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Utilisation of Wood Ash in Cement-Based Materials

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PhD thesis

Technical University of Denmark

Kongens Lyngby, Denmark

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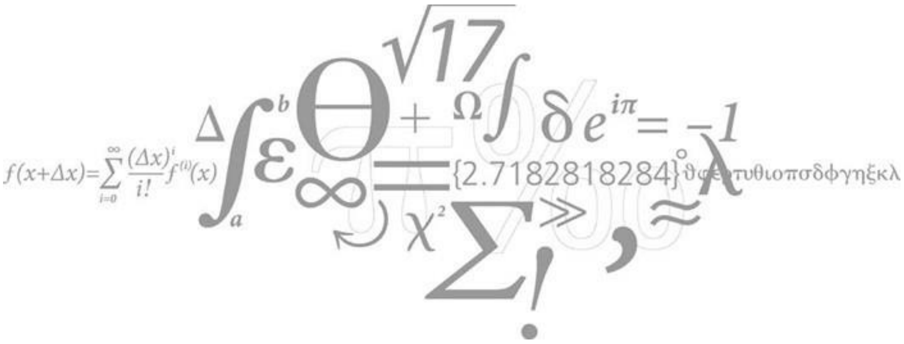

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Preface

The presented thesis compiles the work and findings of my PhD research project, conducted at the Section for Artic Technology and Sustainable Solutions (2017) and later at the Section for Materials and Durability (2018-2020), Department of Civil Engineering at the Technical University of Denmark (DTU). The main supervisor of the project was Professor Lisbeth M. Ottosen (DTU), and the co-supervisors were Associate Professor Gunvor M. Kirkelund (DTU), Associate Professor Pernille E. Jensen (DTU) and Professor Mette R. Geiker (Norwegian University of Science and Technology, NTNU).

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Kgs. Lyngby, November 2020

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I owe my parents Jan and Susan, my sister Anne, my brother Esben, and my good friends Thea and Samuel, my gratitude for their love and support. Especially Samuel, for his indispensable help with both experiments and correction of the final thesis. Finally, I would like to thank my wonderful, always understanding and very patient boyfriend Claes, for always believing in me. Without him, his unconditional support and endless love, this work would not have been possible, and for that, I am forever grateful.

Abstract

Wood ashes originating from combustion of wood and woody biomass were investigated with the aim of utilising wood ash as a partial cement replacement.

The physicochemical properties of wood ashes varied significantly depending on the combustion technique and temperature, the type of woody biomass used etc. Multivariate data analysis of chemical compositions was performed to determine which production parameters yielded the wood ash most suitable for utilisation as a partial cement replacement in cement-based materials. The standards EN 450 [1] and EN 197 [2] were used for the assessment of possible pozzolanic and hydraulic activity, respectively, in the multivariate data analysis. The multivariate data analysis revealed that the combustion technique had the greatest influence on the physicochemical characteristics of the wood ash. It was determined that wood ashes originating from grate combustion had the highest probability of possessing hydraulic properties, while, wood ashes originating from fluidised bed combustion had the highest probability of possessing pozzolanic properties. Based on this analysis, two wood ashes were selected for further investigations: one as the wood ash most likely to possess hydraulic properties and the other as the wood ash most likely to possess pozzolanic properties.

Pozzolanic activity was tested on mixtures with 20% cement replacement with wood ash, and hydraulic activity was assessed based on the phase and strength development of 100% wood ash and water mixtures. Contrary to the results obtained by multivariate data analysis, both of the selected wood ashes displayed hydraulic properties (they set, hardened and developed strength) and neither of them showed pozzolanic activity. Despite both possessing hydraulic properties, a large difference in the strength development of the two wood ash and water mixtures was observed. Subsequent analysis of the phase development determined the formation of ettringite as a major factor in strength development. Formation of ettringite requires aluminium, and upon lack of aluminium formation of gypsum was observed instead, leading to a significantly lower compressive strength development. The difference in strength development of the two wood ash water mixtures was therefore attributed to the difference in aluminium content.

Low-levels of cement replacement and pre-treatment of wood ashes have generally been shown in literature to enhance compressive strength and reduce the risk of durability issues in cement-based materials. In this project, an in-depth analysis of phase and strength development of both untreated and washed samples with wood ashes utilised as low-level cement replacements (10%) has been performed, expanding the knowledge on the influence of such pre-treatments on the performance of wood ashes as low-level cement replacements. A decrease in compressive strength was observed for all cement-wood ash mortars when compared to a reference cement mortar, however, an increase is seen compared to a mortar with a 10% cement replacement with an inert filler. This increase in compressive strength is attributed to the formation of ettringite in all cement-wood ash specimens, due to the aluminium provided by the cement clinker and the increased sulphate content from the wood ash. Washing of wood ashes prior to use was found to remove SO_3 and thus enable regulation of ettringite formation by adjusting the SO_3/C_3A ratio. Based on differences in compressive strength an optimum SO_3/C_3A ratio in the binder of $0.4 \leq$ optimum < 0.5 was proposed. This ratio ensures the maximum contribution to compressive strength from ettringite formation, without excessive ettringite formation leading to microcracking. Several potential durability issues resulting from the presence of oxides in the wood ashes were reduced by a washing pre-treatment (risk of sulphate attack, chloride corrosion and alkali-silica reactions). However, potential durability issues related to the content of CaO_{free}, MgO and LoI were still a risk, thus, other types of treatments could be required. An assessment of the leaching behaviour of heavy metals concluded that none of the wood ashes, untreated or washed, posed any significant environmental risk when used as low-level cement replacements in cement-based materials.

In summary, ettringite was determined to be the most important phase when wood ash was used as a partial cement replacement, due to the contribution to compressive strength. However, even at low-level cement replacement ratios, partial cement replacement with wood ash led to a decrease in the compressive strength of cement-based materials. The hydraulic properties of wood ash could facilitate usage in other types of cement-based materials with lower strength requirements. A washing pre-treatment greatly decreased the risk of several potential durability issues, therefore, further optimisation of wood ash characteristics by pre-treatment may be a viable option to explore in future work.

Resume

Træaske fra forbrænding af træ er blevet undersøgt med det formål, at udnytte træaske som en delvis cement erstatning.

Træaskes fysisk og kemiske egenskaber varierer signifikant afhængig af faktorer som forbrændingsteknik, temperatur og hvilken type træ som er blevet brugt. Multivariat dataanalyse er blevet udført for at for at bestemme, hvilke produktionsparametre som medfører træaske mest egnet til at anvende som delvis cementerstatning i cementbaserede materialer, evalueret ud fra den fysisk og kemiske komposition. Standarderne EN 450 [1] og EN 197 [2] blev inkluderet i multivariate dataanalysen for at vurdere muligheden for henholdsvis pozzolanisk og/eller hydraulisk aktivitet. Den multivariate dataanalyse viste at forbrændingsteknikken havde den største indflydelse på træaskens fysisk-kemiske egenskaber. Yderligere viste den, at træaske fra risteforbrænding har størst sandsynlighed for at besidde hydrauliske egenskaber, mens træaske fra forbrænding i fluidiseret leje har størst sandsynlighed for at besidde pozzolanske egenskaber. Baseret på denne analyse er to træasker udvalgt til yderligere undersøgelser: én træaske, med sandsynlighed for at besidde hydrauliske egenskaber og én træaske, med sandsynlighed for at besidde pozzolanske egenskaber.

Pozzolanske aktivitet blev testet på blandinger med 20% cementerstatning med træaske, og hydraulisk aktivitet blev evalueret ud fra fase- og styrkeudviklingen for prøver med 100% træaske som binder. I modsætning til resultaterne fundet ud fra den multivariate dataanalyse, viste begge de undersøgte træasker sig, at have hydrauliske egenskaber (hærdede og udviklede styrke), og ingen af dem udviste pozzolansk aktivitet. På trods af at begge træasker besidder hydrauliske egenskaber, blev der observeret en stor forskel i styrkeudviklingen for prøver med 100% træaske som binder. Efterfølgende analyse af faseudviklingen afslørede at dannelsen af ettringit var en væsentlig faktor i styrkeudvikling. Dannelse af ettringit kræver aluminium, og i mangel af aluminium blev der i stedet observeret dannelse af gips, hvilket medførte en signifikant lavere trykstyrkeudvikling. Forskellen i styrkeudvikling mellem prøverne, med 100% træaske som binder, blev derfor tilskrevet forskellen i aluminiumindhold.

Forbehandling af træaske og lave cement erstatninger har i litteraturen vist sig at forbedre

trykstyrken og reducere risikoen for holdbarhedsproblemer. I dette projekt er der blevet udført en dybdegående analyse af fase- og styrkeudvikling for prøver med en lav cementerstatning (10%) med både ubehandlede og vaskede træaske. Dette bidrager med viden om hvilken indflydelse sådanne forbehandlinger har på ydeevnen, når træaske bruges som lav cement erstatning. Sammenlignet med en ren cement reference prøve ses der et fald i trykstyrken for alle cement-træaske prøver, til gengæld ses der en stigning i trykstyrken sammenlignet med en 10% cement erstatning med et inert materiale. Denne stigning i trykstyrken tilskrives dannelsen af ettringit i alle cement-træaskeprøver grundet aluminium-indholdet i cementen og det øgede sulfatindhold fra træaskerne. Vask af træaske, mindskede indholdet af sulfat og muliggjorde dermed en regulering af dannelsen af ettringit ved at justere SO_3/C_3A-forholdet. Baseret på forskellene i trykstyrken blev der foreslået et optimalt SO_3/C_3A - forhold i binderen på $0,4 \leq$ optimal $< 0,5$. Dette forhold sikrer det maksimale bidrag til trykstyrken, som et resultat af ettringit dannelsen, uden overdreven dannelse af ettringite, som kan medføre mikrorevner.

Flere mulige holdbarhedsproblemer, som følge af oxidsammensætningen i træasken, blev reduceret ved hjælp af en forbehandlende vask af træasken (risiko for sulfatangreb, kloridkorrosion og alkali-silica-reaktioner). Imidlertid var potentielle holdbarhedsproblemer, relateret til indholdet af CaO_{free}, MgO og LoI, stadig en risiko, og andre typer af forbehandlinger kan derfor være nødvendige. En evaluering tungmetalindholdet og udvaskning konkluderede, at ingen af træaskerne, uvasket eller vasket, udgjorde nogen væsentlig miljørisiko, når træasken blev brugt som en lav cement-erstatning i cementbaserede materialer.

Ettringite er bestemt til at være den vigtigste fase, når træaske blev brugt som delvis cementerstatning på grund af dens bidraget til trykstyrken. Men selv ved lave cementerstatninger førte en delvis cementerstatning med træaske til et fald i trykstyrken. Træaskes hydrauliske egenskaber kan medføre brug af træaske i andre typer cementbaserede materialer med lavere styrkekrav. En vaskeforbehandling reducerede i høj grad risikoen for flere potentielle holdbarhedsproblemer, og yderligere optimering af træaskeegenskaberne ved hjælp af forbehandling kunne være en spænende mulighed at udforske i fremtidigt arbejde.

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List of Abbreviations

Cement chemistry shorthand notations employed in this thesis:

C = CaO
S = SiO_2
A = Al_2O_3
F = Fe_2O_3
M = MgO
H = H_2O
$\bar{C}$ = CO_2
$\bar{S}$ = SO_3

Shorthand notation of anhydrous phases and hydrates in cement systems:

Name	**Shorthand notation / abbreviation**	**Stoichiometric or general formula**
Alite	C_3S	Ca_3SiO_5
Belite	C_2S	Ca_2SiO_4
Aluminate	C_3A	$Ca_3Al_2O_3$
Ferrite	C_4AF	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
Calcium silicate hydrate	C-S-H	$xCaO \cdot SiO_2 \cdot yH_2O$ (variable composition)
Calcium aluminium silicate hydrate	C-A-S-H	$xCaO \cdot Al_2O_3 \cdot SiO_2 \cdot yH_2O$ (variable composition)
Calcium aluminium hydrate	C-A-H	$xCaO \cdot Al_2O_3 \cdot yH_2O$ (variable composition)
Portlandite	CH	$Ca(OH)_2$
Calcite	$C\bar{C}$	$CaCO_3$
Monocarbonate	$C_4A\bar{C}H_{11}$ (Mc)	$3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$
Hemicaronate	$C_4A\bar{C}_{0.5}H_{11.5}$ (Hc)	$3CaO \cdot Al_2O_3 \cdot 0.5Ca(OH)_2 \cdot 0.5CaCO_3 \cdot 11.5H_2O$
Monosulphate	$C_4A\bar{S}H_{12}$ (Ms)	$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$
Ettringite	$C_6A\bar{S}_3H_{32}$ (Et)	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$
Hydrotalcite	Ht	$Mg_6(Al_xFe_{1-x})_2(SiO_4)_y(OH)_{4(3-y)}$

Other abbreviations:

AFm : Alumina, ferric oxide, mono-sulphate
AFt : Alumina, ferric oxide, tri-sulphate

BCF	:	Bubbling fluidised bed
CEM I	:	CEM I 52.5 N (LA), ordinary Rapid Cement from Aalborg Portland
CFA	:	Coal fly ash
CFB	:	Circulating fluidised bed
IC	:	Ion chromatography
ICP	:	Inductively coupled plasma optical emission spectroscopy
LoI	:	Loss on Ignition
PCA	:	Principal component analysis
PLS	:	Projections onto latent structures
REF	:	Reference mixture with 100% CEM I
SAI	:	Strength activity index
SCM	:	Supplementary cementing materials
SDG	:	Sustainable development goal
SEM	:	Scanning Electron Microscope
TGA	:	Thermogravimetric analysis
WA	:	Wood Ash
WA1	:	Wood ash from grate combustion of wood chips at Skærbækværket, sieved to a particle size of < 250µm.
WA1-W	:	WA1 sieved to a particle size of < 250µm and subjected to a washing treatment
WA2	:	Wood ash from circulating fluidized bed combustion of wood chips at Värtaverket, sieved to a particle size of < 250µm.
WA2-W	:	WA2 sieved to a particle size of < 250µm and subjected to a washing treatment
w/b ratio	:	Water-to-binder ratio on weight basis
w/c ratio	:	Water-to-cement ratio on weight basis
wt%	:	Weigh percent
XRD	:	X-ray diffraction
XRF	:	X-ray fluorescence

Structure of the Thesis

The thesis is organized into two parts: the first part sets the frame of the topic and provides an overview of the research conducted.

The first part of the thesis is structured into seven chapters:

1 **Introduction:** This chapter provides a general introduction to the topics of the thesis: environmental problems related to cement production, the current usage of supplementary cementitious materials and utilisation of wood ash.

2 **Knowledge Gaps in the Field:** Knowledge gaps identified in the literature in relation to the topic are identified and described.

3 **Research Methodology:** This chapter provides an overview of the research methodology and experimental techniques used, with further details provided in the appended papers.

4 **Impact of Production Parameters on Physicochemical Characteristics of Wood Ash:** Wood ashes originating from different types of woody fuel and combustion processes are characterised in this chapter. Multivariate modelling is used to identify correlations between production parameters and physicochemical characteristics and assessed in relation to the current standards.

5 **Reaction Mechanisms of Wood Ash:** The reaction mechanisms, pozzolanic or hydraulic activity, of wood ash are determined in this chapter in order to assess the possible influences of WA when used as a partial cement replacement on the compressive strength is assessed. The results are then compared to the multivariate model and the results obtained by the model are reassessed.

6 **Optimisation of Wood Ash for use as a Low-Level Cement Replacement:** The possibility for optimisation of wood ash for improved performance as a partial cement replacement is investigated and discussed in this chapter. The focus is on the phase

development and mechanical responses of mixtures with low-level cement replacements with untreated and treated wood ashes. Potential durability issues and leaching of heavy metals is also assessed.

7. **Main Conclusions:** The main conclusion from the complied findings of this PhD project are summarised and marks the end of the first part of the thesis.

The second part contains three journal papers (2 published and 1 submitted), two conference abstracts (published), and two additional notes (unpublished).

1 Introduction

Cement is the largest manufactured product on Earth (by mass). Cement can be combined with water and mineral aggregates to form cement-based materials like mortar and concrete, and are the second most used substances in the world after water [3]. In 2017, 4.1 billion tonnes of cement were produced worldwide [4], corresponding to 540 kg per person. In addition, sustainable development goals (SDGs) [5] (elaborated in section 1.4) require a substantial expansion of built-up environment, as is reflected by several of the SDGs:

- SDG 4.A Build and upgrade education facilities.
- SDG 7.B By 2030, expand infrastructure and upgrade technology for supplying modern and sustainable energy services.
- SDG 9.4 upgrade infrastructure and retrofit industries to make them sustainable, with increased resource-use efficiency.
- SDG 11.1, ensuring access for all to adequate, safe and affordable housing and upgrading of slums.

These goals will inevitably lead to an increase in the demand for cement-based materials [3], and projections suggest a 50% increase in the production of cement by 2050 [6].

Cement production currently accounts for 8-9% of the global anthropogenic CO_2 emission [6]. For each tonne of cement manufactured, approximately 1 tonne of CO_2 is emitted into the atmosphere [6]. Two sources are mainly responsible for CO_2 emissions linked to the production of cement. Firstly, CO_2 is emitted as a result of the energy consumption during heating of raw materials e.g. limestone and clay in a kiln at ~1450°C to produce clinker phases such as alite, belite, aluminate and ferrite [6,7]. Secondly, the raw material limestone consists mainly of $CaCO_3$ and releases 44wt% of its mass as CO_2 when heated to above 800°C [8]. CO_2 released from limestone accounts for approximately 60% of CO_2 emissions from cement production [3].

One way to decrease the environmental impact of cement is to reduce CO_2 emissions linked to cement production. This could be achieved by increasing the energy efficiency of the kilns, using renewable fuels for heating the raw materials, or producing blended cements with a lower clinker content by replacing a part of the cement clinker with different types of mineral additions [3,9]. Traditionally these types of mineral additions are categorised as supplementary cementitious materials (SCMs) [10]. Replacing parts of the cement clinker in cement-based materials with SCMs is recognised as the fastest solution to reduce CO_2 emissions from the cement and concrete industry [11].

One of the most desirable SCMs is high-quality coal fly ash (CFA), which is ash from combustion of coal in power plants. However, in April 2017, 26 of the 28 EU nations agreed to stop investment into new coal-fired power plants after 2020. This decision was in close accordance with the Paris Agreement and the goal to be 100% reliant on renewable energy by 2050 [12]. This decision has and will continue to result in decreasing availability of high-quality CFA, and in the transformation of many existing power plants to the use of biomass as a fuel source instead of coal. The increased combustion of biomass leads to increasing availability of biomass ashes including wood ash (WA), which is derived from combustion of wood and woody biomass, such as wood chips, pellets and sawdust [13].

The present PhD thesis "*Utilisation of Wood Ash in Cement-Based Materials"* discusses the potential use of WA as a partial cement replacement in cement-based materials creating a more sustainable material for the building industry.

1.1 Wood Ash and Possibilities for Utilisation

The increasing global energy consumption and the goal to provide 100% carbon neutral fuel by 2050 [12] has prompted the need to look for alternative energy sources. Biomass is widely recognised as renewable and does not contribute to the greenhouse effect due to CO_2 neutral conversion, thus making it an environmentally friendly energy source [14]. Biomass is classified as organic material originating from plants, e.g. wood, straw, and bagasse [15]. A rapid increase in the use of biomass as biofuel in heating and power production has been reported in the last decades [16]. Combustion of biofuel inevitably leads to the formation of ashes categorized as biomass ash, hereunder wood ash (WA).

Approximately 10 million tonnes of biomass ash was produced globally in 2018 from electricity production alone, and further quantities were generated from heat production [16]. In Denmark, 31,000 tonnes of WA are produced annually, were approximately 15,000 tonnes are used as fertilizer, and 15,000 tonnes are used for soil improvement [16]. In counties such as Canada, Austria, Switzerland, Portugal, Italy, and Norway less than 10% of the WA they produce is utilised, and the rest ends up in landfills [16,17]. Landfilling of WA can lead to a range of potential problems. The fine particulate WA can easily be rendered airborne, forming a potential health risk to nearby residents, and a source of pollution to the surrounding nature [18]. Landfilling can also lead to leaching of hazardous chemical elements causing contamination of the groundwater [19]. To avoid hazardous contamination properly engineered landfills are required, this makes landfilling of WA expensive with prices reaching 500 Euros pr. tonne [18,20]. Thus, utilisation of WA is of great interest, due to the environmental and economical disadvantages of landfilling, aims to reduce CO_2 emissions and political policies aiming to achieve “zero waste” [21].

Several ways to utilise WA have been proposed in the literature, some of which have already been implemented in practice. Harvesting of biomass from forests leads to the exporting of nutrients from the forest. Much of the nutrients are retained in the WA, thus ash spreading can assist in re-establishing the nutrient balance in forests [22]. Sweden and Denmark use WA in forestry. However, a major drawback is the high solubility of the WA leading to rapid release of nutrients, which can have an adverse effect on vegetation. It is therefore necessary to pelletize the WA before it is used in forestry [16]. In Austria, Canada, Denmark, Germany, Italy and the Netherlands, WA may be used as fertiliser in agriculture depending on the pH, content nutrients CaO, K_2O and SO_2 and trace element concentrations, e.g. cadmium, chromium and mercury. The content of toxic heavy metals and high pH limits the practical application of WA for fertiliser applications [16,23,24].

Different options for utilisation of WA for civil engineering purposes have been proposed; as a raw meal constituent in the production of cement [25], as a sand replacement [26] and as a cement replacement [18,27–30] in cement-based materials. WA as a raw meal addition in cement production is used in Austria, Canada and Italy. However, this type of utilisation necessitates a nearby cement factory needing this specific addition and sufficient production of

WA to match the scale of the cement production [16]. Utilisation of WA in blended cement is not allowed according to the current EU regulations. According to the European standard for fly ash in concrete EN 450 [1], only fly ash derived from co-combustion of pulverised coal and green wood, where the minimum percentage of coal is 50 % by dry mass, is allowed to be used as an SCM. Green wood is defined as wood originating from trees, bushes, stubs, planning, sawdust and shavings used in the form of dust, chips and pellets [1]. Fly ash referred to in EN 197 [2] should conform with EN 450 [1]. EN 197 [2] is used for assessment of the performance characteristics of a cement based on the available performance tests (e.g. setting and strength).

A life cycle assessment conducted by Teixeira et al. [31], compared the potential environmental impact from cradle-to-gate of 1 m^3 of concrete with Portland cement and 0, 20, 40 and 60 % replacement of cement with different types of mineral additions. The assessment showed that the biomass fly ash had the best environmental performance, increasing with the replacement percentage. The environmental impact was assessed based on six categories: global warming, ozone layer depletion, acidification potential, eutrophication potential, formation potential of tropospheric ozone and abiotic depletion potential of fossil resources. A life cycle assessment conducted by da Costa et al. [32] showed that transportation and pre-treatments of the biomass ash had negative effects on the environmental performance. None the less, all scenarios where woody biomass ash was utilised as a cement replacement showed lower environmental impacts (reduces extraction and processing of raw materials, energy consumption required to produce new materials and transportation) than landfilling. In these two studies, only the environmental performance of materials with blended biomass cements were considered and important parameters like material durability and compressive strength were not considered. The improvement in environmental performance amplifies the importance of studying biomass ash in cement-based materials, but also exemplifies the need for investigations of the properties and the technical performance of the material when used in building materials.

1.2 Use of Supplementary Cementitious Materials in cement-based materials

Supplementary cementitious materials (SCMs) cover a wide range of mineral additions used in concrete as supplements for or in addition to Portland cement. According to Thomas [10], the term “SCM” covers materials contributing to the properties of hardened cement-based materials, either through pozzolanic activity (reacting with portlandite from the cement hydration), hydraulic activity (reacting with water, precipitating hydration products similar to those formed with Portland cement) or both.

The variation in the chemical composition between the different types of SCMs is displayed in a CaO-Al_2O_3-SiO_2 ternary diagram in Figure 1.

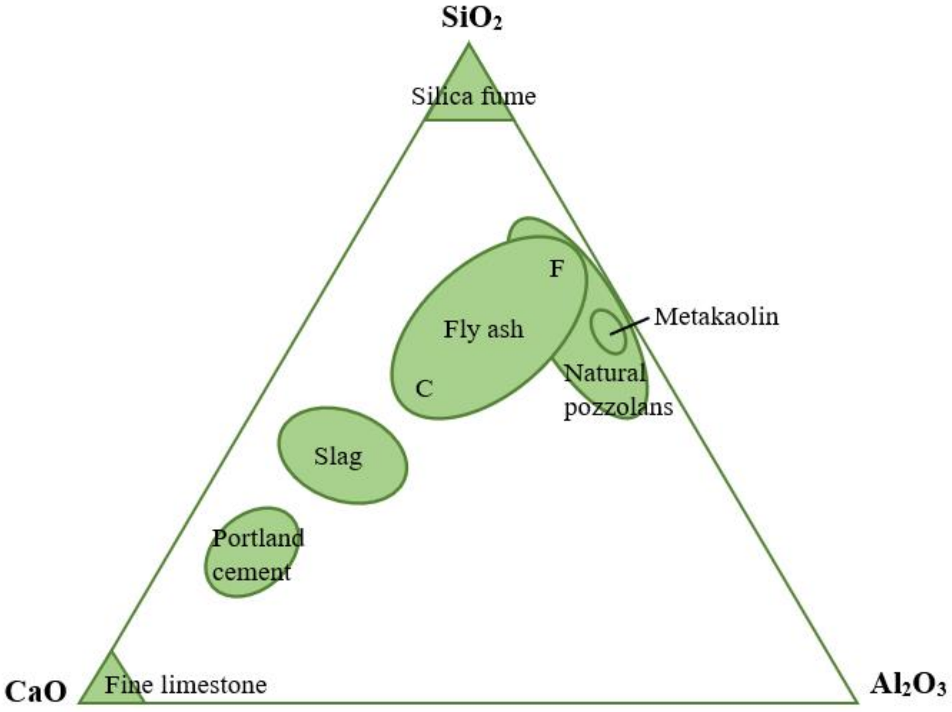

Figure 1. CaO-Al_2O_3-SiO_2 ternary diagram of selected cementitious materials adapted from Lothenbach et al. [9] and Thomas [10]. C: high calcium CFA, F: low calcium CFA.

Silica fume typically consists of 90 % SiO_2 [33] and is a pure pozzolanic material with no hydraulic properties [10]. The composition of fly ash varies considerably, including both high calcium fly ash (type C, ASTM C618 [34]) and low calcium fly ash (type F, ASTM C618 [34]). The composition of low-calcium fly ash overlaps with the composition for the natural pozzolans (e.g. volcanic origin, tuffs, sedimentary materials, etc.), both reacting only pozzolanic. In contrast, high-calcium fly ash has both pozzolanic and hydraulic activity [10]. Metakaolin is a calcined clay also possessing pozzolanic activity [35]. Ground granulated blast furnace slag (slag) has a composition similar to Portland cement, but contains glassy phases. Slag is hydraulic, but unlike Portland cement, it has very little or no cementitious properties, thus is not able to set, harden and develop strength, unless activated by an increase in the pH (> 12) and it is therefore classified as a latent hydraulic material [10,36]. Thomas [10] does not include limestone in his overview of commonly used SCM's, while fine limestone is included by Lothenbach et al. [9]. Limestone is observed (to some extent) to react with alumina, leading to a synergistic performance if limestone and Al-rich SCMs as fly ash are utilised in a triple blended cement [37].

1.2.1 Supplementary Cementitious Materials with pozzolanic properties

A pozzolanic SCM is defined by EN 450 [1]) as a siliceous (S) or siliceous and aluminous material (AS) that in itself possess little or no cementitious value, but which can form compounds having cementitious properties through chemical reactions. The chemical reactions occur between reactive components in the SCM (S and/or AS) and the portlandite (CH) developed during hydration of the Portland clinker [36].

The developed hydration products depend on the reactive components present in the added SCM [10,35], see Eq. 1 and Eq. 2.

$$\text{S} + \text{CH} \rightarrow \text{C-S-H} \qquad \text{(Eq. 1)}$$

$$\text{AS} + \text{H} + \text{CH} \rightarrow \text{C-S-H} + \text{C-A-H} + \text{C-A-S-H} \qquad \text{(Eq. 2)}$$

Typically, the C/S ratio of the C-S-H that is formed by the reaction of silica with portlandite (Eq. 1) is lower than the C-S-H formed by cement hydration. Notably, C-S-H that is formed in the reaction between aluminosilica and portlandite (Eq. 2) contains aluminate [10,33,35].

A partial cement replacement of Portland clinker with a pozzolanic SCM causes a decrease in early strength, however, less than predicted based on the dilution factor. This discrepancy is due to the added fines providing nucleation sites promoting the hydration of the Portland cement fraction [33,38]. In addition, the dilution provides more space for formation of the clinker hydrates, increasing the degree of reaction [38]. The alternation of the hydrate assemblage renders a cement-based material with a partial cement replacement with a pozzolanic SCM with a higher chemical resistance. For instance, addition of pozzolanic SCM leads to a lower content of portlandite in the paste, preventing sulphate attack, and a lower permeability, reducing the mobility of harmful ions [35].

In accordance with EN 450 [1] the content of primary oxides (SiO_2, Al_2O_3 and Fe_2O_3) should be above ≥ 70% by mass in order to ensure proper pozzolanic behaviour of the material.

1.2.2 Supplementary Cementitious Materials with hydraulic properties

A hydraulic binder is defined in EN 197 [2] as a binder which reacts chemically with water, converting the water-binder system into a solid matrix with the ability to set and harden and retain strength and stability even under water. Portland cement is a hydraulic binder. The main hydration products formed by hydration of pure Portland cement are C-S-H, CH, AFm and Aft phases [36].

SCMs with hydraulic properties are generally classified as latent hydraulic, due to their need for an activator [35,36]. A known SCM with latent hydraulic properties is granular blast furnace slag from iron production. Slag itself can hydrate when mixed with water, however, the hydration products form a thin impermeable Si-rich layer on the surface of the grains, preventing further hydration. This can be circumvented by the use of an alkaline activator to increase the pH above 12 in the vicinity of the slag, avoiding formation of this impermeable layer and allowing the continued dissolution of the slag [10]. An activator could be CH or alkali sulphates such as Na_2SO_4 or K_2SO_4 [36]. The main hydration products formed by hydration of slag are similar to those formed in pure Portland cement, however, the content of CH is lower, indicating a partial consumption of CH during the hydration [10]. Slag reacts more slowly than cement. This reduces early-age strength development while increasing long-term strength development. Furthermore, the alternation of hydrate assemblage and microstructure, resulting from use of latent hydraulic additions like slag, renders a cement-based material with improved chemical resistance [10,33].

In accordance with the EN 197 standard [2], Portland cement, defined as a hydraulic material, should comply with a composition of $CaO/SiO_2 > 2$ and slag, defined as a latent hydraulic material, should comply with a composition of $(CaO+MgO)/SiO_2 > 1$.

In general, the term hydraulic SCM refers to a SCM with latent hydraulic properties, and thus needing an activator. However, some mineral additions have hydraulic properties without an external alkaline activator, thus being able to set and develop strength in a simple mineral additions-water system. For these types of systems, formation of AFt phases (Alumina, ferric oxide, tri-sulphate) is the most important process for hardening and strength development [39–41]. This property is seen for some types of high-calcium SCMs [42].

1.3 Wood Ash as a Partial Cement Replacement

Published experimental research on use of WA as a partial cement replacement’s effect on the properties of cement-based materials has shown diverging results [19,27,29,43–46]. For example, the compressive strength of mortar samples with a partial cement replacement with WA was observed by Udoeyo et al. [19], Berra et al. [27], and Elinwa and Mahmood [46] to decrease with increasing replacement rates. On the other hand, Rajamma et al. [29] and Ramos et al. [44] observed a maintained compressive strength for samples with 10 and 20% cement replacements. A major cause for these different observations is the variation in the physicochemical characteristics of WA, which vary significantly depending on how the ash is produced [47]. Therefore, it is vital to determine which physicochemical characteristics a WA should possess to be suitable for utilisation as a partial cement replacement and verify the performance experimentally.

In the following sections (1.3.1, 1.3.2, and 1.3.3) three literature reviews are conducted addressing the following subjects:

1. The physicochemical characteristics of WA.
2. The reaction mechanisms of WA.
3. The influence of pre-treatment of WA on the use as low-level cement replacements.

Only studies, where ash originating from combustion of 100% biomass as fuel, preferably pure wood or woody products (pellets, chips, sawdust, bark) [13], are included.

1.3.1 Relationship between Production Parameters and Physicochemical Characteristics of WA

Determining the physicochemical characteristics of WA is essential when assessing the potential for utilisation. The physicochemical characteristics of WA are dependent on both the wood products, (wood chips or pellet, species of wood, etc.), and the combustion process (temperature, technology, etc.) [18,47,48]. Different types of wood products and combustion processes are used globally for energy production [16], resulting in different types of WAs with different physicochemical characteristics all referred to as WAs. Table 1 provides an overview of selected studies of the influence of production parameters on the physicochemical characteristics of WAs.

Table 1: Selected studies stressing the difference in the physicochemical characteristics of WA

Reference	WA type and production	Major findings
Carević et al. [49]	Ten WAs originating from combustion of wood chips. Five of the WAs originated from grate combustion, four from grate combustion + pulverised fuel combustion and one from bubbling fluidised bed combustion.	Screening of WAs utilised as SCMs. The mean content of oxides in order of decreasing value were determined: CaO > SiO_2 > K_2O > MgO > Al_2O_3 > P_2O_5. The content of heavy metals, alkalis, SO_3 and P_2O_5 are higher for the fly ash fraction compared to the bottom ash fraction. Especially cadmium content was high, raising concerns regarding further utilisation.
Cheah and Ramli [18]	General overview of utilisation of WA as cement replacement.	Overview of work carried out on the use of non-impregnated wood waste ash as a partial replacement of cement in mortar and concrete mixes. The mean content of oxides in order of decreasing value were determined: CaO > SiO_2 > K_2O > MgO > Al_2O_3 > P_2O_5. Especially the type of woody biomass used as fuel and combustion temperature governs the chemical composition of the WAs. Carbonates ($CaCO_3$) and bicarbonates ($Ca(HCO_3)_2$) are predominately found at combustion at below 500°C and oxide compounds such as quick lime (CaO) become more prevalent above 1000°C. Combustion temperature also governs the alkalinity, as a reduction of carbonates and bicarbonates leads to a decrease in the alkalinity. WA produced in a grate fired furnace leads to coarser ash particles, while a fluidised bed furnace produces finer ash particles.
Etiégni and Campbell [47]	Lodgepole pine sawdust combusted an electric furnace.	Increase in combustion temperature, increase in most heavy metal content but decrease in the content of elements such as potassium, sodium and zinc. Subsequent storage conditions can change the chemical composition, as carbon dioxide and moisture can react with the WA and form carbonates ($CaCO_3$), bicarbonates ($Ca(HCO_3)_2$) and hydroxides ($Ca(OH)_2$).
Maschowski et al. [50]	Five WAs, both bottom and fly ash fraction, originating from wood chips. For all samples, the boiler type was fixed bed, but with different total thermal power and flue gas treatments.	The fuel type, boiler size and flue gas treatment showed major influences on ash compositions, leading to some WAs consisting mostly of water-soluble salts and others to higher content of heavy metals. The fly ashes showed elevated concentrations of cadmium to a level of concern for further utilisation, however, the troublesome Cr(VI) was below the detection limit.
Rajamma et al. [29]	Forest residues combusted at a thermal power plant in a boiler with a water-cooled vibrating grate at ~1000°C.	Combustion technology and temperature influence the amount and characteristics of the WA produced. Increases in temperature lead to increases in the amount of organic species volatising in the furnace, leading to an increased content in the fly ash fraction, compared to the bottom ash fraction.
Vassilev et al. [13]	Literature review, including 28 different WAs. Combustion method not specified.	Displayed a significant difference in the oxide content, depending on the type of wood or woody biomass used for combustion. The mean content of oxides in order of decreasing value were determined: CaO > SiO_2 > K_2O > MgO > Al_2O_3 > P_2O_5. The compositional variations were contributed to the type of biomass, biomass combustion and subsequently transport and storage of the WA.

Table 1 illustrate the importance of knowing the production parameters linked to the WA under investigation. Typically, the mean content of oxides in WAs in order of decreasing value was $CaO > SiO_2 > K_2O > MgO > Al_2O_3 > P_2O_5$ [13,18,49]. This trend deviates significantly from traditional CFA, which contains mainly SiO_2 and Al_2O_3, and high-Ca fly ash which contains high amounts of CaO [10]. However, the content of oxides depends on the type of wood product used for combustion [13,18,50]. These observations encourage further studies to link the production parameters and physicochemical characteristics of WAs with current standards, EN 450 [1] and EN 197 [2]. Thus, enabling the determination of which production parameters results in the WA most suitable for utilisation as a partial cement replacement in cement-based materials and what reaction mechanisms can be expected.

1.3.2 Reaction mechanisms of WA

The contribution to the properties of a cement-based material from a partial cement replacement with WA, is mainly linked to the reaction mechanism of WA. Some published studies have determined pozzolanic activity of the WAs [29,44,46], while others have concluded that no pozzolanic activity is present, but that the WAs are hydraulic of nature [27,39,49,51]. An overview of the findings of these studies is presented in Table 2.

Table 2: Selected studies investigating reaction mechanisms of WA

Reference	WA type and production	Major findings
Berra et al. [27]	Three WAs originating from combustion of chestnut wood chips, virgin wood chips and scraps of treated wood. Combustion method not specified.	No pozzolanic activity determined for the WAs according to EN 196 [52]. The increase observed in the compressive strength for the virgin WAs are attributed to hydraulic activity.
Carević et al. [49]	Ten WAs originating from combustion of wood chips. Five of the WAs originated from grate combustion, four from grate combustion + pulverised fuel combustion and one from bubbling fluidised bed	WAs are positioned close to Portland cement in a $CaO\text{-}Al_2O_3\text{-}SiO_2$ ternary diagram, implying greater hydraulic activity than pozzolanic reactivity. The average pH for a fly WA was 13.2 ± 0.3. Correlation between pH and content of $Na_2O_{(eq)}$ shows a linear relationship until $Na_2O_{(eq)}$ ~ 10 mass %, indicating a relatively easy dissolution of the alkalis (~ 10 mass %). Above 10 mass % $Na_2O_{(eq)}$, no further increase is seen for the pH, which reaches a value of ~13.5, displaying the saturation value of the alkalis.

	combustion.	
Demis et al. [53]	WA generated from combustion of wood ash wood products. Combustion method not specified.	No pozzolanic properties observed due to a low content of SiO_2 and considerable amounts of un-burnt carbon. Un-burnt carbon only serves as filler.
Elinwa and Mahmood [46]	WA obtained from sawdust burned by the open burning method using a drum.	Pozzolanic properties due to the compliance with the standards for a pozzolanic material.
Etiégni and Campbell [47]	Lodgepole pine sawdust combusted in an electric furnace.	The WA was found to, when in the presence of water, hydrate and form new chemical compounds and expanded significantly.
Illikainen et al. [39]	Two WAs; one from combustion of peat and wood in a 96 MW circulating fluidized bed boiler and the second from combustion of peat and forest residues in a 246 MW bubbling fluidized bed boiler.	Hydraulic properties (referred to as self-hardening) are seen for both fly ashes and are dependent on the content of reactive calcium, aluminium and sulphate. The main reaction products were ettringite and hydrocaluminate.
Rajamma et al. [29]	Forest residues combusted at a thermal power plant in a boiler with a water-cooled vibrating grate at ~1000°C.	Pozzolanic activity determined for the WA according to EN 196 [52].
Ramos et al. [44]	Wood waste burned at high temperatures for energy production. Combustion method not specified.	Pozzolanic properties determined by the strength activity index test with 20wt% of the cement replaced with pozzolanic materials. The WA complies with the standards for a pozzolanic material.
Steenari and Lindqvist [54]	Wood chips burnt in circulating fluidised bed and bubbling fluidised bed.	The WA hydration and solidification process were studied. $Ca(OH)_2$ forms when WA reacts with water and subsequently $CaCO_3$ due to carbonation. Ettringite formation binds sulphur and aluminium and contributes to the stability.
Ukrainczyk et al. [51]	Forest residues and wood combusted in a fixed bed (moving grate) furnace.	Initially content of $Ca(OH)_2$ increases due to hydraulic activity of the WA. CEM II/A-M (S-V) 42.5N was used, as it contains up to 20% a combination of ground granulated blast furnace slag and coal-derived class F fly ash. A synergistic effect between the WA and pozzolans in the cement is determined, due to alkali-activation of the pozzolans determined by a decrease in the $Ca(OH)_2$.
Vu et al. [55]	WA from combustion of wood chips at a thermal energy production plant.	No pozzolanic properties were observed, due to a low content of SiO_2.

In general, whether a WA possesses pozzolanic or hydraulic properties widely depends on the elements present in the ash. A high content of silica facilitates pozzolanic activity [44,46], while calcium, aluminium and sulphate promote hydraulic activity [39]. According to literature, CaO_{free} increases pH due to hydration of CaO forming excess $Ca(OH_2)$ in a WA-

water mixture [39]. As a consequence of the increase in pH, the amounts of the reactive components increase [10,47], whether the material possesses hydraulic or pozzolanic properties. This encourages an in-depth study of the reaction mechanisms (pozzolanic or hydraulic properties) in order to determine the contribution from a WA when used as a partial cement replacement in cement-based materials.

1.3.3 Pre-treatment of WA to Optimise its use as a Partial Cement Replacement

WA does not meet the physicochemical requirements set by EN 450 [1] for the use of ash as a mineral additive, largely due to high levels of chloride, alkali, CaO and low levels of SiO_2 [1]. These compounds can cause durability issues and have negative effects on mechanical properties complicating use of WA as a partial cement replacement. Different types of pre-treatments can improve the compressive strength and durability, improving the performance of WA as a partial cement replacement. Sieving and subsequent washing can reduce the content of soluble salts (such as chlorides and sulphates), heavy metals and aluminium [28]. An overview of studies implementing WA as a partial cement replacement is given in Table 3. Both pre-treated WA and untreated WA, utilised as received from the power plants, are included.

Table 3: Selected studies investigating the influence of pre-treatment of WA on the properties of cement-based materials.

Reference	WA type and production	Major findings
Berra et al. [27]	Three WAs originating from combustion of chestnut wood chips, virgin wood chips and scraps of treated wood. Combustion method not specified.	The WA from chestnut wood chips was subjected to a two-step washing treatment (liquid/solid ratio = 25) where the WAs are exposed to water for 30 mins/step. Subsequently, the WAs were dried to a constant weight at 80°C. The washing treatment improved the physicochemical properties and compressive strength of the WA, when used as a mineral addition at ages greater than 60 days. In untreated WAs a significant presence of heavy metals, such as As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, were found.
Cheah and Ramli [18]	General overview of utilisation of WA as cement replacement.	Overview of work carried out using wood waste ash as a partial replacement of cement in mortar and concrete mixes. Addition of WA-OPC blended cement leads to significant amounts of ettringite crystals formed within the cement paste matrix.

