Impact of Production Parameters on Physiochemical Characteristics of Wood Ash for Possible Utilisation in Cement-based Materials

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Abstract

Energy production is reorganised to mitigate the pressure on the global environment. This reorganisation leads to an increase in the production of wood ash (WA). Multivariate modelling was used to identify the link between production parameters and the physicochemical characteristics of different WAs and to determine which production parameters result in the WAs most suitable for utilisation in cement-based materials. Based on the multivariate model partial least square, WA originating from circulating fluidised bed combustion of wood chips made from whole trees is the optimal type of WA when utilised as a supplementary cementing material with pozzolanic activity. WA originating from the combustion of wood chips made from whole trees is the optimal type of WA when utilised as a supplementary cementing material with hydraulic activity. Furthermore, the combustion method and type of ash were seen to have the largest influence on the physiochemical characteristics of WAs compared to the other production parameters included in this study.

Keywords: wood ash, supplementary cementitious material, multivariate modelling

1. Introduction

The pressure on the global environment has led to an increase in the demand for renewable energy. In April 2017, 26 of the 28 EU nations, stated they would not invest in new coal-fired power plants after 2020, in close accordance to the Paris Agreement and the goal to provide

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100 % carbon neutral fuel by 2050 (Neslen, 2017). The agreement also includes a demand to reorganise the existing energy sector. Since coal combustion plants already exist, a prevalent option is to transform the existing plants to use alternative, sustainable fuels. One abundant fuel is biomass, defined as an organic material, e.g. plant material such as wood, straw and bagasse (McKendry, 2002).

1.1. Utilisation of WA

Incineration of different types of wood products, e.g. wood pellets or chips, for energy production causes a significant increase in the production of wood ash (WA). 48,000 tonnes WA is produced annually in Denmark (Emineral A/S, 2019). A major portion of the produced WA is land-filled and thus not utilised (Etiégni and Campbell, 1991), which could lead to a range of potential problems. WA consists of fine particulate matter, which is easily airborne by winds. Thus landfilling of WA can be a potential health risk to nearby residents or a source of pollution of the surrounding nature (Cheah and Ramli, 2011a). Further, landfilling of WA can lead to leaching of chemical elements from the WA and thus contamination of the groundwater (Udoeyo et al., 2006). To avoid contamination a properly engineered landfill is required, making landfilling of WA uneconomical (Cheah and Ramli, 2011a). Thus, utilisation of WA is of interest as an alternative to landfilling.

Application of WA in cement-based materials as a supplementary cementitious material (SCM) or filler has been studied in the literature (Berra et al., 2015; Chowdhury et al., 2015; Elinwa and Mahmood, 2002; Rajamma et al., 2009a; Ramos et al., 2013; Siddique, 2012; Udoeyo et al., 2006). The findings of these studies (Berra et al., 2015; Chowdhury et al., 2015; Elinwa and Mahmood, 2002; Rajamma et al., 2009a; Ramos et al., 2013; Siddique, 2012; Udoeyo et al., 2006) vary markedly e.g. in regards to the obtained compressive strength for mortar samples containing WA. Udoeyo et al., (2006), Berra et al., (2015), and Elinwa and Mahmood, (2002) all concluded a decrease in the compressive strength when using WA as a partial cement replacement. Rajamma et al., (2009a) saw no decrease in the compressive strength for a 10 % replacement of cement with WA and Siddique, (2012), Ramos et al., (2013), and Chowdhury et al., (2015) all concluded an initial decrease in the compressive strength, but an increase in the compressive strength over time due to pozzolanic activity. These different results are depending on which type of WA is used. WA physiochemical characteristics vary depending both on the wood products, e.g. wood chips or pellet, and on the combustion process, e.g. temperature, and technology (Cheah and Ramli, 2011a; Siddique, 2008).

Utilisation of WA in cement-based materials is not approved according to EN 450-1, (2012), which is the current European standard for utilisation of fly ashes as mineral admixtures in cement-based materials. Nevertheless, EN 450-1, (2012) will be used as a reference for evaluation of the WAs in this work, as in several previous studies (Berra et al., 2015; Rajamma et al., 2009a; Ramos et al., 2013).

1.2. Environmental perspectives on utilisation of WA in cement-based materials

About 5 % of the global CO_2-emission originates from the production of Portland cement (International Energy Agency (IEA), 2007). Utilisation of WA as a partial cement replacement could potentially contribute to a reduction of the global CO_2-emission and conserve raw materials (Schneider et al., 2011; Teixeira et al., 2016). Utilisation of WA as a partial filler replacement could also conserve raw materials.

Teixeira et al., (2016) conducted a life cycle assessment comparing the potential environmental impact from cradle-to-gate of 1 m^3 of concrete with Portland cement and 0, 20, 40 and 60 % substitutions of cement with different types of by-products (coal fly ash, biomass fly ash, and co-combusted coal and biomass fly ash). They studied cradle-to-gate, as the use and disposal of concrete were assumed to result in the same environmental impacts regardless the type of concrete. Teixeira et al., (2016) included six environmental impact categories: global warming, ozone layer depletion, acidification potential, eutrophication potential, formation potential of tropospheric ozone and abiotic depletion potential of fossil resources. In general, the incorporation of fly ash, regardless of type, reduced the environmental impacts, primarily due to the decrease in the cement consumption, thus the CO_2-emission. They showed that the biomass fly ash had the best environmental performance, increasing with replacement rate.

The life cycle assessment presented by Teixeira et al., (2016) only takes into account environmental impacts and does not take into account the mechanical performance of concretes with biomass fly ash, both parameters that could limit the use. Further, the requirements for binders in cement-based materials, according to EN 450-1, (2012) are comprehensive and conservative. These requrements ensures the necessary durability of a concrete structure, which is another important aspect, not taken into account in the life cycle assessment (Teixeira et al., 2016).

The environmental performance of concrete with WA highly encourages utilisation of biomass fly ash in concrete; however, further studies are required, regarding, e.g. mechanical response, durability, reactivity of WA, influence of WA on the hydration phases and possibilities and influence of pre-treatment of WA, in order to utilise biomass fly ashes in cement-based materials.

1.3. Multivariate modelling

The use of multivariate statistical methods has been applied for several purposes in the literature, e.g. by Pedersen et al., (2015) for evaluation of the efficiency of electrodialytic removal of heavy metals from polluted harbour sediments and by Christensen et al., (2005) for evaluation of biodegradation of mineral oil. Voshell et al., (2018) used multivariate statistical methods to get a better understanding of the origin of the trance elements As, Cd, Cr, Cu, Ni. Pb, Zn, K, Mg, Ca, and Al in biomass ashes.

This work identifies the link between production parameters and the physicochemical characteristics of WA by the use of multivariate statistical analysis. The production parameters were selected by the authors and cover both material and process parameters (see table 1.). The optimal production parameters for WA to be applicable in cement-based materials were identified based on the assumption that requirements described in EN 450-1, (2012) and EN 197-1, (2011) are valid for WA. The production parameters used in this work for multivariate statistical analysis is; the initial water content (of the biofuel), the mean combustion temperature, type of biofuel (wood chips, wood pellets or wood chips and powder), origin of biofuel (whole trees (including logs, bark, buds and pine needles) or logs), and combustion method (circulating fluidized bed (CFB) or grate combustion). The production parameters were supplied by the individual biomass combustion facility. The type of ash is further included as a production parameter (bottom (B), mixed (M) or fly ash (F)). The authors selected these production parameters, based on knowledge available at the individual biomass combustion facility. However, the inclusion of more production parameters, if possible, would result in a more detailed model.

2. Materials and methods

2.1. Investigated WAs

Eleven different types of WA were used in this study, nine different wood ashes from five different biomass combustions facilities in Denmark and two different wood ashes from one biomass combustion facility in Sweden. An overview of the eleven WAs and their production parameters can be found in table 1. Collectively, the eleven WAs used in this study will be referred to as the investigated ashes.

The WAs were sampled from end of March to the beginning of April 2017, except WMFA2, which was collected at the beginning of July 2017. The individual biomass combustion facilities supplied samples of the ashes from deposit storage. All ashes were subsequently stored in closed plastic buckets protected from heat and light sources. The plastic bucket was mixed before sample collection from the bucket in order to ensure a representative ash sample.

