the pellets are falling from a certain height in the fluidized bed. Instead of burning at a high temperature, the temperature of the bed is kept around 780 degrees Celsius. In this way, the pellets are not completely burned and the useful materials like metakaolin and calcium carbonate will remain. Partly the pulp is incinerated at the height of the freeboard; the remaining part is incinerated inside the bed. There, calcium oxide (CaO) present in the paper sludge is sticking on the sand particles creating balls of burned paper sludge which will grow with more sticking CaO particles. For that reason, compared to other fluidized beds, the bed in the paper sludge factory increases in size. There are two options to control the growth of the bed, one is by reducing the pellet amount entering the combustion room and second, by removing fluidized balls between one and three mm and crush them into a maximum size of two mm to keep the bed into shape.

2.3.4 Further installation

After the combustion room the remaining product is guided to the bag house filter by a primary air flow to remove the big and small particles from the gas flow. The system is completely cooled by water that will become steam and can be used in a steam turbine to generate electricity. From the weekly production around 500 MWh of electricity can be generated. However this depends on the pulp supply. Because burning residue during and after combustion is sticking on the wall surface of the combustion room, big air horns producing vibrations and removing the burned paper residue from the walls are used. In the end of the process everything is stored in two silos with a capacity of 300 ton each.

The complete process from bunker until silos is monitored and registered in the control room. At full capacity, the plant can produce 50.000 tons of paper-sludge fly ash per year which constitutes only 1% of the total Dutch cement production per year.

2.4 The by-product fly ash in general

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

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

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

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

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

2.4.1 Coal combustion fly ash

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

The creation of coal combustion fly ash is illustrated in Figure 3, it starts from the moment when the mineral portion of coal is heated above the melting point. From that point, small drops are formed and when they are cooling down the formation of spherical fly ash particles begins. When the temperature of the particles is not above the melting point, less spherical fly ash particles are formed and more fused particles are detected (illustrated in Figure 3). This leads to less small particles of 10 microns and more porous coal particles Figure 4 (CUR, 1992). In general, the production of all fly ashes is similar to the formation of coal combustion fly ash.

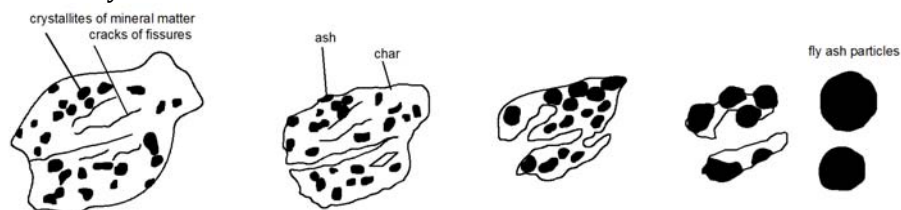


Figure 3: formation of coal combustion fly ash

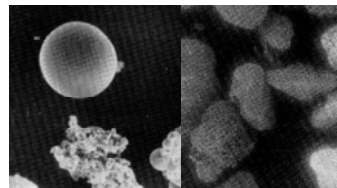


Figure 4 Left, "ideal" fly ash and fused particles. Right, les spherical: fine coal particles

Later, when air pollution problems were recognized, better installations were constructed to collect fly ash using cyclone separators, electrostatic precipitators or bag house filters. Depending on the collection system, varying from mechanical to electric precipitators or bag houses and fabric filters, about 85 to 99.9% of the ash from the flue gases is retrieved in the form of fly ash. Fly ash accounts for 75 to 85% of the total coal ash and the remainder is collected as bottom ash or boiler slag. The current worldwide annual production of coal combustion fly ash is about 500 million tons and forms 75-80% of the total ash production worldwide. Only 3 to 57% of this production is used (Joshi, 1979). The rest is landfilled but this is not economically desirable because of high landfill costs, and environmental risks such as leaching to the ground, thereby creating water and also air pollution. However, the government in the Netherlands aimed to reuse the produced coal combustion fly ash from the beginning. This goal was achieved in 1988, when from the annual production of 712,400 tons fly ash, 98% was reused. This percentage represents the highest amount in the world (CUR, 1992). In 2007, 814.717 tons of fly ash were produced: 506.139 tons of fly ash were used as cement filler and concrete mixtures and 88.054 ton of fly ash were used in the production of pozzolanic cements. In total, this forms 73% of fly ash production (Vliegassunie, 2008). One of the cements is called "Portland fly ash cement" that is classified among other types as described in Figure 5.

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

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

Figure 5: Portland cement types conforming EN-197-1: Composition, specifications and conformity criteria for common cements

2.4.2 Bio-energy fly ash

The increase of using biomass for electricity generation in power plants leads to fly ashes different from the ‘old fashion’ coal combustion fly ash. The bio-energy fly ash created from burning biomass has different characteristics and properties in comparison to coal combustion fly ashes because of different combustion input and therefore, still need to prove their utilization in concrete mixtures. A recent study presents a potential binder with comparable strength properties as coal combustion fly ash (Doudart de la Grée, 2012).

3. Paper sludge fly ash properties

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

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

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

- The first one is a paper sludge fly ash, termed P;
- The second one is a commercial coal combustion fly ash known as: PKVA SMZ (Class F) and is termed F.