		Incorporation of WA as a partial cement replacement at higher levels generally leads to a decrease in the mechanical strength, however, replacement under 10% by total binder weight can produce concrete or mortar with acceptable strength properties.
Doudart de la Grée et al. [28]	Four WAs originating from combustion of waste wood. Two of the WAs originate from grill ovens (furnace) and two of the WAs originate from fluidized beds.	The WAs were subjected to a sieving and washing treatment; WA is sieved to < 500µm, and subsequently, WA and demineralised water are shaken in bottles, filtered (15-30µm) and the retained WA on the filer was flushed with demineralised water and subsequently dried. Washing of the WAs resulted in a reduced chloride content and removal of unburned coal, thus significantly lowing chloride leaching.
Rajamma et al. [29]	Forest residues combusted at a thermal power plant in a boiler with a water-cooled vibrating grate at ~1000°C.	The WA is similar to a class C fly ash, defined by EN 450 [1]. Up to 20% replacement of cement with WA maintains an acceptable mechanical strength but deteriorates rapidly with higher replacement ratios.
Rajamma et al. [30]	Wood or forest biomass residues from logging activities combusted in a grate furnace.	Replacement of cement with more than 10% WA reduced workability, due to the water-absorbing capacity of WA. Partial replacement of cement with WA leads to a decrease in compressive strength, decreasing further with higher replacement rates.
Rosales et al. [56]	Olive biomass bottom ash. Combustion method not specified.	The biomass ash was subjected to 3 different types of pre-treatment: crushing (particle size ≤ 125µm), combustion (800°C at 18 h) and flotation (removal of lightweight particles) as well as combinations of the three. Removal of lightweight particles and crushing of the biomass ash significantly improved the compressive strength of WA containing materials. This is explained by an increase in the content of SiO_2 and $Ca(OH)_2$, as a result of the extraction of lightweight particles, contributing to pozzolanic reactions.

In general, partial cement replacement with WA leads to a decrease in compressive strength, as displayed in Table 3. However, at low-level replacement rates (≤ 10wt%) [18,29,30], the WAs were observed to contribute to enhancement of compressive strength [18] and maintaining acceptable workability [30].

The properties of cement-based materials containing pre-treated WA show a general improvement [27,28,56] compared to cement-based materials with untreated WA [18,29,30]. These pre-treatment methods are worth pursuing further with research into changes in the hydration products linked to the mechanical response, as well as the influence on possible durability issues, heavy metal concentrations and leaching.

1.4 Transforming Our World – The 2030 Agenda for Sustainable Development

This PhD project addresses the possibility for utilisation of WA as a partial cement replacement resulting in a more sustainable consumption of natural resources and a reduction in waste. This is in alignment with SDG 12. SDG 12 is one of 17 SDGs set by 193 countries of the United Nations (UN) collectively aiming to achieve a better and more sustainable future. In the 17 SDGs, it is recognised that ending poverty and other deprivations must go hand-in-hand with strategies that improve health and education, reduce inequality, and spur economic growth – all while combating climate change. Thus the SDGs are a call for action by all these countries to promote prosperity while protecting the environment [5].

SDG 12 recognizes that a rapidly expanding global material consumption and increasing material footprint per capita are problematic issues. Furthermore, SDG 12 recognizes the need for urgent action to ensure that the current rate of material consumption does not lead to over-extraction of available resources [5].

The presented PhD project addresses the following targets within SDG 12 [5]:

- ***SDG 12.2:*** By 2030, achieve the sustainable management and efficient use of natural resources.
- ***SDG 12.5:*** By 2030, substantially reduce waste generation through prevention, reduction, recycling and reuse.
- ***SDG 12.6:*** Encourage companies, especially large and transnational companies, to adopt sustainable practices and to integrate sustainability information into their reporting cycle.

Target 12.6 is included, as the PhD project is conducted in corroboration with the energy companies HOFOR A/S, Ørsted, Fjernvarme Fyn and Aalborg Forsyning. Thus, providing research on the possibility to adopt more sustainable practices, by utilising the residual waste from their power plants.

Figure 2. Sustainable development goal targeted in the PhD project.

2 Knowledge Gaps in the Field

From the literature review presented in Chapter 1, the following gaps (A-C) in our current knowledge regarding wood ash in cement were identified:

A. The results obtained for the potential usage of WA as a partial cement replacement varies significantly in the available literature. This is due to variations in the physicochemical characteristics of WA resulting from different production parameters. In order to determine which production parameters, result in WAs most suitable for use as partial cement replacements, there is a need to understand the correlation between production parameters and the physicochemical characteristics.

B. Whether or not WA possess hydraulic or pozzolanic properties varies significantly in the available literature, as a result of differences in the element content. The possibility for pozzolanic and/or hydraulic activity must therefore be assessed for WAs, in order to evaluate the contributions from WAs when used as a partial cement replacement. This further encourage a reassessment of the results obtained in knowledge gap A based on the actual measured results.

C. WAs have a high content of unwanted compounds, which can cause durability issues. In order to decrease the possible durability issues attributed to the content of soluble alkalis, WA could be subjected to a suitable pre-treatment procedure. The changes in the hydration assemblage and mechanical response as a result of pre-treating WAs, and further the influence on durability issues and leaching of heavy metals, needs to be assessed.

In the presented PhD study, these knowledge gaps (A-C) were investigated. In Chapter 3, Table 4, the research methodology is presented and the correlations between the research methodology, appended papers and knowledge gaps (A-C) are outlined.

3 Research Methodology

The overall research methodology is presented in a process diagram in Figure 3. For a detailed description of the methodologies used in the individual studies, please see the relevant appendices listed in Table 4. Table 4 shows an overview of all appended studies, including their titles and their relations to the knowledge gaps A, B, and C defined in Chapter 2.

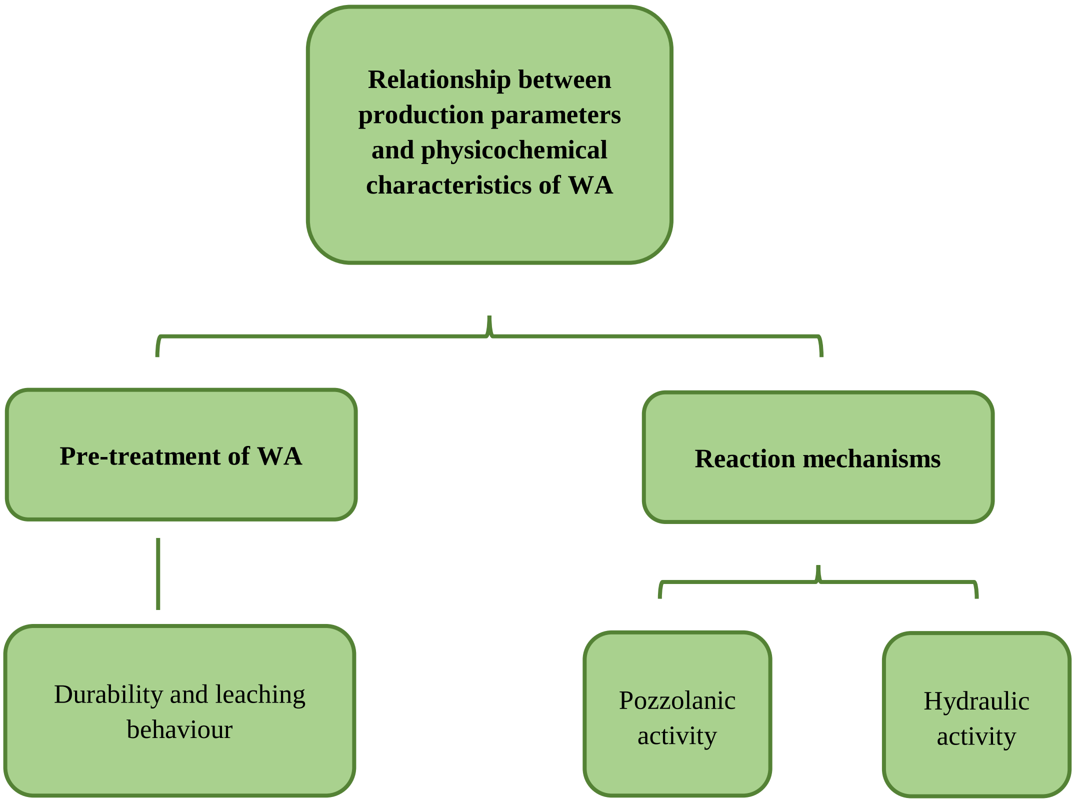

Figure 3: Process diagram of the research methodologies.

In the first part of the experimental work, different types of WAs were characterised and a statistical analysis was performed to link the production parameters to the physicochemical characteristics. This analysis was based on the content of oxides and revealed that fly WA originating from circulating fluidized bed combustion of wood chips (Värtaverket) has the best potential as a material with pozzolanic activity. Fly WA originating from grate combustion of wood chips (Skærbækværket) has the best potential as a material with hydraulic activity. Based on this study WAs from Skærbækværket (hereafter WA1) and Värtaverket (hereafter WA2) were included in all further experiments. WA1 originated from grate combustion and WA2 from circulating fluidised bed (CFB) combustion of wood chips made from whole threes, including bark and needles.

The remaining experimental work was divided into the following branches: 1) reaction mechanisms of WA, 2) pre-treatment of WA for optimal use as a partial cement replacement, and 3) potential durability issues and leaching of heavy metals.

Table 4. Overview of appended papers and the correlation with knowledge gaps A, B, and C (Chapter 2) and methods.

Appended material[1]	Title	Aim	Knowledge gap	Methods
JPI	Impact of Production Parameters on Physiochemical Characteristics of Wood Ash for Possible Utilisation in Cement-based Materials	Use multivariate modelling to identify correlations between production parameters and the physicochemical characteristics among 11 different WAs, and to determine which production parameters result in WAs suitable for utilisation in cement-based materials.	A	XRF, XRD, pH and conductivity measurements, LoI, particle size distribution, IC, multivariate analysis (Appendix A)
CAI	Wood Ashes for Possible Utilisation in Cement-based Materials Evaluated by Multivariate Models	Determine the correlation between production parameters and physicochemical characteristics of WAs by multivariate modelling.	A	XRF, XRD, pH and conductivity measurements, LoI, particle size distribution, IC, multivariate analysis (Appendix A)
JPII	Reaction mechanisms of wood ash for use as a partial cement replacement	Determine which reaction mechanisms result in increases to compressive strength, when WA is used as a partial cement replacement.	B	XRF, pH and conductivity measurements, LoI, particle size distribution, ICP, compressive strength (EN 196-1 [57]), TGA, XRD, CaO_{free} (EN 451-1 [58]), selective dissolution [39,59–61], Frattini (EN 196-5 [52]), SAI [62].

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[1] JP: Journal Paper, AN: Additional Note (unpublished), CA: Conference Abstract

ANI	Impact of strategies for premixing of water and wood ash, when wood ashes are used as partial cement replacement	Investigate different mixing strategies to improve the properties of freshly mixed mortar and the mechanical response of WA containing cement-based materials.	B	XRF, pH and conductivity measurements, LoI, IC, workability (EN 1015 [63], compressive strength (EN 196-1 [57])
JPIII	Phase development and mechanical response of low-level cement replacements with wood ash and washed wood ash	Investigate the influence of replacing 10% cement with WA (untreated and washed) on the phase development and mechanical response of cement-based materials.	B, C	Washing treatment, XRF, pH and conductivity measurements, LoI, particle size distribution, IC, compressive strength (EN 196-1 [57]), SEM, TGA, XRD.
CAII	Prewashed Wood Ash for Utilization in Cement-based Materials	Investigate the influence of washing WAs, originating from wood pellets, on the phase development and mechanical response of cement-based materials.	C	Washing treatment, XRF, pH and conductivity measurements, LoI, particle size distribution, IC, compressive strength (EN 196-1 [57]), SEM, TGA, XRD.
ANII	Leaching Characteristics of Mortars with Wood Ash used as a Low-Level Cement Replacement	Investigate the influence of a 10% cement replacement with WA (untreated and washed) on the total content of heavy metals and leaching behaviour.	C	Washing treatment, total concentration of heavy metals (DS259 [64]), solubility determined leaching (EN 12457 [65]), tank leaching test (NEN 7241 [66]).

All journal papers, additional notes and conference abstracts presented in Table 4 can be found in the section ‘Appended Papers and Additional Notes’. The abbreviations (JP, CA, and AN) presented in Table 4 will from here on be used to reference to the appended materials.

4 Impact of Production Parameters on Physicochemical Characteristics of Wood Ash

This chapter presents the characterisation of different WAs, all originating from combustion of 100% woody biomass, and statistic modelling linking the production parameters to the physicochemical characteristics of the WA. The models are then used to determine correlations between physicochemical characteristics and production parameters and compare them with current standards. EN 450 [1] does not allow for the use of pure WA as a mineral addition in cement-based materials, nevertheless, the requirements given by EN 450 [1] are used as a point of reference to evaluate the WAs in this section, as in other studies [27,29,44]. EN 197 [2] are included for assessment of the hydraulic activity.

This chapter covers an in-depth analysis of the oxide content of all WAs used in this thesis. The multivariate data analysis have been expanded to include WA1 (an expansion on the multivariate data analysis presented in JPI) and ten wood fly ashes recently analysed by Carević et al. [49]. The conclusions of the multivariate analyses are compared to the conclusions drawn in JPI and CAI. Finally, the multivariate data analysis is used to evaluate how well WA1 and WA2, which are the WAs in focus in the main part of the present thesis, act as a typical type of WAs.

4.1 Characterisation of Wood Ash

The WAs investigated in this part of the PhD thesis were collected by employees at Halsnæs Supply A/S, Køge Power Plant, Svebølle Viskinge District Heating Company, Värtaverket, Herningværket, Amagerværket, and Skærbækværket. The 12 different WAs included in the study, and their different appearances are presented in Figure 4.

Figure 4. WAs included in the presented PhD thesis. Diameter of petri dishes = 40 mm.

As it may be seen in Figure 4 the WAs have different appearances, despite all the WAs originating from combustion of 100 % wood or woody products. The different appearances are due to different production parameters and are reflected by differences in the physicochemical characteristics of the WAs [18,47,48]. These differences stress the necessity of a proper description of a WA when presented in scientific literature. Selected chemical characteristics of the WAs included in this thesis, all measured on dried WAs (50°C), are presented in boxplots, and WA1 and WA2 are plotted to show similarities and differences, see Figure 5, Figure 6 and Figure 7.

Figure 5 shows the content of SiO_2, Al_2O_3, Fe_2O_3, the Σ primary oxides and CaO calculated based on the element content. The content of Al_2O_3 (1.6% average) and Fe_2O_3 (1.3% average) are low compared to SiO_2 and especially CaO for all investigated WAs. The values are also low compared to literature, where average values of 4.4% Al_2O_3 and 3.3% Fe_2O_3 were reported [13,18,49]. These higher reported contents are caused by the inclusion of bottom ash fractions which accumulate higher contents of Al_2O_3 and Fe_2O_3 [49]. In the presented thesis, one of the twelve ashes are a bottom ash, four are mixed ashes containing both bottom and fly ash, and seven are fly ashes facilitating a lower average content of Al_2O_3 and Fe_2O_3.

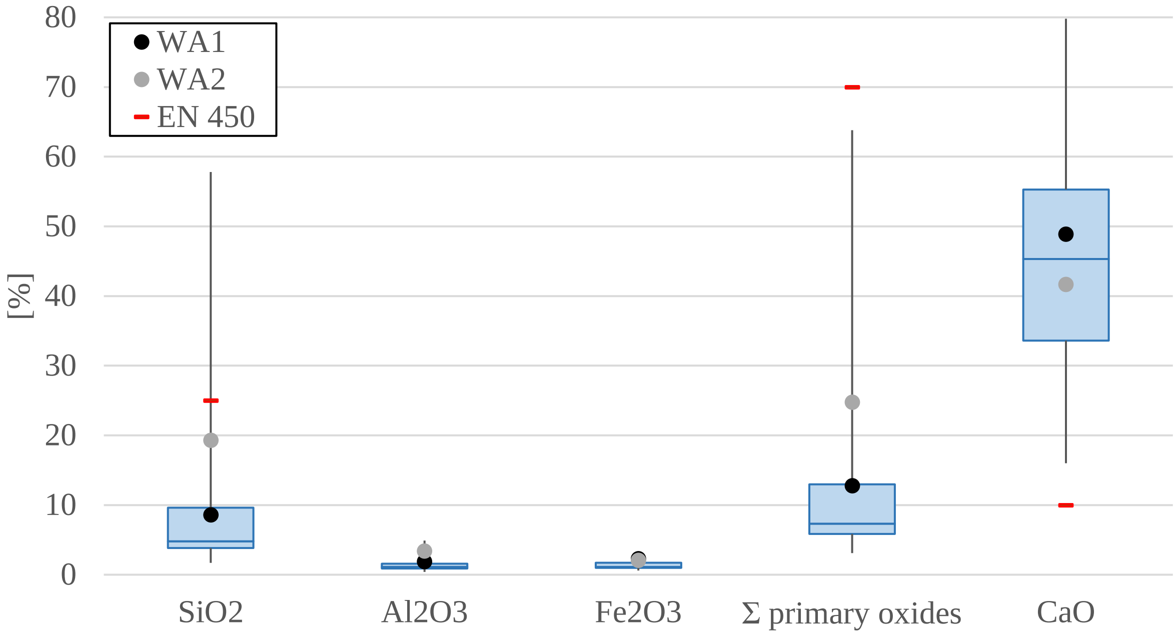

Figure 5. Graphical representation of the calculated content of SiO_2, Al_2O_3, Fe_2O_3, Σprimary oxides and CaO determined by X-ray fluorescence (XRF). WA1: ●, WA2: ●, limits from EN 450 [1]*: -. The data is adapted from JPI and subsequent measurements on WA1.*

SiO_2 achieves a larger interquartile range (25th to the 75th percentile), compared to Al_2O_3 and Fe_2O_3 (Figure 5), and an average value of 11.0%. The maximum value (third quartile + 1.5 · interquartile range) for SiO_2 is significantly above the third quartile (75^{th} percentile), due to ashes from circulating fluidized bed combustion containing higher contents of SiO_2, as the inert sand particles making up the suspension bed can contaminate the fly ash fraction [20]. This is substantiated by the content of SiO_2 in WA2 being located above the third quartile. Of the primary oxides (SiO_2, Al_2O_3 and Fe_2O_3), SiO_2 is seen to be the main determinator for the obtained values of Σ primary oxides, substantiated by the maximum value and location of WA2. According to EN 450 [1] the Σ primary oxides should be above ≥ 70% by mass in order to ensure proper pozzolanic behaviour of the material. None of the WAs included in this thesis comply with this requirement. It should be noted that this requirement does not describe the necessary amount of reactive oxides needed for pozzolanic behaviour. Thus, completely inert quartz complies with this limit but does not contribute with pozzolanic behaviour.

CaO has a large interquartile range with an average of 45.9%. WA1 and WA2 are located in the third and first quartile (75 and 25th percentile), respectively, making them representable for WAs with a high and low content of CaO, respectively (Figure 5). A high content of CaO is expected due to a high content of CaO in the woody products used for combustion, especially wood barks, substantiated in the literature [13,18,49]. EN 450 [1] establishes limits for the content of free calcium oxide and reactive calcium oxide of 1.5% and 10.0%, respectively. The total content of CaO determined here does not indicate how large a fraction is free or reactive. However, due to the high content of CaO there is a great risk of WAs not complying with this requirement. EN 197 [2] establishes that a hydraulic material is to comply with a $CaO/SiO_2 > 2$, referred to as the hydraulic index. Figure 6 presents the hydraulic indices for the WAs studied in this thesis. All tested WAs comply with this requirement, with the exception of the bottom ash sample which is affected by its high SiO_2 content. WA1 and WA2 obtains a hydraulic index of 5.7 and 2.2, respectively.

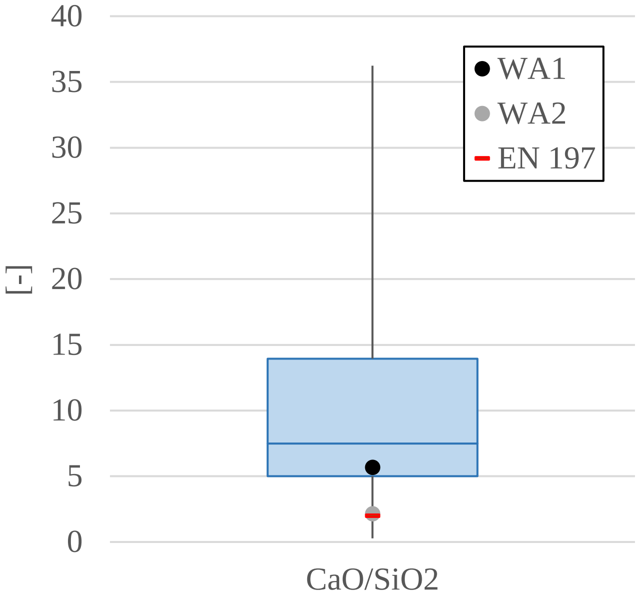

Figure 6. Graphical representation of the calculated hydraulic index. WA1: ●*, WA2:* ●*, and limits from EN 197* [2]*:* -*. The data is adapted from JPI and subsequent measurements on WA1.*

The oxides presented in Figure 7 can facilitate several durability issues for cement-based materials with a partial cement replacement with WA. This is elaborated in section 6.3.1.

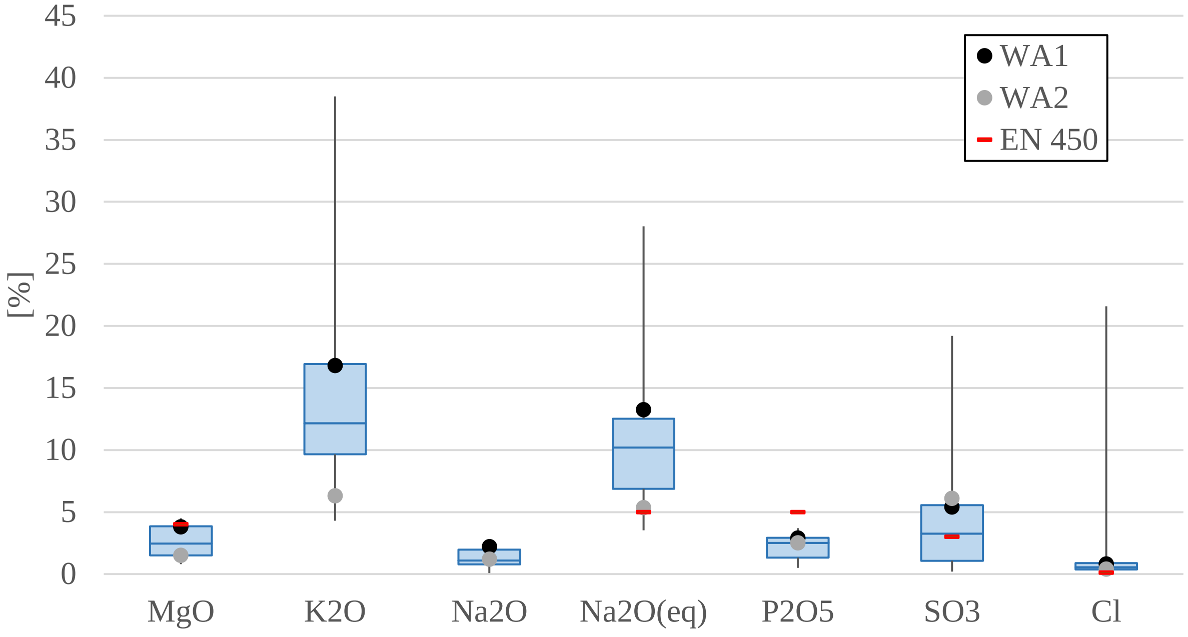

Figure 7. Graphical representation of the calculated content of MgO, K_2O, Na_2O, $Alkali_{(eq)}$, P_2O_5, SO_3 and Cl determined by XRF. WA1: ●, WA2: ●, and limits from EN 450 [1]*: -. The data is adapted from JPI and subsequent measurements on WA1.*

In general, WAs have high values of MgO, K_2O, Na_2O, $Na_2O_{(eq)}$ ($Na_2O + 0.658 \cdot K_2O$ [36]), SO_3 and Cl^- when compared to a traditional EN 450 [1] compliant CFA [49]. Thus several of the WAs tested do not comply with the requirements set by EN 450 [1].

The content of MgO and P_2O_5 in the tested WAs did not vary notably, complying with results obtained by Carević et al. [49] and in contrast to results obtained by Vassilev et al. [13]. The WAs included in this thesis were collected in Denmark and Sweden, WAs included in Carević et al. [49] were collected in the Republic of Croatia, while Vassilev et al. [13] included WAs from several different locations around the world, including Finland, USA and Turkey. The larger interval in the MgO and P_2O_5 are therefore ascribed to variations in growth conditions, wood types etc. For MgO, WA1 and WA2 are located at each end of the interquartile range, making them representable for WAs with high and low contents of MgO, respectively. Though both are still in compliance with the requirement of MgO < 4.0% set by EN 450 [1]. For P_2O_5, both WA1 and WA2 are located in the third quartile and both WA1 and WA2, as well as the rest of the WAs included in this thesis, comply with the requirement of P_2O_5 < 5.0% set by EN 450 [1].

$Na_2O_{(eq)}$, SO_3 and Cl^- all obtain large interquartile ranges, with the high maximum values obtained for $Na_2O_{(eq)}$, SO_3 and Cl^- being caused by the same fly WA sample. This fly WA is considered an outlier, as all other WAs obtain results in a lower range for $Na_2O_{(eq)}$, SO_3 and Cl^-. This outlier is further confirmed by the multivariate data analysis presented in section 4.2.

Only one of the WAs included in the thesis complies with the requirement of $Na_2O_{(eq)} < 5.0\%$, thus the high alkali content can, in general, present a problem when WAs are utilised in cement-based materials. The high $Na_2O_{(eq)}$ values are the result of a high K_2O content, supported in the literature [13,18,49], due to potassium being a plant nutrient [20]. WA1 and WA2 are located at each end of the interquartile range, representing a high alkali WA and a lower alkali WA, respectively.

A high content of SO_3 is seen in the fly ash fraction of WA compared to the bottom and mixed ash fractions [29,49], causing the fly ash fraction of WA to not comply with the requirements from EN 450 [1] of $SO_3 < 3.0\%$. As both WA1 and WA2 are of the fly ash fraction, they are both located around the third quartile. The same applies to the Cl^- content, where a larger concentration is found in the fly ash fraction [29], however, as the values obtained for the WAs included in this thesis do not vary notably, no clear conclusion can be drawn. Only one of the WAs comply with the requirement of $Cl^- < 0.1\%$ established by EN 450 [1]. As WA1 and WA2 are located within the interquartile range, they are both representative for the chloride content in WAs.

In general, WAs do not conform with EN 450 [1]. This was expected, as EN 450 [1] specifies requirements for siliceous fly ash deriving from burning of pulverised coal, with or without co-combustion materials (green wood, municipal sewage sludge etc.), which has pozzolanic properties and consists essentially of SiO_2 and Al_2O_3. None of this resembles pure WA, where the main constituent is CaO, therefore WA should be viewed as a new type of material.

Except for a slightly higher content of $Na_2O_{(eq)}$ and SO_3, WA1 obtains values close to the average values for content of oxides and is therefore, to some extent, representative for the WAs included in this thesis, and thus is included in the further studies. WA2 deviates from the averages with regard to SiO_2 content which facilitates higher content Σ primary oxides and a lower hydraulic index, but is representative with regard to most other parameters. WA2 is included in further studies representing a WA containing oxides, mainly SiO_2, possibly leading to pozzolanic properties. The reaction mechanisms of WA1 and WA2 are addressed further in section 5 and JPII.

Especially, the content of alkalis, sulphate and chloride could present problems for the durability performance of cement-based materials with WA [29,49]. To accommodate these performance issues, Rajamma et al. [29] suggested removal or control of these chemical species. This issue is further addressed in section 6 and JPIII.

The graphic representations of the chemical characteristics of the WAs, Figure 5, Figure 6 and Figure 7, support the observations found in literature [18,47,48] of a varying contents of chemical elements within the different WAs. The most varying oxides in the WAs are CaO, $Na_2O_{(eq)}$ and SO_3. However, the large variation in minimum and maximum values seen for several of the oxides, independent of the fraction type, exemplifies the need for further descriptions of WAs linked to their production parameters.

4.2 Multivariate Analysis

In order to evaluate the different results obtained for the properties of cement-based materials containing WA [19,27,29,43–46], multivariate analysis (see Appendix A) was used. The method was used to analyse the link between the production parameters and the physicochemical characteristics of the WAs and compare them to EN 450 [1] and EN 197 [2], in order to determine which type of production parameters produce the WA most suitable for utilisation as a partial cement replacement.

Two important conclusions were drawn in JPI and CAI:

- 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 for partial cement replacement with pozzolanic activity. It should be noted that the pozzolanic properties of WAs are expected to be limited, and the WAs in general do not comply with the nominative requirements established by EN 450 [1].

- Wood fly ash originating from the combustion of wood chips made from whole trees is the most optimal type of WA for utilisation as a mineral addition with hydraulic activity. This was further substantiated by all but one WA complying with the nominative requirements for hydraulic activity established by EN 197 [2].

The multivariate analyses presented in JPI and CAI are based on the 11 WAs presented in Figure 4, however, WA1 was subsequently included and added to the scientific work presented in this thesis. Furthermore, a new study was published by Carević et al. [49] including physicochemical characterisation of 21 different WAs with associated production parameters stated, encouraging a new multivariate analysis of the enlarged data set including this data.

Carević et al. [49] included ten wood fly ashes (F1-F10), two mixed fly and bottom wood ash (M1-M2), and nine wood bottom ashes (B1-B9). All WAs originated from combustion of wood chips at different temperatures using, a grate combustor, a grate combustor and pulverised fuel combustor or a bubbling fluidised bed (BFB) with quartz sand used as an additive.

Both a principal component analysis (PCA) and projections onto latent structures (PLS) are conducted for the new data set. PLS takes into account both the input (production parameters) and the output (physicochemical characteristics) parameters, while PCA is conducted only for the output parameters. The loading scatter plot for PLS is presented in Figure 8, and the score scatter plot for PCA is presented in Figure 9. The statistic tools included in this sections are elaborated in Appendix A.

In the PLS loading scatter plot, variables that are located close to each other are strongly correlated, and variables that are inversely correlated will be projected opposite to each other, with respect to the axis origin [67].

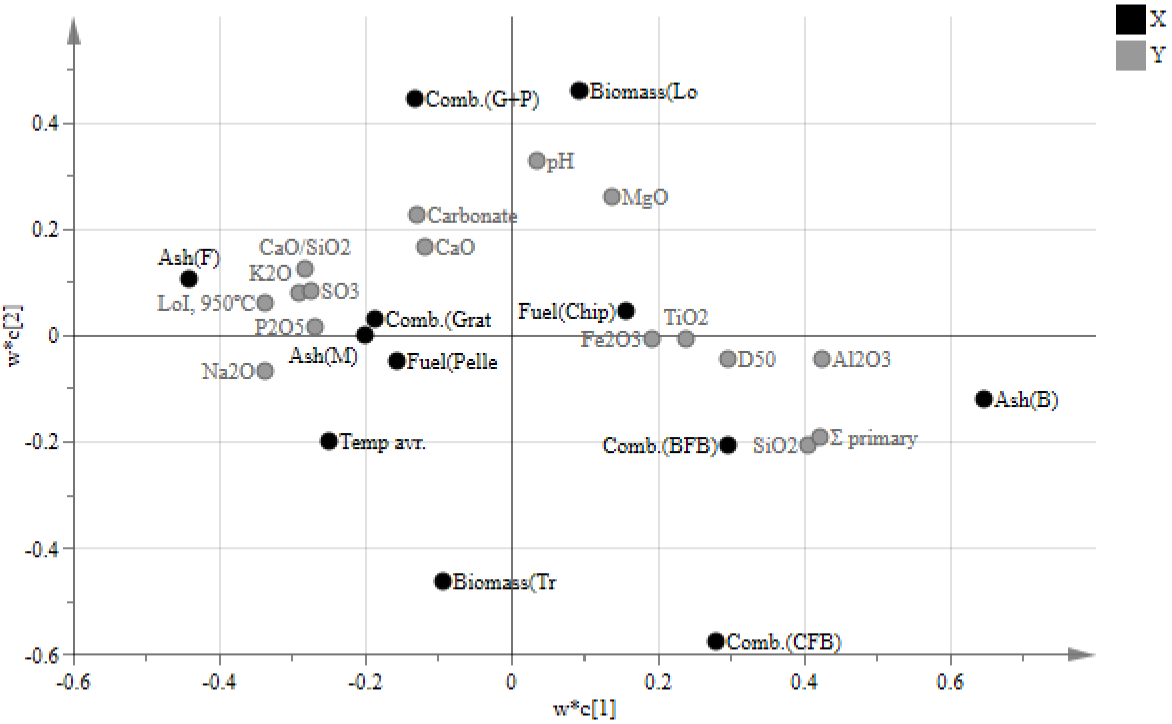

Figure 8. Loading scatter plot from the PLS which gives a graphical summery of the correlation between the physicochemical characteristics and the production parameters. The data is adapted from JPI, with subsequent measurements from WA1 and Carević et al. [49].

Figure 8 substantiates many of the conclusions drawn in JPI. The possibility for pozzolanic activity (based on Σ primary oxides) is primarily related to the content of SiO_2 and Al_2O_3 in the WAs. A higher potential for some extent of pozzolanic activity is primarily seen for bottom ashes, ashes originating from BFB combustion and to some extent also from CFB combustion. The content of SiO_2 is generally low in wood bottom ashes and nearly absent in wood fly ashes [50]. The correlation between BFB and CFB combustion can be attributed to the inert sand particles which make up the suspension bed [20] increasing the content of SiO_2 (however possibly inert) in both the bottom and fly ash. From this analysis, a correlation is seen between WA originating from BFB combustion and to some extent CFB combustion and the Σ primary oxides. Thus these types of ashes could, to some extent, contribute with pozzolanic properties.

The hydraulic index (CaO/SiO_2, Figure 8) is inversely correlated to the Σ primary oxides. The additional WAs from Carević et al. [49] did not further substantiate that WA from chips specifically lead to increased hydraulic activity (as found in JPI). However, a strong correlation between grate combustion and hydraulic index is observed. This is substantiated by CaO being projected close to grate combustion and SiO_2 projected opposite the axis origin in Figure 8. A high content of K_2O, Na_2O, SO_3 and P_2O_5 correlates to a high hydraulic index, which can cause durability problems when WA is used as a partial cement replacement in cement-based materials.

In the PCA score scatter plot, Figure 9, WAs with physicochemical values close to the average are located close to the origin, while WAs outside the circle do not comply with the 95% confidence limit and are considered outliers [67]. WCFA2 is considered an outlier, corresponding with the results presented in Figure 7, section 4.1, and so is B8.

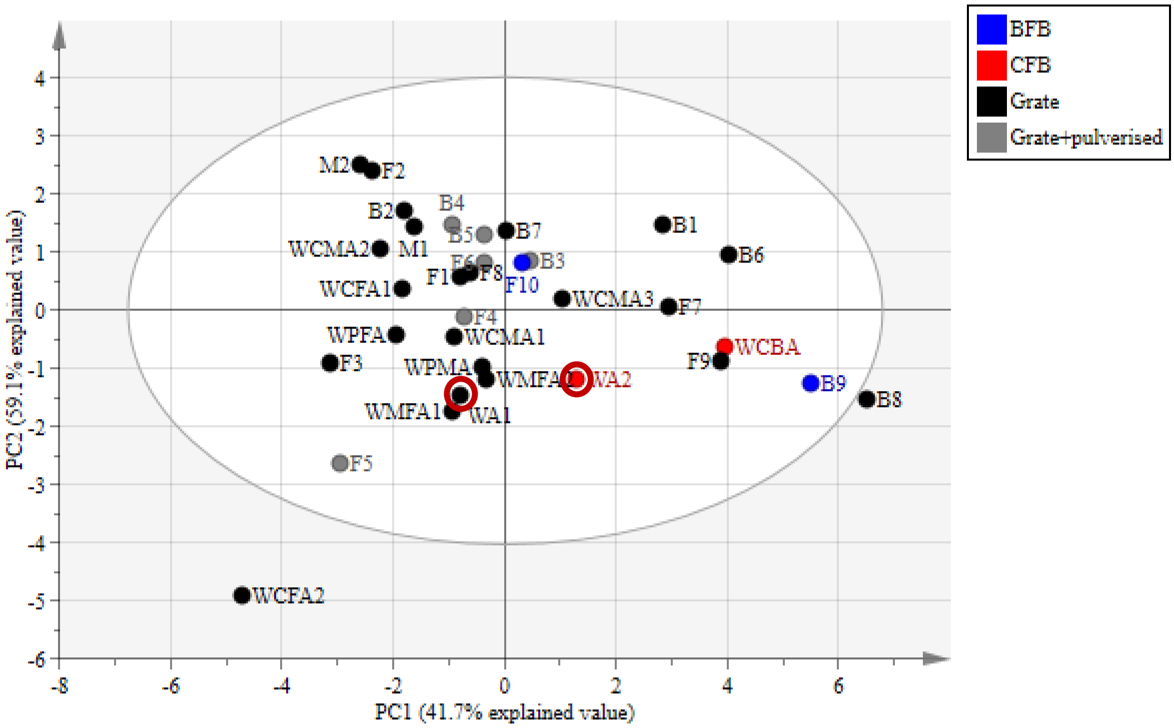

Figure 9. Score scatter plot from the PCA. WA1 and WA2 are marked with red circles. The data is adapted from JPI, subsequent measurements for WA1 and Carević et al. [49].

WA1 and WA2 are marked with red circles in Figure 9. Both WA1 and WA2 are located towards the origin of the plot, thus they are close to the average with the respect to the physicochemical characteristics analysed. As such, WA1 and WA2 can be considered typical types of WAs.

WA1 and WA2 originate from two different types of combustion, grate and CFB combustion, respectively, but from the same type of biofuel (chips) originating from whole trees, including bark and needles. As WA1 and WA2 originate from these two specific types of combustion methods, they each represent the ash type with the best potential to possess either hydraulic activity or pozzolanic activity (to some extend), respectively. This will be addressed further in Chapter 5. Furthermore, both WA1 and WA2 are fly ashes, which can cause durability issues from high contents of K_2O, Na_2O, SO_3, and Cl^- typically correlated with the fly ash fraction, see Figure 5. The consequences of high contents of K_2O, Na_2O, SO_3, and Cl^- and a pre-treatment method as a potential solution are presented in Chapter 6.

5 Reaction Mechanisms of Wood Ash

This chapter contains a resume of the major findings in JPII, were the reaction mechanism of the WAs; pozzolanic and/or hydraulic properties are evaluated. WA1 and WA2, dried at 50°C and sieved to a particle size of ≤ 250μm, were used for the experimental work in this chapter. Details on the sieving method can be found in section 6.1.1. Further details and elaborations on the results discussed in this chapter can be found in JPII. In addition, this chapter contains a comparison between the results obtained by the multivariate data analysis, presented in chapter 4, and the actual measurements presented in this chapter and JPII.

5.1 Pozzolanic Activity

The pozzolanic behaviour of mineral additions used as a partial cement replacements depends on the amount of amorphous silica and aluminosilicate present in the material [10,35]. The content of aluminium in both WA1 and WA2 are low, 1.9 and 4.9% respectively. The content of silica is higher for WA2 (21.8%) than for WA1 (8.6%). However, this difference is attributed to the content of inert sand particles, originating from the circulating fluidised bed which are carried with the flue gas during combustion with the circulating fluidised bed technology ending up in the fly ash fraction [20]. Furthermore, scanning electron microscope images (Figure 10, adapted from JPIII) reveals that the WAs consist of large and fibrous particles. This

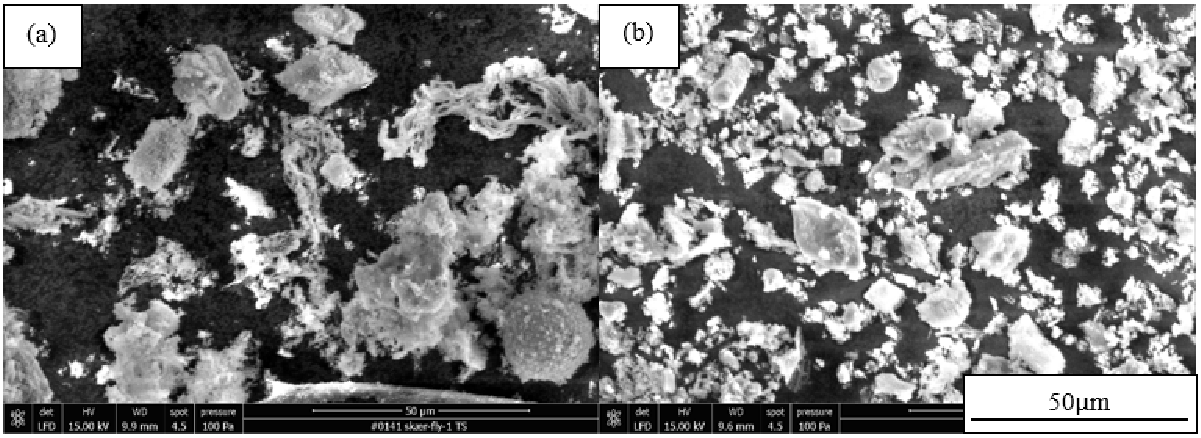

Figure 10. SEM images of WA1 (a) and WA2 (b). Adapted from JPIII.

is a contrast to the typical glassy aluminosilicate spherical particles found in commercial CFA typically contributing to the pozzolanic reactions [68]. Thus, pozzolanic behaviour of the two WAs is initially expected to be very limited or completely absent.

The pozzolanic properties of WA1 and WA2 were tested by both an indirect test (strength activity index (SAI)) measuring the compressive strength to indicate the extent of pozzolanic activity, and a direct method (Frattini test) monitoring the presence of CH and its subsequent reduction as the pozzolanic reaction proceeded. Results from the SAI and Frattini tests are presented in Figure 11. The dotted line in Figure 11 (right) indicates the lower limit of 0.75 established by ASTM C618 [34] for a mineral addition with pozzolanic properties.

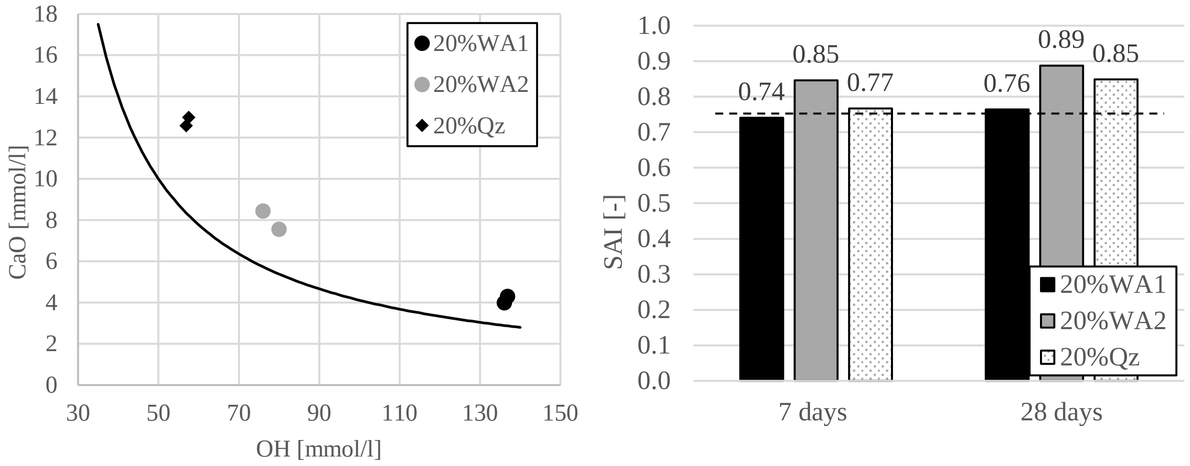

Figure 11: Frattini test results (left) and SAI (right) for three mixtures with 20% replacement of CEM I with WA1, WA2 and Qz (reference quartz). Figures adapted from JPII.