2.2. Characterisation methods

Characterisation was made on dried WA (105 ^{0}C, 24 hours) in order to assure sample without free water. Scanning Electron Microscope (SEM) was used to analyse the morphology. The content of minerals was analysed by X-ray diffractometry (XRD) measured with a PanAnalytical X-ray diffractometer, sat at the PW3064 Spinner stage, with Cu-Kα radiation measuring between 4 °2θ and 100 5 °2θ with a step size of 0.002 °2θ and a sampling time per step of 24.8 s. The XRD plots were qualitatively evaluated using X'Pert HighScore Plus software, with data from the International Centre for Diffraction Data (ICDD). The chemical composition of the investigated WAs was determined by X-ray fluorescence (XRF). The particle size distribution and specific surface area were determined by laser diffraction using a Mastersizer 2000 instrument. The pH and conductivity of the WAs were measured in a 1:2.5 solid to liquid ratio suspension in distilled water with the respective electrodes after 1-hour of stirring with a magnetic stirrer. The suspension was filtered followed by measurement of Cl^- and SO_4^{2-} concentrations by Ion Chromatography. Loss on ignition (LoI) was measured in accordance with CEN (European Committee for Standardization), (2009), i.e. at 550 °C and EN 196-2, (2005), i.e. at 950 °C. The solubility in water was determined: ash and distilled water were mixed to an L/S (liquid-to-solid) ratio 5 and shaken for 1 min. After settling, the water was decanted. This procedure was repeated three times (Kirkelund et al., 2016). Finally, the suspension was filtered and the ash dried and weighed. The carbonate volume was determined by reaction with hydrochloric acid measured by the use of Schreiber equipment (Hamid, 2009). All tests conducted for the characterisation of the WAs were repeated three times, except the XRF analysis. A ternary diagram was plotted for the components CaO, SiO_2 and Al_2O_3. All excess components were subtracted from the total bulk composition before plotting. Thus the ternary diagram displays the relationship between the relative quantities of the three components. SIMCA 14.1 Software is used for conducting the multivariate statistical analysis.

3. Results and discussion

3.1. Physiochemical characteristics of WA

The possibility of using the investigated WAs in cement-based materials has been evaluated based on the physiochemical characteristics measured for the investigated WAs. The characterisation comprises physicochemical characteristics (tables 2 and 3), percentage complying with the filler limit and compliance with category N (table 2), mineralogical composition (table 2 and figure 3) and morphology (figure 4).

3.1.1. Pozzolanic activity

Pozzolanic activity is facilitated by a high amount of SiO_2, Al_2O_3 and Fe_2O_3, referred to as primary oxides, and according to (EN 450, 2012) the $\sum$primary oxides > 70% for a pozzolan. A pozzolan has, in itself, little or no cementitious value but will, in the presence of moisture, react with calcium hydroxide and form compounds possessing cementitious properties (ASTM International C125-15a, 2003).

Pozzolanic activity was reported for WAs in several studies (Chowdhury et al., 2015; Elinwa and Mahmood, 2002; Ramos et al., 2013; S. V. Vassilev et al., 2010), concluded due to a content of primary oxides above 70 % (EN 450, 2012). None of the investigated WAs in this study complies with this limit. The highest content of primary oxides was found for WCBA with a content of primary oxides of 64 %. The rest of the WAs had at a content ≤ 25 %. The primary oxides for the WAs in this study are in the following order $SiO_2 > Al_2O_3 > Fe_2O_3$ for bottom and mixed ashes, except for WPMA, and $SiO_2 > Fe_2O_3 > Al_2O_3$ for fly ashes, except for WCFA3. The WA originating from CFB combustion (WCBA and WCFA3) arrived at the highest amount of primary oxides, mainly due to a high content of SiO_2. A high content of SiO_2 is due to sand particles, which make the suspension bed, and which are carried with the flue gas during combustion with the CFB technology (van Loo and Koppejan, 2010). Sand is considered inert (Wig, 1913), thus a part of the SiO_2 content in WCBA and WCFA3 could be inert bed sand.

The content of primary oxides was above 70 % in the WAs in Chowdhury et al., (2015), Elinwa and Mahmood, (2002), Ramos et al., (2013) and S. V. Vassilev et al., (2010) and in the order $SiO_2 > Fe_2O_3 > Al_2O_3$, an order which corresponds to the findings in this study. Rajamma et al., (2009a) investigated a WA originating from a biomass thermal power plant using forest residues as fuel. The content of primary oxides was 52 % (SiO_2 = 41%, Al_2O_3 = 9%, Fe_2O_3 = 3%), but still argued to contribute to the pozzolanic activity, due to the CaO and OH^- concentrations based on a direct pozzolanic activity test showing a saturation curve well below that of cement, which indicates pozzolanic activity of the WA (Rajamma et al., 2009a). The oxides of the WA investigated by Rajamma et al., (2009a) was similar to WCBA investigated in this study. Thus, WCBA might similarly show pozzolanic behaviour, even though it contains only 64 % primary oxides. The remaining WAs of this study are considered to have very little or no pozzolanic activity, due to the low amount of primary oxides (< 25 %).

3.1.2. Hydraulic activity

Hydraulic activity describes the ability of a material to set and harden, while submerged in water, by forming cementitious products in a hydration reaction (Snellings et al., 2012). Hydraulic activity is governed by the content of SiO_2 and CaO (EN 197-1, 2011) and requirements from (EN 197-1, 2011) is $CaO/SiO_2 > 2$.

Hydraulic activity for WAs was investigated in Berra et al., (2015), Cheah and Ramli, (2011b), and Rajamma et al., (2009a). Berra et al., (2015) investigated the hydraulic index K_3, defined as $(CaO+MgO+Al_2O_3)/SiO_2$. Values of $K_3 > 1$ are an indication of good hydraulic properties (Berra et al., 2015). All WAs was investigated by Berra et al., (2015) and all WAs in the present study, except WCBA, have a hydraulic index above 1. Rajamma et al., (2009a) expected hydraulic reactions of a WA due to a content of CaO above 25%, substantiated by Cheah and Ramli, (2011b) determining WA to be an active hydraulic binder as it is rich in $CaCO_3$ and CaO. However, none of the WAs in Berra et al., (2015), Cheah and Ramli, (2011b) and Rajamma et al., (2009a) complies with the normative compositional requirements set by EN 197-1, (2011).

A CaO-SiO_2-Al_2O_3 ternary diagram with the WAs of the present investigation is plotted in figure 2. All mixed and fly WA are located in the area for SCM with potential hydraulic properties (high content of CaO, low content of SiO_2 and Al_2O_3) and WCBA is in the latent hydraulic area. None of the WAs are located in the sketched areas for fly ash, natural pozzolans or slag. The composition of WCFA3 and WMFA2 are located just outside the sketched area for Portland cement, which is hydraulic, thus properties alike Portland cement could be seen for WCFA3 and WMFA2. The ternary diagram shows that all mixed and fly WA comply with the requirements set by EN 197-1, (2011), i.e. they potential have hydraulic activity. Thus there is a possibility for using mixed and fly WA as SCM partially replacing cement in cement-based materials.

3.1.3. Filler

Fillers are in principle inert and do not react themselves. However, the addition of WA as a filler could still positively influence the suitability of WA in cement-based materials. An inert filler can contribute to the properties of a cement-based material by filling the intergranular voids between the cement grains in the mixture (Deschner et al., 2012; Moosberg-Bustnes et al., 2004). An inert filler can also contribute by having a heterogeneous nucleation effect, acting as nucleation sites for the hydrates in cement, accelerating the hydration reaction and thus improving the compressive strength development (Lawrence et al., 2005; Moosberg-Bustnes et al., 2004; Ye et al., 2007).

The compliance of WA with the filler limit (250µm) (Herholdt et al., 1985; Moosberg-Bustnes et al., 2004) and category N described in EN 450-1, (2012) are highly depending on the type of ash. Only the fly ashes WPFA, WCFA2 and WCFA3, comply with category N (EN 450, 2012), and the same three fly ashes have a > 95 % compliance with the filler limit (table 2). Thus, three fly ashes WPFA, WCFA2 and WCFA3 can be expected to contribute to a decrease in porosity and an increase in compressive strength through the filler effect when utilised in cement-based materials.

