



Evaluating Biomass Ash Properties as Influenced by Feedstock and Thermal Conversion Technology towards Cement Clinker Production with a Lower Carbon Footprint

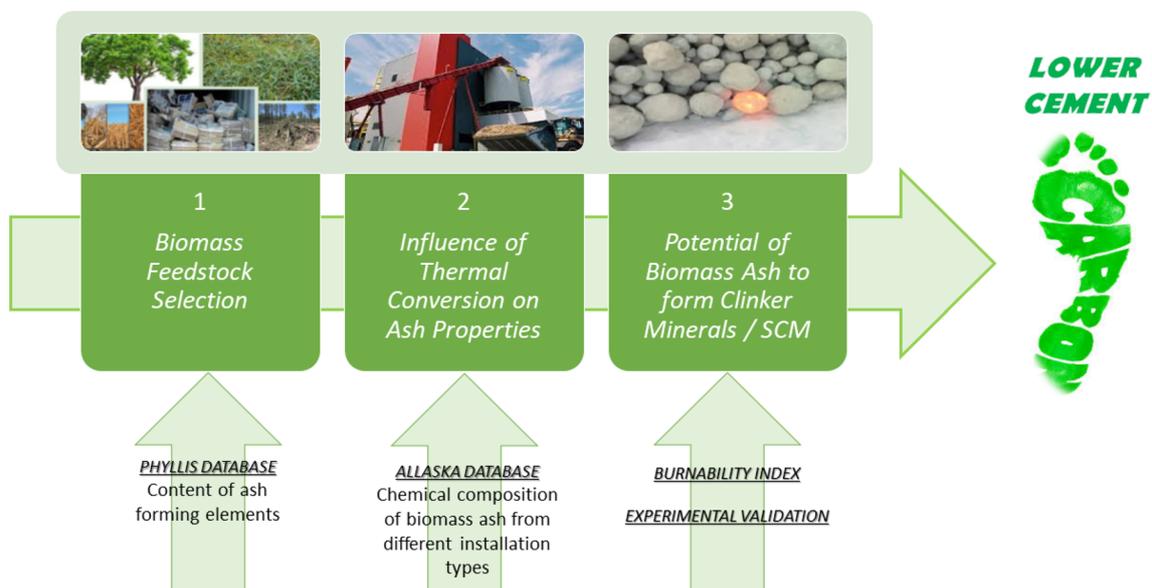
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Abstract

Purpose: This study evaluates the potential of biomass ash as raw clinker material and the influence of biomass feedstock and thermal conversion technology on biomass ash properties. **Methods:** A set of criteria for biomass feedstock and ash properties (i.e. CaO/SiO₂ ratio and burnability) are established. A large dataset was collected and the best combination of biomass feedstock and conversion technology regarding the desired ash quality was identified. **Results:** Wood biomass has the highest potential to provide the right CaO/SiO₂ ratio which is needed to form clinker minerals. Bark content and exogenous Si inclusion in wood biomass have a large influence on the CaO/SiO₂ ratio. Paper sludge is composed of Ca, Si and Al and can potentially serve as a source of cement elements. Wood fly ash from pulverized fuel combustion can substitute a considerable amount of raw clinker materials due to its similar burnability. The replacement ratio is determined by the content of adverse elements in the ash (i.e. MgO₂ and P₂O₅). **Conclusion:** Using biomass ash to lower the CO₂ emission from clinker production depends on the joint effort of bioenergy producers, by providing higher quality biomass ash, and cement makers, by adapting the kiln operation to enable a high level of raw material replacement by biomass ash. The presented evaluation of the ash production chain, from biomass selection through combustion technology and ash management, provides new insights and recommendations for both stakeholders to facilitate this sustainable development.

Graphic Abstract



Extended author information available on the last page of the article

Keywords Biomass ash · Clinker · Raw clinker materials · Cement · Biomass combustion

Statement of Novelty

Biomass ash could represent a valuable source of inorganics able to substitute those already used in the cement industry so to avoid the exploitation of new natural resources and reduce the CO₂ emissions from cement manufacturing. Unfortunately, nowadays biomass ash is mainly landfilled as waste. Several researchers have studied options to use biomass ash residue in cement focusing on already existing biomass ash or case studies of a specific ash stream. This study proposes a novel approach based on a large dataset to evaluate beforehand the potential of biomass ash as substitute for traditional cement materials. The results can support the cement industry and bio-energy plant operators to find innovative solutions for the re-use of this increasingly important waste material.

Introduction

Saving energy and conserving natural resources, as well as reducing CO₂ emissions and managing wastes are becoming more and more important measures to enable a transition towards a circular economy. The cement industry, as one of the largest CO₂ emitting anthropogenic activities, is an important sector that can make a major contribution to these goals. According to Habert et al. [1] around 920 kg CO₂/ton clinker is released during the clinker production process and it has been calculated that the same process accounts for 5–8% of the total anthropogenic CO₂ emissions [2]. During years, the cement industry has increased its efforts to lower CO₂ emissions, including: (i) improving the energy efficiency of the kilns; (ii) replacing fossil based fuels with alternative energy sources (such as animal residues, sewage sludge and waste oil); (iii) substituting the traditional Portland cement with secondary cementitious materials, such as blast furnace slags and coal combustion fly ash [3]. Using fly ash from coal and biomass co-combustion in blended cement is a consolidated practice in Europe due to the pozzolanic properties of such ash [4–6]. Usually, biomass ash differs from coal ash. The high contents of alkali metals and chlorides make pure biomass ash often unsuitable for the established applications of coal fly ash following the EN-450 standard. Hence, most of the biomass ashes are still disposed of in landfills in many countries [7]. Extensive research has been conducted to characterize biomass and biomass ash with the main objectives of (i) understanding the ash formation process and predicting slagging, fouling and

agglomeration phenomena during biomass combustion [8–13], and (ii) finding suitable applications for already existing biomass ash [14–17]. With respect to biomass ash reuse, utilization of woody biomass ash as a partial cement replacement has been progressively investigated [18–21]. General findings are that replacing 10–20% by mass of Portland cement with biomass ash has relatively little effect on plastic and elastic behaviour of the final product [22]. Incorporating high percentages of wood ash (i.e. up to 40% by mass) as a partial cement replacement material in the formulation of concrete mix reduces mechanical strength (compressive, flexural and splitting tensile strength) of concrete [20]. It should be noted that the chemical and physical properties of woody ash and thus the effect when incorporated into the concrete mixture can vary greatly. Several researchers have investigated the use of agricultural waste ashes as constituents in concrete, including rice ash [23, 24], bagasse ash [4] and palm oil ash [25, 26]. Those agro-waste ashes, containing a large amount of silica in amorphous form, have been shown to hold potential for use as pozzolanic material replacing cement. The available literature reflects the current situation in which energy production from biomass is the primary intention and ash utilization is often neglected. In fact, it is common practice to postpone the assessment of ash utilization options until the installation is running. The major reasons for that practise might be found in the variation of biomass ash composition and the generally available option of landfilling of the ash. Recently, due to the development of new concepts such as the circular economy and the environmental and economic benefits that may be obtained from its beneficial reuse, biomass ash is starting to be seen as an integrated part of the biomass energy production chain and some studies have explored also opportunities to replace a portion of cement raw materials with waste and by-products from other processes. Biomass ash contains functional elements such as calcium, silica, alumina and iron that can be used to replace raw materials such as clay, shale and limestone [27, 28] or as secondary cementitious material (SCM), when used in conjunction with traditional ordinary Portland Cement (OPC). Even though biomass ash has been recognized to have potential as a by-product to be used in cement manufacturing, there is still no generally-applicable guidance on (1) the properties that make a biomass ash suitable for application in cement, (2) the available options to use biomass ash for that purpose (e.g. as raw material in the traditional cement kiln, or as secondary cementitious materials), and (3) specific biomass ash properties that control the suitability of the ash for the different application options. Moreover, the

existing literature generally addresses site specific case studies, often dealing with a single ash stream from a specific power plant and geographical region [27, 29], rather than general application principles.

The aim of this work was to evaluate the influence of biomass composition and thermal conversion technology to obtain biomass ash properties that enable its functional use as a raw clinker material. A stepwise approach and criteria have been developed to investigate the potential for formation of the required hydraulic C_3S and C_2S minerals from a combination of suitable biomass feedstock and thermal conversion systems. First, the optimum content of the required inorganic elements in the feedstock was investigated by reviewing a large state of the art database that allowed data selection based on the nature and chemical composition of biomass. Next, a second database was used to evaluate the ash properties as influenced by both feedstock and thermal conversion systems in full scale installations. A typical raw clinker composition was taken as reference. The potential for the formation of the main clinker minerals C_3S and C_2S was assessed by calculating the burnability of the biomass ash. Data from previous reheating experiments with three different ash samples were reviewed to verify the effectiveness of the theoretical criteria to predict burnability values of biomass fly ash and verify the potential formation of C_3S and C_2S minerals. The assessment covers the biomass ash in its “as received” form (i.e. as would be collected from combustion facilities) and after a reheating step to simulate its utilization as raw clinker material in modern cement kilns. Traditional biomass combustors seldomly reach the required clinkerization temperature and, as we will show, biomass ash would most likely need a subsequent heating step to form clinker minerals. Moreover, biomass ash is most likely to be used in conjunction with other raw and/or waste materials in traditional kilns.

With regard to the perspective of partial replacement of raw clinker materials by biomass ash to enable cement production with a lower carbon footprint, a qualitative indication on the amount of CO_2 avoided could be obtained by using the IPCC calculation [30]. The IPCC has proposed an equation to calculate the Environmental Footprint (EF) of the clinker, based on the CO_2 emission factor per mass of CaO contained in the clinker. The EF clinker is equal to 0.785 multiplied by the CaO content (mass fraction) in the clinker. The multiplication factor (i.e. 0.785) is the molecular weight ratio of CO_2 to CaO in the original raw mineral calcite ($CaCO_3$), from which virtually all the CaO in clinker is derived. If it is known that other sources of CaO are being used as kiln feed (i.e. biomass ash) in substantial amounts, the CaO contribution of these non-carbonate feeds should be subtracted from the clinker, thus resulting in a proportionally lower carbon footprint of the clinker. The premise in this work is that biomass ash with burnability values very close

to those of traditional raw clinker materials can in principle substitute traditional raw materials, theoretically up to 100%.

