Contaminated biomass fly ashes - characterization and treatment optimization for reuse as building materials

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Contaminated biomass fly ashes – Characterization and treatment optimization for reuse as building materials

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ABSTRACT

The incineration of treated waste wood generates more contaminated fly ashes than when forestry or agricultural waste is used as fuel. The characteristics of these biomass fly ashes depend on the type of waste wood and incineration process parameters, and their reuse is restricted by their physical, chemical and environmental properties. In this study, four different fly ash types produced by two different incineration plants were analysed and compared to Dutch and European standards on building materials. A combined treatment was designed for lowering the leaching of contaminants and the effect of each treatment step was quantified. A pilot test was performed in order to scale up the treatment. It was found that chlorides (which are the main contaminant in all studied cases) are partly related to the amount of unburnt carbon and can be successfully removed. Other contaminants (such as sulphates and chromium) could be lowered to non-hazardous levels. Other properties (such as particle size, LOI, oxide and mineralogical compositions) are also quantified before and after treatment.

1. Introduction

Worldwide increased concern of the CO_2 emissions and dependency on fossil fuels leads to an increasing use of renewable energy sources in order to decrease the greenhouse emissions. One of the possible renewable energy sources is 100% biomass that can be used as a replacement of coal in power plants. These bio-power plants use mainly ‘waste’ or residue wood streams as fuel to produce heat, which is then consumed in steam turbines to generate electricity to be supplied to the electricity grid. The generated combustion fly ashes are collected and mainly disposed of at landfill sites. However, those responsible for the disposal of fly ash are regularly seeking potential ash utilization options because of high landfilling costs and the increasing banning of these on landfill sites. Nowadays, pulverised coal fly ash is mainly applied in cement- and asphalt-based concrete mixtures due to its physical and chemical properties. Fly ash is a fine material that can be used as filler in concrete mixtures. Also, due to its pozzolanic activity, it can be used as a binder to partly replace cement and therefore reduce the use of natural resources. In the Netherlands the majority of coal combustion fly ash is applied (Vliegasunie, 2008).

The use of biomass as fuel in power plants leads to the production of fly ashes which are different from the ‘conventional’ coal combustion fly ash. These ashes created from burning biomass have different characteristics and properties in comparison to coal combustion fly ash. It has become important to find new ways for the reuse of biomass fly ashes, e.g. in concrete mixtures. The fly ash obtained from the incineration of waste forest wood, agricultural waste and co-firing of biomass and other fuels has been investigated previously (Berra et al., 2015; Cheah and Ramli, 2011; Jaworek et al., 2013; Li et al., 2012; Lima et al., 2008; Pöykiö et al., 2009; Rajamma et al., 2015, 2009). However, the fly ash generated from the burning of contaminated wood has been studied less (Berra et al., 2015) and its reuse has not started because of the following reasons:

1. biomass fly ash is a chemically and physically variable product, which makes its combination with cement more challenging. Its particle size distribution, loss on ignition, density, specific surface area, leaching, as well as pozzolanic/cementitious properties need to be tested to confirm its suitability;
2. biomass fly ash contains contaminants like lead, zinc and chromium and large amounts of chlorides that may have negative influences on the hydration of cement;

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3. as replacement of cement, its slow pozzolanic activity influences the hydration process, consequently lowering the properties of concrete at early ages;
4. so far there is no certified treatment method to sufficiently remove the contaminants and increase the reactivity of contaminated fly ash, which could make its utilization more cost-efficient and sustainable.

The biomass fly ash created from burning biomass has different characteristics and properties in comparison to coal combustion fly ashes because of the different combustion input and therefore, additional research is needed to establish its applicability as building material.

