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

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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 42.5öMPa at 28ödays. Replacement rates of 40% developed a lower strength (30 and 33.5öMPa), but were still suitable for applications. The pulverized fuel ash perform 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.

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 CO_2 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 CO_2 emission per ton of cement is estimated to be around 900 kg, accounting for 5–8% of total human atmospheric CO_2 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

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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) (Obernberger 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 × 40 × 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.

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, 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, 2013) is suitable for an intended use scenario

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[a]	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 20_FA2 20_FA3	40_FA1 40_FA2 40_FA3

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

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, 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 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 HNO_3:$HClO_4$:HF (i.e. 9:1:1) for 10 h 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.

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. Fig. 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

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.

Major elements (% dry)	FA1	FA2	FA3	OPC reference	Coal fly ash (Class C) (Siddique and Khan, 2011; Taylor, 1997) MIN-MAX	Coal fly ash (Class F) (Siddique and Khan, 2011; Taylor, 1997) MIN-MAX	Biomass ash (Energy research center of the Netherlands (ECN), 2012) 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_2O_3	2.8	3.2	8.6	1.9	13–21	20–30	0–14 (3)
Fe_2O_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_2O	7.8	9.35	0.93	0.52	0–2	1–4	0–35 (13)
Na_2O	0.74	1.3	0.77	0.16	0–7	0–3	0–23 (1)
P_2O_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[a]	8.5b	15[b]	4[b]	3[b]	0.3–2	0.4–7	0.1–64 (10)[c]

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

[a] LOI means Loss on Ignition. If not specified the LOI temperature is unknown.
[b] Measured at 950 °C.
[c] Measured at 550 °C.

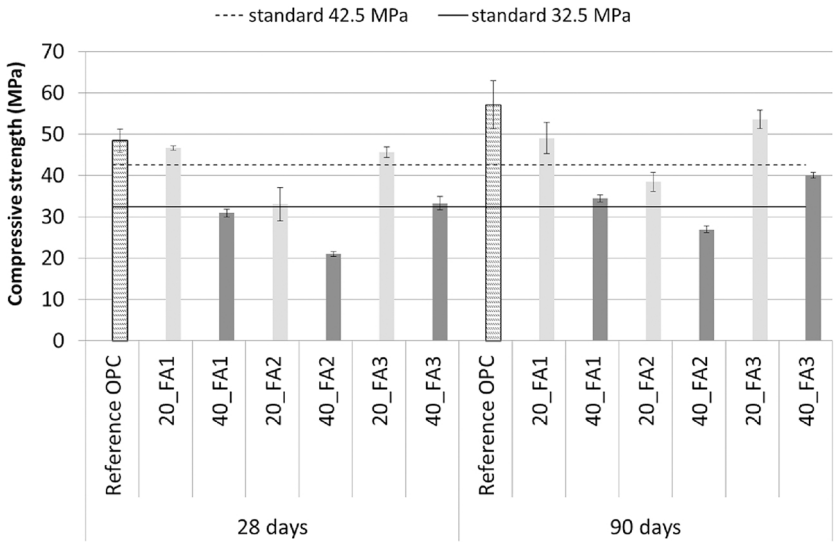

Fig. 1. Compressive strength development of mortars containing FA1, FA2 and FA3 after 28 and 90 days. The vertical bars indicate the standard deviation. The dotted and continuous lines indicate the minimum compressive strength requirements.

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 SiO_2 (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 (2009) (clean wood ash), Udoeyo et al. (2006) (wood waste ash) and Lessard et al. (2017) (biomass fly ash) have substituted 10–30% of cement with biomass ash and measured a compressive strength after 28 days ranging from about 60–97% 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.

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). Fig. 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.