It is important to note that, even though the proposed integrated approach presented in this work may seem straightforward to adopt, it is still complicated to realise for several practical reasons. According to the recent reports of IEA [7], the estimated generation of biomass ash from the power generation facilities amounts globally to about 10 million ton per year and the availability is highly dispersed. Moreover, the biomass input is optimized for energy production purposes, rather than biomass ash quality/reuse options. However, the results of this work remain relevant to provide practical indications on how to evaluate the suitability of biomass ash properties for cement clinker production and on how those are influenced by feedstock and thermal conversion technology. The functionality of an ash as raw material for clinker production depends on chemical, mineralogical and physical properties. The factors with a profound influence on these properties are biomass feedstock, conversion technology and thermal conversion parameters (i.e. residence time and temperature). This evaluation will cover the ash production chain from biomass selection through combustion technology and ash management. Chemical and physical parameters with a beneficial influence on properties of biomass ash that are required for its utilization as raw clinker material will be identified, and the extent to which these properties can be controlled to obtain ash with a high application potential will be assessed.

Biomass Ash as Raw Clinker Material

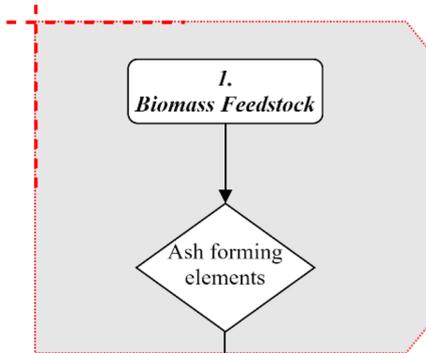
The suitability of a biomass ash to replace raw clinker materials is related to its chemical and mineralogical composition as well as to its physical properties. These properties are influenced by biomass feedstock, type of combustion technology and management of the ash. Taking these properties into account, a stepwise flowchart is proposed here (Fig. 1) to evaluate the biomass ash potential for replacement of raw clinker materials. A typical raw clinker material composition [31] was used to establish a set of criteria for each step of the method. The major oxides composition of the reference raw material for clinker production is: 64.4 mass % CaO, 20.1 mass % SiO_2 , 6.3 mass % Al_2O_3 and 2.4 mass % Fe_2O_3 [31].

The first step of the method evaluates the potential of biomass feedstock as a source of inorganic elements that can be recovered in the ash fraction and potentially form the hydraulic minerals C_3S and C_2S . This evaluation is made by comparing the biomass feedstock composition with the optimum CaO/ SiO_2 ratio of three in the typical raw clinker material. Al_2O_3 and Fe_2O_3 contribute to lowering the melting temperature of the raw material, which promotes the production of C_3S from the reaction between C_2S and unreacted

Steps of the method

Set of criteria

Phyllis Database

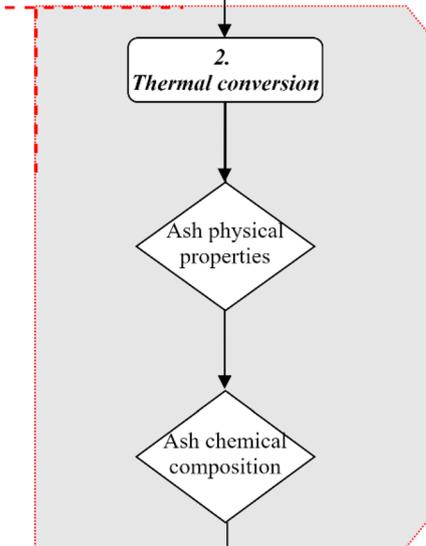


1. Potential of biomass feedstock to form C₃S and C₂S

Criteria 1

- $CaO/SiO_2 = 3$
- $Al_2O_3+Fe_2O_3 = 9\%$ by mass

Allaska Database

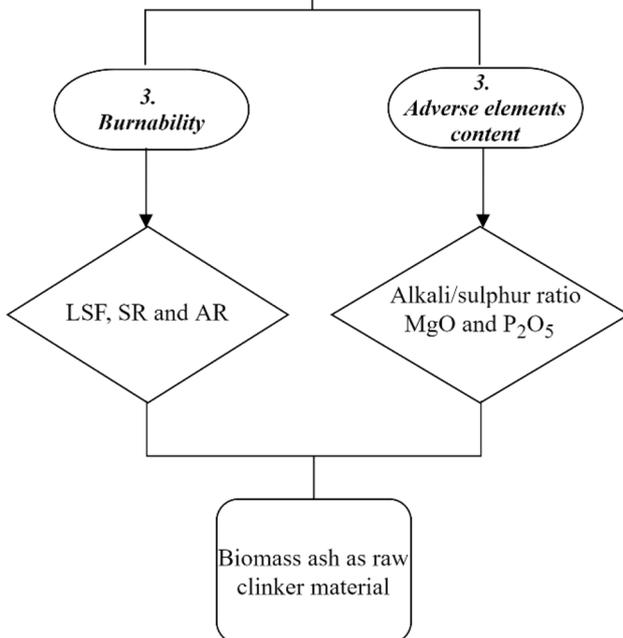


2. Influence of conversion technology on biomass ash properties

Criteria 2

- Homogeneous material
- 45 - 150 um ash particle size

- 64.4% CaO, 20.1% SiO₂, 6.3% Al₂O₃, 2.4% Fe₂O₃



3. Potential of clinkerization of biomass ash and presence of adverse elements into clinker phases

Criteria 3

- | | |
|-------------------|------------------------------------|
| • $LSF = 0.9 - 1$ | • $A/S = 0.8 - 1.2$ |
| • $SR = 2 - 3$ | • $MgO = 4\% - 5\%$ by mass |
| • $AR = 1 - 4$ | • $P_2O_5 = 0.7\% - 4.5\%$ by mass |

Fig. 1 Flow chart for evaluating biomass ash suitability to replace raw clinker materials as influenced by biomass feedstock and thermal conversion. A set of criteria is established for each step of the method (right side of the figure). The potential of clinkerization of biomass ash is assessed by means of parameters that are commonly used in a cement context (Criteria 3). Lime saturation factor (LSF), Silica ratio (SR) and Alumina ratio (AR) are indicative for the ability of a raw material mixture to form the active clinker phases upon heating. Alkali to sulphur ratio (A/S) indicates the potential presence of (undesired) alkali and sulphur into clinker phases

CaO in the kiln. The sum of Al_2O_3 and Fe_2O_3 should equal 9% by mass. In this step, the adverse elements concentration does not yet preclude the selection of potentially suitable biomass feedstock.

The biomass ash composition, mineralogy and physical properties are also affected by the combustion technology, gas cleaning technology and by the management of different ash streams after combustion. Therefore, the second step of the method evaluates the influence of the thermal conversion system on the resulting physical and chemical ash properties (Fig. 1). The particle size distribution and homogeneity of the raw material are known to affect the formation of mineral phases [32, 33]. An insufficient homogeneity could potentially lead to the formation of other than the desired clinker phases. To prevent this effect, the traditional raw material is normally ground to obtain a particle size distribution between 45 and 150 μm [33]. This range was also used as a criterion to ensure homogeneity of the biomass ash (Criteria 2, Fig. 1). Using biomass ash to substitute traditional raw clinker materials also requires control of the major oxides content (CaO, SiO_2 , Al_2O_3 and Fe_2O_3). Therefore, the content of major oxides is directly compared to the typical raw clinker material composition [31] as given in Fig. 1. Theoretically, a biomass ash with the mentioned chemical and physical requirements can form the hydraulic minerals C_3S and C_2S at a temperature of 1450 °C. However, there are also other parameters that need to be in a defined range to ensure an optimal formation of these minerals, usually referred to as the so-called burnability parameters (i.e. step three of the flowchart).

The burnability of a raw mix represents the concentration of free lime (unreacted CaO) that is still present after clinkerization. Low free lime concentrations in the final clinker product indicate that a substantial part of the CaO has reacted with SiO_2 , Al_2O_3 and Fe_2O_3 to form the main clinker phases C_3S , C_2S , C_3A and C_4AF . The burnability is defined by 3 empirical parameters. The Lime Saturation Factor (LSF, Eq. 1) is used to quantify the amount of CaO in the raw material that can be combined with SiO_2 , Al_2O_3 and Fe_2O_3 to form the main clinker phases. Typical LSF values for modern clinkers are 0.92–0.98 [32]. The silica ratio (SR, Eq. 2), usually between 2 and 3, indicates the optimum amount of liquid phases to ensure an efficient

mineral formation at acceptable temperatures and time. The alumina ratio (AR, Eq. 3) is normally between 1 and 4 and expresses the ratio between the aluminates and ferrite phases. This ratio affects the quantity and quality of liquid and the temperature at which it is formed. Burnability values close to those observed for traditional raw materials as reported in Fig. 1 indicate a high replacement potential of biomass ash if introduced together with traditional raw materials.

$$LSF = CaO / (2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3) \quad (1)$$

$$SR = SiO_2 / (Al_2O_3 + Fe_2O_3) \quad (2)$$

$$AR = Al_2O_3 / Fe_2O_3 \quad (3)$$

Finally, the presence of Na_2O , K_2O , Cl, SO_3 (expressed as the A/S ratio, Eq. 4), MgO and P_2O_5 in the biomass ash is considered in order to assess the potential of an excessive inclusion of these adverse elements into the clinker phases and the negative effects that might be connected to such inclusions. Generally, the presence of alkali metals and sulphur leads to a gradual deterioration of the cement quality because of cracking, expansion or loss of strength whereas chloride is associated with corrosion phenomena. The alkali/sulphur ratio (Eq. 4) is used to balance the total input of alkali, sulphur and chloride in raw materials that enter the cement kiln. If present in the right stoichiometric balance, K, Na, S and Cl are considered to be entirely volatile in the cement kiln as alkali chlorides and alkali sulphates. If not, they might be included into clinker phases where they can have the adverse effects described above. In this context, an alkali sulphur ratio (A/S) between 0.8 and 1.2 ensures a good clinker quality because most of the alkalis are stoichiometrically bound in sulphates and chlorides that are mostly volatilized and will not be incorporated or in only minor amounts in the clinker phases.

$$A/S = [(K_2O(mol) + Na_2O(mol)) - Cl(mol)] / SO_3(mol) \quad (4)$$

Commonly, a small amount of MgO in the raw material lowers the melting temperature, thus increasing the quantity of the liquid phases formed and enhancing the formation of C_3S phase. However, when MgO is present in the clinker with a content above 4–5% by mass it might form a mineral phase (i.e. periclase) that lowers the clinker quality. The inclusion of MgO into clinker phases depends mainly on clinkerization temperature and cooling rate. In this work, the total Mg content in the biomass ash is compared with the maximum desired total content in traditional clinker, which is mostly set to 4–5% by mass [31, 32, 34].