The first concern of such by-products is their environmental impact, and how it is evaluated based on the legislation (Landfill Ban Decree, 2012). In the case in which the fly ashes are considered hazardous or unfit for landfilling, a treatment must be envisaged before their disposal can take place. Furthermore, in order not to just lessen their environmental impact, but also to render such secondary materials useful, a number of other factors need to be taken into consideration. A number of utilization routes can be envisaged for these fly ashes, by comparison with the uses of coal combustion fly ash and other secondary building materials in concrete mixes. A first of these routes is application in concrete mixes as inert filler. A second application route is as secondary binder, in which case the chemical interactions between the bio energy fly ashes and water and/or cement becomes of interest. In this case, the bio energy fly ashes must comply with the environmental laws (Soil Quality Regulation, 2013) which define a building material (see Section 3), but a pozzolanic or hydraulic activity is not needed on its part.

In this research different types of fly ashes from two power plants are investigated. Each power plant has its own technology of biomass fly ash generation, which is known to be a factor influencing the quality of the obtained fly ashes (Lima et al., 2008; Rajamma et al., 2009). However, one thing they have in common is that the generated biomass fly ashes cannot be reused as they are because of their concentration of unburned components and harmful substances (metals and salts). To get more insight about these fly ashes in general, background information about the origin of the material and production is very important.

Waste wood can be divided into three different classes, namely A-wood, B-wood and C-wood (National Waste Management Plan, 2010). Not all these types of timber are suitable as fuel for the bio-power plants because of their components. The wood waste used in the bio-power plants considered in this study consists mainly of B-wood, which includes painted, varnished and glued wood, or wood-wool composite boards. Other compositions, such as paper sludge residue or organic municipal waste residues, are also used as fuel.

There are different types of combustion chambers available for the incineration of waste. The two mainly used types are the grill oven (furnace) and the fluidized bed incinerator (Doudart de la Gree, 2012).

The grill oven

The grill oven consists of the following devices: moving tiles for the transport of waste materials; combustion zones; a water basin and an air suction system. The transport tiles can shift and tumble under an angle over each other. The waste undergoes various stages of the combustion process, like drying, degassing, and finally burning under temperatures around 850 °C. After a combustion time of around one hour, the solid combustion residues left on the grate (bottom ash) are water-quenched.

In general, a sufficiently high temperature (above 850 °C), the presence of oxygen (residual content of at least 6% in the flue gases), sufficient stand time (at least two seconds) and thorough mixing of the flue gases should provide a complete burning of the wood.

The fluidized bed incinerator

In this type of incinerator, the biomass is fed to the fluidized bed, which contains a large amount of sand (an inert, non-combustible material). A cyclone separates the solid and unburnt particles from the flue gases and carries it back to the bed.

There are two main types of fluidized beds. In the first one, the velocity is chosen so that the sand and the fuel just perform a bubbling motion. This can be called a stationary fluidized bed or a bubbling fluidized bed (BFB). In the second type, the speed of the airflow is further increased creating flows that are carrying sand and fuel. Such an installation is called a circulating fluidized bed (CFB). Compared to a BFB, the CFB has the advantage that by the greater turbulence the heat transfer will be higher, which means a lower flue stream resulting in a highly efficient system. The disadvantages of the CFB are the higher use of electric power due to the need for an increased airflow and the higher dust concentration in the flue gas. Most of the ashes, however, are simply separated from the flue gas in the cyclone. Unburnt particles from the flue gases are going back to the combustion chamber. That process is controlled by the cyclone. After this, there is another cyclone that captures red-hot ash particles and ash particles greater than 10 μm. The fly ash that is removed by the cyclone is stored in closed fly ash silos.

In general, fly ashes in the grill oven are collected in the following way: coarser particles in the boiler, finer particles in the electrostatic filter and in the cloth filter. In the fluidized bed incinerator, fly ash is collected as follows: coarser particles in the cyclone and finer particles in the electrostatic filter.

2. Materials

The biomass fly ashes used in this study were collected from the cyclone and electrostatic precipitators of two different power plants in The Netherlands. The reason for this approach is that fly ashes generated in power plants are inherently variable materials, because of several factors. Among these are the type and mineralogical composition of the fuel, degree of pulverization, type of furnace and oxidation conditions including fuel ratio and the manner in which fly ash is collected, handled and stored before use.