The results of the Frattini test are presented in an x/y-chart, with CaO [mmol/l] on the y-axis versus OH$^-$ [mmol/l] on the x-axis and the solubility curve of Ca(OH)$_2$ depicted according to EN 196-5 [52] (Figure 11, left). Results below the solubility curve indicate removal of Ca^{2+} from the solution resulting from pozzolanic activity, while results above the curve indicate saturation or oversaturation with Ca(OH)$_2$ and thus no pozzolanic activity. According to the results from the Frattini test neither the WAs or Qz possess pozzolanic activity. The Frattini test relies on the consumption of Ca^{2+} to determine pozzolanic activity. Therefore, high-Ca mineral additions are prone to inaccurate results, due to the presence of soluble Ca^{2+} in the mineral addition [69,70] and/or removal of Ca^{2+} by precipitation as e.g. calcium salts, such as $CaSO_4$ if extra SO_4^{2-} ions are present [70] or possibly other hydrates. Both WAs included in this section are categorised as high-Ca mineral additions (> 20% CaO [33]), possibly contributing with Ca^{2+} and again possible removal of Ca^{2+} not entailed by the pozzolanic activity, but by formation of formation of hydrates such as gypsum and ettringite (please refer to section 5.2), counteracting the increased Ca^{2+} concentration in the solution.

The results from the SAI test are shown in Figure 11 (right), where the dotted line represents the required minimum limit set by ASTM C618 [34]. ASTM C618 requires a SAI above 0.75 after both 7 and 28 days of curing for SCMs with 20% cement replacement to possess pozzolanic properties. 20% WA2 complies with this limit and is thus determined to have pozzolanic properties by the SAI test results. However, 20% Qz (inert) was also determined to have pozzolanic properties by SAI. The SAI relies on measurements of a physical property, strength, which can be affected by hydraulic properties or filler effects [70,71] and then mistaken for pozzolanic properties. The filler effect has two components: 1. the particles can act as nucleation sites for the hydrates [38,72] and 2. the dilution effect, where the partial substitution of cement with an inert filler decreases the amount of clinker grains, resulting in relatively more space for formation of clinker hydrates and thus increases the degree of hydration [38,73]. Particles acting as nucleation sites are limited for mineral additions with the same particle size distribution as cement [38]. 20% Qz has a relatively coarse particle size distribution (please refer to JPII), thus the particles cannot act as nucleation sites for hydrates. As the dilution effect increases the degree of hydration [73], this could explain the increase in strength observed for 20% Qz. Part of the observed SAI response for 20% WA2 could be contributed to the dilution effect, however, as WA2, contrary to Qz, is not considered inert, this contribution is considered limited and the response for 20% WA2 is therefore attributed mainly to its hydraulic properties. WA1 does not comply with the limit set by ASTM C618 [34]. Neither of the filler effects are expected for 20% WA1, due to the particle size distribution and WA1 not expected to be inert. Thus, the low strength could be attributed to formation of hydrates with a limited contribution to the strength development as a result of hydraulic properties of WA1.

The SAI and Frattini test lead to contradictory conclusions regarding the pozzolanic properties of WA2. However, when the low content of silica and aluminosilicate potentially able to enter into pozzolanic reactions, is coupled with the explained positive result for the observed SAI results and the results obtained from the Frattini test, it is concluded that WA2 does not possess any significantly pozzolanic properties.

5.2 Hydraulic Activity

A hydraulic binder is a binder that chemically reacts with water, converting the water-binder system into a solid matrix with the ability to set and harden, and after hardening retains strength and stability even under water [2,74]. In combination with Portland cement, WA1 and WA2 are able to retain stability underwater, while mortars containing 100% WA as binder were, when harden, only stable above water.

In order to test the ability of 100% WA mortar specimens to develop strength, 100% WA mortar specimens were cast in accordance with EN 196-1 [57]. The specimens were cast in 30 x 30 x 30 mm silicone moulds. In order to maintain workability for the WAs without the need for superplasticisers, both WA and reference (REF) specimens were cast with high water to binder (w/b) ratios (0.75). The measured compressive strengths of 100% WA1, 100% WA2 and REF mortars are showed in Figure 12 (left), where a significant difference can be seen between the three mixtures.

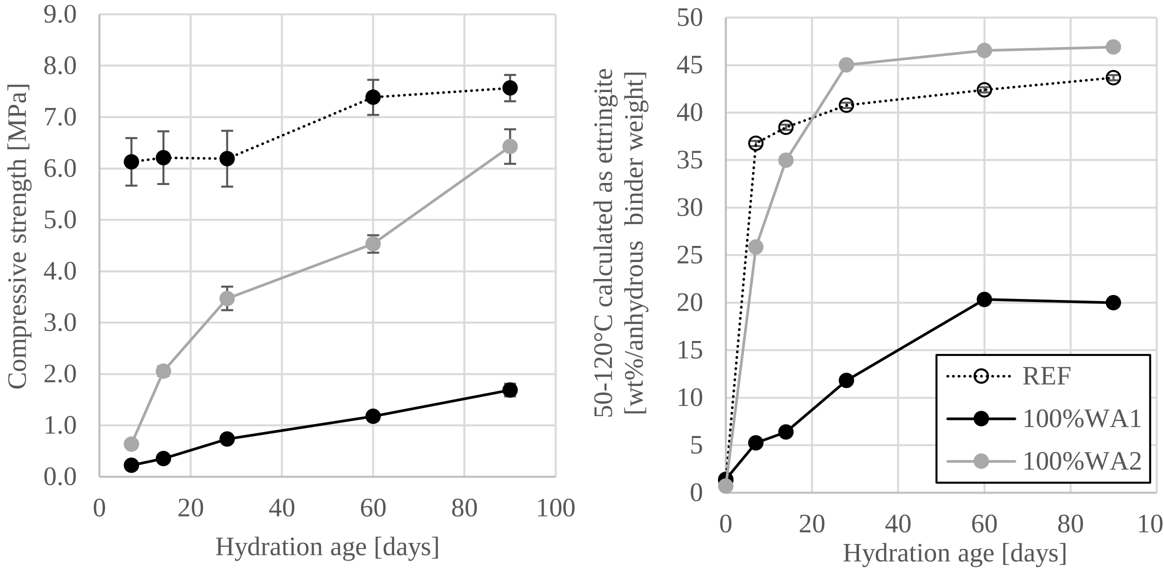

Figure 12. Compressive strength for mortar cubes (w/b = 0.75) (left) and quantification of the weight loss between 50°C and 120°C, calculated as ettringite, normalised to anhydrous binder for wood ash and cement paste samples (right). Samples were investigated after 7, 14, 28, 60 and 90 days of curing at 20°C. Figures adapted from JPII. Standard deviations are shown as error bars.

A rapid increase in the compressive strength for 100% WA2 is seen, increasing from only 10% of the compressive strength of the REF after 7 days of curing, to 85% after 90 days of curing. 100% WA1 obtains only 22% of the compressive strength of REF after 90 days of curing. This shows that both WAs possess hydraulic properties, as mortars with 100% replacement of cement with WA are able to set, harden and develop strength without an external alkali activator; however, at a very different rate.

Phase development has been investigated by both thermogravimetric analysis (TGA) (see Figure 12, right) and x-ray diffraction (XRD) on 100% WA and REF pastes. According to the literature [39,75], ettringite is considered the main contributor responsible for the set, harden and strength development of a water-WA mixture, therefor is the hydrate phase development between 50°C and 120°C is calculated as ettringite (Figure 12, right). Potential interference between the ettringite, C-S-H, AFm phases and gypsum peaks in the TGA measurements (ettringite: 50°C and 120°C [76], C-S-H: 50°C and 600°C, AFm: 60-300°C [77] and gypsum: 100°C and 140°C [77]), can lead to overestimation of the ettringite formed during curing of the water-WA mixtures. No formation of C-S-H were expected for either of the 100% WA pastes, as no pozzolanic activity have been determined (section 5.1), and no monosulfate were detected by XRD. Monocarbonate were determined by XRD for 100% WA2 paste after 14 days of hydration, thus could lead to an overestimation of the ettringite content in 100% WA2 pastes. However, since the main peak lies above 120°C this contribution can be considered limited [77].

Formation of ettringite was determined by XRD for 100% WA2 but not for 100% WA1. The sulphate embedded in WA1 precipitates mainly as gypsum (determined by XRD and TGA). Ettringite formation depends on the presence of sufficient amounts of aluminium, calcium and sulphate in the material [78]. Similar contents of sulphate and calcium are found in WA1 and WA2, thus, differences in phase assemblage are attributed to the difference in the alumina content (1.9wt% for WA1 and 4.9wt% for WA2) facilitating a larger content of ettringite precipitating in 100% WA2 pastes than 100% WA1 pastes.

In the literature [39,54,75], the ability of pure ash-water mixtures to set, harden and develop strength are mainly liked to the formation of ettringite and gypsum. This corresponds to the findings presented in Figure 12; 100% WA2 contains ettringite which leads to a larger increase in the compressive strength than 100% WA1, where only a low content of gypsum was determined corresponding to the lower increase in compressive strength.

5.3 Comparison of MVA Results and the Measurements

Two conclusions have been reached based on the revised multivariate data analysis (MVA) presented in section 4.2:

- WA originating from BFB and to some extent CFB combustion contribute to some extent with pozzolanic properties.
- WA originating from grate combustion with a high SO_3 content contribute with hydraulic properties.

From this WA1 was selected as the WA most likely to have hydraulic properties and WA2 was selected, as the WA most likely to contribute to with pozzolanic properties (although considered minor). The results presented in section 5.1 and 5.2 do not correspond to these conclusions. None of the WAs had detectable pozzolanic properties, while both had hydraulic properties, but were only stable under water in combination with cement. The strength development depended on the formation of ettringite, only detected for WA2, which was dependent on the aluminium content in the two WAs.

The difference between the results in the MVA and the actual measurements can be attributed to the following main causes:

- The MVA does not consider to what extent a WA complies with nominative requirements.
- The hydraulic index included in the MVA did not account for the aluminium content, which is central for evaluating the formation of ettringite.
- The MVA only considered the total oxide content and did not distinguishing between reactive and inert oxides.

In summary, MVA can be a powerful tool when predicting the physicochemical characteristics of a WA based on production parameters. However, if MVA should be used for assessing the potential for application more physicochemical characteristics need to be included (e.g. content of amorphous oxides). Finally, the nominative requirements used for assessing pozzolanic and hydraulic activity must be used with caution.

6 Optimisation of Wood Ash for use as a Low-Level Cement Replacement

The influence of selected pre-treatments (sieving and washing) on the physicochemical characteristics of WA are discussed in this chapter. Furthermore, a resume of the findings presented in JPIII, discussing the influence of pre-treatments on the hydration assemblage and mechanical response of cement-based material where WAs are used as low-level cement replacements, is also given in this chapter. New conclusions are drawn regarding the formation of ettringite based on the findings in chapter 5. Thermodynamic modelling was included in this chapter, which was used for determination of the theoretical phase assemblage as a function of the cement replacement rate with WAs, including both a sieved, and sieved and washed version. The influence of the pre-treatments on potential durability issues and leaching of heavy metals for mixtures with low-level cement replacements are addressed in this chapter.

6.1 Pre-treatment of WA

Pre-treatment of WA, such as washing and sieving, have previously been shown to improve the compressive strength and durability of cement-based materials containing WA as a partial cement replacement [27,28,56]. Based on the chemical composition of WAs presented in chapter 4, the high carbon, alkali, sulphate and chloride contents are causes for concern, due to the risk of loss of soundness, alkali silica reactions and other expansive reactions. This is elaborated further in section 6.3.1. To remedy these issues, two pre-treatment methods have been implemented: sieving and partial sequential extraction (washing). Sieving can reduce the content of unburnt carbon, while washing reduces the content of chloride, sulphate and alkali [28]. Details of the sieving and washing methods can be found in JPIII and have also been included in CAII.

6.1.1 Sieving of WA1 and WA2

Upon receipt of raw WA1 originating from grate combustion and WA2 originating from CFB combustion, a large content of unburnt or partially burnt woody material was noted for WA1, see Figure 13.

Figure 13. WA1 (left) and WA2 (right) as received. Diameter of petri dishes = 40 mm.

The largest constituent in wood is carbon, which constitutes 45 to 50 wt% [79], thus, a high content of carbon is expected in the unburned wood found in WAs. Furthermore, gate combustion often produces fly ashes with 50% or more unburnt carbon, whereas CFB combustion produce well burnt out ashes [80]. This is consistent with observations made for WA1 and WA2.

A high content of unburnt carbon not only changes the colour of the cement-based material to a appear black or dark grey [36], but also affects the water requirements and the rheological properties. Unburnt carbon increases the water required to obtain a normal consistency, due to absorption of water by the unburned carbon particles [10]. In order to limit this effect, EN 450 [1] established a maximum loss on ignition (LoI) of 9.0 wt%. LoI is measured in atmospheric air at 950°C in accordance with EN 196 [81]. However, the measured weight loss is not only related to the presence of unburnt carbon, but also hydrate and/or carbonate phases. As the purpose of the requirement, established in EN 450 [1], is to limit the content of unburnt carbon, it is sufficient to show that the unburnt carbon falls below the established limit. WA2 complies with this limit as received (unburnt carbon ~ 5%), however, more than 10% of WA1 as received is found to be unburnt carbon necessitating removal of unburnt carbon from WA1 by pre-treatment. WA2 was subjected to the same pre-treatment to maintain comparability later tests.

Several methods can be used to separate the unburnt carbon from the ash itself: ash reburning [80], separation by floatation in water [82] or sieving [28,82]. In order to keep the phase composition of the WAs as unaltered as possible the sieving method is used in this thesis. The fraction of WA1 < 250µm was experimentally determined to contain ≤ 1.0% unburnt carbon, see Table 5. Thus, both the WAs were sieved to a particle size < 250µm in order to reduce the unburnt carbon content but keep as much of the ash particles as possible. WA1 > 250µm account for approximately 25% of the total mass of WA1 as received and contained 35.5% unburnt carbon. Figure 14 displays the fraction of WA1 < 250µm and WA1 > 250µm.

Figure 14. WA1 < 250µm (left) and WA1 > 250µm (right). Diameter of petri dishes = 40 mm.

Sieving of WA2 as received was not necessary, however, for comparison between the two WAs, WA2 as received was subjected to the same sieving process as WA1. The fraction of WA2 < 250µm accounted for below 2% of the total mass of WA2 as received and only contained 2.3% unburnt carbon, whereas the fraction of WA2 > 250µm contained 5.7% unburnt carbon, see Table 5. Thus unburnt carbon with a lower particle size can be found in WA2 compared to WA1, consistent with the findings of Girón et al. [83], however still complying with the limit set by EN 450 [1] and are therefore not removed.

The chemical compositions of WA1 < 250µm, WA1 > 250µm, WA2 < 250µm, and WA2 > 250µm are given in Table 5. All WAs were dried at 50°C before the analysis.

Table 5. Chemical composition (wt%) of WA1 < 250µm, WA1 > 250µm, WA2 < 250µm, and WA2 > 250µm dried at 50°C. ± shows the standard deviation.

	WA1 < 250µm	WA1 > 250µm	WA2 < 250µm	WA2 > 250µm
SiO_2	11.0	5.0	23.8	33.1
Al_2O_3	2.4	0.5	5.6	5.8
Fe_2O_3	2.9	3.2	3.1	3.5
CaO	53.6	36.5	44.7	35.8
MgO	4.2	0.4	4.1	5.1
K_2O	14.6	12.1	7.6	4.6
Na_2O	1.0	0.0	0.8	0.5
P_2O_5	2.9	0.5	3.8	4.1
SO_3	5.4	2.7	6.1	3.3
Cl^-	0.8 ± 0.0	0.0 ± 0.0	0.4 ± 0.0	0.0 ± 0.0
SO_4^{-2}	3.8 ± 0.0	1.9 ± 0.0	1.8 ± 0.0	0.0 ± 0.0
Unburnt carbon	≥ 1.0 ± 0.1	35.5 ± 2.4	5.7 ± 0.3	2.3 ± 0.1
LoI	15.0 ± 0.1	51.9 ± 2.4	16.2 ± 0.3	15.06 ± 0.1

6.1.2 Washing of WA1 and WA2

The washing treatment was conducted after sieving. The washing procedure was as follows: 100 g ash was mixed with distilled water to a liquid-to-solid ratio (L/S) of 5 and shaken manually for 1 min [84]. After settling (app. 5 min.), the water was decanted. This procedure was repeated three times, all decantated water was filtered (retention 12-15µm), and the ash was subsequently dried at 50°C.

A graphical representation of the influence of the washing of WA1 and WA2 are presented in Figure 15. WA1 and WA2 subjected to the washing treatment are from here on notated as WA1-W and WA2-W, respectively (W = washed).

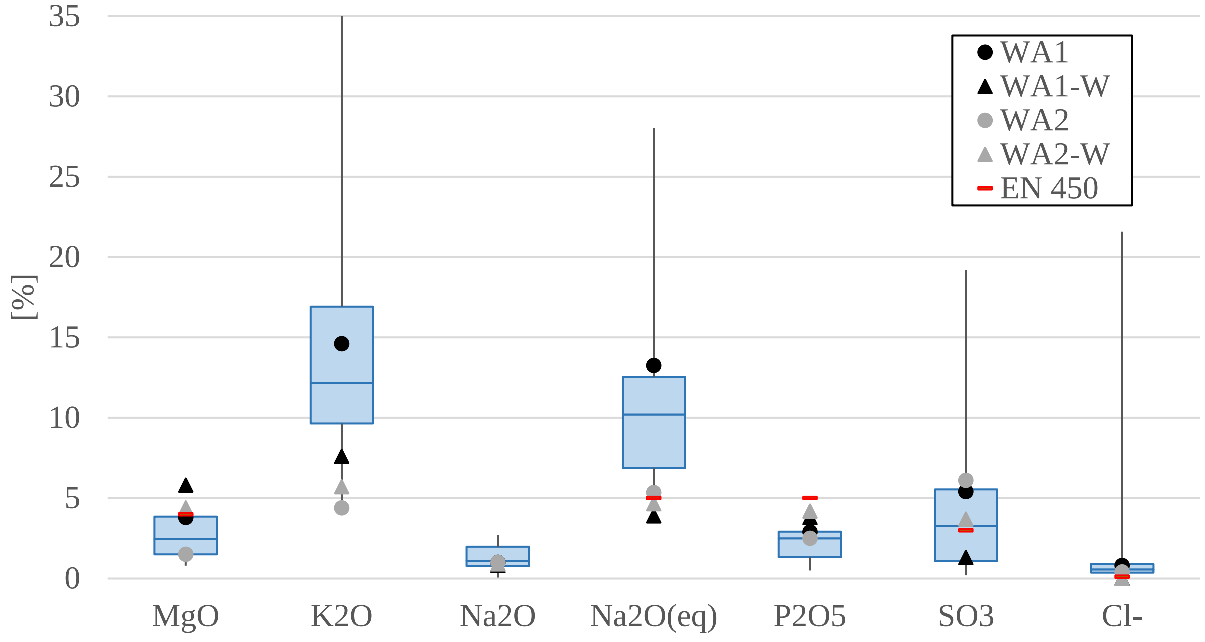

Figure 15. Graphical representation of the content of MgO, K_2O, Na_2O, Alkali$_{(eq)}$, P_2O_5, SO_3 and Cl^- determined by XRF. The WAs are identified with WA1: ●, WA1-W: ▲, WA2: ●, WA2-W: ▲ and limits from EN 450 [1]*: - . The data is adapted from JPIII.*

As determined by Doudart de la Grée et al. [28], a washing treatment leads to a reduction in the chloride, sulphate and alkali content. Figure 15 shows 70% and 13% removal of $Na_2O_{(eq)}$ and 76% and 39% removal of SO_3 in WA1 and WA2, respectively. 100% removal of Cl^- was obtained for both WAs. After the washing, WA1-W and WA2-W comply with the nominative requirements established in EN 450 [1] for $Na_2O_{(eq)}$, and Cl^- and WA1-W comply with the nominative requirements for SO_3. The removal of water-soluble compounds leads to a percent-wise increase in the remaining oxides, graphically displayed in Figure 15 for MgO and P_2O_5, as well as SiO_2, Al_2O_3, Fe_2O_3, and CaO (Table 6).

Washing also leads to changes in the phase composition of the WAs (see JPIII). The portlandite and calcite phases are identified by both XRD and TGA. An increase in the content of calcite after washing is seen by TGA, which might be due to carbonation during the washing treatment. An increase in the portlandite content is seen after washing of WA1, possibly due to the chemical hydration process between CaO and water, whereas a decrease is seen after washing of WA2, potentially due to formation of portlandite and subsequently carbonation of portlandite to calcite [33,39,54,78]. Furthermore, the washing facilitates removal of arcanite from WA1 and sylvite and anhydrite from WA2 (determined by XRD), as these are water soluble salts.

The decrease in the content of sulphate and alkali and the total removal of chloride reduces the risk of loss of soundness, alkali silica reactions and other expansive reactions, which is discussed further in section 6.3.1. The initial presence of calcite has a beneficial impact on the properties of a cementitious material. Calcite provides carbonates which stabilise the AFm phases, and hemi- and monocarbonate, consequently ettringite is stabilised instead of transforming into the AFm phase monosulphate [85,86]. As ettringite has a lager content of hydrate water and is more voluminous, stabilisation of ettringite leads to a reduction in the porosity and an increase in the compressive strength of a cement-based material [35,39,87,88]. The impacts of washing WAs are discussed further in JPIII and CAII.

6.2 Low-Level Cement Replacements with Untreated and Washed Wood Ash

This section includes thermodynamic modelling presenting theoretical phase assemblage when the cement replacement ratio with WAs is increased. This chapter also includes a short resume of the findings in JPIII. These findings elaborate on the differences between utilising washed and unwashed WAs based on the time-dependent phase development and mechanical responses, and utilise the results to determine the necessity of a washing treatment for WAs from a technical perspective.

6.2.1 Replacement Rate (Thermodynamic Modelling)

Thermodynamic modelling predicts the stable phase assemblage based on the composition of the starting material and which solids and solutions are stable under defined conditions. The thermodynamic calculations consider solids, solid solutions, gaseous phases and aqueous electrolytes, and utilise the thermodynamic data (e.g. solubility) of all species (solids, aqueous, gaseous) that can form in the system [89] to predict the amount of hydrate assemblage at different binder compositions and water/binder ratios.

The thermodynamic calculations presented in this thesis were carried out using the Gibbs free energy minimisation program (GEMS) [90,91]. The thermodynamic data used was from the PSI-GEMS database and supplemented with a cement specific database (CEMDATA18.1 [92]) relevant for cementitious materials. For modelling of the C-S-H phase, the CSHQ model proposed by Kulik was used [93], and the solid solution model for Al-Fe siliceous hydrogarnets was used [94]. The predicted effects of the cement-replacement rate with WAs are presented in Figure 16 and Figure 17. For the calculations, 100% degree of reaction between the anhydrous cement and WAs at w/b = 0.5 and 20°C is assumed. In addition, no reaction with CO_2 from the ambient air is assumed. The chemical compositions used as input for the GEMS script are shown in Table 6, where the oxides are measured by XRF analysis and CO_2 content is measured by TGA. The thermodynamic modelling of the predicted effect of increased cement replacement with WA1 and WA1-W are presented in Figure 16, and the predicted effect of increased cement replacement with WA2 and WA2-W are presented Figure 17.

Table 6. Chemical composition (wt%) of CEM I, WA1, WA1-W, WA2, and WA2-W used as input data for thermodynamic modelling in GEMS. The data is adapted from JPIII.

	CEM I	WA1	WA1-W	WA2	WA2-W
SiO_2	19.9	9.8	11.5	22.8	25.2
Al_2O_3	5.5	2.1	2.7	5.4	6.0
Fe_2O_3	3.8	2.6	2.9	3.0	3.1
CaO	64.8	47.9	58.9	42.7	42.8
MgO	1.0	3.8	5.3	3.9	4.2
SO_3	3.2	4.8	1.2	5.8	3.5
K_2O	0.4	13.0	4.0	7.3	5.4
Na_2O	0.3	0.9	0.9	0.8	0.9
Cl-	0.0	0.7	0.0	0.4	0.0
CO_2	1.0	14.3	12.7	8.0	8.8

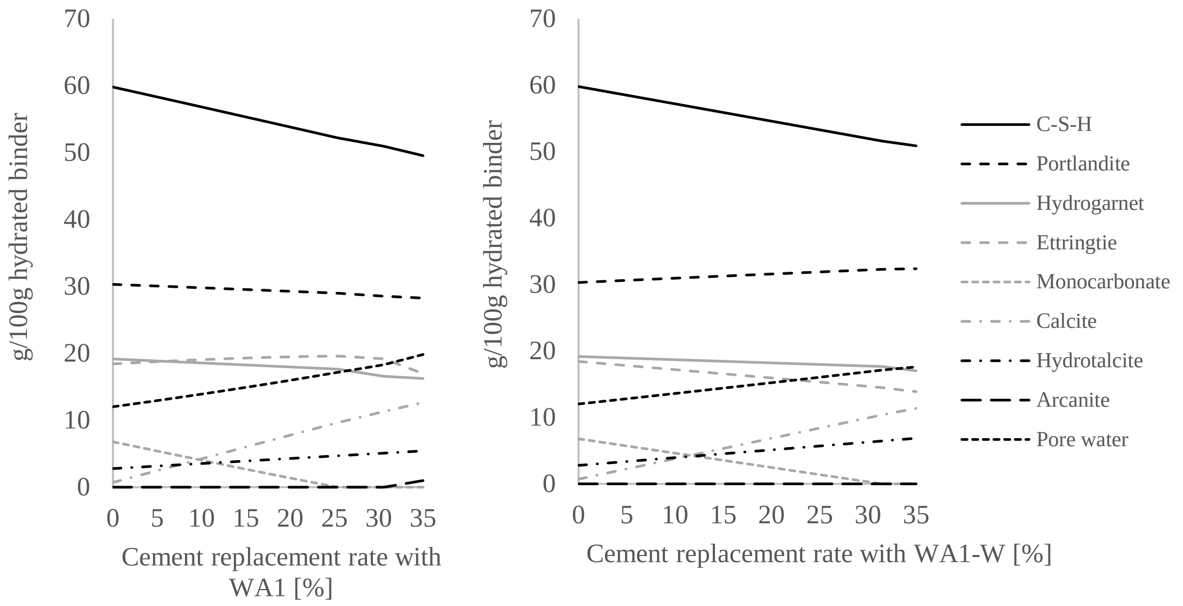

Figure 16. Results of the thermodynamic modelling for an increased cement-replacement rate with WA1 (left) and WA1-W (right). The graphs show predicted values of C-S-H (Calcium silicate hydrate), Portlandite, Hydrogarnet, Ettringite, Monocarbonate, Calcite, Hydrotalcite, Arcanite, and Pore water.

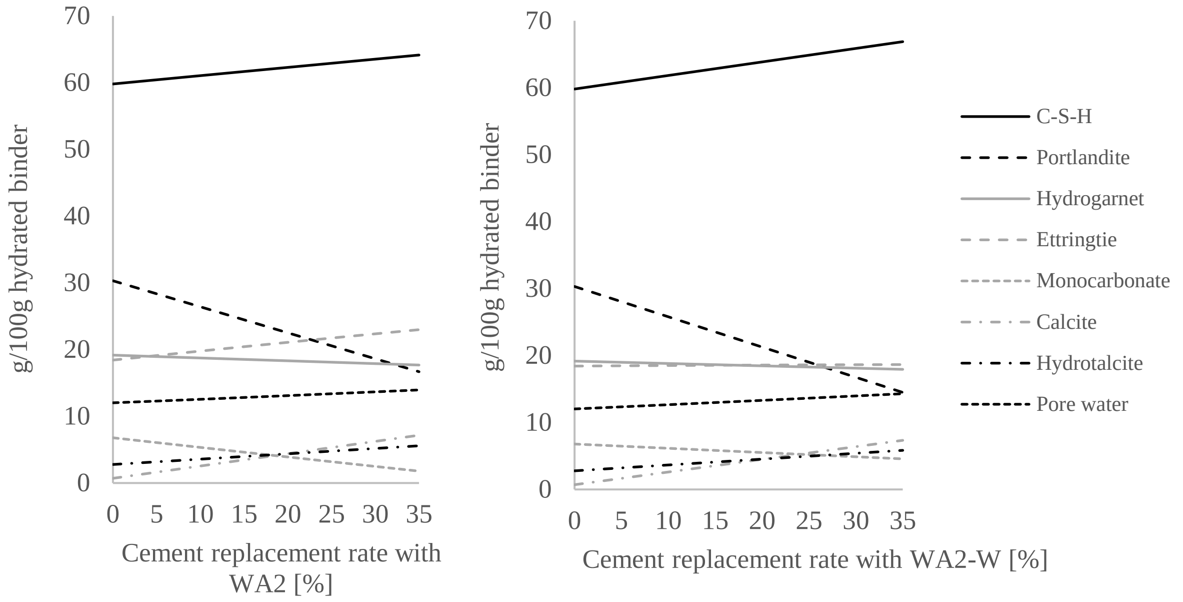

Figure 17 Results of the thermodynamic modelling for an increased cement-replacement rate with WA2 (left) and WA2-W (right). The graphs show predicted values of C-S-H (Calcium silicate hydrate), Portlandite, Hydrogarnet, Ettringite, Monocarbonate, Calcite, Hydrotalcite, and Pore water.

When increasing the cement replacement rate, a decrease is predicted in the content of portlandite for WA2 and WA2-W. As no restrains are applied to the reactivity of the WA components, thermodynamic modelling assumes a pozzolanic reaction between portlandite and the SiO_2 present in WA2 and WA2-W, decreasing the portlandite content and increasing the C-S-H content. Based on the results and discussion presented in section 5.1, were no pozzolanic properties were determine for WA2, as well as knowledge of the combustion technique used to produce WA2, no significant pozzolanic reactions are expected to occur for either WA2 or WA2-W. Thus, the results presented in Figure 17 overestimate the content of C-S-H and underestimate the portlandite content, due to the assumption of 100% reactivity of WA2 and WA2-W. For an increasing replacement rate of cement with either WA1 or WA1-W (Figure 16), a decrease in C-S-H was predicted, where the portlandite content only decreased slightly for WA1 and increased slightly for WA1-W. The decreasing C-S-H content is explained by a low content of SiO_2 leading to an absence of pozzolanic reactivity. The changes in portlandite content are explained by differences in the phase compositions, e.g. a decrease in the ettringite content with increasing replacement rates for WA1-W, increases the amount of CaO available for hydration into portlandite.

By increasing the replacement rate with washed WAs, the ettringite content is either constant (WA2-W) or decreasing (WA1-W). This difference is due to the content of SO_3, where WA2-W obtains a similar SO_3-content as CEM I, while WA1-W obtains a lower content compared to CEM I (Table 6). An increase is predicted for the ettringe content when cement is replaced by WA2, due to a high content of SO_3 compared to CEM I. The ettringite content for cement replacement with WA1 is constant until approximately 30% replacement (Figure 16, left), from where the ettringite content decreases slightly. This corresponds with the point where hydrogarnet ($3CaO\cdot Al_2O_3\cdot 6H_2O$) goes from slightly decreasing to constant and formation of arcanite (K_2SO_4) is predicted to start to occur. The formation of arcanite may be explained by an excess of K^+ in the cement mixture, due to the high content of K_2O in WA1 (Table 6). The formation of arcanite is more favourable under these conditions compared to additional ettringite precipitation. As SO_4^{2-} would no longer be available for the formation of additional ettringite, a decrease in the ettringite content is seen. Hydrotalcite continuous to increase, while hydrogarnet is stabilised, both phases binding the aluminium available as a result of the decrease in the content of ettringite. Furthermore, a low content of aluminium has been measured in WA1 (Table 6), entailing a decrease in the aluminium content as the cement replacement increases.

Monocarbonate decreases for all WAs, due to the reduction of aluminium present in the binder and more aluminium being bound in aluminium containing phases: hydrotalcite and for WA2 also ettringite. This decrease is less significant for WA2 and WA2-W, were on the contrary no formation of monocarbonate is seen for WA1 cement replacement at approximately 25% and for WA1-W cement replacement at approximately 30%, corresponding to the low content of Al_2O_3 measured in WA1 and WA1-W (Table 6), leading to a decrease in the aluminium content when the cement replacement rate increases.

The increase in the content of calcite with increasing replacement rates is due to the initial presence of calcite in the un-hydrated WAs. An increase in the pore water content as a result of increased cement replacement rates is predicted and is most pronounced for WA1 and WA1-W, due to an increase in formation of phases containing less water (hydrotalcite, calcite) with increasing replacement rates.

The thermodynamic calculations give a good indication of which phases should be looked for during experimental work like XRD and TGA. In general, an increase in the partial cement-replacement with WA1 or WA1-W leads to a lower amount of hydrate phases contributing to strength development (C-S-H and ettringite). Meanwhile, an increase in these hydrate phases is generally observed for a partial cement-replacement with WA2 or WA2-W, due to the assumed pozzolanic activity in the model resulting from assumption of 100% reactivity for all of the investigated WAs. As 100% reactivity is unlikely to be realistic, some changes are expected in the phase composition when employing experimental measurements, and the model should subsequently be developed to include degrees of reactivity to account for these changes.

Based solely on the presented thermodynamic models, presented Figure 16 and Figure 17, a partial cement-replacement with WA2 or WA2-W would not be expected to have any significant impact (positive or negative) on compressive strength regardless of the replacement rate, while a negative impact on compressive strength is expected for partial cement-replacement with WA1 or WA1-W with increasing rates.

6.2.2 Phase Development and Mechanical Response

This section includes a summary of the findings in JPIII and new conclusions regarding the formation of ettringite based on the findings in chapter 5 and the influence of the WA and cement chemistry influencing each other. Further, results from ANI are also discussed in this section.

Promising influence on the compressive strength of cement-based materials, with low-level replacement rates (≤ 10wt%) with various types of wood ashes, are seen in the literature [18,29,30]. The thermodynamic models, presented in section 6.2.1, indicate a decrease in compressive strength as a result of an increased replacement of cement with WA1 or WA1-W. Even though the thermodynamic models for WA2 and WA2-W cement replacements indicated a slight increase in the hydration phases which contribute towards increased compressive strength, an overall decrease of compressive strength is expected, as the SiO_2 content in WA2 and WA2-W is considered inert. Therefore, low-level cement replacement rates (10 wt%) with WAs have been chosen for the experimental study presented in this section. 10% replacement of cement with inert quartz (Qz) [95] is also included, as Qz represents a completely inert material, as elaborated in section 5.1.

The necessity for premixing of water and WA prior to casting, in order to ensure proper dispersion of the WA-particles, was investigated in ANI, for WA1, WA2 and a WA originating from combustion of wood pellets. Different results were obtained for the flow values measured by flow table analysis performed in accordance with EN 1015 [63] for WAs when premixing WA with water. WA1 and WA2 showed no improved flow values when the WA was premixed with water, but a WA originating from combustion of wood pellets showed an increase in the flow values by premixing of water and WA for only 15 sec. This leads to the recommendation that for a new WA an initial test of flow values should be conducted in accordance with EN

1015 [63], for a mixture without premixing of water and WA and with miniumum 15 seconds of premixing. If an increase in flow values is observed, it is recommended to follow a premixing procedure when casting with the tested WA to counteract initial flocculation of the WA particles. No increase in flow values were observed when premixing water and WA1 or WA2, thus no premixing procedure was included and WA1 and WA2 were mixed with the cement as dry powders before addition of water.

The mixing design for the specimens tested in this section is elaborated in JPIII. In order to maintain a constant w/b ratio of 0.5 a super plasticiser (Dynamon XTend from Mapei) was added to the mixing water of the mixture with 90% CEM I and 10% WA binder. The necessary amount of super plasticiser was determined according to the flow values measured by flow table analysis performed according to EN 1015 [63].

The developments of the compressive strengths as a function of time when the WAs and Qz were used as partial cement replacements are presented in Figure 18.

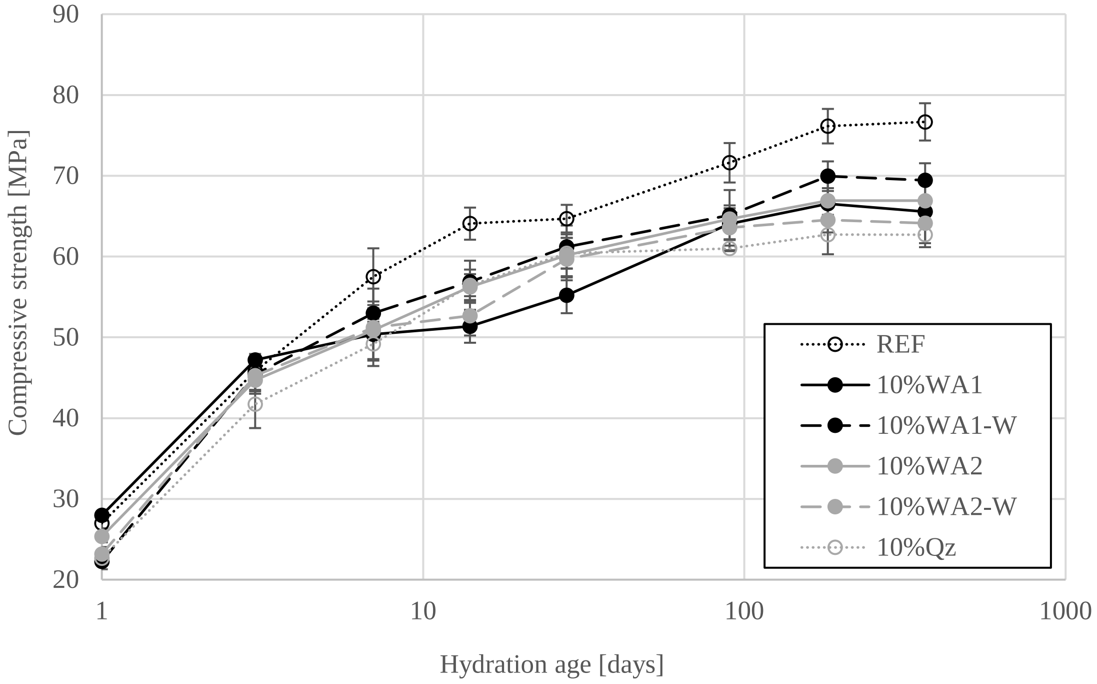

Figure 18. Development of compressive strength of REF and mortars with 10% replacements of cement with WA1, WA1-W, WA2, WA2-W, and Qz after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The compressive strength strength was normalised to an air content of 2 vol% by the use of Bolomeys equation [109]. *The error bars indicate the standard deviation. The figure is adapted from PJIII.*

In general, replacement of cement leads to a decrease of the compressive strength. At early age (1-3 day of hydration) the strengths obtained for 10%WA1 and 10%WA2 mortars are comparable to REF and all mortars with 10%WAs exceed Qz at 3 days of hydration. This trend is indicative of influence from chemical reactions resulting from dissolution of easily soluble salts and leading to strength improving hydration products, a reaction which is agreed upon in literature [35,39,87,88]. At later hydration ages (90 ≤ days of hydration) all 10% WA mortars have (slightly) higher compressive strength than the Qz mortar. At 365 days of hydration the average compressive strength for a mortar with 10% WA1 arrives at 86%, 10% WA2 at 87%, 10% WA1-W at 91%, 10% WA2-W at 84% and Qz at 82% of the compressive strength of REF.

Phase assemblage was determined by XRD. The hydrated phases corresponding to the thermodynamic model were: portlandite, ettringite, calcite and monocarbonate. Neither hydrogarnet, hydrotalcite or arcanite (for WA1) were determined by XRD or TGA. C-S-H is amorphous and cannot be detected by XRD. The differences between the thermodynamic model and the experimental findings are attributed to the assumption of 100% reactivity for all the investigated WAs in the model, leading to differences from the phase compositions obtained by actual measurements. This stresses the need to substantiate modelled results with experimental measurements, but nevertheless combining the two is a powerful predicting tool for predicting stable phase assemblage.

Quantification by TGA of portlandite and mass loss from 50-120°C as a function of time for pastes with 10% cement replacements are displayed in Figure 19.

From 1-3 days of hydration the WA pastes contain a comparable or higher content of portlandite compared to REF. This tendency is due to the additional formation of portlandite for pastes with WAs resulting from the reaction between CaO and H_2O. After 28 days of hydration, the portlandite content in the paste with Qz slightly exceeds the content in the pastes with WAs, as a result of the formation of ettringite at the expense of portlandite [36] in the latter.

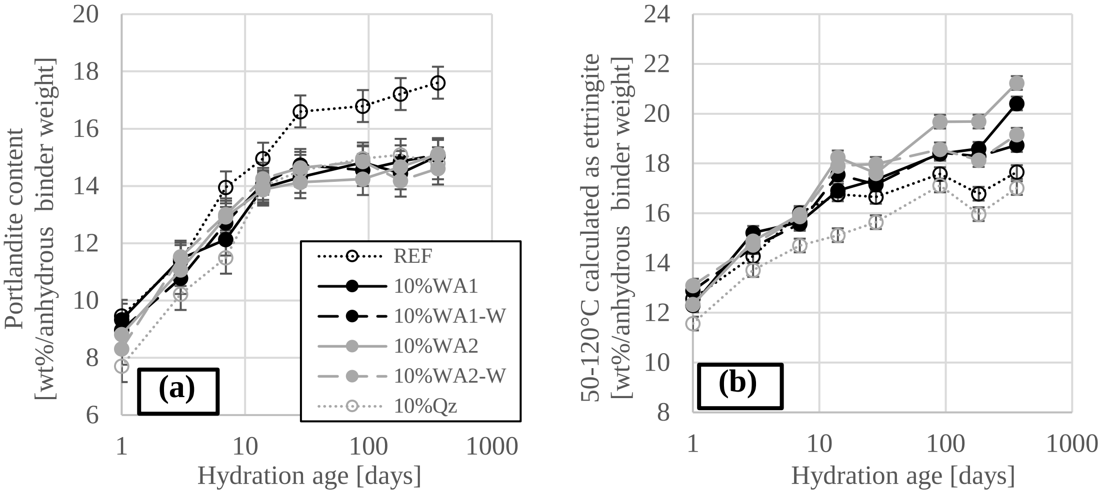

Figure 19. Quantification of Portlandite (a) and mass loss from 50-120°C in TGA calculated as ettringite (b); in paste samples with 10% replacement of cement with WA1, WA1-W, WA2, WA2-W, or Qz; investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C; normalised to the anhydrous binder content. Standard deviations are based on three independent measurements and quantifications of the bound water of a control sample at 28 days of hydration. Figures adapted from JPIII.

As discussed previously (section 5.2) the formation of C-S-H, AFm phases and gypsum cannot be separated from the mass loss corresponding to ettringite as the TGA peaks overlap, thus ettringite measured by TGA may include C-S-H, AFm phases and gypsum. In section 5.2, WA1 was determined not to contribute to the formation of ettringite but instead to the formation of gypsum, whereas formation of ettringite was determined for WA2. However, when blended with cement ettringite is detected, by XRD, for all 10% WA pastes and no gypsum were detected in 10% WA1 paste. This can be explained by the chemistry of the cement and the WAs influencing each other; the WAs contributing to an increased content of SO_3 and the cement contributing with C_3A leading to an increased SO_3/C_3A ratio compared to REF. An increase in the SO_3/C_3A ratio increases the formation of ettringite [33], facilitating formation of ettringite in WA1. No significant contribution to the C-S-H formation is expected as a result of WA hydration (section 5.2), thus the difference between the 10% Qz and the 10% WA pastes (displayed in Figure 19, right) are attributed mainly to formation of ettringite.