When P_2O_5 enters the clinker, it can hinder C_3S formation during clinkerization [32, 35]. At 0.7% by mass of P_2O_5 in the clinker the C_3S content decreases and C_2S increases. At

a P_2O_5 content of 4.5% by mass in clinker the C_3S formation is significantly hindered and the final clinker contains both free lime and C_2S instead of C_3S [35]. This 0.7–4.5% by mass range is taken as reference and indicates the lower boundary concentration (i.e. 0.7% by mass) at which no C_3S reduction is observed and the upper limit (i.e. 4.5% by mass) at which C_3S formation is completely blocked.

Material and Methods

Phyllis Database

The Phyllis two database was updated to the current version within the Phydades European project [36] with the goal of providing public and reliable information on biomass fuels and biomass ashes. The database contains almost 3000 data records of individual fuels including biomass and waste materials. The fossil-based fuels samples (e.g. electronic scrap, automobile shredder residues and cable waste) were excluded from the analysis because these are not CO_2 neutral and would therefore not contribute to lowering the CO_2 footprint of the proposed alternative cement. Samples were classified into three main categories; wood and woody biomass (WWB), herbaceous and agricultural biomass (HAB), organic residues and contaminated biomass (OR-CB), each with sub-categories as reported in the Phyllis two database. This classification is based on a combination of plant physiology and practical considerations. The concentration of elements in the biomass was expressed as total oxides in

the dry ash fraction of the biomass feedstock. Although the partition and speciation of elements in the ashes during combustion might change depending on the chosen conversion technology, this representation provides a first indication of the potential of biomass feedstock as a source of inorganic elements that can be recovered in the ash and potentially form the hydraulic minerals C_3S and C_2S . A triangular diagram was created in order to show the concentration of elements in single biomass feedstock's samples according to the groups and subgroups they belong to (Fig. 2).

ALLASKA Database

The ALLASKA database has been developed within the Ash Program at Värmeforsk [37] with the goal of developing knowledge to encourage the use of ashes, with no or little risk to health and environment in both the short and long-term. The ALLASKA database contains information on geotechnical (111 samples) and leaching properties (322 samples), chemical composition (772 samples), particle size (144 samples) and organic substances content (13 samples) of ash residues originating from the combustion of biomass and waste materials in full-scale power plants with different types of boilers (102 installations). The data can be filtered according to different parameters such as fuel, ash and combustion system types. In this study, the ALLASKA database analysis was limited to those ashes obtained from the combustion of biomass-based fuels. The ash composition was expressed as % of oxides contained in the total dry mass and the considered elements were CaO , SiO_2 , Al_2O_3 ,

Fig. 2 Content of clinker forming elements in biomass feedstock. The typical clinker composition is reported as reference (black circle and parallel lines)

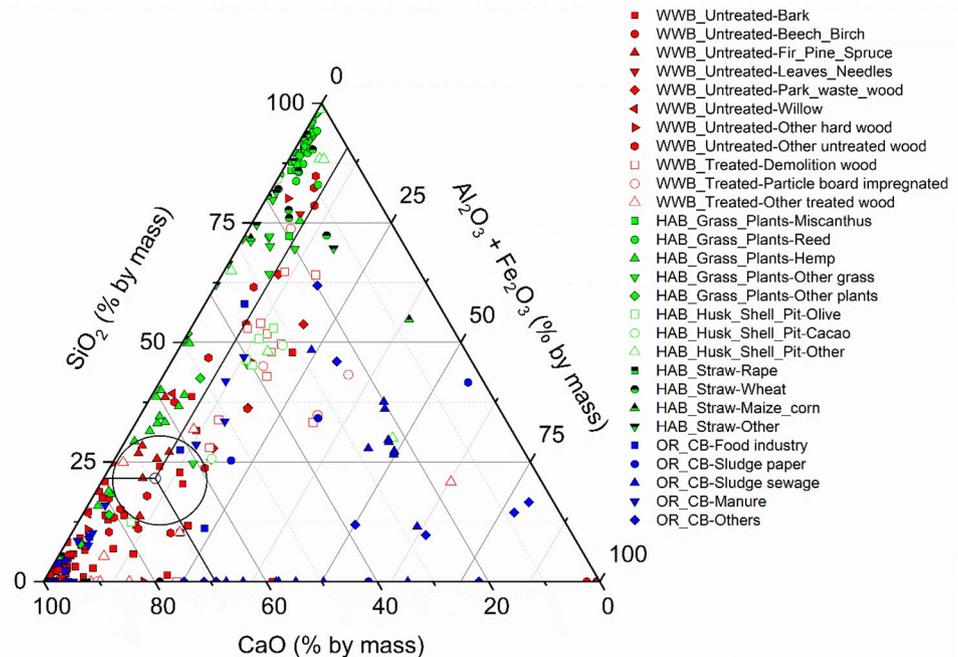
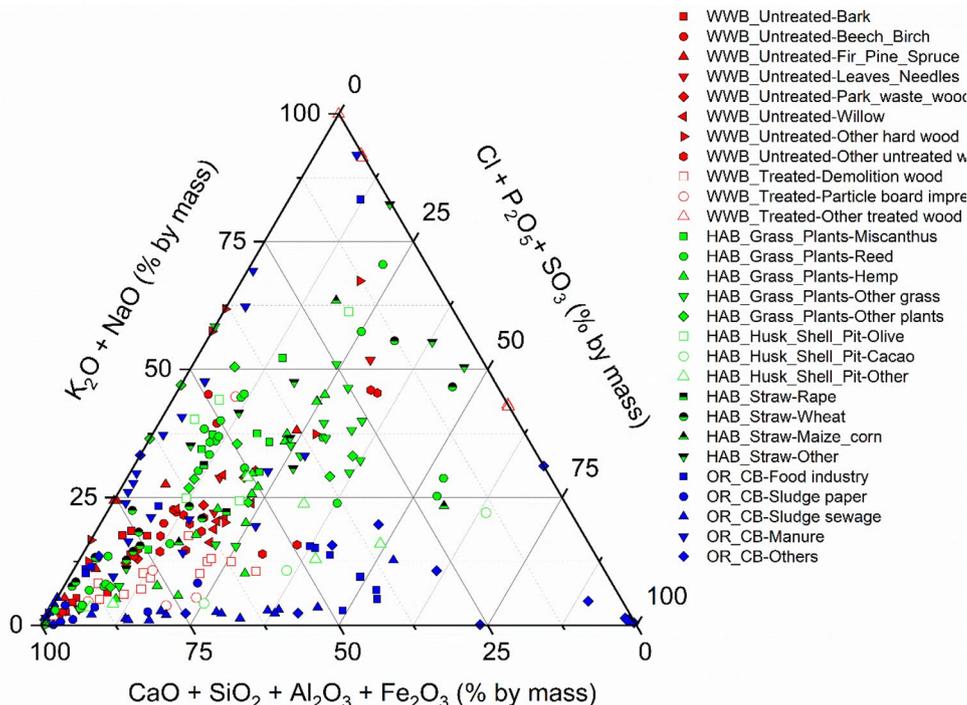


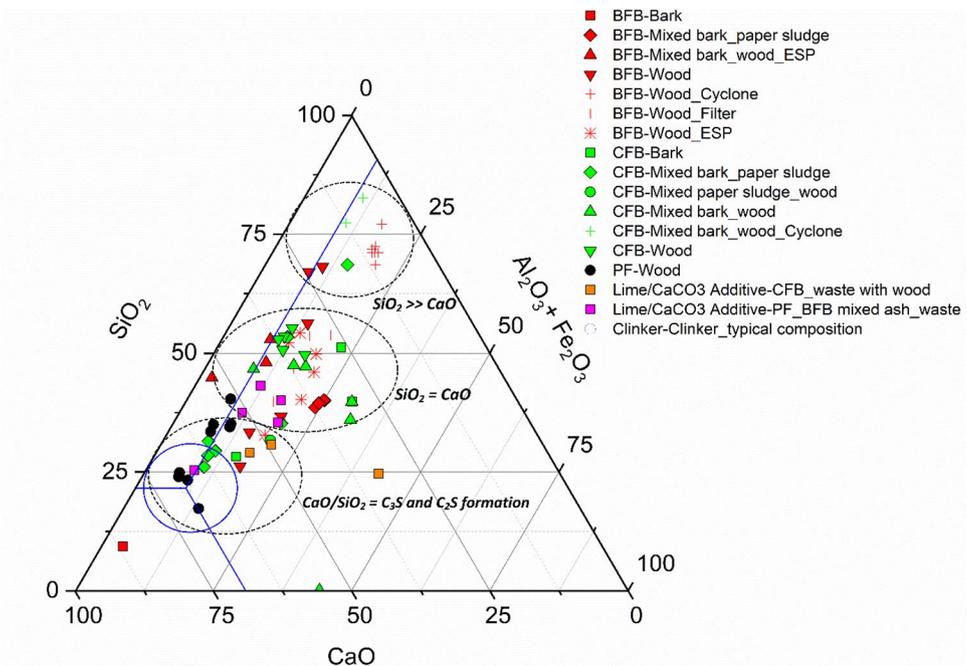
Fig. 3 Content of elements with potential adverse effects on clinker compared to forming oxides



Fe_2O_3 , K_2O , Na_2O , Cl , SO_3 , MgO and P_2O_5 . The data were collected along with information on the type of fuel combusted, plant nominal power, type of ash, ash collecting point, and cleaning system adopted, to allow assessment of the influence of the combustion technology on the resulting ash composition and its suitability for cement replacement. In order to do so the content of cement forming oxides

CaO , SiO_2 , Al_2O_3 and Fe_2O_3 in the dry ash was normalized to 100, plotted in ternary diagrams (Fig. 4) and compared with Criteria 2 (Fig. 1). Successively, the LSF, SR and AR parameters were calculated for the ash samples according to Eqs. 1–3 and plotted in a X-2Y axis graph (Fig. 5) in order to assess the theoretical burnability and investigate the potential of obtaining clinkerization of the ash mixture. Finally,