Since no two installations or plants have all of these factors in common, fly ash from various power plants are likely to be different. The following types of bio-power plant fly ash are examined (Table 1): boiler fly ash (BF1) and cyclone fly ash (BF2) from a plant in Hengelo, in the Netherlands and cyclone fly ash (BF3) and filter fly ash (BF4) from a plant in Alkmaar, in the Netherlands. Using several types of fly ash, a more general approach of treatment and application can be sought.

For example, in the Alkmaar plant, 170,000 t of waste wood (dry biomass) are incinerated every year, compared to 140,000 t of waste wood incinerated by the Hengelo plant. The power plant

Table 1
Terminology of all fly ashes used in this study.

Fly ash name	Fly ash type	Type of incineration bed
BF1	Boiler ash	Grill oven
BF2	Cyclone ash	Grill oven
BF3	Cyclone ash	Fluidized bed
BF4	Filter ash	Fluidized bed
Fly ash	Pulverised coal combustion fly ash	

in Alkmaar delivers 25 MW electricity, which is equal to the electricity use of 60,000 households and the produced heat can be used for 48,000 houses (HVC, 2009).

3. Methods

3.1. Environmental aspects

For example, in the Netherlands, there are two legislative documents that regulate the use of waste materials – Landfill Ban Decree (Landfill Ban Decree, 2012) and the Soil Quality Regulation (SQR, 2013). The Landfill Ban Decree classifies waste streams into inert, non-hazardous, hazardous and no landfill materials, according to their emission level. The Dutch Soil Quality Decree uses similar criteria to divide materials destined to be used in the built sector into non-shaped (granular), shaped (monolithic) and IBC building materials (which need to undergo insulation, management and control measures).

In order to evaluate the fly ash in terms of its environmental impact, a leaching test is performed. The leaching values for elements are determined by EN 12457 (EN 12457, 2002) using a column percolation test; the same standard describes also the shorter cascade test, which is also employed in this study. The emission values stated in the Landfill Ban Decree (2012) are defined by a relative amount of liquid to solid (L/S) of 10. However, this amount is hard to obtain for powder samples.

The fly ash can be seen as a waste or as building material; both products need to fulfil certain requirements. The Landfill Ban Decree (2012) contains requirements that classify waste streams into inert, non-hazardous and hazardous. If the sample does not fulfil these requirements, it cannot be used even for landfill, before it undergoes a certain treatment.

If the fly ash is intended for application in building production it should also fulfil other requirements stated in the SQR (2013). According to the former, fly ash is a non-shaped building material because it is granular. When fly ash is applied into concrete blocks it will become a shaped building material. These concrete blocks will need to fulfil the requirements that are associated with shaped building materials.

The requirements of the SQR (2013) encompass maximum leaching values. The considered elements are those which are mainly available in building materials and can influence the soil quality.

The European standard EN 450 (EN 450, 2012) gives the criteria for the selection of fly ash; only fly ash with certain particle size, (maximum 40% retention on the 45 μm sieve for class N and respectively 12% for class S) and chemical composition and loss on ignition values (under 5% for class A, between 2% and 7% for class B and between 4% and 9% for class C) can be used in concrete production. The ASTM C618 (2001) classifies fly ash based on the lime content. Two classifications of fly ash are produced, fly ash type C and type F, where the key difference between these classes is the amount of calcium, silica, alumina, and iron content in the ashes. Class C fly ash contains more than 20% lime, where it is less than 20% in type F fly ash, keeping in mind that the origin and properties of the combustion material are key factors that determine the parameters of the fly ash, and therefore its performance when added to the concrete mixture. Finally, the amount of fly ash determines the class of cement according to the EN 197-1 (2000) standard. Fly ash addition to concrete generally results in increased workability and, similar to ground granulated blast furnace slag, a slow reaction time and increased strength over a long time. Also, the w/b ratio is reduced when fly ash is applied to the concrete mix. However, also in the case of coal combustion fly ash, the combustion method will highly influence the properties of the obtained ash (Chindaprasirt and Rattanasak, 2010).