3.1 Paper sludge fly ash properties

Paper sludge fly ash possesses pozzolanic activity due to the fact that it contains metakaolin. Metakaolin is obtained from kaolin clay. This fine white clay mineral is composed of aluminium disilicate. When kaolin is heated at a temperature between 500 and 800 degrees Celsius, dehydroxylation of kaolin takes place, forming metakaolin as described by:



When higher temperatures are used, kaolin is burnt and will result in mullite as described by:



Mullite is an unwanted crystalline material because it is not reactive. Metakaolin is a silica-based product that, on reaction with Portlandite ($\text{Ca}(\text{OH})_2$ or CH), produces C-S-H gel at ambient temperature. Metakaolin also contains alumina that reacts with CH to produce additional alumina-containing phases, including C_4AH_{13} , C_2ASH_8 , and C_3AH_6 (Changling et al., 1995; Zhang & Malhotra, 1995).

The major constituents of metakaolin are SiO_2 and Al_2O_3 in the form $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The crystallinity of the products depends principally on the $\text{A}_2\text{S}/\text{CH}$ ratio and reaction temperature (Murat, 1983; Kinuthia et al., 2000; Wild et al., 1998).

3.2 Oxide composition

Table 1 presents the most important oxides in paper sludge fly ash (P), coal combustion fly ash (F) and CEM I 42.5 N. The data is used for oxide engineering. In this method the oxides of different fly ashes are compared with a reference. This way an expectation can be made of how the material will react; the smaller the difference, the better the composition. The calcium and silica oxide amount is similar to that of cement.

Generally, paper-sludge fly ash contains CaO (calcium oxide as free lime, quicklime) 23%, CaCO₃ (calcium carbonate) 41% and Al₂O₃ • 2SiO₂ metakaolin 29% as the main constituents (CDEM, 2003).

Table 1: Oxide composition of different materials obtained by XRF

| Oxide | Paper sludge fly ash (P) [%] | PKVA SMZ (F) [%] | CEM I 42.5 N [%] |
|--------------------------------|------------------------------|------------------|------------------|
| MgO | 2.0 | 1.9 | 1.6 |
| Al ₂ O ₃ | 15.0 | 22.3 | 5.8 |
| SiO ₂ | 22.0 | 55.0 | 18.8 |
| SO ₃ | 1.0 | 1.4 | 4.5 |
| CaO | 57.0 | 4.4 | 62.0 |
| Fe ₂ O ₃ | 0.7 | 8.4 | 3.6 |

3.3 Fineness

Generally a larger amount of particles smaller than 45 microns can result in a better packing and more pozzolanic activity. More pozzolanic activity is due to reaction kinetics: finer particles react faster. Also the workability of the concrete mix will be higher because smaller particles result in a higher Hägermann flow size (CUR, 1992). For other fly ash types a large percentage of particles larger than the 45 microns has been reported to have a negative effect on the 28 and 90 days strengths of normally cured Portland cement fly ash mortars (Mehta, 1984; Diamond, 1985).

Fineness is one of the primary physical characteristics of fly ash that relates to its pozzolanic activity (Joshi, 1970). When examining fly ash for its particle size distribution the NEN-EN-450 sets the limit of 40% for the maximum amount of fly ash retained on the 45 microns mesh sieve on wet sieving, as a quality control measure. Figure 6 illustrates the particle size distribution for five different types of fly ash measured with a Mastersizer 2000 Ver. 5.60 using the laser diffraction method. Figure 6 presents the particle size distribution of the three investigated materials and Figure 7 presents the percentage of particles that are passing through a sieve subdivided from 100% (everything passes) to 0% (nothing passes). The X-axis presents the particle size distribution with increasing dimensions from left to right, while the Y-axis represents a volume percentage from the total sample increasing from the bottom to the top.

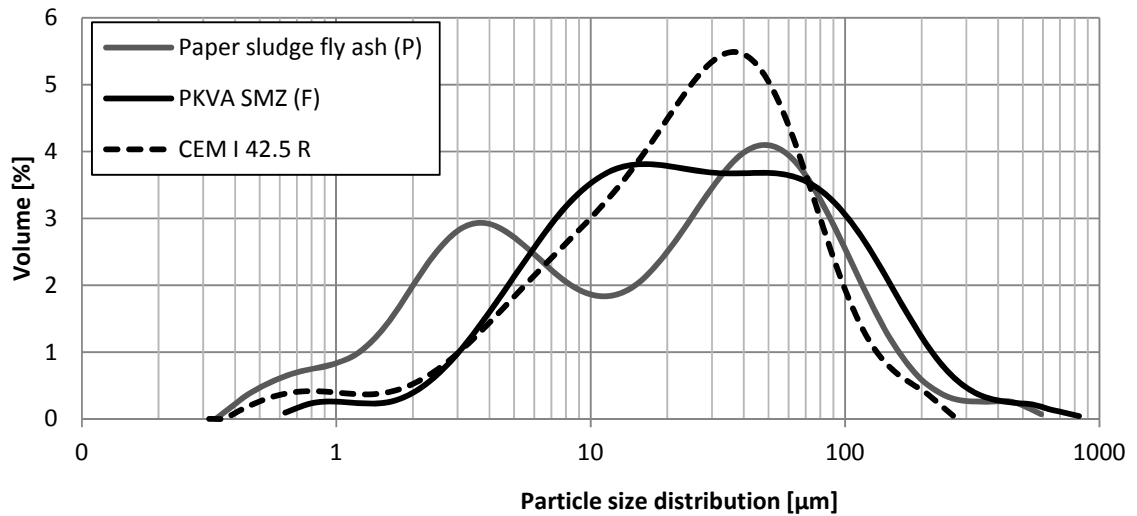


Figure 6: Particle size distribution of paper sludge fly ash (P), coal combustion fly ash (F) and Portland cement