Fig. 4 Cement relevant oxides composition of fly ash (FA) from the ALLASKA database. The FA samples are grouped according to their conversion and biomass type. Samples named “Lime/CaCO₃ additive” indicates fly ash collected from installations using lime/CaCO₃ as a SOX reduction measure (see text for more details). The dotted ovals denote three different clusters according to the CaO and SiO₂ contents of the fly ash as influenced by thermal conversion and ash type. The typical clinker composition is reported as reference (black circle and parallel lines). All values are normalized to 100



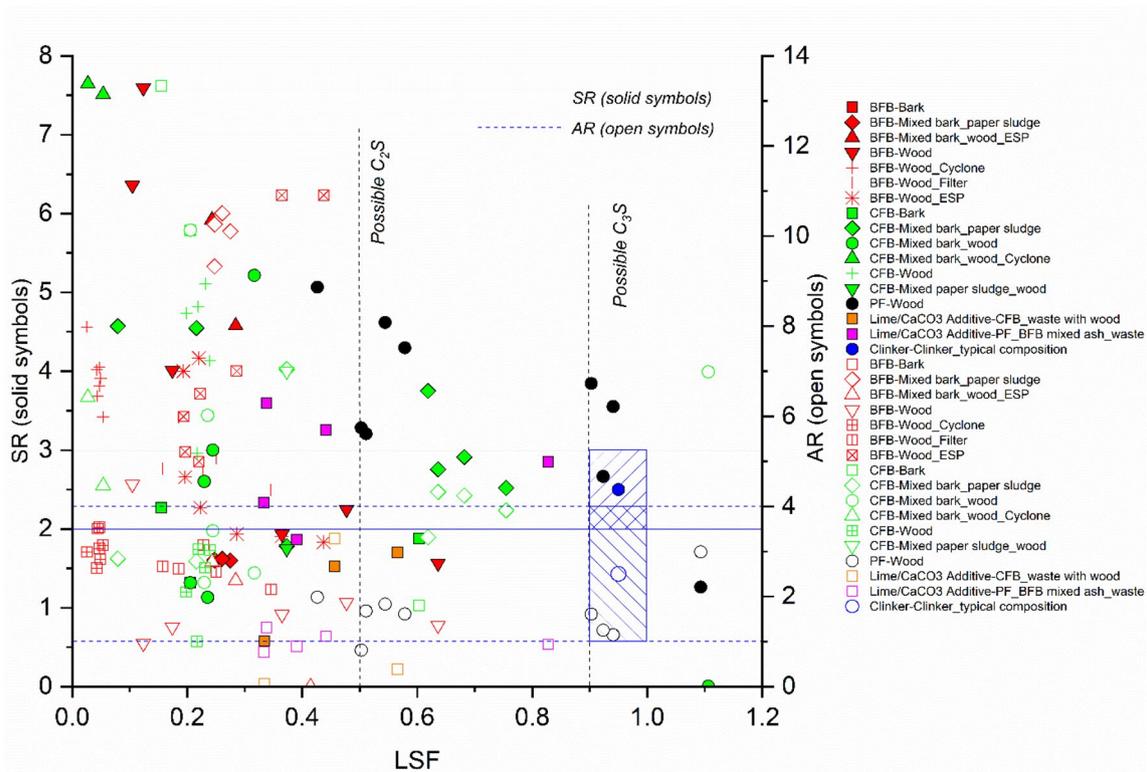


Fig. 5 Burnability parameters of fly ash samples from different conversion technologies. The Lime saturation factor (LSF) indicates the amount of CaO combined with other oxides to form clinker mineral phases. Silica ratio (SR) indicates the amount of liquid produced at relevant temperature. Alumina ratio (AR) indicates the quantity and composition of liquid phases at lower temperature. Each sample is

plotted according to its LSF (X axis), SR (left Y axis closed symbols) and AR (right Y axis open symbols). LSF, SR and AR values for typical clinker are indicated (open and closed blue symbols). The dashed squares in the diagram delimit regions in which the C_3S and C_2S minerals have potential to exist or have already been identified in previous work [44]

the A/S ratio was calculated for biomass ash according to Eq. 4. The molar ratio of alkali was corrected by subtracting the chloride content since alkali chlorides were considered to be completely volatile and therefore not included in the clinker phases. The corrected alkali molar content was plotted against the molar sulphur content (Fig. 6).

Results and Discussion

Biomass Feedstock Composition

Figure 2 displays the content of CaO and SiO_2 together with the sum of $Al_2O_3 + Fe_2O_3$ expressed as oxides % by mass of the total ash content for the different biomass groups, subgroups and specific samples. In Fig. 3 the content of adverse elements is plotted against the content of clinker forming elements for the biomass groups, subgroups and specific samples. Eventhough the adverse elements content does not preclude biomass selection in this step of the flowchart (see Criteria 1, Fig. 1), its concentration can be a preliminary indication of potential degradation of clinker quality.

A general observation from Fig. 2 is that the investigated biomass groups WWB and HAB show two distinct and consistent CaO/SiO_2 ratio distributions with WWB having an higher CaO/SiO_2 ratio then the HAB group. Contrary, the CaO/SiO_2 ratio of OR-CB group is more scattered. The average $Al_2O_3 + Fe_2O_3$ content of the WWB group is close to the optimal value of 9% by mass (Criteria 1, Fig. 1), while the other biomass types (i.e. HAB and OR-CB) contain either a too low or too high content of $Al_2O_3 + Fe_2O_3$. The distribution of adverse elements content in Fig. 3 appears to be more dispersed than was previously observed for clinker forming elements (Fig. 2) and it is difficult to identify a consistent pattern among the different groups and subgroups. Samples belonging to the WWB group generally are located in the bottom-left area of the triangular diagram meaning that the concentration of clinker forming elements is higher than the adverse ones. The HAB group is the most spread out, with a tendency to fall in the central area of the diagram. The concentration of adverse elements in the OR-CB group shows either very high alkali content and low Cl , P_2O_5 and SO_3 content (i.e. manure samples) or viceversa (i.e.

sewage sludge samples). Specific samples of paper sludge (full blue circle in Fig. 3) show a remarkably very low adverse elements content comparing to clinker forming element concentrations.

When we look at subgroups and specific samples in the WWB group we see relatively low CaO/SiO_2 and relatively high $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ in the treated wood subgroup (open red symbols in Fig. 2), while the opposite is observed for the untreated wood subgroup (full red symbols in Fig. 2). This trend can be associated to the inclusion of Si-rich exogenous material such as sand, dust and concrete debris which is collected together with the treated wood and the presence of bark tissue in the untreated wood. The inclusion of exogenous material is common for the treated wood subgroup and contributes significantly to Si, Al and Fe concentrations resulting in a lower CaO/SiO_2 ratio and higher $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ concentration [38] Fig. 2). Specific samples of the untreated wood subgroup might also be subject to exogenous inclusion especially wood samples coming from the maintenance of river banks or parks. Another important factor to take into account is the bark content of wood. Samples of pure bark belonging to the untreated biomass group are enriched in Calcium. Werkelin et al. [39] found the Ca content in bark to be 8 to 19 times higher than in the corresponding wood tissue. Samples of untreated wood might refer to wood with or without bark tissue, which can have an important influence on the CaO/SiO_2 ratio (this information is not always reported in Phyllis). Therefore, samples of bark or bark containing wood with low exogenous inclusions are expected to have the highest CaO/SiO_2 ratio within the WWB group and can also reach the required ratio of three, thus being theoretically suitable for C_3S formation.

The distribution of samples in Figs. 2, 3 suggests a good potential for the WWB group (i.e. bark samples or wood samples with high bark content and low exogeneous inclusion) to contain clinker forming elements and therefore represent a good starting point in the chain to produce ash as substitute for raw clinker material. Contrary, selecting HAB group feedstock cannot produce ash with a suitable Ca/Si ratio, unless Ca is added from an external source, and would potentially decrease the quality of clinker due to the high adverse elements content. Within the OR-CB group, the paper sludge samples have a very high concentration of Ca, Si and Al along with very low concentrations of adverse elements, thus making this biomass feedstock very interesting as a source of cement forming elements.

Biomass Ash Composition

Following Criteria two as defined in the evaluation method (Fig. 1), bottom ash from all installation types was excluded from further consideration. In fact, bottom ash represents the main ash stream produced from a grate stoker furnace with

about 90% by mass of the total ash content of the biomass ending up in this fraction. All ALLASKA bottom ash samples from grate stoker installations show an average passing percentage of 13% for a 125 μm , and 20% passing for a 250 μm mesh size, indicating its coarse nature. Furthermore, this ash fraction is generally very heterogeneous in composition [40]. Therefore, bottom ash from grate stoker combustion was excluded from further consideration. Bottom ash from fluidized bed combustion represents about 30 to 50% by mass of the total produced ash. This ash fraction is often called bed ash because it is mainly composed of bed particles (often quartz sand) coated with alkali oxides, depending on the alkali content of the fuel and the operating temperature. No particular variation in the composition of cement-relevant oxides was observed for bottom ash from fluidized bed combustion, with SiO_2 being the dominant component in all samples with an average value of 65–70% of the total ash by mass. Bottom ash from fluidized bed combustion is very similar in chemical and mineralogical composition as well as in physical properties to sand. It can be applied in the same way as sand is already applied in the building industry, but is also considered not suitable for replacement of raw clinker materials in cement.

Fly ash is the main component of the total produced ash during fluidized bed combustion (around 50 to 70% by mass of the total ash content) and pulverized fuel combustion (> 90% by mass of the total ash content). About 80% and 96% of fly ash from fluidized bed and pulverized fuel combustion, respectively, passes a mesh size of 125 μm . The particle size distribution of these ashes is very similar to that of raw cement materials. At this particle size a high level of homogeneity is expected and no additional grinding is required if fly ash from fluidized bed and pulverized fuel combustion is used as raw material for cement production. Therefore, compositional data of biomass fly ash from bubbling fluidized bed (BFB), circulating fluidized bed (CFB) and pulverized fuel (PF) combustors were retrieved from the ALLASKA database following the method described in Sect. [Mineral composition and thermal treatment of selected biomass ash](#). Figure 4 shows the concentration of CaO, SiO_2 and the sum of Al_2O_3 and Fe_2O_3 of the different biomass fly ash samples. The samples are grouped according to their combustion technology, biomass fuel and ash stream types. Criteria two for biomass ash composition to replace raw clinker material is reported as reference (black circle in Fig. 4).