The ability of fillers to act as nucleation sites depends on the fineness of the particles, the amount of mineral admixture and the affinity of the filler to cement hydrates related to the origin of the mineral admixture (Lawrence et al., 2005). Particles > 215µm can be assumed to be large enough to exclude any heterogeneous nucleation effects (Lawrence et al., 2003; Neville, 1996). This facilitates the fly ashes, and particularly the three fly ashes WPFA, WCFA2 and WCFA3, to have a potential larger contribution to the compressive strength through the heterogeneous nucleation effect, compared to the bottom and mixed WA. Grinding the WAs may lead to an increase in the WAs possibility for utilisation as filler (Berra et al., 2015).

3.1.4 Mineralogy and morphology

The mineralogical composition was determined by XRD (table 2 and figure 3). Quartz, arcanite and calcite were seen to be the predominant mineral components for seven out of the eleven WAs, which is in accordance with Yeboah et al., (2014). Other detected mineral components were portlandite, sylvite, periclase and lime. WCBA differs from the other WAs by having only quartz and wollastonite as identified mineral components.

From the XRD analysis (coal fly ash included for comparison) in figure 3, the amorphous rise was observed from approximately 15°2θ to 35°2θ. A broad amorphous peak is common in XRD studies of coal fly ash due to the poorly ordered atomic structure of the amorphous glass content of the coal fly ash (Bellotto et al., 1989; van Roode et al., 1987; Yeboah et al., 2014), as seen in figure 3. For all the investigated WA no such peak was observed, thus they contain a very limited (if any) amount of amorphous glass.

The lack of amorphous glass is supported by the SEM images, figure 4, for the investigated WA. The SEM images, display all the investigated WA to contain none of the typical glassy aluminosilicate spherical particles, found in commercial coal fly ash (Yeboah et al., 2014). The SEM images, display the investigated WA to consist of large and fibrous wood particles, originating from the biomass (Yeboah et al., 2014). Low content of aluminosilicate leads to a low pozzolanic activity (Shearer, 2014), which is in accordance with the previous findings, stated that pozzolanic activity is expected for the investigates WAs, except for WCBA, based on the content of oxides.

3.2 Multivariate analysis

A statistical analysis of experimental data sets can establish trends and correlations in a system, e.g. assessing the possible relations between the inputs and outputs. In a traditional statistical analysis, e.g. multiple regression analysis, the input variables are assumed independent, which can result in biased results of an analysis, if the input variables are correlated (Pedersen et al., 2015). Biased resuts is, e.g. the case for the chloride content and solubility in water of WAs, which are co-dependent (Wang et al., 2001). Statistical analyses coping with possible collinearity between the variables are the multivariate methods principal component analysis (PCA) and partial least squares (PLS) regression, which in addition provides plots of the data compressed to fewer dimensions than the original dataset (Pedersen et al., 2015).

The production parameters for each of the collected WA are given in table 1, defined as the X-matrix and the measured, individual physicochemical characteristics of the WA are given in tables 2, 3 and 4, defined as the Y-matrix. Combined these tables represent the data set used for the multivariate analysis.

3.2.1. Evaluation of physicochemical characteristics of WA by PCA modelling

PCA is a statistical procedure for identifying differences and similarities in multivariate data. PCA modelling reduces the dimensions of multivariate data by an orthogonal transformation of the variables into a set of linearly uncorrelated variables, referred to as principal components (Voshell et al., 2018). This transformation entails the first principal component to account for as much of the variability from the original data set as possible, and each of the following principal components has the highest variance possible under the constraint that the principal component is orthogonal to the preceding principal component. A detailed description can be found in Jackson, (1991). A loading plot has been obtained by projection of the original variables onto the principal components. The Loading Scatter Plot is used to interpret the relationships between the original variables. In this work, the original variables used for PCA modelling is the physicochemical characteristics of the WAs (Y-matrix), and the obtained Loading Scatter Plot can be seen in figure 1. The influence of each of the original variables on the principal components is reflected by the location of the original variable in the obtained Loading Scatter Plot. Variables with a strong contribution to the variation are projected far from the axis centre (e.g. Al_2O_3 and SiO_2, figure 1), and variables with minor influenced are projected close to the axis centre (e.g. carbonate, figure 1). Variables, which are positively correlated, are found close to each other (e.g. Al_2O_3 and SiO_2, figure 1) and variables, which are negatively correlated, are projected opposite each other with respect to the origin of the plot (e.g. high compliance with the filler limit and a high mean particle size, figure 1) (Pedersen et al., 2015). As the physicochemical characteristics of the WA, in this work, are defined as the Y-matrix, the PCA model is referred to as a PCA-Y model.

Expected correlations between the measured physicochemical characteristics of WA can contribute to the validation of the composed Loading Scatter Plot for the PCA-Y model (figure 1), and subsequently the PLS model. The Loading Scatter Plot (figure 1) displays the principal components 1 and 2. The PCA-Y model is based in total on five principal components, resulting in a model with 25 Loading Scatter Plots and 85% of the correlations between the physicochemical characteristics of WA explained. An example of an expected correlation seen in the Loading Scatter Plot (figure 1) is a high amount of particles, complying with the filler limit (particle size < 250μm (Herholdt et al., 1985)) and category N (maximum 40.0% by mass of the particles retained on a 45μm sieve (EN 450, 2012)). These again correlates with a high specific surface area (SSA) and a low mean size (D50) of the particles, supported by the literature.

Further, the following is displayed by the PCA-Y model:

- The composed PCA-Y model (figure 1) displayed the possible pozzolanic activity (defined as $\sum$primary oxides (EN 450, 2012)) of the investigated WAs to originate only from a high content of SiO_2 and Al_2O_3, as the WAs have a low content of Fe_2O_3. Further, a high pozzolanic activity is seen in the PCA-Y model to entails a low content of CaO and a low LoI measured at both 550°C and 950°C.
- From the composed PCA-Y model, the hydraulic activity (defined as the CaO/SiO_2 ratio (EN 197-1, 2011)) of the WAs is seen to increase with a high content of particles complying with the filler limit (Herholdt et al., 1985; Moosberg-Bustnes et al., 2004), category N (EN 450, 2012), and a high SSA and a low LoI at both 550°C and 950°C, and relatively low pH.
- WA with a high content of particles complying with the filler limit (Herholdt et al., 1985; Moosberg-Bustnes et al., 2004) is correlated to a high content of Fe_2O_3 and $SO_4^{-2,}$ and a low LoI measured at both 550°C and 950°C.

3.2.2. Relationship between production parameters and physicochemical characteristics of WA evaluated by PLS modelling

PLS is a multivariate method used for modelling the quantitative relationships between two data matrices, the descriptor matrix (X-matrix) and the response matrix (Y-matrix) (Wold et al., 2001). In this work, a PLS model was conducted in order to see how the production parameters (X-matrix, table 1) influences on the physicochemical characteristics of WA (Y-matrix, tables 2, 3 and 4). The PLS model is based on four principal components, resulting in a model with 16 Loading Scatter Plots and 90% of the correlations between the production parameters and the physicochemical characteristics of WA explained.

Table 3 summarises the assessment of whether the production parameters and ash type (X-matrix) included in the model have positive (+) or negative (-) influence response, thus leading to an increase or decrease, respectively, on the measurements for the physicochemical characteristics of WA (Y-matrix).

The relative importance of each of the production parameters included in the PLS model can be described by the variable importance in the projection (VIP) plot. The VIP-plot is constructed with respect to all the responses (Y-matrix) and the projections (X-matrix). Production parameters with VIP-values above one are considered to be most relevant for explaining the physicochemical characteristics of WA (Pedersen et al., 2015). VIP-plot for the production parameters, included in this work, is shown in table 4. The production parameters with VIP-values above 1 are the ash types ‘B’ and ‘F’, the combustion methods ‘CFB’ and ‘grate’, and the biofuel ‘chips’. Thus, these production parameters have, according to the conducted model, the largest influence on the physiochemical characteristics of WA (response). The production parameters ash type ‘M’, the types of biofuel ‘chips+powder’ and ‘pellets’, origin of biofuel ‘log’ and ‘tree’, combustion temperature and initial water content of the biofuel had VIP-values between 0.5 and 1, indicating a moderate influence on the physiochemical characteristics of WA (response).