The formation of ettringite enhances compressive strength due to high amounts of hydrate water. Ettringite is voluminous, which leads to a reduction in porosity and consequently to an increase in compressive strength [35,39,87,88]. However, excessive formation of ettringite can cause disruption of the microstructure, due to the voluminous nature of ettringite. This disruption may lead to cracking and a decrease in strength if the stress exceeds the tensile strength of the binder [33], explaining the different results obtained for the compressive strengths of the 10% WA mortars. The adverse effects of excessive formation of ettringite result in an interval for the SO_3/C_3A ratio where optimal compressive strength is obtained. Bogues calculations can be used to calculate the approximate proportions of the four main clinker minerals (alite, belite, ferrite and aluminate) from the measured oxide content of the cement. By the use of Bogues calculations and the content of Al_2O_3 and Fe_2O_3 [36] the content of aluminate (C_3A) in the cement are calculated, and the SO_3/C_3A ratios for mortars with 10% cement replacements with the WAs as follows: WA1 = 0.5, WA1-W = 0.4, WA2 = 0.5, and WA2-W = 0.5. Only WA1-W obtains a compressive strength above 90% of the reference strength while the compressive strength of WA1, WA2 and WA2-W are between 84% and 87%. Thus, the optimal interval the SO_3/C_3A ratio for a cement-based mixture with a partial cement replacement with a WA is determined to be $0.4 \leq \text{optimum} < 0.5$. This provides a target for the optimal removal of SO_3 from a WA, by a washing, in order to obtain the maximum strength contribution from ettringite formation.

According to the presented results, elaborated in JPIII, the content of ettringite is the decisive factor for the compressive strength development of a cement-based material with a low-level cement replacement with either washed or unwashed WA. A washing is, based on the mechanical response, only beneficial when the SO_3 content is decreased enough to avoid cracking but retained sufficiently to ensure formation of ettringite to enhance the compressive strength.

6.3 Durability Issues and Leaching of Heavy Metals

The potential durability and environmental issues when WA is utilised as a partial cement replacement in cement-based materials has been stressed in several studies [29,49,54,96,97]. This section carries on the investigation of cement-based mixtures with low-level cement replacement with WAs, both unwashed and washed versions. Potential durability issues of cement-based materials are assessed based on the chemical composition of the WAs, followed by a short resume of the findings presented in ANII regarding the content of heavy metals and leaching behaviour.

6.3.1 Potential Durability Issues Based on the Chemical Composition

SCMs generally improve the resistance of blended cements towards most degradation mechanisms at equal w/c-ratios [35]. However, as the chemical composition of WAs deviate significantly compared to most traditional SCMs (e.g. CFA and silica fume [35]), several potential durability issues need to be addressed.

Selected chemical components of WA1, WA1-W, WA2, and WA2-W and the chemical requirements specified in EN 450 [1] are presented in Table 7.

Table 7. Chemical composition (wt%) of WA1, WA1-W, WA2, and WA2-W. Chemical requirements specified in EN 450 [1] *are included and exceedances are marked in bold.* $Na_2O_{(eq)}$ *is calculated from* $Na_2O_{(eq)} = Na_2O + 0.658 \cdot K_2O$ [33]. *± defines the standard deviation. The table is adapted from JPIII.*

	WA1	WA1-W	WA2	WA2-W	Requirements specified in EN 450 [1]
Cl^-	**0.8 ± 0.0**	0.0 ± 0.0	**0.4 ± 0.0**	0.0 ± 0.0	≤ 0.10
SO_3	**5.4**	1.3	**6.1**	**3.7**	≤ 3.0
CaO, free	**12.3**	**5.9**	**6.4**	**1.6**	≤ 1.5
$Na_2O_{(eq)}$	**10.8**	3.3	**5.6**	4.4	≤ 5.0
MgO	**4.2**	**5.8**	**4.1**	**4.4**	≤ 4.0
P_2O_5	2.9	3.8	3.8	4.2	≤ 5.0
Unburned carbon	≥ 1.0	≥ 1.0	5.7	6.7	-
LoI	**15.0 ± 0.1**	**19.6 ± 0.1**	**16.2 ± 0.3**	**19.7 ± 0.1**	≤ 9.0

All chloride is removed from the WAs as a result of the washing treatment, and according to EN 450 [1] the chloride content of washed WA are below the chemical requirement. Thus, the chloride content does not impose a durability issue, which would otherwise be to destroy the passive iron oxide film on building reinforcements leading to corrosion of the steel [36].

The content of SO_3 is reduced due to washing none the less only WA1-W complies with the chemical requirement. Sulphate attack can cause deterioration of the cement-based material due to the formation of the expansive compounds gypsum (120% expansion of the solid volume) and ettringite (55% expansion of the solid volume) [36], resulting in cracking and spalling if the stress exceeds the tensile strength of the binder [33]. The severity of the attack depends on the cation associated with the sulphate ion, where calcium sulphate is considered a weak attack leading directly to the formation of ettringite, while sodium sulphate and magnesium sulphate first form the more expansive gypsum and later ettringite [33]. No gypsum was found during hydration of a blended cement with a 10% cement replacement with WA, however indications of excessive amounts of ettringite leading to a decrease in compressive strength at higher SO_3 contents were seen (please refer to JPIII).

Soundness of cement refers to the ability to retain volume after hardening [98]. When blended cements are used excessive amounts of CaO_{free} and crystalline MgO (periclase) imbedded in the mineral additions can potentially cause delayed expansion due to formation of expansive hydration products affecting the volumetric stability [99]. The content of CaO_{free} is significantly decreased by washing of the WAs, as the structure of the CaO renders it more reactive with water than periclase, leading to stabilisation through formation of $Ca(OH)_2$ [78,99]. On the contrary, an increase in the relative MgO content is seen as a result of the washing treatment. Carević et al. [97] tested the soundness of six WAs (fly ash fraction) where one met the MgO content requirement from EN 450 [1] and one meet the CaO_{free} content requirement from EN 450 [1]. The soundness was tested in accordance with EN 196 [100] and all six tested WAs met the requirement for soundness specified in EN 450 [1], even WAs that significantly exceeded the chemical requirements for CaO_{free} and MgO. Thus, the high amounts of CaO_{free} and MgO determined for the WAs included in this thesis (Table 7) do not necessarily pose an issue regarding soundness.

Alkali silica reactions are caused by dissolution of reactive silica from aggregates by the alkali hydroxides in the pore solution forming alkali-silica reaction products. These products can subsequently cause expansion, leading to cracking of the cement-based materials [10]. The unwashed WAs have $Na_2O_{(eq)}$ contents above 5.0%, while the washed WAs have below, thus washing decreases the risk of alkali-silica reactions to an acceptable level by reducing the alkali content of the WAs to acceptable levels.

An increase in LoI and the unburned carbon is seen a result of the washing treatment. As the content of unburned carbon is low, the high LoI measured for all WAs is primarily due to the content of hydrate phases and especially carbonate phases, stressing the importance of distinguishing between unburned carbon and other phases. Mineral additions with a high content of unburned carbon lead to increased absorption of water, due to a high specific surface area for unburned carbon, increasing the amount of free water required for achieving the desired workability [18,30,49]. The workability of mortar mixes with 10% cement replacement with both untreated and treated WAs were measured by the flow table method and presented in JPIII. Even though WA2 and WA2-W have the highest contents of unburned carbon, WA1 and WA1-W required the largest amount of superplasticizer (1.2 g for both compared to 0.6 g and 0.8 g for WA2 and WA2-W, respectively) in order to maintain the same flow values as a reference mortar, stressing the specific surface area and irregular microstructure of the WA particles themselves also plays an important role when assessing the water requirements [99,101].

Overall, the washing treatment aided the WAs notably in meeting the requirements specified in EN 450 [1] by decreaseing the content of chloride, sulphate, CaO_{free}, and $Na_2O_{(eq)}$. The risk of chloride corrosion was thereby reduced, as was the risk of alkali-silica reactions. Only one of the washed WAs complied with the limit for SO_3, thus the potential of gypsum and ettringite formation poses a risk. The content of CaO_{free} decreased due to the washing of WAs, however, the content of MgO could still pose a risk to the soundness of the binder. Based on potentially durability issues a washing step should be included. Further treatments, e.g. thermal treatments in order to remove fine carbon particles or grinding to reduce the particle size [28], could possibly be required before utilisation in cement-based materials is possible, but require further investigation.

6.3.2 Leaching of Heavy Metals

This section presents a summary of the findings in ANII.

Several studies [29,49,54,96] have stressed the possible environment risk when WA is used as a partial cement replacement, due to content of the heavy metals. The total heavy metal concentrations in WA1, WA1-W, WA2, and WA2-W have been determined, and the leaching from mortars have been assessed in two scenarios: worst case scenario at end of life for crushed concrete and the scenario during use i.e. leaching from a cube. The investigation included leaching of Cd, Cr, Cu, Ni, Pb, and Zn from mortars with 10% cement replacement with WA1, WA1-W, WA2, or WA2-W.

According to DS/EN 206 DK NA [102] the use of bioash in a cement-based material must not lead to an increase of the heavy metal content above 25% compared to the initial content in the cement-based material. It should be noted that bioash included in DS/EN 206 DK NA [102] only refers to sewage sludge ash. According to the total concentrations and the requirement set by DS/EN 206 DK NA [102], the heavy metals Cd, Pb, and Zn could propose an environmental risk already from 10% cement replacement with WA1 or WA1-W. For WA2 or WA2-W only Cd does not apply at a 10% cement replacement, Pb does not apply and at a 15% cement replacement, and Zn does not apply at a 25% cement replacement. None of the WAs are an environmental concern with regard to Cr, Cu or Ni, according to DS/EN 206 DK NA [102]. Washing leads to a decrease in Cr, Cu and Pb concentrations in both WA1 and WA2, and in the Zn concentration for WA2, which shows that some of the compounds containing these elements are water soluble.

The washing treatment did not decrease the solubility determined leaching of Cu, Ni and Zn for 10% cement replacement with either WA, however, compared to category 1 set by the Danish Decree BEK nr. 1672 [103], all of specimens with 10% WA, at both L/S 2 and L/S 10 comply. Diffusion-controlled leaching was not detected for Cd from 10% WA2 mortar, Pb from mortars with 10% replacement with any of the WAs, and Zn from mortars with 10% replacement with WA1, WA1-W and WA2-W. A decrease in the content of Cr, Cu, and Ni was obtained as a result of the washing treatment of WA1, and a decrease in the content of Cr and Zn was obtained as a result of a washing treatment of WA2. All measured concentrations of diffusion controlled leaching were considered low and complied with limitations set by the Dutch building material decree (BMD) as used in Quijorna et al. [104]. Neither of the two leaching tests conducted for mortar with 10% WA give rise to major environmental concerns for neither of the untreated or washed WAs.

7 Main Conclusions

In this PhD project, the potential use of wood ash, originating from combustion of 100% wood or wood products, as a partial cement replacement in cement-based materials was researched and discussed. The main conclusions from this research pertain to three main areas of study: 1) the impact of production parameters on the physicochemical characteristics of wood ash, 2) the reaction mechanisms of wood ash for use a partial cement replacement, and 3) the pre-treatment of wood ash to optimise use as a partial cement replacement and reduce potential durability issues and leaching of heavy metals.

Impact of Production Parameters on the Physicochemical Characteristics of Wood Ash.

Multivariate data analysis was used to study the relationship between production parameters and the physicochemical characteristics of wood ashes. The standards EN 450 [1] and EN 197-1 [2] were used to assess the potential of the wood ashes for use as mineral additions (based on their chemical compositions) with either hydraulic and/or pozzolanic properties.

From the multivariate data analysis two important conclusions were drawn: wood ash originating from grate combustion had the highest probability of possessing hydraulic activity, and wood ash originating from fluidised bed combustion had the highest probability of possessing some degree of pozzolanic activity. The differences in the wood ashes characteristics were mainly due to the production parameters, which were linked to the different combustion methods.

Based on the multivariate analysis two wood ashes were selected for further investigation, these being the two wood ashes with the highest probability of possessing hydraulic or pozzolanic properties, respectively. Both wood ashes originated from combustion of wood chips from whole trees, including the bark and needles, while one came from grate and the other from fluidised bed combustion.

Reaction Mechanisms of Wood Ash used as a Partial Cement Replacement.

The potential for hydraulic and pozzolanic properties was investigated experimentally. It was found that neither of the two selected wood ashes possessed pozzolanic properties. Conversely, both wood ashes showed hydraulic behaviour (they could set, harden and retain strength after hardening), although one wood ash had higher compressive strength development than the other. The two wood ashes had similar sulphate and calcium contents but different aluminium contents, leading to the observed differences in their compressive strength developments. The availability of aluminium determined whether ettringite or gypsum was the major hydration product (the latter is formed when aluminium is not present in sufficient quantities to form ettringite). The highest increase in compressive strength was due to the formation of ettringite, therefore the aluminium content in the wood ash was determining for the compressive strength.

The contradictory results obtained from experimental and theoretical investigation of the hydraulic and pozzolanic properties of the wood ashes called for a reassessment of the multivariate data analysis. This stresses the issue in using the EN 450 [1] standard for coal fly ash when assessing a new types of mineral additions for use as partial cement replacements based on their chemical compositions, as the reactivities determined for coal fly ash are not necessarily valid for all types of mineral additions.

Pre-treatment of Wood Ash for Optimal use as a Low-Level Cement Replacement.

In order to improve the durability of concrete containing wood ash as a partial cement replacement, the contents of sulphate, chloride, and alkali were reduced by washing the wood ashes. The wood ashes, both unwashed and washed, were tested as low-level cement replacements (10%). Aluminium originating from the cement clinker led to the formation of ettringite in all the investigated cement-wood ash mixtures, and an optimum SO_3/C_3A ratio of $0.4 \leq \text{optimum} < 0.5$ was proposed. This ratio ensures the maximum contribution to compressive strength from ettringite formation, without excessive ettringite formation leading to microcracking and deterioration of compressive strength.

Potential durability issues were assessed based on the oxide content of both unwashed and washed wood ashes. Washing decreased the content of sulphate, chloride and alkali and thereby reduced the risk of expansive sulphate attack, chloride corrosion and alkali-silica reactions when using wood ash. The content of CaO_{free}, MgO and LoI could still pose a risk to the durability and this risk should be addressed in future work, potentially requiring further pre-treatment of the wood ashes. Wood ashes have been determined to contain heavy metals which can pose an environmental risk when liberated. However, leaching tests (solubility or diffusion controlled) showed that the amount of leaching was below the relevant required limits and therefore no risk was prevalent.

Ettringite was seen to be the most important phase when wood ash was used as a partial cement replacement, due to its contribution to compressive strength development. However, partial cement replacement with wood ash led to an overall decrease in compressive strength compared to a pure cement reference, even when low-level cement replacements were employed. The hydraulic properties displayed for the wood ashes could facilitate usage in other types of cement-based materials with lower strength requirements. Pre-treatment led to clear improvements in the performances of the wood ashes, and therefore further optimization of wood ash characteristics by pre-treatment should be explored in future work.

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Appended Papers and Additional Notes

Journal Paper I

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

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Full length article

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 physiochemicalcharacteristics 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.

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 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., 2009; 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., 2009; 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. (2009) 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

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compressive strength over time due to pozzolanic activity. These different results are dependent on type of WA is used. WA physiochemical characteristics vary depending both on the wood products, e.g. wood chips or pellet, and 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. 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., 2009; 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 ensure 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 physiochemical 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 are; 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 shaked 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 h) 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, set 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

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

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 physiochemical characteristics (tables 2 and 3), percentage complying with the filler limit and compliance with category N (Table 2), mineralogical composition (Table 2 and Fig. 3) and morphology (Fig. 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 Σprimary 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; 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 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. (2009) 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., 2009). The oxides of the WA investigated by Rajamma et al. (2009) 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. (2009). 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. (2009) 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. (2009) 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 Fig. 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 close to 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 potentially 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 size limit (250 µm) (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

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, 2011a, 2011b; 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., 2009; Ramos et al., 2013; Siddique, 2008; Udoeyo et al., 2006; Vassilev et al., 2014; Vassilev et al., 2010; Yeboah et al., 2014) are added for comparison.

	WCBA	WPMA	WCMA1	WCMA2	WCMA3	WPFA	WCFA1
Chemical composition (%)							
SiO_2	57.8	3.4	3.9	4.1	9.4	4.3	3.6
Al_2O_3	4.9	0.9	1.5	0.9	1.3	0.9	0.6
Fe_2O_3	1.1	1.6	0.6	0.7	1.0	2.1	0.9
Σ primary oxides	*63.8*	*5.9*	*5.9*	*5.7*	*11.7*	*7.4*	*5.1*
CaO/SiO_2 (-)	*3.6*	*11.1*	*8.6*	*19.5*	*5.7*	*15.0*	*13.6*
CaO	16.0	37.8	33.6	79.8	53.2	64.4	49.0
MgO	1.5	4.1	2.0	2.7	1.5	4.5	2.8
K_2O	8.9	17.0	16.9	9.9	4.3	22.9	10.1
Na_2O	0.0	1.1	1.1	0.7	0.7	0.9	0.8
P_2O_5	< 0.5	2.7	1.1	3.7	1.1	2.5	3.2
TiO_2	0.2	0.3	0.0	0.0	0.1	0.0	0.0
SO_3	0.2	3.0	0.7	1.2	0.7	6.0	2.5
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
$SO_4{}^{-2}$	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
LoI, 550 °C	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
LoI, 950 °C	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
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
Spread of particle size distribution (μm)	2.5 - 631.0	1.3 – 2187.8	1.4 – 2187.8	1.3 – 2187.8	1.3 – 2187.8	0.5 – 549.5	1.0 – 2187.8
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
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
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 ± 1496.4
$CaCO_3$ (%)	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
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
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 (< 250 μm) (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
Complying with category N (EN 450, 2012)	No	No	No	No	No	Yes	No
Mineralogical compositions of investigated WA determined by XRD analysis. X marks detected minerals.							
Quartz (SiO_2)	X	X	X	X	X	X	X
Portlandite ($Ca(OH)_2$)			X	X	X		
Calcite ($Ca(CO_3)$)		X	X	X	X	X	X
Sylvite (KCl)		X					
Arcintie ($K_2(SO_4)$)		X	X	X			X
Periclase (MgO)		X				X	X
Quick Lime (CaO)						X	X
Wollastonite ($CaSiO_3$)	X						

	WCFA2	WCFA3	WMFA1	WMFA2	EN 450-1 (2012)	EN 197-1 (2011)	Literary review
Chemical composition (%)							
SiO_2	1.7	19.3	5.3	10.3	> 25.0		1.74 – 73.01
Al_2O_3	0.4	3.4	0.9	1.5			0.12 – 28
Fe_2O_3	1.0	2.1	1.1	1.6			0.09 – 27.9
Σ primary oxides	*3.1*	*24.8*	*7.4*	*13.4*	*> 70.0*		

(*continued on next page*)

Table 2 (*continued*)

	WCFA2	WCFA3	WMFA1	WMFA2	EN 450-1 (2012)	EN 197-1 (2011)	Literary review
CaO/SiO$_2$ (-)	*36.2*	*2.2*	*6.3*	*3.1*		*> 2*	
CaO	61.6	41.7	33.6	31.5	< 10.0		1.16 – 83.46
MgO	2.2	3.3	0.8	4.0	< 4.0	< 5.0	0.7 – 14.57
K_2O	38.5	6.3	10.0	14.2			0.11 – 31.99
Na_2O	2.7	1.2	2.6	1.9			0.08 – 29.82
P_2O_5	2.5	2.5	1.4	3.0	< 5.0		0.07 – 13.01
TiO_2	0.0	0.2	0.1	0.2			0.01 – 1.2
SO_3	19.2	4.2	3.5	4.5	< 3.0		0.05 – 12.5
Cl^-	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}	10.2 ± 0.05	1.8 ± 0.0	3.36 ± 0.0	4.2 ± 0.1			0.12 – 0.96
LoI, 550 °C	1.0 ± 0.3	0.8 ± 0.0	9.3 ± 1.5	7.2 ± 0.1			< 0.5
LoI, 950 °C	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)	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)	0.4 – 478.6	0.6 – 478.6	1.1 – 2187.8	1.3 – 2187.8			30 - 600
Specific Surface Area (m^2/g)	1.2 ± 0.01	1.0 ± 0.01	0.1 ± 0.02	0.2 ± 0.02			
pH	12.7 ± 0.0	12.7 ± 0.0	12.8 ± 0.0	13.3 ± 0.01			10.10 – 12.5
Conductivity (mS m^{-1})	3,976.7 ± 141.9	2,380 ± 10.0	3,950.0 ± 364.3	12,160 ± 317.6			
$CaCO_3$ (%)	21.1 ± 0.3	1.5 ± 0.2	22.2 ± 0.4	16.1 ± 0.3			
Water solubility (%)	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 (< 250 µm) (Herholdt et al., 1985; Moosberg-Bustnes et al., 2004)	95.5 ± 0.4	98.6 ± 0.2	48.5 ± 1.9	76.6 ± 4.9			
Complying with category N (EN 450, 2012)	Yes	Yes	No	No			
Mineralogical compositions of investigated WA determined by XRD analysis. X marks detected minerals.							
Quartz (SiO_2)		X	X	X			
Portlandite ($Ca(OH)_2$)	X						
Calcite ($Ca(CO_3)$)	X	X	X	X			
Sylvite (KCl)			X				
Arcintie ($K_2(SO_4)$)	X		X	X			
Periclase (MgO)							
Quick Lime (CaO)							
Wollastonite ($CaSiO_3$)							

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 > 215 μm 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 Fig. 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 Fig. 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 Fig. 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, Fig. 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, 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 physiochemical characteristics of the WA are given in Tables 2–4, defined as the Y-matrix. Combined these tables represent the data set used for the multivariate analysis.

3.2.1. Evaluation of physiochemical 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 physiochemical characteristics of the WAs (Y-matrix), and the obtained Loading Scatter Plot can be seen in Fig. 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, Fig. 1), and variables with minor influence are projected close to the axis centre (e.g. carbonate, Fig. 1). Variables, which are positively correlated, are found close to each other (e.g. Al_2O_3 and SiO_2, Fig. 1) and variables, which are negatively correlated, are projected opposite to each other, with respect to the origin of the plot (e.g. high compliance with the filler limit and a high mean particle size, Fig. 1) (Pedersen et al., 2015). As the physiochemical 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 physiochemical characteristics of WA can contribute to the validation of the composed Loading Scatter Plot for the PCA-Y model (Fig. 1), and subsequently the PLS model. The Loading Scatter Plot (Fig. 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 physiochemical characteristics of WA explained. An example of an expected correlation seen in the Loading Scatter Plot (Fig. 1) is a high amount of particles, complying with the filler limit (particle size < 250 μm (Herholdt et al., 1985) and category N (maximum 40.0% by mass of the particles retained on a 45 μm 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 (Fig. 1) displayed the possible pozzolanic activity (defined as Σprimary 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 physiochemical characteristics of WA evaluated by PLS modelling

PLS is a multivariate method used for modelling the quantitative

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, 550 °C (%)						+			–	+	–	
LoI, 950 °C (%)	–			–	+	+			–	+		
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		+	+			–	–	–			+	–

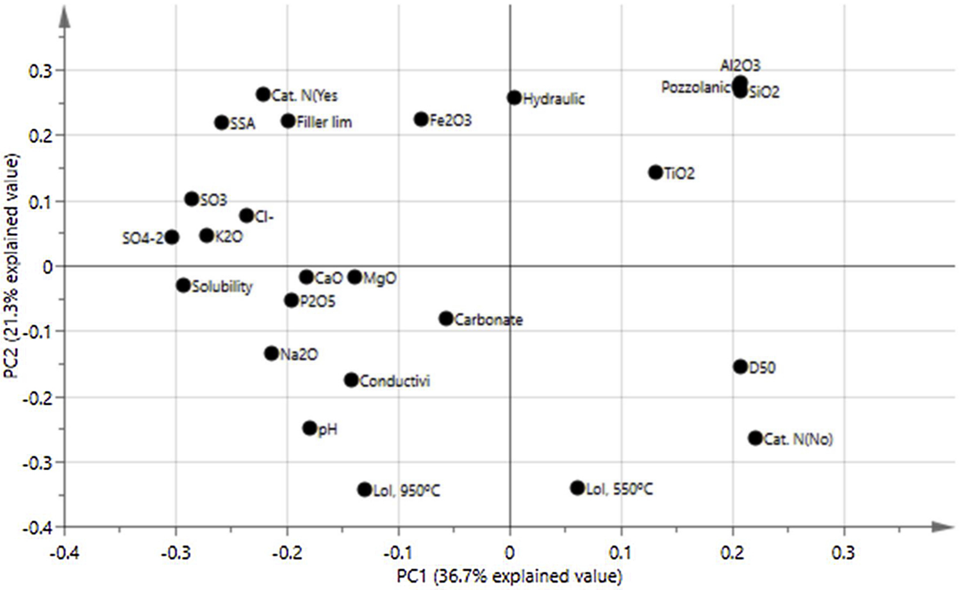


Fig. 1. Loading Scatter Plot for the partial components 1 and 2 from the PCA-Y model conducted for the physiochemical characteristics of WA.

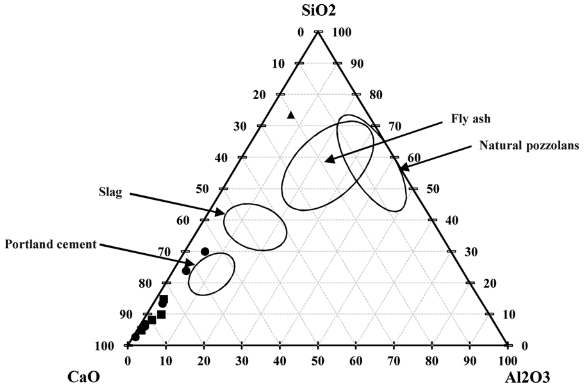


Fig. 2. CaO-SiO_2-Al_2O_3 ternary diagram for the investigated wood ashes. Black triangle ▲: bottom ash, black square ■: mixed ash and black dot ●: fly ash. Ternary diagram adapted from Lothenbach et al. (2011).

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) influence the physiochemical characteristics of WA (Y-matrix, Tables 2–4). 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 physiochemical 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, thus leading to an increase or decrease, respectively, on the measurements for the physiochemical 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

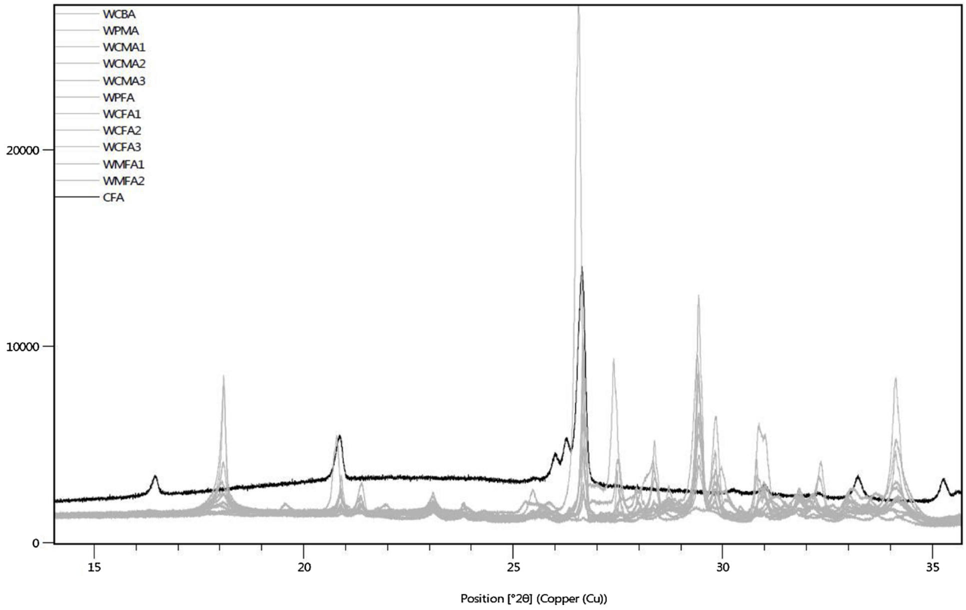
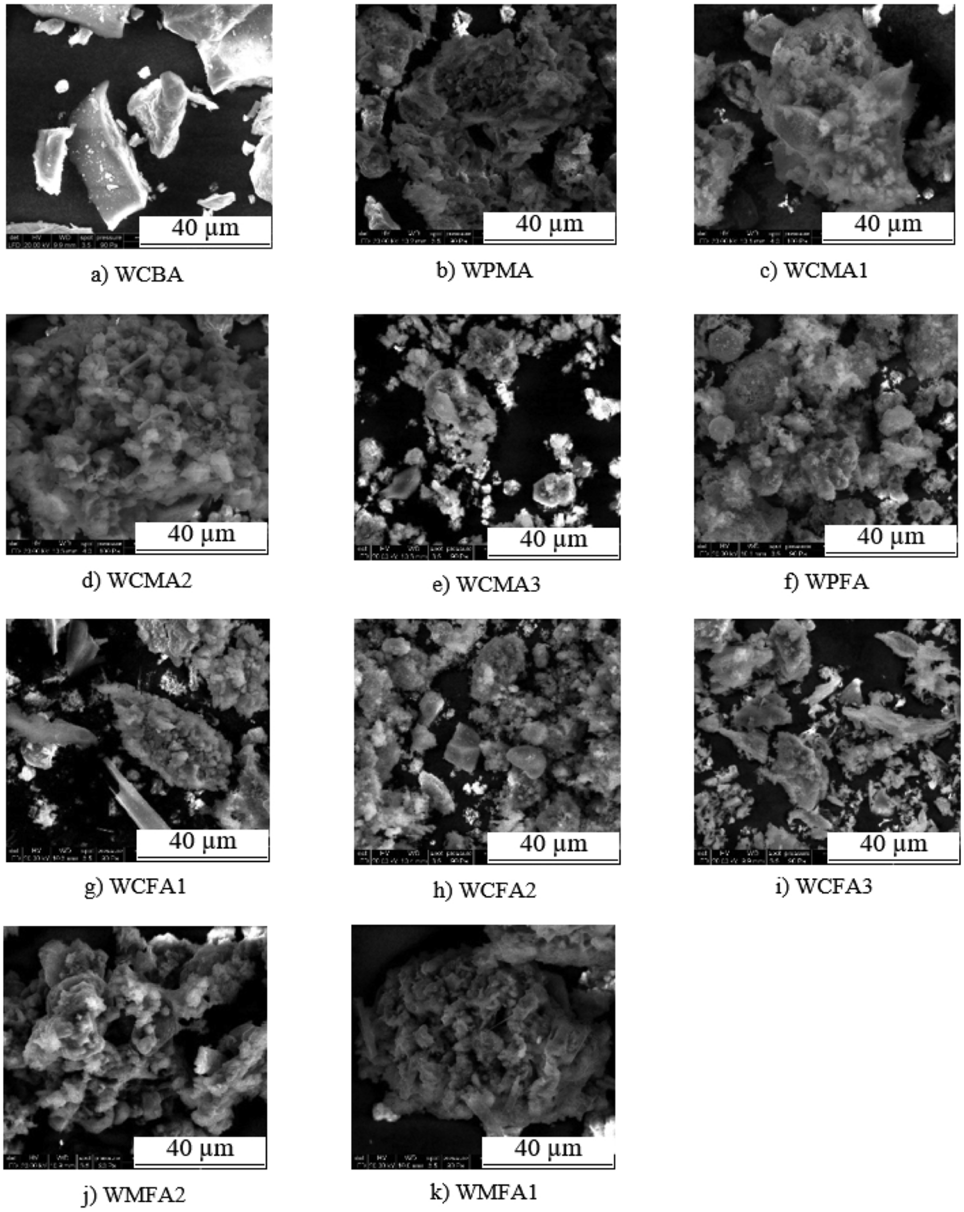


Fig. 3. Comparison between the XRD diffractograms from 15°2θ to 35°2θ (amorphous rise) for the investigated WA and a coal fly ash.



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

Fig. 4. SEM images displaying the 11 investigated WA.

parameters with VIP-values above one are considered to be most relevant for explaining the physiochemical 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 Vassilev et al. (2010) of the combustion technology to have the most significant impact on the properties of biomass ash (ash types excluded). 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 results in 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 (Vassilev et al., 2010).

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

To identify which production parameters results in a suitable WA for utilisation 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.

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

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) also sets limit for the conductivity of the WA of maximum 3600 mS/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 is 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 pozzolanic activity of Σprimary 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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Journal Paper II

JPII: Reaction Mechanisms of Wood Ash for use as a Partial Cement Replacement

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Reaction mechanisms of wood ash for use as a partial cement replacement

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Abstract

An increase in the amounts of wood ashes (WAs) produced by the heating and power industry is seen worldwide. This study investigates two representative WAs for potential use as a partial cement replacement. The WAs originate from combustion of wood chips by grate combustion (WA1) and circulating fluidised bed combustion (WA2). Both WAs were found to possess hydraulic properties, no pozzolanic properties were detected. A substantial difference in strength development was observed between WA1 and WA2 attributed to the phases formed; WA2 contributing the most, ettringite in addition to other phases were formed, while gypsum formed in WA1 pastes.

Keywords: wood ash, hydraulic activity, pozzolanic properties, compressive strength, phase development

1. Introduction

The production of cement is responsible for 8-9% of the total anthropogenic CO_2 emissions [1]. In order to reduce the global carbon footprint, blended cements are produced, where parts of the clinker are replaced with other materials [2]. Traditionally coal fly ash from the combustion of coal has been used in blended cement, however, with the withdrawal of coal-fired power plants, a decrease in the available amounts of coal fly ash is seen. An alternative

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Abbreviations (not standard): WA1: wood ash no. 1, WA2: wood ash no. 2.

to coal biomass is used in the heating and power production, and the amount of ash originating from combustion of different types of biomass increases [3]. Alone from electricity production, approximately 10 million tonnes (year 2018) biomass ash are produced annually worldwide [3]. Potentially biomass ashes could be used as a partial cement replacement for blended cement. One such potential material is wood ash (WA) originating from the combustion of wood and woody products [4].

Mineral additions, used as a partial cement replacement, are divided into pozzolanic, latent hydraulic materials and (partially) inert fillers [2,5]. Pozzolanic materials, e.g. coal fly ash, form cementitious binders in reaction with calcium hydroxides. Latent hydraulic materials react with water and form cementitious binder in the presence of an activator [5]. Wood ash has varying characteristics [6,7] and varying properties when used as a partial cement replacement. Pozzolanic activity has been observed for WA in some studies [8–10] and explained by a high content of silicon, aluminium and iron oxide [9,10] or amorphous silica [8]. Lack of pozzolanic activity was found in [11,12] and explained by limited silicon content in the investigated WAs. Other studies [13–16] reported hydraulic activity for WAs reacting directly with water and forming cementitious products even without activation.

In a recent paper, Sigvardsen et al. [6] presented a multivariate data analysis linking combustion process with reaction mechanisms based on the nominative requirements to fly ash from coal combustion, as no requirements are available for use of WA as partial cement replacement. According to Sigvardsen et al. [6], a WA originating from combustion of biomass (e.g. wood chips, but not limited to) from whole trees (logs, bark, buds and pine needles) by circulating fluidised bed combustion at low temperatures is most likely to possess some pozzolanic properties, while a WA originating from grate combustion from similar biomass is most likely to possess hydraulic activity.

The object of this study was to test the results obtained by the multivariate analysis [6] by investigating the reaction mechanisms (pozzolanic vs hydraulic properties) of two representative WAs from the two different combustion methods; grate combustion and circulating fluidised bed combustion. Both WA originate from combustion of wood chips originating from whole trees, the most commonly used type of biofuel [17].

According to a recently published report by representatives from Austria, Canada, Denmark, Germany, Italy and the Netherlands [3] grate combustion are predominately used for combustion of biomass while circulating fluidised bed combustion are gaining ground in many of the countries. Power-plants using grate or circulating fluidised bed combustion have the highest efficiency when only biomass is used [18] and are the most common type of plants regarding combustion of biomass. This leads to the WAs included in this study to be of the most common type of WA produced.

2. Materials and methods

An overview of notations, including descriptions and the linked methods are provided in Tab. 1.

2.1. Materials

The fly ash fraction of two wood ashes (WAs) were used in this study; WA 1 from Skærbækværket Biomass Power Plant, Denmark and from and WA2 Värtaverket Combined Heat and Power Plant, Sweden. The two power plants use a similar type of wood chips originating from whole trees, including bark and needle, but different combustion methods. Skærbækværket Biomass Power Plant uses grate combustion (600-1,000°C), whereas Värtaverket Combined Heat and Power Plant use circulating fluidised bed combustion (760-930°C).

The WAs were collected by the staff at the power plants and transported in 50L plastic buckets. Each bucket was divided into smaller 20L buckets by taking approximate 100-200g at a time into each bucket. Subsequently, the buckets were closed and stored protected from light, heat and moist sources. The plastic buckets were rotated by hand in order to increase the uniformity of the WA before smaller portions of WA were sampled for testing.

Before use, the WAs were dried at 50°C and sieved to a particle size of $\leq 250\mu m$. This can lead to some extent of carbonation, but it was necessary in order to obtain a controlled water content. Sieving was conducted, since the content of particles $\geq 250\mu m$ consisted only of large remnants of charred wood, accounting for approximately 25% of WA1 and less than 2% of WA2 when received from the power plants. This sieving only removed the large remnants of charred wood, thus smaller particles of charred wood can be found in the fraction $\leq 250\mu m$ [19].

For castings with Portland cement, Rapid Aalborg Cement (CEM I) with 5% limestone filler was used. Inert quartz (Qz) was also used for measurements of strength activity index (SAI).

2.2. Methods

2.2.1. Characterisation of WAs, Qz and CEM I

The content of major chemical element of the WAs, Qz and CEM I was measured by X-ray fluorescence (XRF) spectrometry by the use of a SPECTRO Gmbh X-LAB 2000 with a Pd-tube on samples grounded to a particle size of ≤ 200µm. The equivalent content of oxides was calculated based on the element content. Loss on ignition was measured at 950°C, according to EN 196-2 [20]. The unburnt carbon content was determined from the LoI and thermogravimetric analysis (TGA) measurements. The free calcium oxide contents in the WAs were measured according to EN 451-1 [21].

The pH and conductivity were measured on suspensions of WAs, Qz and CEM I in a 2.5:1 liquid-to-solid ratio in distilled water with radiometer analytical electrodes after 1-hour agitation. The Radiometer analytical electrodes were calibrated against KOH solutions of known concentrations. After filtration, the concentrations of water-soluble Cl^- and SO_4^{-2} were measured in the filtrate with Ion Chromatography (IC).

The particle size distribution was determined for WAs, Qz and CEM I by laser diffraction by the use of Mastersizer 2000. The particle density was measured by the use of a helium gas pycnometer Micrometics AccuPyc 1340 in accordance with EN 196-6 [22].

The crystalline phases in of the WAs and CEM I were identified by X-Ray Diffraction (XRD). The WA was loaded into the sample holder using backloading. A PanAnalytical X-ray diffractometer, sat at the PW3064 Spinner stage for standard powder samples have been used for the measurements. Cu-Kα radiation with a wavelength of 1.54 Å was used as the x-ray source. The samples were measured 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 detection limit of the XRD analysis is 2 wt%.

Thermogravimetric analysis (TGA) was performed on the WAs and CEM I to further identify and to quantify the phases present. Approximate 40 mg of the sample was poured into 85 µl aluminium oxide crucibles (diameter 6.8mm), and the weight loss was measured from room temperature to 900 °C in a NETZSCH STA 449 F3 Jupiter. First, the temperature was raised to 40 °C and kept for 10 min.; then the temperature was increased to 900 °C with a heating rate of 10 °C/min. During the measurements, the cell was purged with 50 ml/min of nitrogen gas. The data were processed using the analysis software Proteus Analyzer.

2.2.2. Determination of pozzolanic reactivity by Frattini test

The pozzolanic reactivity was assessed according to EN 196-5 [23], by measuring the consumption of the $Ca(OH)_2$ during curing (Frattini test). A 20g test sample, consisting of 80% CEM I and 20% of either of the WAs or Qz, were prepared and mixed with 100ml of distilled water. The test was conducted by double determination at both 8 and 15 days. After mixing the samples were sealed in plastic bottles and left in an oven at 40°C until the test of pozzolanic reactivity.

Results are presented in an x/y-chart, with CaO [mmol/l] on the y-axis versus OH^- [mmol/l] on the x-axis. The solubility curve of $Ca(OH)_2$, estimated for an alkaline solution at 40°C, is plotted over OH^- by $[CaO] = 350 / ([OH]-15)$ according to EN 196-5 [23]. Results below the solubility curve of $Ca(OH)_2$ indicates the removal of Ca^{2+} from the solution attributed to pozzolanic activity. Results at or above the solubility curve of $Ca(OH)_2$ indicate saturation or oversaturation with $Ca(OH)_2$ and thus no pozzolanic activity.

2.2.3. Determination of pozzolanic reactivity by strength activity index (SAI)

For testing of the strength activity index (SAI), mortar prisms (40 x 40 x 160mm) were cast according to EN 196-1 [24]. The mix composition was 80% CEM I and 20% of either of the WAs according to ASTM C311/C311M-13 [25]. For comparison, prisms with 20% cement replacement by Qz and 100% CEM I were cast. The w/b was kept at 0.5, but for mixtures containing either of the WAs, super plasticiser (Dynamon XTend from Mapei) were used to achieve standard consistency. The consistency was determinate by flow table according to EN 1015-3 [26]. After 1 day covered and stored in a temperature-controlled room (20°C) the prisms were demoulded and stored in separate boxes for each casting (3 prisms) submerged in 4.5L lime water (3g calcium hydroxide/L distilled water [27]) in a temperature-controlled room (20°C). A total of three mortar prisms were prepared for each mix at each curing age [24].

SAI was measured on prisms at 7 and 28 days of curing [28]. The mortar specimens were split in two with an electro-mechanic test machine (Instron 6022, 10kN) by increasing the load by 0.05 kN/s and the compressive strength were measured for all six pieces of mortar sample with a servohydraulic test machine (Toni Technik 300Ton) by increasing the load by 2.4 kN/s in accordance with EN 196-1 [24]. The air content of mortars was determined in accordance with Osbæck, 1984 [29], by the use of the weight at demoulding and the theoretical air void-free mortar. The compressive strength was then normalised to an air content of 2 vol% by the use of Bolomey's equation [30].

SAI was calculated from Eq. 1 [25].

$$SAI = \frac{A}{B} \tag{1}$$

Where:

A = average compressive strength of test prisms (80% CEM I + 20% WA)

B = average compressive strength of control prisms (100% CEM I).

2.2.4. Compressive strength development of mortar with 100% WA

Mortar cubes were mixed with 100% WAs as prescribed in EN 196-1 [24], but with a constant binder content, w/b = 0.75 and cast in 30 x 30 x 30mm silicone moulds instead of as mortar prisms. The size of the mould complies with the requirements established in EN 12390-1 [31]. A reference mortar was cast with 100% CEM I and w/b ratio = 0.75, notated REF. After 7 days of curing in the covered moulds, the cubes were demoulded and stored, sealed in a box in a temperature-controlled room (20°C) until testing.

