IMPROVING CIRCULARITY OF BIOMASS ASH

A theoretical, experimental,
and modelling approach
to find sustainable solutions
for application in cement or soil

LORENZO TOSTI

Propositions

1. Biomass ash properties can be influenced by fine-tuning the match between feedstock and thermal conversion technology to optimize the suitability of biomass ash for its use in the cement industry.
(this thesis)
2. The use of biomass ash in cement has a lower environmental impact than when the ash is landfilled, while the extent of this impact reduction is determined by the contribution of the ash to the overall strength development of blended cement.
(this thesis)
3. Misinformation can spread faster than a virus and this can lead to more victims than the virus itself.
4. Striving to push recycling rates towards 100% is not a sustainable choice.
5. The transition to a sustainable world can be fully realised only through a consideration of the societal needs.
6. The PhD journey resembles the vinification process as refined wines are seldomly obtained by a short development time.
7. The Dutch master the art of cheese making but not the art of preparing a pasta dish, although they could improve the quality of their pasta dishes by starting to follow the basic rule that pasta is not a side dish.

Propositions belonging to the thesis, entitled

Improving circularity of biomass ash

A theoretical, experimental, and modelling approach to find sustainable solutions for application in cement or soil

Lorenzo Tosti

Wageningen, 15 October 2021

Improving circularity of biomass ash

*A theoretical, experimental, and modelling
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application in cement or soil*

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This research was conducted under the auspices of the Graduate School for Socio-Economic and Natural Sciences of the Environment (SENSE)

Improving circularity of biomass ash

A theoretical, experimental, and modelling approach to find sustainable solutions for application in cement or soil

by Lorenzo Tosti

Thesis

submitted in fulfilment of the requirements for the degree of doctor

at Wageningen University

by the authority of the Rector Magnificus,

Prof. Dr. A.P.J. Mol,

in the presence of the

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to be defended in public

on Friday 15 October 2021

at 4 p.m. in the Aula.

Lorenzo Tosti

Improving circularity of biomass ash

A theoretical, experimental, and modelling approach to find sustainable solutions for application in cement or soil, 214 pages.

PhD thesis, Wageningen University & Research, Wageningen, the Netherlands (2021)

With references, with summary in English

ISBN 978-94-6395-898-1

DOI <https://doi.org/10.18174/550164>

Preface

The work presented in this PhD thesis was carried out at the former *Energy research Centre of the Netherlands (ECN)*, now part of the Netherlands organisation for applied scientific research (TNO) under the supervision of Professor Rob Comans, Dr. André van Zomeren and Dr. Jan Pels from March 2013 to September 2017. The research presented in this thesis is the personal contribution of the PhD candidate to the project “Towards the development of CO₂ neutral renewable cement (BioCement)”. The main aim of this research project was to develop a sustainable biomass ash-based binder able to fully replace Portland cement in concrete product applications. The BioCement project was part of the research program ‘Bio-Based Geo & Civil Engineering for a Sustainable Society (BioGeoCivil)’, funded by the Dutch NWO institute, with the broad aims of developing novel bio-based construction materials that can be used in Civil- and Geo-engineering constructions to enhance the sustainability performance of the sector.

The thesis is organized in three parts, the first of which provides background information and places the findings of the PhD into context (Chapter 1), the second part consists of the papers listed below (Chapters 2, 3, 4 and 5) and the third part draws general conclusions and recommendations (Chapter 6).

Chapter 1: Introduction

Chapter 2: Tosti, L., van Zomeren, A., Pels, J.R. & Comans, R. N. J. (2021). Evaluating Biomass Ash Properties as Influenced by Feedstock and Thermal Conversion Technology towards Cement Clinker Production with a Lower Carbon Footprint. *Waste Biomass Valor.* <https://doi.org/10.1007/s12649-020-01339-0>

Chapter 3: Tosti, L., van Zomeren, A., Pels, J. R., Dijkstra, J. J., & Comans, R. N. J. (2019). Assessment of biomass ash applications in soil and cement mortars. *Chemosphere*, 223, 425-437. <https://doi.org/10.1016/j.chemosphere.2019.02.045>

Chapter 4: Tosti, L., van Zomeren, A., Pels, J. R., & Comans, R. N. J. (2018). Technical and environmental performance of lower carbon footprint cement mortars containing biomass fly ash as a secondary cementitious material. *Resources, Conservation and Recycling*, 134, 25-33, <https://doi.org/10.1016/j.resconrec.2018.03.004>

Chapter 5: Tosti, L., van Zomeren, A., Pels, J. R., Damgaard A., Comans, R. N. J. (2020). Life cycle assessment of the reuse of fly ash from biomass combustion as secondary cementitious material in cement products, *Journal of Cleaner Production*, Volume 245, 2020, 118937, ISSN 0959-6526, <https://doi.org/10.1016/j.jclepro.2019.118937>.

Chapter 6: General discussion and final remarks.

In addition, the following publications, not included in this thesis, were also completed during this PhD project.

Tosti, L., van Zomeren, A., Pels, J. R., & Comans, R. N. J. (2015). Development of new cement formulations containing paper sludge fly ash as secondary cementitious material. *Proceedings of the 9th International Conference on the Environmental and Technical Implications of Construction with Alternative Materials - Resource Efficiency in Construction. Santander, SPAIN, 10–12 June 2015*.

Tosti, L., van Zomeren, A., Pels, J. R., Damgaard, A., & Comans, R. N. J. (2016). Life Cycle assessment of the reuse of fly ash from paper sludge combustion in cement formulations. *Proceedings of the 5th International Conference on Industrial and Hazardous Waste Management “CRETE 2016”, Chania (Crete, Greece), 27– 30 September 2016*.

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Chapter 1

Introduction

Chapter 1

Introduction

1. BACKGROUND AND PROBLEM DEFINITION

Environmental awareness has become increasingly important in our society. The European Commission has initiated the transition of Europe into a highly energy efficient, low-carbon economy. Energy production from renewable sources, saving energy and natural resources, as well as reducing CO₂ emissions while managing wastes are important actions to enable such a transition. The use of biomass for heat and electricity generation is growing rapidly in many countries. The most important renewable energy sources in the EU-28 in 2017 were wood and other solid biofuels, accounting for 42% of primary renewables production (European Commission, 2018). The growing use of biomass for energy purposes results in an increasing amount of biomass ash residues. According to the Waste Hierarchy as defined in the Waste Framework Directive (Directive 2008/98/EC, 2008), the minimum standard for removal of waste is disposal. This means that there is no ban on disposal of biomass ashes in a landfill. The most recent IEA study reports that for four of the five European countries included in the study, landfilling of biomass ash is still the preferred solution (IEA, 2019). However, these residues should be managed in a circular way to achieve a total sustainable energy production from biomass thermal conversion. As an example, fly ash originating from coal combustion power plants has found application as partial cement replacement since the second half of the last century (Hewlett, 2003). Since then, much research has been carried out on the effects of coal fly ash on cement and concrete properties (Cheah et al., 2017; Hemalatha and Ramaswamy, 2017; Hewlett, 2003; Law et al., 2015, 2015; Siddique, 2008). This replacement has in general a positive influence on workability and enhanced durability of the fly ash containing cement and concrete (Hewlett, 2003; Taylor, 1997). The advantages of using coal fly ash resulted in development of national protocols and later also European standards (EN 450-1, 2005) to assess the quality of the coal fly ash in view of its use in cement and concrete. In the Netherlands coal (and co-combusted) fly ash is used in concrete at a large scale (van Loo and Koppejan, 2008).

In EU (15), about 11.6 million tons of coal fly ash were used in construction industry and underground mining in 2016 (ECOBA, 2016).

Given the increased utilization of biomass for energy production, the resulting biomass ash has started to be an integrated part of the biomass energy production system and many different management practices have been proposed or are currently applied in different countries (Lamers et al., 2018). This change of perspective is also encouraged by the development of the circular economy concept and the environmental and economic advantages that may be obtained from beneficial biomass ash reuse.

Cement is an essential ingredient for concrete that is currently the most used construction material worldwide. The global average gross CO₂ emission per ton of cement is about 860 kg accounting for 5-8% of total human atmospheric CO₂ emission (Global Cement and Concrete Association, 2019). The cement industry has a great potential of reducing CO₂ emissions and raw material consumption and it has shown to put a lot of efforts in providing sustainable solutions and a substantial progress has been made throughout the years (Scrivener et al., 2016). Nevertheless, the margin for improvement is still large.

In the past, the utilization of coal ashes has been developed from being a waste to a valuable secondary raw material for utilization in building materials for road construction and civil engineering applications. The same challenge is now facing the biomass energy systems and the cement industry which are called upon to develop management and utilization options for biomass ash following the best practices depicted in the Waste hierarchy of the Waste directive (Lamers et al., 2018). On the other hand, technical and environmental requirements for the application of biomass ash residues in cement or as soil amendment must be met. These requirements are largely dependent on biomass ash chemical and physical properties which in turn are influenced by biomass type and origin, thermal conversion technology and ash removal systems (or flue gas cleaning technology) adopted (Cruz et al., 2019; Jenkins et al., 1998; Li et al., 2013; Obernberger et al., 2006; Saqib and Bäckström, 2015; Vassilev et al., 2013a). Even though several potential applications of biomass ash have been investigated and proposed (Pels and Sarabèr, 2011; Vassilev et al., 2013a, 2013b; Freire et al., 2015; Maresca et al., 2017; Knapp and Insam, 2011; Karlun et al., 2008), only a limited amount of biomass ash is re-used or recycled and most of it is still landfilled (Cruz et al., 2019; IEA, 2019). To valorise biomass ash

residues and increase its utilization and recycling it is necessary to know and be able to predict ash characteristics (including both the technical and environmental characteristics) which are obtained by a given technology (and its typical operating conditions, e.g., temperature) and from a specific type of biomass as fuel, even prior to their production.

2. ASH FROM THERMAL CONVERSION OF BIOMASS

Biomass ash is the residue that is left after thermo-chemical conversion of biomass (combustion, gasification, and pyrolysis) and recovered at different points in the installation. Different methods of biomass thermal conversion have been developed during the years and in principle we can distinguish the following technologies (van Loo and Koppejan, 2008) that are also schematically represented in Figure 1:

Grate stoker (GS): In a GS reactor the fuel is introduced on a grate where primary air passes through. Operational temperature is between 1000-1200 °C. GS is appropriate for firing fuels with large particle sizes, and relatively high moisture contents (up to 65%). Combustion of blended biomass fuel is not commonly practiced.

Fluidised Bed (FB): The reactor usually consists of a vertical steel vessel containing a bed of granular material such as silica sand, limestone, alumina or ceramic material. The bed material is supported by a perforated grid in order to allow air to be injected through diffusers causing the bed to expand and become fluid. Distinctions can be made between bubbling fluidized bed (BFB) and circulating fluidized bed (CFB). In BFB the bed's particle size is comprised between 0.5-1 mm and the air injection velocity is moderate (1-2m/s). This combination of bed particle size and air velocity causes the bed to stay in place in the furnace. In a CFB, a bed material with smaller particle size between 0.2-0.4 mm is employed along with faster air injection velocity of around 5 to 10 m/s allowing the bed material and the fuel to leave the furnace. The bed material is then collected and recirculated into the furnace. Operational temperatures are between 800 and 900 °C. FB technology can convert a wide spectrum of biomass and mixtures of them.

Pulverised Fuel (PF): The fuel and primary air are introduced into the furnace and the thermal conversion of the fuel occurs while it is suspended in air. The injection of secondary air helps to burn the combustion gases. Operational temperature is normally around 1400 °C. This

technology is limited to fuels with particle sizes $<2\text{mm}$ that can be mixed with air and sprayed into the furnace.

Figure 1 Main technologies employed in thermal conversion of biomass.

For each of these three types of installation different ash streams are produced after thermal conversion. Essentially two main streams can be distinguished: bottom ash (BA) and fly ash (FA). When the ash is collected from the discharging point placed at the low end of the furnace, we refer to this ash fraction as bottom ash (BA). The fraction that is entrained with the flue gas and collected afterwards in the flue gas treatment section of the installation is generally referred as fly ash (FA). Both ash fractions are mainly composed by the non-combustible inorganic part and impurities (i.e., sand, soil, dust) present in the fuels and by a residual organic fraction that might be still present in the ash depending on the efficiency of thermal conversion. Depending on the biomass fuel type and thermal conversion system adopted, bottom and fly ashes are produced in different amounts, with a different morphology, chemical and mineral compositions as well as leaching properties. Some studies have investigated the influence of fuel type and thermal conversion technology adopted on the physical-chemical properties and elemental composition of the resulting ash. In general, the chemical composition of biomass ash and its natural pH vary with ash type (Barbosa et al., 2013; Dahl et al., 2009; Maresca et

al., 2017) and are a function of biomass fuel (Vassilev et al., 2013a; Werkelin et al., 2011) and combustion technology (Cruz et al., 2019; Freire et al., 2015; van Loo and Koppejan, 2008).

Inorganic components in biomass used as fuel are highly variable (Jenkins et al., 1998; Olanders and Steenari, 1995; van Loo and Koppejan, 2008) leading to a variable ash elemental composition (Vassilev et al., 2014, 2013a, 2010). Commonly, ashes from the combustion of woody fuels feature high amounts of Ca, Si, Mg and K while ashes from herbaceous fuels are dominated by Si, K and Ca. Moreover, ashes from herbaceous fuels present a lower content of heavy metals. The lower heavy metal uptake is due to significantly shorter rotation periods, higher pH values and lower heavy metal depositions on agricultural soils. There are significant differences in the distribution of nutrient and heavy metal content between bottom ash and fly ash. The volatilization of specific chemical elements in biomass occurs when the combustion temperature is high (800- 1200 °C), and these elements can condensate in the downstream parts of the combustion system and/or adsorb onto fine-sized ash particles (Li et al., 2013; Liao et al., 2007; Misra et al., 1993). The content of metals in biomass ash can have environmental implications when this material is used in specific applications due to the leaching of metals to the surrounding environment (Maresca et al., 2018, 2017). Volatile heavy metals such as Zn and Cd as well as the semi-volatile nutrient K show the highest concentrations in the fine fly ash, while non-volatile elements like Ca, Mg, Si, show the highest concentrations in the bottom ash. Since the combustion temperature in fluidized bed furnaces is usually lower (between 800 and 900 °C) than in fixed bed furnaces (900 to 1400 °C) the enrichment of volatile elements in the fly ash fractions of fluidized bed furnaces is less pronounced compared to fly ashes from fixed bed furnaces (Misra et al., 1993; Obernberger et al., 2006; Saqib and Bäckström, 2015; Vassilev et al., 2014, 2013a, 2013b). The presence of Cadmium (Cd) and to a lesser extent Zinc (Zn) in ash is of particularly relevance due to its potential environmental impacts.

As briefly introduced in the previous paragraph the composition of biomass ash can vary considerably due to different biomass fuel types and compositions within the same fuel types, thermal conversion technology, and ash fraction. Therefore, the identification of a universal suitable application for a given biomass ash is not very likely. Despite the total annual worldwide production of biomass ash is growing fast (almost 500 million tons per year), most part of this material (around 70%) is currently landfilled (Cruz et al., 2019). The main reasons behind the current situation are essentially related to the environmental concern, sustainability,

low market volumes and differences and variations in ash quality (heterogeneity). In addition, there are limitations in technical and regulatory regulations as well as logistics. General issues are also the lack of awareness, lack of knowledge and lack of willingness of plant operators, potential end-users and authorities alike to start or increase utilization (IEA, 2019).

3. MAIN APPLICATIONS FOR BIOMASS ASH

Most common valorisation alternatives for the biomass ashes include construction, civil engineering (e.g. road construction and incorporation in cementitious materials) (Sigvardsen et al., 2019; Teixeira et al., 2019) and soil applications (e.g. soil amendment, fertilizer, pH control) (Cruz et al., 2017; Freire et al., 2015; Maresca et al., 2017; Silva et al., 2019). The wide category of construction products includes direct utilization, e.g., in road construction, and utilization as raw material in the manufacturing of construction products, as secondary cementitious material or filler in concrete and cement, or in lightweight aggregates for concrete. In previous work, BA from grate combustion has been reported to be a suitable sub-base material for road construction and BA from fluidized bed provided an adequate sand substitute in construction and as a low quality filler material in concrete (Ribbing and Bjurström, 2011). Biomass FA has been shown to have binding properties or pozzolanic activity and can replace part of the clinker content in cement, and can thus contribute to reducing CO₂ emissions associated with traditional clinker production (Demis et al., 2014; Salvo et al., 2015; Siddique, 2012).

3.1. Biomass ash as a substitute of raw materials for clinker production or as secondary cementitious material

Cement is a hydraulic binder that sets and hardens by means of hydration reactions and processes when mixed with water. After the hardening process, cement retains its strength and stability even under water. Several types of cement may be produced, such as ordinary Portland cement (OPC), pozzolan-lime cement, calcium aluminate cement, calcium sulfoaluminate cement or geopolymers cement. Ordinary Portland cement (OPC) is the most common type of cement that is used in the construction industry worldwide. It is well known that the primary functional (hydraulic) elements in Portland cement include the following mineral phases: tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A) and tetracalcium aluminate ferrite (C₄AF) (Hewlett, 2003). These minerals are mainly produced by heating a

mixture of limestone and clay (which feature calcium carbonate and silicate as main constituents, respectively) ultimately to a temperature of about 1450 °C in the cement oven (kiln) (Taylor, 1997). This process leads to the production of the final ground mineral mixture that is known as clinker. Around 860 kg CO₂/ton clinker is released during the clinker production process. This emission is due to the decarbonisation of limestone to produce CaO for the clinker phases. Furthermore, carbon-based fuels for the heating of the kiln (and the preheater) release the remaining kg of CO₂/ton clinker (Habert et al., 2010).

Secondary cementitious materials (SCMs) are inorganic substances that can be added to traditional cement. SCMs do normally not contain C₃S and/or C₂S minerals (i.e., the main hydraulic minerals contained in Portland cement) but they contribute to the properties of hardened cement products through either hydraulic or pozzolanic activity, depending on their SiO₂ and Al₂O₃ content. Both types of material do not react with water in the absence of other activating substances. Pozzolanic materials are generally high in SiO₂ and Al₂O₃ (>70% wt.) and sufficiently reactive to form CSH when mixed with water and CaO. Latent hydraulic materials have an intermediate composition between pozzolanic material and Portland cement and act as hydraulic cement if mixed with water and alkaline substances. When considering the performance of SCMs the principal characteristics to be taken into account are their physical properties as particle size distribution and specific surface area, and their chemical properties including oxides composition and amorphous content of oxides (Juenger and Siddique, 2015). Furthermore, when SCMs are added to cement the presence of minor constituents such as Na₂O, K₂O, SO₃ and Cl might cause the deterioration of cement. The combination of elements needed for the cement reactions and the (absence of) elements that can deteriorate the properties of the cement need to be in balance to obtain a good cement quality.

The composition of fly ash to be used in cement is prescribed by the European standard EN-450. In practice the standard allows for the utilization of fly ash from coal combustion or co-combustion of coal with up to 20 wt.% biomass (i.e., virgin wood). At this rate of co-combustion, the properties of the resulting fly ash are dominated by the coal-ash and the material can be used in the same way. A co-combustion rate of 40% wt.% is also allowed if the biomass type is listed in the EN-450 and the resulting ash complies with all requirements (IEA, 2019).

Biomass ash can represent a valuable substitute for traditional raw material since it can contain high amounts of CaO , SiO_2 , Al_2O_3 and Fe_2O_3 depending on the biomass fuel and combustion technology adopted. Replacing part of the limestone as raw material with biomass derived CaO would reduce CO_2 emissions drastically due to (partial) elimination of the limestone calcination process. Alternatively, biomass ash can be blended with traditional cement and act as secondary cementitious material depending on its composition and hydraulic activity and thus reducing the amount of cement needed. Besides reducing greenhouse gas emissions due to lower energy and raw materials consumption, the utilization of biomass ash in clinker production or as secondary cementitious material would result in the additional beneficial effects of avoiding the landfilling of such residues. Understanding the extent to which the quality of biomass ash can be optimized for its use in cement applications and quantifying the potential environmental improvements of cement products containing biomass ash can increase the circularity of both cement and biomass energy industries.

3.2. Soil applications

Biomass ash contains macro and micro-nutrients which are taken away from soil when biomass is harvested. Biomass ash recycling to soil where biomass was grown is considered the best sustainable option since it closes the nutrient cycle. Similarly, return of biomass ash to other forests or soil areas than the biomass growing area is a practice that can help preserving or restoring the original level of nutrients and acid buffering capacity of soil, which are altered by intense harvesting of biomass (Hannam et al., 2018). Besides the nutrient balance, recycling of ash to soil encompasses many aspects that must be taken into account, in particular a) biomass fly ash has a very high pH which may alter the pH of the upper soil layer causing a shock to the flora and fauna with negative consequences for the ecosystems, b) biomass ash quality must be high enough to prevent pollution as a result of the spreading of the ashes (Pels and Sarabère, 2011). European countries with a proven experience on biomass ash recycling to soil (e.g., Denmark, Finland and Austria) have established legislation that allows and controls recycling of biomass ash to forest and agricultural areas based on the total content of elements in the ash. Often ashes do not meet such requirements due to relatively high concentrations of metals (e.g., Cd, Cr, Pb and Zn) even when the ashes originate from clean and untreated biomass. However, the total content of contaminants does not necessarily have a direct relation with the potential release (leaching) and, hence, the risks in a given application scenario. A comprehensive

characterization of different biomass ash types and leaching properties could provide useful information on source-term release from ashes in terms of nutrients and contaminants and improve the potential of utilization in soil.

4. RESEARCH OBJECTIVES AND THESIS OUTLINE

The project “Towards the development of CO₂ neutral renewable cement (BIOCement)” was part of the Dutch national research program “Bio-Based Geo & Civil Engineering for a Sustainable Society (BioGeoCivil)”, funded by the Dutch technology foundation STW (currently NWO-TTW) on novel biobased construction materials that can be used in Civil and Geo engineering construction to enhance the sustainability performance of the sector. The main aim of the BIOCement research project was to develop the scientific basis for methodologies that enable the production of renewable sustainable cement (i.e., “bio-cement”), based on ashes derived from the conversion of biomass fuel. The BIOCement product was intended to be technically identical and environmentally superior to traditional Portland cement, with a significantly lower environmental footprint during its entire life cycle. The research presented in this PhD thesis was conducted as part of the BIOCement project. The main objectives of this thesis are:

- 1) Evaluating the potential of biomass ash as (1) a replacement of traditional raw materials for clinker production or as secondary cementitious material in blended cement formulations, and (2) as soil amendment.
- 2) Evaluating the environmental properties of the ash and ash based obtained products (i.e., BioCement products).

Theoretical, experimental, and modelling approaches have been employed to achieve the mentioned objectives. The specific objectives and research approach of the individual chapters of this thesis are outlined in more detail below.

The functionality of an ash as raw material for clinker production depends on chemical, mineralogical and physical properties. These properties are strongly influenced by the biomass resource utilized as fuel (e.g., type of biomass, plant species or part of plants) and biomass combustion techniques and conditions employed. In *Chapter 2* the chemical and physical

parameters with an advantageous influence on properties of biomass ash that are required for its utilization as raw clinker material are identified, and the extent to which these properties can be controlled to obtain ash with a high application potential is assessed. A novel approach is proposed based on a large dataset of biomass fuel and ash composition. The theoretical approach proposed in Chapter 2 can help to evaluate beforehand the potential of biomass ash as substitute for traditional cement materials. The evaluation covers the entire ash production chain from biomass selection through combustion technology and ash management.

An important concern regarding the application of biomass ashes in cement products and soil is the potential enhanced leaching of contaminants. Nevertheless, there is little information available in the current literature on biomass ash leaching properties and on the potential environmental risks associated with reuse options. In the case of recycling of nutrients contained in the biomass ash, all regulations and recommendations are currently applied based on total content of elements in the ash. *Chapter 3* investigates the pH-dependent availability and leaching of major and trace elements for a wide range of biomass ashes with the aim of identifying common and specific release trends among the different types of biomass ash, fuel and/or thermal conversion technology. Furthermore, a technical and environmental assessment of selected biomass ash for application in soil or in cement mortars is performed, using both the total content and leaching of elements. The main differences and limitations of the two approaches are evaluated with the intent of increasing the knowledge on biomass ash re-use options and identify ash properties that need consideration regarding both functional and environmentally safe recycling of this material.

Based on the results obtained in *Chapter 3*, *Chapter 4* further evaluates the technical and environmental performance of blended cement mortars containing different replacement ratios of selected biomass fly ashes. The technical evaluation includes an assessment based on compressive strength development, an important quality criterion for the construction industry. A combination of different leaching tests is employed to assess the potential environmental impact of cement containing biomass ash under different application scenarios. Results from this work form a basis to assess the sustainability of cement containing biomass ash in a wider perspective, beyond energy and raw material savings. The testing and assessment approach that is presented in *Chapter 4*, may also support the development of a more circular use of cementitious materials in multiple life cycles.

The inclusion of biomass ash in cement results in evidently positive effects such as reduction of energy and raw materials consumption and avoiding landfilling of the biomass ash. On the other hand, some potentially toxic elements present in the biomass ash might be released in the environment during the different life stages of the fly ash containing cement as investigated in **Chapter 3 and 4**. In **Chapter 5** the potential environmental impacts associated with the current waste management practice for biomass ash (reference scenario, i.e. landfilling) and the potential of reuse as a secondary cementitious material in cement are compared by means of a Life Cycle Assessment methodology (LCA). The LCA methodology is extended, contrary to most common studies available in the literature, to both the use phase and the end-of-life phase of cement products. Furthermore, the critical parameters of the modelled systems are identified and the sensitivity of the LCA result to such parameters is quantified. The results described in **Chapter 5** provide new insights in the methodological setup of LCA scenarios for the assessment of alternative materials to replace cement.

Finally, **Chapter 6** is dedicated to the general discussion of the thesis findings. The intent of **Chapter 6** is to reflect on the work conducted and on the implications that the findings can have on the biomass ash management practices and sustainable construction products. Major drawbacks linked with the current regulations and standards governing the utilization of biomass ash are identified and potential improvements are suggested based on the obtained results.

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Chapter 2

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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*Tosti, L., van Zomeren, A., Pels, J.R., Comans, R.N.J.:
Evaluating Biomass Ash Properties as Influenced by
Feedstock and Thermal Conversion Technology towards
Cement Clinker Production with a Lower Carbon Footprint.
Waste Biomass Valor. (2021).
<https://doi.org/10.1007/s12649-020-01339-0>*

ABSTRACT

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. 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. MgO and P₂O₅). The potential of fly ash from fluidized bed combustion to substitute raw materials was shown to be lower than that of wood ash from pulverized fuel due to the lower burnability. 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.

Keywords: *biomass ash; clinker; raw clinker materials; cement; biomass combustion*

1. 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. (2010) around 860 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 (WBCSD - World Business Council for Sustainable Development, 2009). 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 (Schneider et al., 2011). 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 (Cordeiro et al., 2008; Demis et al., 2014; Salvo et al., 2015). 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 (IEA Bioenergy, 2018). 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 (Du et al., 2014; Niu et al., 2010; Nunes et al., 2016; Obernberger et al., 1997; Vassilev et al., 2014; Zevenhoven-Onderwater et al., 2006), and ii) finding suitable applications for already existing biomass ash (Doudart de la Grée et al., 2016; Siddique, 2008; Vassilev et al., 2013a, 2013b). With respect to biomass ash reuse, utilization of woody biomass ash as a partial cement replacement has been progressively investigated (Berra et al., 2015; Cheah and Ramli, 2013, 2011; Siddique, 2012). 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 (Paris et al., 2016). 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 (Cheah and Ramli, 2011). 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 (Chao-Lung et al., 2011; Zain et al., 2011), bagasse ash (Cordeiro et al., 2008) and palm oil ash (Aprianti et al., 2015; Tay and Show, 1995). 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 (Buruberri et al., 2015; Modolo et al., 2017) 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 (Buruberri et al., 2015; Simão et al., 2017), 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 (Eggleston et al., 2006). 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 (IEA Bioenergy, 2018), 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.

1.1. 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 (Figure 1) to evaluate the biomass ash potential for replacement of raw clinker materials. A typical raw clinker material composition (Hewlett, 2003) 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 % SiO₂, 6.3 mass % Al₂O₃ and 2.4 mass % Fe₂O₃ (Hewlett, 2003).

Figure 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.

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 3 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 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 (Figure 1). The particle size distribution and homogeneity of the raw material are known to affect the formation of mineral phases (Taylor, 1997; Telschow, 2012). 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 – 150 μm (Telschow, 2012). This range was also used as a criterion to ensure homogeneity of the biomass ash (Criteria 2, Figure 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 (Hewlett, 2003) as given in Figure 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 3 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 (Taylor, 1997). 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 aluminate 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 Figure 1 indicate a high replacement potential of biomass ash if introduced together with traditional raw materials.

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

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

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

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.

$$A/S = [(K_2O \text{ (mol)} + Na_2O \text{ (mol)}) - Cl \text{ (mol)}] / SO_3 \text{ (mol)} \quad (eq. 4)$$

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 C₃S 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 (Hewlett, 2003; Maclaren and White, 2003; Taylor, 1997).

When P₂O₅ enters the clinker, it can hinder C₃S formation during clinkerization (Staněk and Sulovský, 2009; Taylor, 1997). At 0.7% by mass of P₂O₅ in the clinker the C₃S content decreases and C₂S increases. At a P₂O₅ content of 4.5% by mass in clinker the C₃S formation is significantly hindered and the final clinker contains both free lime and C₂S instead of C₃S (Staněk and Sulovský, 2009). 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 C₃S reduction is observed and the upper limit (i.e. 4.5% by mass) at which C₃S formation is completely blocked.

2. MATERIAL AND METHODS

2.1. Phyllis database

The Phyllis 2 database was updated to the current version within the Phydades European project (European Commission, 2009) 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 CO₂ neutral and would therefore not contribute to lowering the CO₂ footprint of the proposed alternative cement. Samples were classified into 3 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 2 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 (Figure 2).

2.2. ALLASKA Database

The ALLASKA database has been developed within the Ash Program at Värmeforsk (Värmeforsk, 2014) 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 , 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 (Figure 4) and compared with Criteria 2 (Figure 1). Successively, the LSF, SR and AR parameters were calculated for the ash samples according to Equations 1-3 and plotted in a X-2Y axis graph (Figure 5) in order to assess the theoretical burnability and investigate the potential of obtaining clinkerization of the ash mixture. Finally, the A/S ratio was calculated for biomass ash according to Equation 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 (Figure 6).

3. RESULTS AND DISCUSSION

3.1. Biomass feedstock composition

Figure 2 displays the content of CaO and SiO_2 together with the sum of $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ expressed as oxides % by mass of the total ash content for the different biomass groups, subgroups and specific samples. In Figure 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, Figure 1), its concentration can be a preliminary indication of potential degradation of clinker quality.

A general observation from Figure 2 is that the investigated biomass groups WWB and HAB show two distinct and consistent CaO/SiO_2 ratio distributions with WWB having a higher CaO/SiO_2 ratio then the HAB group. Contrary, the CaO/SiO_2 ratio of OR-CB group is more scattered. The average $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content of the WWB group is close to the optimal value of 9% by mass (Criteria 1, Figure 1), while the other biomass types (i.e., HAB and OR-CB) contain either a too low or too high content of $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. The distribution of adverse elements content in Figure 3 appears to be more dispersed than was previously observed for clinker forming elements (Figure 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 Figure 3) show a remarkably very low adverse elements content comparing to clinker forming element concentrations.

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

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 Figure 2), while the opposite is observed for the untreated wood subgroup (full red symbols in Figure 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 (Tarelho et al., 2015) (Figure 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. (2005) 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/SiO₂ 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/SiO₂ ratio within the WWB group and can also reach the required ratio of 3, thus being theoretically suitable for C₃S formation.

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

The distribution of samples in Figure 2 and Figure 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.

3.2. Biomass ash composition

Following Criteria 2 as defined in the evaluation method (Figure 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 (Chandler et al., 1997). 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 Section 3.1.2. 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 2 for biomass ash composition to replace raw clinker material is reported as reference (black circle in Figure 4).

Figure 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 SO_x 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.

A general observation is that the variation of CaO (i.e. 6% < CaO < 86%) and SiO₂ (i.e. 9% < SiO₂ < 82%) concentrations is very high for biomass ashes, while the sum of Al₂O₃ and Fe₂O₃ is showing a substantially smaller variation of about 6% - 30%. The average Al₂O₃+Fe₂O₃ concentration in the biomass samples is about 10% - 15% and close to the reference (Criteria 2, Figure 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 Figure 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. (Tarelho et al., 2015) measured the average particle size of exogeneous material and found that 67% by mass is below $500 \mu\text{m}$ concluding that part of these particles can be entrained with combustion flue gases and, successivly, 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 3. 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 (Pels et al., 2006).