The presented PLS model and VIP-values corresponds to the findings of S. V. Vassilev et al., (2010) of the combustion technology to have the most significant impact on the properties of biomass ash (ash types excluded). S. V. Vassilev et al., (2010) further concluded that WA originating from land clearing wood, pine chips and wood residue results in WAs complying with the limit for the primary oxides set by EN 450-1, (2012) and WA, originating from elm bark, olive wood, poplar bark, spruce bark and willow results in the WA complying with the limit for hydraulic activity set by EN 197-1, (2011). These conclusions corresponds to the findings in the presented PLS model, where the origin of biofuel is found to have the largest influence on the composition of oxides.

The particle size, governing the amount of WA particles to comply with the filler limit, (table 2), is highly dependent on the type of ash, where fly ash has the smallest particles (Cheah and Ramli, 2011a). In addition, the type of biofuel and the combustion temperature also influences the particle size. Wood pellets and high combustion temperature generally facilitates smaller particles, substantiated by Cheah and Ramli, (2011a) and Lecuyer et al., (1996). This correlation is due to the link between the combustion technology and combustion temperature (S. V. Vassilev et al., 2010).

3.3. Evaluation of the relationship between production parameters and physicochemical characteristics of WA for utilisation in cement-based materials by PLS modelling

To identify which production parameters results in a WA suitable in cement-based materials, the PLS model is compared with the chemical requirements set by (EN 450, 2012) and (EN 197-1, 2011), see tables 2 and 4. The standard (EN 450, 2012) only covers fly ashes, thus the ash types in the PLS model are neglected in the following.

3.3.1 Pozzolanic activity

The following points relate the experimental results to the chemical requirements for fly ash with pozzolanic properties set by EN 450-1, (2012):

- CFB combustion and biofuel originating from whole trees processed into wood chips as biofuel contributes to a high content of SiO_2 and thus a high content of primary oxides.
- CFB combustion with a low combustion temperature and biofuel originating from whole trees processed into a combination of wood chips and wood powder as biofuel contributes to a low content of CaO.
- Wood chips as biofuel contribute to a low content of MgO.
- CFB combustion and biofuel originating from wood logs contribute to a low content of P_2O_5.
- A low combustion temperature facilitates a low content of SO_3.
- Biofuel originating from whole trees processed into wood pellets as biofuel contributes to a low content of Cl^-.
- CFB combustion with a low combustion temperature and biofuel originating from wood logs contribute to a low LoI measured at 950 °C.

3.3.2 Hydraulic activity

The following points relate to the chemical requirements for fly ash with hydraulic properties set by EN 197-1, (2011):

- Biofuel originating from whole trees processed into wood chips as biofuel contributes to a high content of SiO_2 and CaO.
- Wood pellets as biofuel contribute to a high content of MgO. However, the content of MgO complies with the limit set by EN 197-1, (2011) for both wood pellets, chips and chips+powder as biofuel.

3.3.3. Filler

The following points relate to the chemical requirements for fly ash complying with the filler limit and category N set by EN 450-1, (2012):

- A high combustion temperature and wood pellets used as biofuel contribute to a high amount of WA particles complying with the filler limit.
- A low initial water content facilitates a WA complying with category N.

3.4 General discussion on utilisation of WA

Based on the physical and chemical characterization of the wood ashes this study shows that WAs have potential for utilisation as a SCM in cement-based materials with hydraulic properties. However, castings of concrete are needed to explore the full potential. To meet industrial use it is necessary to either reconsider the current standard EN 450-1, (2012) or establish a new standard taking into account, among others, the hydraulic properties and the alkali content.

Besides utilisation as a SCM, WA can be utilised as fertiliser. Spreading of WA and recycling of nutrients from wood combustion in the forest counteracts the export of nutrients from the forest when harvesting for energy production, thus creating a closed loop of the nutrients returning to the forest promoting forest growth (Ingerslev et al., 2011; Pitman, 2006). The suitability of WA as fertiliser depends on the retained nutrients in the ash e.g. potassium, phosphorous, calcium and magnesium, which must be relatively high and on the content of heavy metals e.g. arsenic, cadmium, lead, chromium and nickel, which must meet limiting values (Danish Environmental Protection Agency, 2017; Ingerslev et al., 2011). The Danish Environmental Protection Agency, 2017; Ingerslev et al., 2011 also sets limit for the conductivity of the WA of maximum 3600mS/m. The retained nutrients were not included in this study; however, based on the presented model and the measured conductivity, bottom or mixed ash and fly ash only originating from CFB combustion are suitable for recirculation to the forests.

It is not an either-or weather WAs can be used in concrete or as fertilizer. Some of the WAs may find use in concrete or as fertilizer, dependent on their characteristics and local conditions. When considering utilisation of the raw material WA, the utilization with the largest environmental and economic value as possible should be chosen.

4. Conclusion

In this study, WAs from eleven different plants were characterised and PCA and PLS modelling were performed in order to assess the linkage between the production parameters and the physiochemical characteristics of WA. The most important conclusion from the PLS model was the combustion method and type of ash (B or F) to have the largest influence on the WA characteristics. Based on the PLS model, a WA originating from CFB combustion of wood chips made from whole trees (logs, bark, buds and pine needles) at low temperatures are the most optimal type of WA when utilised as an SCM with pozzolanic activity, as these combustion parameters facilitate a higher content of primary oxides. A wood fly ash originating from the combustion of wood chips made from whole trees is the most optimal type of WA when utilised as an SCM with hydraulic activity. When used as filler, WA originating from high-temperature combustion with wood pellets used as a biofuel has the best characteristics. Low initial water content of the biofuel content facilitates the WA to comply with category N, which is consistent with wood pellets facilitating a low particle size, as wood pellets contain significantly less water than wood chips and wood chips + powder.

None of the investigated fly and mixed ashes complied with the normative compositional requirements for indications of pozzolanic activity of $\sum$primary oxides > 70 % (EN 450, 2012). Thus all of the investigated WAs have little or no pozzolanic potential, latter, which is primarily seen for, WAs from grate combustion. The opposite tendency is seen for the hydraulic activity, were all mixed and fly ashes complied with the normative compositional requirements, thus being able to set and harden, while submerged in water, by forming cementitious products in a hydration reaction. Only three of the investigated WAs are found to comply with the filler limit, thus expected to contribute to the compressive strength through the filler effect.

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References

ASTM International C125-15a, 2003. Standard Terminology Relating to Concrete and Concrete Aggregates i, 1–4.

Bellotto, M., Boni, C., Caridi, A., Cereda, E., Chemelli, C., Marcazzan, G.M.B., Parmigiani, F., Scagliotiti, M., Bellagamba, B., 1989. Analysis of Coal Fly Ash by Bulk and Surface Characterization Techniques. MRS Proc. 178, 45.

Berra, M., Mangialardi, T., Paolini, A.E., 2015. Reuse of woody biomass fly ash in cement-based materials. Constr. Build. Mater. 76, 286–296.

CEN (European Committee for Standardization), 2009. European Standard EN 14775: Solid biofuels - Determination of ash content.

Cheah, C.B., Ramli, M., 2011a. The implementation of wood waste ash as a partial cement replacement material in the production of structural grade concrete and mortar: An overview. Resour. Conserv. Recycl. 55, 669–685.

Cheah, C.B., Ramli, M., 2011b. Properties of high calcium wood ash and densified silica fume blended cement. Int. J. Phys. Sci. 6, 6596–6606.

Cheah, C.B., Ramli, M., 2011c. The implementation of wood waste ash as a partial cement replacement material in the production of structural grade concrete and mortar: An overview. Resour. Conserv. Recycl. 55, 669–685.

Chowdhury, S., Maniar, A., Suganya, O.M., 2015. Strength development in concrete with wood ash blended cement and use of soft computing models to predict strength parameters. J. Adv. Res. 6, 907–913.