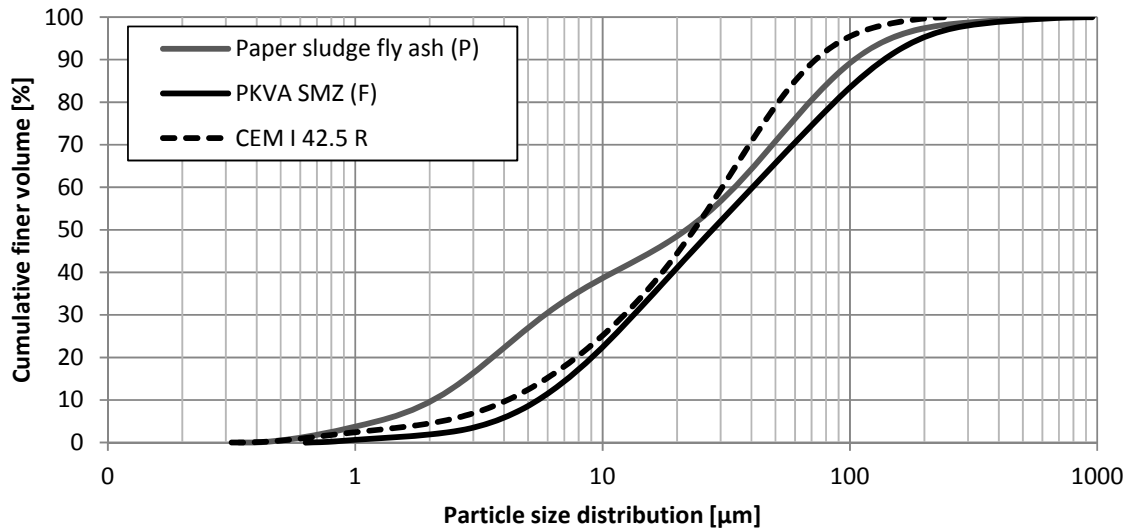


Figure 7: Cumulative finer volume of the paper sludge fly ash (P) compared to coal combustion fly ash (F) and Portland cement.

Compared to coal combustion fly ash (F), paper sludge fly ash (P) has more small particles below 10 microns and more than 50% of the particles are smaller than that of coal combustion fly ash (F). This could be due to metakaolin that is 99.9% finer than 16 microns with a mean particle size of 3 microns; it is well represented and probably is mainly responsible for the pozzolanic activity of the fly ash (Advanced cement technologies, 2012).

So far, both coal combustion fly ash (F) and paper sludge fly ash (P) fulfil the requirements of NEN-EN-450 for maximum retained fly ash on the 45 micron sieve. The fineness of fly ash is also defined by a specific surface area per unit of mass. If the surface area is very large a considerable amount of small particles forming a large active area are available. However, the effect of increase in specific surface area beyond 6000 cm^2/g is reported to be insignificant (Joshi & Marsh, 1986). Table 2 presents the specific surface area of the fly ashes estimated with the Mastersizer 2000 Ver. 5.60 (by assuming all

particles to be spherical). This method, however, does not account the surface associated with the shape of the particles. According to this method the specific surface area of paper sludge fly ash is much higher in comparison with coal combustion fly ash and will have a high reactivity. However, the specific surface area is $> 6000 \text{ cm}^2/\text{g}$ and will probably increase the water demand.

Table 2: Specific surface area of fly ashes

| Bio-power plant | Paper sludge fly ash (P) [cm ² /g] | Coal combustion fly ash (F) [cm ² /g] |
|-----------------------|--|---|
| Specific surface area | 12000 | 2090 |

3.4 Effect of paper sludge fly ash on cement hydration

Paper sludge fly ash as contains approximately of 23%, CaO (calcium oxide) 41% CaCO₃ (calcium carbonate) and 29% Al₂O₃ • 2SiO₂ metakaolin as the main constituents. However, they can slightly vary because varying input from different factories. In concrete, these compounds have the following function: metakaolin is the reactive one with pozzolanic properties. CaCO₃ has no or little pozzolanic properties and will only be used as a filler and is formed by the reaction of calcium oxide and CO₂ according to:



CaO will only absorb large amounts of water and therefore has a negative effect on the concrete because less water can react with cement. At the same time it also has a positive effect, creating portlandite according to:



That is used by fly ash to start its own hydration.

Although, Ca(OH)₂ is produced by the combination of calcium oxide and water, in normal cement mixtures the negative effect of reducing available water for the cement grain makes its application for using it as cement replacement only suitable up to an amount of 10% with a small increase of the water cement ratio (CDEM, 2003).