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 3, see Criteria 1, Figure 1) is combusted as PF, a final fly ash with high potential for clinker substitution can be obtained (Figure 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 Figure 4) can also be found in cluster number 3. 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 (Figure 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) (van Loo and Koppejan, 2008). 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.

3.2.1. 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 3 (Figure 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, Figure 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.

Figure 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 C₃S and C₂S minerals have potential to exist or have already been identified in previous work (Segui et al. 2012).

Samples of PF falling in the possible C₃S range can form C₃S and C₂S 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 C₂S and form C₃S. There is a good potential for C₃S and C₂S formation when this ash type is introduced in a kiln and exposed to the clinkering temperature for a longer time (typically 20 to 40 minutes). 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 C₂S” region in Figure 5) can still contain active phases such calcium silicate (Lothenbach et al., 2011; Tarelho et al., 2015; Vassilev et al., 2014). Segui et al. (2012) for instance detected the presence of C₂S 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 C₂S 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 3. Fly ash presenting a similar set of burnability parameters can contain C₂S which is formed in a CFB at the operational temperature (900 °C - 950 °C). The formation of C₂S in a cement kiln is observed at temperature between 900 °C - 1250 °C and can be basically attributed to the reaction between solid CaO and SiO₂ particles. Calcium has to be supplied in its oxide form to ensure solid-solid reaction with SiO₂ (Telschow, 2012). Calcium in bark is present mainly as calcium oxalate (van Lith et al., 2006; Werkelin et al., 2010) 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 CaCO₃ which decomposes to CaO during combustion. Furthermore, Silica in quartz is less reactive during the clinkerization

process than Silica in clay (Taylor, 1997), 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.

3.2.2. Mineral composition and thermal treatment of selected biomass ash

In this Section, the theoretical predictions made in Sections 1.1 and 3.2.1. will be verified by the analysis of results from previous heating experiment performed on real biomass ash samples. Tosti et al. (2019, 2018) selected three ash samples FA1, FA2, and FA3 from combinations of biomass source and conversion technology on the basis of the criteria described in Section 3.2.1 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 (Tosti et al., 2020).

Carr (2019) 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 hours) 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 (2019). 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.

Table 1 Technical information on fuel type, conversion technology and collection point of three biomass ash samples selected by Tosti et al. (2019, 2018) based on the criteria described in Section 3.2.1. Calculated and reference 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 (2019).

	<i>FA1</i>	<i>FA2</i>	<i>FA3</i>
<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>	<u>Quartz</u> , calcite, arcanite, portlandite, lime	<u>Quartz</u> , calcite, arcanite	<u>Lime</u> , quartz, C_2S , gehlenite, portlandite
<i>Mineral composition after re-heating (Carr, 2019)</i>	Wollastonite, pseudowollastonite	Merwinite, akermanite, α - C_2S	α' H- C_2S , β - C_2S , gehlenite

Mineral composition of FA1 is dominated by quartz with smaller amounts of calcite, arcanite, portlandite and lime. The composition confirms the hypothesis made in Section 3.2 on the negative influence that inclusion of bed sand particles has on the FA as clinker material. Clean wood was used as fuel and generally this feedstock is Ca-rich (see Section 3.1 and Figure 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 Sections 3.2 and 3.2.1. 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 (Hewlett, 2003), and/or the interference of Magnesium in the clinker minerals formation process (Section 1.1). 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 (Figure 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 Section 3.2 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 re-heating 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 C_3S . It is hypothesized that, upon cooling, the C_3S transitioned back to CaO and C_2S (Hewlett, 2003). 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 C_2S 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.

3.2.3. Content of elements in biomass ash with potentially adverse effects on clinker quality

The presence of Na_2O , K_2O , Cl , SO_3 , MgO and P_2O_5 in the biomass ash mixture can adversely affect the quality of the final cement products when biomass ash is used as raw 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 Figure 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 Figure 7 together with the Criteria 3 (Figure 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.

Figure 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 Equation 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, Figure 1) are considered to have a lower probability of adverse alkali effects on cement clinker properties.

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 (Visser and Laughlin, 2004). 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, Figure 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 Figure 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 Figure 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 Figure 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 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).

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 (Figure 1). It is important to underline that in Figure 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 Section 3.2.2.

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% (Kurdowski, 2014). 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.

4. 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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Chapter 3

Assessment of biomass ash applications in soil and cement mortars

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applications in soil and cement mortars.
Chemosphere, 223, 425-437.
<https://doi.org/10.1016/j.chemosphere.2019.02.045>*

ABSTRACT

The pH-dependent availability and leaching of major and trace elements was investigated for a wide range of biomass ash from different fuels and conversion technologies. A technical and environmental assessment of selected biomass ash for application in soil or cement mortars was performed, using both the total content and leaching of elements. A large variation in biomass ash composition, yet consistent pH dependent leaching patterns were observed for most elements and conversion technologies. Chromium showed a distinct behaviour which was hypothesized to reflect redox conditions during conversion of the biomass.

The leaching based approach was found to provide a more realistic assessment of the availability of desired (i.e. nutrients) and undesired elements (i.e. contaminants) in soil systems. When applied to a reference soil at a rate of 2% by weight, the selected biomass ash increased the concentration of particularly Cr, Mo and Zn in soil solution to a level of concern. For cement applications, the release of Ba, Cr and Mo can become of concern during the second life stage, but the release was not attributed to the included biomass ash.

Both soil and cement matrixes were found to control the release of elements such as Cu, V and Ni (soil) and As, Cr and Mo (cement) when compared to the released from pure biomass ash, underlining the importance of evaluating the availability and leaching of desired and undesired elements in the application scenario.

Given current regulatory criteria, beneficial utilization of biomass ash in cement may be more feasible than in soil, but regulatory criteria based on leaching rather than total content of elements may widen the application potential of biomass ash.

Keywords: biomass ash; cement; soil amendment, pH-dependent leaching, availability, regulations

1. INTRODUCTION

Thermal conversion of biomass is an established option to generate power and/or chemicals from renewable sources and to reduce fossil CO₂ emissions. Four thermochemical biomass conversion technologies have been developed: pyrolysis, gasification, direct combustion and liquefaction. The thermal conversion of biomass results also in various residues that are commonly grouped into bottom ash (i.e. BA) and fly ash (i.e. FA). The basic difference between these two ash types is that BA is the fraction that is discharged from the combustion chamber whereas FA is entrained with the flue gas and recovered afterwards by flue gas cleaning techniques. Worldwide production of BA and FA from biomass combustion is currently estimated over 480 Mtons/year (Modolo et al., 2014; Vassilev et al., 2013). In the Netherlands, a scenario study has predicted a volume of ash from co-combustion and biomass stand-alone plants between 2-3 Mton/year in 2030 (Boersma, 2011). Although the technologies for biomass conversion are well developed and largely commercially available, limited research and development has been directed at the management and potential for beneficial utilization of the BA and FA residues (van Eijk et al., 2012). Feasible and acceptable waste management strategies for biomass ash need to be developed to contribute to the sustainability of energy production from biomass. The European Commission has initiated several actions towards a transition from a linear to a circular economy in which wastes are considered as potential resources, and reuse and recycling activities are favoured over disposal. Examples of these actions are the development of the End of Waste strategy (European Commission, 2011) and the revision of the European fertilizer regulation (European Commission, 2016). In the past years, studies have reported overviews on biomass ash properties as influenced by the type of thermal conversion and biomass composition (Obernberger et al., 2006, 1997; van Lith et al., 2006; Vassilev et al., 2014), and have also provided indications of potential bulk applications and reuse options for biomass ash residues. Two general categories have been identified as having the highest application potential for pure biomass ash: i) use in forestry and agricultural soils for fertilizing and liming purposes and ii) use in construction products, i.e. as secondary cementitious material, raw material for cement clinker production (Pels and Sarabr, 2011; Siddique, 2012; van Eijk et al., 2012).

The practice of returning biomass ash to soil can preserve or restore the original level of nutrients and acid buffering capacity of soil, which are altered by intense harvesting of the biomass (Emilsson, 2006).

The category of building products includes direct utilization, e.g., in road construction, and utilization as raw material in the manufacturing of building products, e.g., as secondary cementitious material or filler in concrete and cement, or in lightweight aggregates. BA from

grate combustion has been reported to be a suitable road building material and BA from fluidized bed an adequate sand substitute in construction and as a low quality filler material in concrete (Ribbing and Bjurström, 2011). Biomass FA has been shown to have binding properties or pozzolanic activity and can replace part of the clinker content in cement, and can thus contribute to reducing CO₂ emissions associated with traditional clinker production (Demis et al., 2014; Salvo et al., 2015; Siddique, 2012; Tosti et al., 2018).

Although biomass ash has a potential beneficial use in soil or construction products, this residue is still largely landfilled. This unsustainable practice is due to regulatory barriers as well as concerns about the potential leaching of contaminants to soil ecosystems. In order to facilitate the reuse of biomass ash, and thus the sustainability of biomass conversion, it is very important to assess the benefits and risks associated with its reuse.

The regulations and criteria for the utilization of biomass ash in forestry and agriculture or in construction vary between European countries. In Denmark, Finland and Austria national legislations are in force, whereas Sweden provides recommendations for utilization of biomass ash in forestry and agriculture (Emilsson, 2006). Both criteria and recommendations for utilization of biomass ash in soil are based on total content of elements in the biomass ash (Table 1).

The re-use of biomass ash as partial cement replacement material is not allowed by ASTM C 618 and CEN EN 450-1 that are the standards governing the use of FA as mineral admixtures in concrete. These two standards preclude the use of any material not derived from coal combustion, although biomass co-firing up to 20 wt.% is allowed. The application in construction works (BMUB, 2015; Bodemkwalityteit, 2007) or final disposal in landfills (European Commission, 1999) is generally judged based on the emissions of contaminants from products by leaching processes. The Netherlands has a set of emission limit values for shaped and granular building materials which is included in the Soil Quality Decree (SQD) (Bodemkwalityteit, 2007). In short, this regulation specifies criteria for the (re-)use of mineral materials in construction applications. The SQD includes separate criteria for the use of shaped materials (e.g. bricks or concrete) and granular materials (e.g. steel slag or aggregates from construction and demolition waste). The latter category can be divided in so-called open applications (for relatively clean materials) or closed applications in which isolation measures need to be in place to limit contact with water (e.g. use of a liner system and monitoring requirements for the groundwater). The development of such limit values is based on the impact to soil and groundwater by leaching processes using human- and eco-toxicological limit values as reference. On the contrary, the application of biomass ash for forestry and agriculture purposes is judged based on the total content of elements.

In summary, an important concern regarding the application of biomass ashes in soil or in concrete is the potential enhanced leaching of contaminants. Research has shown that the total content of contaminants does not necessarily have a direct relation with the emission potential (leaching) in an application scenario (Kosson et al., 2002; van der Sloot, 2000). Nevertheless, there is very little information available in the current literature on biomass ash leaching properties and on the potential environmental risks associated with the most promising reuse options for biomass ash (Cruz et al., 2017; Freire et al., 2015; Maresca et al., 2017; van Eijk et al., 2012).

The overall aim of this study is to perform a technical and environmental assessment of biomass ash for application in soil and cement, on the basis of both the total content and the leaching of elements. The main differences and limitations of the two approaches will be discussed with the intent to increase the knowledge on biomass ash re-use options and identify ash properties that need consideration with regard to functional and environmentally safe recycling of this material.

2. MATERIAL AND METHODS

2.1. Samples

A wide range of 21 different biomass ash samples were collected from different laboratory and pilot scale experiments, as well as from full scale installations. The samples included BA and FA originating from various biomass sources that were either converted using combustion or gasification technologies, operating at a range of conversion temperatures (400 to 1400 °C). A general description of the samples is given in Table S1 of the Supplementary Material. Four biomass FA samples (i.e. FA1, FA2, FA3 and FA4) were selected for further investigation of the re-use potential. Sample FA1 originated from a circulating fluidized bed installation that combusts a mixture of clean wood and various clean biomass feedstock like cacao husks or molasses. Sample FA1 was collected from the electrostatic precipitator. Sample FA2 originated from the combustion of wood pellets in a pulverized fuel installation and was collected from the electrostatic precipitator. Sample FA3 was sampled from a bubbling fluidized bed incinerator. The fuel consisted of a mixture with an equal share of recovered paper sludge from the de-inking step of the paper recycling process and recovered waste wood. The sample was collected from the electrostatic filter (90% by mass) and the textile bag filter (10% by mass) flue gas cleaning system. Sample FA4 was collected from a full-scale combined heat and power plant operating with a grate furnace. The fuel for this installation consisted of forest wood from thinning and clipping activities.

2.2. Total composition of biomass ash

Total composition of biomass ash samples (i.e. BA (n=3) and FA (n=19)) was performed by digestion in a Berghof bomb with concentrated HNO_3 (65%): HF (40%): HClO_4 (65%) in the proportion 5: 4.5: 0.5 by weight. About 0.1 gram of sample was weighed and mixed with the acid mixture (10 g) and brought to a final volume of 50 ml by adding HNO_3 (0.1 M). The samples were digested in closed containers in an oven at 190°C for 10 hours, filtered and subsequently analysed with an Inductively Coupled Plasma - Atomic Emission Spectrometer ICP-AES (Varian Vista AX PRO CCD) for major and minor elements.

Total content of chloride was measured in selected samples by fusion with lithium metaborate. About 0.1-0.2 g of sample was mixed with 1 g of LiBO_3 and heated in the oven for 30 minutes at 1150 °C. The fused sample was subsequently dissolved in 1 M HNO_3 and analysed for chloride by ion-chromatography (Dionex IC25 ion-chromatograph with a Dionex AS18 column and a Dionex DS3 conductivity detector).

2.3. Batch pH-static leaching experiments

The biomass ash samples were equilibrated with water for 48 hours at a specific pH value between pH 2 and 12 (including the natural pH of the sample that was not adjusted) according to the EN 14997 (2015). A quantity of 15 g of dry ash was suspended in 150 mL nanopure demineralised water (i.e. at a liquid to solid (L/S) ratio of 10 L/kg) in acid-cleaned 300 mL Polytetrafluoroethylene (PTFE) vessels, under continuous stirring at 20 °C. The suspensions were in contact with the atmosphere. The pH of the different suspensions was controlled using solutions of 1 M HNO_3 and NaOH (analytical grade) and a computerised pH-stat system. After the equilibration period, the suspensions were filtered through 0.45 μm membrane filters. Subsamples of the filtrates were acidified with concentrated HNO_3 (suprapure) and analysed by ICP-AES to obtain solution concentrations of a wide range of elements. It was assumed that total S and P as measured by ICP-AES (Varian Vista AX PRO CCD) represented SO_4^{2-} and PO_4^{3-} , respectively. A carbon analyser (Shimadzu TOC 5000a) was used to determine dissolved inorganic and organic carbon in non-acidified subsamples. Chloride was determined by ion chromatography (see above).

2.4. Soil amendment leaching experiment

The influence of biomass FA on the leaching properties of the ash/soil system was tested by mixing FA1 and FA4 at 0.2 and/or 2% by weight with the reference Euro-Soil 4 (Kuhnt and Muntau, 1994). This soil was sampled (0-30 cm depth after removal of vegetation) in

Normandy (France) and classified as an Orthic Luvizol (Organic carbon: 1.36%; Clay: 20.3%; pH: 6.8). The Euro-Soil 4 composition is reported in Table S3. Samples FA1 and FA4 were selected as representatives for biomass ashes complying (i.e. FA1) or not complying (i.e. FA4) with the Swedish guideline. Next, the amended soils were equilibrated at different pH values using the pH dependence leaching test, carried out in the same way as described in Section 2.3.

In this work, the biomass ash is supposed to be applied into soil all at once in order to reach the 0.2 or 2% percentages (i.e., 15 and 150 ton/ha, respectively). In reality, this is not the case and biomass ash is applied at different time intervals, rather than in a single application. In order to put the ash/soil mixture in perspective we considered a typical soil bulk density of 1500 kg/m³ as an indicative value, a depth of 50 cm (with homogeneous mixing) and an ash dosage of maximum 3 ton/ha in 10 years (Haglund, 2008; Swedish Forest Agency, 2002). This can be a plausible scenario for agricultural use. When this scenario is considered, a 0.2% ash/soil mixture would be reached in 50 years, whereas the 2% mixture would represent an application period of 500 years. In forestry, the biomass ash is spread on top of soil and no ploughing is performed thus we considered that mixing of ash and soil would happen only in the very first layer of soil (i.e. 1 cm). If we assume the same soil density (i.e. 1500 kg/m³) and ash dosage (3 ton/ha in 10 years), 1 cm depth would require 1 year to reach 0.2% ash/soil and 10 years to reach 2% ash/soil.

2.5. Cement applications

Cement mortar samples were prepared by dry mixing of Portland Cement CEM I 42.5N with biomass FA (i.e. FA1, FA2 and FA3) in accordance with the EN 196-1 (2005). The FA4 sample was excluded due to its very high K content that would lead to a poor cement quality. Ordinary Portland cement (OPC) was partly replaced with biomass FA at 20% and 40% by total binder weight. All specimens were prepared with a water-binder weight ratio (w/b) of 1:2 and a sand-binder ratio of 3:1. Rectangular blocks (160 x 40 x 40 mm) were casted and removed from the mould after 24 h of curing. Next, the casted blocks were cured for 28 days in a controlled temperature and humidity room (20 °C and 95% humidity). After 28 days of curing, the specimens were subjected to compressive strength (EN-196-1, 2005) and batch pH-static leaching tests (EN 14429, 2015) after grinding the material to < 1 mm size. These experiments with partial replacement of cement with biomass ash were performed, despite the fact that none of the ashes comply with the current EN 450-1 standard for the utilization of FA from co-combustion of coal with biomass as mineral admixtures in concrete. Currently, the use of biomass fuel in co-combustion of coal is limited to 20 wt.%, while we are using

100% biomass ash. The biomass ashes FA1, FA2 and FA3 do also not comply with the technical requirements of EN 450-1 as described in more detail in Tosti et al. (2018). However, this previous study has shown that replacing 20 and 40% of traditional Portland cement with FA1 and FA3, as we have done here, produced cement mortars that comply with strength requirements of class 42.5 (20% replacement) and class 32.5 (40% replacement) after 28 days of curing (EN-196-1, 2005). In addition, the resulting mortars showed an acceptable environmental performance.

2.6. Comparison of total content and leaching of biomass ash with current quality criteria

The average total content of major and minor elements in BA and FA was compared with an average global soil composition (Mielke, 1979), in order to identify potentially beneficial or unfavourable effects of high or low element contents in biomass ash when used in applications that interact with soil. Next, the total content of individual elements in the ashes was compared with their maximum leachability in order to identify if any relation exists between the two different quantification approaches, and evaluate potential consequences when a regulatory approach based on total content is substituted by a leaching-based approach. The minimum requirements for nutrients and the limit values for contaminants in biomass ash according to the current legislations and recommendations are reported in Table 1. Values in Table 1 vary from country to country, as well as other properties (not listed in Table 1) such as fuel type, content of unburned matter, pH, conductivity, dosage etc. For further detail the reader is referred to Emilsson (2006), Haglung (2008), Ribbing and Bjurström (2011) and Stupak et al. (2008).

It is well known that the pH of materials has a major influence on the leaching of elements (Dijkstra et al., 2006; Kosson et al., 2014). Therefore, the pH dependency of the release from biomass ash was also investigated to evaluate the behaviour of these materials when exposed to different pH, and to identify general trends among ash types.

Finally, the technical and environmental performance of the two application scenarios (i.e. soil and cement) were assessed relative to the existing regulations and criteria. Particular attention was dedicated to the potential use of biomass ash in agriculture or forestry, since the lack of consistent regulations (i.e. contrary to construction products) has been identified among the main reasons that are currently preventing large-scale recycling of biomass ash as potentially functional soil amendments (Cruz et al., 2017; Riding et al., 2015).

Table 1 Nutrient and minor element limits based on total content according to Northern European countries, Austria and Canada, distinguishing applications in agriculture and forestry. Further information can be found in Emilsson (2006), Hannam et al. (2017, 2016), Stupak et al. (2008), Swedish Forest Agency (2002).

	Austria		Canada	Denmark	Finland		Sweden
	Forestry	Agriculture	Soil amendmen	Agriculture & Forestry	Agriculture	Forestry	Forestry
Nutrients (minimum) (g/kg)							
Ca					80	60	125
Mg							15
K					20 (K+P)	10 (K+P)	30
P					20 (K+P)	10 (K+P)	7
Zn							0.5
Minor elements (maximum) (mg/kg)							
As			75		25	30	30
B							800
Cd	8	5	20	15	1.5	17.5	30
Cr	250	250	1060	100	300	300	100
Co			150				
Cu	250	250	2200		600	700	400
Pb	100	250	500	120	100	150	300
Hg			5	0.8	1	1	3
Mo			20				
Ni	100	100	180	30	100	150	70
Se			14				
V							70
Zn	1500	1000	1850		1500	4500	7000

3. RESULTS AND DISCUSSION

3.1. Composition of the biomass ash samples

Total composition of FA1, FA2, FA3 and FA4 samples together with MIN and MAX values for the three categories bottom ash from gasification (BA_GAS), Fly ash from gasification (FA_GAS) and fly ash from combustion (FA_COMB) is reported in Table 2. The biomass ashes showed a large variety in composition due to the different sources of the fuel, ash type and conversion technology.

The most abundant element was Ca with a content of $10^5 - 10^6$ mg/kg dry ash. The content of plant nutrient K was between $10^4 - 10^6$ mg/kg dry ash with no observed distinction among biomass ash categories. The Phosphorous content showed the highest value in the FA_COMB category. The content of Cl showed a large variation ($10^2 - 10^6$ mg/kg dry ash) with a high content in the FA_COMB category as already observed for P. Concerning the content of trace elements, no clear distinction was observed between biomass ash categories, with the exception of Cd that was generally enriched in biomass FA samples. These findings were consistent with other wood ash studies (Freire et al., 2015; Maresca et al., 2017; Vassilev et al., 2010). Mineralogical analysis of the crystalline phases showed that FA samples consists mainly of lime (CaO), Quartz (SiO₂), Portlandite ((Ca(OH)₂) and Arcanite (K₂SO₄). Calcium

silicate and Gehlenite were also present in FA3 samples (Carr, 2019) (see Supplementary Material Figure S1).

Table 2 Total composition of FA1, FA2, FA3 and FA4 samples together with MIN and MAX values for the three categories Bottom ash from gasification (BA_GAS), Fly ash from gasification (FA_GAS) and Fly ash from combustion (FA_COMB). All values are expressed in mg/kg of dry ash. Between brackets the number of samples in each category. Full dataset is reported in the Supplementary Material Table S2.

	FA1	FA2	FA3	FA4	BA_GAS (n=3)		FA_GAS (n=9)		FA_COMB (n=9)	
					MIN	MAX	MIN	MAX	MIN	MAX
pH*	12.8	12.9	12.7	10.3	10.3	12.2	10.3	12.7	10.7	12.8
As	12.0	< 6.80	88.0	113	0.843	55.3	0.062	93.0	6.80	113
Ba	669	1771	831	38.9	97.3	1426	91.6	3647	38.9	1771
Ca	190361	197209	402533	24602	16644	31945	10941	87932	24602	402533
Cd	22.9	7.97	3.02	40.1	0.183	0.208	0.071	7.51	0.100	40.1
Cl	6563	8217	2995	124898	950	15925	645	18684	2995	124898
Co	7.9	13.5	10.9	1.60	2.36	11.0	1.96	20.1	1.60	15.4
Cr	69.8	109	160	151	72.4	232	12.9	444	69.8	1913
Cu	121	141	559	280	23.3	313	15.5	506	30.7	559
K	64779	77638	7761	373686	7357	149226	5643	143453	7761	373686
Mo	15.1	21.9	< 1.90	40.0	5.36	12.9	1.50	37.7	1.90	547
Na	5472	9317	5705	26757	1371	6231	1171	13795	194	26757
Ni	36.8	47.6	55.7	8.60	51.0	114	5.71	68.4	8.60	316
P	15783	9864	1375	5991	474	37748	308	46567	1375	27413
Pb	163	50.2	279	1277	10.5	873	0.762	4698	6.33	1277
S	15441	12837	5856	116416	985	9202	105	8025	372	116416
Sb	4.7	< 17.0	< 7.50	21.3	0.00	24.8	0.00	42.0	3.60	21.3
Se	0.600	9.25	< 3.10	5.60	0.095	0.856	0.150	1.89	0.150	9.30
Sn	3.20	31.6	5.48	36.7	1.19	2.78	0.150	58.4	0.600	36.7
V	27.8	33.8	18.7	3.50	6.03	73.0	2.45	27.5	3.50	77.0
Zn	1400	884	2564	10820	58.8	1411	52.0	3913	8.83	10820

*Natural pH measured at L/S 10

3.2. Comparison of total composition of biomass ash and soil

Figure 1 shows a double log plot of the average weight percentages for elements in natural soil (data taken from Kirby and Rimstidt (1993) based on a globally averaged dataset for soil composition as reported in Mielke (1979)) versus the average weight percentage in biomass BA (n=3) and FA (n=18) samples. Figure 1 gives a preliminary indication of the content of elements that is generally higher in biomass ash than in average soil. This assessment is important because the applications of biomass ash could result in a net accumulation of heavy metals or other harmful substances in soil and their subsequent transfer to crops and/or surface or groundwater. At the same time, for specific soil amendment purposes such as nutrient (re)supply and/or pH control, elements such as Ca, K and P should be present at elevated levels in the ash. For any application of specific biomass ash in a specific soil, a more detailed assessment is appropriate, for which we provide considerations and suggestions below.

The thick solid line in Figure 1 represents equal contents in biomass ash and soil matrices. The thin solid lines indicate tenfold higher or lower element content in biomass ash relative to soil. These graphs show averaged contents of major and minor elements in ash over the whole range of biomass sources and conversion technologies. Figure 1 clearly shows a lower content of the major elements Al, Fe and Si in the biomass ash and an approximately one order of magnitude higher content of phosphorus, some heavy metals (Cd, Cu, Pb and Zn) and chloride Calcium, Magnesium and Potassium contents are also generally higher in biomass ash, indicating potentially functional properties as soil amendment.

Figure 1 Double log plot of average element contents (weight%) in biomass BA ($n=3$) and FA ($n=19$) samples versus natural soil (Kirby and Rimstidt, 1993). The thick solid line represents equal contents in both materials. Each of the thin dotted lines represent one order of magnitude depletion or enrichment relative to the average content in soils.

3.3. Total content versus potential leachability of elements in biomass ash

In this Section, we explore relationships between the total content and the leachability of major and minor elements in biomass ash. Figure 2 shows the total content of As, Ca, Cr, K, Mo, Ni, P and Pb in the biomass ash (x-axis) versus the potential leachability of elements estimated at the pH value at which their mobility is generally highest (Dijkstra et al., 2008; Freire et al., 2015), (i.e. for metals, measured at pH around 2, for oxyanions Mo and Sb measured in the range $8 < \text{pH} < 12$) at L/S of 10 L/kg. The selected elements were representative of a linear or non-linear correlation as explained later in the text. Data for other measured elements is presented in the Supplementary Material (Figure S2).

Figure 2 Total content of As, Ca, Cr, K, Mo, Ni, P and Pb versus the potential leachability expressed in mg/kg (48h, L/S=10 L/kg) at pH 2 or $8 < \text{pH} < 12$ (only for oxyanion-forming Mo and Sb) of the biomass ash samples. Continuous black line indicates a ratio 1:1 where total content equals the maximum leached amount from the biomass ash. When available, the limit values (MIN-MAX) from Table 1 were plotted on both X and Y-axis in order to identify any discrepancies between judgement based on total content vs. potential leachability. Canadian regulation (Hannam et al., 2016) is used only for Co and Mo limits.

The potentially leachable amount of elements can be interpreted as the maximum amount of elements that is expected to be released from the biomass ash in the long term. In some cases, (i.e. Ca, K, Mo, Na, Zn, Cl and P) the total content and potentially leachable concentrations can get very close and show dependency (i.e. elements with a high and largely pH-independent solubility). In these cases, the total content provides a good indication of the potential release from the biomass ash. Other elements (i.e. As, Ba, Cr, Co, Ni, Pb, Sb, Se, Sn and V), however, show a potential leachability that is mostly 1-2 orders of magnitude lower than their total content, with little correlation between the two measurements (see Figure 2 and Figure S2). If we look at the recommendations and limits in Table 1, a judgment based on total content would preclude the use of 32% of the total ash samples due to exceeding the limit for As content, 54% due to Cr, 60% due to Ni and 41% due to Pb. When a hypothetical

judgment based on potential leachability is used, this would result in exclusion of only 4% of total biomass ash due to As, 4% due to Cr, 4% due to Ni and 22% due to Pb.

Figure 3 Graphical representation of the concept of total content, maximum leachability and actual leaching from materials or materials exposed to different conditions. Black curve represents typical cation behaviour whereas the red curve indicates the behaviour of oxyanionic species. The red area highlights the pH range of soil and the grey area the pH of cement.

The results discussed in this Section show that the total content of As, Ba, Cr, Co, Ni (for Ni only when the total content is of about 10^2 mg/kg dry ash), Pb, Sb, Se, Sn and V is not representative of the maximum amount that can be potentially leached from the biomass ash. Moreover, the actual release is also a function of the pH (both natural pH of biomass ash or imposed by the application scenario) as shown in Figure 3. The actual release is very important for a more realistic assessment of biomass ash quality (e.g. nutrients content) and potential risk associated with contaminants in reuse applications.

3.4. pH dependent leaching behaviour of biomass ash

In this Section we evaluate the leaching of the different biomass ash samples in response to a pH change. The aim was to measure the actual release, in addition to the potentially leachable concentrations, and to identify common and specific pH-dependent release trends among the different types of biomass ash, fuel and/or combustion technology. Figure 4 shows the pH-dependent leaching behaviour of K, Cr, Mo and Zn in the tested biomass ash samples. These elements were selected as representatives of typical pH dependent leaching behaviour (i.e. cations, oxyanions and elements forming soluble compounds).

Generally, the trends in the pH dependent leaching behaviour were similar for most ash samples indicating that the chemical processes that control the release of individual elements

are consistent for this wide range of different biomass ash samples. However, distinct differences in the absolute levels of leached concentrations at comparable pH were observed among the different samples. This observation can be explained by differences in the potential leachable amounts of elements in individual ash samples. The natural pH of biomass ash samples varies between 10 and 13 (at an L/S ratio of 10 L/kg, after 48h equilibration, see Table 2). At this pH range the actual release from biomass ash is lower than the potential leachability as described in Section 3.3. Figure 4 and Figure S3 (Supplementary Material) show a difference between the release measured at natural pH and the potential release of up to 3 orders of magnitude for Cd, Co, Cu, Ni and Zn. Accordingly, the release at natural pH results in an extremely lower concentration when compared with the total content.

An exception is represented by Mo and, to a lesser extent, V. For these two elements the natural pH of ash coincides with the pH of potential leachability. Another exception is represented by Cl and K. The leached concentrations of Cl and K, elements that are normally present in highly soluble phases (i.e. NaCl, KCl), are essentially independent of solution pH, but rather controlled by their total content in the ash. The described leaching trends are very similar to those observed in previous studies on FA from coal combustion (Kosson et al., 2009) and biomass ash (Freire et al., 2015; Maresca et al., 2017).

Despite the wide variation in the absolute leached amounts of contaminants, the leaching behaviour as a function of the pH was generally very consistent among the different ashes, with a few exceptions, notably one observed for Cr release. The release pattern and level of Cr showed a distinct relation with the applied conversion technology (Figure 4). These differences were probably related to the oxidation state of Cr in the biomass ash, i.e. Cr (III) (immobile) and Cr (VI) (mobile) as has previously been observed in studies of leaching mechanisms in cement (van der Sloot et al., 2008; van der Sloot, 2000). Based on our observations, we hypothesize that the conditions during biomass gasification and combustion lead to a different oxidation state of Cr in the ash.

One of the FA sample (i.e. sample ID #1, see Supplementary Material, Table S1) in Figure 4 showed an exceptionally high Cr leaching over the whole pH domain. This sample was collected from a lab-scale experiment. The total content of Cr in this sample is unusually high and it is thought that the source of Cr is contamination as a result of corrosion of the stainless steel reactor that was used in the laboratory experiment.

Overall, we conclude that the consistent pH-dependent leaching patterns for individual elements shown in Figure 4 and Figure S3 in the Supplementary Material point at similar geochemical processes that determine their release from this wide range of biomass ash samples.

The pH-dependent leaching test provides essential information on the effect of pH changes that occur in different ash re-use or disposal scenarios on the leaching of contaminants. However, interactions with the surrounding environment (e.g. soil or cement matrices) are also very important in determining the net release from the complete system composed of biomass ash plus soil or cement, as will be further investigated in Sections 3.5 and 3.6.