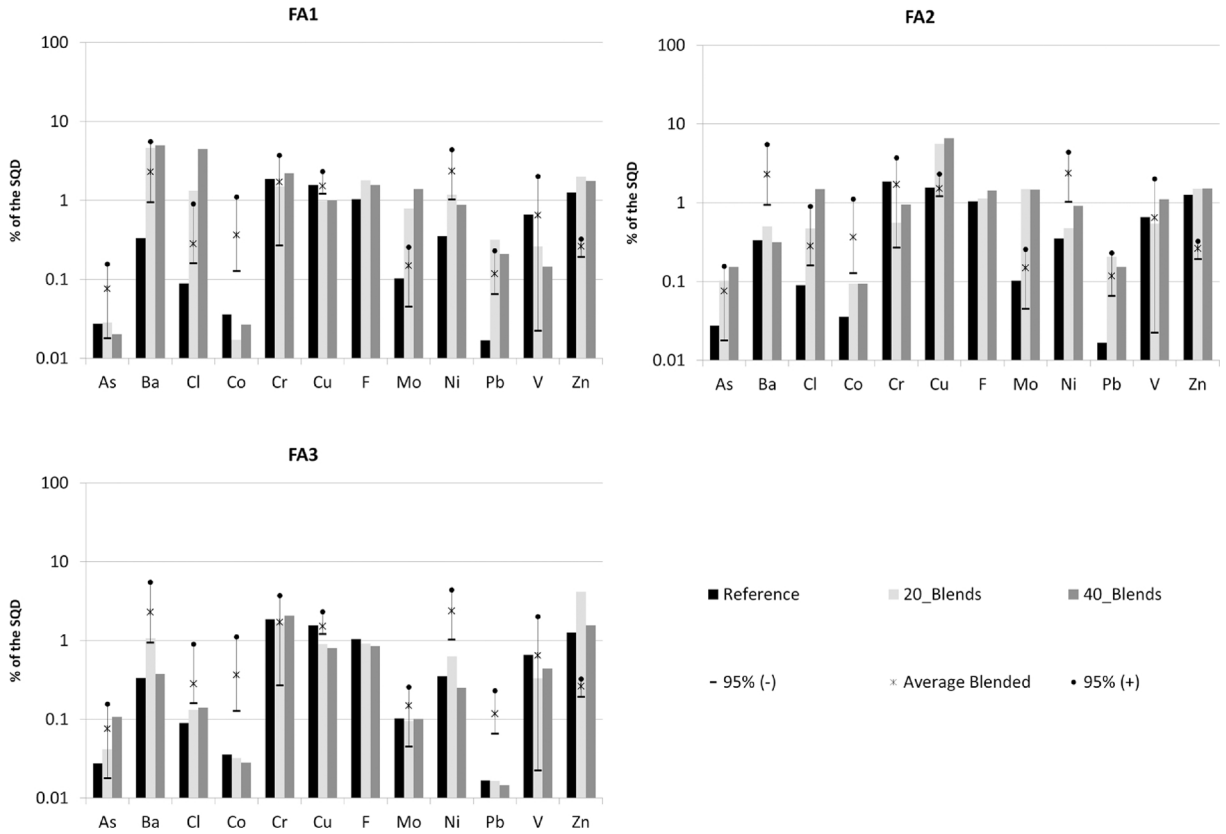

Fig. 2. Cumulative release after 64 days of reference mortar and mortars containing biomass fly ash. The range of pH measured during experiments is between 11.3 and 12.1. The cumulative release is expressed as percentage of the maximum allowed release of the Dutch Soil Quality Decree for shaped construction 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.