The compressive strength of the cubes was measured after 7, 14, 28, 60 and 90 days of curing in accordance with EN 196-1 [24] with an electro-mechanic test machine (Instron 6025, 100kN) by increasing the load by 2.4 kN/s [24]. All specimens were tested perpendicular to the direction of casting as a laitance layer of 2-3mm was seen on the reference specimens. The measured compressive strength was normalised to an air content of 2 vol% as described in section 2.2.3.

2.2.5. Casting and testing of 100% WA paste samples for phase development

Paste samples were prepared with 100% WA with high water to binder (w/b) ratio = 0.75 in order to maintain workability. The pastes were mixed using a high shear mixer (Whip Mix Power Mixer Model B). The mixing procedure was adapted from EN 196-1 [24]: mixing for 90 s, resting for 90 s, and mixing for 60 s. A reference was also cast with 100% CEM I and w/b ratio = 0.75, notated REF. The pastes were cast in 18 ml Nalgene LDPE sample vials with snap closure (diameter 27.1mm) and stored sealed in a temperature-controlled room (20°C, >90% RH) until testing.

2.2.5.1. Double solvent exchange

Double solvent exchange was used for curing stoppage [32] for the paste specimens after 7, 14, 28, 60 and 90 days of curing. Four 2 mm thick slices (diameter 27.1 mm) were cut from the middle of the cured paste sample. The slices were crushed in a porcelain mortar to pass through a 1 mm sieve. Approximately 3g of the crushed sample was immersed in 50 mL isopropanol. The suspension was shaken for 30 sec, left to rest for 5 min, and subsequently decanted. This isopropanol treatment was performed twice, and then the suspension was vacuum-filtered. The crushed sample was then immersed in 10 mL diethyl ether, shaken for 30 sec, left to rest for 5 min., and vacuum-filtered. The crushed paste sample was shortly subjected to an oven drying process (8 min. at 40°C) to remove the easily volatile diethyl ether [32]. Just before testing, the paste samples were further crushed in a porcelain mortar, until the whole paste sample was able to pass through a 63µm sieve [32]. The crushed paste sample was subdivided into two, and TGA and XRD analysis were conducted right away.

2.2.5.2. X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was performed on the same powdered paste samples as used for the pH and TGA, after the double solvent exchange treatment, drying and grinding. The XRD analysis was performed as described in section 2.2.1.

2.2.5.3. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was performed on the same powdered paste samples as used for the pH and XRD, subsequent to the double solvent exchange treatment, drying and grinding. The TGA was performed as described in section 2.2.1.

The loss of bound water and decomposition of portlandite, ettringite and calcite were measured by TGA. The loss of bound water and weight loss of ettringite and calcite were determined by the use of a horizontal step between 50°C and 550°C [33], 50°C and 120°C [34], and 600-800°C [32], respectively. The temperature interval used for ettringite also includes AFm phases and C-S-H [34], which can lead to an overestimation of the amount of ettringite formed. Portlandite was measured by the use of a tangential step between 400°C and 550°C [33]. The equations for the quantification of the bound water (H), portlandite (CH), ettringite (Et) and calcite (C) relative to the anhydrous mass binder weight (c.f. [32]) are given in Eqs. (2)-(9).

$$H_{measured} = WL_{50-550} \tag{2}$$

$$H_{anhydrous} = \frac{H_{measured}}{weight\ at\ 550°C} \tag{3}$$

$$CH_{measured} = WL_{400-550} \cdot (74/18) \tag{4}$$

$$CH_{anhydrous} = \frac{CH_{measured}}{weight\ at\ 550°C} \tag{5}$$

$$Et_{measured} = WL_{50-120} \cdot (1255/(32 \cdot 18)) \tag{6}$$

$$Et_{anhydrous} = \frac{\mathrm{C_6As_3H_{32}}_{measured}}{weight\ at\ 550°C} \tag{7}$$

$$\mathrm{C}_{measured} = WL_{600-800} \cdot (100/44) \tag{8}$$

$$\mathrm{C}_{anhydrous} = \frac{\mathrm{C\overline{C}}_{measured}}{weight\ at\ 550°C} \tag{9}$$

3. Results

3.1 Characteristics of unreacted binders and filler (WAs, Qz and CEM I)

The chemical composition of the unhydrated materials, WA1, WA2, Qz, and CEM I are presented in Tab. 2 and the physical properties are presented in Tab. 3. The particle size distributions for WA1, WA2, Qz, and CEM I are displayed in Fig. 1. The mean particle size were 15, 9, 24, and 13 for WA1, WA2, Qz, and CEM I respectively (Tab. 3). Fig. 2 and Tab. 4 included the crystalline phases in both unhydrated WAs and CEM I. CEM I contained alite, belite, ferrite and C_3A. Both WA1 and WA2 contained portlandite, quartz, lime and calcite. Further WA1 contained arcanite (K_2SO_4), and WA2 contains anhydrite ($CaSO_4$) and sylvite. DTG curves of unhydrated WAs and CEMI are displayed in Fig. 3.

3.2. Pozzolanic activity

The Frattini test is a direct method to measure the possible pozzolanic activity of a material [35], monitoring the presence of $Ca(OH)_2$ and its subsequent reduction as the pozzolanic reaction proceeds. The result is given in Fig. 4. All results from the Frattini test are observed above the solubility curve of $Ca(OH)_2$ indicating no pozzolanic activity for neither of the WAs nor the Qz.

The strength activity test is an indirect method measuring a physical property indicating the extent of pozzolanic activity of a material [35]. The results for the investigated 20%WAs can be found in Tab. 5. For pozzolanic activity, ASTM C618 [28] requires a strength activity index (SAI) above 0.75 compared to the reference after 7 and 28 days of curing for specimens containing a binder from 20% of the material tested and 80% CEM I. 20%WA1 achieved a SAI of 0.74 and 0.76, 20%WA2 achieved a SAI of 0.85 and 0.89, and 20% Qz achieved a SAI of 0.77 and 0.85 at 7 and 28 days of curing, respectively. Thus the SAI test indicate pozzolanity of WA2.

3.3. Compressive strength development of mortar cubes with either WA1, WA2 or CEM I

The compressive strength development of mortar cubes with either 100%WA1, 100%WA2 or plain CEM I (REF) are presented in Fig. 5. The mortar cubes with WA had at all time a lower compressive strength than the cubes with REF. For 100%WA2, a significant increase in the compressive strength was seen from 0.6MPa at 7 days of curing to 6.4MPa at 90 days of curing, reaching 85% of the compressive strength of REF. 100%WA1 only increased in compressive strength from 0.2MPa at 7 days of curing to 1.7MPa at 90 days of curing, reaching 22% of the compressive strength of REF.

3.4. Phase development

The phase development in plain CEM I (REF), 100%WA1 and 100%WA2 pastes were analysed by XRD and TGA. The phase development in the paste specimens determined by XRD is presented in Fig. 2 and summarised in Tab. 4. For REF depletion of alite was seen after 28 days of curing. Portlandite and ettringite were seen in REF at all ages (7-90 days), in addition increasing amounts of hemicarbonate and some monocarbonate were seen.

The hydrated 100%WA1 pastes were by XRD found to contain portlandite, quartz, calcite, potassium sulfate (arcanate) and gypsum. Lime and ettringite present in the unhydrated WA1 were note observed in the hydrated 100%WA1, while portlandite and gypsum were not found the unhydrated WA1. The hydrated 100%WA2 pastes were by XRD found to contain Portlandite, ettringite, quartz and calcite at 7 days of curing, while lime anhydrite and sylvite present in the unhydrated WA2 were not detected. At 14 days monocarbonate was detected in addition to Portlandite, ettringite, quartz and calcite. At later age (≥ 14 days) depletion of portlandite was seen. The identified phase assemblage for the 100%WAs pastes is supported by literature [13,15].

The weight loss (DTG)curves measured by TGA confirmed the hydrate phases identified by XRD in REF: ettringite, hemicarbonate, monocarbonate and portlandite, see (Fig. 3 (a)). The DTG curves for 100%WA2 pastes (Fig. 3 (c)) confirmed the presence of ettringite, portlandite and calcite, while the DTG curves for 100%WA1 confirmed the presence of gypsum, portlandite and calcite. In addition, a weight loss below 100^{o}C was observed for the hydrated pastes of both WAs (not in the unhydrated WAs). The peak appears at the decomposition temperature of, among others C-S-H and monosulfate, but peak is sharper (the temperature interval more narrow) than expected for C-S-H, and monosulfate was not found by XRD (Fig. 4; Tab. 4), and the peak remains unidentified.

Quantification of bound water, portlandite, and calcite in the pastes, and weight loss in the temperature range 50-120 ^{o}C calculated as ettringite are presented in Fig. 6. The weight loss between 50-120 ^{o}C is calculated as the weight loss due to ettringite, as ettringite is considered the main contributor responsible for the set, harden and strength development of a water-WA mixture [15,36]. The standard deviations of these quantifications are based on three independent quantifications of the bound water, portlandite, ettringite and calcite of a reference sample at 28 days of curing. The standard deviation was 0.67wt% for the quantification of bound water, 0.56wt% for the quantification of portlandite, 0.27wt% for the quantification of ettringite and 0.33wt% for the quantification of calcite. The standard deviation is illustrated as error bars in Fig. 6.

A larger amount of bound water was seen for REF compared to the 100%WA pastes at all ages (Fig. 6 (a)). Further, the amount of bound water for 100%WA2 exceeded 100%WA1 at all ages, mainly due to an initial larger amount after 1 day.

Also, the amount of portlandite in REF determined by TGA exceeded the content determined in the 100%WA pastes (approximately 16 vs 5 and 1wt% after 28 days' curing). Comparing the WAs, the content of portlandite was higher for 100%WA1 than for 100%WA2 (Fig. 6 (b)).

The weight loss observed in the temperature range 50 - 120°C is interpreted, based on XRD, as amount of ettringite in 100%WA2 increased notably from zero to 28 days of curing and exceeded REF at 28 days of curing (Fig. 6 (c)). No further development was observed from 28 days of curing.

Also, the 100%WA1 pastes had a weight loss in the temperature range 50 - 120°C. However, based on XRD this weight loss is not interpreted as ettringite, but attributed to the decomposition of unidentified phases. The rate of development of the phases decomposing in the temperature range 50 - 120°C was slower and the final value lower than observed for 100%WA2. A slight increase in the amount of hydrate phases between 50 - 120°C were seen for 100%WA1 (increase 7wt%) from 7 to 60 days of curing until it became constant.

An initial increase is seen in the calcite content from unhydrated to hydrated materials which might be a result of carbonation during the double solvent exchange. The calcite content for REF was constant from 7 days of curing (Fig. 6 (d)), indicating no synergetic reaction between the limestone filler and alumina in CEM I [37]. 100%WA1 had a significantly higher calcite content compared to 100%WA2, and for both 100%WA pastes the calcite content was seen to decrease by 5-7wt% during curing (Fig. 6 (d)).

4. Discussion

The two WAs investigated in this study originated from combustion of wood chips by grate combustion (WA1) or circulating fluidised bed combustion (WA2). As mentioned in the introduction, WAs from the two combustion processes are, based on a multivariate data analysis [6], most likely to possess hydraulic (WA1) or pozzolanic properties (WA2). Below results from the present study are summarised and discussed.

4.1. Pozzolanic properties

4.2.1 Comparison to requirements in EN 450

In order to assess the applicability of the WAs as a partial cement replacement, the oxide content of the WAs was assessed based on the requirements in the fly ash standard EN 450 [38]. It should, however, be noted that EN 450 [38] covers fly ash from coal combustion; thus, the assessment is only indicative. EN 450 [38] specifies requirements for the chemical and physical properties for coal fly ash used in mortar and grouts. According to EN 450 [38], the sum of the content of SiO_2, Al_2O_3 and Fe_2O_3 shall not be less than 70% by mass for a pozzolanic material. None of the WAs investigated in this study meet this requirement, see Tab. 2. Thus, based solely on the oxide composition and the criteria established in EN 450 [38], a pozzolanic behaviour of WA1 and WA2 can be expected to be very limited or absent.

The pozzolanic behaviour depends on the amount of amorphous silica and aluminosilicate present in the material [5,39]. The aluminium content was low in both WAs (1.9 and 4.9% respectively), compared to traditional coal fly ash (> 18%) [39]. Higher content of silicon was seen for WA2 compared to WA1, 21.8 versus 8.6%, but still lower than required for fly ash coal combustion (> 32%) [39]. WA2 originates from fluidised bed combustion, where fine inert quartz of elutriated bed material is carried with the flue gas during combustion and ending in the fly ash fraction [40]. This might explain the difference in the silica content between WA1 and WA2, however, this also leads to the expectation that much of the silica in WA2 was inert.

4.2.2. Frattini test

The results of the Frattini test are presented in Fig. 4 in accordance with EN 196-5 [23] as an x/y-chart, with CaO [mmol/l] on the y-axis versus OH^- [mmol/l] on the x-axis, and the solubility curve of $Ca(OH)_2$. Results appearing below the solubility curve indicate the removal of Ca^{2+} from the solution which is attributed to pozzolanic activity, and results above the solubility curve indicate saturation or oversaturation with $Ca(OH)_2$ and thus no pozzolanic activity. All tested samples (REF, 20%WA1, 20%WA2 and 20%Qz) remained saturated with portlandite over the 28 days testing period and did not show sufficient consumption of portlandite to be categorised as a pozzolan. A drawback of the Frattini test is the reliance on a) the removal of Ca^{2+} from the solution attributed solely to the pozzolanic reactions and b) no contribution of Ca^{2+} from the mineral addition tested. This might incorrectly lead to negative results for high-Ca mineral additions which can possibly act as a source for soluble Ca^{2+} [41,42] and a false positive response in case of removal of Ca^{2+} due to precipitation of, e.g. $CaSO_4$ if extra SO_4^{2-} ions are present [42]. Based on the content of CaO > 20% in the WAs, both WAs can be categorised as high-Ca mineral additions [43] (Tab. 2), potentially contributing with soluble Ca^{2+}. Formation of gypsum was seen for WA1 and formation of ettringite was seen for WA2 (see Tab. 4.), counteracting the increased Ca^{2+} and leading to a consumption of Ca^{2+} not entailed by the pozzolanic activity. Nevertheless, based on the low content of silica and aluminosilicate potentially able to enter into pozzolanic reactions of the WAs, the results obtained from the Frattini test are considered reliable, and none of the WAs are, based on the combined chemical analysis (oxide composition of the unreacted ashes) and the Frattini test, expected to possess any significantly pozzolanic properties.

4.2.3. Strength activity index

From the results of the SAI test (Tab. 5), WA2 appeared to possess pozzolanic properties achieving a SAI of 0.85 and 0.89 after 7 and 28 days of curing, respectively, meeting the requirements set by ASTM C618 [28] of minimum compressive strength relative to a reference sample at 0.75 after both 7 and 28 days reaction. However, so did the inert Qz, achieving a SAI of 0.77 and 0.85 after 7 and 28 days of curing. In contrast, WA1 did not possess pozzolanic properties according to the SAI test, achieving a SAI of 0.74 and 0.76 after 7 and 28 days of curing. These results are contradictory to the results obtained by the Frattini test for WA2, and the WA2 compliance with the SAI acceptance criteria might be attributed to the WA possible possessing hydraulic properties. The positive results for Qz highlight a clear drawback of the SAI test, due to uncertainty in whether the observed strength development is actually due to pozzolanic activity or due to hydraulic properties or filler effects as expected for Qz [42,44]. Based on the relatively coarse particle size distribution (Fig. 1), neither nucleation nor packing effects were expected for Qz. The increase in the compressive strength seen for the 20%Qz mortar might be explained by dilution of cement paste, providing more space and water for the cement reaction. Following this argument, (part of) the observed response of WA2 might also be due to a dilution effect. However, a dilution effect would then also have been expected for WA1.

In summary, based on the low content of silica and aluminosilicate, the results from the Frattini test, and explaining the positive response of WA2 to the SAI test by hydraulic properties, none of the WAs are expected to possess any significant pozzolanic properties.

4.2. Hydraulic properties

The definition of a hydraulic binder is a binder that chemically reacts with water, converting the water-binder system into a solid matrix with the ability to set and harden and, after hardening, retaining strength and stability even under water [45]. In a blended system with Portland cement (CEM I), the WAs investigated in this study retained stability even under water, but the 100% WA mortars were, when hardened, not stable in water.

4.2.1 Comparison to requirements in EN 197-1

To assess the applicability of the WAs as a partial cement replacement, the hydraulic properties of the WAs were assessed based on the requirements to oxide contents in the European cement standard EN 197-1 [45]. It should, however, be noted that EN 197-1 does currently not approve the use of WA as a partial cement replacement, and thus the assessment is only indicative. According to EN 197-1 [45] a Portland cement clinker, defined as a hydraulic material, should comply with a CaO/SiO_2 ratio above 2 and granulated blast furnace slag, defined as a material possessing hydraulic activity when suitably activated, should comply with a $(CaO+MgO)/SiO_2$ ratio above 1. The WAs investigated in this study meet both requirements, see Tab. 2.

4.2.2 Compressive strength development

A significant difference was seen between the compressive strength development measured for the 100%WA mortar cubes and the REF mortar cubes. REF had the highest compressive strength at all ages (reaching 7 MPa after 90 days) and 100%WA1 the lowest compressive strength at all ages (see Fig. 5). 100%WA2 did not exceed the REF, but the compressive strength of 100%WA2 was increasing substantially from obtaining 10% of the compressive strength of REF at 7 days of curing to obtaining 85% of the compressive strength of REF at 90 days of curing. In comparison, 100%WA1 obtained 4% of the compressive strength of REF at 7 days of curing and 22% of the compressive strength of REF at 90 days of curing.

In summary, both investigated WAs appear to possess hydraulic properties as the 100%WA mortars were able to set, harden and develop strength, however, at a very different rate and extent and only when cured above water.

4.2.3. Phase development

The hydraulic properties of the WAs were further assessed through XRD and TGA of the reaction products formed in pastes of 100%WA. The development of crystalline phases identified by XRD is illustrated in Fig 2. and Tab. 4, summarising data for both WAs and CEM I. Based on TGA the amounts of selected phases were quantified; Fig. 6 illustrates the development with time of bound water, portlandite, calcite, and ettringite (and other phases decomposing in the temperature range 50-120°C).

Ettringite and phases decomposing in the temperature range 50-120°C

According to the literature [15,36,46,47], the formation of ettringite and gypsum are the most important phases for the setting and strength development of WA-water mixtures. Formation of ettringite leads to a relatively high increase in compressive strength, as ettringite has a high content of hydrate water (32 moles vs. 12 mole for AFm [5]). An increase in the hydrate volume are seen upon ettringite formation, leading to a reduction in the porosity [5,15]. As displayed in Fig. 6 (c), hydrated 100%WA2 contained a large content of ettringite, exceeding REF from 28 days of curing. No ettringite was found in 100%WA1 by XRD; instead, SO_3 appeared to precipitate as gypsum (Tab. 4). The TG curves indicate potential presence of monosulfate (Fig. 3). However, this was not confirmed by XRD and monosulphate is not stable in the presence of gypsum as it would react to form ettringite [48].

Ettringite precipitates when sufficient amounts of aluminium, calcium and sulfate are present [49]. WA1 and WA2 have similar total content of calcium and sulfate, thus the observed difference in the ettringite content might be attributed to the difference in the alumina content; 1.9wt% for WA1 and 4.9wt% for WA2. The alumina present in WA1 appeared to precipitate as hydrogarnet, if no monosulfate is considered to be present, see Fig. 3.

Hemi- and monocarbonate were determined for REF (by both XRD and TGA) and monocarbonate was found in 100%WA2 pastes (by XRD). Hemi- and moncarbonate decompose between 60-300°C [32], which could lead to an overestimation of ettringite for REF and 100%WA2 pastes, however, since the main peak lies above 120°C, this contribution is considered limited.

Portlandite

Portlandite has been determined in the literature as a hydrate phase which can form during curing of a WA-water mixture [15,49]. Initially, a similar content of portlandite was seen for

100%WA1 and 100%WA2, see Fig. 6 (b). Between 7 and 14 days of curing, a further increase was seen in the portlandite content of 100%WA1, maybe due to the difference in the content of free CaO between WA1 and WA2 (Tab. 2). At later age, the portlandite content was decreasing for both WAs.

The decrease in the portlandite content detected for 100%WA2 from 7 to 28 days of curing, corresponds to the formation of ettringite (Fig. 6 (c)). From 28 days of curing the portlandite content of 100%WA2 close to 0, corresponding to the constant content of ettringite (Fig. 6 (c)) from 28 days of curing.

The decrease in portlandite, seen for 100%WA1 from 14 to 60 days of curing, might be due to the formation of C-S-H through pozzolanic reactions as observed for other WAs by Illikainen et al. [15]. However, the amount of C-S-H precipitating as a result of pozzolanic reactions can be considered limited, both based on the TG curves (Fig. 3 b) and the results obtained by the Frattini test. Another explanation could be formation of gypsum from sulfate and portlandite, determined from 7 days of hydration by XTD (Tab. 4).

Calcite

A decrease in the calcite content was seen for both 100%WA1 and 100%WA2. The decrease in calcite for 100%WA2 is attributed to the formation of monocarbonate determined by XRD. Monocarbonate was not determined for 100%WA1, and no other phases could be identified explaining the decrease in calcite.

4.3. Comparison to the Multivariate Data Analysis and perspectives

As previously described, Sigvardsen et al. [6] presented a multivariate data analysis investigating which types of WAs would be expected to possess hydraulic and/or pozzolanic properties based on the total content of oxides and nominative requirements. The conclusions were:

- WA originating from grate combustion of wood chips made from whole trees (in this study represented by WA1) appears as the optimal type of WA when utilised as mineral additions with hydraulic activity.

- WA originating from circulating fluidised bed combustion of biomass from whole trees at low temperatures (in this study represented by WA2) is most likely to contribute to some extent with pozzolanic properties.

From the presented study, the WAs were found to possess very limited or no pozzolanic properties and both, however, most distinguishable for WA2, possessed hydraulic properties.

The difference between the conclusions of the multivariate data analysis [6] and the observations in this study might be attributed to several reasons;

- The multivariate analysis only considered the relative amount of oxides and did not take into consideration to what extent the WAs complied with the nominative requirements established in EN 450 [38] and 197-1 [45].
- The multivariate analysis only considered the total amount of oxides not differentiating between reactive and inert parts.
- The hydraulic index included in the multivariate data analysis did not take into account the aluminium content.

Multivariate data analysis can be a powerful predicting tool, however, when assessing the possible pozzolanic or hydraulic properties of a mineral addition, the total content of oxides does not necessarily predict the actual performance. For future use of multivariate data analysis for assessing the possible use of a mineral admixture, more physicochemical characteristics of the mineral admixture need to be included, e.g. the amorphous oxide content. Furthermore, the nominative requirements need to be used with.

5. Conclusion

Two representative WAs originating from combustion of wood chips by grate combustion (WA1) and circulating fluidised bed combustion (WA2) of wood chips were investigated in this study. When mixed with water, both WAs were able to set, harden and develop strength, and thus found to possess hydraulic properties. Mortars of 100%WA2 obtained substantially more strength than mortars of 100%WA1. This was explained by a difference in the hydrate phases, mainly gypsum was found in hydrated pastes of WA1, while ettringite was found in hydratedWA2. Neither of the WAs were categorised as a pozzolanic.

The difference in main reaction products was attributed primarily to the content of aluminium in 100%WA2, facilitating ettringite formation and the free CaO content in 100%WA1 facilitating precipitation of portlandite and subsequent formation of gypsum.

6. Acknowledgement

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Table 1. Overview of methods and notations.

	Property/ Method	WA1	WA2	Qz	CEM I			
Unhy-drated	Elemental composition	x	x		x			
	Particle size distribution	x	x	x	x			
	LoI	x	x		x			
	Free CaO	x	x					
		100% WA1	100% WA2	100% Qz	REF	20% WA1	20% WA2	20% Qz
Hydrated	Strength activity index on mortar prims				x	x	x	x
	Frattini test on WA in water				x	x	x	x
	Compressive strength on mortar cubes	x	x	x	x			

	Phase development (TGA, XRD) on paste samples	x	x	x	x

Table 2. Chemical composition (%) of unreacted WA1, WA2, Qz and CEM I. ± defines the standard deviation.

	WA1	**WA2**	**Qz**	**CEM I**
SiO_2	8.6	21.8	99.4	19.7
Al_2O_3	1.9	4.9	0.10	5.4
Fe_2O_3	2.3	2.7	0.03	3.8
CaO	48.9	45.2	0	64.1
MgO	3.8	4.0	0	1.0
K_2O	16.8	7.2	0	0.4
Na_2O	2.2	0.8	0	0.3
SO_3	5.4	5.8	0	3.2
$SiO_2 + Al_2O_3 + Fe_2O_3$	12.9	29.4	0	-
CaO / SiO_2	5.7	2.1	-	-
$(CaO + MgO) / SiO_2$	6.1	2.3	-	-
Cl^-	0.8 ± 0.0	0.4 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
SO_4^{-2}	3.8 ± 0.0	1.8 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
LoI, 950ºC	15.0 ± 0.1	16.2 ± 0.3	0.0 ± 0.0	1.9 ± 0.0
Unburnt carbon	≥ 1.0	5.7	-	-
Free CaO	12.3 ± 0.7	6.4 ± 0.2	-	-

Table 3. Physical characteristics of unreacted WA1, WA2 and CEM I. ± defines the standard deviation.

	WA1	**WA2**	**Qz**	**CEM I**
pH	13.0 ± 0.1	12.7 ± 0.1	7.7 ± 0.1	12.8 ± 0.0
Mean particle size (D50)	15 ± 0.5	9 ± 0.2	24.6 ± 0.4	13 ± 0.1
Particle density (kg/m^3)	2740	2710	2650	3180

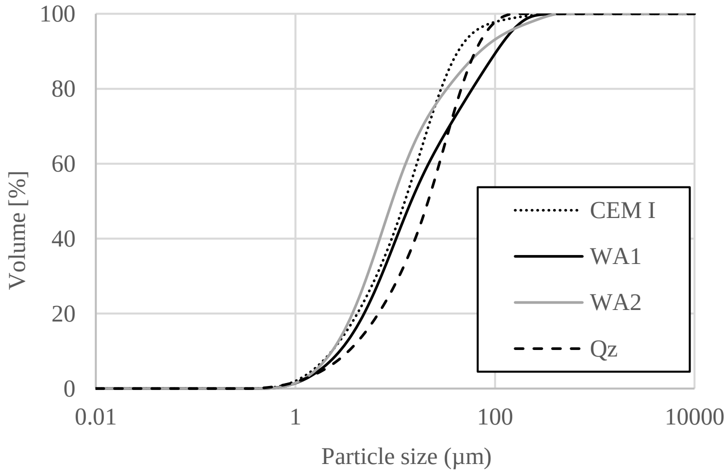
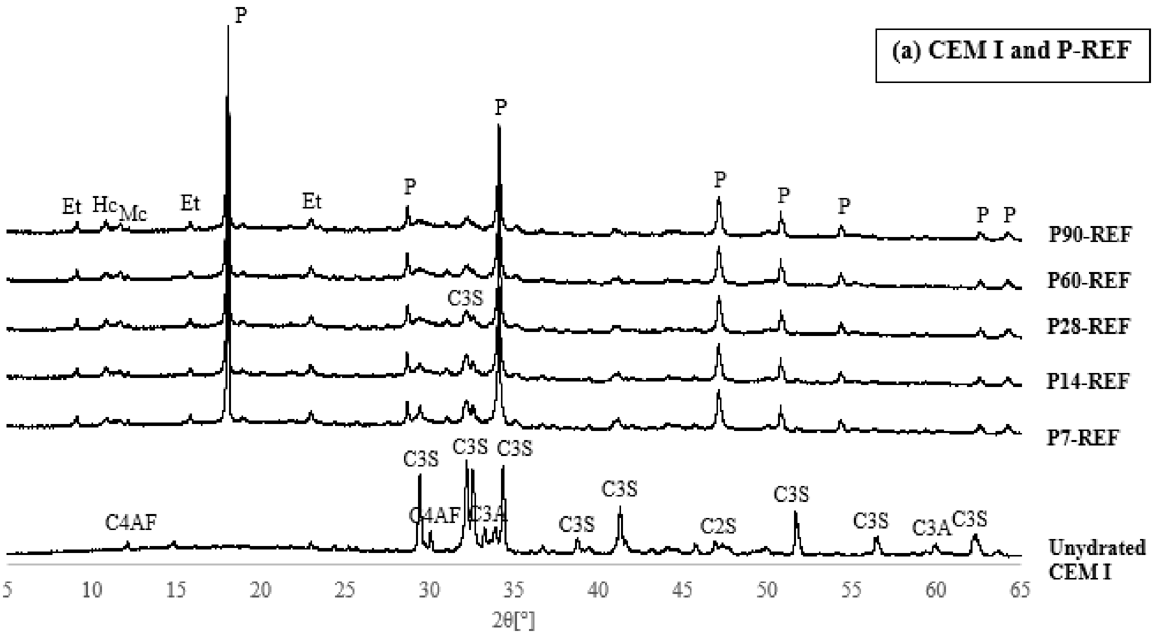
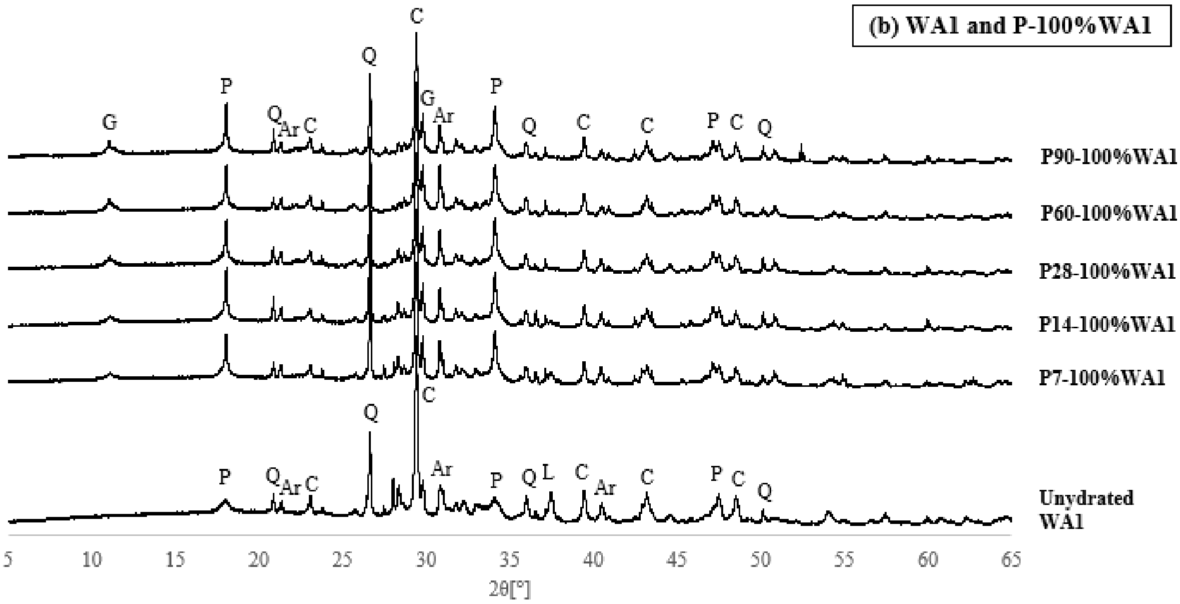


Figure 1. Particle size distribution of unreacted CEMI, WA1, WA2 and Qz, determined by laser diffraction.


(a) CEM I and P-REF
P
Et
Hc
Mc
Et
Et
P
P
P
P
P
P
P
P90-REF
P60-REF
C3S
P28-REF
P14-REF
P7-REF
C3S
C3S
C3S
C3S
C3S
C4AF
C4AF
C3A
C3S
C2S
C3S
C3A
C3S
Unydrated CEM I
5
10
15
20
25
30
35
40
45
50
55
60
65
2θ[°]


(b) WA1 and P-100%WA1
C
Q
P
G
Q
Ar
C
G
Ar
P
Q
C
C
P
C
Q
P90-100%WA1
P60-100%WA1
P28-100%WA1
P14-100%WA1
P7-100%WA1
C
Q
Ar
P
Q
Ar
C
P
Q
L
C
Ar
C
P
C
Q
Unydrated WA1
5
10
15
20
25
30
35
40
45
50
55
60
65
2θ[°]

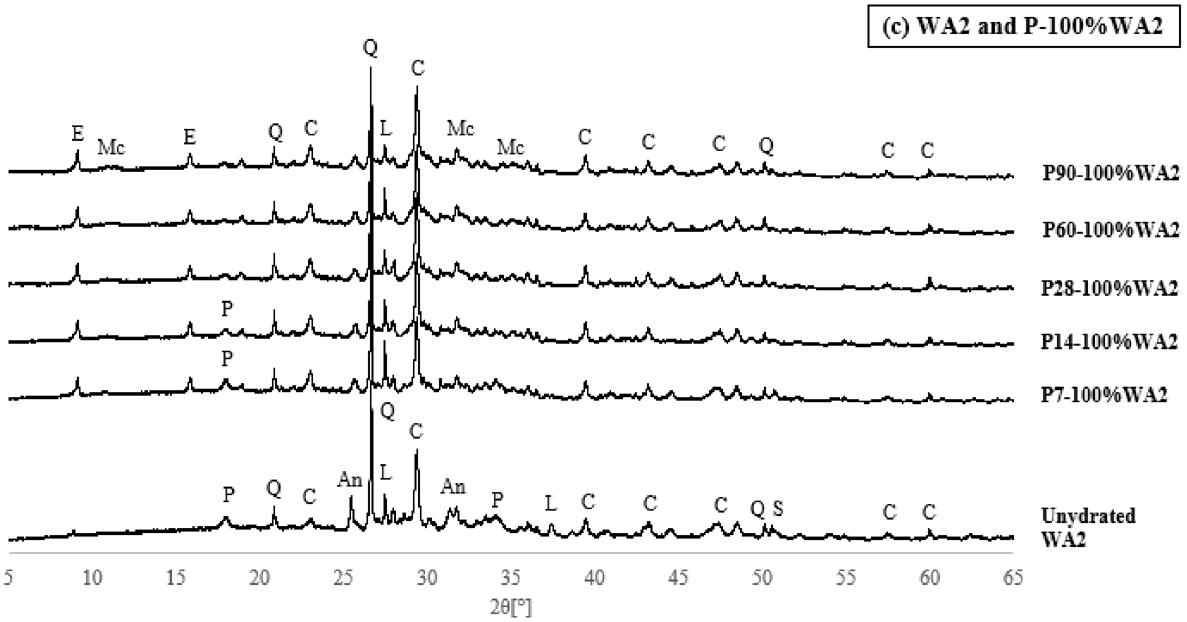
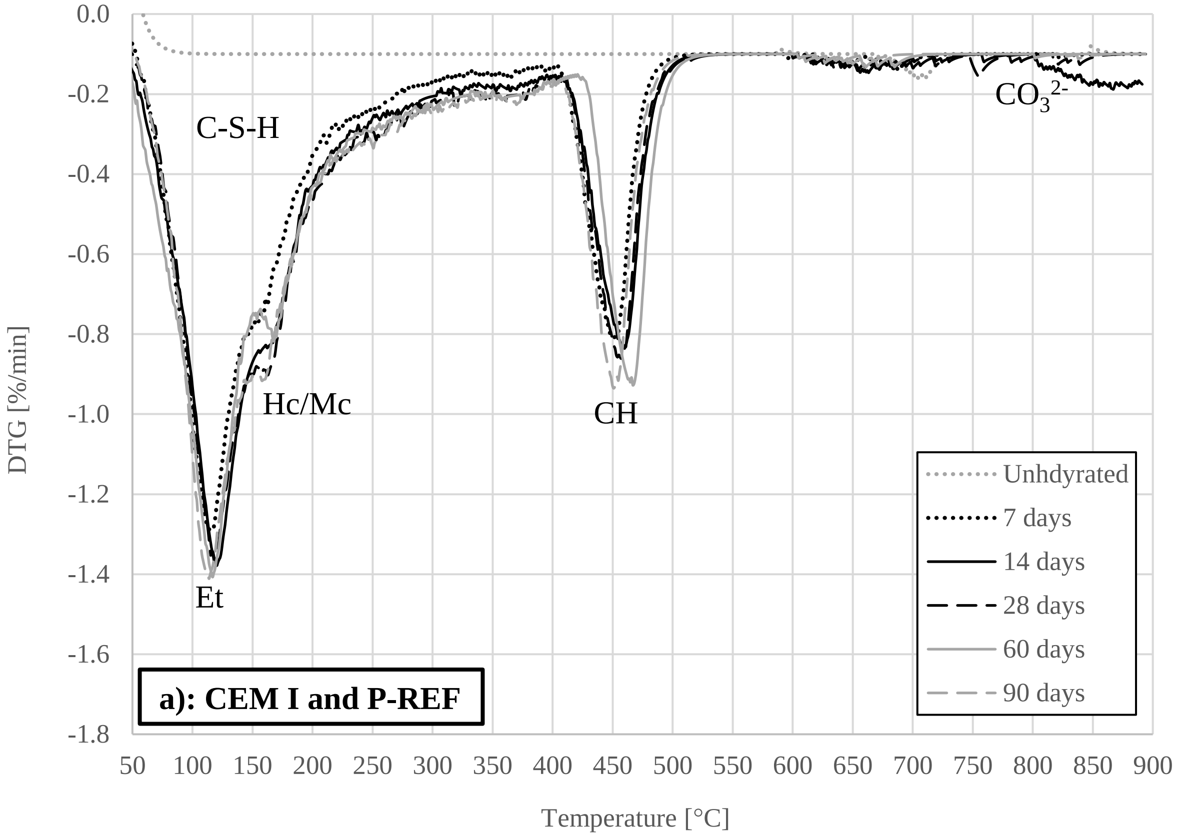


Figure 2. XRD patterns between 5 °2θ and 65 °2θ for the unreacted materials and hydrated pastes, (a) Unhydrated CEMI and cured REF pastes, (b) Unhydrated WA2 and cured 100%WA1 pastes and (c) Unhydrated WA2 and cured 100%WA2 pastes. Et: Ettringite, Hc: Hemicarbonate, Mc: Monocarbonate, P: Portlandite, G: Gypsum, Ar: Arcanite, C: Calcite, L: Lime, An: Anhydrite, S: Sylvite.

Table 4. Crystalline phases for unhydrated CEM I, WA1 and WA2, and for 100%WA1, 100%WA2 and REF paste samples investigated after 7, 14, 28, 60 and 90 days of curing at 20°C determined qualitatively by XRD diffraction.

	Alite	Belite-β	Ferrite	C_3A	Lime (CaO)	Arcanite (K_2SO_4)	Anhydrite ($CaSO_4$)	Sylvite (KCl)	Portlandite	Ettringite	Quartz	Calcite	Monocarbonate	Hemicarbonate	Gypsum ($CaSO_4 \cdot 2(H_2O)$)
Unhydrated CEM I	x	x	x	x											
Unhydrated WA1					x	x				x	x	x			
Unhydrated WA2					x		x	x		x	x	x			
P7-REF	x								x	x					
P7-100%WA1						x			x		x	x			x
P7-100%WA2									x	x	x	x			
P14-REF	x								x	x			x	x	
P14-100%WA1						x			x		x	x			x
P14-100%WA2									x	x	x	x	x		
P28-REF	x								x	x			x	x	
P28-100%WA1						x			x		x	x			x
P28-100%WA2										x	x	x	x		
P60-REF									x	x			x	x	
P60-100%WA1						x			x		x	x			x
P60-100%WA2										x	x	x	x		
P90-REF									x	x			x	x	
P90-100%WA1						x			x		x	x			x

P90-100%WA2	x	x	x	x



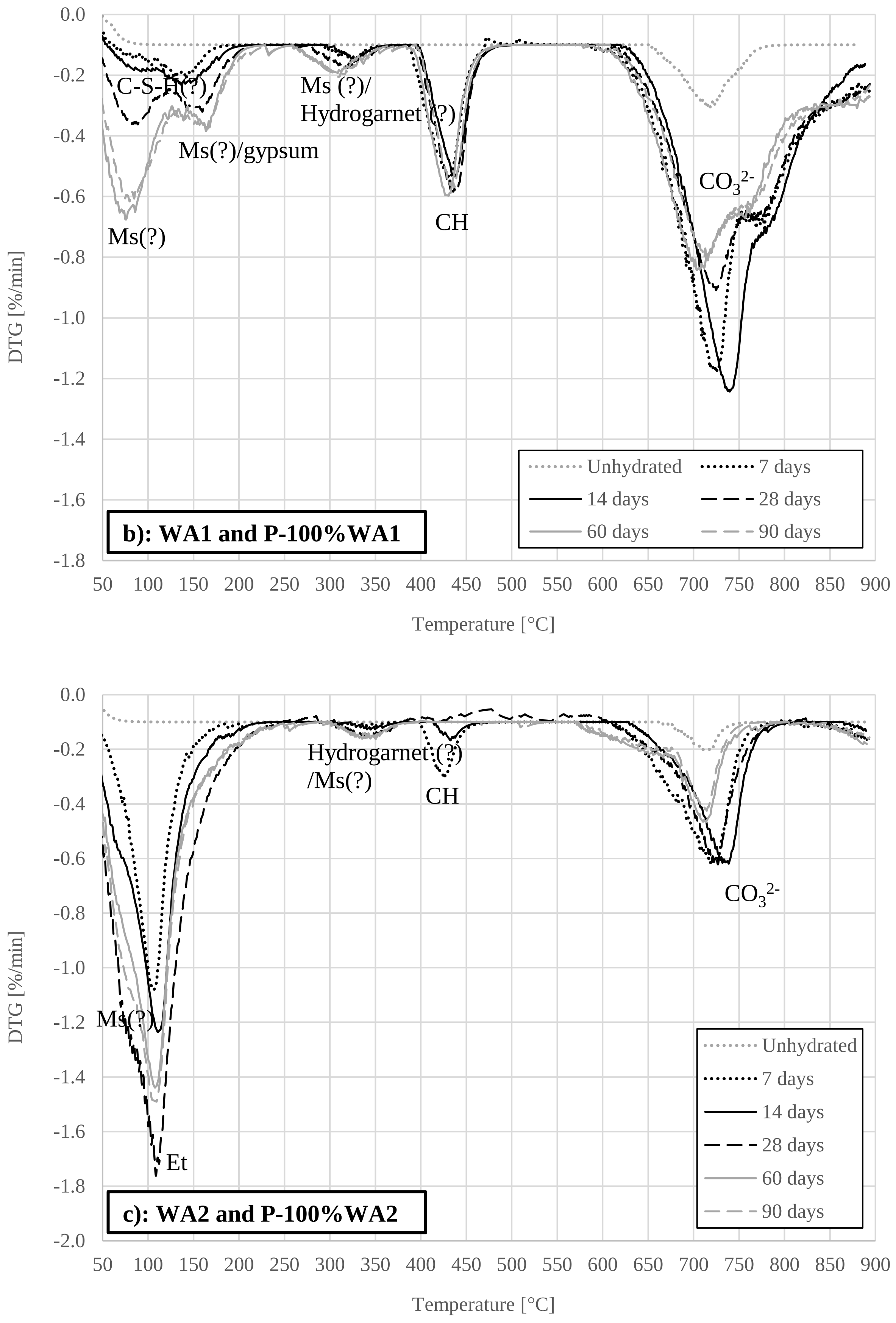


Figure 3. DTG curves of unhydrated and hydrated CEM I, WA1 and WA2 paste samples. (a) Unhydrated CEMI and cured REF pastes, (b) Unhydrated WA2 and cured 100%WA1 pastes and (c) Unhydrated WA2 and cured

100%WA2 pastes at 7, 14, 28, 60, and 90 days of curing. C-S-H: Calcium-silicate-hydrate, Mc: Monocarbonate, Hc: Hemicarbonate, Et: Ettringite, CH: portlandige, Ms: Monosulfate.