A general observation is that the variation of CaO (i.e. $6\% < \text{CaO} < 86\%$) and SiO_2 (i.e. $9\% < \text{SiO}_2 < 82\%$) concentrations is very high for biomass ashes, while the sum of Al_2O_3 and Fe_2O_3 is showing a substantially smaller variation of about 6–30%. The average $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ concentration in the biomass samples is about 10–15% and close to the reference (Criteria 2, Fig. 1). The type of biomass combusted

or the combustion technology adopted does apparently not have a major influence on the resulting $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ concentration. However, the speciation and morphology of these oxides may still be different. From Fig. 4 three clusters have been indicated to distinguish important aspects related to the conversion system that influence the resulting CaO and SiO_2 content in the ash:

Cluster 1 $\text{SiO}_2 \gg \text{CaO}$ is represented by ash with high SiO_2 (> 65%) and low CaO contents. All the samples collected from cyclones that are used to capture the relatively coarse fractions during the flue gas cleaning belong to Cluster 1. This fraction is composed mostly of the coarse fragmented bed particles and the exogenous material (e.g. particles of soil and dust from the feedstock), thus explaining the high SiO_2 content of this fraction compared to the filter and ESP ash. The samples of BFB_Wood and CFB_Mixed bark_paper sludge which are also found in the cluster 1 area are assumed to be either cyclone ash or to have been mixed with a cyclone ash fraction since no further information could be retrieved from the ALLASKA database. The cyclone fly ash fraction should be collected separately from the fine filter ash fraction in order to avoid dilution of Ca and enable application of the latter in cement production (as further discussed below).

Cluster 2 $\text{SiO}_2 \approx \text{CaO}$ Is characterised by comparable values of SiO_2 and CaO, with SiO_2 still being the prevailing element. This condition is common for most of the investigated fly ash samples from both BFB and CFB and is related to inclusion of fragmented bed particles and exogenous inert material introduced during processing of the biomass. The particle size, density and volume of the bed material in the installation is controlled by the operator and fairly constant. On the other hand, the properties of the exogenous inert material introduced during processing of the biomass are more heterogeneous and can influence the SiO_2 content of the fine fly ash fraction. In fact coarse exogenous material can still be sufficiently small to be entrained with the flue gas and to reach the fine ash fraction, influencing its composition. Tarelho et al. [38] measured the average particle size of exogeneous material and found that 67% by mass is below 500 μm concluding that part of these particles can be entrained with combustion flue gases and, successively, be collected in the cleaning gas section. These results indicate that careful handling and processing of biomass by avoiding the inclusion of soil, dust and other inert materials can reduce the amount of silicon ending up in the fine ash fraction, thus improving the quality of the ash in terms of its CaO/ SiO_2 ratio.

Cluster 3 CaO/SiO_2 suitable for C_3S and C_2S formation is represented by ash with high CaO (> 55–60%) and relatively low SiO_2 contents. Samples from PF_wood combustion and CFB_mixed bark_paper sludge are found in this part of the diagram with a relatively low variation in composition.

PF_wood samples show more variation compared to CFB_mixed bark_paper sludge that falls in a more confined area of cluster three. This observation can be explained by the fact that a specific residue stream such as de-inking sludge or fibre sludge is expected to maintain a stable composition over time as a result of the industrial treatment process. Moreover, the paper sludge has a high ash content and its chemical composition dominates the resulting ash composition when paper sludge is co-combusted with other fuels such as wood. This effect has been noticed at a co-combustion level of 20% by mass of sludge [41].

The variation of fly ash from PF combustion is related to variations in the wood mixture that is used as fuel. The PF technology does not involve the use of bed material so inclusion of extra Si is limited to the contribution from the exogeneous material only. Nevertheless, when a suitable wood composition (i.e. CaO/ SiO_2 ratio of three, see Criteria 1, Fig. 1) is combusted as PF, a final fly ash with high potential for clinker substitution can be obtained (Fig. 4, black full circle inside the reference).

Samples where lime or calcium carbonate are used for SO_x emission reduction (Lime/ CaCO_3 Additive labelled samples in Fig. 4) can also be found in cluster number three. However, the variation is higher for these samples when compared to PF_wood combustion and CFB_mixed bark_paper sludge samples. Furthermore, when the Sulfur concentration in biomass is high, as is the case for sludges (Fig. 3), SO_x emission is usually reduced by injecting alkaline agents such as limestone/lime or NaOH. When limestone or lime are used as alkaline agents, high SO_x reduction efficiency can be obtained only through injecting the additive in stoichiometric excess. CaSO_4 along with unreacted limestone/lime are then collected in the fine particle cleaning system (i.e. ESP or baghouse filter) [42]. The fly ash fraction recovered after limestone or lime injection is therefore rich in Ca. However, this is often also associated with a high Sulfur content with potentially negative effects on clinker quality as described below.

Burnability of Fly Ash as Raw Material for Cement Production

Figure 5 shows the set of parameters that defines the burnability of pure biomass fly ash, together with Criteria three (Fig. 1). This assessment has the aim to explore the potential of biomass fly ash to form the desired C_3S and C_2S phases during clinker formation. Although not specifically quantified in this study, biomass ash can also be added in mixtures with traditional raw materials to achieve the desired burnability. A first observation is that a substantial number of biomass fly ash samples from FB combustion display LSF values between 0.1 and 0.4, which is significantly lower than

the reference (Criteria 3, Fig. 1). These low LSF values indicate that insufficient CaO is available in the biomass ash to form C_3S and C_2S and, hence, these ashes have a low potential as clinker raw material replacement.

Samples of PF falling in the possible C_3S range can form C_3S and C_2S in similar proportion to that observed in traditional clinker. These results indicate that the combination of Ca rich wood fuel combusted in a PF installation results in fly ash with similar chemical composition and burnability parameters as traditional raw clinker material. PF installations operate normally at 1400 °C, thus very close to clinkerization temperature. However, the time during which fly ash is exposed to 1400 °C during pulverized combustion is within the order of seconds, which is supposed to limit the formation of liquid phases needed for CaO to react with C_2S and form C_3S . There is a good potential for C_3S and C_2S formation when this ash type is introduced in a kiln and exposed to the clinkering temperature for a longer time (typically 20 to 40 min). The calculated LSF, SR and AR parameters for PF_wood indicate a potentially high replacement rate of traditional raw cement materials.

Biomass ash with a lower LSF and SR and AR ratios in the observed range (i.e. “possible C_2S ” region in Fig. 5) can still contain active phases such calcium silicate [12, 38, 43]. Segui et al. [44] for instance detected the presence of C_2S mineral in fly ash from the combustion of a mixture of paper sludge and waste wood in a fluidized bed (LSF=0.5, SR=2, AR=10, at 850 °C). Fly ash with LSF around 0.5 and up to 0.9 can potentially produce C_2S and therefore still be relevant as substituting raw material. The samples of fly ash from combustion of bark and mixed bark with paper sludge in a CFB installation have an LSF value between 0.6 and 0.8. SR and AR parameters are very close to the reference Criteria three. Fly ash presenting a similar set of burnability parameters can contain C_2S which is formed in a CFB at the operational temperature (900 °C–950 °C). The formation of C_2S in a cement kiln is observed at temperature between 900 °C and 1250 °C and can be basically attributed to the reaction between solid CaO and SiO_2 particles. Calcium has to be supplied in its oxide form to ensure solid–solid reaction with SiO_2 [33]. Calcium in bark is present mainly as calcium oxalate [45, 46] and is most likely released upon combustion in the form of ultrafine CaO particles. The same holds for de-inking paper sludge where Ca is present mainly as $CaCO_3$ which decomposes to CaO during combustion. Furthermore, Silica in quartz is less reactive during the clinkerization process than Silica in clay [32], while de-inking sludge contains a high concentration of inorganics such as kaolin and clay which are used as coatings in the paper. Therefore, formation of hydraulic C_2S minerals in fly ash is likely improved by the combustion of bark and/or de-inking paper sludge. The relatively low operational temperature of a fluidized bed (900 °C) avoids any liquid formation, and the formation of

C_3S during fluidized bed combustion is not expected. Since fly ash from bark and/or de-inking paper sludge is likely to contain already C_2S in the ash, these materials could be used directly as a C_2S rich binder added to traditional clinker. Alternatively, this ash type could still represent an important source of elements for clinker production if exposed for a sufficient time to the right temperature.

Mineral Composition and Thermal Treatment of Selected Biomass Ash

In this Section, the theoretical predictions made in Sects. [Biomass ash as raw clinker material](#) and [Burnability of fly ash as raw material for cement production](#) will be verified by the analysis of results from previous heating experiment performed on real biomass ash samples.

Tosti et al. [47, 48] selected three ash samples FA1, FA2, and FA3 from combinations of biomass source and conversion technology on the basis of the criteria described in Sect. [Burnability of fly ash as raw material for cement production](#) in order to study (i) the leaching of major and trace elements from raw biomass ash and cement products containing biomass ash (ii) to perform a technical and environmental assessment of such cement products (iii) to evaluate the sustainability of application of biomass ash in cement as an alternative to landfilling [49].

Carr [50] performed heating experiments on the same samples to study the potential formation of hydraulic minerals. Initially, the optimum firing temperatures were identified by measuring the temperature at which chemical reactions and mineralogical transformation occurred with digital scanning calorimetry coupled with thermogravimetric analysis (DSC/TGS). Subsequently, the author placed the samples in a furnace (i.e. Carbolite), exposing them to the identified temperatures for different residence times (i.e. 1, 2, 4 and 6 h) and at different ramping rates (i.e. 5 °C/min and 10 °C min). Changes in mineral composition were detected by means of XRD analysis. Further details of the experimental setup and XRD scans can be found in Carr [50]. Table 1 shows technical information on selected biomass ash, LSF, AR and SR factors, firing temperature and mineral composition before and after re-heating experiment. It should be noted that the experimental conditions reported in the present work are different from modern kiln conditions. Therefore, results from the experiments serve the single purpose to estimate the potential formation of C_3S and C_2S minerals in a set of samples selected on the basis of the criteria proposed in this paper.