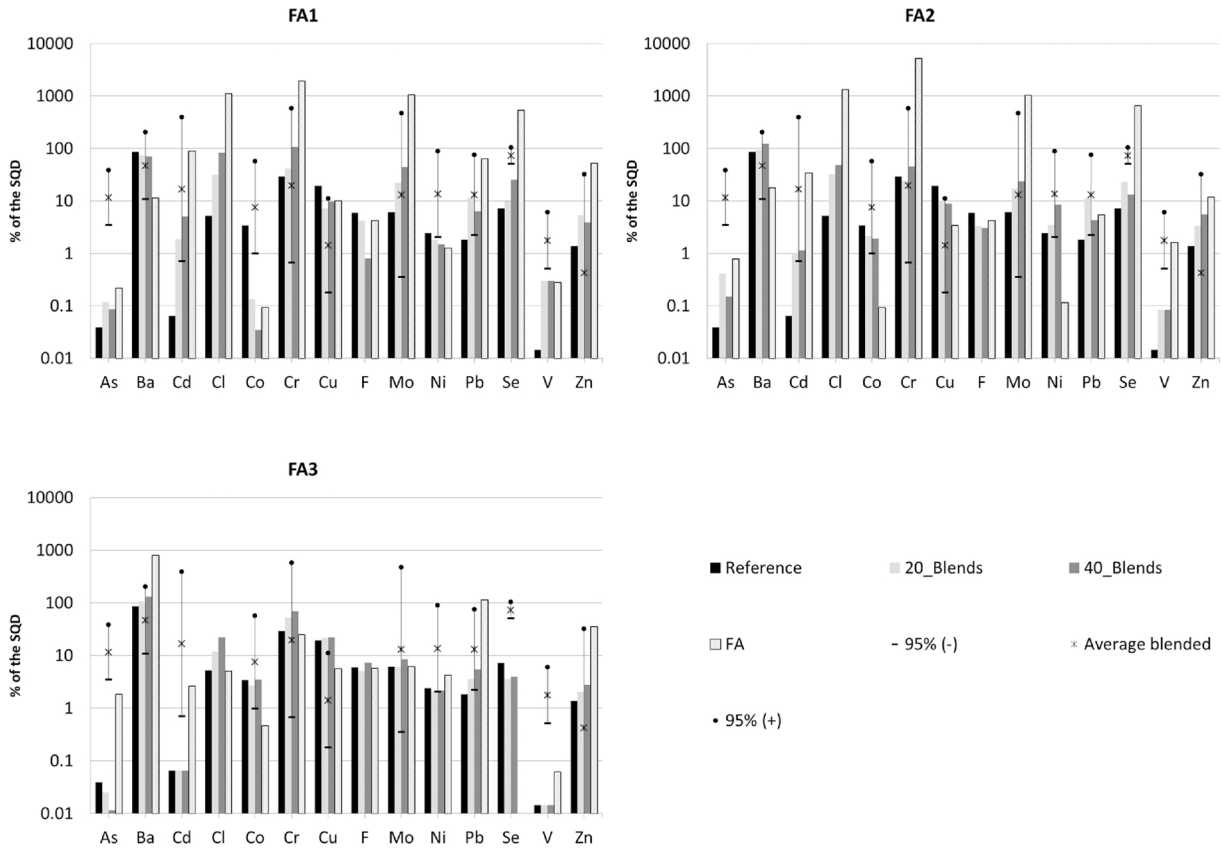

Fig. 3. Release of the batch tests on the crushed cement mortars and the corresponding pure fly ashes at L/S 10 and natural pH. The pH range of pure fly ash is 12.7–13 whereas for mortars is between 12.5–12.7. The release is expressed as percentage of the SQD limit value. The black cross indicates the average of blended cements (van der Sloot et al., 2008) with corresponding 95% confidence level.

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.

Fig. 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).

When the relative emissions from the crushed fly ash mortars (Fig. 3) are compared to the relative emissions of the monolithic fly ash mortars (Fig. 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 Section 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 Section 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

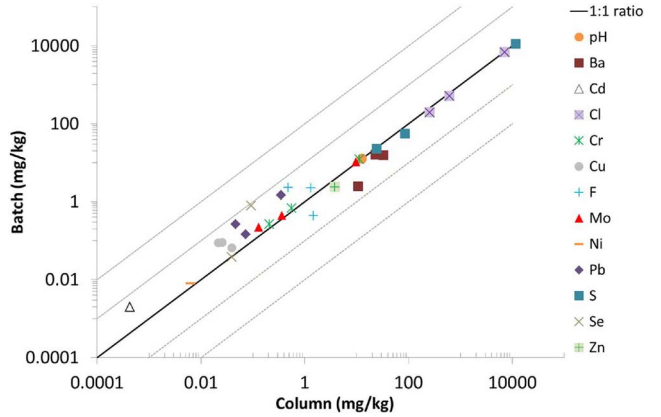

Fig. 4. Comparison between batch and column data for samples FA1, 20_FA1 and 40_FA1 at liquid to solid (L/S) ratio of 10. The black line indicates a ratio of 1,i.e. equal emissions between both methods. The grey dotted lines indicate a factor 10 and 100 of variation.

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).

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. Fig. 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 (Fig. 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. Fig. 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.