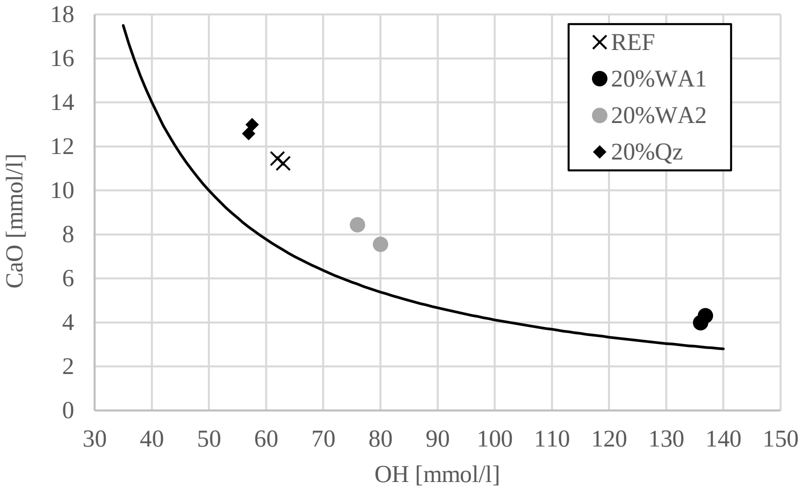


Figure 4. Frattini test results for a reference mixture and three mixtures with 20% replacement of CEM I with WA1, WA2 and Qz, respectively.

Table 5. Measured compressive strength for 20%WA1, 20%WA2, 20%Qz and REF mortar prims, air content, compressive strength normalised to an air content of 2 vol% by the use of Bolomeys equation [30] and calculated SAI.

	Compressive strength (MPa)	SD	Air content (%vol)	Normalised compressive strength (MPPa)	Strength activity index (SAI)
M7-REF	59.5	3.6	1.1	57.5	-
M7-20%WA1	44.1	0.7	1.0	42.6	0.74
M7-20%WA2	50.3	0.7	1.0	48.7	0.85
M7-20%Qz	45.9	0.9	1.0	44.1	0.77
M28-REF	69.9	1.8	1.1	64.7	-
M28-20%WA1	51.1	1.3	1.0	49.4	0.76
M28-20%WA2	59.4	1.4	1.0	57.4	0.89
M28-20%Qz	57.2	1.4	1.0	54.9	0.85

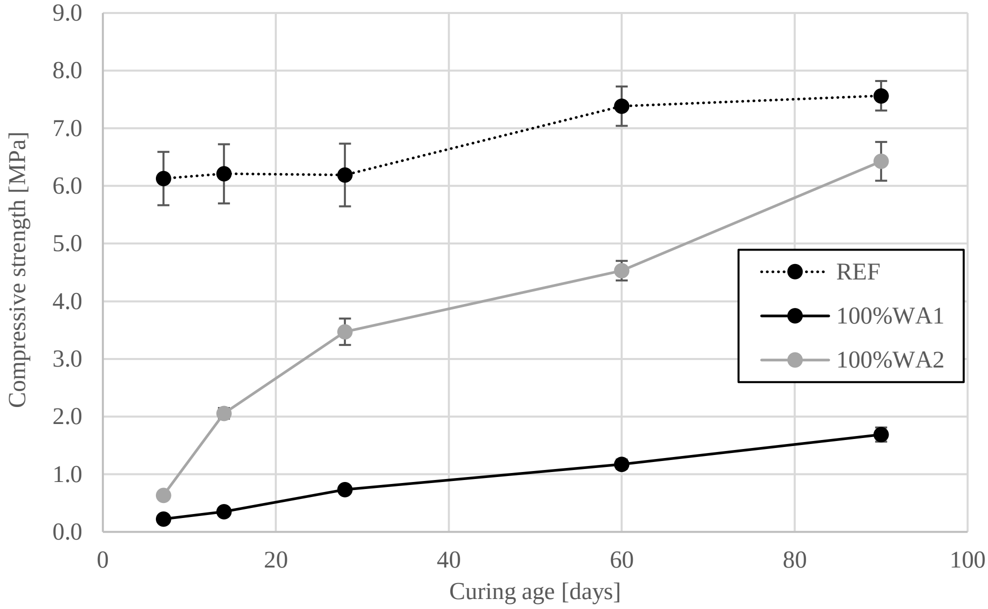


Figure 5. Compressive strength for 100%WA1, 100%WA2 and REF mortar cubes investigated after 7, 14, 28, 60 and 90 days of curing at 20°C. The compressive strength normalised to an air content of 2 vol% by the use of Bolomeys equation [30]. The error bars defines the standard deviation.

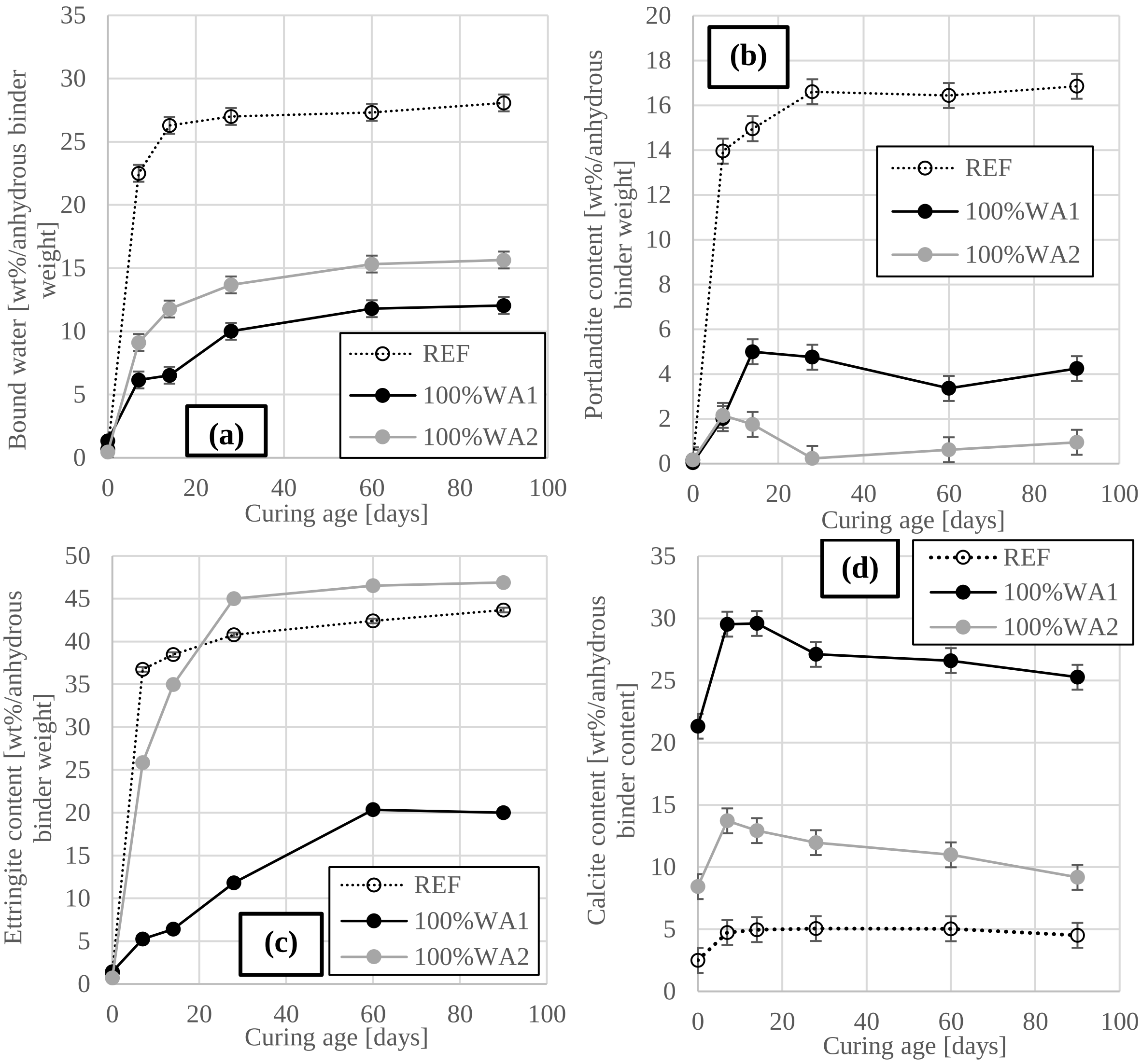


Figure 6. Quantification of bound water (a), portlandite (b), ettringite (c) and calcite (d) normalised to anhydrous binder for 100%WA1, 100%WA2 and 100% CEM I paste samples investigated after 7, 14, 28, 60 and 90 days of curing at 20°C. Unhydrated 100%WA1, 100%WA2 and CEM I are included as 0. The standard deviations of these quantifications are based on three independent measurements and quantifications of the bound water, portlandite, ettringite and calcite of a control sample at 28 days of curing. The error bars defines the standard deviation.

Journal Paper III

JPIII: Phase Development and Mechanical Response of Low-level Replacements with Wood Ash and Washed Wood Ash

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Phase development and mechanical response of low-level cement replacements with wood ash and washed wood ash

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Abstract

A significant increase is seen worldwide in the amounts of wood ashes (WAs) produced by the heating and power industry. This study investigates the potential utilisation of two different WAs as low-level cement replacements, in an untreated and a washed version. Phase development and mechanical response were investigated. Results indicated ettringite formation mainly to contribute to the strength development until excessive formation. Indications of an optimum SO_3/C_3A ratio for mixtures with a low-level cement replacement with WA was between 0.4 and 0.5. Washed WA originating from grate combustion appeared to be most promising of the tested WAs in cement-based materials.

Keywords: Wood ash, low-level cement replacement, phase development, mechanical response, cement-based material.

1. Introduction

Cement production accounts for 8-9% of the total anthropogenic CO_2 emissions [1], and the percentage is increasing due to a growing need for cement in developing countries [2]. One

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Abbreviations (not standard): WA1: untreated wood ash no. 1, WA2: untreated wood ash no. 2, WA1-W: wood ash no. 1 exposed to a preliminary washing treatment, WA2-W: wood ash no. 2 exposed to a preliminary washing treatment.

way to decrease the associated CO_2 emissions from cement production is the use of blended cement where a part of the cement is substituted with other materials. The production of ash deriving from biomass, organic materials such as wood, is increasing due to a withdrawal of the traditional coal-fired power plants in Europe [3], substituting coal with biomass in the heating and power production [4]. Currently, approximately 10 million tonnes of biomass ash are produced annually worldwide alone from the electricity production, thus for heat-only production, additional quantities of biomass ash can be added to the quantities [4]. This leads to a series of potentially new types of materials which can be used as a partial cement substitution in blended cement. Such a potential new material could be wood ash (WA), originating from combustion of wood and wood products [5].

The performance of wood ash in mortar and concrete, studied in the literature [5–11], vary significantly depending on the physicochemical characteristics of the WA utilised, again depending on, e.g. the type of wood fuel and combustion process used for the energy production [12,13]. This is clearly seen, e.g. from compressive strength measurements of mortar samples with a partial cement replacement of cement with different WAs; Udoeyo et al. [11], Berra et al. [6], and Elinwa and Mahmood [10] all saw a decrease in the compressive strength with increasing replacement rates, while Rajamma et al. [14] and Ramos et al. [7] observed a maintained compressive strength for samples with 10 and 20% cement replacements compared to a reference sample. Further, the properties of a WA can be improved by different types of pre-treatments; Berra et al. [6] included a washing step, Doudart de la Grée et al. [15] included both a sieving and washing step, and Rosales et al. [16] included grinding, heating and removal of remnants of charred wood, all pre-treatments improving the compressive strength measurements of cement-based materials with WA as a partial cement replacement. Washing of the WA reduces the content of soluble salts (such as chlorides and sulfates) [15]. These promising results encourage further studies, including pre-treatments and following both the strength and the phase development over time, as the latter has not been included in any of the previous studies, in order to increase the knowledge on how pre-treatment of WA influences the two. Based on previous studies, only low-level replacements (10wt%) of cement with WA, have seen to be feasible based on the compressive strength. This study continues these investigations on low-level replacements in order to determine the effects on the compressive strength and phase development at low-level cement replacements with WA.

The objectives of this study are: (1) to determine the impact of sieving and washing treatment of the WAs on the physicochemical characteristics; (2) to investigate the impact of a low-level cement replacement with WA on the mechanical response and phase development as a function of time; and (3) to determine the influence of sieving and washing treatments before utilisation of WA as a low-level cement replacement according to the strength and phase development.

In the presented study, two types of WA originating from different types of combustion but using the same type of biofuel were investigated. The two investigated WAs originate from combustion of wood chips. One originates from grate combustion, and the other from circulating fluidised bed combustion. Wood chips for the energy production are one of the most commonly used biomasses, and the use has increased in consumption over the last 20 years (841% increase in the consumption of wood chips for the energy production since 2000 [17]). According to a recently published report by representatives from Austria, Canada, Denmark, Germany, Italy and the Netherlands [4] grate combustion is predominately used for combustion of biomass, but circulating fluidised bed combustion is gaining ground in many of the countries. These types of plants, grate or circulating fluidised bed combustion, have the highest efficiency when solely biomass is used [18], and are the most common type of plants regarding combustion of biomass. This means that the two chosen WAs represent common types of WAs.

2. Materials and methods

2.1. Materials

The materials used for this study were Portland cement, Rapid Aalborg Cement from Aalborg Portland, Denmark (CEM I), inert quartz (Qz) [19], and two types of wood fly ash, sampled at Skærbækværket Biomass Power Plant, Denmark (WA1) and Värtaverket Combined Heat and Power Plant, Sweden (WA2). WA1 is a residue from grate combustion (600-1,000°C). WA2 is a residue from circulating fluidised bed combustion (760-930°C). The fuel used at both plants was a similar type of wood chips originating from whole trees, primary pine trees, including bark and needles [20]. After sampling, the WAs were stored in closed plastic buckets protected from moist, heat and light sources. The buckets were rotated by hand in order to increase the uniformity of the WA before smaller portions of WA for further treatment were sampled. The WA samples were divided into two portions. The WAs were dried at 50°C and sieved. The sieving removed the particles $\geq 250\mu m$, which consisted only of larger remnants from charred wood. The larger remnants of charred wood accounted for approximately 25% of WA1 and < 2% of WA2 when received from the power plants. Smaller particles of charred wood, which can be found in the fraction ≤ 250μm [15], are not removed. One portion of each WA was subjected to drying at 50°C and sieving to a particle size of ≤ 250µm (termed WA1 and WA2). The other portion was washed after drying and sieving (termed WA1-W and WA2-W). The washing procedure was as follows: 100 g ash was mixed with distilled water to a liquid-to-solid ratio (L/S) of 5 and shaken manually for 1 min [21]. After settling (app. 5 min.), the water was decanted. This procedure was repeated three times, the suspension was filtered (retention 12-15μm), and the ash was subsequently dried at 50°C.

2.2 Methods

2.2.1 WA characterisation

Selected characteristics of the WAs, CEM I and Qz, are given in Tab. 2. Loss on ignition (LoI) was measured at 950°C, according to EN 196-2 [22]. The element content was determined by X-ray fluorescence (XRF) spectrometry measured by the use of a SPECTRO Gmbh X-LAB 2000 with a Pd-tube on samples ground to a particle size of less than 200μm. The software used was TQ-3945r, and the equivalent content of oxides was calculated based on the element content. Cl^- and SO_4^{-2} were measured with Ion Chromatography (IC) on a 1:2.5 solid-to-liquid ratio suspension in distilled water after 1 hour of agitation. The free calcium oxide contents in the WAs were measured according to EN 451-1 [23].

The particle size distribution was found by laser diffraction by the use of Mastersizer 2000. The pH was measured for all materials in 1:2.5 solid-to-liquid ratio suspensions in distilled water with a pH electrode after 1-hour agitation. The electric conductivity was determined on the same suspension with an electrical conductivity meter. The particle density was measured by the use of a helium gas pycnometer Micrometics AccuPyc 1340 in accordance with EN 196-6 [24].

The crystalline phases in the materials were identified by XRD. The WA was loaded into the sample holder using backloading. A PanAnalytical X-ray diffractometer, sat at the PW3064 Spinner stage for standard powder samples have been used for the measurements. Cu-Kα radiation with a wavelength of 1.54 Å was used as the x-ray source. The samples were measured 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). A semiquantitative analysis has been performed in X'Pert HighScore Plus software, determining approximate amounts (in %) of the crystalline phases. The detection limited of the XRD analysis is 2 wt%. Grain morphology was analysed by the use of Scanning Electron Microscope (SEM)-images performed on a FEI Quanta 200. The pictures were magnified X1500, and the accelerating voltage of the beam was 20 keV with a large field detector under low vacuum conditions.

The thermogravimetric analysis (TGA) was performed on both WAs and WA-Ws. Approximate 40 mg of the sample was poured into 85 µl aluminium oxide crucibles (diameter 6.8mm), and the weight loss was measured from room temperature to 900 °C in a NETZSCH STA 449 F3 Jupiter. First, the temperature was raised to 40 °C and held for 10 min.; then the temperature was increased to 900 °C with a heating rate of 10 °C/min. During the measurements, the cell was purged with 50 ml/min of nitrogen gas. The data were processed using the analysis software Proteus Analyzer. The unburned carbon content was determined from LoI and TGA measurements.

2.2.2. Paste preparation and double solvent exchange

Six paste mixes were prepared, one reference and with 10% replacements of cement either with one of the four WAs or Qz with a constant w/b = 0.5. The pastes were mixed using a high shear mixer (Whip Mix Power Mixer Model B). The mixing procedure was adapted from EN 196-1 [25]: mixing for 90 s, resting for 90 s, and mixing for 60 s. The pastes were cast in 5 ml polythene tubes (diameter 12 mm) and stored for one day in a temperature-controlled room (20°C, <80% RH). The pastes were demoulded and transferred into larger 25 ml vials (diameter 25 mm), subsequently filled with lime water (3 g calcium hydroxide/L distilled water [26]) and stored in a temperature-controlled room (20°C). The pastes were tested after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration.

Double solvent exchange was used for hydration stoppage [27]. Four 2 mm thick slices (diameter 12 mm) were cut from the middle of the cured paste samples. The slices were crushed in a porcelain mortar until the whole paste sample could pass through a 1 mm sieve. Approximately 3g of the crushed sample was immersed in 50 mL isopropanol. The suspension was shaken for 30 sec, left to rest for 5 min, and subsequently decanted. This isopropanol treatment was performed twice, and then the suspension was vacuum-filtered. The crushed sample was then immersed in 10 mL diethyl ether, shaken for 30 sec, left to rest for 5 min., and vacuum-filtered [27]. The crushed cement paste (< 1mm) sample was shortly subjected to an oven drying process (8 min. at 40°C) in order to remove the easily volatile diethyl ether. This method does not alter the hydrate products significantly [27]. For the TGA and XRD analysis, the paste samples were further crushed in a porcelain mortar, right before test execution, until the whole paste sample could pass through a 63µm sieve [27].

2.2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed on pastes subsequently to the double solvent exchange treatment, drying and crushing. The TGA was performed as described in section 2.2.1. From the TGA measurements, the loss of bound water and decomposition of ettringite and calcite were determined by the use of a horizontal step and decomposition of portlandite was determined by the use of a tangential step. The step for bound water was 50°C and 550°C [27], for ettringite 50°C and 120°C [28], for portlandite 400°C and 550°C [27], and for calcite 550-800°C [27], respectively. It should be noted that the temperature interval for ettringite also includes carbonate AFm phases and C-S-H [28]. However, the included mass loss due to carbonate AFm phases was expected to be very small as the main peak of the carbonate AFm phases was determined to be above 120°C (approximately 160°C) as displayed in Fig. 5. The mass loss due to decomposition of C-S-H cannot be separated from the mass loss corresponding to ettringite as the TGA peaks overlap. This might lead to an overestimation of the amount of ettringite formed. However, this is acceptable as the WAs are not expected to contribute significantly to the formation of C-S-H compared to the formation of ettringite [29] due to a low content of silica in the WA, and the increase due to C-S-H can therefore mainly be attributed to the cement hydration. The equations for the quantification of the bound water (H), portlandite (CH), ettringite ($C_6As_3H_{32}$) and calcite ($C\bar{C}$) relative to the dry mass or clinker content (c.f. [27]) are given in Eqs. (1)-(12).

$$H_{measured} = WL_{50-550} \tag{1}$$

$$H_{anhydrous} = \frac{H_{measured}}{weight\ at\ 550°C} \tag{2}$$

$$H_{Clinker} = \frac{H_{measured}}{weight\ at\ 550°C} \times \frac{100}{\%clinker} \tag{3}$$

$$CH_{measured} = WL_{400-550} \cdot (74/18) \tag{4}$$

$$CH_{anhydrous} = \frac{CH_{measured}}{weight\ at\ 550°C} \tag{5}$$

$$CH_{Clinker} = \frac{CH_{measured}}{weight\ at\ 550°C} \times \frac{100}{\%clinker} \tag{6}$$

$$\mathrm{C_6As_3H_{32}}_{measured} = WL_{50-120} \cdot (1255/(32 \cdot 18)) \tag{7}$$

$$\mathrm{C_6As_3H_{32}}_{anhydrous} = \frac{\mathrm{C_6As_3H_{32}}_{measured}}{weight\ at\ 550°C} \tag{8}$$

$$\mathrm{C_6As_3H_{32}}_{clinker} = \frac{\mathrm{C_6As_3H_{32}}_{measured}}{weight\ at\ 550°C} \times \frac{100}{\%clinker} \tag{9}$$

$$\mathrm{C\bar{C}}_{measured} = WL_{550-800} \cdot (100/44) \tag{10}$$

$$\mathrm{C\bar{C}}_{anhydrous} = \frac{\mathrm{C\bar{C}}_{measured}}{weight\ at\ 550°C} \tag{11}$$

$$\mathrm{C\bar{C}}_{Clinker} = \frac{\mathrm{CaCO_3}_{measured}}{weight\ at\ 550°C} \times \frac{100}{\%clinker} \tag{12}$$

The standard deviations of these quantifications were based on three independent measurements and quantifications of the bound water (H), portlandite (CH), ettringite ($C_6As_3H_{32}$) and calcite ($C\bar{C}$) of a control sample at 28 days of hydration.

2.2.4. X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was performed on the same pastes used for the TGA subsequently to the double solvent exchange treatment, drying and crushing. The XRD analysis was performed, as described in section 2.2.1. Semiquantitative analysis was performed in X'Pert HighScore Plus software, determining approximate amounts (in %) of the crystalline phases.

2.2.5. Preparation of mortar samples and compressive strength testing

Mortar mixes were prepared according to the mixing procedure prescribed in EN 196-1 [25] with a constant w/b = 0.5. One control mix without WA (REF), five mixes with 10%, and five mixes with 20% replacements of cement (in accordance with ASTM C311/C311M-13 [30]), either with one of the four WAs or Qz. WA or Qz was added to the unhydrated cement before mixing. Super plasticiser (Dynamon XTend from Mapei) was added to the mixing water and in order to achieve standard consistency, thus keeping a constant w/b ratio. The consistency was determined by flow table according to EN 1015-3 [31] for mixes containing WA or Qz, see Tab. 1. Mortar prisms (40 x 40 x 160 mm) were cast in accordance with EN 196-1 [25]. Three mortar prisms were prepared for each of the mixes for each of the hydration ages. After 1 day in a temperature-controlled room (20°C, <80% RH) the three prisms from each mix were demoulded and stored in separate boxes submerged in lime water (3 g calcium hydroxide/L distilled water [26]) in a temperature-controlled room (20°C). The mortar specimens with 10% replacements were tested after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration and the mortar specimens with 20% replacements were tested after 7 and 28 days of hydration [32].

After hydration, the compressive strength of the mortar specimens was determined according to EN 196-1 [25]. The mortars were split in two with an electro-mechanic test machine (Instron 6022) by increasing the load by 0.05 kN/s [25], and the compressive strength was measured for all the subsequent six pieces of mortar with a servohydraulic test machine (Toni Technik 300Ton) by increasing the load by 2.4 kN/s [25]. The air content of mortars was determined in accordance with Osbæck [33] by the use of the weight at demoulding and the theoretical air void free mortar. The compressive strength was then normalised to an air content of 2 vol% by the use of Bolomeys equation [34]. SAI was calculated according to ASTM C311/C311M-13 [30].

3. Results

3.1 Characteristics of WAs and Qz

DTG curves for all materials are displayed in Fig. 1. Some prehydration of CaO resulting in portlandite formation were seen for the washes ashes as a result of the washing treatment. The chemical composition of the materials is presented in Tab. 2 and the physical properties are presented in Tab. 3. A total below detection limit of Cl^- and SO_4^{2-} and a reduction in the content of alkali metals K_2O and Na_2O are results from the washing of WAs. Tab. 4 displays the crystalline phases for the materials and hydration of CaO to $Ca(OH)_2$ is seen for washed WAs. The grain morphology is shown by SEM images (Fig. 3). This reveals large, angular particles for both WAs. A layer of soluble compounds covers the untreated WAs, Fig. 3 (a) and (c), seen as minor particles covering larger particles. When the WAs were washed, Fig. 3. (b) and (d), this layer was removed. More spherical particles were found in WA1-W compared to WA2-W. The washing did not improve LoI of the WAs, which are high (≥ 15%) for all WAs. The unburned carbon content was ≤ 1% for both WA1 and WA1-W and 6 and 7% for WA2 and WA2-W respectively.

3.2. Strength activity index

For pozzolanic activity, the ASTM C618 [32] requires an SAI above 0.75 compared to the reference after 7 and 28 days of hydration for a mortar sample containing 20% possible pozzolan and 80% CEM I as binder. The SAI are presented in Tab. 5 and only WA1 mortar does not comply with the limit. The washing treatment leads to an increase in the SAI for both types of WAs. Qz also complies with the limit, even though it being completely inert.

3.3. Compressive strength development

At 1 day of hydration, the compressive strength of the WA1 mortar is comparable to REF, see Fig. 4 and Tab. 6. The rest of the WA mortars obtains a slightly lower compressive strength, and a tendency is seen, where the washed WA mortars are more comparable with the Qz mortar. At 3 days the compressive strength for all WA mortars is comparable to REF and higher than the Qz mortar. From 7 days of hydration, the compressive strength of REF exceeds all WA and Qz mortars. At 90 ≤ days of hydration, all WA mortars have a slightly higher compressive strength compared to the Qz mortar. The WA1-W mortar exceeds the compressive strength of all other WA mortars, followed by, in decreasing order, the WA2, WA1 and WA2-W mortar.

3.4. Phase development

The phase development was analysed by XRD and TGA. Tab. 7 is an overview of the detected phases in the pastes determined by XRD. Depletion of alite was seen after 3 days of hydration for all pastes. Depletion of belite and ferrite are seen after 14 days of hydration for WA1-W and Qz paste, and for the remaining pastes after 28 days of hydration. Portlandite and ettringite were detected in all pastes from 1 days of hydaration and monocarbonate was detected in all pastes from 14 ≤ days of hydration. Quartz is detected in WA, and Qz pastes, at all hydration ages. Calcite is detected at 1 day of hydration for all WA pastes. However, dissolution of the calcite is seen for WA2 and WA2-W pastes since no calcite is detected again before 90 days of hydration.

Differential thermogravimetric (DTG) curves, determined with TGA for all pastes at 28 days of hydration, are presented in Fig. 5. The DTG curves show peaks of weight changes related to the decomposition of ettringite (Et) and C-S-H, monocarbonate (Mc) and portlandite (CH). Above 550°C, calcite decomposes by emitting CO_2 [27], substantiating the change from hydration to carbonation to be at 550°C as used in the formulas (1) – (12).

Quantification of bound water, portlandite, ettringite/C-S-H and calcite in all pastes are presented in Fig. 6, 7, 8 and 9, (a) calculated as wt%/anhydrous binder weight and (b) calculated as wt%/clinker content. The standard deviation was 0.67%wt for the quantification of bound water, 0.56%wt for the quantification of portlandite, 0.27%wt for the quantification of ettringite and 0.33%wt for the quantification of calcite. This is illustrated as error bars in the figures 6-9.

3.4.1. Bound water

At 1-3 days of hydration, a slightly larger amount of water was bound in the WA pastes compared to REF, see Fig. 6 (a)). After 7 days of hydration, the amount of bound water in REF and WA pastes were comparable. At 14 and 28 days of hydration, the amount of water bound in REF slightly exceeds the amount bound in the WA pastes. At 365 days the amount of bound water in REF and WA pastes are in the same range, but with a slightly higher amount of bound water in WA2 and WA2-W pastes compared to WA1 and WA1-W pastes. Qz had the lowest content of bound water of all pastes.

3.4.2. Portlandite

At 1-3 days of hydration, the portlandite content in WA and Qz pastes is similar or slightly higher than REF (Fig. 7 (a)). At 7 days, the portlandite content for REF paste increases compared to WA and Qz pastes, which remains comparable for the rest of the hydration period.

3.4.3. Ettringite

Ettringite has been determined for both REF and WA pastes at all ages (Tab. 7). A comparable ettringite content (Fig. 8 (a)) is seen for WA pastes from 1 to 7 days of hydration. From 14 ≤ days of hydration, the ettringite content in the WA pastes exceeds REF. This is especially notable for WA2 paste from 90 days of hydration and, at later ages (182 ≤ days of hydration), the same is seen for WA1 paste. Qz had the lowest content of ettringite at all ages.

3.4.4. Calcite

A clear difference is seen in the calcite content between WA1 and WA1-W pastes, and WA2 and WA2-W pastes at all ages (Fig. 9 (a)), with WA1 and WA1-W pastes having the highest content of calcite. The calcite content decreased from 1-90 days of hydration for all pastes followed by an increase after 90 days.

3.4.5. Dilution effect

In the pastes, the most reactive part (the cement) is replaced with a less or non-reactive material (WA or Qz). In order to take this dilution effect into account when analysing the results, the amount of bound water, portlandite, ettringite and calcite are calculated as wt%/clinker content, see Fig. 6, 7, 8 and 9 (b). The WA pastes have a higher amount of bound water than REF, and Qz pastes at all ages, see Fig. 6 (b). From 28 days of hydration, a slight increase in the portlandite content is seen for REF compared to WA and Qz pastes (Fig. 7 (b)). For the ettringite (Fig. 8 (b)) and calcite content (Fig. 9 (b)), Qz exceeds the contents calculated for REF.

4. Discussion

In the following section, the objectives 1-3 outlined in section 1 will be discussed based on the results presented in section 3.

4.1. Impact of the washing on the physicochemical characteristics of the WAs

Washing of the WAs resulted in a slight increase of the particle size distribution (Fig. 2) by removing the soluble fraction consisting of compounds with smaller particle sizes. This is supported by the SEM images (Fig. 3). Fig. 3 (a) and (c) reveals a layer of smaller compounds covering the particles of the raw WAs. These compounds are removed by washing, see Fig. 3. (b) and (d), and are thus assumed soluble, probably salts with Cl^- and SO_4^{2-} and the alkali metals, K and Na such as KCl, K_2SO_4 (Tab. 4) and NaCl, Na_2SO_4, as these chemical elements are removed to below detection limit or significantly reduced (Tab. 2). No decrease of neither LoI nor the unburned carbon content is seen as a result of the washing. The sieving effectively removed unburned carbon from WA1 and WA1-W, however, smaller particles (≥ 250µm) of unburned carbon are found in WA2 and WA2-W, containing 6 and 7% unburned carbon, respectively. The unburned carbon can lead to an increase in the water requirement [12,35,36]. However, this was not seen for the WAs investigated in this study. The high LoI measured for all WAs are primarily due to the content of hydrate phases and especially carbonate phases and not a high content of unburned carbon. The content of free CaO is decreased by the washing, however, it could still present an issue regarding soundness of the blended cement.

Several other issues are possible when utilising these WAs as a partial cement replacement, e.g. P_2O_5 can cause delayed set, alkalis can cause alkali silica reactions and SO_3 can cause sulfate attack. In relation to the durability, washing improves the possible use of WAs as a partial cement replacement, but further treatments will possibly be required before utilisation in cement-based materials is possible. However, as these issues are not investigated in this study, this needs to be addressed further in a subsequent study.

The washing further caused a difference in the phase composition of the WAs. From the DTG curves (Fig. 1) of the unhydrated materials, C-S-H (as no ettringite was determined by XRD) and an increase in the calcite content can be found in the washed WAs. The increase in calcite is substantiated by the XRD (Tab. 4.) and is due to removal of other water-soluble compounds and carbonation. Portlandite has been determined for all WAs by the XRD (Tab. 4.), but the DTG curves (Fig. 1) reveals a difference in the impact of the washing on the Portlandite content between the two types of WAs. The content of portlandite increases after the washing of WA1, but decreases for WA2. For both washed WAs, a chemical prehydration process between CaO and the content of water forming portlandite following reaction (13) is expected [29], as no CaO are found in the washed WAs (Tab. 4.) and a significant reduction is seen in the content of free CaO (Tab. 2) are seen. Subsequently, carbonation occurs in WA2-W, decreasing the content of portlandite and leading to calcite formation, following reaction (14) [37–39].

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{13}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{14}$$

The initial content of portlandite and calcite in the untreated ashes are a consequence of water and CO_2 in the air during ash storage at the power plants, following reactions (13) and (14).

Arcanite (K_2SO_4) was determined in WA1 by XRD WA1, see Tab. 4. Formation of arcanite in the ash is due to a higher release of alkali metals by volatilisation facilitated by the high temperatures in grate combustion, compared to a fluidised bed system [40]. Arcanite is water-soluble and is removed during the washing, and thus it is not present in WA1-W (Tab. 4).

Sylvite (KCl) and anhydrite ($Ca(SO_4)$) were identified in WA2 by XRD, see Tab. 4. Thus, in WA2 potassium is primarily bound with chloride rather than sulfate, and sulfate is bound primarily to calcium. Anhydratie is a result of a sulphation process at the power plant were limestone are added to capture SO_2, an important process in a fluidised bed system, precipitating anhydrite [40]. Neither sylvite nor anhydrite is present in WA2-W (Tab. 4) because these compounds are water-soluble, and the lime present in WA2 is hydrated to portlandite following reaction (13).

The initial presence of calcite has a beneficial impact on the properties of a cementitious material due to the potential formation of hemi- and monocarbonate. These AFm phases are more stable than monosulfate in the presence of carbonates [41], and as a consequence, ettringite does not transform into monosulfate, but is stabilised. Stabilisation of ettringite leads to an increase in compressive strength, as ettringite has a lager content of hydrate water and is more voluminous, leading to a reduction in the porosity [29,42–44]. Reactions (13) and (14) can occur during hydration of cement paste with partial cement replacement with WA due to hydration of CaO and subsequently carbonation [39], as CaO is present in both WA1 and WA2 and $Ca(OH)_2$ is present in all WAs (Tab. 4.).

4.2. Impact of the partial cement replacement of cement with WA on SAI, mechanical response and phase development

4.2.1. Strength activity index

From the results from the SAI test (Tab. 5), WA1-W, WA2 and WA2-W are seen to possess pozzolanic properties, meeting the requirements set by ASTM C618 [32] at both 7 and 28 days of hydration. A decrease of 20% and 15% decrease in the strength compared to REF are seen for Qz at 7 and 28 days of hydration, respectively, thus Qz complies with the requirements set by ASTM C618 [32]. However, Qz is completely inert and does not contribute through either nucleation processes or particle packing, due to the large particle size of Qz comparted to CEM I (Fig. 2) [45].

The SAI test an indirect method measuring a physical property indicating the extent of pozzolanic activity of a material [46]. According to the literature [47–49], there are several drawbacks of this method. An unreactive material can be misread as having pozzolanic properties, e.g. due to nucleation processes and particle packing effects [50,51] and other hydrate phases contributing to the compressive strength cannot be distinguished from the hydrate phases resulting from pozzolanic activity. Further ASTM C618 [32] requires measurements only at 7 and 28 days of hydration, which for some types of pozzolans is inadequate, e.g. coal fly ash shows very little pozzolanic reactivity 28 days of hydration [38]. Amorphous silica and aluminosilicate leads to pozzolanic activity [52]. Due to the WAs consisting of large and fibrous particles (Fig. 3) and not the typical glassy aluminosilicate spherical particles found in commercial coal fly ash [53], the amount of amorphous glass are considered to be limited in the WAs. Further, the content of silica in WA1 and WA1-W are low (< 13%), see Tab. 2. The silica content in WA2 and WA-2-W is higher (23.8 and 26.5%, respectively), but this can be attributed to inert sand particles, which make the suspension bed and are carried with the flue gas during combustion with the circulating fluidised bed technology ending up in the fly ash fraction [40]. Thus a very limited pozzolanic reaction with silica [43] can be expected and the increase in strength can mainly be due to the WAs contributing through hydration of other hydrate phases, like ettringite, contributing to an increase in compressive strength [42]. No contribution through heterogeneous nucleation processes from WAs are expected either due to their particle size distribution being equivalent or larger than CEM I, see Fig. 2 [45].

4.2.2. Mechanical response

The development of compressive strength, when WAs are used as a partial cement replacement, is seen in Fig. 4. At 1 day of hydration WA1 and WA2 mortars have compressive strength comparable to the compressive strength of REF, and higher compressive strength compared to the mortars with WA1-W, WA2-W and Qz. The compressive strength of the mortar with WA1 is comparable to REF at both 1 and 3 days of hydration. All mortars containing WA, has a slightly higher compressive strength than the mortar with Qz at 1-7 days of hydration.

No contribution through heterogeneous nucleation processes from the WAs are expected, as described in section 4.2.1, thus the increase in the compressive strength of WA mortars being comparable to REF and not Qz at yearly age indicates an influence from chemical reactions due to dissolution of easily soluble salts leading to strength improving hydration products [29,42–44].

At late age, 90 ≤ days of hydration, all WA mortars have a higher compressive strength than the Qz mortar. The low compressive strength of Qz is due to the inert nature of the Qz and a low density (2650kg/m^3 compared to 3180kg/m^3 for CEM I), resulting in a larger volume based addition of Qz, leading to relatively less space available for the hydrate formation further decreasing the strength.

At 365 days of hydration the average compressive strength for mortar with WA1 arrives at 86%, WA2 at 87%, WA1-W at 91%, WA2-W at 84% and Qz at 82% compared to the compressive strength of REF. The lower compressive strength of WA mortars reflects the dilution effect, decreasing the amount of hydrated cement and the larger volume based addition of the WA compared to CEM I. However, the increase in compressive strength compared to Qz indicates that the WA mortars facilitates the development of phases contributing to an increase in the compressive strength.

4.2.3. Phase development

4.2.3.1. Bound water

An increase in the amount bound water is seen for WA pastes at 1-3 days of hydration (Fig. 6 (a)) compared to REF. Such increase can be explained by the dissolution of easily soluble salts enhancing the initial growth of hydrated phases. From 14 to 90 days of hydration, the bound water in REF exceeds all WA pastes, but at 365 days of hydration, all WA pastes have approximately the same amount of bound water as the REF, indicating a continuous hydration of phases in the WA pastes compared to REF. WA2 and WA2-W pastes contain a slightly higher amount of bound water compared to WA1 and WA1-W pastes. This is explained by WA2 and WA2-W binding more water in phases such as ettringite (see Fig. 8).

The amount of bound water for WA pastes exceeds Qz at all ages (Fig. 6 (a)). These observations correspond to the WAs contributing through a quick initial dissolution of the particles at early age and development of phases contributing to the compressive strength at later ages.

4.2.3.2. Portlandite

Initially (1-7 days), the content of portlandite for all pastes with WAs exceeds the content of portlandite for pastes with Qz (Fig. 7 (a)). The increase in portlandite, compared to Qz, can be explained by an additional formation of portlandite due to a reaction between CaO in the WAs and H_2O (Eq. 13).

After 28 days of hydration, the portlandite content in WA pastes is slightly exceeded by the portlandite content of Qz when the dilution effect is considered (Fig. 7 (b)). This is explained by consumption of portlandite in the WAs either as a result of, to a minor extent, the pozzolanic reaction or formation of ettringite occurring at the expense of portlandite, aluminium and sulfate [41].

4.2.3.3. Ettringite/C-S-H

As discussed previously (section 2.2.3.) the formation of C-S-H cannot be separated from the mass loss corresponding to ettringite as the TGA peaks overlap, thus ettringite discussed in this section can include C-S-H. Some initial C-S-H is determined for washed WAs, however, based on the discussions presented in section 4.2.1. and 4.2.2. the WAs are not expected to contribute significantly to the formation of C-S-H compared to the formation of ettringite, substantiated by the literature [29]. Further, ettringite has been determined for both REF and WA pastes by XRD at all ages (Tab. 7).

A difference is seen at 1 day of hydration for the ettringite content between pastes with untreated and washed WAs (Fig. 8), corresponding to the initial C-S-H content and not ettringite found in WA1-W and WA2-W (Fig. 1.) A rapid increase in the ettringite content is seen for WA1 and WA2 from 1 to 3 days of hydration, corresponding to the dissolution of SO_4^{2-} in the untreated ashes (Fig. 8.).

All WA pastes have a higher content of ettringite than Qz at all ages and REF from 28 days of hydration, see Fig. 8 (a). The increase mainly contributed to the ettringite formation in WA pastes is attributed to an increase in the SO_3/C_3A ratio [38] and not formation of C-S-H. The content of ettringite was highest in the paste with WA2, corresponding well to WA2 having the largest initial content of SO_3 (Tab. 2). WA1 has the second-largest initial content of SO_3 and the second-largest content of ettringite at 182 ≤ days of hydration. These tendencies are consistent with the increased amount of bound water (Fig. 6 (b)) in WA pastes. Due to the amount of hydrate water, ettringite is voluminous, which leads to a reduction in the porosity and consequently to an increase in compressive strength [29,42–44]. At 182 ≤ days of hydration, the washed WA pastes have a lower ettringite content, compared to the untreated WAs, due to a lower SO_3 content (Tab. 2).

There was no decrease in the ettringite content due to stabilisation as a result of the presence of calcite and formation of monocarbonate (determined by the TGA, Fig. 5, and XRD Tab. 7.).

4.2.3.4. Calcite

A significant difference in the content of calcite at 1 day of hydration is seen between pastes with WA1 and WA1-W, WA2 and WA2-W, and Qz and REF, see Fig. 9 (a). This is due to a difference in the initial content of the materials: calcite contribution from WA and 5 % limestone filler in CEM I. WA1 and WA1-W pastes have approximately 2 wt% higher content of calcite than WA2 and WA2-W pastes (Fig. 9 (a)), attributed to a higher initial content of calcite in WA1 and WA1-W (Fig. 1).

A decrease in calcite content is seen for all pastes from 1-90 days of hydration, especially profound for WA pastes, due to formation of mono- and hemicarbonate at the expense of calcite (determined by the TGA, Fig. 5, and XRD Tab. 7.). An increase in the calcite content is seen from 90 ≤ days of hydration (Fig. 9 (a) and (b)), due to carbonation at later ages for WA pastes.