Christensen, J.H., Hansen, A.B., Karlson, U., Mortensen, J., Andersen, O., 2005. Multivariate statistical methods for evaluating biodegradation of mineral oil. J. Chromatogr. A 1090, 133–145.

Dahl, O., Nurmesniemi, H., Pöykiö, R., Watkins, G., 2009. Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler. Fuel Process. Technol. 90, 871–878.

Danish Environmental Protection Agency, 2017. Bekendtgørelse om anvendelse af bioaske til jordbrugsformål (Bioaskebekendtgørelsen) (in Danish). Danish Environ. Prot. Agency 1–16.

Deschner, F., Winnefeld, F., Lothenbach, B., Seufert, S., Schwesig, P., Dittrich, S., Goetz-Neunhoeffer, F., Neubauer, J., 2012. Hydration of Portland cement with high replacement by siliceous fly ash. Cem. Concr. Res. 42, 1389–1400.

Elinwa, A.U., Mahmood, Y.A., 2002. Ash from timber waste as cement replacement material. Cem. Concr. Compos. 24, 219–222.

Emineral A/S, 2019. Emineral A/S [WWW Document]. URL http://www.emineral.dk/

EN 196-2, 2005. Methods of testing cement - Part 2: Chemical analysis of cement.

EN 197-1, 2011. Cement - Part 1: Composition, specifications and conformity criteria for common cements.

EN 450, 2012. Fly ash for concrete - Part 1: Definition, specifications and conformity criteria.

Etiégni, L., Campbell, A.G., 1991. Physical and chemical characteristics of wood ash. Bioresour. Technol. 37, 173–178.

Hamid, Y.S.A., 2009. Dissolution kinetics of carbonates in soil. Szent István University.

Herholdt, A.D., Justesen, C.F.P., Christensen, P.N., Nielsen, A., 1985. Beton-Bogen (In Danish). Cementfabrikkernes tekniske oplysningskontor, Aalborg Portland.

Illikainen, M., Tanskanen, P., Kinnunen, P., Körkkö, M., Peltosaari, O., Wigren, V., Österbacka, J., Talling, B., Niinimäki, J., 2014. Reactivity and self-hardening of fly ash from the fluidized bed combustion of wood and peat. Fuel 135, 69–75.

Ingerslev, M., Skov, S., Sevel, L., Pedersen, L.B., 2011. Element budgets of forest biomass combustion and ash fertilisation - A Danish case-study. Biomass and Bioenergy 35, 2697–2704.

International Energy Agency (IEA), 2007. Tracking Industrial Energy Efficiency and CO2 Emissions.

Jackson, J.E., 1991. A User's Guide To Principal Components, John Willy & Sons, Inc. New York.

Kirkelund, G.M., Ottosen, L.M., Jensen, P.E., Goltermann, P., 2016. Greenlandic waste incineration fly and bottom ash as secondary resource in mortar. Int. J. Sustain. Dev. Plan. 11, 719–728.

Lanzerstorfer, C., 2015. Chemical composition and physical properties of filter fly ashes from eight grate-fired biomass combustion plants. J. Environ. Sci. (China) 30, 191–197.

Lawrence, P., Cyr, M., Ringot, E., 2005. Mineral admixtures in mortars effect of type, amount and fineness of fine constituents on compressive strength. Cem. Concr. Res. 35, 1092–1105.

Lawrence, P., Cyr, M., Ringot, E., 2003. Mineral admixtures in mortars Effect of inert materials on short-term hydration. Cem. Concr. Res. 33, 1939–1947.

Lecuyer, I., Bicocchi, S., Ausset, P., Lefevre, R., 1996. Physico-Chemical Characterization and Leaching 1, 15–28.

Lothenbach, B., Scrivener, K., Hooton, R.D., 2011. Supplementary cementitious materials. Cem. Concr. Res. 41, 1244–1256.

McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. Bioresour. Technol 83, 37–46.

Moosberg-Bustnes, H., Lagerblad, B., Forssberg, E., 2004. The function of fillers in concrete. Mater. Struct. 37, 74–81.

Neslen, A., 2017. The end of coal: EU energy companies pledge no new plants from 2020 (Accessed 16th of November, 2018). Guard.

Neville, A.M., 1996. Properties of concrete, 4th ed. Wiley, New York.

Pedersen, K.B., Kirkelund, G.M., Ottosen, L.M., Jensen, P.E., Lejon, T., 2015. Multivariate methods for evaluating the efficiency of electrodialytic removal of heavy metals from polluted harbour sediments. J. Hazard. Mater. 283, 712–720.

Peyronnard, O., Benzaazoua, M., 2011. Estimation of the cementitious properties of various industrial by-products for applications requiring low mechanical strength. Resour. Conserv. Recycl. 56, 22–33.

Pitman, R.M., 2006. Wood ash use in forestry - A review of the environmental impacts. Forestry 79, 563–588.

Rajamma, R., Ball, R.J., Tarelho, L.A.C., Allen, G.C., Labrincha, J.A., Ferreira, V.M., 2009a. Characterisation and use of biomass fly ash in cement-based materials. J. Hazard. Mater. 172, 1049–1060.

Rajamma, R., Ball, R.J., Tarelho, L.A.C., Allen, G.C., Labrincha, J.A., Ferreira, V.M., 2009b. Characterisation and use of biomass fly ash in cement-based materials. J. Hazard. Mater. 172, 1049–1060.

Ramos, T., Matos, A.M., Sousa-Coutinho, J., 2013. Mortar with wood waste ash: Mechanical strength carbonation resistance and ASR expansion. Constr. Build. Mater. 49, 343–351.

Schneider, M., Romer, M., Tschudin, M., Bolio, H., 2011. Sustainable cement production-present and future. Cem. Concr. Res. 41, 642–650.

Shearer, C.R., 2014. The Productive Reuse of Coal, Biomass and the Productive Reuse of Coal, Biomass and Co-Fired Fly Ash. Georgia Institute of Technology.

Siddique, R., 2012. Utilization of wood ash in concrete manufacturing. Resour. Conserv. Recycl. 67, 27–33.

Siddique, R., 2008. Waste Materials and By-Products in Concrete. Springer Berlin Heidelberg, Berlin, Heidelberg.

Snellings, R., Mertens, G., Elsen, J., 2012. Supplementary Cementitious Materials. Rev. Mineral. Geochemistry 74, 211–278.

Teixeira, E.R., Mateus, R., Camõesa, A.F., Bragança, L., Branco, F.G., 2016. Comparative environmental life-cycle analysis of concretes using biomass and coal fly ashes as partial cement replacement material. J. Clean. Prod. 112, 2221–2230.

Udoeyo, F.F., Inyang, H., Young, D.T., Oparadu, E.E., 2006. Potential of wood waste ash as an additive in concrete. J. Mater. Civ. Eng. 18, 605–611.

van Loo, S., Koppejan, J., 2010. The Handbook of Biomass Combustion and Co-firing. Taylor & Francis Ltd.

van Roode, M., Douglas, E., Hemmings, R.T., 1987. X-ray diffraction measurement of glass content in fly and slags. Cem. Concr. Res. 17, 183–197.

Vassilev, S. V., Baxter, D., Andersen, L.K., Vassileva, C.G., 2010. An overview of the chemical composition of biomass. Fuel 89, 913–933.

Vassilev, S. V., Baxter, D., Vassileva, C.G., 2014. An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types. Fuel 117, 152–183.

Vassilev, S. V, Baxter, D., Andersen, L.K., Vassileva, C.G., 2010. An overview of the chemical composition of biomass. Fuel 89, 913–933.

Voshell, S., Mäkelä, M., Dahl, O., 2018. A review of biomass ash properties towards treatment and recycling. Renew. Sustain. Energy Rev. 96, 479–486.

Wang, K.S., Chiang, K.Y., Lin, K.L., Sun, C.J., 2001. Effects of a water-extraction process on heavy metal behavior in municipal solid waste incinerator fly ash. Hydrometallurgy 62, 73–81.

Wig, R.J., 1913. The Progress of the Work of the Bureau of Standards in Cement and Concrete. ACI J. Proc. 9.

Wold, S., Sjöström, M., Eriksson, L., 2001. PLS-regression: A basic tool of chemometrics. Chemom. Intell. Lab. Syst. 58, 109–130.