Figure 4 Leaching of K, Cr, Mo and Zn as a function of pH in all biomass ash samples. Red square indicates bottom ash samples from gasification processes, black square indicates fly ash from gasification and blue squares represent fly ash samples from combustion processes. Open circles indicate the natural pH of each ash without pH adjustment. The dotted grey areas indicate a typical pH range for soil (4 to 8) and cement (10.5 to 12.5).

3.5. Recycling of biomass ash to soil

An assessment based on the total content of elements would exclude utilization of FA1, FA2, FA3 and FA4 in agriculture according to the limit values reported in Table 1. Common exceeding elements are Cd, Cr, Pb and Zn depending on the specific country. According to the Swedish guidelines FA1 is suitable for forestry and FA2 is almost compliant with a Cr content of 109 mg/kg (i.e. limit for Cr is 100 mg/kg) utilization, whereas FA3 and FA4 have a content of 160 and 151 mg/kg and are hence not suitable.

Calculated contents of elements in theoretical mixtures of 2% FA1, FA2, FA3 and FA4 in soil were compared to the Dutch SQD criteria for utilization of contaminated soil (Dirven-

Van Breemen et al., 2007). Complete information on criteria and element contents in amended soils can be found in Table S3. This comparison resulted for all four ash-soil mixtures in an amended soil quality that complies with most of the limits for residential use. Two exceptions were observed. The Ni content was higher in all of the amended soils, since the high content of Ni contained in Euro-Soil 4 (48 mg/kg) already exceeded the limit for residential application (39 mg/kg). The second exception was observed for the Zn and Cd content of the soil amended with 2% FA4. This addition of FA4 resulted in an increase of the Zn and Cd content to above the limit for residential application. When we disregard the Ni data that are determined by the selected soil, rather than by the biomass ashes, it can be concluded that FA1, FA2 and FA3, when mixed at 2%, comply with the criteria for residential soil application, but that FA4 does not comply.

Soil amendment experiments were performed using FA1 and FA4 for the assessment of the availability of nutrients and contaminants in the soil/ash system. In this Section, we investigate the pH dependent release (Figure 5) of macronutrients Ca, K and P and trace elements (including potential contaminants) from the Euro-Soil 4 reference soil sample, pure FA1 and FA4 from clean wood combustion, and the soil mixed with 0.2 and 2 wt.% of these FA samples. The applied dosage represents an equivalent of 15 and 150 ton/ha if biomass ash was to be spread in the soil (i.e. bulk density of 1500 kg/m³) all at once (see Section 2.4 for more details). Leached concentrations of trace elements were compared with the Dutch Maximum Tolerable Risk (MTR) values in groundwater (Verschoor et al., 2007), as a first indication of possible risks of these biomass ash types and application levels in soil. When leached concentrations are lower than the MTR values, it is considered that these levels do not pose an unacceptable risk for the groundwater.

The original pH of the soil was 6.8 and increased slightly after addition of 2% FA to a value of 7.0 (2 wt.% FA1) and 7.2 (2 wt.% FA4), due to the presence of alkali and alkaline earth metal oxides and carbonates in these FA samples (Figure 5). When Ca-rich FA is used as liming agent in acidic soils, a larger than 2 wt.% amendment rate may be required to reach an appropriate soil pH between 6-7 (Cruz et al., 2017). Amending FA1 and FA4 to soil had a general positive effect on the availability of most nutrients (i.e. Ca, K, Mg) and Na and Cl (see Figure S4 of the Supplementary Material). The release of K, Na and Cl reflected the amendment rates of the FA, indicating that these elements are present mainly as soluble compounds that are readily released when mixed with soil. Conversely, phosphorus is in a poorly soluble form at relevant soil pH values, and only a very small fraction was released from the ash to the soil during the test time. The availability of P in the amended soil with 2 wt.% FA1 and 2 wt.% FA4 at the natural pH (i.e. pH 7 and 7.2 respectively) increased by

about a factor of 2 compared to the availability of P in the reference soil at natural pH (i.e. pH 6.8) (see the release of P between pH 6 and 8 in Figure 5). Since the pH variation is limited, the increased P availability was attributed to the FA addition.

Figure 5: Release of Ba, Ca, Cr, K, Ni and P as function of pH for two biomass FA samples from clean wood combustion (i.e. FA1 and FA4) and mixtures with soil (i.e. 0.2 and 2 wt.% of FA_1 and 2 wt.% of FA_4, respectively). The release from the pure FA and from the reference soil is also shown. The

natural pH values are indicated by open circles for the pure FA (i.e. pH 12.8 (FA1) and pH 10.3 (FA4) and reference soil (i.e. pH 6.8), open diamond for the addition of 0.2 wt.% of FA1 (i.e. pH 7) and open squares for the addition of 2 wt.% of FA1 (i.e. pH 7) and FA4 (i.e. pH 7.2) to soil. Solid black line specifies the Maximum Tolerable Risk (MTR) limits for groundwater quality which are expressed as mg/kg.

With regard to the release of trace elements, the mixture of 0.2% FA1 essentially showed no significant difference when compared with the soil reference. This observation can be extended to all the other investigated elements reported in the Supplementary Material, Figure S4.

At 2% amendment rate and natural pH values an increased released of trace elements was observed for both FA1 and FA4, the latter showing generally higher levels and for a broader range of elements (Figure 5 and Figure S4 in the Supplementary Material). Some of the elevated trace elements in biomass ash, such as Zn and Se (Figure 1), but also Mo and B, may function as beneficial micronutrients in soil applications, provided that they do not leach at undesirably high (i.e. toxic) levels. When the release of elements from amended soil with 2% of FA1 and FA4 was compared with MTR values, we could distinguish three situations. In the first, the addition of biomass ash caused an increase in the release but below MTR values at the natural pH of mixtures. This situation was observed for As, Ba and Pb (only for 2% FA4 since the solution concentration of the 2% FA1 mixture is below detection limit). A second situation was observed for Cu, Ni and V, for which the concentration at natural pH in the soil solution reference (red open circle in Figure 5) were already above the MTR values. Addition of FA1 or FA4 resulted in no significant alteration of these values. The third situation referred to Cd, Co, Cr, Mo, Sb, Se and Zn, for which the FA addition caused the concentration in soil solution at natural pH to increase above the MTR values. In particular, Cr, Mo and Zn showed a substantial increase. The mixture containing 2% of FA4 resulted in a Cr release of about 55 times that of the reference soil, resulting in a concentration of about one order of magnitude higher than MTR limit.

The above analysis of actual leaching properties of biomass ash shows that the effects of ash application directly to soil may be substantially different from those assumed on the basis of the total content or potential leachability as shown in Section 3.3. For macronutrients such as Ca and P the different total contents in FA1 and FA4 have been shown to result in a very similar enhanced availability in the amended soil, while for the mobile macronutrient K the effect is in line with the difference in total content. These elements showed a maximum leachability close to total content. In addition, leached concentrations of contaminants allow

for a more direct comparison with undesirable (e.g. MTR) concentration levels in groundwater.

Another important observation is that the soil matrix can mitigate the sometimes large differences in the concentrations of elements leached from individual FA samples (e.g. Cu, Ni and V) due to processes such as precipitation, sorption or complexation which affect their mobility.

3.6. Utilization as secondary cementitious material

The utilization of the ashes as secondary cementitious material was investigated on the basis of the crushed mortars made with samples FA1, FA2 and FA3.

The first reason for this approach was to follow a single consistent framework for comparison of the ash characteristics in the two investigated application routes. The cement product characteristics and leaching properties are described in Tosti et al. (2018). The second reason for this approach was that use of crushed mortars is regarded as the second life phase of the cement mortars where it is expected that most of the leaching takes place. Since in the first phase, e.g. in intact concrete structures, the exchange with the environment is minimal, the leaching of crushed mortar is particularly relevant for the assessment of the environmental risk associated with the reuse of biomass ash in concrete products over the entire life cycle. Figure 6 shows the pH dependent release of Cr, Mo, Se and Zn from the pure FA samples that were used as secondary cementitious material (FA1, FA2 and FA3), as well as and from the resulting cement mixtures. In addition, the average release of all other FA samples considered in this study is reported, together with the 95% confidence interval. Measured concentrations below the detection limits were set equal to the detection limit. The pH dependent release of OPC was included as a reference. Complete information is reported in the Supplementary Material, Figure S5.

Figure 6 shows that the pH-dependent release patterns and magnitude for Ba, Cr, Mo, and Zn from OPC (reference) and from the blended cement samples are very similar. This observation can be extended to all other elements reported in Supplementary Material (Figure S5) with the exception of Cd, Cl, Co and Sn at alkaline pH. For these elements the displayed difference between OPC and blended cements were related to different detection limits applied. Concerning pure biomass FA, an interesting observation is that leaching pattern of FA3 followed the pattern of OPC (reference) while FA1 and FA2 did not (e.g. Cr and S). What distinguishes FA3 is its very high Ca, and relatively low K, Cl and P content (Table 2). The natural pH of FA1, FA2 and FA3 is comparable. Apparently, with regard to leaching, the cement chemistry was dominant over the chemistry of the biomass ash in the blended cements,

even at 40% replacement, as was also evidenced by the different pH-dependent release patterns and magnitude for the pure biomass ash samples.

The inclusion of biomass ash into the cement matrix has a considerably lower influence on the net release from the mixture compared to that of biomass ash amendment to the soil matrix, even though higher percentages of biomass ash were added to cement compared to soil (Figure 5 and Figure 6). The release of most of the regulated elements remained below the limits of the SQD at the natural pH of the materials (see Figure 6 and Figure S5 in the Supplementary Material). The release of Cr and Ba at the natural cement pH was very close to the SQD limit. The release of these elements from blended cement was somewhat increased by the inclusion of FA1 and to a certain extent FA3 at the natural pH, but they were all still below the SQD limits. The inclusion of biomass FA plays a minor role. As shown in Figure 6 and described in Tosti et al. (2018), the carbonation of crushed cement can increase the leaching of particularly (oxy)anions up to a point which is above the SQD (i.e. Cr) or very close (i.e. Mo, V).

Similar to our findings for the soil application scenario (e.g. with regard to Cu, V and Ni; see Figure 5), the cement matrix plays a major role in controlling the net leaching of many of the investigated elements, such as As, Cr and Mo, when biomass ash is used in cement. These observations underline that it is essential to evaluate and interpret the (pH-dependent) availability and leaching of both desired (e.g. nutrients) and undesired (contaminants) elements in the environment in which biomass ash is applied.

Figure 6 Leaching of Ba, Cr, Mo and Zn as function of pH in pure biomass FA and cement products. Ordinary Portland Cement (OPC) is added as reference cement. The black dotted line represents the average leaching at different pH for all biomass ash samples investigated in this study (see Table 2). Grey dotted lines report the 95% confidence level. The red line indicates the SQD limit value for open application of granular materials. The natural pH of pure biomass ash samples and blended cement is indicated by asterisks and open symbols respectively.

4. CONCLUSIONS

In this study, we have characterized the pH-dependent availability and leaching of major and trace elements, including potential nutrients and contaminants, for a wide range of FA and BA samples that originate from different biomass fuel and energy conversion techniques. In addition, a technical and environmental assessment was performed of the suitability of selected biomass ash for application in soil or cement mortars. The biomass ashes showed a large variety in composition due to the different sources of the fuel, ash type and conversion technology. Despite this large variation, the actual leaching behaviour of biomass ashes as a function of pH showed quite consistent patterns for most elements and biomass conversion technologies. Chromium was a noticeable exception and showed distinct features that we hypothesize reflect oxidising/reducing conditions during conversion of the biomass.

When the total composition of elements in biomass ash was compared with their potential leachability at low pH, some elements (i.e. Ca, Cd, K, Mo, Na, Zn, Cl and P) show a good correlation, while others (i.e. As, Ba, Cr, Co, Ni, Pb, Sn and V) do not. A substantial part of the total content of the latter elements was found to be not accessible for leaching even at extreme pH conditions. We demonstrated that an assessment based on total element content leads to different conclusions on the applicability of biomass ash as soil amendment than when based on potential leachability. We conclude that an approach based on potential leachability instead of total content does provide a more realistic assessment of the availability of both desired (i.e. nutrients) and undesired (contaminants) in soil systems, and could help improving the usability of biomass ash as soil amendment. This approach could enhance opportunities towards the use of biomass ash as a potentially valuable resource, e.g. with regard to the recycling of nutrients to the soil, and reduce landfilling.

Three FA samples were used to replace cement by 20 and 40% of total binder weight, for which it was shown earlier that the technical performance of produced mortars complies with strength requirements for class 42.5 and 32.5 cement, respectively. Here, we have shown that these mortars also complied with environmental leaching criteria for construction products. In addition, the emissions during a second life phase of the cement mortars (e.g. as recycled and aged aggregates) should preferably be taken into account to assess the environmental consequences of such applications over their entire life cycle. We have demonstrated how such an assessment, that would be appropriate for alkaline construction materials in general, can be made on the basis of the pH dependence leaching test.

Returning biomass ash to soil would be beneficial from the viewpoint of closing element cycles. However, our results suggest that individual ashes may have insufficient total amounts of nutrients (e.g. Ca and P) or too high amounts of trace elements (e.g. As, Cu, Cr, Ni, Pb and

V) under the current guidelines for this application. Although not currently considered in prevailing regulations, we have shown that an approach based on leaching could lead to substantially different results and a potentially more realistic quantification of element availability in soil applications. Given current regulatory criteria, the beneficial utilization of biomass ash in cement may be more feasible than direct soil application. However, an assessment and regulatory criteria based on the leaching rather than total content of elements may widen the application of biomass ash.

Finally, we recommend that biomass ash applications should be assessed also from a lifecycle perspective, in order to account for all additional processes and associated environmental impacts.

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Supplementary Material

Table S1 List of samples investigated in this study. G or C notations identify the thermal conversion technique adopted i.e. gasification (G) or combustion (C). Technologies are divided in bubbling fluidized bed (BFB), circulating fluidized bed (CFB), pulverizing fuel or fixed bed. FA1, FA2, FA3 and FA4 samples were subject of further investigation as described in Sections 2.4 and 2.5 of the manuscript.

<i>Ash type</i>	<i>Sample ID</i>	<i>Fuel</i>	<i>Conversion</i>	<i>Technology</i>	<i>Conversion Temp. (°C)</i>
Fly ash	FA1	Mixed wood (clean)	C	BFB	850
Fly ash	FA2	Wood (clean) pellets	C	Pulverized fuel	1400
Fly ash	FA3	Demolition wood/papersludge	C	CFB	850
Fly ash	FA4	Wood (clean)	C	Pulverized fuel	1000
Fly ash	#1	Wood (beech)	C	Lab-scale CFB	-
Fly ash (cooler)	#2	Wood	C	Pilot-scale BFB	850
Fly ash (cyclone)	#3	Wood	C	Pilot-scale BFB	850
Fly ash (mix)	#4	Wood	C	Pilot-scale BFB	850
Fly ash	#5	Wood	C	BFB	-
Fly ash	#6	Cacao	G	Pilot -scale CFB	822
Fly ash	#7	Wood pellets	G	Pilot -scale CFB	-
Fly ash	#8	Grass/paper sludge	G	Pilot -scale CFB	811
Fly ash	#9	Grass	G	Pilot -scale CFB	809
Fly ash	#10	Chicken manure	G	Pilot -scale CFB	750
Fly ash	#11	Straw	G	Pilot -scale CFB	750
Fly ash	#12	Wood pellets	G	Pilot -scale CFB	760
Fly ash	#13	Wood pellets	G	Pilot -scale CFB	900
Fly ash	#14	Wood demolition (cat B)	G	Pilot -scale CFB	-
Bottom ash	#15	Wood pellets	G	Co-current fixed bed	700
Bottom ash	#16	Cacao	G	Lab-scale BFB	822
Bottom ash	#17	Straw	G	Lab-scale BFB	750

Table S2 Complete dataset of the investigated samples. Content of elements is expressed as mg/kg of dry ash. For information on fuel type and conversion technology the reader can refer to the sample ID as reported in Table S1.

FA_COMB					
Sample ID	#1	#2	#3	#4	#5
As	21.1	7.80	30.6	17.1	14.5
Ba	591.9	310.0	419.9	355.1	477.4
Ca	151995	94943	198530	137414	190361
Cd	0.100	2.70	6.00	4.05	12.5
Cl	N.A	N.A	N.A	N.A	N.A
Co	4.09	13.8	15.4	14.4	9.91
Cr	1912	122	178	145	89.5
Cu	30.7	56.9	136	89.6	98.6
K	11751	24369	32247	27599	64778
Mo	13.9	320	546	413	19.4
Na	194.2	10925	11927	11336	5472
Ni	315	97.5	112	103	38.6
P	1426	27412	26108	26877	15783
Pb	6.33	70.6	187	118	149
S	372	5278	13296	8565	8913
Sb	4.24	N.A	3.60	N.A	3.92
Se	0.150	N.A	N.A	N.A	1.82
Sn	2.15	5.80	8.20	6.78	0.600
V	4.31	51.1	77.0	61.7	45.8
Zn	8.80	308	690	464	846

<i>FA_GAS</i>									
<i>Sample ID</i>	<i>#6</i>	<i>#7</i>	<i>#8</i>	<i>#9</i>	<i>#10</i>	<i>#11</i>	<i>#12</i>	<i>#13</i>	<i>#14</i>
As	1.60	10.4	6.26	5.36	0.060	2.1	51.8	83.8	93.0
Ba	352	395	189	205	157	91.6	1519	2065	3647
Ca	31939	10941	87931	45851	48672	14247	19108	25956	48089
Cd	0.070	0.070	0.070	0.070	0.070	0.078	0.292	0.088	7.51
Cl	645	N.A	6429	11849	18684	11251	837	760	N.A
Co	9.82	2.42	4.07	4.00	4.97	1.96	8.00	11.2	20.1
Cr	46.4	29.1	62.3	59.5	31.7	12.9	204	254	444
Cu	362	22.1	62.9	52.1	506	15.5	217	199	416
K	118298	8560	48112	68653	143453	43692	5642	7077	7382
Mo	3.78	1.50	7.12	9.65	37.7	8.36	3.65	5.82	7.46
Na	2905	1171	4751	6755	13794	1725	2403	2407	4604
Ni	68.3	21.6	28.3	25.6	39.8	5.71	28.4	50.7	30.3
P	35453	307	6719	8457	46567	3022	333	457	1328
Pb	22.4	0.760	10.6	20.3	7.48	19.4	1701	329	4697
S	5255	105	4727	4728	8025	1348	1751	1569	4960
Sb	1.44	4.16	3.42	1.70	N.A	0.211	23.0	42.0	34.4
Se	0.622	0.150	0.534	0.686	1.89	0.819	1.74	0.213	0.150
Sn	0.149	2.71	6.95	4.71	0.307	1.42	19.5	21.2	58.3
V	13.7	2.45	27.4	26.2	24.8	6.79	6.18	9.21	10.1
Zn	1153	56.0	212	224	1366	51.9	1752	710	3912

<i>BA_GAS</i>			
<i>Sample ID</i>	<i>#15</i>	<i>#16</i>	<i>#17</i>
As	55.3	2.07	0.843
Ba	1426	171	97.3
Ca	31945	27665	16644
Cd	0.188	0.207	0.183
Cl	950	1477	15924
Co	10.9	10.2	2.36
Cr	232	189	72.4
Cu	157	313	23.2
K	7356	149226	58693
Mo	5.36	7.13	12.9
Na	6231	1371	1588
Ni	75.7	113	51.0
P	474	37747	3465
Pb	872	10.4	10.5
S	2329	9202	984
Sb	24.7	N.A	N.A
Se	0.571	0.856	0.094
Sn	2.79	1.76	1.20
V	72.9	12.2	6.03
Zn	1410	420.7	58.7

FA1)

FA2)

FA3)

Figure S1 Qualitative mineralogical composition of the samples FA1, FA2 and FA3 (Carr, 2019).

Figure S2 Total content of Ba, Cd, Cl, Cu, Na, Sb, Se, Sn, V and Zn versus the maximum leached concentration expressed as the emission in mg/kg (48h, L/S=10 L/kg) at pH around 2 or $8 < \text{pH} < 12$ (only for oxyanions forming elements Mo and Sb) of the biomass ash samples. Continuous black line indicates a ratio 1:1 meaning total content equals the maximum leached amount from the biomass ash. When available, the limit values (MIN-MAX) from Table 1 where plotted on both X and Y-axis in order to evidence any discrepancy between judgment based on total content Vs maximum leached. Canadian (Hannam et al., 2016) regulation is used only for Co and Mo limits.

Figure S3 Leaching of As, Ba, Ca, Cd, Cl, Co, Cu, Ni, P, Pb, Se and V as a function of pH in all biomass ash samples. Red square indicates bottom ash samples from gasification processes, black square indicates fly ash from gasification and blue squares represent samples from combustion processes. Open red, black and blue circles indicate the natural pH of bottom ash, fly ash from gasification and fly ash from combustion samples respectively without pH adjustment. The dotted grey areas indicate a typical pH range for soil (4 to 8) and cement (10.5 to 12.5)

Table S3 Limit values for utilization of contaminated soil and construction products for different applications. Content of elements in the EURO soil used in the experiments and theoretical content of 2% wt. FA1, FA2, FA3 and FA4 containing soil. The fly ash composition is reported in Table 2 of the manuscript. All values are expressed in mg/kg.

	Soil Quality				EURO Soil 4 b	2%FA1	2%FA2	2%FA3	2%FA4
	Background values	Residential	Industrial	Construction products*					
As	20	27	76	0.90	6.2	6.4	6.2	8.2	8.8
Ba	190	550	920	22	113	136	179	143	112
Cd	0.60	1.2	4.3	0.04	0.50	1.1	0.70	0.57	1.5
Cl	-	-	-	616	-	-	-	-	-
Co	15	35	190	0.54	7.8	7.8	7.9	7.9	7.6
Cr	55	62	180	0.63	36	37	38	39	38
Cu	40	54	190	0.90	23	26	26	36	30
Hg	0.15	0.83	4.8	-	0.03	-	-	-	-
Mo	1.5	88	190	1	0.06	0.36	0.50	0.10	0.86
Ni	35	39	100	0.44	48	47	48	48	47
Pb	50	210	530	2.30	26	29	26	32	55
Sb	4	15	22	0.32	-	-	-	-	-
Se	-	-	-	0.15	-	-	-	-	-
Sn	6.5	180	900	0.40	0.07	0.14	0.81	0.20	0.93
V	80	97	250	1.80	35	35	35	35	35
Zn	140	200	720	4.50	80	113	100	141	342

*Soil Quality Decree (SQD) limit values refer to the leaching of elements express as mg/kg at natural pH and L/S 10 for open application

Figure S4 Release of As, Cd, Co, Cu, Mg, Mo, P, Pb, Sb, Se, Sn, V and Zn as function of pH for two different biomass fly ash samples (i.e. FA1 and FA4) and mixtures with soil (i.e. 0.2% and 2% of FA_1 mixed with soil and 2% of FA_4 mixed with soil). The release of pure fly ashes is also shown along with the reference soil. The natural pH values are indicated by open circles for the pure fly ash and open diamond for the addition of 0.2% of FA1 and open squares indicate the addition of 2 wt. % of FA1 and FA4 to soil. Solid black line specifies the MTR limits for groundwater quality which are expressed as mg/kg.

Figure S5 Leaching of As, Cd, Cl, Co, Cu, Ni, Pb, S, Sb, Se, Sn and V as function of pH in pure biomass fly ash and cement products. The black dotted line represents the average leaching at different pH of all biomass ash samples investigated in this study. Grey dotted lines reports the 95% confidence level. The red line indicates the SQD limit value for open application of granular materials. The natural pH of pure biomass ash samples and blended cement is indicated by asterisks and open symbols respectively.

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Chapter 4

Technical and environmental performance of lower carbon footprint cement mortars containing biomass fly ash as a secondary cementitious material

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Tosti, L., van Zomeren, A., Pels, J. R., & Comans, R. N. J. (2018). Technical and environmental performance of lower carbon footprint cement mortars containing biomass fly ash as a secondary cementitious material. Resources, Conservation and Recycling, 134, 25-33, <https://doi.org/10.1016/j.resconrec.2018.03.004>

ABSTRACT

This study evaluated the mechanical and environmental properties of cement mortars containing fly ash from biomass combustion as a secondary cementitious material.

Cement mortars with 20 and 40% wt. replacement of Portland cement with fly ash from two types of installations were tested for their compressive strength and leaching behaviour.

Substitution of 20% Portland cement with wood fly ash complied with the reference standard for compressive strength of 42.5 MPa at 28 days. Replacement rates of 40% developed a lower strength (30 and 33.5 MPa) but were still suitable for applications. The pulverised fuel ash performs substantially worse. We conclude that the biomass fly ash from fluidized bed combustion performs as a functional secondary cementitious material in cement, whereas the functionality of pulverized fuel fly ash is insufficient.

The release of environmentally relevant elements from all the tested specimens fulfilled the Dutch leaching criteria for reuse. During second life as a granular construction material the release of Ba, Cr, Mo and V increased to a level of concern. However, this release was found to be similar to that of existing blended cements and was controlled by cement chemistry.

The technical performance of cement mortars was influenced by the type and ratio of fly ash mixed with cement. However, the environmental performance was driven by the cement matrix that controlled the release of contaminants.

Using biomass fly ash as a secondary cementitious material can reduce the carbon footprint of concrete by 40% while maintaining good technical and environmental performance.

Keywords: Blended cement, leaching, biomass ash, compressive strength, secondary cementitious material

1 INTRODUCTION

Cement is an essential ingredient for concrete that is currently the most used construction material worldwide with an annual output, in 2009, of 2.8 Gtons (WBCSD - World Business Council for Sustainable Development, 2009). For traditional cement production, different raw materials such as limestone and clay need to be mined, blended in specific proportions, ground and heated at high temperature in a rotary kiln. This process is energy and resource intensive and results in considerable CO₂ emissions due to the decomposition of calcium carbonate (limestone) into calcium oxide and the combustion of fossil fuels during the heating of the mixture. The global average gross CO₂ emission per ton of cement is estimated to be around 900 kg, accounting for 5-8% of total human atmospheric CO₂ emission (Habert et al., 2010). Over the last years, many efforts have been made to reduce the carbon footprint of the cement industry, including: i) improving the energy efficiency of the kilns; ii) replacing fossil fuels with alternative energy sources such as animal residue, sewage sludge and waste oil; iii) substitution of the traditional Portland cement with alternative cementitious materials, such as blast furnace slags and coal combustion fly ash.

The substitution of traditional cement with biomass fly ash is progressively being investigated due to the growing use of biomass for sustainable energy production and the corresponding large amount of biomass fly ash produced (Berra et al., 2015; Rajamma et al., 2015; Siddique, 2012). Besides reducing greenhouse gas emissions due to lower energy and raw materials consumption, the addition of biomass ash to cement could result in the beneficial effects of avoiding the landfilling of the biomass combustion residues. On the other hand, some potentially dangerous substances present in the biomass ash might be released in the environment during different life stages of cement containing fly ash. At present, the use of fly ash as a mineral admixture in concrete is regulated by the European standard EN 450-1 (2005). In practice, this standard precludes the use of any material not derived from coal combustion. This prerequisite limits the use of biomass ash in cement because coal-fired power plants can use only up to 20% biomass to replace coal. At this percentage, the characteristics of the fly ash from co-combustion of coal and biomass (normally clean wood) is dominated by the coal-ash and can be used in the same applications. Higher percentages of biomass ash generally lead to a higher content of alkali and phosphorus (Boersma, 2011; Sarabèr, 2014; van Loo and Koppejan, 2008). The elevated levels of these constituents make the biomass ash unsuitable for the established application of coal fly ash according to EN-450. In many countries most of the biomass ash is still landfilled (van Eijk et al., 2012).

However, several researchers have demonstrated that biomass fly ash can be effectively used as cement replacement to produce concrete with acceptable strength and durability performances (Cheah and Ramli, 2011). The effects of biomass ash on the technical cement properties can vary depending on the physical-chemical properties of the ash. These properties are determined by the type of biomass feedstock combusted (i.e., ash forming elements present in the biomass and their mode of occurrence) (Oberberger et al., 1997; van Lith et al., 2006), the thermal conversion technology adopted (i.e., pulverized fuel combustion, fluidized bed, grate stoker) and the flue gas cleaning system (Sarabèr, 2014; Tarelho et al., 2015).

A general observation is that strength properties of cement and concrete mixtures decreases with increasing wood ash contents but, when pozzolanic activity is present, strength increases with age (Siddique, 2012, 2008; Wang et al., 2008). Normally this observation is attributed to the low hydraulic activity of biomass fly ash with consequential dilution of active phases contained in cement (Cheah and Ramli, 2013; Rajamma et al., 2015). The maximum replacement ratio at which acceptable compressive strength is maintained is around 10 - 20% of total binder weight (Cheah and Ramli, 2012, 2011; Corinaldesi et al., 2016; Rajamma et al., 2015; Rajamma, 2009). Lothenbach et al. (2011) also stated that fly ash with a high Calcium content can contain reactive crystalline phases such as dicalcium silicates which can contribute to strength development by forming hydrated products. Therefore, we focus on ashes with a relatively high Ca content to study the cement performance in combination with higher replacement rates (20-40%).

Most studies have focused mainly on the technical performance of cement containing biomass ash. To date, little is known about the environmental compatibility of products containing biomass ash when exposed to different utilization scenarios (Berra et al., 2011). Fly ash from biomass combustion can contain significant amounts of hazardous elements (Saqib and Bäckström, 2015) even if the fuel is regarded as clean fuel (Pels et al., 2004). Other studies have shown that the use of alternative materials in cement (e.g. coal fly ash, blast furnace slags) can affect the potential release of hazardous substances from these products (Kosson et al., 2009, 2014; van der Sloot et al., 2008). Thus, when biomass ash is used in cement, part of the contaminants could be released from the product during its service life (e.g., application of material in intact structures) and potential second life applications (e.g., reuse of recycled concrete aggregates as road sub-base) (Engelsen et al., 2017, 2012, 2010; van Zomeren et al., 2015). Release of contaminants might threaten the environment and restrict re-use of biomass ash in products.

In this study we evaluate both the technical and environmental performance of blended cement mortars containing different replacement ratios of biomass fly ash. Combination of different leaching tests is employed to assess the potential impact of cement containing biomass ash under different application scenarios. Results from this work could form a basis to assess the sustainability of cement containing biomass ash in a wider perspective, beyond energy and raw material savings. The testing and assessment approach that is presented here, may also support the development of a more circular use of cementitious materials in multiple life cycles.

2 MATERIALS AND METHODS

2.1 Biomass Fly Ash

Three biomass fly ashes (i.e. FA1, FA2 and FA3) were investigated in this study. The samples had a particle size <1 mm and were stored dry in the laboratory. Sample FA1 originates from a circulating fluidized bed installation that combusts a mixture of clean wood and either cacao husks, molasses or other clean biomass streams that were occasionally added. The sample FA1 was collected from the electrostatic precipitator. Sample FA2 originates from the combustion of wood pellets in a pulverized fuel installation and was collected from the electrostatic precipitator.

Sample FA3 was sampled from a bubbling fluidized bed incinerator. The fuel consisted of a mixture with an equal share of recovered paper sludge from the de-inking step of the paper recycling process and recovered waste wood. The fly ash was collected from the electrostatic filter (90% by mass) and the textile bag filter (10% by mass) flue gas cleaning system. The investigated biomass ashes cover a fairly wide range of commonly used biomass fuels and conversion technologies and can, therefore, be considered representative for future biomass ash use in cement products.

2.2 Preparation of blended cement mortars

Cement mortar samples were prepared by dry mixing of Portland Cement CEM I 42.5N with biomass fly ash in accordance with the European standard EN 196-1 (2005). Both 20% and 40% (by total binder weight) of the Ordinary Portland cement (OPC) was replaced with biomass fly ash. Table 1 shows the mix design of the cement mortars. All specimens were prepared with a water-binder weight ratio (w/b) of 1:2 and a sand-binder ratio of 3:1. Rectangular blocks (160 x 40 x 40 mm) were casted and removed from the mold after 24 h of

curing. Next, the molds were cured for 28 days in a controlled temperature and humidity room (20 °C and 95% humidity). After 28 days of curing, the specimens were subjected to compressive strength (EN-196-1, 2005) and leaching tests.

Table 1 Composition and sample IDs of the studied cement mortar recipes. The percentage of replacement of traditional Portland cement (OPC reference) by fly ash (FA1, FA2 or FA3) refers to the total binder weight.

		Reference	20 Blends	40 Blends
Portland Cement (CEM I 42.5-N)	wt%	22.2	17.8	13.3
Fly Ash*	wt%	-	4.4	8.9
Sand	wt%	66.7	66.7	66.7
Water	wt%	11.1	11.1	11.1
Sample ID	sample code	OPC reference	20 FA1	40 FA1
			20 FA2	40 FA2
			20 FA3	40 FA3

*Different types of FA were used (i.e. FA1, FA2 and FA3).