4. Treatment of paper sludge fly ash

Two investigations are performed in order to chemically upgrade paper sludge fly ash. The first one is to treat paper sludge fly ash with water to reduce the amount of free lime and instead increase the amount of portlandite that could be used to activate the pozzolanic reaction of metakaolin, or at least reduce the water demand of paper sludge fly ash. The second one is to thermally treat paper sludge fly ash to remove calcite by releasing carbon dioxide and therefore increase the concentration of free lime that later will be treated with water to increase the amount of portlandite.

4.1 Water demand

To calculate the amount of water that is needed to form portlandite, a study is performed to investigate the water demand by using XRF data, to see how much quicklime could be turned into portlandite. Figure 9 presents the XRF-data that illustrates that 57% of the total composition is CaO.

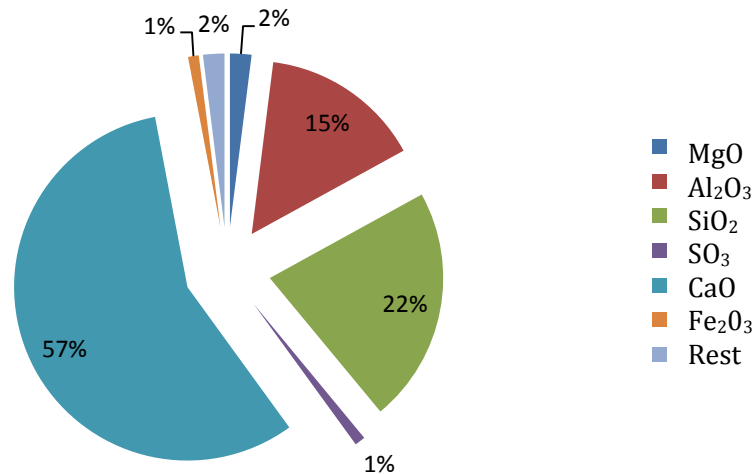


Figure 8: Oxide composition paper sludge fly ash

The molar mass of CaO is 56 g/mole and the molar mass of water is 18 g/mole. To transfer all the CaO into water an certain amount is needed (equation 5):

$$\frac{m_w}{m_c} = \frac{M_w}{M_c} * x_c \quad (5)$$

were M_w is the molar mass of H₂O. M_c is the molar mass of CaO and x_c is the percentage CaO in the fly ash , resulting in:

$$\frac{m_w}{m_c} = 0.18 \text{ (m/m)}$$

This water demand would be needed if all quicklime would be free lime and would absorb water. From Paragraph 3.4 it is known this is not true and that the water concentration should be around 0.7 (m/m). The reason is that XRF identifies elements not compounds,

and the result of the analysis is exposed in % of oxides. In the case of paper sludge fly ash, all Ca is considered by XRF to be CaO, but actually it will be a mixture of CaO, CaCa₃ and other minor Ca-counting phases. However, from practical experiments that will be discussed later, it is found that lowering the water demand is not applicable. This was visibly observed by an insufficient change of colour and the possibility of particles to flare up. Indicating that the water has had only partial access to the particles.

4.2 Water treatment

In order to sufficiently distribute the water that is needed to treat paper sludge fly ash, a special sprayer is used distribute fine water droplets. The quantity of water added to the paper sludge fly ash is measured using a balance. The principle is illustrated in Figure 9.



Figure 9: Left, distributed paper sludge on balance. Right, water spray

The effect of the water spray can be visually observed by a change in colour: water-sprayed paper sludge fly ash possesses of a darker grey colour.

Figure 10 presents an example of the colour change. From the middle to the top water is distributed and the bottom, left and right edge is tried to be avoided. The two regions are separated by the black line surrounded with a white glow.



Figure 10: Comparison original (light region) and water treated (dark region) paper sludge fly ash separated by a dark line surrounded with a white glow.

4.3. Effect of thermal and water treatment

To investigate the efficiency of the water treatment two tests are performed. The first analysis is performed by using X-ray diffraction to check the effect of treatments and to make sure no side effects occur. Analyses are performed using copper radiation with a step size of 0.02 degrees and 1-second count time. Pattern processing was done using EVA software and the ICDD pattern database. The results are presented in Figure 11.