Ye, G., Liu, X., De Schutter, G., Poppe, A.M., Taerwe, L., 2007. Influence of limestone powder used as filler in SCC on hydration and microstructure of cement pastes. Cem. Concr. Compos. 29, 94–102.

Yeboah, N.N.N., Shearer, C.R., Burns, S.E., Kurtis, K.E., 2014. Characterization of biomass and high carbon content coal ash for productive reuse applications. Fuel 116, 438–447.

Table 1. Production parameters and ash type (X-variables for multivariate statistical analysis)

	Ash type	**Combustion method**	**Initial water content [%]**	**Type of biofuel**	**Origin of biofuel**	**Combustion temperature [ºC]**
WCBA	Bottom	CFB	24-40	Wood Chips	Whole trees	760-930
WPMA	Mixed	Grate	5-8	Wood Pellets	Logs	800
WCMA1	Mixed	Grate	35-45	Wood Chips	Logs	800-900
WCMA2	Mixed	Grate	35-50	Wood Chips	Whole trees	800-900
WCMA3	Mixed	Grate	40-45	Wood Chips	Logs	800-900
WPFA	Fly	Grate	5-8	Wood Pellets	Logs	1,000-1,100
WCFA1	Fly	Grate	35-50	Wood Chips	Whole trees	800-900
WCFA2	Fly	Grate	40-45	Wood Chips	Logs	800-900
WCFA3	Fly	CFB	25-40	Wood Chips	Whole trees	760-930
WMFA1	Fly	Grate	25-50	Wood Chips and Powder	Whole trees	900-1,000
WMFA2	Fly	Grate	40-45	Wood Chips and Powder	Whole trees	1,000-1,100

Table 2. Chemical composition and physical characteristics of investigated WA (Y-variables for multivariate statistical analysis) and mineralogical composition. * For category C. ± defines the standard deviation. Requirements for fly ash utilised in cement-based materials (EN 450, 2012), requirements for hydraulic activity (EN 197-1, 2011) and values from literature (Berra et al., 2015; Cheah and Ramli, 2011b, 2011c; Chowdhury et al., 2015; Dahl et al., 2009; Elinwa and Mahmood, 2002; Illikainen et al., 2014; Lanzerstorfer, 2015; Peyronnard and Benzaazoua, 2011; Rajamma et al., 2009b; Ramos et al., 2013; Siddique, 2008; Udoeyo et al., 2006; Vassilev et al., 2014; S. V Vassilev et al., 2010; Yeboah et al., 2014) are added for comparison.

	WCBA	**WPMA**	**WCMA 1**	**WCMA 2**	**WCMA 3**	**WPFA**	**WCFA 1**	**WCFA 2**	**WCFA 3**	**WMFA1**	**WMFA2**	EN 450-1, (2012)	EN 197-1, (2011)	**Literary review**
Chemical composition (%)														
SiO_2	57.8	3.4	3.9	4.1	9.4	4.3	3.6	1.7	19.3	5.3	10.3	> 25.0		1.74 – 73.01
Al_2O_3	4.9	0.9	1.5	0.9	1.3	0.9	0.6	0.4	3.4	0.9	1.5			0.12 – 28
Fe_2O_3	1.1	1.6	0.6	0.7	1.0	2.1	0.9	1.0	2.1	1.1	1.6			0.09 – 27.9
Σ primary oxides	*63.8*	*5.9*	*5.9*	*5.7*	*11.7*	*7.4*	*5.1*	*3.1*	*24.8*	*7.4*	*13.4*	*> 70.0*		
CaO/SiO_2 (-)	*3.6*	*11.1*	*8.6*	*19.5*	*5.7*	*15.0*	*13.6*	*36.2*	*2.2*	*6.3*	*3.1*		*> 2*	
CaO	16.0	37.8	33.6	79.8	53.2	64.4	49.0	61.6	41.7	33.6	31.5	< 10.0		1.16 – 83.46
MgO	1.5	4.1	2.0	2.7	1.5	4.5	2.8	2.2	3.3	0.8	4.0	< 4.0	< 5.0	0.7 – 14.57
K_2O	8.9	17.0	16.9	9.9	4.3	22.9	10.1	38.5	6.3	10.0	14.2			0.11 – 31.99
Na_2O	0.0	1.1	1.1	0.7	0.7	0.9	0.8	2.7	1.2	2.6	1.9			0.08 – 29.82
P_2O_5	< 0.5	2.7	1.1	3.7	1.1	2.5	3.2	2.5	2.5	1.4	3.0	< 5.0		0.07 – 13.01
TiO_2	0.2	0.3	0.0	0.0	0.1	0.0	0.0	0.0	0.2	0.1	0.2			0.01 – 1.2
SO_3	0.2	3.0	0.7	1.2	0.7	6.0	2.5	19.2	4.2	3.5	4.5	< 3.0		0.05 – 12.5
Cl^-	0.001 ± 0.0002	0.9 ± 0.03	1.0 ± 0.01	0.3 ± 0.003	0.05 ± 0.005	0.5 ± 0.01	0.6 ± 0.08	21.6 ± 1.2	0.5 ± 0.004	1.83 ± 0.2	0.52 ± 0.008	< 0.1		0.1 – 1.74
SO_4^{-2}	0.02 ± 0.0	4.1 ± 0.1	0.43 ± 0.0	1.3 ± 0.0	0.2 ± 0.0	5.6 ± 0.1	3.4 ± 0.4	10.2 ± 0.05	1.8 ± 0.0	3.36 ± 0.0	4.2 ± 0.1			0.12 – 0.96
LoI, 550ºC	0.0 ± 0.0	0.7 ± 0.4	9.8 ± 1.0	1.9 ± 1.2	1.7 ± 0.3	0.5 ± 0.3	8.4 ± 0.4	1.0 ± 0.3	0.8 ± 0.0	9.3 ± 1.5	7.2 ± 0.1			< 0.5
LoI, 950ºC	0.4 ± 0.1	9.9 ± 0.2	23.2 ± 1.5	19.7 ± 1.8	7.6 ± 0.3	15.3 ± 0.3	25.0 ± 0.2	16.7 ± 0.1	10.2 ± 0.1	25.4 ± 1.1	18.3 ± 0.2	< 9.0*		0.66 – 95.9
Physical characteristics														
Mean particle size, D_{50} (μm)	184.5 ± 1.8	94.5 ± 12.8	257.1 ± 29.9	65.1 ± 3.6	534.7 ± 54.2	18.3 ± 0.3	61.7 ± 3.9	10.5 ± 0.1	10.8 ± 0.0	273.9 ± 29.4	90.2 ± 11.0			3.2 – 1,440