Mineral composition of FA 1 is dominated by quartz with smaller amounts of calcite, arcanite, portlandite and lime. The composition confirms the hypothesis made in Sect. [Biomass ash composition](#) on the negative influence that inclusion of bed sand particles has on the FA as clinker

Table 1 Technical information on fuel type, conversion technology and collection point of three biomass ash samples selected by Tosti et al. [47, 48] based on the criteria described in Sect. [Burnability of fly ash as raw material for cement production](#). Calculated and refer-

ence LSF, SR and AR cement factors are reported together with qualitative mineral analysis of the ash samples before and after the re-heating experiments at optimal temperature for hydraulic mineral formation as obtained by Carr [50]

	FA1	FA2	FA3
<i>Biomass fuel</i>	Mix of clean wood	Wood pellets	Paper sludge/waste wood
<i>Combustion technology</i>	Circulating fluidized bed	Pulverized fuel	Bubbling fluidized bed
<i>Ash type</i>	Electrostatic precipitator	Electrostatic precipitator	Electrostatic filter and bag filter
<i>LSF (ref. 0.9–1)</i>	0.7	1.7	2.1
<i>SR (ref. 2–3)</i>	3.6	1.6	1.7
<i>AR (ref. 1–4)</i>	0.8	0.3	2.3
<i>Optimal re-heating temperature (°C)</i>	1210	1214	1238
<i>Mineral composition “as received”</i>	Quartz, calcite, arcanite, portlandite, lime	Quartz, calcite, arcanite	Lime, quartz, C ₂ S, gehlenite, portlandite
<i>Mineral composition after re-heating</i> [50]	Wollastonite, pseudowollastonite	Merwinite, akermanite, α-C ₂ S	α’H-C ₂ S, β-C ₂ S, gehlenite

material. Clean wood was used as fuel and generally this feedstock is Ca-rich (see Sect. [Biomass feedstock composition](#) and Fig. 2). The FA1 sample, however, shows an LSF value of 0.7 that is lower than the reference and a value of 3.6 for SR that is higher than the reference. Even though burnability values would place FA1 sample within the area of “C₂S formation”, no presence of C₂S has been detected after reheating. The observed lack of C₂S is consistent with the low reactivity of Silica in quartz during the clinkerization process, compared to amorphous Silica, as described in Sects. [Biomass ash composition](#) and [Burnability of fly ash as raw material for cement production](#). This observation highlights the importance of the mineral form in which the elements are provided. A theoretically sufficient LSF value may thus not lead to the formation of C₂S and C₃S when Silica is predominantly provided by sand particle inclusions (e.g. as FA1).

The sample of FA2 is composed of quartz, calcite and arcanite. The LSF and AR burnability values of FA2 sample are outside of the reference range whereas the SR fall within this range. However, the presence of C₂S is detected after reheating but no C₃S. The lack of C₃S is attributed to the C₃S transitioned back to CaO and C₂S upon cooling [31], and/or the interference of Magnesium in the clinker minerals formation process (Sect. [Biomass ash as raw clinker material](#)). The AR ratio is lower than the reference value but is not considered to significantly influence the observed lack of C₃S formation in the FA2 sample. This last hypothesis is also supported by the formation of both akermanite and merwinite after reheating, which are Calcium-rich minerals with the chemical formulas Ca₂MgSi₂O₇ and Ca₃MgSi₂O₈, respectively, indicating that reaction between Ca, Mg and Si is favoured over the formation of C₃S. Sample FA3 is predominantly composed of lime with smaller amounts of quartz, C₂S, gehlenite and portlandite. The Calcium content

in FA3 is very high due to paper sludge used as fuel (Fig. 2), resulting in a very high LSF value compared to the reference. SR and AR values are within the reference ranges. This ash contains already C₂S mineral in its “as received” form as suggested also in Sect. [Biomass ash composition](#) highlighting its potential use as secondary cementitious material to be mixed directly with cement. After reheating of FA3 the amount of C₂S increases but no C₃S is formed. This absence is also associated with the likely transitioning of C₃S back to CaO and C₂S during cooling of the ash.

Table 1 shows that hydraulic minerals (i.e. C₂S) can be formed from FA2 and FA3 when these are exposed to a reheating step (like in a cement kiln). All optimal temperatures are at least 200 °C below traditional firing temperatures. However, none of the samples yielded any C₃S. It is hypothesized that, upon cooling, the C₃S transitioned back to CaO and C₂S [31]. The results shown in Table 1 confirm that clean biomass combusted in a pulverized fuel installation has higher potential to substitute raw clinker material than when combusted in a fluidized bed. These results also show that the presence of Mg should be minimized and controlled during biomass selection as fuel. Fly ash from paper sludge and similar fuels combusted in a fluidized bed can already contain C₂S and thus be used directly as secondary cementitious material in cement formulation. Alternatively, such ashes can represent a good source of raw material for clinker production due to their burnability values very close to the reference.

Content of Elements in Biomass Ash with Potentially Adverse Effects on Clinker Quality

The presence of Na₂O, K₂O, Cl, SO₃, MgO and P₂O₅ in the biomass ash mixture can adversely affect the quality of the final cement products when biomass ash is used as raw

Fig. 6 Alkali to Sulphur molar ratio (A/S) of biomass fly ash. The molar content of Alkali metals (K_2O and Na_2O) is corrected by the molar content of Cl according to Eq. 4, in order to account for the portion of alkali that is easily volatilized as alkali chlorides and therefore not included in the clinker phases. The remaining alkali is assumed to combine with sulphur to form alkali sulphates. The black dotted line represents a fixed A/S ratio of 1 (± 0.2 , grey dotted lines). Samples with A/S ratio within this A/S range (= Criteria 3, Fig. 1) are considered to have a lower probability of adverse alkali effects on cement clinker properties

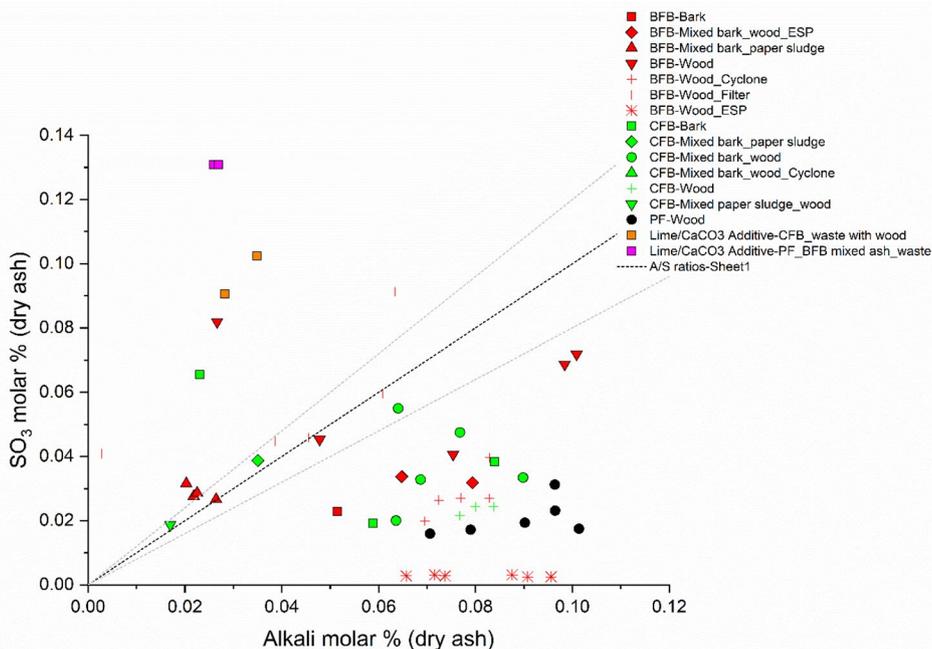
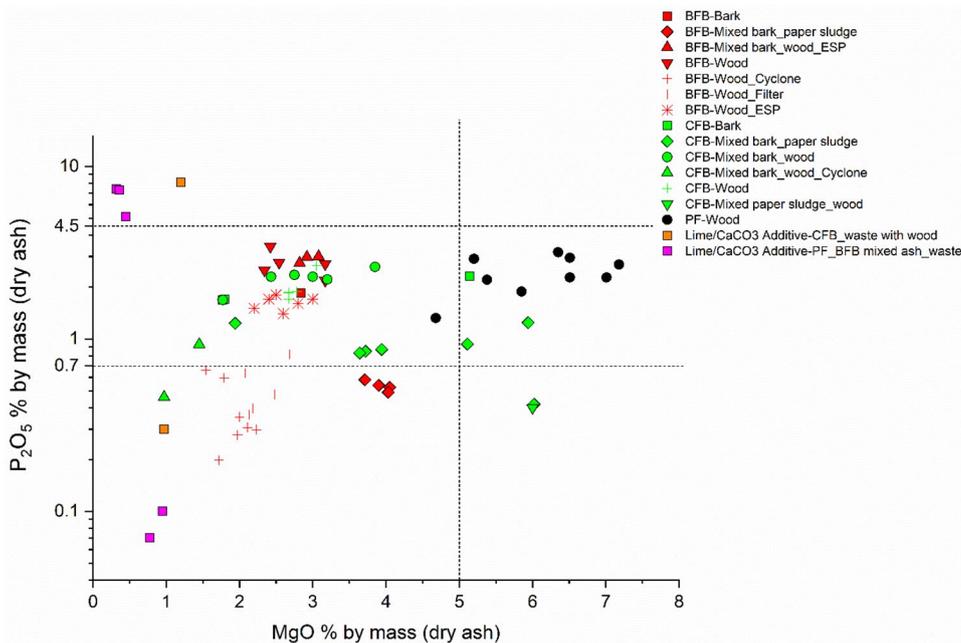


Fig. 7 MgO and P_2O_5 content in biomass fly ash samples. Small inclusion of MgO into clinker phases is beneficial and enhances C_3S production. MgO content higher than 5% by mass in the clinker (vertical dotted line) can promote the formation of adverse mineral phases for clinker quality. P_2O_5 hinders C_3S formation above a concentration of 0.7% by mass in the clinker, while the formation of C_3S is totally blocked above 4.5% by mass (horizontal dotted lines)



material for clinker production. Figure 6 shows the molar content of alkali metals and SO_3 in biomass fly ash samples. According to the criteria in Fig. 1 an A/S ratio between 0.8 and 1.2 indicates a good quality of the clinker. The total content of MgO and P_2O_5 in the biomass ash is plotted in Fig. 7 together with the Criteria 3 (Fig. 1) to assess potential formation of adverse mineral phases due to excessive MgO and reduction of C_3S formation by excess P_2O_5 in the clinker. The assessment is performed assuming the biomass ash replacing 100% of the traditional raw material.