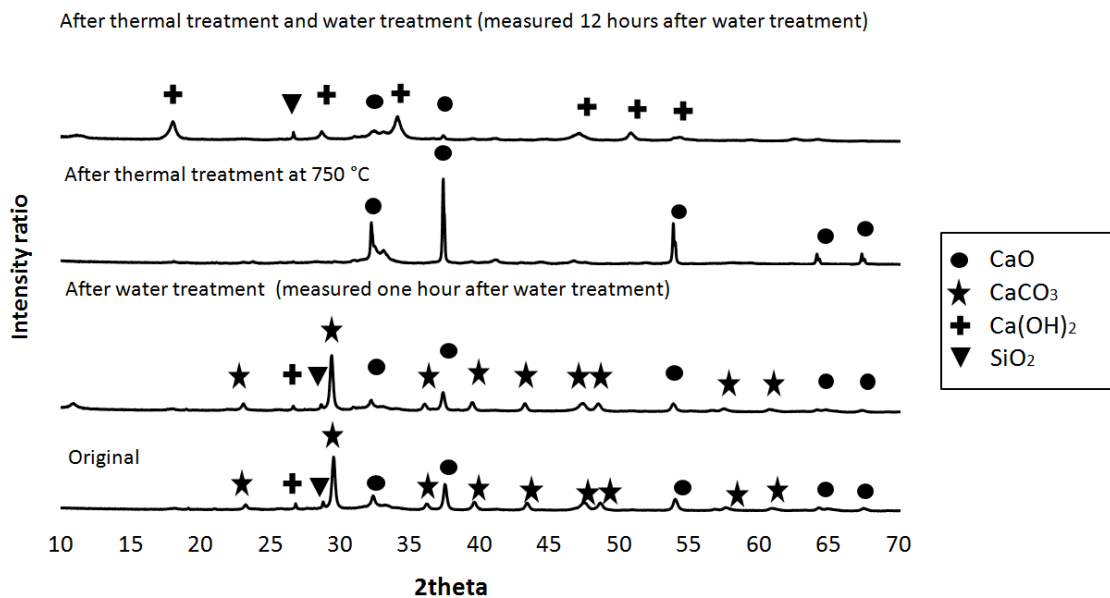


Figure 11: XRD-pattern of original and treated paper sludge fly ash

By looking at X-ray diffraction patterns illustrated in Figure 11, it can be seen that the original paper sludge fly ash consists of a high content of calcite and some small peaks of quicklime and quartz. One hour after the water treatment, the quicklime is reduced but not

completely consumed. At that time no formation of portlandite was detected. However, after twelve hours the formation of portlandite could be detected (not illustrated in Figure 11). The effect of thermal treating paper sludge fly ash for one hour at 750 degrees Celsius is also investigated. After thermally treatment no calcite or portlandite could be detected and only free lime was detected. Finally a thermal treated and water treated paper sludge fly ash is investigated after 12 hours. As expected all calcite is turned into lime and later into portlandite. Still not all lime is transformed into portlandite, which is later confirmed by the second analysis with thermo gravimetric analysis (TGA).

The second analysis is performed by using TGA to make a prediction of available percentages of quicklime, portlandite and calcite by measuring the mass loss when increasing temperature. The results are presented in Table 3 and Figure 12.

Table 3: Mass loss of original and treated paper sludge fly ash and predicted % of calcium compounds.

| | Original | Thermal treated at 750 °C | Thermal and water treated | Water treated using 20% m/m |
|--------------------------|----------|---------------------------|---------------------------|-----------------------------|
| 20-150 [°C] | -0.14 | -0.05 | -1.53 | -1.72 |
| 150-350 [°C] | -0.15 | -0.06 | -3.63 | -2.58 |
| 350-600 [°C] | -0.6 | -0.56 | -9.08 | -2.71 |
| 600-900 [°C] | -16.35 | -0.17 | -0.93 | -14.07 |
| Ca(OH) ₂ [%]* | 2.47 | 2.30 | 37.33 | 11.14 |
| CaCO ₃ [%]** | 33.44 | 0.35 | 1.90 | 28.78 |
| CaO [%]*** | 21.09 | 54.35 | 17.77 | 17.08 |