Using fly ash in new concrete can be beneficial for the environment, since landfilling is not required and less cement needs to be produced. The other advantage of using fly ash in concrete is that it slows down the hydration process and so reduces the hydration heat accumulation, which makes it good for bulky constructions to reduce heat related cracking. However, the hydration of fly ash does take a longer time to start than Portland cement. In the construction industry often a high construction speed is desired, which often corresponds with rapid hardening.

EN 450 (2012) gives criteria for coal combustion fly ash concerning properties like particle size distribution and chemical composition. It is stated that the pozzolanic activity of fly ash is determined by the content of SiO_2 and Al_2O_3, and that the reactive form of SiO_2 should be at least 25% (m/m). Additional requirements are:

1. loss of ignition $\leqslant$ 5% (m/m).
2. chloride content $\leqslant$ 0.10% (m/m) = 1000 (mg/kg).
3. sulphate content $\leqslant$ 3.0% (m/m) = 30,000 mg/kg.
4. free calcium oxide $\leqslant$ 1.0% (m/m) = 10,000 mg/kg.

Besides these, the maximum sieved residue on the 45 μm sieve is $\leqslant$40% (m/m).

3.2. Physical and chemical analysis

XRF and XRD

The X-ray fluorescence (XRF) analyses were performed on pressed powder tablets using an EDX Panalytical Epsilon 3^X.

For X-ray diffraction (XRD) the samples were analysed using a Rigaku-Geigerflex spectrometer using Cu Kα radiation and a 2θ angle between 25° and 50°.

Thermogravimetry

The thermal analysis was performed using a Netzsch STA F1 in oxidizing atmosphere (synthetic air). The materials were heated with 10 °C/min up to 950 °C.

Particle size distribution

The materials were analysed using a Malvern Mastersizer 2000 and the Fraunhofer approximation. The specific surface area was approximated by assuming all particles to be spherical.

Washing and Cl titration

Water treatment is used to remove water soluble compounds (mostly chlorides). For this, four steps are performed:

1. fly ash in combination with demineralised water is shaken in bottles using a "Stuart reciprocating shaker SSL2" to remove soluble chlorides and metal ions.
2. the water is separated from the fly ash using 15–30 μm filters.
3. the fly ash retained on the filter is flushed with demineralised water to remove remaining water with soluble minerals.
4. the remaining fly ash is dried to remove the available water content.

A chemical method (described below) is used to determine the chloride content of the solid or liquid samples, based on the precipitation reaction of chlorides with silver ions (in this case, silver nitrate being the source).

Chloride content of the solid material

For measuring the chloride content of solid materials, two grams solid material (biomass fly ash), together with 37 ml of demineralised water and 3 ml of nitric acid is combined in a bottle. The mix is then stirred using a magnetic stirrer on a heating plate of

45 °C for 15 min. Afterwards, the solution is filtered and flushed with demineralised water until a volume of filtrate of 100 ml is obtained. From this, 2–10 ml, depending on the chloride content, can be measured using Metrohm 785 DMP Titrino with a 0.01 M solution of silver nitrate.

4. Properties

4.1. Leaching

The leaching values of the different fly ashes from the bio-power plant compared to the classifying values for L/S = 10 according to the Soil Quality Regulation (2013) are presented in Table 2. It can be seen that all the employed biomass fly ashes qualify as hazardous (BF1, BF2 and BF3) or no-landfill (BF4). The values in *italics* represent the “non-hazardous” category, the ones in **bold** belong to the “hazardous” class and the underlined ones to the “no landfill” one.

The chloride, chromium, lead and sulphate contents are above the limit, which means that the fly ashes cannot go to landfill before having a pre-treatment to remove unwanted elements. The cleaning process can be a chemical treatment, immobilization using binders or washing techniques, as will be described in Section 5.