Most biomass ash samples show an unbalanced A/S ratio with values higher than 1.2, due to the generally relatively high content of alkali in wood and woody biomass and low S content. Samples from fluidized bed combustion show on average an A/S ratio closer to the reference ratio compared to the pulverized fuel samples. The fluidised bed technologies are known to trap part of the alkalis in the silica bed material, leading to fly ash fractions with a relatively low alkali content [51]. In particular, samples from FB combustion of wood mixed with paper sludge have

a A/S ratio within or very close to the reference range. This can be explained by the combined alkali trapping effect of the fluidized bed and the very low alkali and S content of paper sludge. Adding paper sludge to wood and woody biomass could lead to fly ash with an adequate A/S ratio to limit the inclusion of alkali and SO_3 in the clinker phases, while these materials are also close to compositional requirements for potential formation of C_2S and C_3S (i.e. Criteria 1, Fig. 1).

During pulverized fuel combustion the inorganics present in the biomass fuel are recovered almost entirely in the fly ash. Although such ash samples from woody biomass were identified as potentially suitable to substitute up to 100% of traditional raw material, such high replacements can result in an excessive inclusion of alkali into the clinker phases with adverse consequences for the durability of cement. Pulverized fuel combustion is applied only to clean wood biomass due to technical reasons. Therefore, only a limited flexibility is allowed in the choice of biomass fuel for this combustion technique. This restriction implies that obtaining an appropriate A/S ratio should involve an external SO_3 rich source (e.g. ash from sludge combustion see Fig. 3).

Samples containing waste (e.g. MSW, industrial wastes) present extremely low A/S ratio. Generally, this is related to the combined effect of high concentrations of Cl and S in the waste. In some cases, the Cl concentration is so high that, when subtracted from the numerator in the A/S ratio, a negative value results (not shown in Fig. 6). Such high Cl and S concentrations are a limiting factor for using these ash types as raw clinker material, due to their adverse effects on corrosion in reinforced concrete and product durability. High SO_3 content in fly ash is not always linked to high Cl (e.g. when sludge is used as fuel, see also Fig. 3). As discussed earlier this type of ash is interesting as source of SO_3 to obtain an acceptable A/S ratio in a mixture of ash samples with otherwise suitable properties in accordance with the reference criteria.

Figure 7 shows the content of MgO and P_2O_5 in the biomass fly ash together with reference values as described in the Criteria 3 (Fig. 1). It is important to underline that in Fig. 7 the concentration of MgO and P_2O_5 in the ash is compared with reference concentration in the clinker. There is no detailed research available on the fraction of these elements that will be incorporated into clinker phases during clinkerization. Therefore, in this paper a worst-case scenario is adopted, assuming that the entire content of these elements in the ash passes into the clinker.

The MgO content of biomass ash is generally below the maximum reference value (i.e. 5% by mass). An exception is observed for pulverized fuel samples and some samples from fluidized bed combustion. However, the MgO content is not very far from the reference value. This means that even if most of the MgO in the biomass ash is included in the

clinker phases, this would likely result in an acceptable level. Therefore, MgO is not considered an important limiting factor for most biomass fly ash substitution of clinker raw material, although it could be undesirable for specific fly ash from pulverized fuel combustion as shown in Sect. [Mineral composition and thermal treatment of selected biomass ash](#).

A different situation is observed for the P_2O_5 content. In this case only few ash samples show a P_2O_5 content lower than the lower reference value of 0.7% by mass. At this concentration of P_2O_5 in the clinker, C_3S formation starts to diminish. Most of the biomass ash samples show P_2O_5 concentrations of around 3% by mass. Assuming that a substantial amount of P_2O_5 in the ash will be transferred to the clinker phases, P_2O_5 concentrations of around 3% would result in reduced C_3S formation. A content of 1% of P_2O_5 in clinker is considered to decrease the C_3S content by 10% [52]. This aspect could thus represent a limiting factor for utilization of biomass fly ash as raw clinker material. Further research is required to evaluate what proportion of P_2O_5 in biomass ash can be incorporated into clinker phases, and how this proportion is related to the P-speciation in specific ash types, in order to test the conservative assumption made in this paper. Moreover, a thorough investigation of the P-speciation in biomass ash may enable the development of further criteria to narrow down the P-fraction that can be transferred to the clinker phases.

Conclusions

Using biomass ash as raw material for cement clinker production is identified as a potentially valuable and feasible option to reduce CO_2 emissions, and to reduce the volume of biomass ash that is landfilled. The results show how combustion of specific biomass feedstock such as bark can help obtaining the desired CaO/ SiO_2 ratio of the ash. Wood and woody biomass can also provide a suitable CaO/ SiO_2 ratio that is limited mostly by the inclusion of exogenous material (e.g. sand). In order to enhance the suitability of biomass ash for substitution of raw clinker materials, the amount of exogenous material in the biomass fuel should be minimized, while increasing the bark content of fuel mixtures can be used to obtain the desired CaO/ SiO_2 ratio. Control of the chemical composition of the biomass feedstock, e.g. by dedicated blending of fuel mixtures, can further contribute to obtain a suitable ash for clinkerization.

We have shown that biomass ash quality can both be positively and negatively influenced by thermal conversion systems. Two combinations of biomass fuel/thermal conversion were identified as most promising for raw clinker replacement purposes. The combination of wood biomass with low exogenous inclusion and high bark content combusted in a pulverized fuel installation holds the highest replacement

potential, followed by fluidized bed combustion of combined paper sludge and wood/bark. The previously measured formation of hydraulic mineral C_2S from two of such samples, when exposed to a re-heating step similar to conditions in a cement kiln underpins this potential. C_3S formation could not be verified, which is attributed to the transition of C_3S to $CaO + C_2S$ during cooling, interference of MgO on C_3S formation and the low reactivity of Si in quartz. The MgO , P_2O_5 alkali, sulphur and chloride content of ash are identified as properties that can potentially limit the replacement rate of traditional raw clinker materials by biomass ash. Further investigation of particularly the P-speciation in biomass ash may enable the development of criteria to narrow down the P-fraction that can adversely affect hydraulic mineral formation.

Potentially suitable biomass feedstock (e.g. wood mixed with bark) can still result in an unsuitable ash for substitution of traditional cement raw materials. Particularly, cyclone ash from fluidized bed combustion contains fragmented bed particles that increase the Si content and result in an insufficient Ca/Si ratio. Mixing the cyclone ash with other ash fractions also negatively influences the burnability and, hence, the replacement potential of the ash. While it is currently still common practice to mix different ash streams, we recommend to collect and separate cyclone ash from the fine filter ash, when aiming for an ash quality suitable for substitution of traditional cement raw materials. Despite these potential limitations, we conclude that application of fly ash from fluidized bed combustion of paper sludge and wood/bark as a secondary cementitious material is identified as an alternative option to produce cement with a lower carbon footprint.

A concerted effort is recommended by both the cement industry (e.g. by adjusting kiln operation to accept the higher content of alkalis in biomass ash) as well as by the bioenergy industry (e.g. by optimizing ash quality) to support the use of biomass ash as raw material for clinker production. We recommend further research to investigate the effect of potentially suitable biomass ash as identified in this study, on the final clinker quality and the durability of the cement products.

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References

1. Habert, G., Billard, C., Rossi, P., Chen, C., Roussel, N.: Cement production technology improvement compared to factor four objectives. *Cem. Concr. Res.* **40**, 820–826 (2010). <https://doi.org/10.1016/j.cemconres.2009.09.031>
2. WBCSD-World business council for sustainable development.: Cement industry energy and CO_2 performance “Getting the numbers right.” (2009). <http://www.wbcd.org/Pages/EDocument/EDocumentDetails.aspx?ID=11095>. Accessed 10 Dec 2020
3. Schneider, M., Romer, M., Tschudin, M., Bolio, H.: Sustainable cement production—present and future. *Cem. Concr. Res.* **41**, 642–650 (2011). <https://doi.org/10.1016/j.cemconres.2011.03.019>
4. Cordeiro, G.C., ToledoFilho, R.D., Tavares, L.M., Fairbairn, E.M.R.: Pozzolanic activity and filler effect of sugar cane bagasse ash in Portland cement and lime mortars. *Cem. Concr. Compos.* **30**, 410–418 (2008). <https://doi.org/10.1016/j.cemconcomp.2008.01.001>
5. Demis, S., Tapali, J.G., Papadakis, V.G.: An investigation of the effectiveness of the utilization of biomass ashes as pozzolanic materials. *Constr. Build. Mater.* **68**, 291–300 (2014). <https://doi.org/10.1016/j.conbuildmat.2014.06.071>
6. Salvo, M., Rizzo, S., Caldirola, M., Novajra, G., Canonico, F., Bianchi, M., Ferraris, M.: Biomass ash as supplementary cementitious material (SCM). *Adv. Appl. Ceram.* **114**, S3–S10 (2015). <https://doi.org/10.1179/1743676115Y.0000000043>
7. IEA bioenergy: options for increased use of ash from biomass combustion and co-firing. <https://www.ieabioenergy.com/publications/options-for-increased-use-of-ash-from-biomass-combustion-and-co-firing/>. Accessed 10 Dec 2020
8. Du, S., Yang, H., Qian, K., Wang, X., Chen, H.: Fusion and transformation properties of the inorganic components in biomass ash. *Fuel* **117**, 1281–1287 (2014). <https://doi.org/10.1016/j.fuel.2013.07.085>
9. Niu, Y., Tan, H., Wang, X., Liu, Z., Liu, H., Liu, Y., Xu, T.: Study on fusion characteristics of biomass ash. *Bioresour. Technol.* **101**, 9373–9381 (2010). <https://doi.org/10.1016/j.biortech.2010.06.144>
10. Nunes, L.J.R., Matias, J.C.O., Catalão, J.P.S.: Biomass combustion systems: a review on the physical and chemical properties of the ashes. *Renew. Sustain. Energy Rev.* **53**, 235–242 (2016). <https://doi.org/10.1016/j.rser.2015.08.053>
11. Obernberger, I., Biedermann, F., Widmann, W., Riedl, R.: Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. *Biomass Bioenergy* **12**, 211–224 (1997). [https://doi.org/10.1016/S0961-9534\(96\)00051-7](https://doi.org/10.1016/S0961-9534(96)00051-7)
12. Vassilev, S.V., Baxter, D., Vassileva, C.G.: An overview of the behaviour of biomass during combustion: part II. Ash fusion and ash formation mechanisms of biomass types. *Fuel* **117**, 152–183 (2014). <https://doi.org/10.1016/j.fuel.2013.09.024>
13. Zevenhoven-Onderwater, M., Öhman, M., Skrifvars, B.-J., Backman, R., Nordin, A., Hupa, M.: Bed agglomeration characteristics of wood-derived fuels in FBC. *Energy Fuels* **20**, 818–824 (2006). <https://doi.org/10.1021/ef050349d>
14. Doudart de la Grée, G.C.H., Florea, M.V.A., Keulen, A., Brouwers, H.J.H.: Contaminated biomass fly ashes – characterization and treatment optimization for reuse as building materials. *Waste Manag.* **49**, 96–109 (2016). <https://doi.org/10.1016/j.wasman.2015.12.023>
15. Siddique, R.: Wood ash. In: *Waste materials and by-products in concrete*, pp. 303–321. Springer Berlin Heidelberg, Berlin, Heidelberg (2008)