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 Fig. 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 Fig. 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 aging. 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 (Fig. 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 behaviour 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

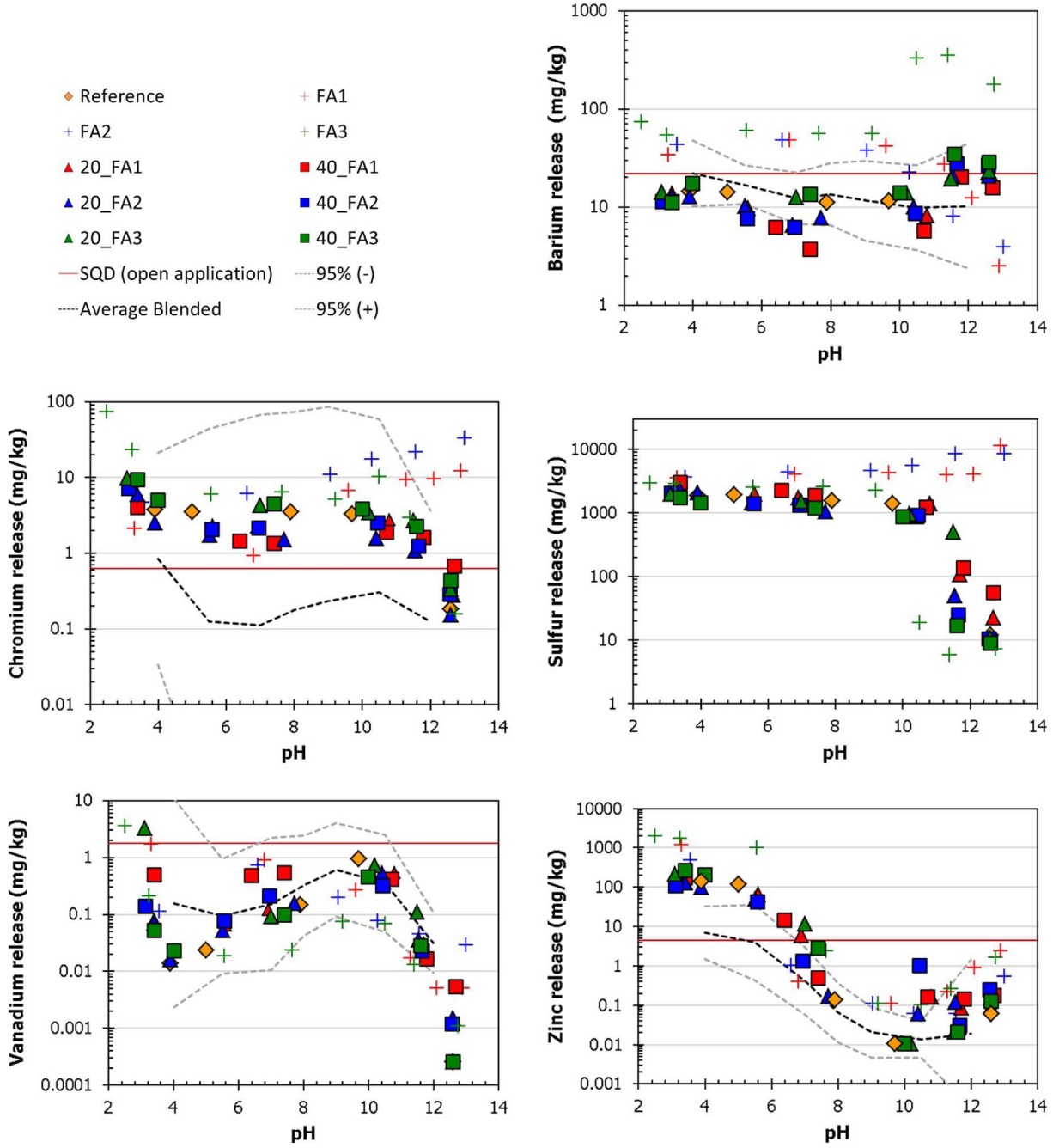

Fig. 5. Leaching behaviour of Ba, Cr, S, V, Zn, as a function of pH. Samples FA1, FA2 and FA3 are reported together with the corresponding blended mortars and reference OPC. The black dotted line represents the average of blended cements and the grey dotted lines the 95% confidence level. The red line indicates the SQD limit values for open application of granular construction materials. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

solely related to the inclusion of fly ash but also to the cement leaching properties. The pH dependent leaching behaviour 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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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.resconrec.2018.03.004.

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