2.3 Leaching tests

The release of inorganic elements from the pure biomass ashes, the 20% blends, 40% blends and the reference was measured by means of three leaching tests: tank leaching test (FprCEN/TS 16637-2, 2013), parallel batch extraction test at different L/S ratios (EPA, 2012) and the pH dependence leaching test (EN 14429, 2015). Selection of an appropriate combination of leaching tests to characterize the environmental performance of cement mortars during a determined use or second life scenario was based on the physical form of materials (i.e. granular or monolithic) and the anticipated application conditions. The tank leaching test (FprCEN/TS 16637-2, 2013) is suitable for an intended use scenario in which the product is intact and shaped and the release of substances to the surrounding environment is primarily diffusion controlled. The parallel batch extraction test at different L/S ratios (EPA, 2012) is adopted to evaluate a second life stage in which the material is used in a granular form and exposed to more direct contact with (percolating) water. The partition of elements between solid and liquid phase is determined by the liquid to solid ratio and controlled by advection and solubility mechanisms. Finally, the pH is known to be the main controlling factor for the speciation of chemicals in the solution and solid phase. Different processes such as complexation, precipitation and sorption to mineral phases are controlled by pH. Therefore, the pH dependence leaching test (EN 14429, 2015) was selected to assess the response of leaching to the change in surrounding environmental conditions.

In the tank leaching test (FprCEN/TS 16637-2, 2013), the intact mortars were placed in a plastic vessel (i.e. HDPE, pre cleaned with HNO_3) with the exposed surfaces completely submerged in water. The liquid to surface area ratio (L/A) was 76.4 l/m^2 . The leachant (demineralized water) was renewed at predetermined time intervals up to a cumulative time of 64 days. The test results provide the mass released per unit surface area as a function of time. This test was performed on 20_blends, 40_blends and reference OPC.

The particle size of the mortar samples was reduced with a jaw crusher ($<1 \text{ mm}$) for the leaching tests using granular materials. When the biomass ash was tested no further particle size reduction was required. In the parallel batch extraction procedure (EPA, 2012) 20-100 g of ash or crushed mortars was placed in plastic bottles (i.e. LDPE, pre cleaned with HNO_3) and different amounts of water were added to reach the desired liquid to solid (L/S) ratios (i.e. 1, 2, 5, 10 l/kg). The contact time was 48 h. The test results provide the release per mass unit as a function of the L/S ratio.

In the pH dependence leaching test (EN 14429, 2015) various amounts of acid and base were added to about 15 g of the granular material at a liquid to solid (L/S) ratio of 10 l/kg, obtaining a final pH ranging from 2 to 12.5 at an equilibration time of 48 h.

2.4 Chemical analysis

The samples for total content analysis were prepared after digestion of solid samples in a mixture of $\text{HNO}_3\text{:HClO}_4\text{:HF}$ (i.e. 9:1:1) for 10 hours at 190°C . The digests were analysed for Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V and Zn by ICP-OES. All leachates from the various leaching tests were analysed for elements As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, S, Sb, Se, Sn, V and Zn by ICP-MS. Only the Zn concentrations in leachates from the tank test on 20_FA1, 40_FA1, 20_FA2 and 40_FA2 samples were measured by ICP-AES, as well as the concentrations of Cu, S and Zn from batch test on all samples. Chloride and fluoride were analysed by ion chromatography. More detailed information and detection limits values are reported in the supplementary material.

3 RESULTS AND DISCUSSION

3.1 Biomass fly ash and cement mortars composition

Table 2 shows the chemical composition of samples FA1, FA2, FA3 and the OPC reference. Concentration ranges for coal fly ash and biomass ash are also reported for comparison. Table 2 shows that the total content of most major elements is fairly comparable for the three ash

types and differences are generally within a factor 2-3. An exception is the K and P content which is around one order of magnitude higher in samples FA1 and FA2 compared to FA3. Normally, wood biomass is enriched in K and P compared to paper sludge, thus explaining the higher concentration of these elements in FA1 and FA2. Even though K and P are known for their deteriorating properties in cement mortars, these elements do not have hazardous properties. All tested biomass fly ash samples (especially FA3) contain a relatively high CaO content in comparison to coal fly ashes. Potassium is generally more concentrated in biomass fly ash than coal fly ash.

With regard to trace elements, the use of demolition wood in the fuel mixture is responsible for the higher content of As, Cu, Cr and Zn in sample FA3 compared to FA1 and FA2 as was also indicated by (Krook et al., 2004; Saqib and Bäckström, 2015). When the concentration of minor elements in FA1, FA2 and FA3 is compared with typical range of coal fly ash and biomass ash, no significant difference is observed with the exception of Chloride which is generally higher in biomass ash than in coal fly ash. Additionally, Mo concentration in FA1 and FA2 and Sr content in FA1, FA2 and FA3 samples are close to maximum values of the range reported in literature for biomass fly ash. The content of minor elements is higher in the biomass fly ash studied than in the OPC reference, with the exception of Co and Se. This observation implies that inclusion of coal fly ash or biomass fly ash into cement would result in cement mortars with higher concentrations of trace elements, in proportion to the replacement rates of traditional OPC cement.

Table 2 Chemical composition of the pure FA1, FA2 and FA3 ash samples, reference OPC. Typical composition ranges of fly ash from coal combustion (Class C and Class F) and biomass fly ash are also reported for comparison.

	FA1	FA2	FA3	OPC reference	Coal fly ash (Class C) (Siddique and Khan, 2011; Taylor, 1997)	Coal fly ash (Class F) (Siddique and Khan, 2011; Taylor, 1997)	Biomass ash (Energy research center of the Netherlands (ECN), 2012)
Major elements (% dry)					MIN-MAX	MIN-MAX	MIN-MAX (average value)
CaO	26	27	56	14	12-30	0-8	9-65 (34)
SiO ₂	34	24	18	69	23-50	45-64	0-57 (13)
Al ₂ O ₃	2.8	3.2	8.6	1.9	13-21	20-30	0-14 (3)
Fe ₂ O ₃	1.7	2.7	1.3	0.97	4-22	4-24	0-8 (2)
MgO	3.3	4.9	2.9	0.47	1-7	1-2	0-18 (5)
K ₂ O	7.8	9.35	0.93	0.52	0-2	1-4	0-35 (13)
Na ₂ O	0.74	1.3	0.77	0.16	0-7	0-3	0-23 (1)
P ₂ O ₅	3.6	2.3	0.32	0.15	-	-	0-17 (5)
SO ₃	3.9	3.2	1.5	0.66	1-12	0-5	0-13 (3)
LOI*	8.5**	15**	4**	3**	0.3-2	0.4-7	0.1-64 (10)***
Minor elements (mg/kg dry)					MIN-MAX (Kosson et al., 2009; Van der Sloot et al., 1985)		MIN-MAX (Energy research center of the Netherlands (ECN), 2012; Saqib and Bäckström, 2015)
As	12	< 6.8	88	< 6.8	10-200		2-392
B	273	267	88	11	30-390		45-800
Ba	669	1770	831	164	600-2000		110-4000
Cd	22	7.9	3.1	0.55	2-15		6-21
Cl	6563	8216	2995	470	<500		3000-40000
Co	7.9	13	11	57	20-70		9-124
Cr	69	109	160	21	70-200		47-651
Cu	121	141	559	44	60-300		74-864
F	N.A.	10	219	N.A.	140-180		N.A.
Li	14	41	10	11	N.A.		N.A.
Mn	4736	8513	741	153	100-1200		2200-29000
Mo	15	22	< 1.9	< 4.2	8-30		3-12
Ni	37	48	56	19	0-300		26-88
Pb	163	50	279	11	20-100		108-1900
Sb	4.6	< 17	< 7.5	< 17	3-15		2-64
Se	0.57	9.2	< 3.1	13	2-50		N.A.
Sn	3.2	31	5.5	< 4.3	4-10		4-60
Sr	733	1065	821	239	N.A.		450-970
Ti	1103	1224	2225	548	4000-13000		140-10400
V	28	34	19	24	150-720		6-90
Zn	1400	883	2563	143	70-1680		1290-17200

* LOI means Loss on Ignition. If not specified the LOI temperature is unknown

** measured at 950 °C

*** measured at 550°C

3.2 Compressive strength of cement mortars

The technical properties of the cement mortars with OPC/fly ash blends and the OPC control were evaluated by means of compressive strength measurements. The main objective of the

measurement is to explore to which extent biomass fly ash could replace part of the OPC while achieving an acceptable compressive strength. It is common practice to set the reference value of the compressive strength development at 28 days of curing time. In this study, the compressive strength development after 90 days is also reported to account for the contribution of minerals with a delayed hydration which might be contained in (or formed from) the studied biomass fly ash. Figure 1 shows the compressive strength of the samples after 28 days (left) and 90 days (right).

The reference sample gained the highest strength and the strength decreased with increasing biomass fly ash replacement rates. This general trend is in line with previous findings (Cheah and Ramli, 2011; Siddique, 2012; Wang et al., 2008). The 20_FA1 and 20_FA3 samples reached a compressive strength of 46.7 and 45.6 MPa after 28 days, respectively, representing 96 and 94 % of the reference. The average strength development of these samples complies with the minimum requirement of 42.5 MPa after 28 days. After the same hydration time, the samples with a higher replacement ratio (40_FA1 and 40_FA3) developed a compressive strength of 30 and 33.5 MPa, respectively, representing 63 and 70 % of the reference. It is observed that replacement of 20 or 40% of cement with FA1 and FA3 resulted in a lower strength loss than what would be expected based on the corresponding dilution of the OPC binder. Contrary, the 20_FA2 developed a compressive strength of 33.1 MPa after 28 days (68% of the control) and the 40_FA2 of 21 MPa (43 % of the control). The observed loss of strength due to FA2 inclusion is larger than the binder dilution effect which denotes a deteriorating effect of FA2 on mechanical strength of cement blends. From these observations, we conclude that biomass fly ash from fluidized bed combustion (FA1 and FA3) is suitable as active material when added to cement formulation and contribute to strength development, whereas this effect is absent in the pulverized fuel fly ash (FA2).

The observed differences in the cementitious activity of biomass fly ash are related to the presence and amount of different mineral forms in the ash, as well as to ash particle size, shape and organic content (Juenger and Siddique, 2015). More insights in the different processes contributing to strength can be derived from the delayed compressive strength developments (90 days).

FA1 (at both replacement rates) initially (28 days) achieved good compressive strengths but showed a significant reduction in further strength development at 90 days, relative to the control. This behaviour of initially rapid and subsequently limited strength development can be attributed to an optimal particle packing rather than a delayed cementitious functionality. FA1 does not show pozzolanic activity despite the high Si content. Silicon in the fly ash

fraction from fluidized bed results from the inclusion of fragmented bed material, i.e. quartz with no pozzolanic property.

Contrary to FA1 blends, the 20_FA3 and 40_FA3 mortars showed a larger strength development between 28 and 90 days. This behaviour of FA3 is probably related to the presence of the hydraulic mineral belite. The potential formation of belite during biomass combustion has been demonstrated by Tosti et al. (2017). Based on those results, the authors hypothesize that the combination of calcium-rich biomass (i.e. bark, paper sludge) combusted in a fluidized bed installation can promote the formation of dicalcium silicates due to an enhanced interaction between solid CaO (from the biomass) and SiO₂ (from the bed material) particles. Belite is known to react slower than alite and by replacing the OPC with FA3, the alite fraction of the blend is reduced, while the belite fraction is increased. The results of compressive strength measurement after 28 and 90 days in this study are in good agreement with literature findings. More in detail Rajamma et al. (2009) (clean wood ash), Udoeyo et al. (2006) (wood waste ash) and Lessard et al. (2017) (biomass fly ash) have substituted 10 to 30% of cement with biomass ash and measured a compressive strength after 28 days ranging from about 60 to 97 % of the pure reference cement. After 90 days the compressive strength ranged between 61 and 77 % of the reference cement.

Substituting 20% wt. of the traditional cement with biomass fly ash from Ca-rich biomass fuels combusted in a fluidized bed (i.e. FA1 and FA3) can thus produce mortars that comply with the strength requirement of 42.5 MPa after 28 days. Higher replacement ratios can still result in mortars that comply with the compressive strength criterion of 32.5 MPa (e.g non-structural application). In particular, mortar containing FA3 can develop a relatively high strength close to the reference 42.5 MPa after 90 days due to the presence of hydraulic minerals.

Figure 1 Compressive strength development of mortars containing FA1, FA2 and FA3 after 28 and 90 days. The vertical bars indicate the standard deviation. The dotted and continuous lines indicate the minimum compressive strength requirements.

3.3 Leaching of substances during service life of the products

In this study, the Dutch Soil Quality Decree (SQD) is taken as reference to judge the environmental performance of the intact mortar samples. The SQD sets the maximum allowed release of inorganics, expressed as mg/m^2 , after a testing period of 64 days using a tank leaching test (NEN 7375, almost identical to the EU standard FprCEN/TS 16637-2 for construction products). Figure 2 shows the cumulative emissions after 64 days for all samples expressed as percentage of the limit values of the SQD for shaped construction materials. The release is also compared with the average release of currently used blended cements (van der Sloot et al., 2008). When the concentration in the leachate was below the detection limit, the detection limit was used for calculation of the emission. The leaching of Cd, Sb, Se and Sn was found to be below the detection limits in all leachate fractions for all the samples. Therefore, these elements are not reported here (complete information is reported in the supplementary material).

Generally, the difference between the cumulative emission of elements from the 20, 40_blends and the reference is within a factor of 5. However, some substances Ba (FA1) and Cl, Mo and Pb (FA1 and FA2) show a difference of a factor of 10 or more. Of these elements only Cl seems to be sensitive to the replacement ratio showing a higher release in the 40_blends compared to the 20_blends. Despite these elevated levels relative to the reference

mortar sample, the cumulative emission of all regulated elements remains below 10% of the SQD limit values for all the investigated samples and replacement ratios. The leaching of the new cement mortars including biomass ash is acceptable (all elements are at least a factor 10 below the limit values) and does not lead to substantially different emissions when the control sample and the ranges in blended cements are considered.

Figure 2 Cumulative release after 64 days of reference mortar and mortars containing biomass fly ash. The range of pH measured during experiments is between 11.3 and 12.1. The cumulative release is expressed as percentage of the maximum allowed release of the Dutch Soil Quality Decree for shaped construction materials. The average release from commercial blended cements (van der Sloot et al., 2008) is indicated by the black cross together with the 95% confidence level.

3.4 Leaching of crushed mortars and pure fly ash

After the intended use phase, the intact cement mortars (or the concrete products) are generally crushed and potentially re-used as concrete aggregate in road foundations and/or embankments. This physical change affects the release mechanism of substances from a more diffusion controlled release to a percolation controlled release. Generally, the release from granular materials at different L/S ratio is measured by means of a column percolation test (Kosson et al., 2002). In this work, a parallel batch extraction test (see section 2.3) was used as a proxy for the percolation test as previously investigated by (Di Gianfilippo et al., 2016;

Lopez Meza et al., 2008). The reasons for this were: i) the total amount of FA2 available for leaching tests was insufficient to perform the percolation test.; ii) sample FA3 showed hydraulic properties causing the material to solidify during the equilibration period in the percolation test. In a preliminary experiment, the increased volume caused breakage of the column. Hence, it was chosen to perform a single type of leaching test on all samples rather than a combination of either the batch leaching tests or the percolation test on different samples. A comparison of the results of both test methods performed on samples FA1 20_FA1 and 40_FA1 is discussed below.

Figure 3 shows the release of the batch tests at L/S 10 expressed as percentage of the limit value of the SQD (open application) for all crushed mortars and the corresponding pure fly ash samples. The release is also compared with the average release from batch leaching test (EN 12457-2) on crushed blended cements (van der Sloot et al., 2008). The leaching of Sb and Sn was found to be below the detection limits in all leachate fractions for all the samples including pure fly ash. Therefore, these elements are not reported here (complete information is reported in supplementary material).

Figure 3 Release of the batch tests on the crushed cement mortars and the corresponding pure fly ashes at L/S 10 and natural pH. The pH range of pure fly ash is 12.7 – 13 whereas for mortars is between 12.5 – 12.7. The release is expressed as percentage of the SQD limit value. The black cross

indicates the average of blended cements (van der Sloot et al., 2008) with corresponding 95% confidence level.

When the relative emissions from the crushed fly ash mortars (Figure 3) are compared to the relative emissions of the monolithic fly ash mortars (Figure 2), it can be seen that the release of Ba and Cr in all crushed samples increase substantially towards, or even above, the SQD limit values. This observation implies that the leaching from the initial monolithic products might not fulfil the limit value for re-use when materials are crushed in the end of life scenario (see also paragraph 3.5). The release of chloride and Mo does also increase to values higher than 10% of the SQD limit values for samples containing FA1 and FA2. The relatively high release of Ba and Cr is mainly due to the Portland cement since the high release of these elements observed in the pure fly ash is not reflected proportionally in the blended mortars. The increased release of the relatively soluble elements (Cl and Mo) is predominantly caused by the changed leaching mechanism from a diffusion controlled regime to a percolation dominated regime. In addition, the increased release of these soluble elements is also related to the relatively high concentrations in the fly ash samples FA1 and FA2. Nevertheless, the release of Ba, Cr and Mo are all within the observed ranges for blended cements that was taken from literature. Most other elements show a release that is below 10% of the SQD limits. Differences in the leaching of these elements between blends and reference cement mortar can generally be attributed to differences in detection limits of the analytical measurements (e.g. As, Cd, V and Zn), see supplementary material for more details. The release of substances from the crushed mortars give a first indication of the expected performance of the mortars in a second life scenario as granular application (e.g. road foundation, embankment). However, this comparison does not yet include the potential effects of weathering and carbonation on the release of substances. Those effects will be addressed in paragraph 3.5.

Finally, the release from pure FA1 and FA2 is higher than the corresponding 20_blends and 40_blends for all the investigated elements where the release of Cl, Cr, Mo and Se is significantly above the SQD limit values. In case of pure FA3, release of Ba and Pb is above the SQD limit. However, introducing FA1, FA2 and FA3 into cement leads to a reduction of the leaching of the mentioned elements with an effect higher than that which could be attributed to dilution only. Apparently, these elements are also chemically bound in mineral phases and/or adsorbed to reactive surfaces in the mortars as has also been observed for coal fly ash in concrete (Kosson et al., 2014).

Figure 4 Comparison between batch and column data for samples FA1, 20_FA1 and 40_FA1 at liquid to solid (L/S) ratio of 10. The black line indicates a ratio of 1, i.e. equal emissions between both methods. The grey dotted lines indicate a factor 10 and 100 of variation.

The comparison between results from the batch leaching test and the column test (both at L/S 10) was performed on samples FA1, 20_FA1 and 40_FA1. This comparison aimed at assessing the magnitude of variation between batch and column release data and to check the validity of comparing batch test results to the SQD limit values that are derived for column test results. Since the detection limits in the batch test were a factor of 20 higher compared to the column test, values below the detection limit are not reported. Figure 4 shows that the results from the present article are mostly in reasonably good agreement with the column test in particular for concentrations above 100 mg/kg. Our results are in a good agreement with Di Gianfilippo et al. (2016) and Lopez Meza et al. (2008). However, results from different matrices (and combustion technologies) can lead to specific differences as observed by the variation in leaching of Cu from MSWI bottom ash due to enhanced release of DOC in the batch tests (Di Gianfilippo et al., 2016). In the presented comparison, most elements are within a factor of 3 of difference. The elements Ba, Cl, Cr and Mo, which were observed to be very close to the SQD limits (Figure 3), even show a lower variation between 1.1 and 1.7. The only exception is the release of Ba from one of the pure fly ash sample (FA1), which shows a factor of 4.3 lower release from the batch test in comparison to the column test. At lower concentrations, the variation increases up to a factor 10 for elements such as Cd, Pb and Se. However, the difference in this low concentration range shows an overestimation of the release when data from batch test is used. From the validation results we conclude that using data from batch tests instead of column tests is acceptable to obtain an impression of the anticipated changes in leaching when these materials are size reduced for a second life phase.

3.5 Leaching behaviour as a function of pH

In addition to physical changes (i.e. crushing), mortars can be subject to pH variation due to a change in the exposure scenario or natural aging (i.e. carbonation). The pH is known to be a major factor that determines the leaching of many substances (Dijkstra et al., 2006; Kosson et al., 2014; Meima and Comans, 1999). Consideration of the effect of pH changes on the release of elements is very important when evaluating the long term leaching behaviour of mortars at different environmental application conditions. Figure 5 shows the release of Ba, Cr, S, V and Zn, as a function of pH for the mortars and the pure fly ash samples. Values below detection limit were reported as equal to the detection limit. Complete information can be found in the supplementary material.

Figure 5 Leaching behavior of Ba, Cr, S, V, Zn, as a function of pH. Samples FA1, FA2 and FA3 are reported together with the corresponding blended mortars and reference OPC. The black dotted line represents the average of blended cements and the grey dotted lines the 95% confidence level. The red line indicates the SQD limit values for open application of granular construction materials.

In general, the leaching patterns of Ba, Cr, S, V and Zn as function of pH are similar for all the investigated mortar specimens. The release of all elements in Figure 5 (but also the other elements shown in the supplementary information) is mostly within the observed bandwidth of currently used blended cements (dotted lines in Figure 5). Particularly the pH interval between 8 and 12.5 is important when assessing the leaching response to a change of pH as a potential consequence of different exposure and/or ageing. Cationic elements such as Ba, Cd,

Co, Ni, Pb and Zn are not expected to be of concern when the cement is crushed and aged. A pH reduction due to carbonation corresponds to a lower release within the relevant pH window of 8-12.5. On the other hand, for (anionic) Cr, Mo, Se and V the carbonation process might result in an increased release up to values very close to or exceeding (i.e. Chromium) the SQD limit. It is thus very important to consider the leaching properties of (blended) cement samples for the different scenarios in which they may be exposed during their service life, next life and/or the end of life phase.

When the release from pure fly ash is compared to the release from blended cements we see a distinction for Ba, Cr, S and Mo and Se (reported in the supporting information), especially at the cementitious materials relevant pH values between 10 and 13. This difference between the pure fly ashes and the corresponding blends can reach up to two orders of magnitude (i.e. Ba, Cr, Mo and S). The observed difference implies different leaching mechanisms underlying the release of these elements. As already observed from the batch test results at natural pH (Figure 3), the inclusion of fly ash (FA1 and FA2) is partially contributing to the higher release of more soluble elements. However, the consistency of the pH dependent leaching behavior observed for the blends and reference mortars, as well as for the blends and the average of the worldwide dataset, shows that the cement chemistry mainly controls the leaching of elements.

Based on the obtained results we conclude that the release of elements is strongly pH dependent and, in view of long term assessment, this factor could influence the release from cement mortars.

4 CONCLUSIONS

In this study, the technical and environmental performance of cement mortars containing three types of biomass fly ash was assessed; fly ashes from combustion of clean wood in a fluidized bed (FA1) and a pulverized fuel installation (FA2), as well as fly ash from combustion of paper sludge mixed with demolition wood in a fluidized bed (FA3).

Replacement of 20% wt. of traditional Portland cement with FA1 and FA3 produced cement mortars that complied with strength requirements for structural concrete application of 42.5 MPa after 28 days. Replacement of 40% wt. of traditional cement with FA1 and FA3 resulted in a lower compressive strength, but still compliant with the requirement of 32.5 MPa for lower strength (non-structural) applications. The ash from the pulverized fuel installation (FA2) resulted in a substantially lower compressive strength performance, albeit that the 20%

replacement ratio reached the lower strength application requirement. In evaluating the environmental performance of the cement mortars, the monolithic leaching test on the hardened mortars showed a very similar cumulative release of elements for all the mortars containing biomass fly ash and the OPC control sample. The release was also in line with that of other blended cements currently used in the building industry, while the release of all relevant elements was below 10% of the Dutch limit values for construction products. The physical change of the crushed mortars, which reflects their potential second life application as a granular construction material, caused the release to increase relative to the monolithic form, with values for Ba and Cr much closer to the allowed limits. However, this observation is not solely related to the inclusion of fly ash but also to the cement leaching properties. The pH dependent leaching behavior of Ba, Cr, Mo and S from the pure fly ash samples and their corresponding blended mortars clearly showed that the chemical leaching mechanisms in the pure fly ash samples are no longer visible when these ashes are blended in the cement mortars. Therefore, we conclude that the release of the identified relevant elements Ba and Cr is essentially controlled by the cement matrix, even at 40% fly ash replacement rates. The release of Ba, Cr, Mo and V from cement mortars might increase especially during a second life stage, where the mortars are in a granular form and carbonation/aging processes contribute to a decreasing pH. The importance of a set of leaching tests that reflect the environmental performance of the cement mortars during their entire life cycle has been demonstrated. The partial replacement of traditional cement by biomass derived fly ash can be a promising option to reduce the carbon footprint of concrete up to 40% while maintaining good technical and environmental properties of products. Further research focusing on optimizing fly ash properties to ensure a good technical performance of blended cement, and on the release of contaminants in multiple life cycles of mortars that include biomass fly ash, is recommended to facilitate maximum replacement of traditional cement and a corresponding further reduction of the carbon footprint.

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Supplementary Material

Table S1 Cumulative release after 64 days as measured from shaped mortars. All data is expressed as mg/m². The pH of the water in contact with mortar is also reported in the first row. All elements were measured by ICP-MS except for those indicated by (*) which were measured by means of ICP-AES

	20_FA1	40_FA1	DTL (64)	Reference	DTL (64)	Average Blended	95% (-)	95% (+)	SQD
pH	12.1	12.2		11.4		11.3			
As	7.39E-02	5.26E-02	4.13E-02	7.12E-02	1.22E-02	1.98E-01	4.61E-02	4.05E-01	2.60E+02
Ba	6.93E+01	7.40E+01	6.19E-02	5.00E+00	1.83E-02	3.45E+01	1.40E+01	8.28E+01	1.50E+03
Cd	1.80E-02	1.80E-02	1.80E-02	3.06E-03	3.06E-03	3.64E-02	3.47E-02	4.09E-02	3.80E+00
Cl	1.46E+03	4.90E+03	3.67E+02	9.85E+01	3.06E+01	3.10E+02	1.73E+02	9.89E+02	1.10E+05
Co	1.03E-02	1.60E-02	1.03E-02	2.15E-02	3.06E-03	2.20E-01	7.58E-02	6.65E-01	6.00E+01
Cr	1.82E+00	2.64E+00	4.13E-02	2.23E+00	1.22E-02	2.05E+00	3.19E-01	4.44E+00	1.20E+02
Cu	9.65E-01	9.94E-01	8.17E-01	1.53E+00	6.11E-02	1.48E+00	1.17E+00	2.27E+00	9.80E+01
F	4.51E+01	3.90E+01	1.83E+01	2.59E+01	1.83E+01	N.M.	N.M.	N.M.	2.50E+03
Mo	1.13E+00	1.99E+00	3.71E-01	1.48E-01	1.10E-01	2.14E-01	6.40E-02	3.68E-01	1.44E+02
Ni	9.55E-01	7.14E-01	6.19E-02	2.85E-01	1.83E-02	1.91E+00	8.21E-01	3.54E+00	8.10E+01
Pb	1.28E+00	8.38E-01	8.25E-02	6.72E-02	2.44E-02	4.69E-01	2.59E-01	9.23E-01	4.00E+02
Sb	3.30E+00	3.30E+00	3.30E+00	9.78E-01	9.78E-01	9.69E-02	3.35E-02	2.56E-01	8.70E+00
Se	2.06E-01	2.06E-01	2.06E-01	6.11E-02	6.11E-02	N.M.	N.M.	N.M.	4.80E+00
Sn	1.03E+00	1.03E+00	1.03E+00	3.06E-01	3.06E-01	4.56E-01	3.34E-01	6.91E-01	5.00E+01
V	8.37E-01	4.64E-01	1.03E-01	2.11E+00	3.06E-02	2.07E+00	7.09E-02	6.41E+00	3.20E+02
Zn	1.60E+01 (*)	1.41E+01 (*)	1.22E+01	1.01E+01	1.83E-01	2.10E+00	1.52E+00	2.58E+00	8.00E+02

	20_FA2	40_FA2	DTL (64)	Reference	DTL (64)	Average Blended	95% (-)	95% (+)	SQD
pH	11.8	11.8				11.3			
As	2.65E-01	3.96E-01	2.15E-01	7.12E-02	1.22E-02	1.98E-01	4.61E-02	4.05E-01	2.60E+02
Ba	7.52E+00	4.73E+00	3.23E-01	5.00E+00	1.83E-02	3.45E+01	1.40E+01	8.28E+01	1.50E+03
Cd	5.39E-02	5.39E-02	5.39E-02	3.06E-03	3.06E-03	3.64E-02	3.47E-02	4.09E-02	3.80E+00
Cl	5.19E+02	1.63E+03	3.67E+02	9.85E+01	3.06E+01	3.10E+02	1.73E+02	9.89E+02	1.10E+05
Co	5.63E-02	5.65E-02	5.39E-02	2.15E-02	3.06E-03	2.20E-01	7.58E-02	6.65E-01	6.00E+01
Cr	6.69E-01	1.13E+00	2.15E-01	2.23E+00	1.22E-02	2.05E+00	3.19E-01	4.44E+00	1.20E+02
Cu	5.46E+00 (*)	6.47E+00 (*)	5.35E+00	1.53E+00	6.11E-02	1.48E+00	1.17E+00	2.27E+00	9.80E+01
F	2.83E+01	3.59E+01	1.83E+01	2.59E+01	1.83E+01	N.M.	N.M.	N.M.	2.50E+03
Mo	2.14E+00	2.12E+00	1.94E+00	1.48E-01	1.10E-01	2.14E-01	6.40E-02	3.68E-01	1.44E+02
Ni	3.86E-01	7.38E-01	3.23E-01	2.85E-01	1.83E-02	1.91E+00	8.21E-01	3.54E+00	8.10E+01
Pb	8.20E-01	6.09E-01	4.31E-01	6.72E-02	2.44E-02	4.69E-01	2.59E-01	9.23E-01	4.00E+02
Sb	2.98E-01	2.37E-01	1.72E+01	9.78E-01	9.78E-01	9.69E-02	3.35E-02	2.56E-01	8.70E+00
Se	2.06E-01	2.06E-01	2.06E-01	6.11E-02	6.11E-02	N.M.	N.M.	N.M.	4.80E+00
Sn	5.39E+00	5.39E+00	5.39E+00	3.06E-01	3.06E-01	4.56E-01	3.34E-01	6.91E-01	5.00E+01
V	1.74E+00	3.53E+00	1.00E-01	2.11E+00	3.06E-02	2.07E+00	7.09E-02	6.41E+00	3.20E+02
Zn	1.20E+01 (*)	1.22E+01 (*)	1.22E+01	1.01E+01	1.83E-01	2.10E+00	1.52E+00	2.58E+00	8.00E+02

	20_FA3	40_FA3	DTL (64)	Reference	DTL (64)	Average Blended	95% (-)	95% (+)	SQD
pH	<i>11.7</i>	<i>11.6</i>				<i>11.3</i>			
As	1.08E-01	2.80E-01	1.22E-02	7.12E-02	1.22E-02	1.98E-01	4.61E-02	4.05E-01	2.60E+02
Ba	1.60E+01	5.65E+00	1.83E-02	5.00E+00	1.83E-02	3.45E+01	1.40E+01	8.28E+01	1.50E+03
Cd	3.44E-03	3.06E-03	3.06E-03	3.06E-03	3.06E-03	3.64E-02	3.47E-02	4.09E-02	3.80E+00
Cl	1.44E+02	1.55E+02	1.15E+02	9.85E+01	3.06E+01	3.10E+02	1.73E+02	9.89E+02	1.10E+05
Co	1.93E-02	1.70E-02	3.06E-03	2.15E-02	3.06E-03	2.20E-01	7.58E-02	6.65E-01	6.00E+01
Cr	2.03E+00	2.48E+00	1.22E-02	2.23E+00	1.22E-02	2.05E+00	3.19E-01	4.44E+00	1.20E+02
Cu	8.80E-01	7.87E-01	6.11E-02	1.53E+00	6.11E-02	1.48E+00	1.17E+00	2.27E+00	9.80E+01
F	2.29E+01	2.14E+01	1.38E+01	2.59E+01	1.83E+01	N.M.	N.M.	N.M.	2.50E+03
Mo	1.37E-01	1.46E-01	1.10E-01	1.48E-01	1.10E-01	2.14E-01	6.40E-02	3.68E-01	1.44E+02
Ni	5.10E-01	2.04E-01	1.83E-02	2.85E-01	1.83E-02	1.91E+00	8.21E-01	3.54E+00	8.10E+01
Pb	6.65E-02	5.81E-02	2.44E-02	6.72E-02	2.44E-02	4.69E-01	2.59E-01	9.23E-01	4.00E+02
Sb	9.78E-01	9.78E-01	9.78E-01	9.78E-01	9.78E-01	9.69E-02	3.35E-02	2.56E-01	8.70E+00
Se	6.11E-02	6.11E-02	6.11E-02	6.11E-02	6.11E-02	N.M.	N.M.	N.M.	4.80E+00
Sn	3.06E-01	3.06E-01	3.06E-01	3.06E-01	3.06E-01	4.56E-01	3.34E-01	6.91E-01	5.00E+01
V	1.05E+00	1.41E+00	3.06E-02	2.11E+00	3.06E-02	2.07E+00	7.09E-02	6.41E+00	3.20E+02
Zn	3.34E+01	1.25E+01	1.83E-01	1.01E+01	1.83E-01	2.10E+00	1.52E+00	2.58E+00	8.00E+02

Table S2 Release from batch test at L/S 10 expresses as mg/kg. The natural pH is also reported in the first row. All elements were measured by ICP-MS except for Cu, S and Zn which were measured by ICP-AES.