Spread of particle size distribution (µm)	2.5 - 631.0	1.3 – 2,187.8	1.4 – 2,187.8	1.3 – 2,187.8	1.3 – 2,187.8	0.5 – 549.5	1.0 – 2,187.8	0.4 – 478.6	0.6 – 478.6	1.1 – 2,187.8	1.3 – 2,187.8	30 - 600
Specific Surface Area (m^2/g)	0.04 ± 0.02	0.2 ± 0.02	0.1 ± 0.0	0.3 ± 0.04	0.1 ± 0.01	0.7 ± 0.01	0.4 ± 0.03	1.2 ± 0.01	1.0 ± 0.01	0.1 ± 0.02	0.2 ± 0.02	
pH	11.9 ± 0.0	12.3 ± 0.1	13.0 ± 0.1	12.8 ± 0.0	12.6 ± 0.0	13.1 ± 0.0	13.0 ± 0.1	12.7 ± 0.0	12.7 ± 0.0	12.8 ± 0.0	13.3 ± 0.01	10.10 – 12.5
Conductivity ($mS\ m^{-1}$)	184.6 ± 7.8	1,894.3 ± 125.0	3,053.3 ± 100.7	2,253.3 ± 196.3	1,067.7 ± 103.8	4,760 ± 535.1	4,980.0 ± 1,496.4	3,976.7 ± 141.9	2,380 ± 10.0	3,950.0 ± 364.3	12,160 ± 317.6	
$CaCO_3$ (%)	21.4 ± 0.2	27.6 ± 0.5	19.3 ± 0.3	16.0 ± 0.9	12.1 ± 0.4	26.5 ± 3.4	16.9 ± 0.2	21.1 ± 0.3	1.5 ± 0.2	22.2 ± 0.4	16.1 ± 0.3	
Water solubility (%)	0.5 ± 0.4	14.1 ± 0.2	11.8 ± 0.6	9.0 ± 0.5	2.2 ± 0.2	17.9 ± 3.4	8.9 ± 0.5	43.6 ± 1.2	6.8 ± 0.4	14.8 ± 0.3	24.1 ± 1.2	
Percentage of WA complying with the filler limit and compliance with Category N (EN 450, 2012) ***(Yes = comply/No = does not comply)***												
Percentage complying with the filler limit (<250µm) (Herholdt et al., 1985; Moosberg-Bustnes et al., 2004)	72 ± 0.6	78 ± 4.6	49.7 ± 2.5	72.3 ± 1.9	31.3 ± 2.1	98.2 ± 0.7	65.7 ± 1.0	95.5 ± 0.4	98.6 ± 0.2	48.5 ± 1.9	76.6 ± 4.9	
Complying with category N (EN 450, 2012)	No	No	No	No	No	Yes	No	Yes	Yes	No	No	
Mineralogical compositions of investigated WA determined by XRD analysis. X marks detected minerals.												
Quartz (SiO_2)	X	X	X	X	X	X	X		X	X	X	
Portlandite ($Ca(OH)_2$)			X	X	X			X				
Calcite ($Ca(CO_3)$)		X	X	X	X	X	X	X	X	X	X	
Sylvite (KCl)		X								X		
Arcintie ($K_2(SO_4)$)		X	X	X			X	X		X	X	
Periclase (MgO)		X				X	X					
Quick Lime (CaO)						X	X					
Wollastonite ($CaSiO_3$)	X											

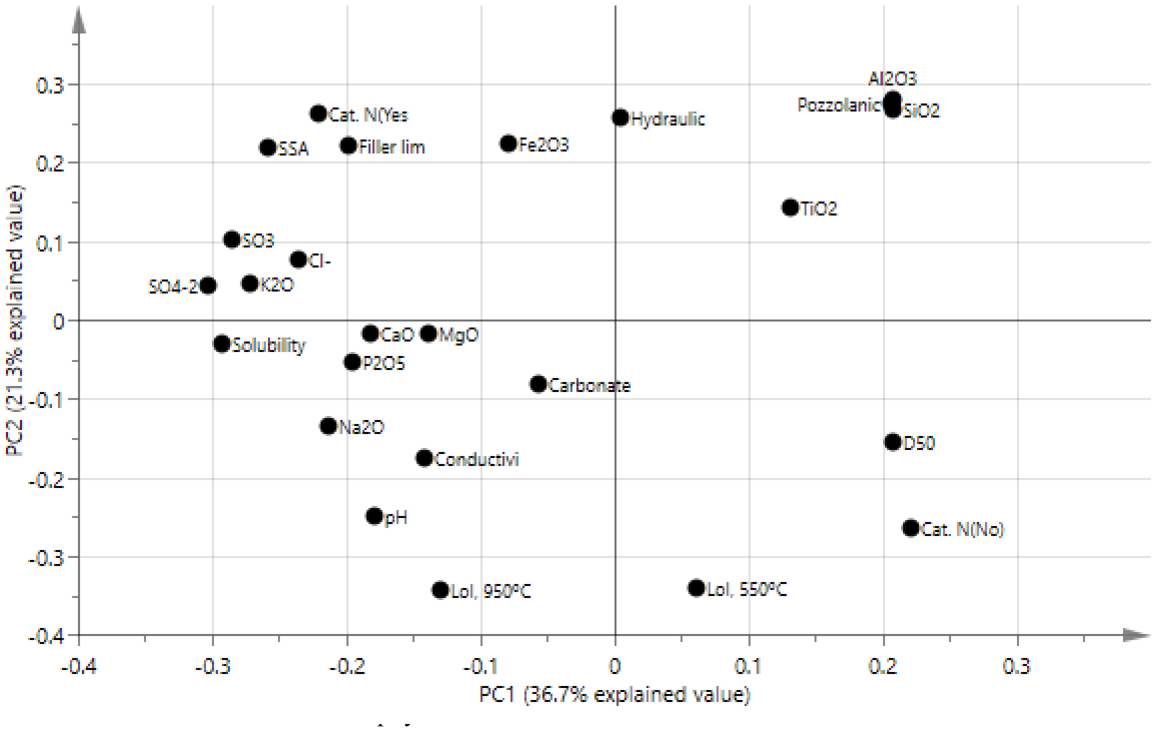


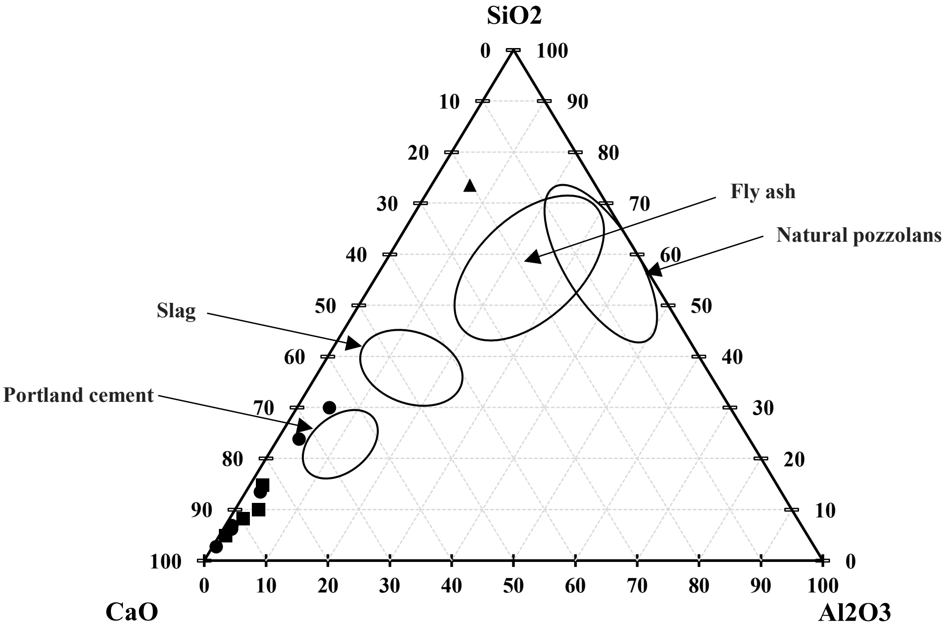
Table 3. Overview of relationships between the production parameters and the wood ash characteristics based on the PLS analysis. High values for the wood ash characteristics are achieved by high (+) or low values (-) of the given production parameter.

	Ash type: B	**Ash type: F**	**Combustion temperature, middle**	**Combustion method: CFB**	**Combustion method: Grate**	**Type of biofuel: Chips+Powder**	**Ash type: M**	**Type of biofuel: Chips**	**Origin of biofuel: Log**	**Origin of biofuel: Tree**	**Type of biofuel: Pellets**	**Initial water content, middle**
SiO_2 (%)	+			+	-			+	-	+		
Al_2O_3 (%)	+			+	-				-	+		
Fe_2O_3 (%)							-	-			+	-
Σ primary oxides (%)	+			+	-			+	-	+	-	
SiO_2/CaO (-)								+	-	+		
CaO (%)	-		+	-	+	-			+	-		
MgO (%)								-			+	
K_2O (%)	-							-	+	-	+	
Na_2O (%)	-	+	+			+						
P_2O_5 (%)	-	+		-	+				-	+		
TiO_2 (%)				+	-				-	+		
SO_3 (%)	-	+	+									
Cl^- (%)	-							+	+	-	-	
SO_4^{-2} (%)	-	+	+				-	-	+	-	+	
LoI, 550ºC (%)						+			-	+	-	
LoI, 950ºC (%)	-			-	+	+			-	+		
Mean particle size, D_{50} (µm)	+	-	-			+	+	+			-	+
SSA (m^2/g)	-	+	+			-	-					-
pH	-		+	-	+							
Conductivity (mS cm^{-1})	-	+	+			+						
Carbonate content (%)						-		-	+	-	+	-
Water solubility (%)	-	+	+	-	+	+		-	+	-	+	
Category N (Y = + /N = -)		+					-					-
<250 µm		+	+			-	-	-			+	-

Table 4. VIP values of the variables in the X-matrix in descending order.