4.3. Impact of washing on phase and compressive strength development

Several differences were seen between the two types of WAs, before and after washing when utilised in as low cement-replacements in cement-based materials. More ettringite is found in pastes with untreated WA, compared to pastes containing washed WA, due to a larger SO_3 content in untreated WAs. The washing leads to a higher content of calcite due to removal of soluble and carbonation occurring during washing. In general, the contribution to the compressive strength from the WAs is mainly due to the formation of ettringite as a result of an increased SO_3/C_3A ratio and stabilisation by calcite forming monocarbonate [41]. However, excessive formation of ettringite can lead to micro-cracking and a decrease in strength if the stress exceeds the tensile strength of the binder [38]. This can explain the different results obtained for WA mortars, where WA1-W obtains a compressive strength above 90% the reference strength and the compressive strength of WA1, WA2 and WA2-W all arrive at between 84-87%.

A sufficient amount of ettringite is precipitated in WA1-W in order to increase the strength, but low enough not to facilitate micro-cracks. The content of C_3A in the clinker can be calculated by the use of Bogue calculations based on the content of Al_2O_3 and Fe_2O_3 [41], and the SO_3/C_3A ratios are calculated for the WAs: WA1 = 0.5, WA1-W = 0.4, WA2 = 0.5, and WA2-W = 0.5. This indicates the optimum SO_3/C_3A ratio of a mixture with a partial cement replacement with WA to be: $0.4 \leq$ optimum < 0.5. This provides an indication of a sufficient removal of the SO_3 from a WA by a washing treatment order to obtain a sufficient, but not excessive amount of ettringite contributing positively to the strength development. The washing removed 76% of the SO_3 from WA1 and only 39% of SO_3 from WA2, thus further treatment should be conducted for WA2-W indicating WA1-W to be more promising as a low-level partial cement replacement.

Again, it should be noted that washing improves the possible use of WAs as a partial cement replacement, but further treatments will possibly be required before utilisation in cement-based materials is possible, especially considering several possible durability issues.

5. Conclusion

Two wood ashes (WAs), originating from two different power plants using circulating fluidised bed combustion and grate combustion, respectively, were investigated in an untreated as well as washed version for the purpose of low cement replacements (10%) in cement-based materials. The time-dependent development of bound water, portlandite, ettringite(/C-S-H) and calcite were measured in cement pastes with 10% replacement with the WAs. In general, increased content of bound water, ettringite and calcite, and decreased content of portlandite were seen for all pastes with WA compared to the Portland cement reference.

If only the mechanical response is considered, the results indicate that the WAs contributes to a minor extent to the compressive strength through pozzolanic reactions and the main contribution to the compressive strength are determined to be the ettringite content. However, excessive formation of ettringite leads to micro-cracking and a decrease in strength. Thus, the optimal ettringite content, contributing to the strength and not to micro-cracking, are found based on the SO_3/C_3A ratio for mixtures with low-level cement replacement with WA between 0.4 and 0.5.

For the two WAs investigated in this study, washed WA originating from grate combustion appears to be more promising as a low-level cement replacement a cement-based material compared to both untreated and washed WA originating from circulating fluidised bed combustion based on the compressive strength development.

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Table 1. Consistency measured by flow table. The value SP to obtain REF are calculated via linear interpolation of the measured flow values in order to obtain a flow value equal to the average flow value of REF.

	SP	**Measure 1**	**Measure 2**	**Measure 3**	**Measure 4**	**Average**	**SP to obtain REF**
	[g]	**[mm]**	**[mm]**	**[mm]**	**[mm]**	**[mm]**	**[g]**
REF no. 1	0	173.0	176.0	176.2	175.0	174.3	-
REF no. 2	0	167.0	175.6	175.5	176.2		
WA1 no. 1	0.5	148.8	146.2	146.9	144.8	146.7	1.2
WA1 no. 2	1.0	183.8	184.6	177.1	178.7	181.0	
WA1 no. 3	2.4	206.7	201.9	206.5	207.0	205.1	
WA1-W no. 1	0.6	148.8	148.1	143.0	152.3	147.8	1.2
WA1-W no. 2	1.0	169.1	173.7	166.8	159.1	167.2	
WA1-W no. 3	1.5	182.8	194.2	181.6	191.1	187.4	
WA2 no. 1	0.5	172.2	178.9	171.6	166.5	172.3	0.6
WA2 no. 2	0.8	183.6	182.5	179.8	185.1	182.7	
WA2 no. 3	1.0	184.9	189.0	177.4	181.0	183.1	
WA2-W no. 1	0.5	174.0	172.4	164.4	164.0	166.9	0.8
WA2-W no. 2	0.8	175.4	164.2	159.8	173.5	168.2	
WA2-W no. 3	1.0	185.2	181.9	184.6	182.4	183.5	

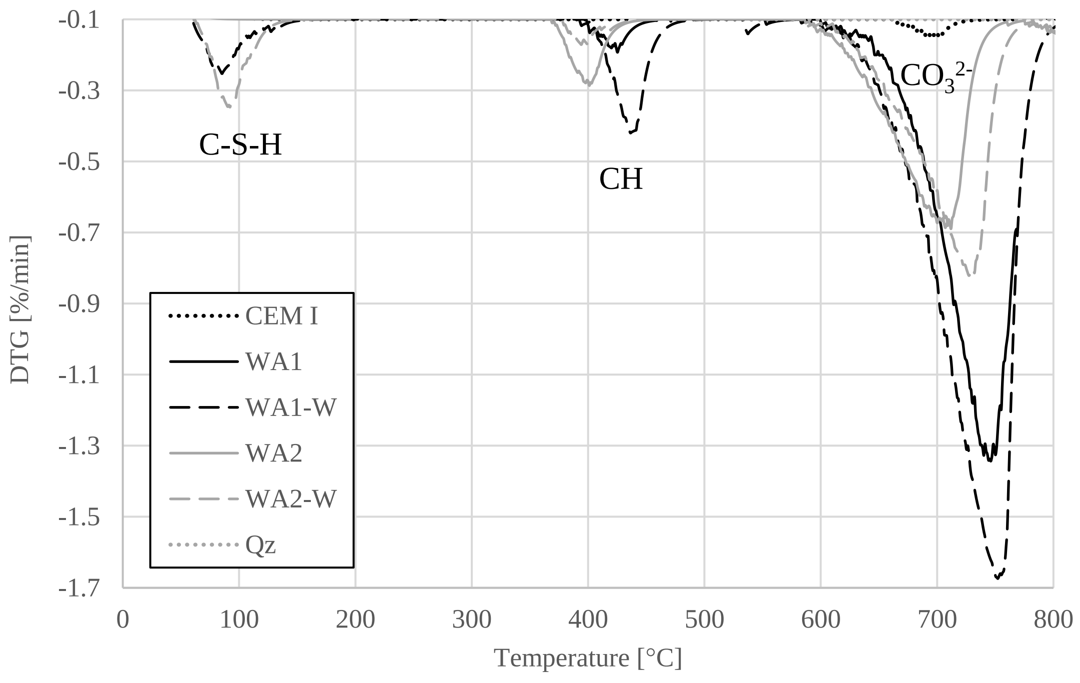

Figure 1. Differential thermosgravimetric (DTG) curves for unhydrated materials. C-S-H: Calium silicate hydrate, CH: Portlandite.

Table 2. Chemical composition (%) of CEM I, WA1, WA1-W, WA2, WA2-W, and Qz. ± defines the standard deviation. ND: not determined.

	CEM I	**WA1**	**WA1-W**	**WA2**	**WA2-W**	**Qz**
SiO_2	19.7	11.0	12.7	23.8	26.5	99.4
Al_2O_3	5.4	2.4	3.0	5.6	6.3	0.10
Fe_2O_3	3.8	2.9	3.2	3.1	3.3	0.03
CaO	64.1	53.6	65.0	44.7	45.0	0
MgO	1.0	4.2	5.8	4.1	4.4	0
K_2O	0.4	14.6	4.4	7.6	5.7	0
Na_2O	0.3	1.0	1.0	0.8	0.9	0
P_2O_5	0.3	2.9	3.8	3.8	4.2	0
SO_3	3.2	5.4	1.3	6.1	3.7	0
CaO, $_{free}$	ND	12.3	5.9	6.4	1.6	0
Cl^-	0.0 ± 0.0	0.8 ± 0.0	0.0 ± 0.0	0.4 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
SO_4^{-2}	0.0 ± 0.0	3.8 ± 0.0	0.0 ± 0.0	1.8 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
LoI, 950ºC	1.9 ± 0.0	15.0 ± 0.1	19.6 ± 0.1	16.2 ± 0.3	19.7 ± 0.1	0.0 ± 0.0
Unburned carbon	-	≥ 1.0	≥ 1.0	5.7	6.7	-

Table 3. Physical characteristics of CEM I, WA1, WA1-W, WA2, WA2-W, and Qz. ± defines the standard deviation.

	CEM I	**WA1**	**WA1-W**	**WA2**	**WA2-W**	**Qz**
pH	12.8 ± 0.0	13.0 ± 0.1	12.5 ± 0.0	12.7 ± 0.1	12.5 ± 0.2	7.7 ± 0.1
Conductivity (mS m^{-1})	18.1 ± 0.2	76.6 ± 0.4	11.1 ± 0.1	29.0 ± 1.3	11.9 ± 0.2	40.0 ± 2.5
Particle density (kg/m^3)	3180	2740	2640	2710	2650	2650

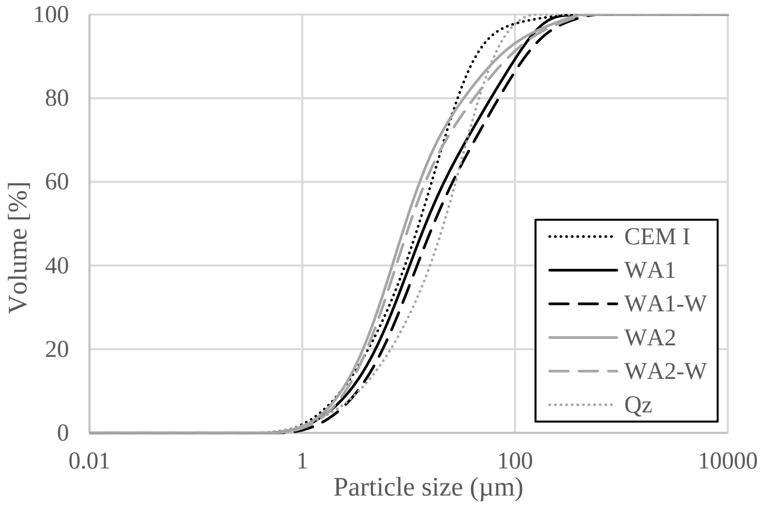

Figure 2. Particle size distribution of CEM I, WA1, WA1-W, WA2, WA2-W, and Qz, determined by laser diffraction.

Table 4. Crystalline phases for unhydrated materials determined qualitatively by XRD diffraction. x: < 15%, xx: ~ 25%, xxx: ~ 50% and xxxx: ~ 100% of crystalline phases identified according to semiquantitative analysis.

	Alite	Belite-β	C_3A	Ferrite	Portlandite	Lime	Quartz	Calcite	Sylvite	Arcanite	Anhydrite
CEM I	xxx	x	x	x							x
WA1					x	x	xx	xxx		x	
WA1-W					x		xx	xxx			
WA2					x	x	xxx	xx	x		x
WA2-W					x		xxx	xxx			
Qz							xxxx				

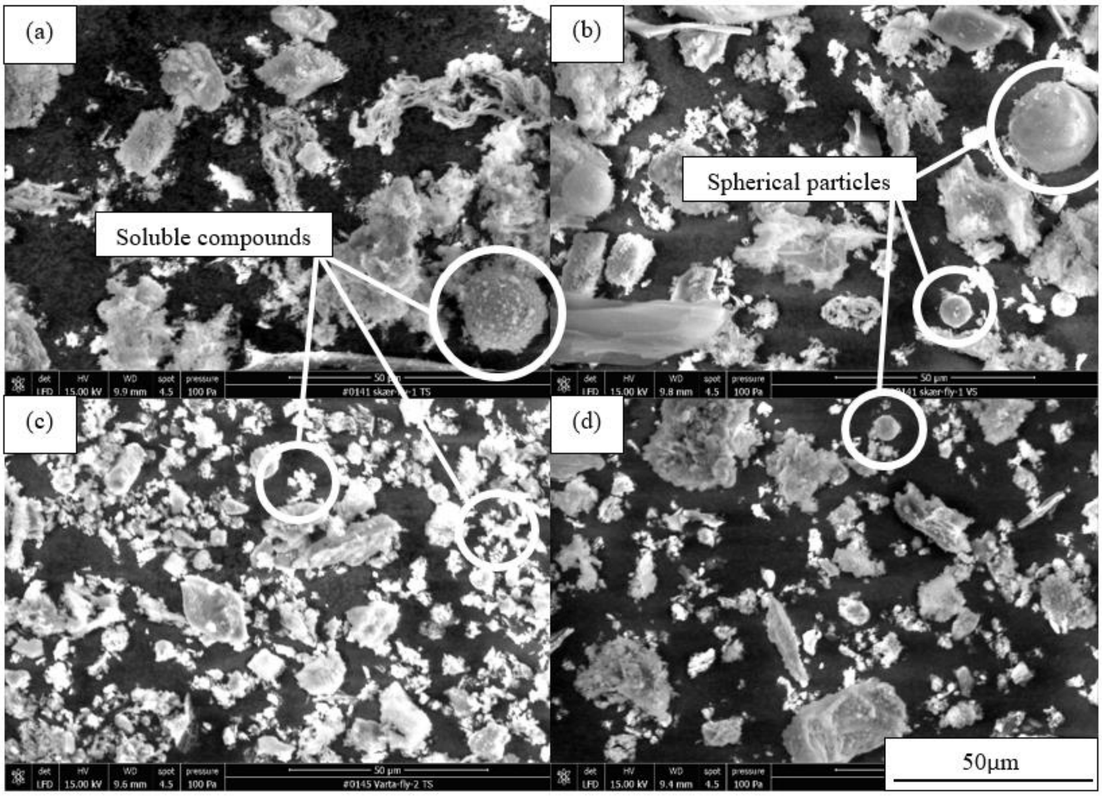

Figure 3. Grain morphology of (a) WA1, (b) WA1-W, (c) WA2 and (d) WA2-W.

Table 5. Measured compressive strength, air content, compressive strength normalised to an air content of 2 vol% by the use of Bolomeys equation [34] and SAI calculated according to ASTM C311/C311M-13 [30].

	Compressive strength (MPa)	SD	Air content (%vol)	Normalised compressive strength (MPa)	SAI
M7-REF	59.5	3.6	1.1	57.5	-
M7-20%WA1	44.1	0.7	1.0	42.6	0.74
M7-20%WA1-W	50.4	1.1	1.1	46.7	0.81
M7-20%WA2	50.3	0.7	1.0	48.7	0.85
M7-20%WA2-W	49.3	0.4	1.1	46.04	0.80
M7-20%Qz	45.9	0.9	1.0	44.1	0.77
M28-REF	69.9	1.8	1.1	64.7	-
M28-20%WA1	51.1	1.3	1.0	49.4	0.76
M28-20%WA1-W	59.3	2.7	1.1	55.0	0.85
M28-20%WA2	59.4	1.4	1.0	57.4	0.89
M28-20%WA2-W	57.0	0.7	1.1	53.24	0.82
M28-20%Qz	57.2	1.4	1.0	54.9	0.85

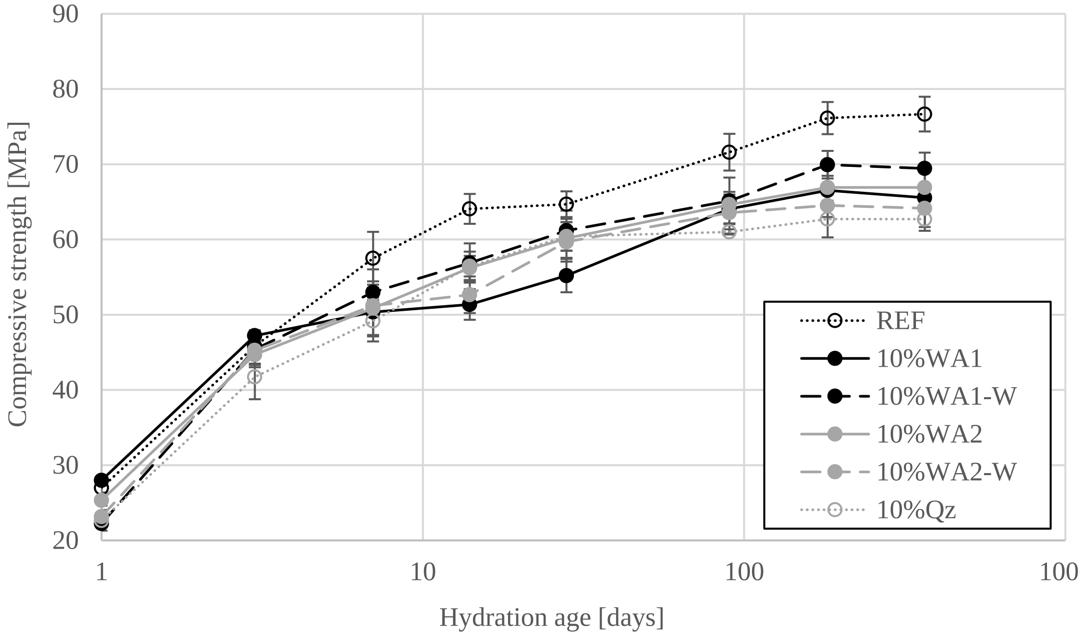

Figure 4. Development of compressive strength of REF and mortars with 10% replacements of cement with WA1, WA1-W, WA2, WA2-W, and Qz after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The compressive strength normalised to an air content of 2 vol% by the use of Bolomeys equation [34]. The error bars defines the standard deviation.

Table 6. Measured compressive strength, air content and compressive strength normalised to an air content of 2 vol% by the use of Bolomeys equation [34].

	Compressive strength (MPa)	SD	Air content (%vol)	Normalised compressive strength (MPa)
M1-REF	27.9	0.6	1.1	27.0
M1-10%WA1	30.1	0.7	0.1	28.0
M1-10%WA1-W	23.2	1.0	0.9	22.3
M1-10%WA2	26.1	0.7	1.2	25.3
M1-10%WA2-W	24.8	0.9	0.2	23.2
M1-10%Qz	23.8	0.9	0.8	22.7
M3-REF	47.4	1.6	1.1	45.8
M3-10%WA1	50.8	0.8	0.1	47.2
M3-10%WA1-W	47.4	2.2	0.9	45.4
M3-10%WA2	46.1	1.7	1.2	44.7
M3-10%WA2-W	48.4	1.9	0.2	45.3
M3-10%Qz	43.8	3.1	0.8	41.7
M7-REF	59.5	3.6	1.1	57.5
M7-10%WA1	54.2	3.5	0.1	50.4
M7-10%WA1-W	55.3	3.2	0.9	53.0
M7-10%WA2	52.5	3.7	1.2	50.9
M7-10%WA2-W	54.8	1.2	0.2	51.2
M7-10%Qz	51.6	2.9	0.8	49.2
M14-REF	67.1	2.1	1.1	64.1
M14-10%WA1	55.3	2.2	0.1	51.4
M14-10%WA1-W	59.4	2.7	0.9	56.9
M14-10%WA2	58.0	1.6	1.2	56.2
M14-10%WA2-W	56.4	2.6	0.2	52.7
M14-10%Qz	59.2	2.0	0.8	56.4
M28-REF	69.9	1.8	1.1	64.7
M28-10%WA1	59.4	2.4	0.1	55.2
M28-10%WA1-W	63.9	2.8	0.9	61.2
M28-10%WA2	62.1	2.7	1.2	60.2
M28-10%WA2-W	63.9	2.8	0.2	59.7
M28-10%Qz	63.6	1.8	0.8	60.4
M90-REF	74.1	2.5	1.1	71.6
M90-10%WA1	68.9	2.1	0.1	64.1
M90-10%WA1-W	68.0	3.2	0.9	65.1
M90-10%WA2	66.7	1.1	1.2	64.6
M90-10%WA2-W	68.0	3.0	0.2	63.6
M90-10%Qz	64.0	0.4	0.8	61.0
M182-REF	78.8	2.2	1.1	76.1
M182-10%WA1	71.6	2.1	0.1	66.5
M182-10%WA1-W	73.0	1.9	0.9	69.9
M182-10%WA2	69.1	2.8	1.2	66.9
M182-10%WA2-W	69.1	1.7	0.2	64.5
M182-10%Qz	65.8	0.4	0.8	62.7
M365-REF	77.0	2.5	1.1	76.7
M365-10%WA1	70.5	1.4	0.1	65.6
M365-10%WA1-W	71.5	2.2	0.9	69.4
M365-10%WA2	69.1	2.4	1.2	66.9
M365-10%WA2-W	68.6	2.7	0.2	64.1
M365-10%Qz	67.9	1.6	0.8	62.7

Table 7. Crystalline phases for paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C determined qualitatively by XRD diffraction. x: < 15%, xx: ~ 25% and xxx: ~ 50% of crystalline phases identified according to semiquantitative analysis.

	Lime	Alite	Belite-β	Ferrite	Portlandite	Ettringite	Quartz	Calcite	Monocarbonate
P1-REF		xx	xx	x	xx	x			
P1-10%WA1	x	xx	xx	x	xx	x	x	x	
P1-10%WA1-W		xx	xx	x	xx	x	x	x	
P1-10%WA2	x	xx	xx	x	xx	x	x	x	
P1-10%WA2-W		xx	xx	x	xx	x	x	x	
P1-10%Qz		xx	x	x	x	x	xx		
P3-REF		xx	xx	x	xx	x			
P3-10%WA1		x	xx	x	xx	xx	x	x	
P3-10%WA1-W		xx	xx	x	xx	xx	x	x	
P3-10%WA2		x	xx	x	xxx	xx	x		
P3-10%WA2-W		x	xx	x	xx	xx	x		
P3-10%Qz		x	x	x	xx	xx	xx		
P7-REF			xx	x	xx	xx			
P7-10%WA1			xx	x	xx	xx	x	x	
P7-10%WA1-W			xx	x	xx	xx	x	x	
P7-10%WA2			x	x	xxx	xx	x		
P7-10%WA2-W			x	x	xx	xx	x		
P7-10%Qz			x	x	xx	xx	xx		
P14-REF			xx	x	xxx	xx			x
P14-10%WA1			x	x	xxx	xx	x	x	x
P14-10%WA1-W			x	x	xxx	xx	x	x	x
P14-10%WA2			x	x	xxx	xx	x		x
P14-10%WA2-W			x	x	xxx	xx	x		x
P14-10%Qz			x	x	xxx	xx	xx		x
P28-REF			x	x	xxx	xx			x
P28-10%WA1					xx	xx	x	x	x
P28-10%WA1-W			x	x	xx	xx	x	x	x
P28-10%WA2			x	x	xx	xx	x		x
P28-10%WA2-W			x	x	xx	xx	x		x
P28-10%Qz					xxx	xx	xx		x
P90-REF					xxx	xx			x
P90-10%WA1					xxx	xxx	x	x	x
P90-10%WA1-W					xxx	xx	x	x	x
P90-10%WA2					xxx	xx	x	x	x
P90-10%WA2-W					xxx	xx	x	x	x
P90-10%Qz					xxx	xx	xx		x
P182-REF					xxx	xx			x
P182-10%WA1					xxx	xxx	x	x	x
P182-10%WA1-W					xxx	xx	x	x	x
P182-10%WA2					xxx	xx	x	x	x
P182-10%WA2-W					xxx	xx	x	x	x
P182-10%Qz					xxx	xx	xx		x
P365-REF					xxx	xx			x
P365-10%WA1					xxx	xxx	x	x	x
P365-10%WA1-W					xxx	xx	x	x	x
P365-10%WA2					xxx	xxx	x	x	x
P365-10%WA2-W					xxx	xx	x	x	x
P365-10%Qz					xxx	xx	xx		x

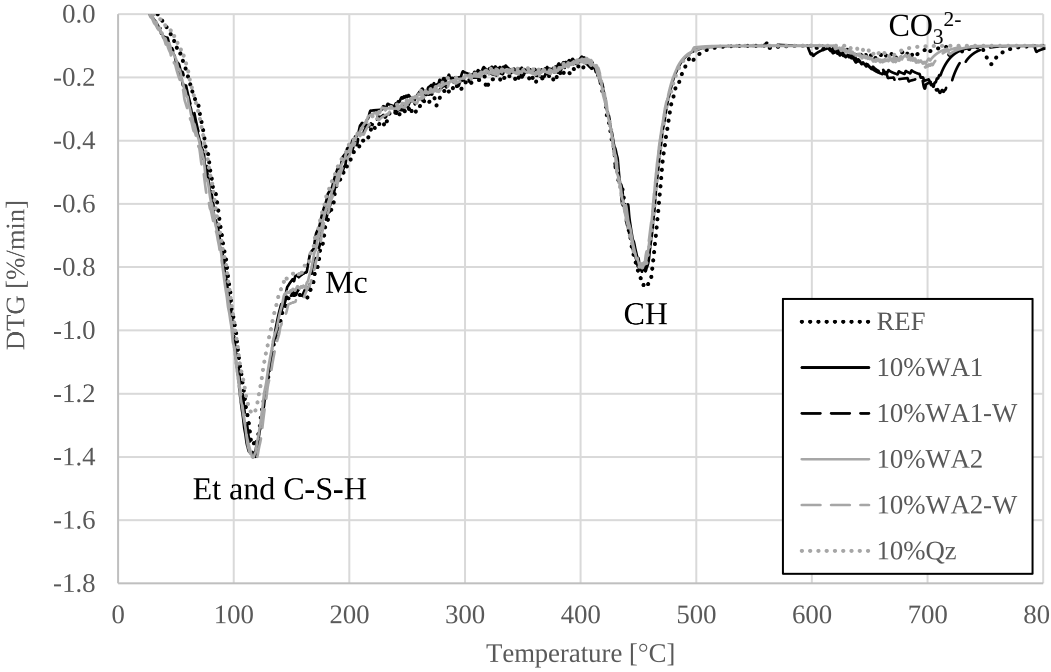

Figure 5. Differential thermosgravimetric (DTG) curves for paste samples investigated at 20°C after 28 days of hydration. Et: Ettringite, C-S-H: Calium silicate hydrate, Mc: Monocarbonate, CH: Portlandite.

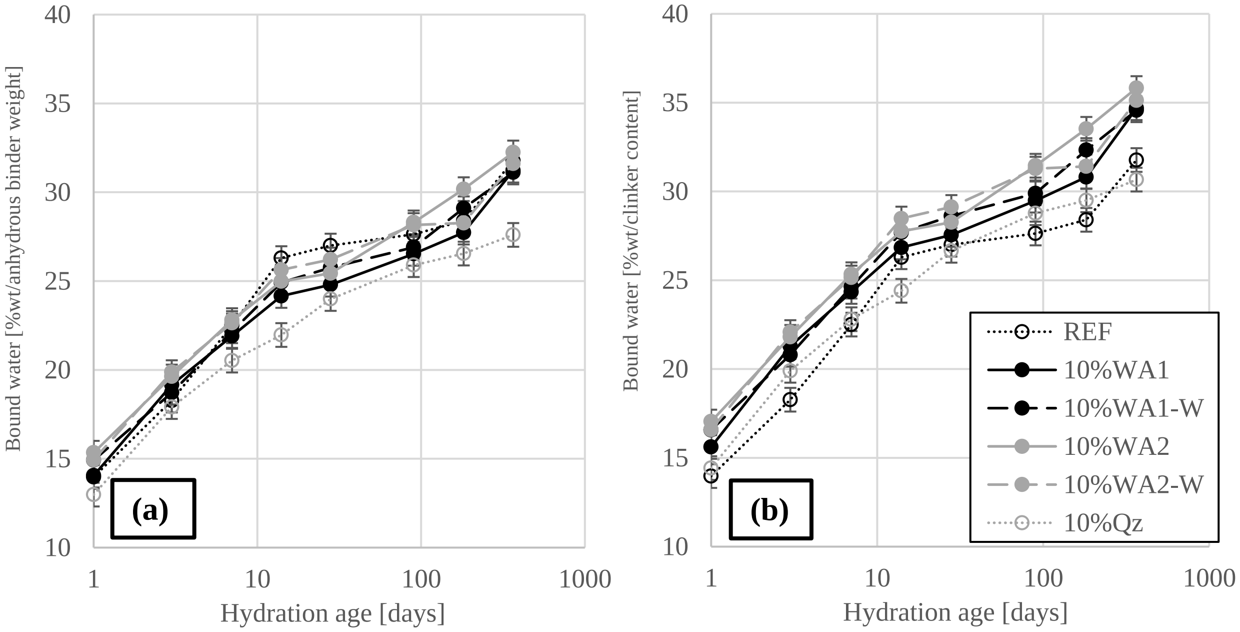

Figure 6. Quantification of bound water in paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The results are normalised to the anhydrous binder (a) and clinker content (b). Standard deviations are based on three independent measurements and quantifications of the bound water of a control sample at 28 days of hydration.

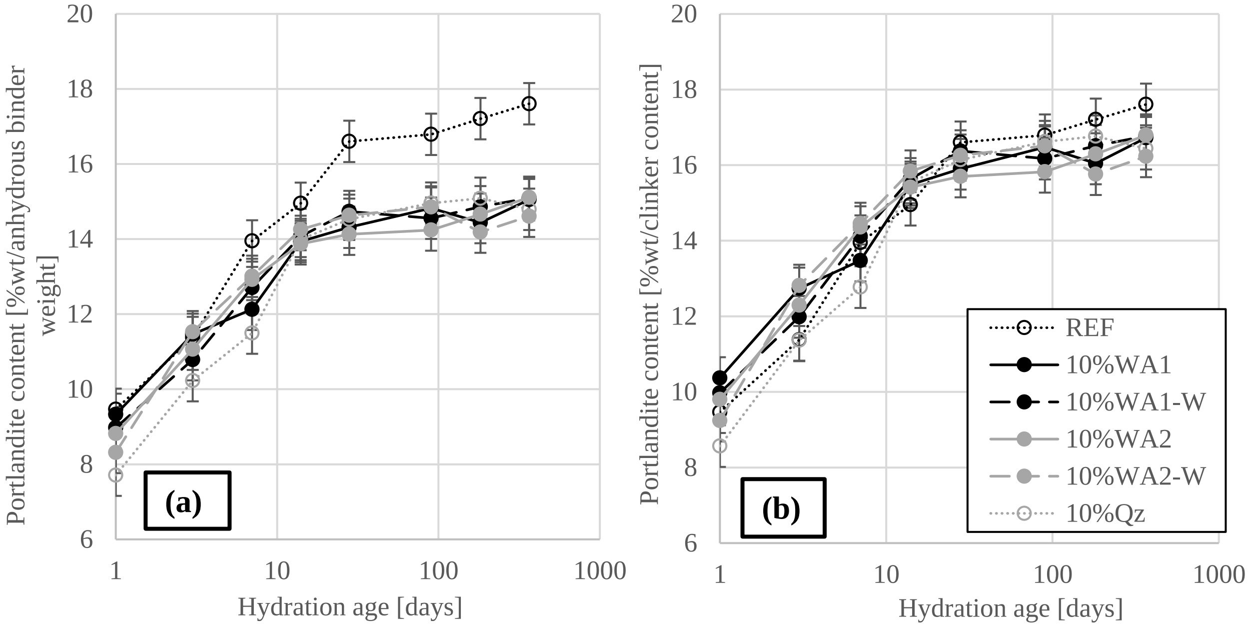

Figure 7. Quantification of portlandite in paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The results are normalised to the anhydrous binder (a) and clinker content (b). Standard deviations are based on three independent measurements and quantifications of the portlandite of a control sample at 28 days of hydration.

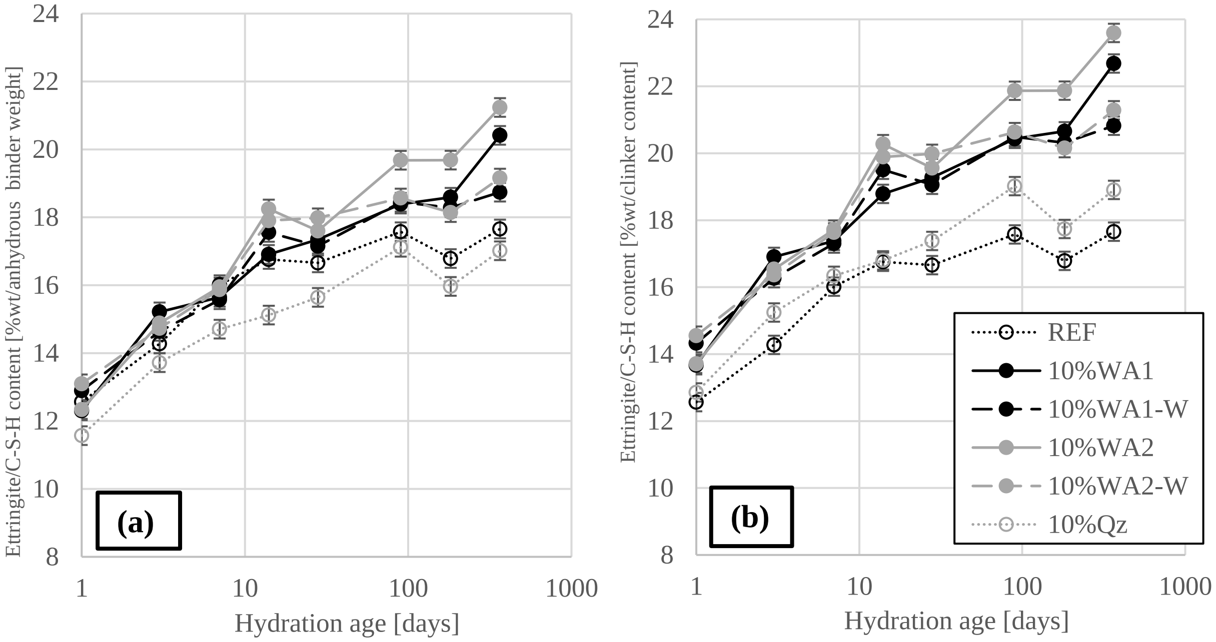

Figure 8. Quantification of ettringite/C-S-H in paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The results are normalised to the anhydrous binder (a) and clinker content (b). Standard deviations are based on three independent measurements and quantifications of the ettringite of a control sample at 28 days of hydration.

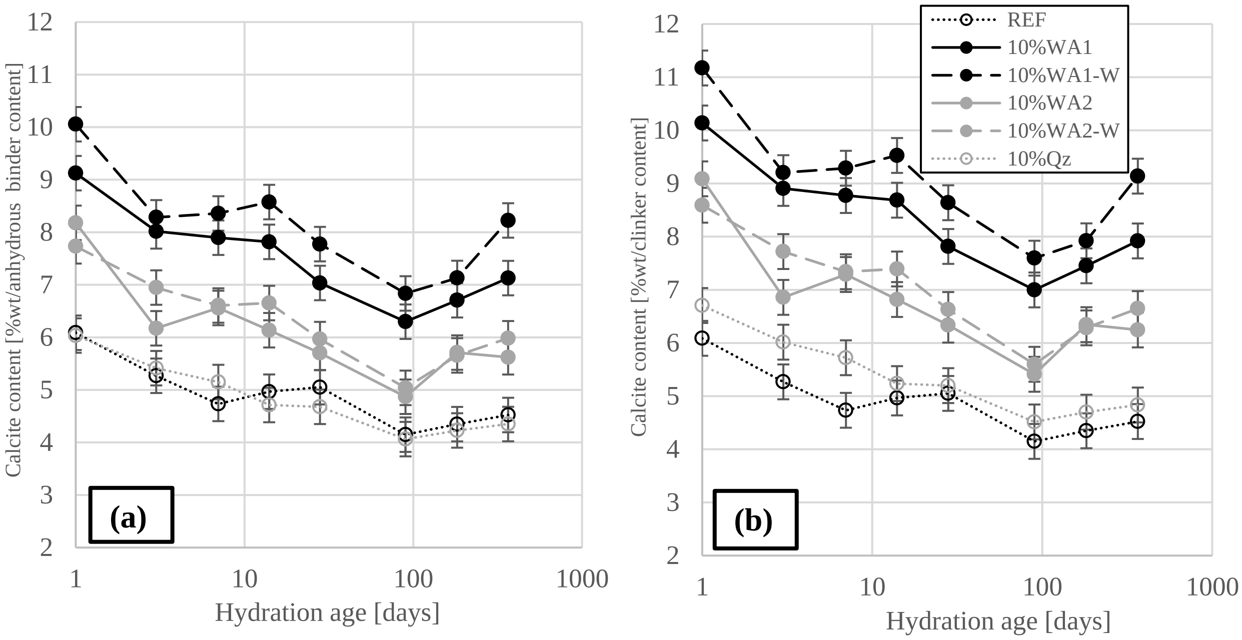

Figure 9. Quantification of calcite in paste samples investigated after 1, 3, 7, 14, 28, 90, 182 and 365 days of hydration at 20°C. The results are normalised to the anhydrous binder (a) and clinker content (b). Standard deviations are based on three independent measurements and quantifications of the calcite of a control sample at 28 days of hydration.

Conference abstract I

CAI: Wood Ashes for Possible Utilisation in Cement-based Materials Evaluated by Multivariate Models

Authors: N. M. Sigvardsen, L.M Ottosen

Platform presentation

Sustain, 2018, Kgs. Lyngby Denmark

Wood Ashes for Possible Utilisation in Cement-based Materials Evaluated by Multivariate Models

Nina Marie Sigvardsen[1], Lisbeth M. Ottosen[1]

1: Technical University of Denmark

As a result of the necessity to mitigate the pressure on the global environment several actions have been taken. 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 100 % carbon neutral fuel by 2050 [1]. The Paris Agreement leads to an increase in the demand for renewable energy and a reorganisation of the existing energy sector, e.g. from the use of coal to alternative, sustainable fuels for energy production by transforming existing plants. Wood is considered an alternative, sustainable fuel for energy production. Coal fly ash (CFA) is utilised in the production of cement or as a cement replacement, reducing the consumption of cement and the associated CO_2 emission. However, the withdrawal of coal-fired power plants results in a decrease in the availability of CFA. Opposite the availability of new types of ashes will increase, such as wood ash (WA) from wood combustion. These new types of ashes are often landfilled, which is both uneconomical and contaminating, making utilisation of alternative ashes, such as WA, in cement-based materials of interest.

Utilisation of WA in cement-based materials depends on the physiochemical characteristics of WA, which again depends on the parameters of production such as the utilised wood fuel, e.g. wood chips or pellet, and on the combustion process, e.g. temperature, and technology [2]. Multivariate modelling was used to identify the link between production parameters and the physicochemical characteristics of WA 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. The combustion method and type of ash (bottom, fly or mix of bottom and fly ash) were seen to have the largest influence on the physiochemical characteristics of WAs compared to the other production parameters included in this study.

Literature

[1] A. Neslen, The end of coal: EU energy companies pledge no new plants from 2020, Guard. (2017). https://www.theguardian.com/environment/2017/apr/05/the-end-of-coal-eu-energy-companies-pledge-no-new-plants-from-2020.

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

Conference abstract II

CAII: Prewashed Wood Ash for Utilization in Cementitious Materials

Authors: N. M. Sigvardsen, J. Pedersen, L.M Ottosen

Poster and pitch presentation

The 2nd International Conference on Sustainable Building Materials, 2019, Eindhoven, Netherlands

Prewashed wood ash for utilization in cement-based materials

Nina Marie Sigvardsen[1], Julie Pedersen[1] and Lisbeth M. Ottosen[1]

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Abstract

In the transition towards a more sustainable energy system, renewable energy sources, e.g. wood, are of significant importance in the withdrawal of the coal-fired power plants. This leads to a decrease in the availability of the by-product coal fly ash, which is traditionally used in the concrete production, and to an increase in the residual waste, wood ash. The performance of wood ash in cementitious materials varies markedly throughout the literature depending on the physicochemical characteristics, determined by, e.g. the wood product, temperature, combustion method, and on pretreatment of the wood ash before utilization. This aim of this study was to determine the influence from the physicochemical characteristics of wood ash from grate combustion of wood pellets and the properties of cementitious materials. The work includes both with partial cement replacements with the untreated (marked WA) and prewashed WA (marked WA-W).

The WA was divided into two portions. One portion was subjected to a washing treatment as follows: WA 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 and the suspension was vacuum-filtered. The morphology of the particles for cement, WA and WA-W was evaluated with SEM. Cementitious materials with 10 wt% cement replacement with WA and WA-W, respectively, were investigated. The w/b-ratio for all mixes was kept at 0.55. The workability was determined according to EN 196-3, the setting time according to EN 196-3 and the compressive strength at 7, 14, 28, 60 and 90 days according to EN 196-1. Development of phases were measured on cement paste with 10 wt% cement replacement with WA and WA-W, respectively, by XRD and TGA at 7, 14, 28, 60 and 90 days. Reference tests were conducted for all test with 100 wt% cement.

Use of WA and WA-W in the mortar mix resulted in a decrease in the workability due to the water absorption of the WA and WA-W and a delay in the setting time compared to reference mixtures. A more distinctive decrease in the compressive strength was seen for WA compared to WA-W. The delayed setting time and the decrease in compressive strength can both be attributed to the clinker dilution effect for both ashes. The rounded particles (filler effect) determined by SEM and the increase in portlandite content determined by TGA for WA-W can explain the higher compressive strength when WA-W is utilized compared to WA. The phase development showed a decrease for portlandite and the ettringite content for pastes containing WA and WA-W, more profound for WA. Thus, the washing treatment of wood ash from grate combustion of wood pellets facilitates a wood ash more suitable for utilization in cement-based materials.

Utilization of wood ash in cementitious materials presents new challenges. However, due to the possibility for hydraulic activity and the particles to function as a filler, the potential for wood ash as a partial cement replacement should be taken into consideration for new and sustainable cementitious materials.

Keywords: wood ash, prewashing, cementitious materials

DTU Civil Engineering
Department of Civil Engineering

Prewashed wood ash for utilization in cementitious materials

Nina Marie Sigvardsen[1], Julie Pedersen[1] and Lisbeth M. Ottosen[1]
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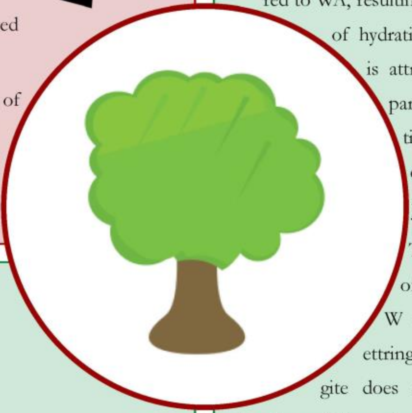
Introduction

- Transitioning towards a more sustainable energy system
- Withdrawal of the coal-fired power plants → limited availability of the coal fly ash
- Wood is being used as fuel in an increasing number of power plants → amount of wood ash increases.

Research questions: Can wood ash be used as cement replacement? Is prewashing beneficial as a pretreatment?



Materials and Methods

- The wood ash was divided into two portions: WA (raw) and WA-W (subjected to a washing treatment, L/S = 5).
- Morphology evaluated by SEM.
- Oxide compostion by TGA and LoI.
- Phase development: cement paste samples, w/b-ratio = 0.55, 10 wt% cement replacement.
- Strength development: mortar samples, w/b -ratio = 0.55, 10 wt% cement replacement.