	<i>FA1</i>	<i>20_FA1</i>	<i>40_FA1</i>	<i>DTL</i>	<i>Reference</i>	<i>DTL</i>	<i>Average blended</i>	<i>95% (-)</i>	<i>95% (+)</i>	<i>SQD</i>
<i>pH</i>	12.9	12.7	12.7	-	12.6	-	12	-	-	-
<i>As</i>	4.0E-03	4.3E-03	4.4E-03	4.0E-03	3.5E-04	2.0E-04	1.0E-01	3.1E-02	3.4E-01	9.0E-01
<i>Ba</i>	2.5E+00	1.6E+01	1.6E+01	6.0E-02	1.9E+01	3.0E-04	1.0E+01	2.4E+00	4.5E+01	2.2E+01
<i>Cd</i>	3.6E-02	1.1E-03	2.0E-03	1.0E-03	5.2E-05	5.0E-05	6.6E-03	2.8E-04	1.6E-01	4.0E-02
<i>Cl</i>	6.9E+03	1.9E+02	5.2E+02	6.0E+00	3.2E+01	5.0E-01				6.2E+02
<i>Co</i>	1.0E-03	1.1E-03	1.1E-03	1.0E-03	1.8E-02	5.0E-05	4.0E-02	5.3E-03	3.0E-01	5.4E-01
<i>Cr</i>	1.2E+01	2.6E-01	6.7E-01	4.0E-03	1.8E-01	2.0E-04	1.2E-01	4.2E-03	3.6E+00	6.3E-01
<i>Cu</i>	9.0E-02	6.5E-02	8.7E-02	1.0E-01	1.8E-01	1.0E-01	1.3E-02	1.6E-03	1.0E-01	9.0E-01
<i>F</i>	2.3E+00	2.3E+00	4.4E-01	3.0E-01	3.3E+00	3.0E-01				5.5E+01
<i>Mo</i>	1.1E+01	2.2E-01	4.4E-01	3.6E-02	6.1E-02	1.8E-03	1.3E-01	3.5E-03	4.7E+00	1.0E+00
<i>Ni</i>	6.0E-03	8.1E-03	6.5E-03	6.0E-03	1.1E-02	3.0E-04	6.0E-02	9.0E-03	3.9E-01	4.4E-01
<i>Pb</i>	1.5E+00	2.6E-01	1.5E-01	8.0E-03	4.3E-02	4.0E-04	3.0E-01	5.1E-02	1.7E+00	2.3E+00
<i>S</i>	1.1E+04	2.3E+01	5.6E+01	2.0E+01	1.2E+01	2.0E+00				
<i>Sb</i>	3.2E-01	3.2E-01	3.2E-01	3.2E-01	1.6E-02	1.6E-02	7.3E-02	2.0E-02	2.7E-01	3.2E-01
<i>Se</i>	8.0E-01	2.2E-02	3.8E-02	2.0E-02	1.1E-02	1.0E-03	1.1E-01	7.6E-02	1.6E-01	1.5E-01
<i>Sn</i>	1.0E-01	1.0E-01	1.0E-01	1.0E-01	5.0E-03	5.0E-03	2.7E-02	4.2E-03	1.7E-01	4.0E-01
<i>V</i>	1.0E-02	1.0E-02	1.0E-02	1.0E-02	5.2E-04	5.0E-04	3.2E-02	9.3E-03	1.1E-01	1.8E+00
<i>Zn</i>	2.4E+00	2.2E+00	2.2E+00	2.0E+00	2.1E-01	2.0E-01	1.9E-02	2.5E-04	1.4E+00	4.5E+00

	<i>FA2</i>	<i>20_FA2</i>	<i>40_FA2</i>	<i>DTL</i>	<i>Reference</i>	<i>DTL</i>	<i>Average blended</i>	<i>95% (-)</i>	<i>95% (+)</i>	<i>SQD</i>
<i>pH</i>	13	12.6	12.5	-	12.6	-	12	-	-	-
<i>As</i>	7.0E-03	4.0E-03	4.0E-03	4.0E-03	3.5E-04	2.0E-04	1.0E-01	3.1E-02	3.4E-01	9.0E-01
<i>Ba</i>	3.9E+00	2.1E+01	2.7E+01	6.0E-02	1.9E+01	3.0E-04	1.0E+01	2.4E+00	4.5E+01	2.2E+01
<i>Cd</i>	1.4E-02	1.0E-03	1.0E-03	1.0E-03	5.2E-05	5.0E-05	6.6E-03	2.8E-04	1.6E-01	4.0E-02
<i>Cl</i>	8.2E+03	2.0E+02	3.0E+02	6.0E+00	3.2E+01	5.0E-01				6.2E+02
<i>Co</i>	1.0E-03	1.2E-02	1.0E-02	1.0E-03	1.8E-02	5.0E-05	4.0E-02	5.3E-03	3.0E-01	5.4E-01
<i>Cr</i>	3.3E+01	1.5E-01	2.9E-01	4.0E-03	1.8E-01	2.0E-04	1.2E-01	4.2E-03	3.6E+00	6.3E-01
<i>Cu</i>	3.0E-02	9.0E-02	8.0E-02	1.0E-01	1.8E-01	1.0E-01	1.3E-02	1.6E-03	1.0E-01	9.0E-01
<i>F</i>	2.3E+00	1.8E+00	1.7E+00	3.0E-01	3.3E+00	3.0E-01				5.5E+01
<i>Mo</i>	1.0E+01	1.7E-01	2.4E-01	3.6E-02	6.1E-02	1.8E-03	1.3E-01	3.5E-03	4.7E+00	1.0E+00
<i>Ni</i>	6.1E-03	1.5E-02	3.7E-02	6.0E-03	1.1E-02	3.0E-04	6.0E-02	9.0E-03	3.9E-01	4.4E-01
<i>Pb</i>	1.2E-01	2.6E-01	9.9E-02	8.0E-03	4.3E-02	4.0E-04	3.0E-01	5.1E-02	1.7E+00	2.3E+00
<i>S</i>	8.4E+03	2.0E+01	2.0E+01	2.0E+01	1.2E+01	2.0E+00				
<i>Sb</i>	3.2E-01	3.2E-01	3.2E-01	3.2E-01	1.6E-02	1.6E-02	7.3E-02	2.0E-02	2.7E-01	3.2E-01
<i>Se</i>	9.8E-01	3.5E-02	2.0E-02	2.0E-02	1.1E-02	1.0E-03	1.1E-01	7.6E-02	1.6E-01	1.5E-01
<i>Sn</i>	1.0E-01	1.0E-01	1.0E-01	1.0E-01	5.0E-03	5.0E-03	2.7E-02	4.2E-03	1.7E-01	4.0E-01
<i>V</i>	2.9E-02	1.0E-02	1.0E-02	1.0E-02	5.2E-04	5.0E-04	3.2E-02	9.3E-03	1.1E-01	1.8E+00
<i>Zn</i>	2.0E+00	2.0E+00	2.0E+00	2.0E+00	2.1E-01	2.0E-01	1.9E-02	2.5E-04	1.4E+00	4.5E+00

	<i>FA3</i>	<i>DTL</i>	<i>20_FA3</i>	<i>40_FA3</i>	<i>DTL</i>	<i>Reference</i>	<i>DTL</i>	<i>Average blended</i>	<i>95% (-)</i>	<i>95% (+)</i>	<i>SQD</i>
<i>pH</i>	12.7	-	12.6	12.6	-	12.6	-	12	-	-	-
<i>As</i>	2.0E-02	2.0E-02	2.3E-04	2.1E-04	2.0E-04	3.5E-04	2.0E-04	1.0E-01	3.1E-02	3.4E-01	9.0E-01
<i>Ba</i>	1.8E+02	3.0E-02	2.3E+01	2.9E+01	3.0E-04	1.9E+01	3.0E-04	1.0E+01	2.4E+00	4.5E+01	2.2E+01
<i>Cd</i>	5.0E-03	5.0E-03	5.2E-05	5.2E-05	5.0E-05	5.2E-05	5.0E-05	6.6E-03	2.8E-04	1.6E-01	4.0E-02
<i>Cl</i>	3.1E+01	5.0E-01	7.3E+01	1.3E+02	5.0E-01	3.2E+01	5.0E-01				6.2E+02
<i>Co</i>	5.0E-03	5.0E-03	1.5E-02	1.9E-02	5.0E-05	1.8E-02	5.0E-05	4.0E-02	5.3E-03	3.0E-01	5.4E-01
<i>Cr</i>	1.6E-01	2.0E-02	3.3E-01	4.4E-01	2.0E-04	1.8E-01	2.0E-04	1.2E-01	4.2E-03	3.6E+00	6.3E-01
<i>Cu</i>	5.0E-02	1.0E-01	2.0E-01	2.0E-01	1.0E-01	1.8E-01	1.0E-01	1.3E-02	1.6E-03	1.0E-01	9.0E-01
<i>F</i>	3.2E+00	3.0E-01	2.8E+00	4.0E+00	3.0E-01	3.3E+00	3.0E-01				5.5E+01
<i>Mo</i>	1.8E-01	1.8E-01	6.0E-02	8.4E-02	1.8E-03	6.1E-02	1.8E-03	1.3E-01	3.5E-03	4.7E+00	1.0E+00
<i>Ni</i>	3.0E-02	3.0E-02	9.1E-03	9.5E-03	3.0E-04	1.1E-02	3.0E-04	6.0E-02	9.0E-03	3.9E-01	4.4E-01
<i>Pb</i>	2.6E+00	4.0E-02	8.2E-02	1.2E-01	4.0E-04	4.3E-02	4.0E-04	3.0E-01	5.1E-02	1.7E+00	2.3E+00
<i>S</i>	7.2E+00	2.0E+00	1.1E+01	9.0E+00	2.0E+00	1.2E+01	2.0E+00				
<i>Sb</i>	1.6E+00	1.6E+00	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	7.3E-02	2.0E-02	2.7E-01	3.2E-01
<i>Se</i>	N.M.	N.M.	5.4E-03	5.9E-03	1.0E-03	1.1E-02	1.0E-03	1.1E-01	7.6E-02	1.6E-01	1.5E-01
<i>Sn</i>	5.0E-01	5.0E-01	5.0E-03	5.0E-03	5.0E-03	5.0E-03	5.0E-03	2.7E-02	4.2E-03	1.7E-01	4.0E-01
<i>V</i>	5.0E-02	5.0E-02	5.2E-04	5.2E-04	5.0E-04	5.2E-04	5.0E-04	3.2E-02	9.3E-03	1.1E-01	1.8E+00
<i>Zn</i>	1.6E+00	2.0E-01	2.1E-01	2.1E-01	2.0E-01	2.1E-01	2.0E-01	1.9E-02	2.5E-04	1.4E+00	4.5E+00

Figure S1 Release of elements at L/S 10 as function of pH. All elements were measured by ICP-MS except for Cu, S and Zn which were measured by ICP-AES.

Chapter 5

Life cycle assessment of the reuse of fly ash from biomass combustion as secondary cementitious material in cement products

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*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.
Journal of Cleaner Production. 245, 118937 (2020).
<https://doi.org/10.1016/j.jclepro.2019.118937>*

ABSTRACT

In this study, we performed a life cycle assessment of the reuse of biomass fly ash as secondary cementitious material in cement mortars as alternative to a reference landfill scenario of the ash. Since biomass ash does contain enhanced levels of elements that are of potential concern for the environment or human exposure, the performed Life Cycle Assessment (LCA), in addition to CO₂ savings, takes into account the impact on all non-toxic categories and human toxicity/carcinogenicity during service and second life stages. Results showed that utilization of biomass ash in cement is preferable over landfill for all the non-toxic categories at both cement replacements rates of 20 and 40 wt.%. In detail, the reduction of CO₂-eq. was found to be between 11-26 % when biomass ash was blended with cement instead of being landfilled. The hydraulic activity of biomass ashes was found to be a critical parameter in this scenario, as it had impacts on the global warming potential (and all other investigated non-toxic categories), and it is therefore crucial to consider the uncertainty related to this aspect in LCA studies. Cement containing biomass ash performed better, on average, when compared with the reference landfill scenario regarding the impact to human toxicity (carcinogenic) category. Contrary, only the utilization in cement for one particular ash type (from paper sludge combustion) showed a better performance than the reference scenario for the ecotoxicity (ET) category. The impact to human toxicity carcinogenic (HTc) and ecotoxicity (ET) was mainly dominated by the leaching of Cr from landfilling of pure biomass fly ash (reference scenario) and the leaching of Ba, Cu, Cr (VI) and Zn from the second life stage of cement products (i.e., reuse of the crushed cement after service life in road base applications). However, this impact was acceptable when emissions are compared to existing EU landfill directive and regulations on the reuse of secondary materials in construction works. The novel LCA approach performed in this study, which includes impacts of leached contaminants during both the service and second life phase of cement, has shown that the reuse of biomass ash as secondary cementitious materials has a beneficial effect on the majority of the impact categories, with no unacceptable leaching risks.

Keywords: Biomass fly ash, Cement, Life cycle assessment (LCA), Leaching, Second life

1. INTRODUCTION

Cement production accounts for about 5-8% of total anthropogenic CO₂ emissions, mainly due to the conversion of CaCO₃ (limestone) into calcium oxide and the combustion of fossil fuel during heating of the raw material mixture. Many efforts have been made to reduce these emissions, including the (partial) substitution of the traditional Portland cement with alternative cementitious materials such as blast furnace slags and fly ash from coal combustion (Barcelo et al., 2013). The growing use of biomass for sustainable energy production and the corresponding large amount of biomass ash produced, has initiated investigations of the substitution of traditional Portland cement with biomass ash residues (Rajamma, 2009; Siddique, 2012). A scenario study has been conducted to determine volumes and characteristics of biomass ashes in the Netherlands for the 2020-2030 timeframe (Boersma, 2011; Saraber and Overhof, 2010). In this study, emphasis has been put on biomass residues from co-firing and stand-alone biomass combustion/gasification technologies. The analysis forecasts an ash volume from co-combustion and stand-alone biomass plants of 2-3 Mton/year in 2030. These biomass conversion plants are estimated to achieve a growth of up to 125 PJ by 2020, which involves around 6 Mton of biomass combusted per year. The utilization of biomass ash as alternative binder in traditional cements has been identified as bulk application with a potential profitable market in a long term perspective (Paris et al., 2016; Pels and Sarabr, 2011; van Eijk et al., 2012). This application could contribute substantially to the reduction of greenhouse gas emissions from cement production (Imbabi et al., 2012; Meyer, 2009; Rahla et al., 2019). The inclusion of biomass ash in cement would also result in two additional beneficial effects: 1) reduction of the consumption of energy and raw materials by the cement industry, 2) reduction in the direct landfilling of the biomass combustion residues. On the other hand, some potentially toxic elements present in the biomass ash might be released in the environment during the different life stages of the fly ash containing cement (e.g. reuse of the cement aggregates after initial use in structural applications) (Tosti et al., 2019).

Life cycle assessment (LCA) is increasingly being used as a tool to assess the environmental impacts associated with different management options for waste and residues (Laurent et al., 2014) including valorisation of biomass ash residues in cement products (Teixeira et al., 2016). However, the impact assessment of inorganic contaminants released by leaching from ash residues and cement remains a difficult task and is often neglected in LCA studies (Van den Heede and De Belie, 2012). A few studies (mainly using MSWI bottom ash) have addressed the environmental impact of leaching through LCA based on results from field or laboratory leaching tests (Allegrini et al., 2015; Di

Gianfilippo et al., 2016; Olsson et al., 2006). Barbosa et al. (2013) concluded that formulations containing biomass ash presented emission levels of chemical species similar to those observed for the reference formulation and reduced ecotoxicological levels. In general, these studies have shown that the leaching behaviour of materials under different conditions may have an important influence on the LCA results and, therefore, should be considered when choosing between different management strategies.

The aim of this work is i) to compare the potential impacts associated with the current waste management practice for biomass ash (reference scenario, i.e. landfilling) and the potential of reuse as a secondary cementitious material in cement, ii) to identify the critical parameters of the modelled systems (i.e. substance emissions and processes contributing to impacts), and iii) to identify the sensitive parameters in terms of methodological choices, assumptions and data selection with regard to final results. The novelty of this work is that the use of biomass fly ash in cement is not only assessed for the use scenario in cement applications but also in the subsequent life phase when the demolition waste is reused as a sub-base material in road constructions. The results of this study also provide new insights in the methodological setup of LCA scenarios for the assessment of alternative materials to replace cement.

2. MATERIALS AND METHODS

2.1. Biomass fly ash

Three biomass fly ashes (FA1, FA2 and FA3) were investigated in this study. The samples had a particle size <1 mm and were stored dry in the laboratory. Sample FA1 originated from a circulating fluidized bed installation that combusts a mixture of clean wood and cacao husks, molasses or other clean biomass streams that were occasionally added. The sample FA1 was collected from the electrostatic precipitator. The sample FA2 originated from the combustion of wood pellets in a pulverized fuel installation and was collected from the electrostatic precipitator. The sample FA3 was taken from a bubbling fluidized bed incinerator. The fuel consisted of a mixture with an equal share of recovered paper sludge from the de-inking step of the paper recycling process and recovered waste wood. The fly ash was a mixture collected from the electrostatic filter (90% by mass) and the textile bag filter (10% by mass) cleaning system units. The investigated biomass ashes cover a fairly wide range of biomass fuels and conversion technologies and can, therefore, be considered representative for future biomass ash use in cement products.

2.2. Blended cement mortars

Mortar samples were prepared by dry mixing the Portland Cement CEM I 42.5N with FA in its “as received” form in accordance with the European standard EN 196-1 (2005). Ordinary Portland cement was replaced with both 20 and 40 wt. % of FA1, FA2 or FA3. These combinations resulted in six test samples that are referred to in this paper as 20_FA1, 40_FA1; 20_FA2, 40_FA2 and 20_FA3 and 40_FA3, respectively. In addition, a reference sample of pure Ordinary Portland Cement was also casted (OPC). Prisms (160 x 40 x 40 mm) were cured for 28 days in a controlled temperature and humidity room (at 20 °C and 95% humidity). All specimens were prepared with a water-binder weight ratio (w/b) of 1:2 and a sand-binder ratio of 3:1. After curing the specimens were subjected to compressive strength (EN-196-1, 2005) and leaching tests (see Section 2.3 for more details).

2.3. Leaching tests

Results from standardized leaching tests were used as input for the LCA model in order to estimate the potential release of contaminants during the proposed management scenarios. In particular two different tests were used in this work: tank leaching tests (FprCEN/TS 16637-2, 2013) and parallel batch extraction tests at different liquid to solid (L/S) ratios (EPA, 2012). In short, results from the tank leaching tests were used as input to model the service life of cement (i.e. release from monolithic material), whereas results from the batch tests were used to model the landfill and end of life scenario (i.e. release from granular materials at different L/S). Section 2.5 and Sections 3, 4 and 5 of the Supplementary Material provide for more details on the modelling aspects. A detailed description of the mentioned tests and the obtained results is reported in Tosti et al. (2018).

2.4. LCA methodology

2.4.1. Goal, scope and model

This study was conducted according to the requirements of ISO 14044 (ISO, 2006) and the ILCD Handbook (EC-JRC, 2010). The goal of the study is to compare the potential impacts associated with the current waste management of fly ash from biomass combustion (i.e. landfilling) with its potential reuse as secondary cementitious material (SCM) in cement formulations as an alternative management strategy. In particular, the analysis aims at verifying whether the expected CO₂ reductions from using biomass ash in cement are also supported by a similar environmental performance as ordinary cement applications throughout the entire life cycle. A reference scenario in which biomass ash is landfilled and traditional Portland cement is used was compared to an alternative scenario in which landfilling is avoided and a blended cement (containing biomass ash) is used. Due

to the nature of the alternative scenario, this study has a goal encompassing two services: 1) the handling, treatment and/or use of one ton of biomass ash and 2) the production of cement material (i.e. pure or mixed with biomass ash). Cement replacement with biomass ash was investigated at two levels: 20 and 40 wt. % of total binder weight. Therefore, two functional units are defined for the application of 1 ton of biomass fly ash, as collected from the incineration plant, in the production and use of cement: FU₂₀ for producing, using and re-using a total of 5 ton of cement when biomass ash is used to substitute 20% of cement, and FU₄₀ for 2,5 ton of cement (with 40% substitution). Since these formulations result in a lower compressive strength than that of pure OPC (Tosti et al., 2018), additional OPC was accounted for in order to reach the same compressive strength for all formulations, as further explained below. Biomass fly ash is considered to enter the system without any impacts in agreement with the zero burden assumption (Ekvall et al., 2007). A temporal horizon of 100 years was selected for the analysis and The Netherlands was adopted as reference geographic area for the model assumptions in particular for the landfill scenario. Even though the impact from the recycling of ashes might be higher in a longer time horizon, the fate of products after second life stage and at timeframes of over 100 years is highly uncertain and, therefore, disregarded in this study. The Life cycle impact assessment (LCIA) included the midpoint impact categories recommended by the European Commission in the International Reference Life Cycle Data System (ILCD) Handbook (Hauschild et al., 2013), as outlined in Table S1 of the Supplementary Material. The LCA modelling software EASETECH version 2.3.6 (Clavreul et al., 2014) that was developed at DTU in Denmark was used in this study.

2.4.2. Scenarios description, system boundaries and assumptions

Two scenarios were considered in this study (Figure 1).

Figure 1 Flow chart representation of the LCA reference scenario and the LCA scenario for the use of biomass ash in cement. The dashed line indicates the boundary conditions for the LCA models. The reference scenario includes the traditional cement production (i.e., Ordinary Portland Cement OPC), while the BIOCement scenario takes into account the additional cement needed to maintain the compressive strength of the OPC reference. Only transport to the landfill site (i.e., reference scenario) and the cement plant (i.e., BIOCement scenario) is included.

Reference scenario: In the reference scenario, it was assumed that biomass fly ash is disposed in an industrial waste landfill situated in The Netherlands. Biomass fly ash is transported from the energy plant to the landfill site (situated at 100 km distance) where it is disposed. The landfill site was assumed to have a height of 20 meter and to remain open for the first 30 years with a net leachate production rate of 300 mm/year. After the final covering of the landfill the net leachate production rate was assumed to diminish to 5 mm/year throughout the remaining 70 years. These assumptions were used, together with the density of FA1, FA2 and FA3, to calculate the final liquid to solid ratio (L/S) (Table 1) following the approach described in Section 3 of the Supplementary Material. Leaching of inorganic substances from the landfill at the calculated L/S was included in the study as described below in Section 2.5. Part of the generated leachate is sent to the wastewater treatment plant

(WWTP) (see Table 1 for collection efficiencies). The electricity consumption in the WWTP was also accounted for. The reference scenario involves, in parallel to the landfilling process, the modelling of the pure OPC cement production (see Table 2 for process detail), the cement service and second life stages, that would happen anyway when biomass ash is landfilled instead of used as secondary cementitious material (see Figure 1).

Table 1 Dataset used to model the reference scenario. The leachate generation and efficiencies for the removal of individual substances in the WWTP are reported in the Supplementary Material (Table S3).

Reference scenario					Process used in the model
		FA1	FA2	FA3	
Transport	km	100	100	100	Truck, 28t-32t, Euro6, highway_EASETECH Database (Clavreul et al., 2014)
Infiltration rate (30 years)	mm/y	300	300	300	Leachate_Landfill_Treatment_ emission to surface water (Olesen and Damgaard, 2014)
Infiltration rate (70 years)	mm/y	5	5	5	
Layer	m	20	20	20	
Density FA	kg/m³	690	750	916	
Leachate collection efficiency* (10 years)	%	95	95	95	
Leachate collection efficiency (90 years)	%	90	90	90	
Cumulative liquid to solid ratio (L/S) (100years)	L/kg	0.7	0.6	0.5	
Electricity consumption	kWh/kg	0.00044 3	0.00044 3	0.00044 3	Electricity, high voltage, production mix; NL (Ecoinvent Centre, 2017)

**Remaining leachate assumed to be stored in the landfill*

BIOCement: In this scenario, biomass fly ash is used as secondary cementitious material in cement for outdoor pavement construction, thus considering all benefits derived from avoiding landfill. The BIOCement scenario is composed of three stages: i) mixing biomass FA with traditional OPC cement, ii) service life of cement containing biomass fly ash (50 years), and iii) utilization of crushed cement as road subbase for 50 years (i.e. second life). First, biomass fly ash is transported from the energy plant to the facility (200 km) where it is mixed with traditional cement. This step requires electricity for the mixing and the corresponding electricity consumption was taken from Hewlett (2003). After a pavement service life of 50 years, the cement is crushed, and the aggregates are subsequently reused as a subbase material for road construction. The leaching of inorganic substances during the service and second life phases was also considered.

Inclusion of biomass ash in cement decreases the compressive strength after curing time of 28 days by about 3 to 50% depending on fly ash types and replacement ratios, as shown in Tosti et al.,

(2018). To obtain comparable results, the performance of cement systems with biomass ash as SCM was compared to an average strength of 48.4 MPa which was the measured average compressive strength of pure OPC. The additional OPC requirement per kg of fly ash was calculated to compensate for the loss in strength and to obtain a comparable basis by adding OPC to the BIOCement until the average strength value of 48.4 MPa is reached (see Table 2 for values and Section 2, Table S2 of the Supplementary Material for calculations). The production of pavement and road construction processes were not included in the boundaries since these processes are not considered to be affected by the utilization of biomass ash in cement. The inclusion of fly ash in cement could affect the durability of products and consequently the life time and maintenance operations required. However, this aspect is difficult to quantify and there is currently no method available in LCA that relates cement durability to fly ash content. Therefore, the maintenance process was considered to be the same for the reference and BIOCement scenarios. The model described in this section was also applied to the traditional OPC cement application in the parallel reference scenario (Figure 1). Only different leaching data are used for the calculation of the release of inorganic substances from OPC and BIOCement. Complete information on the leaching dataset can be found in the Supplementary Material Sections 4 and 5, Tables S4 and S5.

Table 2 Dataset used to model the different BIOCement scenarios. The complete list of leaching values of elements for the service life and second life phases are reported in the Supplementary Material (Tables S4 and S5).

BIOCement scenario								Process used in the model
		20_FA1	20_FA2	20_FA3	40_FA1	40_FA2	40_FA3	
Transport Fly ash	km	200	200	200	200	200	200	Truck, 28t-32t, Euro6, highway_EASETECH Database (Clavreul et al., 2014)
Electricity for Additional Blending	kWh/kg FA	0.035	0.035	0.035	0.035	0.035	0.035	Electricity, high voltage, production mix; NL (Ecoinvent Centre, 2017)
Additional OPC*	kg/kg FA	0.04	0.32	0.06	0.36	0.57	0.31	Cement production, Portland; Europe without Switzerland (Ecoinvent Centre, 2017)

*the amount of additional OPC expressed as kg/kg of FA is equivalent to the % of strength lost due to FA addition when compared to the average strength of pure OPC (48.4 MPa as average compressive strength value of 6 measurements performed in the lab). Complete calculation is reported in Section 2, Table S2 of the Supplementary Material.

2.5. Emissions from leaching

Results from laboratory leaching tests were taken as the basis for estimation of potential release during the life cycle phases within the 100 years time frame considered in the two scenarios. The leaching during the service life phase (i.e. monolithic) was calculated as total element mass released following a simplified diffusion model which takes the cumulative release (mg/m^2) measured during the standardized tank test after 64 days into account (Birgisdottir, 2005; Kosson et al., 1996). Complete information is reported in Section 4 of the Supplementary Material.

The assessment of the release of inorganics from the granular materials (i.e. from the landfilled fly ash in the reference scenario, and from the second life phase of the cement aggregates) required an estimation of the expected amount of water in contact with the residues within a given time horizon, i.e. the L/S ratio. The expected L/S ratios of the different scenarios were estimated following the approach proposed by Kosson et al. (2002) as reported in the Supplementary Material (i.e. Section 5). The measured release from batch tests was then used to calculate the concentration of elements in the leachate from landfilling of biomass ash and the release from cement aggregates during the second life stage at the estimated L/S ratios (see Sections 3 and 5 in the Supplementary Material). For landfilling of biomass ash, the process included in EASETECH (i.e., *Leachate_Landfill_Treatment_emission_to_surface_water*) was used to model the leachate generation at the calculated L/S and elements' removal efficiencies in the waste water treatment plant (Table S3 in the Supplementary Material). All emissions from WWTP were considered to be emitted to surface water.

Leaching emissions from the service life and second life of cement products were inventoried as cumulative emissions to industrial soil. The USEtox model used in the LCA considers two soil types, agricultural and industrial. However, it is not considered common practise that cement is used in agricultural setting. This approach, as reported by Allegrini et al. (2015), set the boundaries between the natural environment and the techno-sphere at the interphase between the material (i.e. cement pavement and layer of crushed cement below the road) and soil. The partitioning of contaminants into the natural environment between water and soil is determined completely by the fate modelling included in the USEtox model (Rosenbaum et al., 2008). This approach was used consistently in both the reference and the BIO Cement scenarios and was considered appropriate for the scope of this work. Chromium release from cement products is considered to be in the oxidation state Cr (VI). This assumption was based on results obtained from pH dependent leaching tests on the same cement products investigated in this study (Tosti et al., 2018) and other literature on construction and demolition waste (Butera et al., 2015).

2.6. Sensitivity and uncertainty analysis

Several assumptions were made in this study with regard to the release of elements, ash transportation distances and need for additional OPC. To assess the influence of these assumptions, a sensitivity analysis was performed starting with a perturbation analysis to identify the most sensitive parameters. Sensitivity analysis is subsequently conducted to investigate these sensitive inputs and to analyse the importance of assumptions made in the input model on the final result. The parameters for the perturbation analysis were identified through a contribution analysis to identify the most important processes. A total of 73 parameters for the reference scenario and 33 parameters for the use in cement scenario were tested in the perturbation analysis. This analysis included multiples runs of the model where each of the parameters was augmented by 10% of its default value and the model was run with a singular augmented parameter value. The result was then compared with the default scenario (i.e. all parameters set to their default value) and sensitivity ratios (SR) were then calculated for each parameter to identify the most sensitive parameters. The SR is defined as the ratio between the change in the result of the particular parameter variation and the default result, divided by the ratio between the change in the parameter value and the default parameter value (see Section 7.2 in Supplementary Material). To compare different sensitivity ratios in each scenario and each impact category, normalized sensitivity ratios (NSR) were calculated. The NSR is defined as the ratio between the sensitivity ratio of one parameter in one impact category and the maximum absolute value among all SRs in the same impact category. All relevant information and equations are reported in Section 7.2 of the Supplementary Material. After the identification of the most sensitive parameters (i.e. 7 parameters for reference scenario and 5 parameters for the biomass ash in cement scenario), an uncertainty analysis was carried out. The analysis was done with a probability distribution set for each parameter value. A Monte Carlo analysis (10000 random variables) was performed subsequently to assess the propagation of the uncertainty through the model.

3. RESULTS AND DISCUSSION

3.1. Contribution analysis

Figure 2 shows the contribution of processes to the total characterized potential impacts for Climate change (Global Warming Potential, GWP_{100}), Human toxicity, cancer effects (HTc), Human toxicity, non-cancer effects (HTnc) and Ecotoxicity freshwater (ET) categories. The impacts on the GWP_{100} category are consistent with those on all the non-toxic categories (Ozone depletion (ODP), Particulate

matter (PM), Ionising radiation human health (IR), Photochemical ozone formation (POF), Terrestrial acidification (AP), Eutrophication Terrestrial (TEP), Eutrophication Freshwater (FEP) Eutrophication Marine (MEP) and Depletion of abiotic resources (ADP)) since they all show a comparable trend with that of GWP₁₀₀. In the remainder of the article, we therefore focus on global warming and toxicity impacts, but in Supplementary Material Section 6, Table S6-S11, all ILCD impact categories are included.

The contributions to potential impacts have been aggregated into five groups: cement production, transport of biomass fly ash, landfill, leaching from service life and second life stages. For illustrative purposes, the discussion in this paragraph focuses on the 20_FA1 scenario, replacement of 20% wt. of OPC with biomass fly ash FA1, since the results in the total impacts are similar for all scenarios investigated including the 40% replacement. Complete information on characterized impact values for all categories and for all scenarios can be found in Section 6 of the Supplementary Material.