All these materials need to undergo treatment to remove the detrimental substances. However, if it is impossible to fulfil all the non-shaped building material requirements it can be used in a shaped building material; part of the elements will then be immobilized and therefore not hazardous substances anymore (van Eijk, 2001).

4.2. Particle size distribution

Fineness is one of the primary physical characteristics of fly ash that relates to its pozzolanic activity (Joshi, 1970). When examining fly ash for its particle size distribution (PSD) the EN 450 (EN 450, 2012) sets the limit of 40% for the maximum amount of fly ash retained on the 45 μm mesh sieve on wet sieving, as a quality control measure.

The fly ashes BF1 and BF2 examined with the Mastersizer are sieved to a maximum particle size of 250 μm. However, from the results presented in Table 3, about 10% of the particles still have a larger size. This is due to the fact that some particles are needle-shaped, so when falling vertically they will slip through the sieve mesh openings.

For using fly ash as filler, fly ash should contain fine spherical particles instead of the fused forms, as mentioned in Section 3.2. So far BF4 fulfils this requirement and the requirements of EN 450 (EN 450, 2012) for maximum retained fly ash on the 45 μm sieve.

4.3. X-ray fluorescence

Table 4 lists the mass percentages of the most important oxides present in the analysed samples of the biomass fly ashes, while Table 5 presents the maximum and minimum values of the

Table 2

Classification of inert, non-hazardous, hazardous and no-landfill elements in the fly ashes (L/S = 10, column test EN 12457) according to the Landfill Ban Decree (2012) in mg contaminant/kg dry matter. Values for the analysed biomass fly ashes are presented, obtained in 2010 for BF1 and BF2 and in 2011 for BF3 and BF4, together with the range in parentheses, when available. The values in *italics* represent the “non-hazardous” category, the ones in **bold** belong to the “hazardous” class and the underlined ones to the “no landfill” one.

	Inert (mg/kg)	Non-hazardous (mg/kg)	Hazardous (mg/kg)	No landfill (mg/kg)	BF1 (mg/kg)	BF2 (mg/kg)	BF3 (mg/kg)	BF4 (mg/kg)
Sb	<0.06	*0.06–0.7*	**0.7–5**	>5	<0.3 (<0.3–0.6)	<0.3 (0.3–0.6*)	<0.3	<0.3
As	<0.5	*0.5–2*	**2–25**	>25	<0.6 (0.48*–0.6)	<0.6 (0.5*–0.6)	<0.6	<0.6
Ba	<20	*20–100*	**100–300**	>300	<3 (1.1*–3.1)	<3 (2.1*–9.1*)	5.68	*20.9*
Cd	<0.04	*0.04–1*	**1–5**	>5	<0.3 (0.02*–0.3)	<0.3 (0.02*–0.3)	<0.3	<0.3
Cl^-	<800	*800–15,000*	**15,000–25,000**	>25,000	*2400* (1647*–5764*)	*8300* (7200–34,314*)	**21,000**	80,000
Cr	<0.5	*0.5–10*	**10–70**	>70	**13.9** (0.8*–13.9)	**15.4** (0.23*–23.3*)	<3	<3
F^-	<10	*10–150*	**150–500**	>500	*<50* (4.5*–50)	*<50* (16.9*–50)	*<50*	*<50*
Cu	<2	*2–50*	**50–100**	>100	<1.5 (0.2*–1.5)	<1.5 (0.22*–1.5)	<1.5	<1.5
Hg	<0.01	*0.01–0.2*	**0.2–2**	>2	*<0.07* (0.003*–0.07)	*<0.07* (0.003*–0.07)	*<0.07*	*<0.07*
Pb	<0.5	*0.5–10*	**10–50**	>50	**28.8** (0.27*–28.8)	50 (30.37*–524.58*)	*<3*	515
Mo	<0.5	*0.5–10*	**10–30**	>30	*<3* (2.2*–3.7*)	*<3* (2.4*–4.2*)	*<3*	*<3*
Ni	<0.4	*0.4–10*	**10–40**	>40	*<3* (0.23*–3)	*<3* (0.23*–3)	*<3*	*<3*
Se	<0.1	*0.1–0.5*	**0.5–7**	>7	*<0.07* (<0.07–0.22)	*<0.15* (0.15–2.2*)	*0.161*	*0.358*
SO_4^{2-}	<1000	*1000–20,000*	**20,000–50,000**	>50,000	*19,000* (17,940*–35,881*)	*20,000* (14,950*–20,000)	*15,000*	*15,000*
Zn	<4	*4–50*	**50–200**	>200	*10.9* (3.9*–19.5)	*32.3* (11.4*–36.1)	*11*	*14.5*