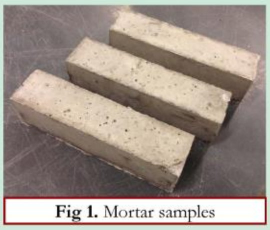


Fig 1. Mortar samples

Characterization

wt [%]	WA	WA-W
Al_2O_3	0.7	1.7
SiO_2	3.2	10.5
Fe_2O_3	1.22	1.24
CaO	42.0	32.2
K_2O	13.3	2.2
MgO	2.7	6.3
MnO	1.5	1.0
Na_2O	1.3	0.4
P_2O_5	2.0	3.0
SO_3	0.6	0.1
Cl	0.64	0.0
LoI	18.0	24.0

Table 1. XRF and LoI

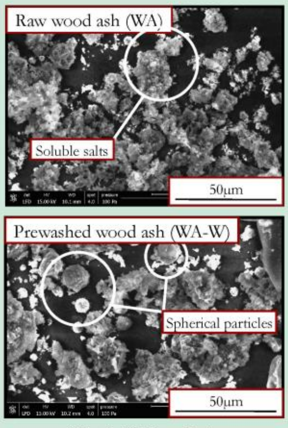


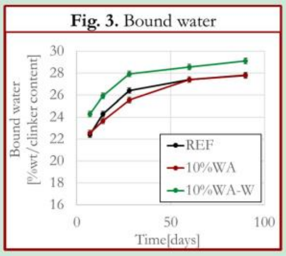
Fig. 2. SEM analysis

Phase and strength development

Bound water

More water is bound for WA-W compared to WA, resulting in a higher degree of hydration for WA-W. This is attributed to spherical particles with low particle size, thus a higher reactivity.

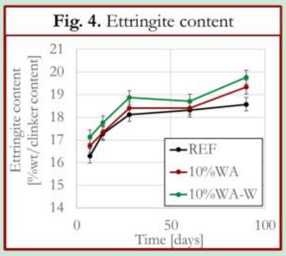
Fig. 3. Bound water



Ettringite content

The higher degree of hydration for WA-W results in a higher ettringite content. Ettringite does not decrease as a function of time due to stabilization of monocarbonate.

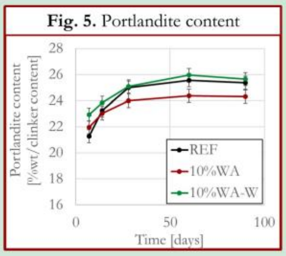
Fig. 4. Ettringite content



Portlandite content

No decrease as a function of time is seen, indicating no pozzolanic reaction.

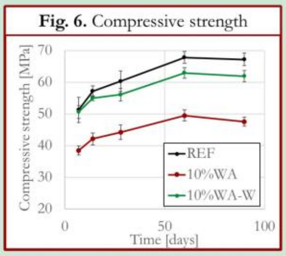
Fig. 5. Portlandite content



Compressive strength

The low compressive strength of WA indicates a prolonging of the induction period due to an increased sulfate content in the pore solution, postponing the crystallization of portlandite and formation of C-S-H. WA-W shows a higher compressive strength, attributed to a higher content of voluminous ettringite, a higher degree of hydration and spherical particles with a low particle size (filler effect).

Fig. 6. Compressive strength



Conclusion

- Prewashing of wood ash results in an SCM more suitable for utilization as a partial cement replacement. The degree of hydration is improved, and a higher content of voluminous ettringite and spherical particles improves the compressive strength.
- Utilizing raw wood ash results in a lower degree of hydration and a postponement of crystallization of portlandite and formation of C-S-H.

Acknowledgement

The work was supported by the Department of Civil Engineering at the Technical University of Denmark and Emineral A/S. HOFOR Amagerværket is acknowledged for supplying the ash.

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Additional Note I

ANI: Impact of strategies for premixing of water and wood ash, when wood ashes are used as partial cement replacement (not published)

Authors: N. M. Sigvardsen

Not published

Additional Note I: Impact of strategies for premixing of water and wood ash, when wood ashes are used as partial cement replacement.

Results from the investigation of the impact of premixing wood ash (WA) and water, when wood ash is used as a partial cement replacement, on flow properties and compressive strength are presented in this additional note.

Fresh cement-based materials are considered Bingham fluids, which are defined by the physical parameters yield stress and plastic viscosity [1]. While the plastic viscosity describes the ease of the flow [2], the yield stress describes the required shear stress necessary to initiate flow [2–4]. The yield stress reflects the extent of flocculation, thus the strength of the attractive interparticle forces responsible for flocculation [1]. Flocculation of the particles is due to low zeta potentials and by van der Waals forces [5].

The yield stress is affected by the water content of the paste and is more sensitive to changes in the binder composition than the plastic viscosity [6], thus, the yield stress has been selected for investigation in this study. As a cement-based material stops flowing when the applied shear stress (gravity) is below the yield stress, flow properties can be related to the yield stress [4,7].

Due to the high water-solubility of WA, (please refer to JPI in the current thesis), an increase in the release of ions into the mixing water, compared to a pure cement binder, can be expected. This can potentially influence the zeta potential and consequently the yield stress. The increased release of ions can further facilitate an increase or decrease in the compressive strength of mortar samples with a partial cement replacement by WA, e.g. alkalis usually lead to an increase in the early strength (≤ 2 days of hydration) and a decrease in the later strength [8].

Materials and methods

Three different WAs were investigated in this study; Amagerværket (WA-A), Skærbækværket (WA1), and Värtaverket (WA2). Production parameters for the WAs are presented in Table 1.

Table 1. Production parameters for WAs

	WA-A	WA1	WA2
Production parameters			
Combustion method	Grate	Grate	Curculating fludized bed
Type of biofuel	Wood pellets	Wood chips	Wood chip
Origin of biomass	Logs	Whole trees	Whole trees
Combustion temperature	1,000 – 1,100°C	600 – 1,000°C	760 – 930°C

WA characterisation

The element content was determined by X-ray fluorescence (XRF) spectrometry measured on a SPECTRO Gmbh X-LAB 2000 with a Pd-tube on samples ground to a particle size of less than 200µm. TQ-3945r (software) was used for the analysis, and the oxide content was calculated based on the measured element content. Loss on ignition (LoI) was measured at 950°C, according to EN 196-2 [9]. The pH of each WA was measured by a pH electrode in a 1:2.5 solid to liquid ratio suspension in distilled water after 1-hour of stirring with a magnetic stirrer. The water solubility was determined by mixing 100g WA with distilled water at a 1:5 solid to liquid ratio and shaken manually for 1 min [10]. This procedure was repeated three times, the suspension was filtered (filter retention was 12-15µm), the ash (retentate) was dried at 50°C, and subsequently weighed to calculate the water-soluble fraction. The content of water-soluble cations and anions were measured, on a 1:2.5 solid to liquid ratio suspension of WA in distilled water after 24-hour agitation, using inductively coupled plasma atomic emission spectroscopy (ICP/OES) and ion chromatography (IC), respectively. Results are presented in Table 2.

Mortar samples, flow values and compressive strength

Mortar mixes were prepared as prescribed in EN 196-1 [11], modified with a w/b = 0.55 for all mixtures. Four mixtures were tested: One control mixture (REF) and three mixtures with 10% cement replacements with each of the WAs, respectively. Four different mixing strategies were tested: one with no premixing (0 sec), and three with premixing of WA and water (15 sec, 2.5 hours, and 24 hours). Premixing was performed by mixing the WA and 4/5 of the water in a container and placed it on an agitating table for 15 sec, 2.5 hours, or 24 hours. The last 1/5 water was added to the premixed WA and water during mixing of the mortars.

The flow values were measured for each casting, according to EN 1015 [12]. Three mortar prisms were cast, in accordance with EN 196-1 [11], for each mixing strategy for each compressive strength test. The mortar prisms were demoulded after 1 day of storage in a temperature-controlled room (20°C) and stored in separate boxes submerged in lime water (3 g/L calcium hydroxide in distilled water [13]) in the temperature-controlled room (20°C). The compressive strengths of the mortar prisms were tested after 1, 2, 3, 7, and 28 days of hydration according to EN 196-1 [11]. First the mortar prisms were split into two by the use of an electro-mechanic test machine (Instron 6022) by increasing the load by 0.05 kN/s [11] until the prism split in two. The compressive strength of the subsequent pieces of mortar were then tested with a servohydraulic test machine (Toni Technik 300Ton) by increasing the load by 2.4 kN/s [11] until failure.

Main results

The physicochemical characteristics in Table 2 show significant differences between each WA. The variations in WA are greatly determined by the combustion method, please refer to JPI in the current thesis.

Table 2. Physicochemical characteristics of WAs and CEM I

	WA-A	WA1	WA2	CEM I
Chemical composition (%)				
SiO_2	3.2	11.0	23.8	19.7
Al_2O_3	0.7	2.4	5.6	5.4
Fe_2O_3	1.2	2.9	3.1	3.8
CaO	42.0	53.6	44.7	64.1
MgO	2.7	4.2	4.1	1.0
K_2O	13.3	14.6	7.6	0.4
Na_2O	1.3	1.0	0.8	0.3
P_2O_5	2.0	2.9	3.8	0.3
SO_3	3.7	5.4	6.1	3.2
LoI, 950ºC	16.7 ± 0.1	15.0 ± 0.1	16.2 ± 0.3	1.9 ± 0.0
Physical characteristics				
Water solubility (%)	15.7 ± 0.1	8.4 ± 0.3	1.7 ± 0.2	-
pH	13.61 ± 0.0	13.2 ± 0.1	12.7 ± 0.1	12.8 ± 0.0

Table 3 shows that WA1 has the largest content of water-soluble chloride, and WA-A has the largest content of water-soluble sulfate.

Table 3. Selected water-soluble ions in WA suspensions (mol/l) (<DL = below detection limit)

	WA-A	WA1	WA2
Cl^-	0.6 ± 0.0	0.9 ± 0.0	0.4 ± 0.0
SO_4^{-2}	1.5 ± 0.0	1.6 ± 0.0	0.5 ± 0.0
Ca^{2+}	< DL	0.2 ± 0.0	0.1 ± 0.0
K^+	< DL	< DL	7.0 ± 0.1
Na^+	0.5 ± 0.0	0.3 ± 0.0	0.2 ± 0.0
Ca^{2+}/SO_4^{-2}	0.02	0.12	0.11

The flow values for the three WAs with different premixing times are presented in Figure 1.

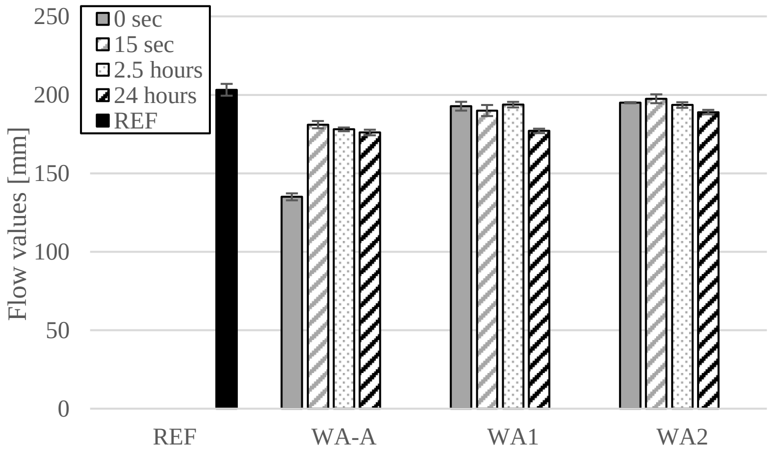

Figure 1. Flow values for mortars with different premixing durations. Standard deviations are shown by error bars.

All WA mortars obtained lower flow values than the reference (REF). Little to no difference is seen between the flow values for WA2 mortars with different premixing times. On the contrary, the flow value for WA-A without premixing was considerably lower than with premixing, while WA1 had a lower flow value after 24 hours premixing.

The development in compressive strength of the WA and REF mortars is shown in Figure 2 to Figure 4.

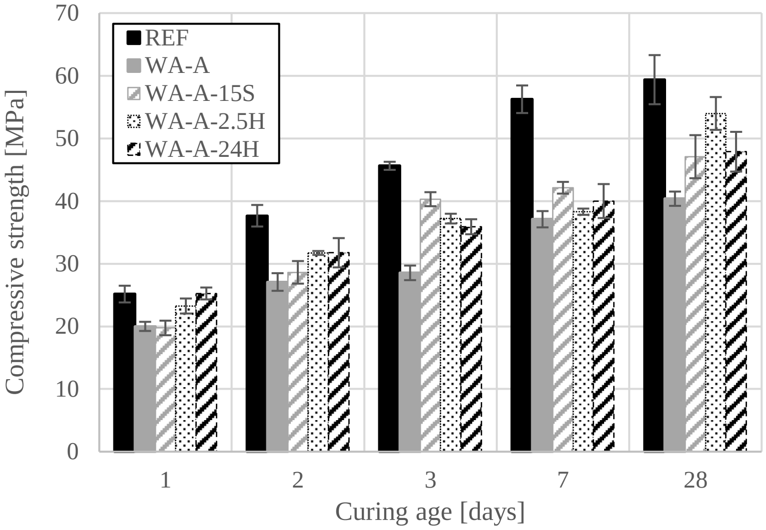

Figure 2. Compressive strength of mortar prisms with 10% cement replacement with WA-A and REF at 1, 2, 4, 7, and 28 days of hydration, with and without premixing of water and WA. Standard deviations are shown by error bars.

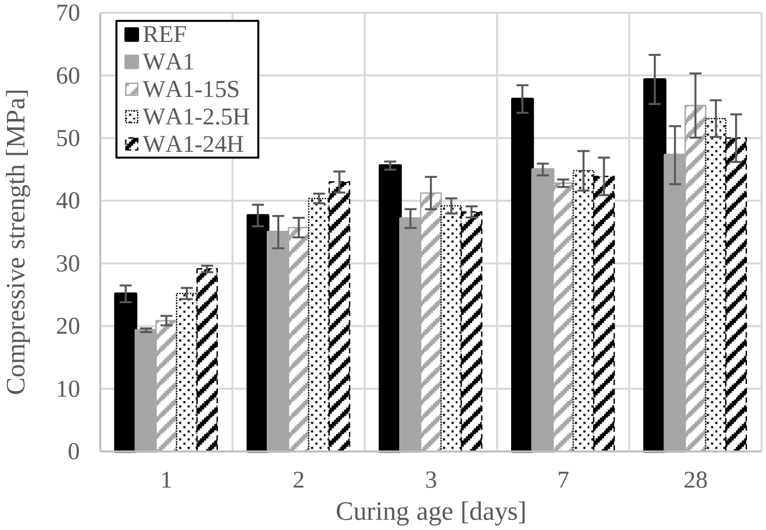

Figure 3. Compressive strength of mortar prisms with 10% cement replacement with WA1 and REF at 1, 2, 4, 7, and 28 days of hydration with and without premixing of water and WA. Standard deviations are shown by error bars.

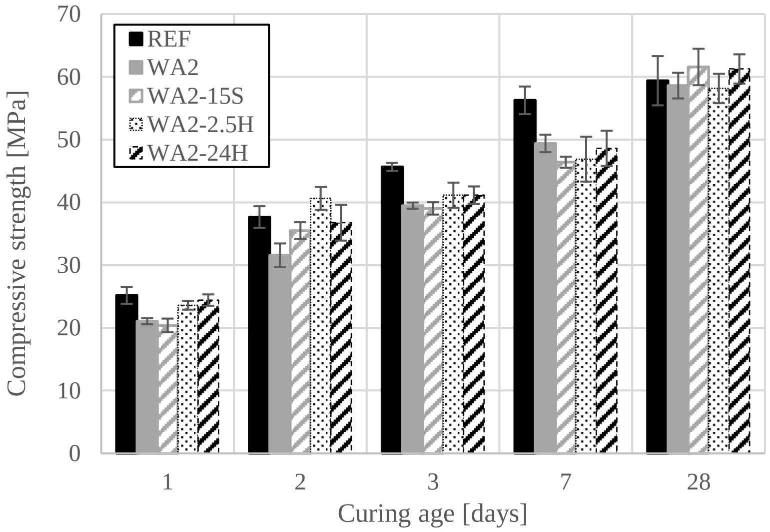

Figure 4. Compressive strength of mortar prisms with 10% cement with WA2 and REF at 1, 2, 4, 7, and 28 days of hydration with and without premixing of water and WA. Standard deviations are shown by error bars.

For all WA mortars a difference was seen between the compressive strength at 1 and 2 days of hydration, increasing the compressive strength when premixing of WA and water is applied. A general tendency of higher compressive strength at early age correlating with longer mixing times is evident for all WA mortars, except WA2-24H at 2 days of hydration.

Between 3 and 7 days of curing, all WA mortars obtained lower compressive strength than REF without a clear correlation between the premixing durations. An increase in strength is seen as a result of the premixing for WA-A mortars, while no significant difference is seen between premixing and no premixing for WA1 and WA2 mortars.

At 28 days all mortars containing WA2 obtain compressive strength at the same level as REF, i.e. there was no loss in compressive strength by the partial replacement of cement with WA2. For mortars with WA-A and WA1 a slight relation between the compressive strength and premixing is observed, with premixed mortars obtaining a higher compressive strength than mortars with no premixing.

Discussion

A large difference is seen between the flow values for WA-A with and without premixing of water and WA-A regardless of the premixing duration. This can most likely be attributed to the dispersion of WA particles, when water and WA-A are premixed, leading to a lower degree of flocculation of the WA-A particles in the mortar mix, increasing the flow value and decreasing the yield stress. No significant difference is seen between the flow values for WA1 and WA2, thus no significant flocculation of the WA1 and WA2 particles is expected. However, an investigation of the microstructure is necessary in order to eliminate flocculation entirely.

The zeta potentials of cement and mineral additions were determined by Lowke and Gehlen [14] to increase with the molar concentration ratio of Ca/SO_4. An increase in the zeta potential also facilitates an increase in flow values due to low flocculation of the particles. The molar Ca/SO_4 concentration ratios were calculated based on the water-soluble ions presented in Table 3 and are as follows WA-A = 0.02, WA1 = 0.12 and WA2 = 0.11, thus it follows that: WA1 ≈ WA2 > WA-A.

The WAs generally have a high LoI compared to traditional coal fly ash. The presence of organic material leads to absorption of water molecules by the particles [6,15,16]. The relationship between LoI values for the WA are: WA2 ≈ WA-A > WA1.

The different WA replacements increases the average flow values in the following order: WA2 ≈ WA1 > WA-A. The observed order corresponds to the molar Ca/SO_4 concentration ratios and the increase in zeta potential, and does not correspond to the water absorption by the WAs due to LoI. Thus, the flow values are more dependent, to some extent, on flocculation of the particles in WA cement mixtures, depended on the water-soluble ions, than the water availability. This stresses the difference between the three different types of WAs, where some are prone to flocculation of the WA particles leading to a decrease in the flow values, if the WA particles is not properly dispersed before mixing.

A slight correlation can be seen between the flow values and compressive strength for WA-A, in that all premixed samples (except WA-A-15s at 1 day of hydration) obtain higher compressive strength than mortars without premixing. At 2 days of hydration, comparable strength is observed between the WA1 mortars and REF, and to some extent also between WA2 mortars and REF. As no general correlation in flow values or pre-mixing time are observed, the compressive strength is attributed to the high content of alkalis, calcium, chloride and sulfate, which can act as hydration accelerators [17]. This leads to an increase in the early compressive strength (≤ 2 days of hydration) and a decrease in the later strength (≥ 3 days of hydration) [8], corresponding with the compressive strength at ≥ 3 days of hydration. In general, when WA1 or WA2 are used as partial cement replacements no clear correlation is observed between the premixing time of the WAs and water and the resulting compressive strength.

Conclusion

In some cases, the dispersion of WA particles prior to mixing, by premixing of water and WA, are associated with improvements in the flow properties of cement-based materials. Not all WAs benefit from a premixing method, it is therefore necessary to conduct initial tests of new WAs. The flow values should be determined in accordance with EN 1015 [12], for a mixture with (minimum 15s) and without premixing of water and WA. If an improvement of the flow values is observed with premixing, it would be recommended to include a premixing procedure when casting with the WA.

Acknowledgement

This note is based on experimental work performed by MSc students Jonas Holmer Bigom and Oliver Kragelund Vittrup at DTU, who are acknowledged for their skilled and thorough execution of the experiments. Värtaverket Combined Heat and Power Plant, Skærbæk Power Plant and Amager Power Plant are acknowledged for supplying the investigated wood ashes.

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Additional Note II

ANII: Leaching Characteristics of Mortars with Wood Ash used as a Low-Level Cement Replacement (not published)

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Not published

Additional Note II: Leaching Characteristics of Mortars with Wood Ash used as a Low-Level Cement Replacement.

WAs could potentially present an environmental risk due to their content of the heavy metals: Cd, Cr, Cu, Ni, Pb, and Zn [1,2]. This additional note focuses on the heavy metal content and leaching properties of mortars with a low-level cement replacement with WA.

Materials and Methods

Two WAs were investigated in this study, one from Skærbækværket Biomass Power Plant, Denmark (WA1) and one from Värtaverket Combined Heat and Power Plant, Sweden (WA2). Traditional coal fly ash (CFA) from Amagerværket, Denmark is included as a reference for comparison. An overview of the production parameters for WA1, WA2 and CFA are provided in Table 1.

Table 1. Production parameters for WA1, WA2, and CFA.

	WA1	WA2	CFA
Production parameters:			
Ash type	Fly ash	Fly ash	Fly ash
Combustion method	Grate	Curculating fludized bed	Pulverized coal-fired boiler
Type of biofuel	Wood chips	Wood chip	Coal
Origin of biomass	Whole trees	Whole trees	-
Combustion temperature	600 – 1,000°C	760 – 930°C	1500°C

Both WAs were divided into two portions. The first portion was dried at 50°C and sieved to a particle size of ≤ 250μm (henceforth noted as WA1 and WA2). The second portion was subjected to a washing treatment (henceforth noted as WA1-W and WA2-W). The washing was performed by mixing 100 g ash with 500 g distilled water, shaking manually for 1 min [3] and then precipitating (app. 5 min.). After precipitation, the water was decanted and the WA was dried at 50°C until constant mass. This procedure is further elaborated in JPIII in the current thesis.

Concentrations of Cd, Cr, Cu, Ni, Pb and Zn were measured after pre-treatment of the ash in accordance with DS259 [4]: 1.0 g ash and 20.0 ml (1:1) HNO3 were heated to 120 °C at 200 kPa for 30 minutes then filtered through a 0.45 µm filter. The heavy metal concentrations in the filtrate were then measured by inductively coupled plasma – optical emission spectrometry (ICP-OES).

Mortar cubes (50 x 50 x 50mm) were cast with ordinary Portland cement (CEM I) and with 10% cement replaced by each of the four wood ashes and CFA, respectively. Three cubes were cast with each composition. The mixtures were prepared in accordance with EN 196 [5], cast in 50 x 50 x 50mm moulds and after 1 day in a temperature-controlled room (20°C), the cubes were demoulded and cured for 21 days in an incubator with 90 ± 1% RH at 20°C.

The solubility determined leaching of heavy metals was measured in accordance with EN 12457 [6] on cubes crushed to a particle size ≤ 4 mm at liquid-to-solid ratios of 2 and 10. The concentrations of Cd, Cr, Cu, Ni, Pb and Zn were measured in the leachate using ICP-OES. This test simulated the worst-case end-of-life scenario where the concrete is completely crushed and exposed to water.

Tank leaching tests were to simulate the leaching properties of pollutants during the service-life of the concrete [7]. The tank leaching of heavy metals was determined on cubes submerged in water acidified with 1.0 M HNO_3 to pH 4 at a L/S = 4 in accordance with NEN 7345 [8]. 20 mL of leachate was extracted after, 0, 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days, and 20 mL of water was added to the vessel containing the submerged cube to replace the extracted leachate. The concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the leachate were determined by ICP-OES.

Main Results

The total concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the four wood ash samples, CFA and CEM I are presented in Table 2.

Table 2. Elemental compositions of WA1, WA1-W, WA2, WA2-W, CFA, and CEM I, and regulation limits from the Danish Decree BEK nr. 1672 [9], category 1. ± indicates the standard deviation.

	WA1	WA1-W	WA2	WA2-W	CFA	CEM I	Regulation limit, cat 1
Total concentrations (mg/kg)							
Cd	10.9 ± 0.2	16.0 ± 0.4	9.8 ± 0.5	11.1 ± 0.3	0.3 ± 0.1	0.4 ± 0.1	0 – 0.5
Cr	23.7 ± 1.1	22.4 ± 1.1	28.8 ± 0.8	27.7 ± 0.8	29.9 ± 0.8	33.7 ± 0.7	0 – 500
Cu	155 ± 4	131 ± 2	77.5 ± 12.5	74.6 ± 1.5	15.3 ± 0.3	139.6 ± 3.2	0 – 500
Ni	20.4 ± 0.8	23.1 ± 0.5	19.5 ± 0.2	21.2 ± 0.4	15.1 ± 0.5	24.3 ± 0.6	0 – 30
Pb	85.9 ± 2.2	83.2 ± 1.6	56.2 ± 13.5	54.5 ± 1.1	26.2 ± 1.1	16.7 ± 0.5	0 – 40
Zn	1,700 ± 46	1,800 ± 31	386 ± 43	371 ± 4.0	18.1 ± 2.1	184 ± 15	0 – 500

The concentrations of the all heavy metals included in the current investigation, with the exception of Cr, are higher in WA1 than in WA2, especially Zn which is 4.4 times higher, see Table 2. Likewise, in the washed WAs the concentrations in WA1-W are higher than in WA2-W, except for Cr. The washing reduces the concentrations of Cr, Cu and Pb for both WAs, and also for Zn in WA2. While, increased concentrations of Cd, and Ni are seen for both WAs and also for Zn in WA1, as a result of the washing.

Danish Decree BEK nr. 1672 [9] set the requirements for waste being used in construction work. Three categories are defined by the concentrations of heavy metals in the material, where category 1 is approved for the greatest number of applications and therefore has the strictest requirements. Due to the concentration of Zn in WA1 and WA1-W, and Cd and Pb in all WAs exceeding the limit set by category 1, see Table 2, all WAs tested here were placed in category 2.

The solubility determined leaching concentrations of Cd, Cr, Cu, Ni, Pb and Zn at L/S = 2 and L/S = 10 are shown in Figure 1.

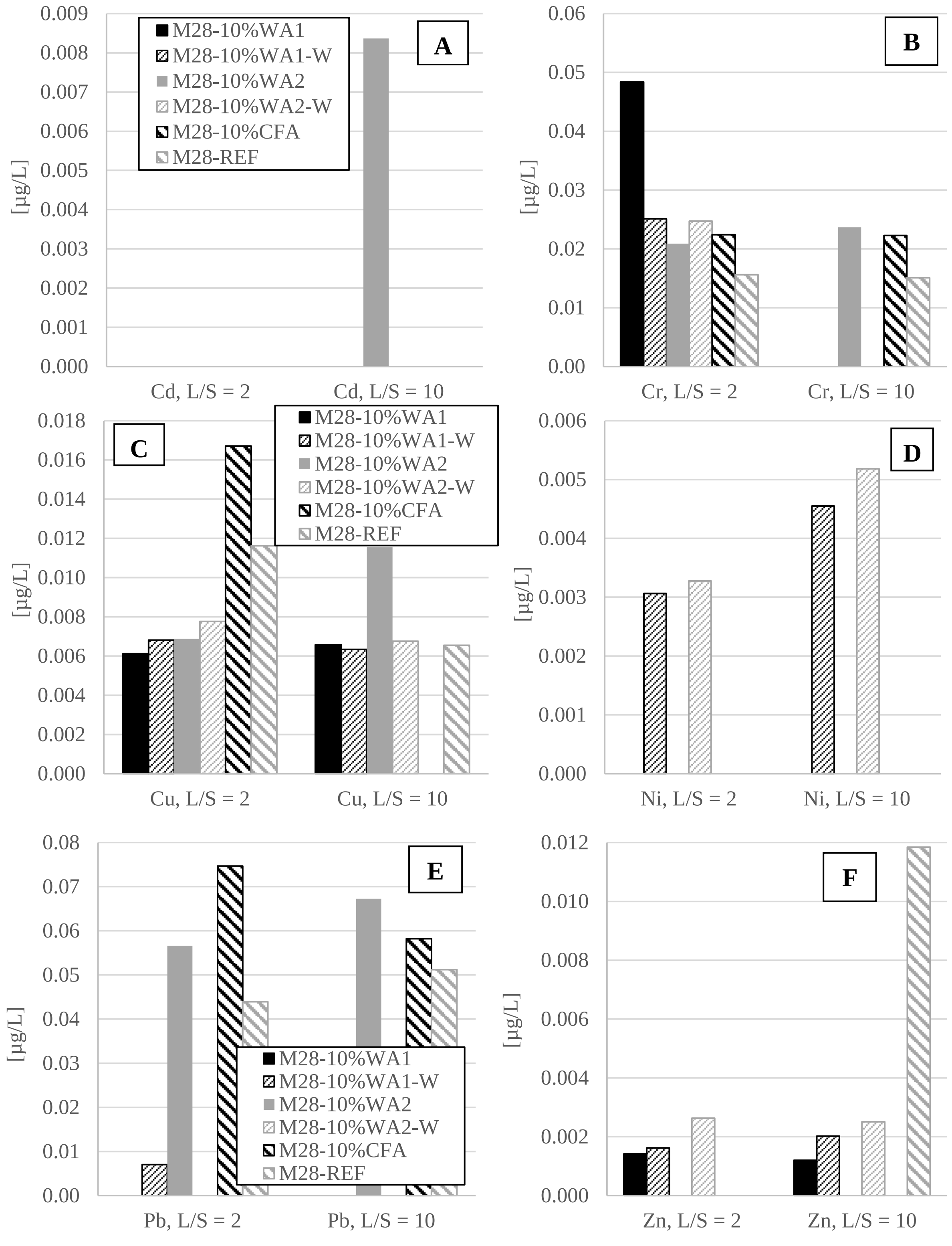

Figure 1. Solubility determined leaching of Cd (A), Cr (B), Cu (C), Ni (D), Pb (E), and Zn (F) in µm/L measured on crushed WA, CFA and REF mortar cubes at L/S = 2 and L/S = 10.

Notably, washing of the WAs did not lead to decreased leaching of Cu, Ni and Zn. On the contrary, the leaching of these heavy metals was higher from the mortars with washed WAs than the mortars with untreated WAs (except Cu for L/S = 10). Increased leaching was generally observed for L/S 10 compared to L/S 2, except for Cr where the opposite trend is observed. This suggests that leaching for the majority of the heavy metals is solubility controlled. The Cr leaching from pure WA is highly pH dependent, at an alkaline pH of 12-13 Cr starts to leach rapidly [10]. The lower leaching of Cr at L/S 10 is likely because pH in this leachate was slightly lower than in the leachate at L/S 2.

Often concrete is crushed and used under e.g. road constructions, therefore the limiting values of the Danish Decree BEK nr. 1672 [9] based on crushed concrete are a highly relevant comparison for leaching results. Three categories according to the heavy metal concentrations and leaching of heavy metals based on leaching tests are given in EN 12457 [6]. Category 1 is the strictest category, having the most approved applications among the three categories. Category 1 is restricted by: 2µg Cd/L, 10µg Cr/L, 45µg Cu/L, 10µg Ni/L, 10µg Pb/L, and 100µg Zn/L, to which all of the WAs at both L/S 2 and L/S 10 comply.

The tank leaching test was conducted according to NEN 7345 [8]. Samples were measured over 64 days (after 0, 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days) and the measured heavy-metal concentrations were very low throughout the experiments. The highest leached concentration measured for each heavy metal is listed in Table 3. The limiting values regulated in Dutch building material decree (BMD) used in Quijorna et al. [7] are also used here for comparison.

Table 3. The highest concentrations of diffusion controlled leaching of Cd, Cr, Cu, Ni, Pb, and Zn [mg/m^2] for WA, CFA and REF mortar cubes measured at 0, 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days. Regulation limit in mg/m^2 from the Dutch Building Material Decree [7].

Heavy metal	WA1	WA1-W	WA2	WA2-W	CFA	CEM I	Regulation limit
Cd	0.1	0.1	0.0	0.1	0.0	0.1	12
Cr	1.1	0.5	1.5	0.7	0.9	1.1	1500
Cu	1.9	1.0	0.6	0.9	0.4	0.5	540
Ni	2.1	1.1	0.8	1.7	0.6	0.6	525
Pb	0.0	0.0	0.0	0.0	0.0	0.9	1275
Zn	0.0	0.0	0.4	0.0	0.6	0.6	2100

From the results presented in Table 3, it is evident that the tank leaching of heavy metals from WA mortars are very limited, all lying significantly below the regulation limit.

Discussion

When compared to CFA, all WAs have higher total concentrations (Table 2) of Cd, Cu, Ni, Pb and Zn, but lower concentrations of Cr. The concentrations of Cd, Pb, and Zn for all WAs and Cu for WA1 are higher than for pure CEM I. According to the standard DS/EN 206 DK NA [11], the addition of a bio-ash to a cement-based material must not lead to an increase in the heavy metal content above 25% of the initial content in the cement-based material. It should be noted that the bio-ash included in DS/EN 206 DK NA [11] only refers to sewage sludge ash. The percentage increase or decrease in the content of heavy metals for the cement and WA blends, with increasing replacement rates are presented in Table 4 and Table 5. Values exceeding the 25% limit are highlighted in bold.

Table 4. Heavy metal contents of Cd, Cr, Cu, Ni, Pb, and Zn as percentwise increases compared to pure CEM I as a result of increasing the level of cement replacement with WA1 or WA1-W.

	Replacement rate with WA1					Replacement rate with WA1-W				
	10%	15%	20%	25%	30%	10%	15%	20%	25%	30%
Cd	***262***	***393***	***524***	***655***	***786***	***389***	***584***	***778***	***973***	***1168***
Cr	-3	-4	-6	-7	-9	-3	-5	-7	-8	-10
Cu	1	2	2	3	3	-1	-1	-1	-2	-2
Ni	-2	-2	-3	-4	-5	0	-1	-1	-1	-1
Pb	***41***	***62***	***83***	***103***	***124***	***40***	***60***	***79***	***99***	***119***
Zn	***82***	***124***	***165***	***206***	***247***	***88***	***131***	***175***	***219***	***263***

Table 5. Heavy metal contents of Cd, Cr, Cu, Ni, Pb, and Zn as percentwise increases compared to pure CEM I as a result of increasing the level of cement replacement with WA2 or WA2-W.

	Replacement rate with WA2					Replacement rate with WA2-W				
	10%	15%	20%	25%	30%	10%	15%	20%	25%	30%
Cd	***235***	***352***	***470***	***587***	***705***	***267***	***401***	***535***	***668***	***802***
Cr	-1	-2	-3	-4	-4	-2	-3	-4	-4	-5
Cu	-4	-7	-9	-11	-13	-5	-7	-9	-12	-14
Ni	-2	-3	-4	-5	-6	-1	-2	-3	-3	-4
Pb	24	***35***	***47***	***59***	***71***	23	***34***	***45***	***56***	***68***
Zn	11	16	22	***27***	***33***	10	15	20	***25***	***31***

For 10% replacement of cement with WA1 or WA1-W, Cd, Pb, and Zn all exceed the 25% increase limit (Table 4, bold). For 10% replacement of cement with WA2 or WA2-W only Cd exceeds the 25% limit, at 15% replacement Pb also exceeds the limit and at 25% replacement Zn also exceeds the limit (Table 5, bold). Thus according to DS/EN 206 DK NA [11], the content of Cd, Pb and Zn could constitute an issue if the cement replacement levels are not regulated.

From the data presented in Figure 1 and Table 3, both solubility and diffusion determined leaching are limited.

The solubility determined leaching of Cd (Figure 1, A) is absent for all ashes except for WA2 mortar at L/S = 10, but only at 0.0084 µg/L which is neglectable compared to the 10 µg/L limit. Pb (Figure 1, E) is absent for all ashes except for WA2 mortar at L/S = 10, reaching the same values as traditional CFA. Lower amounts of Zn (Figure 1, F) than in traditional CFA are found in WA1, WA1-W and WA2-W mortars, although values increase with an increase of the L/S ratio. According to DS/EN 206 DK NA [11], Cu and Ni (Figure 1, C and D) do not present a problem when using either of the WAs as a partial cement replacement, but the solubility determined leaching is seen to increase as a result of an increase in the L/S ratio. An increase in the solubility determined leaching indicates that more of the heavy metal can be dissolved in the water before equilibrium is achieved. For Cr (Figure 1, B) the opposite tendency is observed, here the concentration decreases as a result of an increase in the L/S ratio. This is attributed to a slightly higher pH at the lower L/S ratio [6], and the heavy metal solubility not being concentration but pH dependent.

Ni and Cr are the heavy metals mostly leached by diffusion determined leaching, see Table 3. All concentrations measured for diffusion determined leaching are very low, and neither Ni or Cr are determined to pose an issue regarding the total content of heavy metals restricted by DS/EN 206 DK NA [11].

Conclusion

Fly ash from combustion of wood and woody products contains heavy metals of environmental concern, Cd, Cr, Cu, Ni, Pb, and Zn. According to DS/EN 206 DK NA [11], only Cd, Pb and Zn could potentially pose a risk. However, both the soluble and diffusion determined leaching of heavy metals from mortar cubes with 10% cement replacements was determined to be very low. This indicates the blended cements have a high heavy metal immobilization capacity, and thus pose little risk to the environment.

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Appendices

Appendix A: Multivariate Analysis

Multivariate analysis (MVA) is a set of statistical models used to analyse patterns in multidimensional data by considering several data variables at once. This is achieved by reducing the number of dimensions, making it simpler to visualise and analyse trends in the data set. MVA has been widely used in numerous areas including data compression [105], e.g. developing and optimising different processes [67]. This appendix introduces the multivariate models, principal component analyses (PCA) and projections onto latent structures (PLS), used in this PhD project.

Principal Component Analysis

Principal component analysis (PCA) identifies differences and similarities in large data set by simplifying the variation without loss of systematic information [106].

PCA is based on a matrix (X) of data, where the rows represent objects (N), and the columns represent the values recorded for each observation, termed variables (K) [67], see Figure 20. In JPI, N are the types of wood ash samples, and K are the recorded physicochemical characteristics of each of the wood ash samples. This results in an X matrix with N = 11 objects and K = 28 variables.

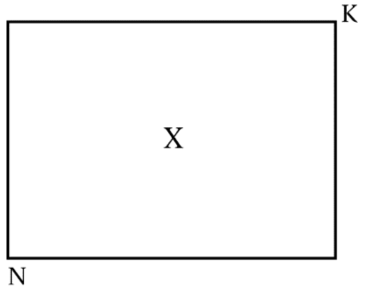

Figure 20. X matrix with N objects and K variables. Figure adapted from Dunn, 2019 [67].

For a simplified geometrical explanation of the method, we consider an X matrix with only 3 variables, K = 3, hence a 3-dimensional space (Figure 21). The N objects are presented as a swarm of points.

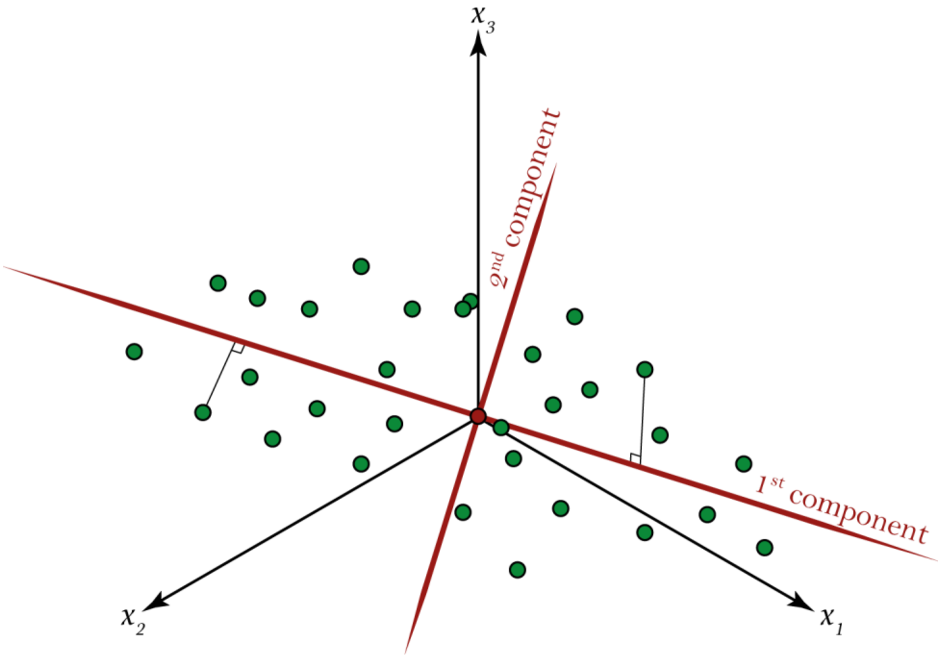

Figure 21. A 3-dimensional descriptor space (3 variables) with a swarm of data point. Figure adapted from Dunn, 2019 [67].

A best-fit line, 1st principal component (PC1), is drawn through the swarm of points, see Figure 21. The objects in the swarm are subjected to a 90-degree projecting of each object onto the line. The distance from this projected point on the line to the origin (intersection of axes) is referred to as a score value. There is one score value for each object, so we obtain N score values. PC1 is determined as the best fit-line, best explaining all the observation with minimum residual error (distance from the point to the projected point on PC1). Principal components are also known as latent variables [67].

The 2nd principal component (PC2) starts at the origin and is orthogonal to PC1, where the minimum residual error (distance from the point to the projected point on PC2), is found [67], see Figure 21.

PC1 and PC2 define a plane, which is the latent variable model with two principal components. If more principal components are added, it will be referred to as a hyperplane. If there still is a systematic variation left after fitting PC1 and PC2, additional principal components are fitted orthogonal to the previous component, until no more systematic variation can be found [67].

Loading plots are obtained by projecting the original variables (K) onto the principal components based on the loadings. Loading is a measure of how the original variables contributed to creating the principal component. This can be graphically displayed, by plotting the original variables (K) against each other in loading plots, e.g. PC1 vs PC2. Variables that are strongly correlated will have approximately the same loading and will appear close to each other. Variables that are inversely correlated will be projected opposite to each other, with respect to the axis centre. Further variables with a strong contribution to the variation will be plotted far from the origin (intersection of axes) and variables with minor contribution will be plotted close to the origin [67].

Projections onto Latent Structures

Projections onto latent structures (PLS) calculate the relation between a descriptor matrix (X) and a response matrix (Y) [106], thus describing the correlation between the X and Y matrix.

For both matrices, X and Y, the rows represent objects (N). The columns that represent variables in the X-matrix (descriptors) are given by K, and columns representing variables in the Y-matrix (responses) are given by M [67]. In JPI, N are the types of wood ash samples, K are the production parameters, and M are the measured physicochemical characteristics for each of the wood ash samples. This results in a X matrix with N = 11 objects and K = 6 variables, and a Y matrix with N = 11 objects and M = 28 variables.

The relationship between all these variables [67] can be obtained by combining the loadings w^* and c [107] in a loading plot. w^* combines the original X variables (K) to form the X scores, where c displays the correlation between the original Y variables (M) and the X scores [108]. The loadings w^* and c is combined into one vector w*c for the loading plot, and from this plot interpretation of how the X and Y variables are combined as well as how the X variables (K) relates to the Y variables (M), is possible [108]. Similar to PCA, strongly correlated variables are projected close to each other, inversely correlated variables are projected opposite each other, variables with a strong contribution are plotted far from the origin, and variables with a minor contribution are plotted close to the origin [67].

The importance of each descriptor in the model, with respect to the correlation between the descriptor matrix (X) and the response matrix (Y), can be described by the variable importance in the projection (VIP). Descriptors with VIP values above 1 are considered to have a large influence on the responses, while descriptors with VIP values between 0.5 – 1 are considered to have a moderate influence on the responses [106].