The results in Figure 2 show that for both the BIOCEment scenario and the reference scenario the cement production contributes almost entirely (i.e. 98%) to the impact on GWP₁₀₀. Emission of CO₂ is the main contributor to the impact on GWP₁₀₀ category. The processes responsible of the CO₂ emission are carbonation of limestone and production of thermal energy required to reach the sintering temperature in the cement kiln as already observed in previous literature (Huntzinger and Eatmon, 2009; Mohammadi and South, 2017; Van den Heede and De Belie, 2012).

The cement production is also contributing to the HTnc category for about 85% of the total impact in the case of the BIOCEment scenario and for 95% in the reference scenario. When taking a closer look to the underlying data (see Table S12, Section 6 of the Supplementary Material), it becomes clear that in this category the emissions of Hg to air from cement production is mainly responsible for the impact on the HTnc.

About 60% of the total impact to the category HTc in the reference scenario is due to the leaching of inorganics from landfill and second life stage (Figure 2). The impact to the HTc category in the 20_FA1 scenario is determined for about 50% by the leaching of inorganics in the second life stage. In particular, the release of Cr to surface water (i.e. during landfill) and industrial soil (i.e. during second life) is contributing almost entirely to the impact on the HTc category. The rest of the impact is determined by cement production for both reference and BIOCEment scenario.

Concerning the impact to the ET category in the BIOCEment scenario, this is determined for more than 80% by the release of Ba, Cu, Cr, Sb and Zn from second life stage. In the reference scenario, the impact to ET category is divided between cement production and release from second life of cement with a relatively smaller contribution (i.e. less than 15%) from service life stage. Percentages

of contribution slightly change depending on type of biomass ash and the replacement ratio. It is interesting to note that transport of fly ash provides an almost negligible contribution to all impact categories. Only in the case of impact to HTnc, transport contributes for about 10% of the total impact.

The only observed difference in contribution to potential impacts among fly ash types is observed for the reference scenario when FA3 is assessed (see Section 6, Tables S10 and S11 of the Supplementary Material). Here, the contribution of the landfill process to HTc impact is minor: less than 10% of total impact instead of about 40%. This difference is related to the substantially lower Cr release in comparison to the other fly ash types.

Figure 2 Percentage of contribution of processes to the total impact for the reference scenario (i.e. FA1) and BIOCement scenario (i.e. 20_FA1). The results are considered representative for all other scenarios.

3.2. Comparison of scenarios

In Figure 3, the internally normalized results from the modelling of scenarios are shown for GWP₁₀₀, HTc, HTnc and ET impact categories. Generally, the BIOCement scenario has lower average potential impact values compared to the reference when GWP₁₀₀ and all other non-toxic categories (ODP, PM, IR, POF, AP, TEP, FEP, MEP, ADP) are considered. As observed during the contribution analysis, the cement production process is dominating the impacts to GWP₁₀₀ and, therefore, the

observed differences between the reference and BIOCEment scenarios in terms of non-toxic impacts are consistent with the lower amount of OPC cement used in the latter scenario. The total amount of cement in the BIOCEment scenario is determined by the hydraulic activity of the biomass fly ash. The differences are small, but FA2 shows the lowest hydraulic activity and, therefore, requires a relatively high amount of additional cement (see Table 2) to maintain the strength development properties of the reference system. Thus, FA2 has also a slightly higher impact in the GWP₁₀₀ category. This observation is particularly evident in the 40_FA2 scenario in which replacing 40% of cement with FA2 resulted in a limited (only 15%) reduction of the impact on GWP₁₀₀ (and other non-toxic categories) compared to the reference scenario. When FA3 is used in the 40% formulation the impact in the same category is 26% lower than the reference.

The ability of biomass ash to develop strength is a crucial parameter that should be measured and accounted for as outlined in Table 2. This approach allows for a more uniform basis in LCA studies for the possible re-use of different biomass ash types in cement.

The impacts of FA1 and FA2 (both for 20% and 40% replacement) on HTc are substantially lower than the reference scenario, with FA2 performing better than FA1. Contrary, FA3 shows a higher impact on HTc than the reference scenario. The magnitude of impacts is related to the different release of elements from pure FA during landfill. In particular, as previously observed in the contribution analysis, the release of Cr to fresh water from the landfill (after WWTP) process has a significant influence on the HTc impact results of the reference system. Therefore, a cleaner ash will give a higher relative impact than a more contaminated ash, as the difference to the landfill scenario becomes lower. Leaching of Cr from the biomass ash is very important in determining the impact on HTc of the reference scenario (see also Section 3.3). When biomass ash is added to cement, the leaching of chromium is controlled by the cement matrix and results in a more consistent release (Tosti et al., 2018). The different relative impacts on HTc that are observed for the different BIOCEment scenarios (Figure 3) are, therefore, predominantly determined by the leaching properties of the landfilled ashes in the reference scenario. In particular, pure FA2 shows a relatively high leaching, which reduces its relative impact (compared to the other ash types) when applying it in cement, due to the mitigating effect of the cement matrix on the leaching of biomass ash (Tosti et al., 2018). Contrary, FA3 is a relatively “clean” ash (particularly regarding Cr release) with a Chromium concentration in the leachate generated during landfill of FA3 of around 0.06 mg/L. This low concentration implies a very small cumulative Cr released to fresh water after WWTP. As result, the cumulative leaching during second life of 20 and 40_FA3 specimens makes the BIOCEment scenario performs worse than reference in the HTc category.

As was also observed for GWP₁₀₀ category, the different impacts to HTnc are consistent with the lower amount of cement used when fly ash is added to cement due to Hg emissions to air from cement production process. Hence, the impacts to HTnc are mainly determined by the lower use of OPC cement in the BIOCEment system rather than by the direct impact from the added fly ash.

The higher impact to ET category when BIOCEment is compared to reference systems for FA1 and FA2 is due to different detection limits obtained for the analysis of dissolved Zn in leachates from pure cement (no ash addition) and from FA1 and FA2 containing cement at both replacement ratios (Tosti et al., 2018). We have, therefore, conservatively used the detection limit value as input for this LCA study, which has resulted in higher than reference impacts for FA1 and FA2.

Figure 3 Comparison of results expressed as percentage of the corresponding reference scenario (internal normalization).

3.3. Sensitivity analysis and uncertainty analysis

Table 3 summarizes the parameters in the reference and BIOCEment scenarios for which the model is most sensitive (i.e., with a NSR > 0.8) in relation to the impact categories GWP₁₀₀, HTc, HTnc and ET. Tables with all normalized sensitivity ratios (NSR) values are reported in Section 7.2 of the Supplementary Material. It is important to stress that during perturbation analysis, the cement production process (and the corresponding emissions), was not entered as a parameter in the model and, therefore, no NSR was calculated for that process. This decision was based on the fact that the goal of the study was to investigate the influence of biomass fly ash addition to cement as alternative option to landfilling and, therefore, only the “additional OPC” production needed to maintain the same cement strength in the case of biomass ash inclusion was entered as a parameter in the model.

A general observation from Table 3 (and S14-S19 for details) is that the model is sensitive to just a few parameters for every impact category, and that these parameters are consistent among different

ash types. For instance, the release of Ba and Cr from the second life stage of cement are sensitive parameters for all fly ashes with respect to the HTnc and HTc categories in the reference and ash utilization in cement scenario, respectively. The transport and the additional OPC parameters influence the results on GWP₁₀₀ (and all other non-toxic categories), independently from the biomass ash type.

Table 3 Parameters resulting from perturbation analysis with a normalized sensitivity ratio (NSR) higher than 0.8. GWP₁₀₀ is reported as representative of all non-toxic impact categories. The complete list of NSR values for all parameters is reported in Section 7.2 of the Supplementary Material.

		FA1	FA2	FA3
Reference	GWP ₁₀₀	Transport	Transport	Transport
	HTc	Infiltration Rate, Layer, Density, Leaching from landfill (Cr)	Infiltration Rate, Layer, Density, Leaching from landfill (Cr)	Leaching from second life (Cr) of traditional cement
	HTnc	Leaching from second life (Ba) of traditional cement	Leaching from second life (Ba) of traditional cement	Leaching from second life (Ba) of traditional cement
	ET	Leaching from second life (Ba) of traditional cement	Infiltration Rate, Layer, Density, Leaching from second life (Ba) of traditional cement	Leaching from second life (Ba) of traditional cement
BIOCement (20 and 40%)	GWP ₁₀₀	Production of additional OPC	Production of additional OPC	Production of additional OPC
	HTc	Leaching from second life (Cr)	Leaching from second life (Cr)	Leaching from second life (Cr)
	HTnc	Leaching from second life (Zn)	Production of additional OPC (Hg emission)	Leaching from second life (Ba)
	ET	Leaching from second life (Cu), Leaching from second life (Zn)	Leaching from second life (Zn)	Leaching from second life (Cr)

However, some differences are observed in the sensitive parameters among biomass ash types and the corresponding cements replacements. The HTc category of the reference scenario for FA1 and FA2 is sensitive to landfill parameters (i.e. infiltration rate, FA height layer, bulk density of FA. See Section 7.1 Table S13 of the Supplementary Material for the description and values of parameters) and leaching of Cr from the pure biomass ash. A difference in the sensitivity of the model to parameters is observed also in the BIOCement scenario for the HTnc category. In this case, the low hydraulic activity of FA2 required a relatively high amount of additional cement, which influences the impact on the HTnc (mainly due to the emission of Hg to air associated with additional cement production). This is not the case for FA1 and FA3 where the variation of leaching values of Zn and Ba from the second life stage of cement (i.e. of cement aggregates in road base) has the largest

influence on the resulting impact to HTnc. The leaching of Cu and Zn from the second life stage are the most sensitive parameters that affect the impact to the ET category in the BIO Cement scenarios. Values of NSR are reported in Section 7.2 of the Supplementary Material.

Since sensitivity of parameters does not necessarily confer uncertainty of results, the uncertainty of the model results was evaluated by assigning probability distributions to the most sensitive parameters shown in Table 3 and, subsequently, quantifying the error propagation by means of Monte Carlo analysis (details are provided in Section 7.3 of the Supplementary Material). The results of the uncertainty analysis are shown in Figure 4 as normalized values expressed in person equivalent (PE).

In this type of data representation, the characterized results obtained from the analysis are divided by a normalization value that is called Person Equivalent (PE), which is a quantification of the environmental impact in a specific category caused annually by the activities of an inhabitant of the affected area (EC-JRC, 2010). In the presented study, Europe was selected as area of interest. The normalization values are reported in Table S1 of the Supplementary Material.

The identified uncertainty, as reflected in the error bars (95% confidence interval as calculated by the EASETECH software) in Figure 4, is relatively small for the three biomass ashes for the categories GWP₁₀₀ and all the other non-toxic categories. Hence, the conclusions from the comparison between the reference and BIO Cement scenarios do not change, i.e. that the use of fly ash in cement is beneficial. This observation can be explained by the fact that the most sensitive parameter (i.e. additional OPC, see Table 3) affecting GWP₁₀₀ and all the other non-toxic categories show a small deviation around the average value in this study (see Table S20 of the Supplementary Material).

The uncertainty is relatively large for the category HTc and is mainly related to release of Cr from the second life stage of cement. Nevertheless, the difference in HTc impact between these two scenarios is still significant and the uncertainty bars do not overlap when comparing these scenarios (except for 40_FA1 and 40_FA3 where the uncertainty bars overlap between both scenarios).

Regarding the toxic categories, it is important to also quantify the actual risks associated to those emissions, which is determined by concentrations and not the aggregated cumulative release as used in an LCA study. Therefore, in this study, a first check was performed by comparing the leaching properties of biomass ash and biomass ash containing cement with regulatory limits as specified in the EU Landfill Directive (European Commission, 1999) and the Dutch Soil Quality Decree (Bodemkwaliteit, 2007), respectively. All three biomass ashes and the corresponding blended cements comply with the criteria for landfilling of hazardous material (Table S21 of the Supplementary Material) and application as monolithic and/or granular material in construction (Tosti et al., 2018), respectively. Based on these findings, we conclude that for those cases where the

impacts to toxic categories is overlapping (e.g. HTc in 40_FA1, and HTc in 40_FA3, see Figure 4) no ranking can be made between the reference and ash utilization in cement scenarios, but that no unacceptable risk is associated with that impact.

Figure 4 Normalized results from uncertainty analysis, error bars are the 95% confidence intervals. The results are expressed as person equivalent per functional units. Since the amount of cement used to produce 20 or 40% fly ash containing mixtures changes, the results can be compared only for identical (i.e. 20% or 40%) replacement ratios.

4. CONCLUSIONS

In this study, the potential environmental impacts associated with the reuse of biomass fly ash as secondary cementitious material, as an alternative management option to landfilling, were evaluated by means of a life cycle assessment (LCA). Both the service life phase (cement application) as well as the second life phase of cement products (use of cement aggregates in road base) were taken into account, with focus on the cumulative release of potentially toxic elements during a life cycle of 100 years.

Effects on non-toxic impact categories

Life cycle assessment modelling of management options for 1 ton of biomass ash has demonstrated that the utilization of biomass ash into cement is preferable over landfilling for all non-toxic impact categories considered: Global warming potential (GWP), Ozone depletion (ODP), Particulate matter (PM), Ionising radiation human health (IR), Photochemical ozone formation (POF), Terrestrial acidification (AP), Eutrophication Terrestrial (TEP), Eutrophication Freshwater (FEP), Eutrophication Marine (MEP) and Depletion of abiotic resources (ADP). This preference was demonstrated for all types of biomass ash investigated at cement replacement ratios of 20 and 40%. Cement production was the most important process for all non-toxic impact categories accounting for about 85 to 98 % of total impacts. The hydraulic activity of biomass ash in cement determines the total amount of traditional (OPC) cement needed to obtain the same compressive strength between the reference and BIOCement scenarios and, therefore, the lower impact to those categories determined by the cement production process. Biomass ash from the combustion of clean wood in a circulating fluidized bed installation (i.e. FA1), and biomass ash from the combustion of paper sludge and recovered waste wood in a bubbling fluidized bed incinerator (i.e. FA3) were found to perform better than biomass ash originating from the combustion of wood pellets in a pulverized fuel installation (i.e. FA2). The lower impact to global warming was found to be between 11 (i.e. FA2) and 18% (i.e. FA1) of the reference scenario when biomass ash replaces 20% of cement, and between 15 (i.e. FA2) and 26% (i.e. FA3) at a replacement rate of 40%. Uncertainty related to variability of the most sensitive parameters did not appear to be critical for the resulting impacts on all non-toxic categories investigated. Based on these conclusions we can recommend that using a higher amount of fly ash is beneficial for the non-toxic categories and this amount will in practice be limited by the physical strength requirements for the application.

Effects on toxic impact categories

The impact to human toxicity carcinogenic (HTc) and ecotoxicity (ET) was determined by the leaching of metals whereas the impact to human toxicity non carcinogenic (HTnc) was determined by cement production as for non-toxic categories.

Comparison between the reference and the BIOCEment scenarios showed that cements containing FA1 and FA2 perform better, on average, than blends containing FA3 regarding the impact to HTc category. Contrary, only BIOCEment scenario containing FA3 showed a better performance than the reference for the ecotoxicity (ET) category. These observed performance differences between the reference and BIOCEment scenarios are mainly determined by the leaching properties of biomass ash itself. Leaching from biomass fly ash determines the concentrations of contaminants in the leachate generated during landfilling and, therefore, the impact on human toxicity of the reference scenario.

Consideration of the uncertainty of leaching data from pure biomass ash and all the investigated cement specimens resulted in a different ranking of scenarios particularly when the human toxicity carcinogenic category was assessed. However, a higher impact on the toxic categories does not necessarily imply an actual risk associated with the investigated scenarios in this work. Comparison of leaching values with regulatory criteria for soil quality and landfill leachate is strongly advised to assess whether actual risks may occur.

General conclusion

Methodologically, this study has demonstrated the importance of considering the hydraulic activity of fly ash and the strength development of the blended cement, as well as the leaching of metals from the alternatively landfilled fly ash, in LCA modelling of the reuse of biomass fly ash as secondary cementitious material. For the selected range of broadly representative types of biomass ashes that were evaluated in this study, we have shown that the use of biomass ash in cement was beneficial with regard to the majority of the impact categories, while not conferring any additional risk.

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1. LCIA method

The ILCD methods contains the impact categories recommended by the European Commission in the International Reference Life Cycle Data System (ILCD) Handbook (EC-JRC, 2010) and described in Hauschild et al. (2013). Normalization references are based on (Benini et al., 2014)

Table S1 Impact categories used in this study. Due to the very similar results obtained in the different scenario for the non-toxic categories the results are discussed only for GWP₁₀₀ but extended to all the non-toxic categories.

Impact category	Characterization model	Abbreviation	Unit	Normalization value	Unit
Climate change midpoint	IPPC 2007	GWP ₁₀₀	kg CO2-Eq	9.22E+03	kg CO2-Eq/PE/year
Ozone depletion	WMO	ODP	kg CFC-11 Eq	2.16E-02	kg CFC-11 Eq/PE/year
Human toxicity, cancer effects	USEtox	HT _c	CTUh	3.69E-05	CTUhPE/year
Human toxicity, non-cancer effects	USEtox	HT _{nc}	CTUh	5.33E-04	CTUhPE/year
Particulate matter	Humbert 2009	PM	kg PM2.5-eq	3.80E+00	kg PM2.5-eqPE/year
Ionising radiation human health	ReCiPe 2008 v 1.05	IR	kBq U235 eq	1.13E+03	kBq U235 eqPE/year
Photochemical ozone formation	ReCiPi 2008 v 1.05	POF	kg NMVOC	3.17E+01	kg NMVOCPE/year
Terrestrial acidification	Accumulated Exceedance	AP	mol H+ eq.	4.73E+01	mol H+ eq.PE/year
EutrophicationTerrestrial	Accumulated Exceedance	TEP	mol N eq.	1.76E+02	mol N eq.PE/year
Eutrophication Freshwater	ReCiPe 2008 v 1.05	FEP	kg P eq.	1.48E+00	kg P eq.PE/year
Eutrophication Marine	ReCiPe 2008 v 1.05	MEP	kg N eq.	1.69E+01	kg N eq.PE/year
Ecotoxicity freshwater	USEtox	ET	CTUe	8.74E+03	CTUePE/year
Depletion of abiotic resources mineral fossil & renewable	CML 2002	ADP	kg Sb eq.	1.01E-01	kg Sb eq.PE/year

2. Additional OPC calculation

Table S2 shows the results of compressive strength measurements performed on the reference OPC and BIOCement containing FA1, FA2 and FA3 in accordance with European standard (EN-196-1, 2005). The measurement was replicated six times and, subsequently, the average value was calculated together with its standard deviation. The amount of additional OPC needed to keep up with the loss of strength of blended cement due to biomass fly ash inclusion was expressed as the percentage of the difference between the compressive strength of BIOCement and reference OPC (average measured strength, Table S2). This value was input in the model as kg of additional OPC per kg of biomass fly ash blended with cement (e.g. a loss in strength of 36% would result in the addition of 0.36 kg of OPC for each kg of biomass fly ash blended with cement).

Table S2 Results from the compressive strength tests performed on reference OPC and BIOCement containing FA1, FA2 and FA3 at 20 and 40% replacement ratio. The tests were performed according to EN (EN-196-1, 2005). Additional details can be found in Tosti et al. (2018) and (Carr, 2019)

Scenario	Measured compressive strength 28 days (MPa)						Average	STDV	% of traditional cement needed to keep up with strength value of the reference
OPC reference (CEM I 42.5N)	44,39	45,49	48,94	49,92	48,92	52,83	48,41	3,07	0
20_FA1	47,21	47,06	45,61	46,95	46,96	46,42	46,70	0,60	4
40_FA1	31,96	29,88	31,73	31,65	29,81	30,36	30,90	0,99	36
20_FA2	35,51	33,68	34,73	24,36	36,39	33,70	33,06	4,39	32
40_FA2	21,47	21,34	20,31	21,37	21,42	19,97	20,98	0,66	57
20_FA3	44,93	46,08	45,66	45,08	48,10	43,81	45,61	1,44	6
40_FA3	35,12	34,39	33,30	34,65	31,59	30,77	33,30	1,77	31

3. Emissions from landfill

The calculation of emissions from landfill was based on the process present in EASETECH database called “*Leachate_Landfill_Treatment_emission to surface water*”. This process starts with the module “leachate generation” which defines the amount of leachate produced during a time frame and the concentration of substances in the leachate. The amount of leachate generated is dependent on the net infiltration of water to the landfilled waste. The leachate generation per kg waste is calculated based on a chosen time horizon, a chosen height of waste layer, and a chosen bulk density of the waste. The concentration of substances in the leachate

fraction was input in the model as a concentration (mg/l) at a given L/S after laboratory test on the pure fly ash samples FA1, FA2 and FA3. The expected L/S ratio after 100 years for landfill was estimated according to Kosson et al. (2002) (Eq. 1) and resulted in a L/S ratio between 0.5 and 0.7 depending on density of FA (see Table S3). However, data from laboratory experiment (batch test) was available only at L/S 1. In this work, data from real laboratory measurements was preferred to extrapolation of the concentration at lower L/S.

$$\frac{L (l)}{S (kg)} = \frac{T (years) \times P (mm \cdot years^{-1})}{\rho (kg \cdot m^{-3}) \times h (m)} \quad (Eq. 1)$$

Finally, the generated leachate solution is collected from the bottom of the landfill and sent to the waste water treatment plant with a collection efficiency of 95% for the first 10 years and 90% for the remaining 90 years. Waste water treatment plant removal efficiency are specific for each elements and reported in Table S3. After treatment the collected leachate is discharge to surface water.

Table S3 Dataset for the reference scenario for the three different type of ash. Leachate production from the pure fly ash has been taken from Tosti et al. (2018) whereas data for substance removal efficiency of the WWTP have been taken from EASETECH process “Leachate_Landfill_Treatment_emission to surface water” documented in Olesen and Damgaard (2014).

Landfill parameters				
		FA1	FA2	FA3
Transport	km	100	100	100
Infiltration rate (30 years)	mm/y	300	300	300
Infiltration rate (70 years)	mm/y	5	5	5
Layer	m	20	20	20
Density FA	kg/m ³	690	750	916
Electricity consumption	kWh/kg	0.000443	0.000443	0.000443
Leachate collection efficiency (10 years)	%	95	95	95
Leachate collection efficiency (90 years)	%	90	90	90
Cumulative liquid to solid ratio (L/S) (100years)	L/Kg	0.7	0.6	0.5
Leachate generation				
		FA1	FA2	FA3
As	mg/L	0.003	0.0888	0.0004
Ba	mg/L	0.235	0.239	22.24833
Cd	mg/L	0.0166	0.0152	0.0001
Cl	mg/L	6916	0.3	60.1
Co	mg/L	0.00005	0.0002	0.006955
Cr	mg/L	9.753	33.378	0.06825
Cu	mg/L	0.03	0.03	0.0224
F	mg/L	0.015	0.015	0.53
Mo	mg/L	6.975	5.82	0.01218
Ni	mg/L	0.0046	0.0006	0.00522
Pb	mg/L	0.0928	0.0508	0.271374
S	mg/L	7090	11900	1.103333
Sb	mg/L	0.0006	0.0032	0.032
Se	mg/L	0.472	0.828	0.002
Sn	mg/L	0.0004	0.0032	0.01
V	mg/L	0.0052	0.082	0.001
Zn	mg/L	0.00237	0.00225	0.1804

Substances removal efficiency				
		FA1	FA2	FA3
As	%	87	87	87
Ba	%	100	100	100
Cd	%	28	28	28
Co	%	27	27	27
Cl	%	15	15	15
Cr	%	14.4	14.4	14.4
Cr6	%	1.6	1.6	1.6
Cu	%	6	6	6
Mo	%	15	15	15
Ni	%	43	43	43
Pb	%	8	8	8
Sb	%	15	15	15
Se	%	15	15	15
Sn	%	15	15	15
V	%	94	94	94
Zn	%	38	38	38

4. Emission from service life of cement

The leaching during the service life is expressed as percentage of leached mass of elements compared to the total content of element in the products. First, the total mass of leached elements was calculated according to Eq.2 for a time frame of 50 years. The calculation of the diffusion coefficients (D_e) for each element was based on the cumulative release (mg/m^2) measured during the tank test after 64 days. Availability of elements (C_o) was taken from pH dependent test at $\text{pH} < 3$ (Tosti et al., 2018).

$$M = 2 \times A (\text{m}^2) \times \frac{\%wet}{100} \times \rho (\text{kg} * \text{m}^{-3}) \times C_o (\text{mg} * \text{kg}^{-1}) \times \sqrt{\frac{D_e (\text{m}^2 * \text{s}^{-1}) \times t(\text{years})}{\pi}} \quad (\text{Eq.2})$$

The available surface for leaching was supposed to be wet for 30% of the service life time horizon which was set to 50 years. Bulk density of materials was between 2000 and 2250 kg/m^3 for all the investigated blended cement mortars. Table S4 shows the leaching of considered elements during the service life of blended cements and reference. The model described in this section refers to the BIO Cement scenario but it has to be applied also to the parallel system considered in the landfill scenario. The only difference consists in the leaching data used for the calculation of the inorganics release accordingly to the specimen investigated.

Table S4 Dataset for the release from the service life of cement containing fly ash as well as reference pure cement. Data have been elaborated from Tosti et al. (2018).

<i>Leaching from service life</i>								
		<i>20_FA1</i>	<i>20_FA2</i>	<i>20_FA3</i>	<i>40_FA1</i>	<i>40_FA2</i>	<i>40_FA3</i>	<i>CEM (Ref)</i>
As	% TOT content	0.0215	0.0248	0.0153	0.0135	0.0176	0.0238	0.0371
Ba	% TOT content	0.5949	0.3250	0.0290	0.4596	0.2086	0.0064	0.0266
Cd	% TOT content	0.0076	0.0172	0.0116	0.0042	0.0109	0.0060	0.0220
Cl	% TOT content	1.9650	1.6433	0.1357	3.8364	3.1255	0.0756	0.3246
Co	% TOT content	0.0005	0.0005	0.0014	0.0010	0.0009	0.0015	0.0010
Cr	% TOT content	0.1342	0.1069	0.0291	0.1480	0.1067	0.0298	0.0919
Cu	% TOT content	0.0370	0.0346	0.0109	0.0302	0.0273	0.0034	0.0658
Mo	% TOT content	0.4042	0.3325	0.1253	0.5280	0.3995	0.1595	0.1116
Ni	% TOT content	0.0963	0.0876	0.0352	0.0622	0.0531	0.0129	0.0369
Pb	% TOT content	0.0704	0.1547	0.0024	0.0266	0.0716	0.0008	0.0200
Sb	% TOT content	0.5165	0.4415	0.2564	0.6223	0.4415	0.3426	0.2277
Se	% TOT content	0.0834	0.0717	0.0220	0.1474	0.1031	0.0343	0.0186
Sn	% TOT content	0.5643	0.2413	0.2621	0.5995	0.1559	0.2397	0.2750
V	% TOT content	0.0769	0.0732	0.1002	0.0413	0.0377	0.1826	0.2306
Zn	% TOT content	0.0925	0.1254	0.0725	0.0495	0.0728	0.0271	0.3098

5. Emissions from second life of cement products

Concerning the second phase (reuse as road sub base), the release after 50 years was estimated by applying the same equation for L/S calculation described for the reference landfill scenario (Eq.1). In this case, the equation was adjusted considering a net infiltration rate of rain water under the road pavement of 10% whereas the annual precipitation rate is approximately 800 mm/year. Density of crushed cement was approximately 1250 kg/m³ for all the samples and was calculated from a column test experiment performed in Tosti et al. (2018). The thickness of road sub-base layer was considered 30 cm according to Butera et al. (2015). The theoretical reached L/S ratio was around 10 for all the investigated blended cements and therefore the cumulative release at L/S 10 measured in the batch test was used.

Table S5 Dataset for the leaching from second life stage (granular material) of cement containing fly ash as well as reference pure cement. Data have been taken from Tosti et al. (2018).

		<i>Leaching from second life</i>						
		<i>20_FA1</i>	<i>20_FA2</i>	<i>20_FA3</i>	<i>40_FA1</i>	<i>40_FA2</i>	<i>40_FA3</i>	<i>CEM (Ref)</i>
As	kg/kg	4.32E-09	4.00E-09	2.27E-10	4.36E-09	4.00E-09	2.06E-10	3.51E-10
Ba	kg/kg	1.62E-05	2.06E-05	2.35E-05	1.56E-05	2.70E-05	2.89E-05	1.90E-05
Cd	kg/kg	1.08E-09	1.00E-09	5.15E-11	2.02E-09	1.00E-09	5.16E-11	5.16E-11
Cl	kg/kg	1.94E-04	2.01E-04	7.31E-05	5.17E-04	2.97E-04	1.35E-04	3.22E-05
Co	kg/kg	1.08E-09	1.16E-08	1.45E-08	1.09E-09	1.02E-08	1.90E-08	1.85E-08
Cr6	kg/kg	2.64E-07	1.52E-07	3.30E-07	6.73E-07	2.87E-07	4.39E-07	1.85E-07
Cu	kg/kg	1.08E-06	9.00E-08	1.96E-07	1.09E-06	8.00E-08	1.96E-07	1.75E-07
Mo	kg/kg	2.21E-07	1.73E-07	6.05E-08	4.42E-07	2.35E-07	8.40E-08	6.14E-08
Ni	kg/kg	8.10E-09	1.54E-08	9.07E-09	6.55E-09	3.74E-08	9.49E-09	1.06E-08
Pb	kg/kg	2.61E-07	2.56E-07	8.16E-08	1.45E-07	9.94E-08	1.24E-07	4.25E-08
Sb	kg/kg	3.45E-07	3.20E-07	1.65E-08	3.49E-07	3.20E-07	1.65E-08	1.65E-08
Se	kg/kg	2.16E-08	3.46E-08	5.36E-09	3.79E-08	2.00E-08	5.88E-09	1.07E-08
Sn	kg/kg	1.08E-07	1.00E-07	5.15E-09	1.09E-07	1.00E-07	5.16E-09	5.16E-09
V	kg/kg	1.08E-08	1.00E-08	5.15E-10	1.09E-08	1.00E-08	5.16E-10	5.16E-10
Zn	kg/kg	2.16E-06	2.00E-06	2.06E-07	2.18E-06	2.00E-06	2.06E-07	2.06E-07

6. Contribution analysis

Tables reported in the following section show the characterized results for all the investigated impact categories. The processes have been grouped into five main contributions. “Cement” includes also the additional OPC cement needed to keep up with strength loss due to biomass fly ash inclusion.

Table S6 Characterized results for all the impact categories of the reference and BioCement scenario 20_FA1.