* From 350-600 °C $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$

** From 600-900 °C $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$

*** Values are obtained by subtracting the found portlandite and calcite from the quicklime found by XRF

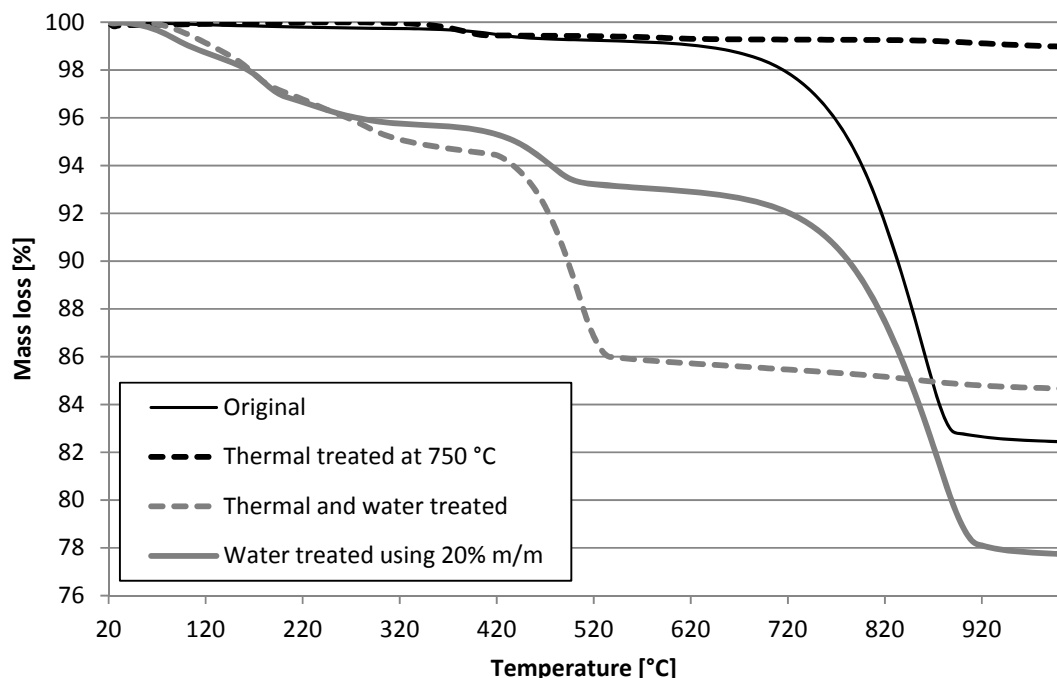


Figure 12: Mass loss of original and treated paper sludge fly ash

From XRD results and Table 3 it can be clearly seen that there is a decrease of calcite after thermal treatment, and that it almost completely turned into quicklime. Furthermore, after thermal and water treatments there is a large increase of portlandite. It can however be concluded that not all the free lime is used for the formation of portlandite. When only water-treated, the amount of portlandite is increased but the amount of quicklime is not significantly reduced. Observing the results of TGA and XRD there is still 17% of quicklime available after treatments. It is possible, that the calcium oxide content obtained from XRD could include other Ca- containing compounds than calcite, portlandite and quicklime.

5. Results

To investigate if after different treatment steps the flexural and compressive strength results of paper sludge fly ash are improved, mortars are made using a replacement factor of 10%. Furthermore the effect of paper sludge fly ash on coal combustion fly ash is investigated to see if the activation can be accelerated by formation of portlandite. Results can be divided into two groups.

The first group consist of 10% replacement of cement with:

- Original paper sludge fly ash termed P 10%;
- Thermally treated paper sludge fly ash termed PT 10%;
- Thermal and water treated paper sludge fly ash termed PTW 10%;
- Water treated paper sludge fly ash termed PW 10%.

The second group consist of 10 % coal combustion fly ash with:

- 10% thermally treated paper sludge fly ash termed PT 10% + F 10%;
- 10% thermal water treated paper sludge fly ash termed PTW 10% + F 10%;
- 10% water treated paper sludge fly ash termed PW 10% + F 10%.

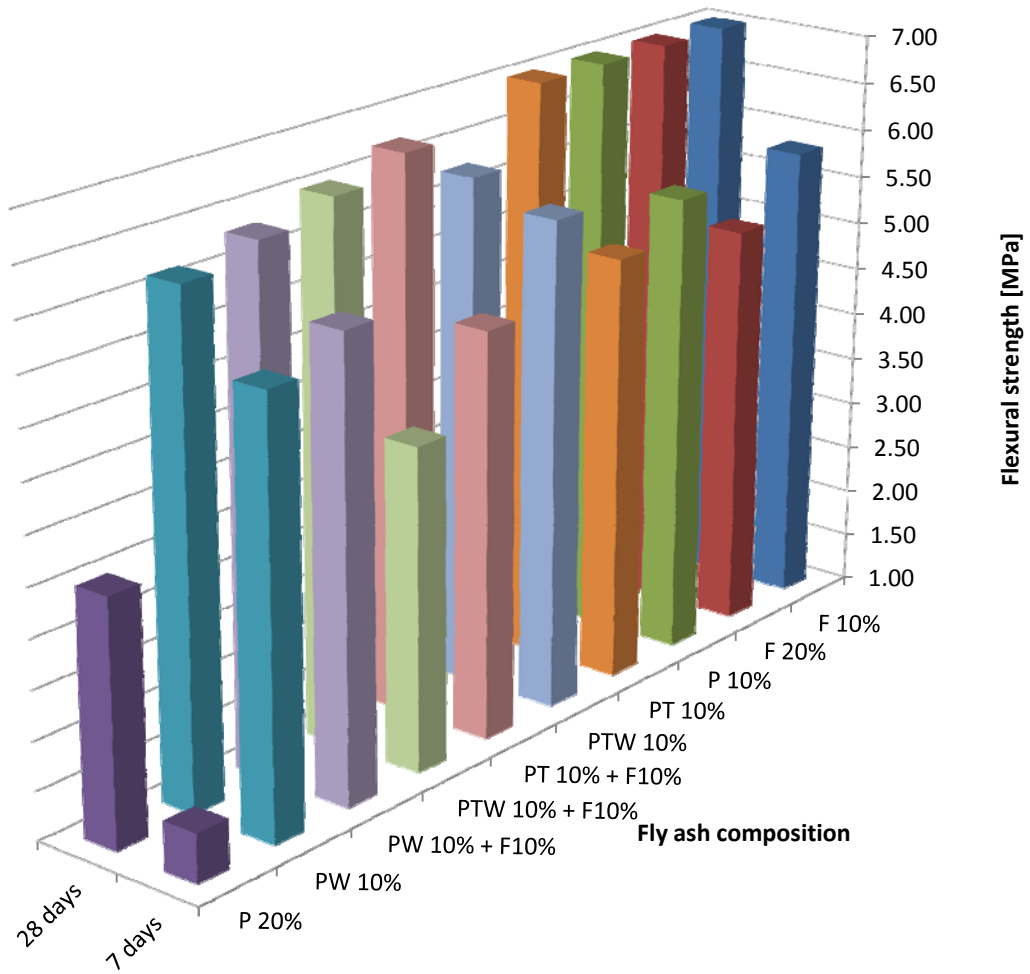
Additionally mortars are made with 10% (F 10%) and 20% coal combustion fly ash (F 20%) and an additional 20% original paper sludge fly ash (P 20%).