* Value recalculated from a different L/S ratio.

Table 3

PSD characteristics of all four bio fly ashes and the reference powder coal fly ash, before and after treatment (notations from Table 7).

	BF1	BF2	BF3	BF4	R	BF1-T1	BF1-T2	BF2-T	BF3-T
D_{min} (μm)	1.7	2.2	0.7	0.7	0.6	0.8	0.7	0.7	0.7
d_{10} (μm)	18	8.7	10	3.8	5.0	5	4	6	7
d_{50} (μm)	110	110	38	13	25	31	31	34	34
d_{60} (μm)	138	130	47	19	30	40	40	42	46
d_{80} (μm)	202	187	75	40	106	63	63	68	80
d_{90} (μm)	255	235	110	69	120	82	83	90	113
D_{max} (μm)	479	417	631	209	832	158	158	182	275

concentrations of the main contaminants for the four different biomass power plant fly ashes, also obtained by XRF. These main contaminants were chosen based on leaching tests, as described above. The samples for the concentration measurements are collected twice per year at the corresponding power plant. It can be seen that for each plant the concentration of the components varies. This is due to the different fuel types, the combustion process and the collecting point of each plant, as mentioned in Section 2. The content of all elements is reported in milligrams of element per kilogram of dry matter (mg/kg ds).

4.4. Carbon content/loss on ignition test

Biomass fly ash can be classified by colour (Lima et al., 2008; Rajamma et al., 2009); this quality is important for aesthetic reasons but can also be used to distinguish particles that contain a large amount of iron oxide and unburnt coal. These particles are dark, blackish in colour and changes in their concentration can affect the overall colour of the fly ash. Fig. 1 presents the four different biomass fly ashes investigated in this research. The BF1 and BF2 fly ashes are much darker than the BF3 and BF4 ones, which indicates a higher carbon content. The BF3 and BF4 fly ashes consist of agglomerated particles.

The BF2 cyclone fly ash has a consistency more like fine powder (particle size under 0.125 mm) and the BF1 boiler fly ash – like a mix of fine powder and coal dust. From an aesthetic point of view, the amount of fly ash that is used can have an influence on the colour of the final concrete. In Fig. 1 only unburnt coal particles (black) can be distinguished from the other particles in the samples; other unburnt particles have a similar colour as the rest of the sample and are therefore hard to detect visually.

The BF1 boiler fly ash has a large amount of unburned coal, which is mainly due to the combustion installation of the grill oven instead of a fluidized bed oven, where a less efficient combustion takes place. The fact that the BF2 cyclone fly ash and BF3 and BF4 ashes have a comparable amount of loss on ignition (LOI) is probably due to the fact that the LOI of the BF1 and BF2 ashes is mostly carbon, while in the BF3 and BF4 ashes consist of other elements. To investigate the amount of unburned coal, the fly ashes are sieved from 500 to 125 μm; a relationship between the specific surface of the particles and their carbon content has been documented in Girón et al. (2013).

It is found that BF1 boiler fly ash consists of 13.1% coarse carbon particles (above 500 μm, a discarded fraction) and that the carbon particles also remain in the lower sieve diameters as illustrated in Table 4 (measured LOI). However, the BF2 cyclone fly ash has only 0.7% coarse carbon particles larger than 500 μm and the carbon

Fig. 1. Pictures of the four different fly ashes from both biomass power plants (Doudart de la Gree, 2012).