16. Vassilev, S.V., Baxter, D., Andersen, L.K., Vassileva, C.G.: An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. *Fuel* **105**, 40–76 (2013). <https://doi.org/10.1016/j.fuel.2012.09.041>
17. Vassilev, S.V., Baxter, D., Andersen, L.K., Vassileva, C.G.: An overview of the composition and application of biomass ash: part 2. Potential utilisation, technological and ecological advantages and challenges. *Fuel* **105**, 19–39 (2013). <https://doi.org/10.1016/j.fuel.2012.10.001>
18. Berra, M., Mangialardi, T., Paolini, A.E.: Reuse of woody biomass fly ash in cement-based materials. *Constr. Build. Mater.* **76**, 286–296 (2015). <https://doi.org/10.1016/j.conbuildmat.2014.11.052>
19. Cheah, C.B., Ramli, M.: The engineering properties of high performance concrete with HCWA–DSF supplementary binder. *Constr. Build. Mater.* **40**, 93–103 (2013). <https://doi.org/10.1016/j.conbuildmat.2012.10.010>
20. Cheah, C.B., Ramli, M.: The implementation of wood waste ash as a partial cement replacement material in the production of structural grade concrete and mortar: an overview. *Resour. Conserv. Recycl.* **55**, 669–685 (2011). <https://doi.org/10.1016/j.resconrec.2011.02.002>
21. Siddique, R.: Utilization of wood ash in concrete manufacturing. *Resour. Conserv. Recycl.* **67**, 27–33 (2012). <https://doi.org/10.1016/j.resconrec.2012.07.004>
22. Paris, J.M., Roessler, J.G., Ferraro, C.C., DeFord, H.D., Townsend, T.G.: A review of waste products utilized as supplements to Portland cement in concrete. *J. Clean. Prod.* **121**, 1–18 (2016). <https://doi.org/10.1016/j.jclepro.2016.02.013>
23. Chao-Lung, H., Anh-Tuan, B.L., Chun-Tsun, C.: Effect of rice husk ash on the strength and durability characteristics of concrete. *Constr. Build. Mater.* **25**, 3768–3772 (2011). <https://doi.org/10.1016/j.conbuildmat.2011.04.009>
24. Zain, M.F.M., Islam, M.N., Mahmud, F., Jamil, M.: Production of rice husk ash for use in concrete as a supplementary cementitious material. *Constr. Build. Mater.* **25**, 798–805 (2011). <https://doi.org/10.1016/j.conbuildmat.2010.07.003>
25. Aprianti, E., Shafiqh, P., Bahri, S., Farahani, J.N.: Supplementary cementitious materials origin from agricultural wastes – a review. *Constr. Build. Mater.* **74**, 176–187 (2015). <https://doi.org/10.1016/j.conbuildmat.2014.10.010>
26. Tay, J.-H., Show, K.-Y.: Use of ash derived from oil-palm waste incineration as a cement replacement material. *Resour. Conserv. Recycl.* **13**, 27–36 (1995). [https://doi.org/10.1016/0921-3449\(94\)00012-T](https://doi.org/10.1016/0921-3449(94)00012-T)
27. Buruberri, L.H., Seabra, M.P., Labrincha, J.A.: Preparation of clinker from paper pulp industry wastes. *J. Hazard. Mater.* **286**, 252–260 (2015). <https://doi.org/10.1016/j.jhazmat.2014.12.053>
28. Modolo, R.C.E., Senff, L., Ferreira, V.M., Tarelho, L.A.C., Moraes, C.A.M.: Fly ash from biomass combustion as replacement raw material and its influence on the mortars durability. *J. Mater. Cycle Waste Manag.* (2017). <https://doi.org/10.1007/s10163-017-0662-9>
29. Simão, L., Justi, J., Lóh, N.J., Hotza, D., Raupp-Pereira, F., Labrincha, J.A., Montedo, O.R.K.: Waste-containing clinkers: valorization of alternative mineral sources from pulp and paper mills. *Process Saf. Environ. Prot.* **109**, 106–116 (2017). <https://doi.org/10.1016/j.psep.2017.03.038>
30. Eggleston, H.S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K.: IPCC guidelines for national greenhouse gas inventories (2006). <http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.htm>. Accessed 10 December 2020
31. Hewlett, P.: Lea's chemistry of cement and concrete. Butterworth-Heinemann, Oxford (2003)
32. Taylor, H.F.W.: Cement chemistry. Thomas Telford, London (1997)
33. Telschow, S.: Clinker burning kinetics and mechanism. Technical University of Denmark, Denmark (2012)
34. Maclaren, D.C., White, M.A.: Cement: its chemistry and properties. *J. Chem. Educ.* **80**, 623 (2003). <https://doi.org/10.1021/ed080p623>
35. Staněk, T., Sulovský, P.: The influence of phosphorous pentoxide on the phase composition and formation of Portland clinker. *Mater. Charact.* **60**, 749–755 (2009). <https://doi.org/10.1016/j.matchar.2008.11.013>
36. European commission: phydades - standardization of analysis methods for biomass and ash: project information, <http://p29596.typo3server.info/36.0.html>. Accessed 10 Dec 2020
37. Värmeforsk: ash program: environmentally friendly utilisation of ashes, <http://www.varmeforsk.se/allaska-en>. Accessed 10 May 2018
38. Tarelho, L.A.C., Teixeira, E.R., Silva, D.F.R., Modolo, R.C.E., Labrincha, J.A., Rocha, F.: Characteristics of distinct ash flows in a biomass thermal power plant with bubbling fluidised bed combustor. *Energy* **90**, 387–402 (2015). <https://doi.org/10.1016/j.energy.2015.07.036>
39. Werkelin, J., Skrifvars, B.-J., Hupa, M.: Ash-forming elements in four scandinavian wood species. Part 1: summer harvest. *Biomass Bioenergy* **29**, 451–466 (2005). <https://doi.org/10.1016/j.biombioe.2005.06.005>
40. Chandler, A.J., Eighmy, T.T., Hjelmar, O., Kosson, D.S., Sawell, S.E., Vehlow, J., van der Sloot, H.A., Hartlén, J.: Municipal solid waste incinerator residues. Elsevier, Amsterdam (1997)
41. Pels, J.R., de Nie, D.S., Kiel, J.H.A. 2006 GASASH. Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management.
42. van Loo, S., Koppejan, J.: The handbook of biomass combustion and co-firing. Routledge, London (2008)
43. Lothenbach, B., Scrivener, K., Hooton, R.D.: Supplementary cementitious materials. *Cem. Concr. Res.* **41**, 1244–1256 (2011). <https://doi.org/10.1016/j.cemconres.2010.12.001>
44. Segui, P., Aubert, J.E., Husson, B., Measson, M.: Characterization of wastepaper sludge ash for its valorization as a component of hydraulic binders. *Appl. Clay Sci.* **57**, 79–85 (2012). <https://doi.org/10.1016/j.clay.2012.01.007>
45. van Lith, S.C., Alonso-Ramírez, V., Jensen, P.A., Frandsen, F.J., Glarborg, P.: Release to the gas phase of inorganic elements during wood combustion. Part 1: development and evaluation of quantification methods. *Energy Fuels* **20**, 964–978 (2006). <https://doi.org/10.1021/ef050131r>
46. Werkelin, J., Skrifvars, B.-J., Zevenhoven, M., Holmbom, B., Hupa, M.: Chemical forms of ash-forming elements in woody biomass fuels. *Fuel* **89**, 481–493 (2010). <https://doi.org/10.1016/j.fuel.2009.09.005>
47. Tosti, L., van Zomeren, A., Pels, J.R., Dijkstra, J.J., Comans, R.N.J.: Assessment of biomass ash applications in soil and cement mortars. *Chemosphere* **223**, 425–437 (2019). <https://doi.org/10.1016/j.chemosphere.2019.02.045>
48. Tosti, L., van Zomeren, A., Pels, J.R., Comans, R.N.J.: Technical and environmental performance of lower carbon footprint cement mortars containing biomass fly ash as a secondary cementitious material. *Resour. Conserv. Recycl.* **134**, 25–33 (2018). <https://doi.org/10.1016/j.resconrec.2018.03.004>
49. Tosti, L., van Zomeren, A., Pels, J.R., Damgaard, A., Comans, R.N.J.: Life cycle assessment of the reuse of fly ash from biomass combustion as secondary cementitious material in cement products. *J. Clean. Prod.* **245**, 118937 (2020). <https://doi.org/10.1016/j.jclepro.2019.118937>
50. Carr, N.N. 2019 Biomass derived binder: development of the scientific basis for methodologies that enable the production of renewable sustainable cement based on ashes derived from the conversion of biomass residues as determined by qualitative

mineralogical analysis. <https://doi.org/https://doi.org/10.4233/uuid:12821467-3df9-40ab-a297-159497650b8c>

51. Visser, H.J.M., Laughlin, K.: Ash and elemental balance for a medium and large scale fluidised bed combustion test. ECN Publication, Petten (2004)
52. Kurdowski, W.: Portland cement clinker. In: Cement and concrete chemistry, pp. 21–127. Springer Netherlands, Dordrecht (2014)

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