5.1 7 and 28 days flexural and compressive strength

Before the samples are cured, fresh mortars are investigated on the workability and where needed Glenium 51 (with concentration of 35%) super plasticiser (SP) is added to achieve a spread of 140 mm. The recipes are presented in Table 4. After one day the samples are demolded and cured under water for 7 and 28 days. The seven days compressive and tensile strength are illustrated in Figure 13 and Figure 14. The results are obtained by taking the average of 2 samples.

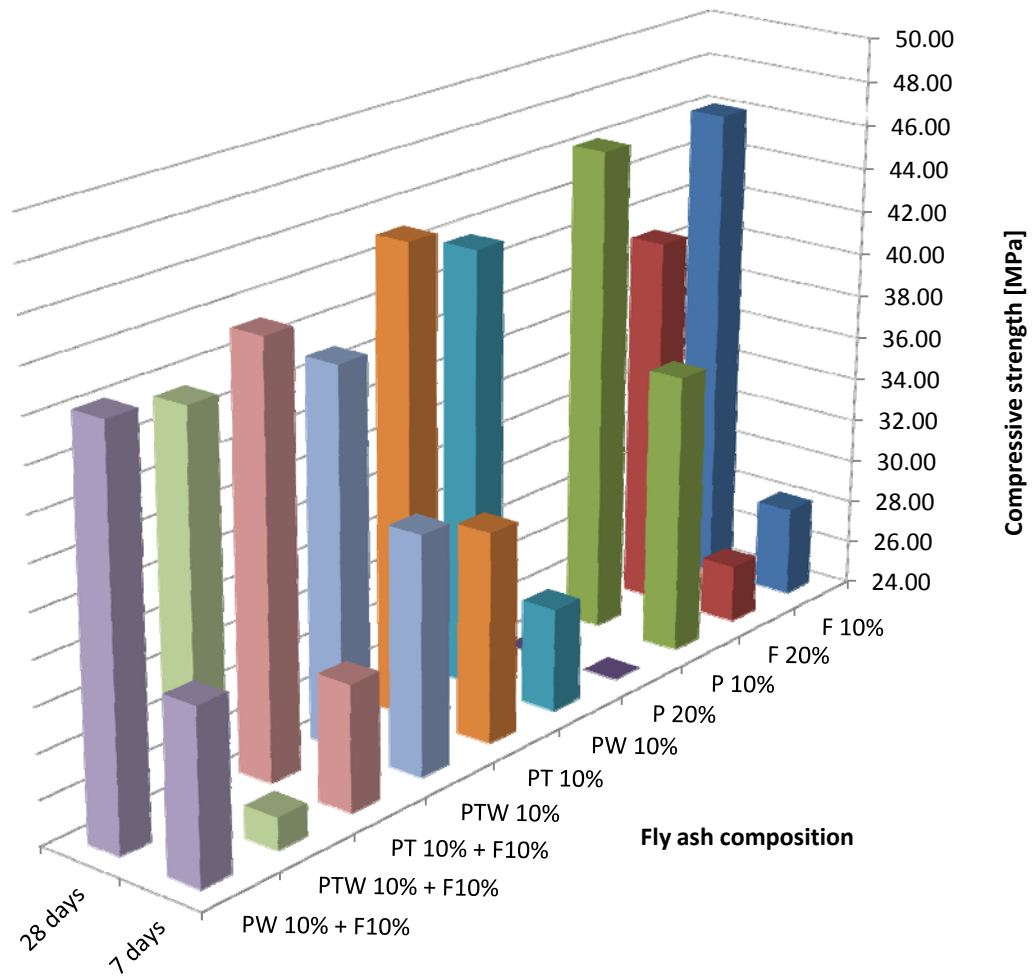
Table 4: Recipes for 7 and 28 days flexural and compressive strength

| Recipes | SP [ml] | CEM I [g] | Paper sludge fly ash [g] | Coal combustion fly ash [g] |
|-----------------------------|------------|--------------|-----------------------------|--------------------------------|
| 7 & 28 days F 10% | - | 405 | - | 45 |
| 7 & 28 days F 20% | - | 360 | - | 90 |
| 7 & 28 days P 10% | 2 | 405 | 45 | - |
| 7 & 28 days P 20% | 2 | 360 | 90 | - |
| 7 & 28 days PT 10% | 2 | 405 | 45 | - |
| 7 & 28 days PTW 10% | 0.5 | 405 | 45 | - |
| 7 & 28 days PW 10% | 0.5 | 405 | 45 | - |
| 7 & 28 days PT 10% + F 10% | 0.5 | 360 | 45 | 45 |
| 7 & 28 days PTW 10% + F 10% | 0.5 | 360 | 45 | 45 |
| 7 & 28 days PW 10% + F 10% | 0.5 | 360 | 45 | 45 |



| | 7 days flexural strength [Mpa] | 28 days flexural strength [Mpa] |
|------------------|--------------------------------|---------------------------------|
| ■ F 10% | 5.83 | 7.48 |
| ■ F 20% | 5.21 | 7.24 |
| ■ P 10% | 5.78 | 7.37 |
| ■ PT 10% | 5.40 | 7.10 |
| ■ PTW 10% | 6.02 | 6.26 |
| ■ PT 10% + F10% | 5.17 | 6.71 |
| ■ PTW 10% + F10% | 4.30 | 6.51 |
| ■ PW 10% + F10% | 5.68 | 6.32 |
| ■ PW 10% | 5.39 | 6.15 |
| ■ P 20% | 1.50 | 3.50 |