	Climate change, kg CO ₂ -Eq		Ozone depletion, kg CFC-11 Eq		Human toxicity, cancer effects, CTUh		Human toxicity, non-cancer effects, CTUh		Particulate matter, kgPM _{2.5} -eq		Ionising radiation, kBq U235 eq		Photochemical ozone formation, kg NMVOC	
	Reference	20_FA1	Reference	20_FA1	Reference	20_FA1	Reference	20_FA1	Reference	20_FA1	Reference	20_FA1	Reference	20_FA1
Cement	4.34E+03	3.52E+03	1.24E-04	1.01E-04	7.50E-06	6.07E-06	1.88E-04	1.52E-04	6.32E-01	5.11E-01	7.04E+01	5.71E+01	7.38E+00	5.97E+00
Transport	5.32E+00	2.66E+01	1.91E-09	9.57E-09	8.04E-09	4.02E-08	2.01E-06	1.01E-05	3.38E-04	1.69E-03	7.54E-03	3.77E-02	5.91E-03	2.96E-02
Landfill	2.85E-01	0.00E+00	1.23E-11	0.00E+00	8.91E-06	0.00E+00	7.58E-08	0.00E+00	2.51E-05	0.00E+00	2.22E-04	0.00E+00	3.51E-04	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.04E-07	1.05E-06	1.76E-06	1.97E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.80E-06	6.92E-06	5.28E-06	1.22E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SUM	4.35E+03	3.55E+03	1.24E-04	1.01E-04	2.17E-05	1.41E-05	1.97E-04	1.76E-04	6.33E-01	5.13E-01	7.04E+01	5.71E+01	7.39E+00	6.00E+00

	Terrestrial acidification, mol H ⁺ eq.		Eutrophication Terrestrial, mol N eq.		Eutrophication Freshwater, kg P eq.		Eutrophication Marine, kg N eq.		Ecotoxicity freshwater, CTU _e		Depletion of abiotic resources, mineral fossil & renewable kg Sb eq.	
	Reference	20_FA1	Reference	20_FA1	Reference	20_FA1	Reference	20_FA1	Reference	20_FA1	Reference	20_FA1
Cement	9.85E+00	7.96E+00	2.90E+01	2.34E+01	4.84E-02	3.93E-02	2.49E+00	2.01E+00	3.24E+02	2.62E+02	1.53E-02	1.24E-02
Transport	8.83E-03	4.41E-02	2.64E-02	1.32E-01	4.54E-06	2.27E-05	2.12E-03	1.06E-02	2.20E+00	1.10E+01	4.70E-06	2.35E-05
Landfill	4.02E-04	0.00E+00	1.36E-03	0.00E+00	4.97E-09	0.00E+00	1.24E-04	0.00E+00	1.92E+01	0.00E+00	1.22E-07	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.93E+01	1.03E+02	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.72E+02	6.76E+02	0.00E+00	0.00E+00
SUM	9.86E+00	8.00E+00	2.90E+01	2.36E+01	4.85E-02	3.93E-02	2.49E+00	2.02E+00	6.07E+02	1.05E+03	1.53E-02	1.24E-02

Table S7 Characterized results for all the impact categories of the reference and BioCement scenario 40_FA1

	Climate change, kg CO ₂ -Eq		Ozone depletion, kg CFC-11 Eq		Human toxicity, cancer effects, CTUh		Human toxicity, non-cancer effects, CTUh		Particulate matter, kgPM _{2.5} -eq		Ionising radiation, kBq U235 eq		Photochemical ozone formation, kg NMVOC	
	Reference	40_FA1	Reference	40_FA1	Reference	40_FA1	Reference	40_FA1	Reference	40_FA1	Reference	40_FA1	Reference	40_FA1
Cement	2.17E+03	1.63E+03	6.20E-05	4.70E-05	3.75E-06	2.81E-06	9.39E-05	7.04E-05	3.16E-01	2.37E-01	3.52E+01	2.65E+01	3.69E+00	2.77E+00
Transport	5.32E+00	2.66E+01	1.91E-09	9.57E-09	8.04E-09	4.02E-08	2.01E-06	1.01E-05	3.38E-04	1.69E-03	7.54E-03	3.77E-02	5.91E-03	2.96E-02
Landfill	2.85E-01	0.00E+00	1.23E-11	0.00E+00	8.91E-06	0.00E+00	7.58E-08	0.00E+00	2.51E-05	0.00E+00	2.22E-04	0.00E+00	3.51E-04	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.52E-07	7.99E-07	8.82E-07	8.57E-07	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.40E-06	8.82E-06	2.64E-06	6.12E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SUM	2.18E+03	1.66E+03	6.20E-05	4.70E-05	1.53E-05	1.25E-05	9.95E-05	8.75E-05	3.17E-01	2.38E-01	3.52E+01	2.66E+01	3.70E+00	2.80E+00

	Terrestrial acidification, mol H ⁺ -eq.		Eutrophication Terrestrial, mol N eq.		Eutrophication Freshwater, kg P eq.		Eutrophication Marine, kg N eq.		Ecotoxicity freshwater, CTUe		Depletion of abiotic resources, mineral fossil & renewable kg Sb eq.	
	Reference	40_FA1	Reference	40_FA1	Reference	40_FA1	Reference	40_FA1	Reference	40_FA1	Reference	40_FA1
Cement	4.92E+00	3.69E+00	1.45E+01	1.09E+01	2.42E-02	1.83E-02	1.25E+00	9.33E-01	1.62E+02	1.22E+02	7.66E-03	5.74E-03
Transport	8.83E-03	4.41E-02	2.64E-02	1.32E-01	4.54E-06	2.27E-05	2.12E-03	1.06E-02	2.20E+00	1.10E+01	4.70E-06	2.35E-05
Landfill	4.02E-04	0.00E+00	1.36E-03	0.00E+00	4.97E-09	0.00E+00	1.24E-04	0.00E+00	1.92E+01	0.00E+00	1.22E-07	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.46E+01	4.92E+01	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.59E+01	3.94E+02	0.00E+00	0.00E+00
SUM	4.93E+00	3.73E+00	1.45E+01	1.10E+01	2.42E-02	1.83E-02	1.25E+00	9.43E-01	3.14E+02	5.76E+02	7.67E-03	5.76E-03

Table S8 Characterized results for all the impact categories of the reference and BIOcement scenario 20_FA2.

	Climate change, kg CO ₂ -Eq		Ozone depletion, kg CFC-11 Eq		Human toxicity, cancer effects, CTUh		Human toxicity, non-cancer effects, CTUh		Particulate matter, kgPM _{2.5} -eq		Ionising radiation, kBq U235 eq		Photochemical ozone formation, kg NMVOC	
	Reference	20_FA2	Reference	20_FA2	Reference	20_FA2	Reference	20_FA2	Reference	20_FA2	Reference	20_FA2	Reference	20_FA2
Cement	4.34E+03	3.77E+03	1.24E-04	1.08E-04	7.50E-06	6.50E-06	1.88E-04	1.63E-04	6.32E-01	5.48E-01	7.04E+01	6.12E+01	7.38E+00	6.40E+00
Transport	5.32E+00	2.66E+01	1.91E-09	9.57E-09	8.04E-09	4.02E-08	2.01E-06	1.01E-05	3.38E-04	1.69E-03	7.54E-03	3.77E-02	5.91E-03	2.96E-02
Landfill	2.62E-01	0.00E+00	1.13E-11	0.00E+00	2.81E-05	0.00E+00	1.54E-06	0.00E+00	2.31E-05	0.00E+00	2.04E-04	0.00E+00	3.23E-04	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.04E-07	1.12E-06	1.76E-06	1.80E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.80E-06	3.95E-06	5.28E-06	1.26E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SUM	4.35E+03	3.80E+03	1.24E-04	1.08E-04	4.09E-05	1.16E-05	1.98E-04	1.87E-04	6.33E-01	5.50E-01	7.04E+01	6.12E+01	7.39E+00	6.43E+00

	Terrestrial acidification, mol H ⁺ eq.		Eutrophication Terrestrial, mol N eq.		Eutrophication Freshwater, kg P eq.		Eutrophication Marine, kg N eq.		Ecotoxicity freshwater, CTUe		Depletion of abiotic resources, mineral fossil & renewable kg Sb eq.	
	Reference	20_FA2	Reference	20_FA2	Reference	20_FA2	Reference	20_FA2	Reference	20_FA2	Reference	20_FA2
Cement	9.85E+00	8.53E+00	2.90E+01	2.51E+01	4.84E-02	4.21E-02	2.49E+00	2.16E+00	3.24E+02	2.81E+02	1.53E-02	1.33E-02
Transport	8.83E-03	4.41E-02	2.64E-02	1.32E-01	4.54E-06	2.27E-05	2.12E-03	1.06E-02	2.20E+00	1.10E+01	4.70E-06	2.35E-05
Landfill	3.70E-04	0.00E+00	1.25E-03	0.00E+00	4.57E-09	0.00E+00	1.14E-04	0.00E+00	6.48E+01	0.00E+00	1.12E-07	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.93E+01	9.80E+01	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.72E+02	4.91E+02	0.00E+00	0.00E+00
SUM	9.86E+00	8.57E+00	2.90E+01	2.52E+01	4.85E-02	4.21E-02	2.49E+00	2.17E+00	6.52E+02	8.81E+02	1.53E-02	1.33E-02

Table S9 Characterized results for all the impact categories of the reference and BIOcement scenario 40_FA2

	Climate change, kg CO ₂ -Eq		Ozone depletion, kg CFC-11 Eq		Human toxicity, cancer effects, CTUh		Human toxicity, non-cancer effects, CTUh		Particulate matter, kgPM _{2.5} -eq		Ionising radiation, kBq U235 eq		Photochemical ozone formation, kg NMVOC	
	Reference	40_FA2	Reference	40_FA2	Reference	40_FA2	Reference	40_FA2	Reference	40_FA2	Reference	40_FA2	Reference	40_FA2
Cement	2.17E+03	1.82E+03	6.20E-05	5.22E-05	3.75E-06	3.13E-06	9.39E-05	7.83E-05	3.16E-01	2.63E-01	3.52E+01	2.95E+01	3.69E+00	3.08E+00
Transport	5.32E+00	2.66E+01	1.91E-09	9.57E-09	8.04E-09	4.02E-08	2.01E-06	1.01E-05	3.38E-04	1.69E-03	7.54E-03	3.77E-02	5.91E-03	2.96E-02
Landfill	2.62E-01	0.00E+00	1.13E-11	0.00E+00	2.81E-05	0.00E+00	1.54E-06	0.00E+00	2.31E-05	0.00E+00	2.04E-04	0.00E+00	3.23E-04	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.52E-07	5.86E-07	8.82E-07	9.79E-07	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.40E-06	2.71E-06	2.64E-06	6.91E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SUM	2.18E+03	1.84E+03	6.20E-05	5.22E-05	3.45E-05	6.47E-06	1.01E-04	9.63E-05	3.17E-01	2.65E-01	3.52E+01	2.95E+01	3.70E+00	3.11E+00

	Terrestrial acidification, mol H ⁺ eq.		Eutrophication Terrestrial, mol N eq.		Eutrophication Freshwater, kg P eq.		Eutrophication Marine, kg N eq.		Ecotoxicity freshwater, CTU _e		Depletion of abiotic resources, mineral fossil & renewable kg Sb eq.	
	Reference	40_FA2	Reference	40_FA2	Reference	40_FA2	Reference	40_FA2	Reference	40_FA2	Reference	40_FA2
Cement	4.92E+00	4.10E+00	1.45E+01	1.21E+01	2.42E-02	2.03E-02	1.25E+00	1.04E+00	1.62E+02	1.35E+02	7.66E-03	6.38E-03
Transport	8.83E-03	4.41E-02	2.64E-02	1.32E-01	4.54E-06	2.27E-05	2.12E-03	1.06E-02	2.20E+00	1.10E+01	4.70E-06	2.35E-05
Landfill	3.70E-04	0.00E+00	1.25E-03	0.00E+00	4.57E-09	0.00E+00	1.14E-04	0.00E+00	6.48E+01	0.00E+00	1.12E-07	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.46E+01	4.67E+01	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.59E+01	2.63E+02	0.00E+00	0.00E+00
SUM	4.93E+00	4.14E+00	1.45E+01	1.22E+01	2.42E-02	2.03E-02	1.25E+00	1.05E+00	3.60E+02	4.56E+02	7.67E-03	6.41E-03

Table S10 Characterized results for all the impact categories of the reference and BIOCEment scenario 20_F43.

	Climate change, kg CO ₂ -Eq		Ozone depletion, kg CFC-11 Eq		Human toxicity, cancer effects, CTUh		Human toxicity, non-cancer effects, CTUh		Particulate matter, kgPM _{2.5} -eq		Ionising radiation, kBq 1/235 eq		Photochemical ozone formation, kg NMVOC	
	Reference	20_F43	Reference	20_F43	Reference	20_F43	Reference	20_F43	Reference	20_F43	Reference	20_F43	Reference	20_F43
Cement	4.34E+03	3.54E+03	1.24E-04	1.01E-04	7.50E-06	6.11E-06	1.88E-04	1.53E-04	6.32E-01	5.15E-01	7.04E+01	5.75E+01	7.38E+00	6.01E+00
Transport	5.32E+00	2.66E+01	1.91E-09	9.57E-09	8.04E-09	4.02E-08	2.01E-06	1.01E-05	3.38E-04	1.69E-03	7.54E-03	3.77E-02	5.91E-03	2.96E-02
Landfill	2.14E-01	0.00E+00	9.24E-12	0.00E+00	4.81E-08	0.00E+00	1.17E-06	0.00E+00	1.88E-05	0.00E+00	1.66E-04	0.00E+00	2.63E-04	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.04E-07	3.91E-07	1.76E-06	1.84E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.80E-06	8.64E-06	5.28E-06	3.57E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SUM	4.35E+03	3.57E+03	1.24E-04	1.01E-04	1.29E-05	1.52E-05	1.98E-04	1.68E-04	6.33E-01	5.16E-01	7.04E+01	5.75E+01	7.39E+00	6.04E+00

	Terrestrial acidification, mol H ⁺ -eq.		Eutrophication Terrestrial, mol N eq.		Eutrophication Freshwater, kg P eq.		Eutrophication Marine, kg N eq.		Ecotoxicity freshwater, CTUe		Depletion of abiotic resources, mineral fossil & renewable kg Sb eq.	
	Reference	20_F43	Reference	20_F43	Reference	20_F43	Reference	20_F43	Reference	20_F43	Reference	20_F43
Cement	9.85E+00	8.01E+00	2.90E+01	2.36E+01	4.84E-02	3.96E-02	2.49E+00	2.03E+00	3.24E+02	2.64E+02	1.53E-02	1.25E-02
Transport	8.83E-03	4.41E-02	2.64E-02	1.32E-01	4.54E-06	2.27E-05	2.12E-03	1.06E-02	2.20E+00	1.10E+01	4.70E-06	2.35E-05
Landfill	3.02E-04	0.00E+00	1.02E-03	0.00E+00	3.72E-09	0.00E+00	9.30E-05	0.00E+00	1.97E+01	0.00E+00	9.14E-08	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.93E+01	7.82E+01	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.72E+02	1.85E+02	0.00E+00	0.00E+00
SUM	9.86E+00	8.06E+00	2.90E+01	2.37E+01	4.85E-02	3.96E-02	2.49E+00	2.04E+00	6.07E+02	5.38E+02	1.53E-02	1.25E-02

Table S11 Characterized results for all the impact categories of the reference and BIOcCement scenario 40_FA3

	Climate change, kg CO ₂ -Eq		Ozone depletion, kg CFC-11 Eq		Human toxicity, cancer effects, CTUh		Human toxicity, non-cancer effects, CTUh		Particulate matter, kgPM _{2.5} -eq		Ionising radiation, kBq 1/235 eq		Photochemical ozone formation, kg NMVOC	
	Reference	40_FA3	Reference	40_FA3	Reference	40_FA3	Reference	40_FA3	Reference	40_FA3	Reference	40_FA3	Reference	40_FA3
Cement	2.17E+03	1.59E+03	6.20E-05	4.58E-05	3.75E-06	2.74E-06	9.39E-05	6.86E-05	3.16E-01	2.30E-01	3.52E+01	2.58E+01	3.69E+00	2.69E+00
Transport	5.32E+00	2.66E+01	1.91E-09	9.57E-09	8.04E-09	4.02E-08	2.01E-06	1.01E-05	3.38E-04	1.69E-03	7.54E-03	3.77E-02	5.91E-03	2.96E-02
Landfill	2.14E-01	0.00E+00	9.24E-12	0.00E+00	4.81E-08	0.00E+00	1.17E-06	0.00E+00	1.88E-05	0.00E+00	1.66E-04	0.00E+00	2.63E-04	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.52E-07	3.10E-07	8.82E-07	9.53E-07	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.40E-06	4.27E-06	2.64E-06	1.12E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SUM	2.18E+03	1.62E+03	6.20E-05	4.58E-05	6.45E-06	7.36E-06	1.01E-04	8.07E-05	3.17E-01	2.32E-01	3.52E+01	2.59E+01	3.70E+00	2.72E+00

	Terrestrial acidification, mol H ⁺ -eq.		Eutrophication Terrestrial, mol N eq.		Eutrophication Freshwater, kg P eq.		Eutrophication Marine, kg N eq.		Ecotoxicity freshwater, CTUe		Depletion of abiotic resources, mineral fossil & renewable kg Sb eq.	
	Reference	40_FA3	Reference	40_FA3	Reference	40_FA3	Reference	40_FA3	Reference	40_FA3	Reference	40_FA3
Cement	4.92E+00	3.59E+00	1.45E+01	1.06E+01	2.42E-02	1.78E-02	1.25E+00	9.08E-01	1.62E+02	1.18E+02	7.66E-03	5.59E-03
Transport	8.83E-03	4.41E-02	2.64E-02	1.32E-01	4.54E-06	2.27E-05	2.12E-03	1.06E-02	2.20E+00	1.10E+01	4.70E-06	2.35E-05
Landfill	3.02E-04	0.00E+00	1.02E-03	0.00E+00	3.72E-09	0.00E+00	9.30E-05	0.00E+00	1.97E+01	0.00E+00	9.14E-08	0.00E+00
Leaching from service life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.46E+01	3.81E+01	0.00E+00	0.00E+00
Leaching from second life	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.59E+01	7.65E+01	0.00E+00	0.00E+00
SUM	4.93E+00	3.63E+00	1.45E+01	1.07E+01	2.42E-02	1.78E-02	1.25E+00	9.18E-01	3.15E+02	2.44E+02	7.67E-03	5.61E-03

Table S12 Percentage of contribution of elements to the total impact on GWP100, HTc, HTnc and ET impact categories. The percentages refer to reference and BIOcement scenario for FAI but can be considered representative for all other biomass fly ash scenarios. Percentage of contribution of elements to the total impact on categories might slightly change depending on FA types.

	GWP₁₀₀ % of the total impact		HTc % of the total impact		HTnc % of the total impact		ET % of the total impact
Carbon dioxide	98	Chromium	92	Mercury	60	Zinc	23
		Mercury	5,4	Zinc	11	Chromium	20
		Arsenic	1	Arsenic	8	Barium	15
				Barium	3	Copper	10
						Antimony	6

7. Sensitivity analysis

7.1. Parameters

Table S13 shows the list of parameters tested in the perturbation analysis. A brief explanation of the function of the parameter in the model is also given.

Table S13 List of parameters tested in the perturbation analysis

Reference		BIOCement	
Parameter	Comments	Parameter	Comments
Transport_FA	Transport distance	Transport_FA	Transport distance
Inf_rate_30	Infiltration rate (mm/year) for the first 30 years and remaining 70 years	Blending	Electricity requirement for mixing cement with fly ash
Inf_rate_70		Additional_OPC	Additional OPC to compensate strength loss
Layer	Height of landfill layer	Use_leachAs	Release of elements to soil during the service life of cement as described in paragraph 4
Dens_FA	Density of fly ash	Use_leachBa	
WWTP_elec	Electricity requirement of the WWTP	Use_leachCd	
Dist_1	Leachate collection efficiency first 10 years and remaining 90 years	Use_leachCl	
Dist_2		Use_leachCo	
Leach_gen As	Leaching value (mg/L) from pure biomass fly ash as measured during batch test at L/S 1	Use_leachCr	
Leach_gen Ba		Use_leachCu	
Leach_gen Cd		Use_leachMo	
Leach_gen Cl		Use_leachNi	
Leach_gen Co		Use_leachPb	
Leach_gen Cr		Use_leachSb	
Leach_gen Cu		Use_leachSe	
Leach_gen F		Use_leachSn	
Leach_gen Mo		Use_leachV	
Leach_gen Ni		Use_leachZn	
Leach_gen Pb		Sec_leachAs	Release of elements to soil during the second life stage as described in Section 5
Leach_gen S		Sec_leachBa	
Leach_gen Sb		Sec_leachCd	
Leach_gen Se		Sec_leachCl	
Leach_gen Sn		Sec_leachCo	
Leach_gen V		Sec_leachCr6	
Leach_gen Zn		Sec_leachCu	
Spec As	Removal efficiency of the WWTP	Sec_leachMo	
Spec Ba		Sec_leachNi	
Spec Cd		Sec_leachPb	
Spec Co		Sec_leachSb	
Spec Cl		Sec_leachSe	
Spec Cr		Sec_leachSn	
Spec Cr6		Sec_leachV	
Spec Cu		Sec_leachZn	
Spec Mo			
Spec Ni			
Spec Pb			
Spec Sb			
Spec Se			
Spec Sn			
Spec V			
Spec Zn			
Use_leachAs	Release of elements to soil during the service life of cement as described in Section 4.		
Use_leachBa			
Use_leachCd			
Use_leachCl			
Use_leachCo			
Use_leachCr			
Use_leachCu			
Use_leachMo			
Use_leachNi			
Use_leachPb			
Use_leachSb			
Use_leachSe			
Use_leachSn			
Use_leachV			
Use_leachZn			

Reference			
Parameter	Comments		
Sec_leachAs	Release of elements to soil during the second life stage as described in Section 5		
Sec_leachBa			
Sec_leachCd			
Sec_leachCl			
Sec_leachCo			
Sec_leachCr6			
Sec_leachCu			
Sec_leachMo			
Sec_leachNi			
Sec_leachPb			
Sec_leachSb			
Sec_leachSe			
Sec_leachSn			
Sec_leachV			
Sec_leachZn			

7.2. Perturbation analysis

The perturbation analysis was conducted by calculating the Normalised Sensitivity Ratio (NSR) in order to highlight the parameters the model is more sensitive to. NSR is defined as:

$$NSR_i = \frac{SR_i}{\max(|SR_i|)}, \text{ where } SR = \frac{\frac{\Delta \text{result}}{\text{initial_result}}}{\frac{\Delta \text{parameter}}{\text{initial_parameter}}} \quad (\text{Eq.3})$$

The NSRs for all parameters are reported in the following tables. To simplify the interpretation of the perturbation analysis, colours were chosen in order to define when the parameters showed a low, medium and high sensitivity

Negligible	NSR < 0.1
Low	0.1 < NSR < 0.5
Medium	0.5 < NSR < 0.8
High	0.8 < NSR = 1
∅	By increasing/decreasing the parameter, no change was observed in the results.

Table S14 reports NSRs values for the parameters in the reference scenario whereas Table S15 reports NSRs for the parameter in the BIOCement scenario. The replacement ratio was found not to affect significantly the resulting NSRs, therefore, only the ash type is reported.

Table S14 Normalized sensitivity ratios (NSR) values of the reference scenario for FA1

Parameter	GWP ₁₀₀	ODP	HTc	HTnc	PM	IR	POF	AP	TEP	FEP	MEP	ET	ADP
Transport FA	1.00	1.00	0.00	0.44	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.03	1.00
Inf rate 30	0.05	0.01	0.96	0.02	0.07	0.03	0.06	0.04	0.05	0.00	0.06	0.26	0.02
Inf rate 70	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Layer	0.05	0.01	0.91	0.02	0.07	0.03	0.05	0.04	0.05	0.00	0.05	0.25	0.02
Dens FA	0.05	0.01	0.91	0.02	0.07	0.03	0.05	0.04	0.05	0.00	0.05	0.25	0.02
WWTP elec	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dist 1	0.01	0.00	0.11	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.03	0.00
Dist 2	0.04	0.00	0.42	0.01	0.05	0.02	0.04	0.03	0.03	0.00	0.04	0.12	0.02
Leach gen As	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cr	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.00
Leach gen Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Mo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Leach gen Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Leach gen Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec As	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cr	0.00	0.00	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Spec Cr6	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.00
Spec Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Mo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachAs	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachBa	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCr	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00
Use leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00
Use leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachPb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00
Use leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachV	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.00
Use leachZn	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.65	0.00

Parameter	GWP ₁₀₀	ODP	HTc	HTnc	PM	IR	POF	AP	TEP	FEP	MEP	ET	ADP
Sec leachAs	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachBa	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
Sec leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCr6	0.00	0.00	0.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.67	0.00
Sec leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.00
Sec leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Sec leachPb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00
Sec leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachZn	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.30	0.00

Table S15 Normalized sensitivity ratios (NSR) values of the reference scenario for FA2

Parameter	GWP ₁₀₀	ODP	HTc	HTnc	PM	IR	POF	AP	TEP	FEP	MEP	ET	ADP
Transport FA	1.00	1.00	0.00	0.44	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.03	1.00
Inf rate_30	0.05	0.01	0.96	0.29	0.07	0.03	0.05	0.04	0.05	0.00	0.05	0.88	0.02
Inf rate_70	0.00	0.00	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00
Layer	0.04	0.01	0.91	0.28	0.06	0.02	0.05	0.04	0.04	0.00	0.05	0.83	0.02
Dens FA	0.04	0.01	0.91	0.28	0.06	0.02	0.05	0.04	0.04	0.00	0.05	0.83	0.02
WWTP elec	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dist 1	0.01	0.00	0.11	0.05	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.11	0.00
Dist 2	0.03	0.00	0.42	0.18	0.05	0.02	0.04	0.03	0.03	0.00	0.04	0.41	0.02
Leach gen As	0.00	0.00	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
Leach gen Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cr	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.79	0.00
Leach gen Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Mo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Leach gen Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00
Leach gen Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec As	0.00	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
Spec Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cr	0.00	0.00	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00
Spec Cr6	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00
Spec Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Mo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Spec Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00
Spec Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Parameter	GWP100	ODP	HTc	HTnc	PM	IR	POF	AP	TEP	FEP	MEP	ET	ADP
Use leachAs	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachBa	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCr	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00
Use leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00
Use leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachPb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00
Use leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachV	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.00
Use leachZn	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.65	0.00
Sec leachAs	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachBa	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
Sec leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCr6	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.67	0.00
Sec leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.00
Sec leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Sec leachPb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00
Sec leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachZn	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.30	0.00

Table S16 Normalized sensitivity ratios (NSR) values of the reference scenario for FA3

Parameter	GWP ₁₀₀	ODP	HTc	HTnc	PM	IR	POF	AP	TEP	FEP	MEP	ET	ADP
Transport FA	1.00	1.00	0.00	0.44	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.03	1.00
Inf rate 30	0.04	0.00	0.01	0.25	0.05	0.02	0.04	0.03	0.04	0.00	0.04	0.27	0.02
Inf rate 70	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Layer	0.04	0.00	0.01	0.24	0.05	0.02	0.04	0.03	0.04	0.00	0.04	0.26	0.02
Dens FA	0.04	0.00	0.01	0.24	0.05	0.02	0.04	0.03	0.04	0.00	0.04	0.26	0.02
WWTP elec	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dist 1	0.01	0.00	0.00	0.04	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.04	0.00
Dist 2	0.03	0.00	0.00	0.16	0.04	0.01	0.03	0.02	0.03	0.00	0.03	0.17	0.01
Leach gen As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cr	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Mo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Leach gen Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Leach gen Zn	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Spec As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Ba	0.00	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00
Spec Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cr	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cr6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Mo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Spec Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spec Zn	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Use leachAs	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachBa	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCr	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00
Use leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00
Use leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachPb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00
Use leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachV	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.00
Use leachZn	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.65	0.00
Sec leachAs	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachBa	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
Sec leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Sec leachCr6	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.67	0.00
Sec leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.00
Sec leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Parameter	GWP ₁₀₀	ODP	HTc	HTnc	PM	IR	POF	AP	TEP	FEP	MEP	ET	ADP
Sec leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Sec leachPb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00
Sec leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachZn	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.30	0.00

Table S17 Normalized sensitivity ratios (NSR) values of the BIOCement scenario when FA1 substitutes cement.

Parameter	GWP ₁₀₀	ODP	HTc	HTnc	PM	IR	POF	AP	TEP	FEP	MEP	ET	ADP
Transport FA	0.17	0.00	0.00	0.17	0.08	0.02	0.11	0.13	0.13	0.01	0.12	0.01	0.04
Blending	0.60	1.00	0.00	0.05	0.33	0.72	0.36	0.32	0.35	0.67	0.36	0.00	0.34
Additional OPC	1.00	0.97	0.00	0.11	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.01	1.00
Use leachAs	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachBa	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Use leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCr	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00
Use leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Use leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachPb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00
Use leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Use leachZn	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.00
Sec leachAs	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachBa	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00
Sec leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCr6	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00
Sec leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
Sec leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachPb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSb	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.43	0.00
Sec leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Sec leachZn	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.93	0.00

Table S18 Normalized sensitivity ratios (NSR) values of the BIOCement scenario when FA2 substitutes cement

Parameter	GWP ₁₀₀	ODP	HTc	HTnc	PM	IR	POF	AP	TEP	FEP	MEP	ET	ADP
Transport FA	0.02	0.00	0.00	0.17	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.00
Blending	0.07	0.12	0.01	0.05	0.04	0.08	0.04	0.04	0.04	0.07	0.04	0.00	0.04
Additional OPC	1.00	1.00	0.12	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.10	1.00
Use leachAs	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachBa	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
Use leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCr	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00
Use leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Use leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachPb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.00
Use leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
Use leachZn	0.00	0.00	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.00
Sec leachAs	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachBa	0.00	0.00	0.00	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.00
Sec leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCr6	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00
Sec leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00
Sec leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachPb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSb	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.72	0.00
Sec leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Sec leachZn	0.00	0.00	0.00	0.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00

Table S19 Normalized sensitivity ratios (NSR) values of the BIOCement scenario when FA3 substitutes cement

Parameter	GWP ₁₀₀	ODP	HTc	HTnc	PM	IR	POF	AP	TEP	FEP	MEP	ET	ADP
Transport FA	0.11	0.00	0.00	0.71	0.05	0.01	0.07	0.08	0.08	0.01	0.07	0.03	0.03
Blending	0.36	0.63	0.00	0.21	0.20	0.44	0.22	0.20	0.22	0.41	0.22	0.01	0.21
Additional OPC	1.00	1.00	0.01	0.77	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.04	1.00
Use leachAs	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachBa	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachCr	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00
Use leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
Use leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachPb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.00
Use leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Use leachV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00
Use leachZn	0.00	0.00	0.00	0.56	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.56	0.00
Sec leachAs	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachBa	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.51	0.00
Sec leachCd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachCr6	0.00	0.00	1.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
Sec leachCu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.33	0.00
Sec leachMo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachNi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachPb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSb	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00
Sec leachSe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachSn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sec leachZn	0.00	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.00

7.3. Uncertainty analysis

The parameters identified as the most sensitive parameters after perturbation (i.e. red cells in tables presented in Section 7.2) were characterized with a probability distribution in order to carry out Monte Carlo simulation and quantify the propagation of error through the model and the uncertainty of results. In Table S20 the type of distribution and deviation around the average value of parameters are reported. The average values of parameters were already reported in Table S3, Table S4 and Table S5.

Table S20 Type of distribution and deviation assigned to the most sensitive parameters as identified from perturbation analysis. ND describe a normal distribution around the average value whereas TD is a triangular distribution. The deviation in ND is described as percentage of the average value. For the TD a lower and upper values are defined.

Parameter	Type of distribution	Deviation
Transport_FA	ND	50%
Inf_rate_30	ND	10%
Layer	TD	Low 10, UPP 30
Dens_FA	ND	10%
Leach_gen_Cr	ND	25%
Sec_leachCr6	ND	25%
Sec_leachBa	ND	25%

Parameter	Type of distribution	Deviation		
Additional_OPC	ND	3.6%(FA1)	7.6%(FA2)	4.8%(FA3)
Sec_leachBa	ND	25%		
Sec_leachCr6	ND	25%		
Sec_leachCu	ND	25%		
Sec_leachZn	ND	25%		

For the scope of this work the deviation was considered to be normal distributed around the average values. The percentage of deviation was assumed to be of an arbitrary value of 50% for transport and layer of landfill and 10% for infiltration rate and density of fly ash. Concerning leaching of elements the deviation was set to 25% and was based on results obtained from the validation studies conducted for the European standard: Characterisation of waste: Leaching - Compliance test for leaching of granular waste materials and sludges - part 2 (NEN-EN 12457-2, 2002). The only value derived from laboratory measurements was the deviation of the *Additional_OPC* parameter. This equals the average across 20 and 40% replacement of standard deviation on compressive strength measurements (total of six measurements) used to calculate the additional OPC cement requirements.

8. Landfill directive

Table S21 Limits value for landfill of hazardous and non-hazardous waste as reported in the EU landfill directive (European Commission, 1999). Concentrations of regulated elements in samples of pure biomass ash FA1, FA2 and FA3 are also reported for comparison reason.

	<i>Hazardous mg/kg at L/S 10</i>	<i>Non-hazardous mg/kg at L/S 10</i>	<i>FA1 mg/kg at L/S 10</i>	<i>FA2 mg/kg at L/S 10</i>	<i>FA3 mg/kg at L/S 10</i>
As	25	2	0.00	0.01	0.02
Ba	300	100	2.49	3.89	177
Cd	5	1	0.04	0.01	0.01
Cl	25000	15000	6880	8155	31.2
Cr	70	10	12.13	32.71	0.16
Cu	100	50	1.00	1.01	0.10
F	500	150	2.30	2.33	3.16
Mo	30	10	10.6	10.3	0.18
Ni	40	10	0.01	0.01	0.03
Pb	50	10	1.47	0.12	2.59
Sb	5	0.7	0.32	0.32	1.60
Se	7	0.5	0.80	0.98	N.A.
Zn	200	50	2.36	2.03	1.60

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Chapter 6

General discussion and final remarks

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1. THE CIRCULAR APPROACH

6

In the current policy of the European Union, circularity is the adopted approach to create a more sustainable society. According to the concept of circular economy the value of products and materials should be maintained as long as possible and waste generation and down cycling should be avoided when possible. Alternatively, a cascade approach (i.e., the sequential and consecutive use of resources) should be followed (Campbell-Johnston et al., 2020; Directorate-General for Environment (European Commission), 2018). The cement industry has been using wastes from other industries (i.e., coal fly ash) since decades now with good results especially when it comes to improving the technical properties of blended cements. Obtaining specific technical ameliorations has been the moving principle behind using wastes rather than the potential to improve the environmental profile of cement products. Although this incentive was already one step forward in comparison with a complete “linear” economy where waste was always landfilled, it is still representative of an old conception that prioritizes the technical aspect and the economical profits over the environmental benefits linked with the use of the material for a next application in the same or another sector. The new concept of circular economy changes this paradigm by assigning a sort of value to the environmental profile of products that, often, can be translated also into economic profit. The circularity concept has pushed many industries, including the cement industry, to strive in obtaining a reasonable balance between technical and environmental properties of products. Consequently, waste materials are now more and more seen as by-products or can even obtain an end-of-waste status when certain criteria and conditions are fulfilled (European Commission, 2008). These policy developments together with the technological developments in various fields have significantly

improved the synergy between industries where waste materials from one producer can be a resource for another producer.