Table 4
Oxide composition of the four fly ash types obtained by XRF, compared to that of coal combustion fly ash; LOI determined under oxidizing atmosphere is also included.

Oxide	Boiler fly ash (BF1) (% mass)	Cyclone fly ash (BF2) (% mass)	Cyclone fly ash (BF3) (% mass)	Filter fly ash (BF4) (% mass)	Coal combustion fly ash (% mass)
CaO	33.2	28.5	30.9	49.7	4.7
SiO_2	22.2	33.3	19.1	6.6	52.7
Al_2O_3	3.7	4.8	7.1	2.7	21.5
Fe_2O_3	6.7	5.7	4.4	2.7	9.7
SO_3	7.7	6.5	10.5	11.7	1.7
Cl	0.82	1.18	4.24	8.02	0.00
Remaining oxides	23.0	16.3	19.1	13.0	7.9
LOI (oxidizing atmosphere)	2.7	3.7	4.7	5.7	1.7

Table 5
Contaminants concentration ranges of the four bio fly ashes obtained by XRF.

Element (symbol)	Boiler fly ash (BF1) (mg/kg ds)	Cyclone fly ash (BF2) (mg/kg ds)	Cyclone fly ash (BF3) (mg/kg ds)	Filter fly ash (BF4) (mg/kg ds)
Antimony (Sb)	28–49	65–300	67	110
Bromide (Br^-)	15–59	15–150	130	420
Chloride (Cl^-)	990–5600	5300–27,000	23,000	83,000
Fluoride (F^-)	2–6.8	6.9–100	5	2.1
Copper (Cu)	210–380	210–620	830	890
Molybdenum (Mo)	4.6–5.8	7.1–13	8.8	11
Selenium (Se)	<4	4–9.4	4	4
Sulphate (SO_4^{2-})	9800–15,000	11,000–16,000	7200	6100
Vanadium (V)	23–27	39–45	39	30
Zinc (Zn)	1100–3300	2700–10,000	4600	3000

particles are almost entirely filtered out using the 125 μm sieve diameter. The remaining fly ash <125 μm constitutes 41.5% of the total amount of fly ash, which means that it is much more suitable for application in concrete than the BF1, based on its finer particles that are reacting faster and have less/non carbon content. All four BFA samples have LOIs between 2.7% and 5.7% (Table 4), which are lower than other types of forestry ashes (Girón et al., 2013, 2012).

4.5. X-ray diffraction

XRD provides knowledge about the mineral composition of the fly ashes (Fig. 2). The reference coal combustion fly ash is mainly constituted of quartz (SiO_2), hematite (Fe_2O_3) and mullite ($2Al_2O_3{\cdot}SiO_2$). Quartz is also the main constituent of all the four investigated fly ash, followed by Ca-containing compounds ($CaSO_4$, $CaCO_3$, CaO or $Ca(OH)_2$) and TiO_2 in various crystalline phases. These results are in line with the findings of (Campbell, 1990; Cheah and Ramli, 2011; Elinwa and Ejeh, 2004; Elinwa and Mahmood, 2002; Etiégni and Campbell, 1991). Chlorides were hard to detect by XRD, being in too low quantity to be clearly visible (phases under 10% by mass are expected to be hard to identify). Still, the BF4 fly ash diffractograms permitted the identification of halite (NaCl). This is in line with the XRF composition which shows that BF4 contains the largest amount of chlorides from all the investigated fly ashes. The largest fraction of BF1 (particles larger than 500 μm) were also expected to contain a high amount of chlorides and indeed, NaCl could also be observed by XRD as present in its mineralogical composition.