Figure 13: Flexural strength results of different fly ash compositions for 7 and 28 days water curing



| | 7 days compressive strength [Mpa] | 28 days compressive strength [Mpa] |
|------------------|-----------------------------------|------------------------------------|
| ■ F 10% | 28.09 | 46.06 |
| ■ F 20% | 26.60 | 41.03 |
| ■ P 10% | 36.79 | 46.20 |
| ■ P 20% | 8.00 | 16.00 |
| ■ PW 10% | 28.66 | 43.77 |
| ■ PT 10% | 33.47 | 45.11 |
| ■ PTW 10% | 34.70 | 40.97 |
| ■ PT 10% + F10% | 29.63 | 43.26 |
| ■ PTW 10% + F10% | 25.42 | 41.56 |
| ■ PW 10% + F10% | 31.71 | 42.19 |

Figure 14: Compressive strength results of different fly ash compositions for 7 and 28 days water curing

6. Conclusions and discussions

6.1 Discussion

So far, from the obtained strength results the following conclusions can be drawn. At first, samples containing 10% treated paper sludge fly ash (either thermal, water- or combined treatment) give lower strength results than the original paper sludge fly ash, indicating that treatment of fly ash is so far not increasing its potential. However, combining paper sludge fly ash with coal combustion fly ash indeed increased the strength results for all obtained treatment methods, indicating that paper sludge fly ash is able to activate coal combustion fly ash, increasing its strength at 28, and even already at 7 days.

It is however uncertain if treatment methods need to be applied and if so, how much water is needed and how much portlandite is needed for the activation of coal combustion fly ash. This uncertainty is more described in the next paragraphs.

6.1.1 *Thermally treated*

From the results it seems that thermal treated paper sludge fly ash (PT 10%) performs acceptably at both 7 and 28 days, but not better than the original untreated paper sludge fly ash (P 10%). This could be because quicklime absorbed too much water, and less water was available for cement, resulting in a lower strength. However, the strength decrease is <1% (could be considered as measurement error) in comparison with the original, indicating that the water demand was estimated correctly. The combination of PT 10% with coal combustion fly ash (F 10%) performed better than the same replacement factor only than with 20% coal combustion fly ash (F 20%). When comparing PT 10% with water treated paper sludge fly ash (PW 10%), higher strength results are found for PT 10%. It seems that the high lime content of PT 10% is used more sufficient for different hydration products (increasing the strength), while PW 10% has only available portlandite that will leach out when not needed.

6.1.2 *Water treated*

At early age, PW 10% exhibits a decrease of flexural and compressive strength, suggesting that metakaolin is activated by the water treatment before the paper sludge fly ash is used in mortars. This was expected because the calculated water demand of 10% was increased to a water demand of 20% as the lower water demand seemed to have no effect. However, TGA shows that there is still available quicklime that never reacted with water. After 28 days the compressive strength of PW 10% is only 1.5 MPa lower than that of PT 10%, meaning that the effect on metakaolin is not high or may even not occur. Furthermore, no expansion was observed for any created samples.

It seems that not all quicklime reacts with water. However, there could be other available compounds in paper sludge fly ash that absorb/react with water, even faster than quicklime does.

6.1.3 *Paper sludge with coal combustion fly ash*

The effect of water treatment is clearly seen by the results obtained by thermal and water treated paper sludge fly ash (PTW 10%) and the one with added 10% coal combustion fly ash added (PTW 10% + F 10%). Coal combustion fly ash decreased the water demand, making more water available for cement and paper sludge fly ash to hydrate. In this way

strength results of PTW 10% + F 10% are higher than without coal combustion fly ash, even though the cement content is 10% lower. Furthermore the strength results with coal combustion fly ash is for every treatment higher than strength results obtained from P 20% or 20% coal combustion fly ash (F 20%).

It seems that the water demand is very important and when adjusted probably higher strength results will be obtained.

Finally, the 7 days strength results when combining paper sludge fly ash (either thermal, water-or combined treatment) and coal combustion fly ash are lower than that without coal combustion fly ash. This is due to the low early strength contribution of coal combustion fly ash and the high early strength contribution of paper sludge fly ash. However, comparing it with F 20%, strength increase is found because of early strength development paper sludge fly ash.

6.1 Conclusions

Combining paper sludge fly ash with coal combustion fly ash increases the strength results for all obtained treatment methods, indicating that paper sludge fly ash is a good alternative to replace 50% of coal combustion fly ash, increasing strength at 28 and even at 7 days by its activation properties.

6.2 Recommendation

Recommendations for further research could be:

- Increasing replacement percentages of paper sludge fly ash with coal combustion fly ash and other fly ashes;
- Determine optimum water cement ratio's to increase strength results;
- Investigate if water treatment method could be improved because there is still quicklime available after water treatment;
- Investigate the effect of untreated paper sludge fly ash with coal combustion fly ash;
- Perform X-ray diffraction measurements with smaller step size (< 0.02) and count time (< 1.0) for more accurate results (finding more small compounds);
- So far maximum 35% of cement can be replaced with coal combustion fly ash (EN-197-1). By combining paper sludge fly ash the application of coal combustion fly ash could perhaps be increased.

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