2. EFFORTS TO LOWER CO₂ FOOTPRINT OF CEMENT

The production of cement releases CO₂ through two sources: the decomposition of limestone into free lime and the combustion of fossil fuel to heat the raw materials needed to form the clinker minerals. The global average gross CO₂ emissions per ton of clinker is around 860 kg (Global Cement and Concrete Association, 2019). Because of growing commitments towards the decarbonization of industry and mitigation of greenhouse gases emissions, also the concrete industry is challenged and called to reduce its emissions (Biesbroek et al., 2010; Tol, 2018). Moreover, cement production is associated with depletion of natural resources which do not fulfil the principles of the circular economy (Aguiar et al., 2018). Therefore, many steps have been taken to reduce the CO₂ emissions in the cement industry and to reduce the natural resource use including: i) improving energy efficiency of the kilns, ii) replacing fossil fuel with renewable energy sources, and iii) substituting part of Portland cement with other cementitious materials. The latter has been identified as one of the opportune strategies for the reduction of negative environmental effects associated with cement manufacturing (Araos et al., 2016; Barcelo et al., 2013; Castellani et al., 2016). On this account, several types of materials also known as secondary cementitious materials (SCMs) have been extensively studied over the past decades (Cordeiro et al., 2009, 2008; da Costa et al., 2018; Law et al., 2015; Mo et al., 2017; Siddique, 2008; Vejmelková et al., 2012). Fly ash from coal combustion is a typical example of a waste material which has been used by the cement industry throughout the years especially due to the demonstrated pozzolanic activity of coal fly ash. However, in the light of increased awareness and commitments to climate change, and CO₂ reduction emission, coal combustion became an undesired source of primary energy (Zhao et al., 2020). In fact, coal combustion power plants generate CO₂ (also SO₂ and NO_x), and their operation is expected to be reduced in the near future. The decrease in CO₂ emissions is closely related to the abandonment of coal-based energy production has already taking place in several countries. In the European Union, GHG emissions should be cut to almost zero by 2050 (Biesbroek et al., 2010; Figueiredo et al., 2019; Saint Akadiri et al., 2020). The objective established by the mid-term and long-term energy strategies can be achieved only by progressively moving away from traditional coal combustion and towards renewable energy sources (Martí-Ballester, 2019; Scarlat et al., 2015). As a consequence, coal fly ash may become scarce compared to the present and its replacement

by other available and suitable SCMs may turn into a necessity (Castillo Castillo and Angelis-Dimakis, 2019; Fořt et al., 2021).

3. AIMS OF THE PhD RESEARCH

In this context, the work proposed in this thesis aimed at exploring the potential of biomass ash to substitute the traditional raw materials for clinker production or as secondary cementitious materials in blended cement formulations ensuring a base standard quality of cement products with a better environmental performance. Since the concepts of circularity and sustainability imply closing the loop of raw materials (e.g., including nutrients) the option of returning some specific biomass ash (i.e., *Chapter 3*) to soil for closure of the mineral balance was also investigated in parallel to the cement applications (i.e., *Chapters 3 and 4*). Harvesting of specific biomass types (e.g., wood, herbaceous) leads inevitably to nutrient removal from soils on which this biomass was grown and, if no countermeasures are taken, to reduction of the soil quality in the end. A common practice consists of leaving specific parts of the tree (e.g., foliage, small branches) in the forest to restore the nutrient cycle as much as possible, as these parts contain most of the nutrients in a tree. Recently, whole tree harvesting is increasingly applied in Europe as the marketability of the woody residues has increased. This trend is in line with the policy of the EU to reach a complete circular economy by 2050 (de Vries et al., 2021). By harvesting the entire above-ground part of the tree, the biomass removed by harvest can be 30% larger than compared to conventional stem-only harvesting (Aherne et al., 2012; Pels and Sarabèr, 2011). It is therefore also an option to combust these residues for energy recovery and to find suitable solutions for the biomass ash. The main findings of this thesis regarding both cement and soil applications of biomass ash will be discussed below. Lastly, general conclusions and perspectives on the circularity of biomass ash will be presented.

4. FINDINGS OF THE PhD RESEARCH

4.1. Potential of biomass ash as raw clinker material

An important hypothesis of this thesis is that biomass ash composition can be partially controlled throughout the energy chain (i.e., biomass used as fuel, combustion process adopted

and ash management practices) to obtain a material suitable to replace traditional raw clinker materials (mainly C_3S and C_2S minerals). To verify this hypothesis, we cross-checked data from two important databases (i.e., Phyllis (Energy research center of the Netherlands (ECN), 2012) and ALLASKA (Värmeforsk, 2014)) containing a large amount of data on biomass fuel and ash compositions and investigated the existing relations between the biomass fuels, the combustion process, and the properties of the generated biomass ash (i.e. *Chapter 2*). Common parameters used by the cement industry were applied here to assess the suitability of biomass ash as replacement of the traditional raw materials for clinker production or as secondary cementitious materials. The conclusion from *Chapter 2* pointed out that the combination of wood biomass with low exogenous inclusion (e.g., material that is collected involuntarily with biomass such as sand, soil, dust etc.) 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. However, the possibility to directly produce the right amount of the most important cement minerals (C_3S and C_2S) already in biomass ash from a selected match of biomass feedstock and combustion equipment was found to be not feasible. This observation suggests that the research effort should be directed towards mixing of biomass ash with traditional raw materials to obtain the right amount of cement minerals. Another option is to use biomass ash directly as secondary cementitious material provided that the ash already contains the C_2S mineral which has hydraulic properties. This option was found feasible for ash from combustion of a mixture of paper sludge and wood in a fluidized bed.

In this sense, the work conducted in *Chapter 2* gives valuable suggestions on the biomass fuel type to be combusted to obtain the desired balance between clinker forming elements and also informs on common practices that should be avoided to maintain a high quality of biomass ash. For example, bark and paper sludge have been identified as a suitable source of Ca but when these are combusted in a fluidized bed conversion technology (using a sand bed), a significant amount of sand is generally added to the final biomass ash composition. This combination of feedstock property and combustion technology leads to an undesired lower Ca/Si ratio. Samples of wood from riverbank maintenance activities and park pruning and trimming activities should also be avoided when considering applications of the ash as cement replacement since they are subject to soil, sand, stones and debris inclusions which are difficult to control and lead to very unpredictable ash compositions. Accurate cleaning is otherwise suggested (e.g., by means of vibrating bed) to minimize such unwanted inclusions.

A controlled and certified system for the “biomass ash value chain” that would guarantee the biomass fuel type combusted, the basic specs of the thermal conversion system adopted, and the biomass ash management practices, is recommended to improve the potential of biomass ash for cement application. In fact, certification can enable consistency of the quality of biomass ash batches. The bio-energy sector would then be able to provide a stable amount of biomass ash with given properties for this market. Biomass ash could be divided into classes according to its certified quality and be directed towards the corresponding suitable application. In summary, the application of biomass ash in cement formulations is expected to gain in importance and it is recommended to initiate work on developing standard tests for European (CEN) or international (ISO) standards for which the framework developed in Chapter 2 can form the starting point. In addition, it is recommended to organise the supply chain and application of biomass ash by an overarching “ash management” organisation that could ensure the quality of (mixed) ash streams. Potentially, the model of the Dutch organisation for coordination, management, and supply of coal fly ash (Vliegassunie) could be suitable for biomass ash too.

4.2. Biomass ash as secondary cementitious material or in soil applications

From the method developed in *Chapter 2*, wood derived biomass ash has been identified as the biomass ash with the highest potential to partially substitute raw clinker materials or also as secondary cementitious material. However, returning biomass ash to soil to partly close mineral balances could be a more sustainable utilization pathway for biomass ash although the work in this thesis shows that this option is not straightforward. The application of ash as soil improvement and/or fertilizer is conceptually more appropriate than mixing in cement since it closes the nutrient loop, thus avoiding nutrient depletion and a general soil quality deterioration. At the same time, some drawbacks are associated with this practice due to the relatively low nutrient availability in biomass ash, the potentially high metal content, and the potentially rapid pH increase of soil due to the high alkalinity of biomass ash. In a future circular economy, wood will be used in a cascading approach meaning that, after one or more recycling steps, it will be finally used for energy conversion. In most cases, the generated biomass ash will be contaminated with undesired components (metals) and, hence, it is doubtful whether these ashes would still be suitable for application in the soil.

Currently, criteria and recommendations for utilization of biomass ash in soil are based on total content of elements in the biomass ash. This approach was challenged in *Chapter 3* by comparing it with a leaching based approach. The chemical composition of biomass ash is characterized by large variation whereas the leached amount as a function of pH was shown to have consistent patterns that can be understood using basic principles of geochemistry. When the total content of elements in biomass ash was compared with the maximum potential leachability, the relatively mobile elements (i.e., Ca, Cd, K, Mo, Na, Zn, Cl and P) show a good correlation, while the relatively immobile elements (i.e., As, Ba, Cr, Co, Ni, Pb, Sn and V) do not show a correlation with the total content. A substantial part of the total content of the latter elements was found to be not accessible for leaching even at extreme pH conditions, implying a reduced environmental concern during application. An approach based on leaching could lead to substantially different results and a potentially more realistic quantification of elements released in soil applications in comparison to regulations based on total content. An approach of leaching assessment and new regulations could help improve the usability of biomass ash as soil amendment. Furthermore, leached concentrations of contaminants allow for a more direct comparison with undesirable (i.e., Maximum Tolerable Risk (MTR)) concentration levels in groundwater. This is extremely important when assessing the risk associated with the reuse of biomass ash in soil. When specific biomass ash samples were selected from the set of samples assessed in *Chapter 2* and tested as soil amendment in lab experiments, the concentrations of Cr, Mo and Zn in soil solutions at natural pH condition showed a substantial increase higher than the MTR. This implies that biomass ash can be potentially dangerous for the environment and that a leaching based approach can be helpful in evaluating the biomass ash usability while ensuring a safe use.

The re-use of biomass ash as partial cement replacement material is not in accordance with ASTM C 618 and EN 450-1 that are the standards governing the use of fly ash as mineral admixtures in concrete. These two standards preclude the use of any material not derived from coal (co-)combustion. In *Chapter 3* and *4* experiments with partial replacement of cement with the selected biomass ash based on the framework and criteria developed in *Chapter 2* were performed, despite the fact that none of the ashes comply with the current standard. The technical evaluation included an assessment based on compressive strength development, an important quality criterion for the building industry. A combination of different leaching tests was employed to assess the potential environmental impact of cement containing biomass ash under different application scenarios. In the Netherlands, the environmental properties of

construction products are regulated in the Soil Quality Decree (SQD). In the SQD, the leached levels for inorganic components are based on an eco-toxicological risk assessment, where 95% of the ecosystem does not indicate any demonstrable negative effects of the emissions from the construction product resulting from a service life of 100 years. When the cement specimens containing biomass ash were tested against the SQD limits, the release of environmentally relevant elements from all samples fulfilled the Dutch leaching criteria for reuse. The technical performance of cement mortars was influenced by the type and ratio of fly ash mixed with cement. The inclusion of 20 and 40% by weight of fly ash from wood and a mixture of wood and paper sludge combusted in a fluidized bed resulted in acceptable compressive strength values for different applications. Ash from wood combustion in a pulverized fuel installation (i.e., 40% by weight) performed the worst and failed to reach an adequate strength after 28 days.

Another aspect that was considered is the fate of the biomass-containing cement materials in a second (or subsequent) life phase. During a second life phase of the cement product (e.g., after demolition of a building) where the concrete is in a granular form and carbonation/aging processes contribute to a decreasing pH, the release of Cr, Mo and V increased to a level of potential concern for all blended cement formulations. In particular, the release of Cr was found to be higher than the SQD in all samples, whereas the release of Mo was above SQD in cement blends containing fly ash from a circulating fluidized bed installation that combusts a mixture of clean wood and fly ash from the combustion of wood pellets in a pulverized fuel installation. However, the release of all investigated inorganic compounds from existing common blended cements formulations was also found to not fully comply with the SQD in a granular second life application. The release of elements was also found to be controlled by the cement chemistry rather than by the included biomass ash. In this respect, biomass-ash containing cement does not perform environmentally worse than traditional cement formulations.

The conclusions from *Chapter 3* and *4* have evidenced some limits related to the current regulations and standards which govern the reuse of biomass ash in soil (total content versus leaching) and cement products (exclusion of biomass ash). The importance of a set of leaching tests that reflect the environmental performance of the biomass ash during its entire life cycle and in different applications has been highlighted instead. In particular, the realization of a circular approach regarding the use of biomass as renewable material and fuel would definitely benefit from a leaching-based approach by providing important information on the availability

of nutrients contained in the biomass ash for soil amendment purposes and the potential environmental risk due to the spreading of biomass ash in soils. Concerning the reuse of pure biomass ash in cement, the leaching approach has demonstrated that the release of environmentally relevant elements is essentially controlled by the traditional cement matrix and not substantially influenced by the biomass ash chemical composition. Moreover, a satisfying strength development at 28 days was obtained for investigated cement samples containing biomass ash. A revision of the EN 450 standard to consider the inclusion of pure biomass ash in the list of allowed fly ash types is suggested, also in view of ongoing developments towards sustainable energy production.

4.3. Life cycle assessment of biomass ash as secondary cementitious material

According to the findings of *Chapters 2, 3 and 4* the most practical reuse option for biomass ash is as secondary cementitious material. This application would have a substantial benefit on the carbon footprint of cement due to the reduction of CO₂ emissions that are associated with traditional cement production processes (i.e., calcination of limestone). On the other hand, potential release of inorganic compounds during the use and end of life stages could shift the potential impacts to human and eco toxicity related limitations. In *Chapter 5* a holistic Life Cycle Assessment methodology (LCA) was employed to verify and eventually quantify the mentioned trade-off between benefits and burdens of biomass ash inclusion in cement products. The current waste management practice for biomass ash (i.e., landfilling) was compared to reuse of biomass ash as a secondary cementitious material in cement since, as explained before, this was found to be the most reasonable scenario for biomass ash reuse.

A reduction of the impact on global warming potential (GWP) and all other non-toxic categories assessed was observed for the different replacement ratios of traditional cement with biomass ash modelled (i.e., 20 and 40% by weight) when compared to landfilling. In detail, the reduction of GWP was found to be between 11-26 % when biomass ash was blended with cement instead of being landfilled. The GWP reduction and all other non-toxic impacts were related essentially to the strength development of cement formulations. To perform a fair comparison between traditional cement and cement that includes biomass fly ash, the specimens must have the same functionality. The functionality of specimens was defined by their compressive strength developed after 28 days. The gaps between the compressive strength of the specimens were

assumed to be filled by adding traditional cement to the biomass ash containing blends. It was observed that the amount of additional traditional cement needed to keep up with the partial strength loss that was detected by the replacement with biomass ash determined most of the impacts on GWP and all other non-toxic impact categories. Therefore, biomass ash (with low CO₂ footprint) that shows a high compressive strength would need less traditional cement (with a larger CO₂ footprint) to obtain similar performance.

Chapter 5 gives important insight in how to consider strength development in LCA studies of alternative cements and in the uncertainty of results when this parameter is disregarded. It is thus suggested to include strength losses into LCA studies that aim at assessing or comparing the environmental performance of biomass ash containing cements. However, this thesis does not assess the potential effects of durability issues of cement containing biomass ash in LCA results. Durability issues might decrease the lifetime of biomass ash containing products with a consequential reduction of environmental performances. Another relevant observation is that the impact to human toxicity carcinogenic (HTc) and ecotoxicity (ET) LCA categories was found to be mainly dominated by the leaching of Cr from landfilling of pure biomass fly ash (reference scenario) and the leaching of Ba, Cu, Cr (VI) and Zn from the second life stage of biomass ash containing cement products (i.e., reuse of the crushed cement after service life as granular construction material in road base applications). Potential impacts to (eco)-toxic categories of inorganic emissions due to leaching is often disregarded in LCA studies since (i) leaching is difficult to model, (ii) modelling a specific scenario requires data from laboratory tests that can be expensive (iii) current commercial LCA databases include generic and not customizable processes only related to landfilling. *Chapter 5* provides a list of parameters for each impact category to which the LCA model is most sensitive (including the non-toxic categories). The methodological approach proposed in *Chapter 5* can help LCA practitioners in the construction sector on the modelling of the use and end of life phases of cement blended with biomass ash.

In this thesis, the LCA modelling was taken a step further beyond the state of the art by including leaching test results and environmental criteria from *Chapter 4* in the LCA model. Based on this combination of findings it can be stated that including biomass ash into cement is a more sustainable option than landfilling. The impacts on non-toxic categories are reduced and potential toxic impacts do not represent an unacceptable risk.

The European community has put a lot of effort in assessing the sustainability of construction products and has come up with a CEN/TC350 series of standards. The series of standards developed by this Technical Commission (TC) defines practices at the product level (i.e., EN 15804) and the building level (i.e., EN 15978), and they comprehend the assessment of environmental (including 7 LCA impact categories), economic and social aspects of construction works. These standards are applicable to marketable products such as Portland cement and concrete of different classes including those classes which include by-products from industries (e.g., steel slags and coal fly ash). These standards assist on performing a LCA but do not provide benchmarks of reference values for the different environmental impact categories considered. Therefore, no comparison of environmental performance between different products is possible. Moreover, pure biomass ash is currently excluded since it is not allowed in cement formulations according to EN 450. It is reasonable to assume that once the scope of EN 450 will be widened to also include pure biomass ash (or another standard will be developed for that purpose) the same quality and environmental assessments described in the series of standard CEN/TC 350 will apply. In this sense biomass ash is still behind its potential for beneficial reuse, and what is really missing it is not a dedicated standard or regulation but a common framework on how to assess the most sustainable reuse option among the various alternatives for biomass ashes (e.g., as raw material for clinker, as secondary cementitious material, as fertilizer, soil improver or stabilizer). Life cycle assessment represents an optimal methodology to choose the most sustainable option between the available alternatives for reuse and recycling of biomass ash since LCA methodology has the potential to simultaneously account for environmental and technical properties. Currently there are no specific LCA guidelines that harmonize the methodology to calculate and compare impacts of biomass ash (and other types of incineration ash) when re-used or recycled in construction products, forestry soils, fertilizers, or other applications. The lack of a common approach leads to difficulties when it comes to comparison of LCA studies due to different system boundaries, different impact methods employed, different allocation procedures adopted etc. A harmonized method would increase comparability of results. Furthermore, the credibility of LCA findings would also benefit from applying a harmonized methodology. The assessment of the sustainability of biomass ash management options would become more straightforward if harmonized rules were to be developed. To strengthen utilization possibilities on a supranational scale, improved knowledge exchange is required. This thesis has provided guidance on how to model the life cycle and assess the sustainability of the reuse of biomass ash (and the approach is equally

relevant for any other type of incineration ash) in cement products as alternative to landfilling, and the most influencing parameters have been identified.

5. CONCLUSIONS AND PERSPECTIVE ON CIRCULARITY OF ASH FROM THERMAL CONVERSION OF BIOMASS

The production of biomass ash is going to grow in the coming years and its penetration in the circular economy market for industrial by products is also expected to become a reality. In fact, utilising biomass ash in cement products rather than landfilling has an environmental advantage from a life cycle perspective as it was demonstrated in this thesis.

Biomass ash can be successfully used as raw material for clinker production and substitute a large part of the raw feed minerals. The specific stream of fly ash from clean wood combusted in a pulverized fuel installation has the highest potential of replacement of raw clinker materials. However, mixing of different biomass ash streams to resemble the traditional raw clinker materials will be the key to a potentially 100 % biomass ash based clinker. This practice can be successful only if the biomass-conversion system-ash management chain is going to be controlled and certified.

The direct use of biomass ash as secondary cementitious material is also expected to be feasible for specific biomass ash types. This is the case of fly ash from fluidized bed combustion of a mixture of paper sludge and wood. The direct use as secondary cementitious material is suggested for all those biomass ashes that show already hydraulic and/or pozzolanic activity. When the biomass ash contributes to strength development, the replacement of 20 and 40% by weight of Portland cement with biomass ash produces blended cement suitable for application such as non-structural application, pavements, and roads.

From a circular perspective, the inclusion of biomass ash as such in in clinker or cement and concrete products contributes to circularity but should not preclude the future circularity of the resulting materials. When biomass ash is used in cement, the obtained biomass ash containing products will also be introduced in the cement/concrete cycle. The circularity of cement/concrete products is not expected to be affected by inclusion of biomass ashes from an environmental perspective, since the environmental performance of cement blended with biomass ash is equal to that of traditional cement during all the considered life stages.

Looking again at the circularity of biomass ash one may argue that harvesting of biomass subtracts nutrients from the soil and that if these are not returned to the soil, the nutrient cycle is not closed.

Two main scenarios which are related with the energy production from biomass and supposed to influence the beneficial utilization of biomass ash are identified below:

1. Biomass as renewable fuel. In this scenario biomass (wood) is grown to function as fuel for energy production. If the biomass is combusted within a restricted distance from where it was grown, the biomass ash obtained in this scenario could be used to restore the nutrient balance or in general as soil amendment. It should be noted that biomass ash does not contain the macro nutrient Nitrogen which should be compensated by using fertilizer. Biomass ash from this scenario can still contain significant concentrations of metals. A leaching based approach should be applied to obtain a more realistic evaluation of the potential risk associated with spreading of ash to the soil.
2. Biomass as a raw material/product. The biomass (wood) is first destined for a different use then energy production (e.g., paper making, furniture making, and construction materials) and after one or more recycling steps is used for energy production. The biomass ash originating from this scenario is most likely contaminated and difficult to trace back to the origin where the biomass was grown. For this type of ash use in cement should be preferred over the use in soil.

Depending on the general scenario depicted, biomass ash can be used as a substitute for raw clinker materials, a secondary cementitious material, or as a soil amendment. These applications improve the circularity of biomass ash by avoiding this material to be landfilled but rather be used in applications. Using biomass ash as clinker raw material or secondary cementitious material can contribute to save traditional resources and energy that are employed during conventional cement production. The reuse of biomass ash in soil can help to balance the nutrients that are taken away with biomass harvesting.

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Summary

The growing use of biomass for energy production and the corresponding substantial amounts of biomass ash generated calls for development of sustainable utilization options rather than landfilling. Next to reducing the amount of biomass ash sent to landfills, the reuse of biomass ash in cement products can decrease the greenhouse gas emissions of the cement industry due to lower energy and raw materials consumption associated with traditional cement production process. Alternatively, the biomass ash can be employed in soil to restore the natural balance of elements taken up by the original harvested biomass, or as a fertilizer to provide macro- and micronutrients which are essential for plant growth.

In this thesis, three potential options of biomass ash utilization were investigated:

- 1) Biomass ash as a valuable source of inorganic elements able to substitute raw materials already used in the cement industry.
- 2) Biomass ash as a direct replacement of the traditional Portland cement in blended formulations.
- 3) Biomass ash as soil amendment.

Each of the above mentioned options requires different functionality of biomass ash. Required biomass ash functionality, in turn, is defined by its chemical, mineralogical and physical properties. These properties are strongly influenced by the biomass feedstock (e.g., type of biomass, plant species or specific parts of plants) and biomass thermal-conversion techniques and conditions employed. Together with the technical functionality of an ash, the environmental aspect must be also considered when valorising biomass ash as secondary material. The potential enhanced leaching of contaminants represents a relevant concern regarding the application of biomass ashes in cement products and as soil amendment. Additionally, the environmental impacts associated with the entire life cycle of biomass ash applications should be considered in order to avoid any environmental impact-shifting. Focusing exclusively on the reduction of greenhouse gas emissions still can result in a product

with an overall higher environmental impact compared to traditional solutions. However, there is little information available in the current literature on biomass ash leaching properties, the potential environmental risks and the life cycle impacts which are associated with biomass ash valorisation options. This thesis aimed at:

1. Evaluating the potential of biomass ash as a replacement of traditional raw materials for clinker production, as secondary cementitious material in blended cement formulations or as soil amendment.
2. Evaluating the environmental properties (including the Life Cycle Assessment) of the ash and ash based obtained products.

The first part of the thesis (*Chapter 2*) is dedicated to exploring to which extent the biomass ash composition can be controlled by fine tuning of the biomass feedstock, thermal conversion and the ash management chain. In *Chapter 2*, the most suitable biomass ash type was assessed to replace raw materials in cement clinker production or to serve as secondary cementitious material. The assessment was based on a novel tailored approach using a large dataset of biomass fuel and ash compositions. The conclusion from *Chapter 2* pointed out that the highest replacement potential can be reached by a combination of wood biomass with low exogenous inclusions and a high bark content that is combusted in a pulverized fuel installation. This type of ash can potentially substitute a considerable amount of raw clinker materials. Fly ash from fluidized bed combustion of combined paper sludge and wood/bark was identified as having the required properties to perform as a secondary cementitious material. The theoretical approach proposed in *Chapter 2* can help to evaluate beforehand the potential of biomass ash as substitute for traditional cement materials. Next to the selection procedure based on technical properties, it was found important to investigate the environmental aspect of biomass ash.

Chapter 3 investigated the pH-dependent leaching and the leaching potential of major and trace elements for a wide range of biomass ashes with the aim of identifying common and specific release trends among the different types of biomass ash, the feedstock and/or the conversion technology. Next to this, a technical and environmental assessment of selected biomass ash for application in soil or in cement mortars was performed, using two approaches: one based on the total element content, and one based on the leaching of elements. Results showed that there is a correlation between the leaching of relatively mobile elements (i.e., Ca, Cd, K, Mo, Na, Zn, Cl and P) and their total content, but the same correlation was not observed for the relatively immobile elements (i.e., As, Ba, Cr, Co, Ni, Pb, Sn and V). Therefore, the majority of the total

content of immobile elements was found to be non-leachable even at extreme pH conditions, implying a reduced environmental concern during application. Considering these findings, an approach based on leaching leads to different conclusions in comparison to current regulations that are based on the total content of elements. An assessment approach based on leaching can increase the utilization rates of biomass ash in soil. In addition, leaching values can be directly compared to existing limits for soil or groundwater concentrations to assess the risk more realistically. Soil and cement matrices were found to control the release of some desired and undesired elements, thus underlining the importance of the application scenario when assessing environmental performance of biomass ash.

Based on the results obtained in *Chapter 3*, the study of cement blends with selected biomass ash was developed further in *Chapter 4*. *Chapter 4* evaluates the technical and environmental performance of blended cement mortars containing different replacement ratios of selected biomass fly ashes. The technical evaluation consisted in measuring the compressive strength development. A combination of different leaching tests and comparison with emission criteria specified in the Dutch Soil Quality Decree (SQD) was employed to assess the potential environmental impact of cement containing biomass ash under different application scenarios. Cement mortars with 20 and 40% by weight replacement of Portland cement with biomass fly ash from two types of installations were tested for their compressive strength and leaching behaviour. The inclusion of 20 and 40% by weight of fly ash from wood and a mixture of wood and paper sludge combusted in a fluidized bed resulted in acceptable compressive strength values for different applications. When the blended cement specimens were tested against the SQD leaching limits, the release of environmentally relevant elements from all samples fulfilled the criteria for reuse. The technical performance of cement mortars was influenced by the type and ratio of fly ash mixed with cement. However, the environmental performance was driven by the cement matrix that controlled the release of contaminants. The results of *Chapter 4* thus showed that the use of biomass fly ash as a secondary cementitious material can potentially reduce the carbon footprint of cement formulations while maintaining acceptable technical and environmental performance.

In *Chapter 5* the potential environmental life cycle impacts associated with the current waste management practice for biomass ash (reference scenario, i.e., landfilling) and the potential of reuse as a secondary cementitious material in cement are compared by means of a Life Cycle Assessment methodology (LCA). Results showed that utilization of biomass ash in cement is

the currently available risk limits based on soil or ground water concentrations of regulated elements, thus offers a more realistic evaluation of the risk associated.

Specific types of biomass ash were found to be able to replace up to 40% of cement in blended specimens without significantly reducing the compressive strength at 28 days. The technical properties of blended cement were influenced by the quality of biomass ash, but the release of elements by leaching was essentially determined by the cement matrix. The addition of biomass ash up to 40 % by weight to cement formulation did not affect the environmental performance of the cement material. Considering the life cycle perspective, the use of biomass ash in cement is always a more sustainable option than landfilling. The novel LCA approach developed in this thesis has identified a significant influence of the technical properties (i.e., compressive strength loss) on the results in all non-toxic environmental impact categories. The LCA thus showed that technical properties of biomass ash should always be accounted for in life cycle assessments in addition to its environmental properties.

Acknowledgements

I would like to express my deepest appreciation to my promotor Prof. Rob Comans for his constructive criticism and valuable advice that I received during the entire time I spent under his supervision. Thank you for always pushing me and challenging me to improve as a scientist.

I would also like to extend my sincere gratitude to my supervisor Dr André van Zomeren for his relentless support. Your insightful suggestions cannot be underestimated. I really enjoyed the time we spent together both inside and outside the working environment.

I am grateful to Dr Jan Pels for his support on the initial part of my PhD, for his feedback on the thesis chapters and for introducing me to the biomass ash world.

Many thanks to all my ex-colleagues at ECN for the support and the nice talks during the coffee breaks and group outings. Special thanks to Petra Bonouvrie for her assistance during the time I spent in the laboratory. I am also grateful to dr. ing. Joris Dijkstra for his valuable contribution to the work performed in Chapter 3.

I would like to recognize the assistance I received from Natalie Carr on cement related matters and the advice from Anders Daamgard on the LCA modelling approach adopted in Chapter 5.

Particularly helpful to me during the last stretch of my PhD was the people from my actual research group in Siena who always encourage me during the finalization of the thesis.

I wish to thank all the friends I have found along the way (Masoud, Lili, Varun, Leo, Chiara, Tommaso, Sascha, Sol, Aki, Eline, Billy, Joan and all the crazy members of the “Den Helder crew”) as well as the friends from “Odeon”. I share with you the sweetest and funniest memories of my time in The Netherlands.

A huge hug to Gianna for designing the cover.

I am deeply indebted to Tania. The completion of my dissertation would not have been possible without your unwavering support. You are the most precious gift I brought back with me from The Netherlands.

Thanks to my family for never letting me feel alone despite the distance. In times when the load of distance began to be felt, my brothers would arrive in The Netherlands washing away all fears. Thanks “Banda Fratelli”!

My biggest thank goes to Luisa. You had the courage and the madness to follow me on this journey. You drove me when I was lost or too tired to continue. Well, look how far we have come!

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The SENSE Research School declares that **Lorenzo Tosti** has successfully fulfilled all requirements of the educational PhD programme of SENSE with a work load of 33.7 EC, including the following activities:

SENSE PhD Courses

- o Environmental research in context (2013)
- o Research in context activity: 'Organizing committee of the BioGeoCivil Summit' (2015)

Other PhD and Advanced MSc Courses

- o Life Cycle Assessment training course using the EASETECH software, Technical University of Denmark (2014)
- o Project and time management, Wageningen Graduate Schools (2014)
- o Scientific writing, Wageningen Graduate Schools (2016)

External training at a foreign research institute

- o Advanced use of SimaPro, Pré-Sustainability, The Netherlands (2015)
- o Material flow analysis, STAN software utilization workshop, Austria (2016)

Oral Presentations

- o *Development of new cement formulations containing paper sludge fly ash as secondary cementitious material.* 9th International Conference on the Environmental and Technical Implications of Construction with Alternative Materials - Resource Efficiency in Construction, 10 –12th June 2015, Santander, Spain
- o *Life Cycle assessment of the reuse of fly ash from paper sludge combustion in cement formulations.* 5th International Conference on Industrial and Hazardous Waste Management, 27- 30 September 2016, Chania, Greece
- o *Life cycle assessment (LCA) of cement containing biomass fly ash as secondary cementitious material (SCM).* BioGeoCivil Summit, 18 -19 November 2015, Delft, The Netherlands
- o *Towards the Development of CO₂-Neutral Renewable Cement (BioCement): Aims of the project and preliminary results.* Jong-ECN EXPO, 21 August 2014, Petten, The Netherlands

SENSE coordinator PhD education

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The research described in this thesis was financially supported by the Dutch Organisation for Scientific Research (NWO), Domain Applied and Engineering Sciences (formerly Technology Foundation STW).

Financial support from Wageningen University and Research for printing this thesis is gratefully acknowledged.

Cover picture and design by Benedetta Giannoni.

Printed by ProefschriftMaken.nl

2021