Variable	**VIP-value**
Ash type: F	1.27
Combustion method: CFB	1.16
Combustion method: Grate	1.16
Ash type: B	1.13
Type of biofuel: Chips	1.09
Ash type: M	0.98
Type of biofuel: Chips+Powder	0.95
Initial water content, average	0.95
Type of biofuel: Pellets	0.90
Combustion temperature, average	0.82
Origin of biofuel: Log	0.70
Origin of biofuel: Tree	0.70

Figure 2. CaO-SiO$_2$-Al$_2$O$_3$ ternary diagram for the investigated wood ashes. Black triangle ▲: bottom ash, black square ■: mixed ash and black dot ●: fly ash. Ternary diagram adapted from Lothenbach et al., (2011).



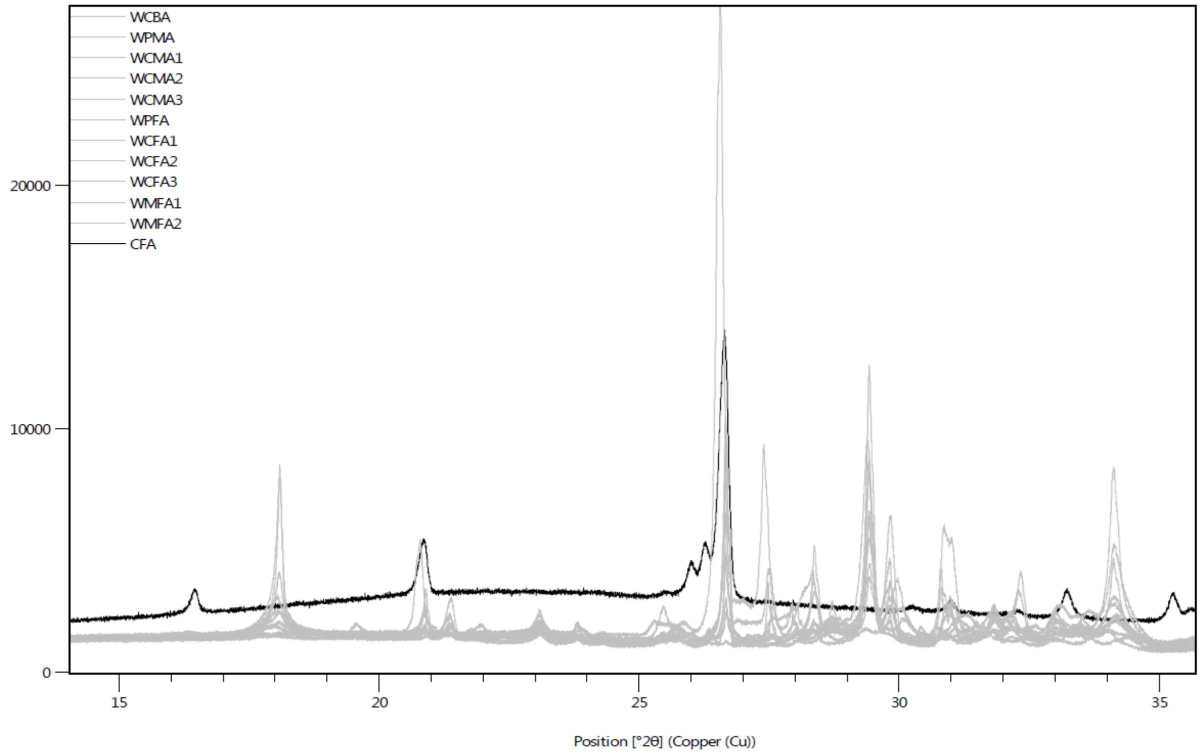
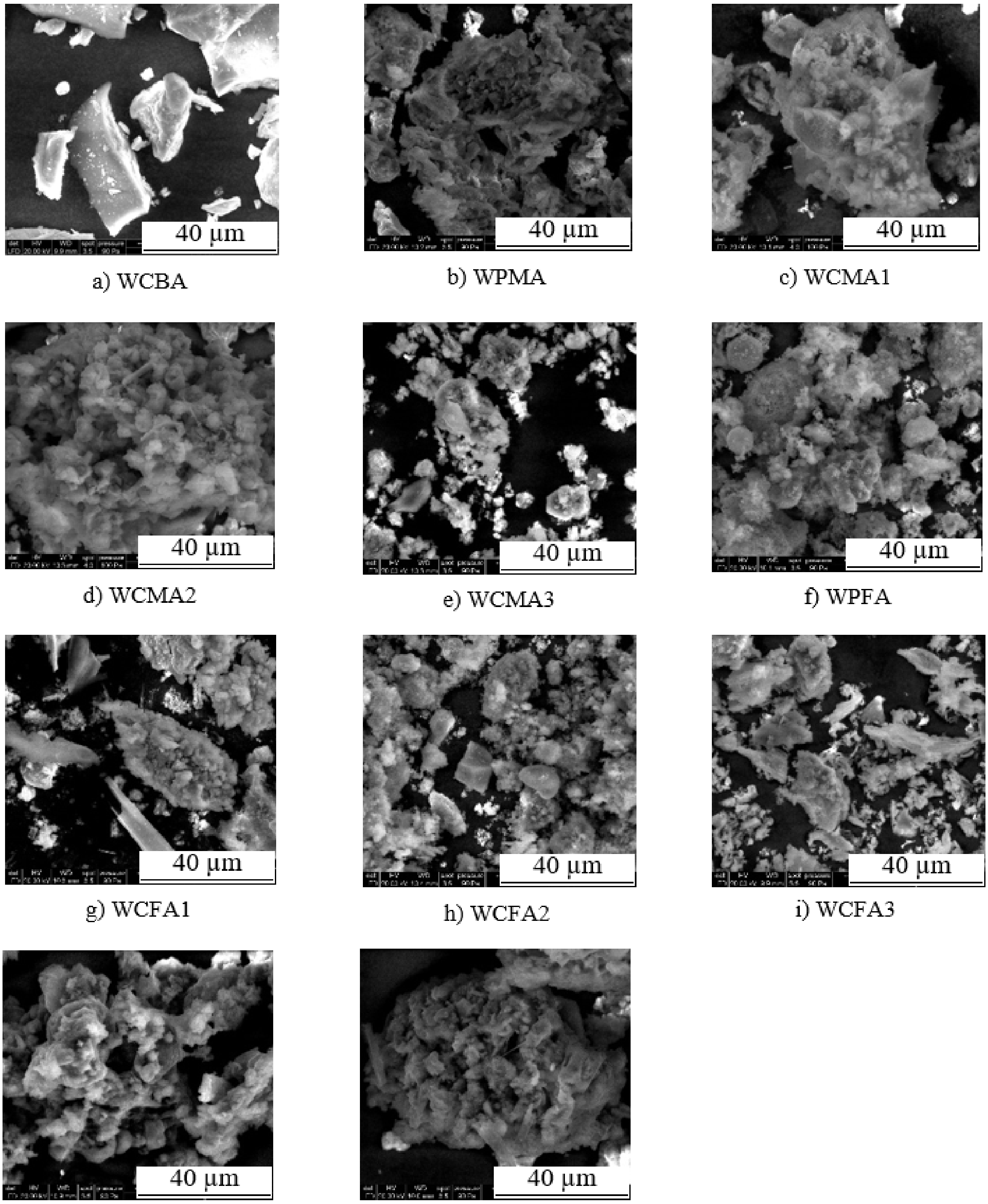


Figure 3. Comparison between the XRD diffractograms from 15°2θ to 35°2θ (amorphous rise) for the investigated WA and a coal fly ash.



a) WCBA b) WPMA c) WCMA1 d) WCMA2 e) WCMA3 f) WPFA g) WCFA1 h) WCFA2 i) WCFA3 j) WMFA2 k) WMFA1

Figure 4. SEM images displaying the 11 investigated WA.