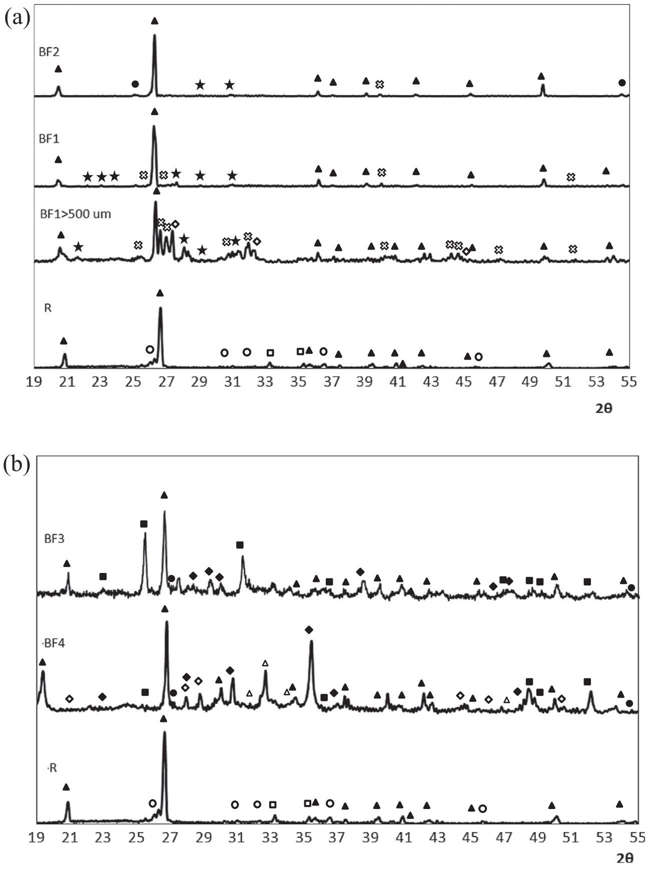

Fig. 2. (a) X-ray diffractograms of the R (reference) and BF1, BF1 > 500 μm and BF2 bio fly ashes, (b) X-ray diffractograms of the R (reference), BF3 and BF4 bio fly ashes. $CaSO_4$ (▲); $2Al_2O_3{\cdot}SiO_2$ (○); TiO_2 (●); SiO_2 (■); $Ca(OH)_2$ (△); $CaCO_3$ (◆); Fe_2O_3 (□); NaCl (◇); CaO (★); K-containing phase of the type $K_2Pb_2(CrO_4)_3$ or $K_2Ca_2(SO_4)_3$ (x).

5. Treatment methods

The treatments steps used in this research depend on the biomass fly ash and moreover the compounds which it consist of. In general the following treatment methodology will be used:

Firstly, carbon particles are removed, because of the negative effect on the chloride removal. Secondly, the fly ash is washed to reduce the soluble salts (such as chlorides and sulphates), heavy metals and aluminium content and in the end grinding can be performed to decrease the PSD and possibly increase the reactivity of the biomass fly ashes.

5.1. Sieving

This treatment is needed for biomass fly ashes with a high content of carbon. Using a sieve of 500 μm, coarse carbon particles will be removed. In this way the LOI will be reduced, as well as the chloride content of the fly ash.

5.2. Thermal treatment and air-filtering

This treatment is needed for biomass fly ashes with a high content of fine carbon particles (<40 μm). These fly ashes can be recognized by their black appearance, even after Treatment 1. For this treatment, two options (2a and 2b) are available: treatment 2a is a thermal treatment (Kuboňová et al., 2013; Lindberg et al., 2015) and treatment 2b is a separation by electrostatic filters (both for industrial use). However, in the laboratory the thermal treatment is performed by using an oven and electrostatic filters are replaced by a shaking device with air suction. These measures should give similar end results as the above described industrial processes. The choice of which method to use depends on whether there are phases present that can change when a thermal treatment is used.

If there is a possibility of phase change, Treatment 2a is not an option and Treatment 2b can be applied. Treatment 2b uses a

Table 6
Removed chlorides from boiler fly ash BF1 with different parameters (percentage removed is calculated from the original 5226 mg/kg).

	20 °C, 120 rpm (mg/kg)	20 °C, 240 rpm (mg/kg)	60 °C, 120 rpm (mg/kg)	60 °C, 240 rpm (mg/kg)
%Cl removed L/S = 2	37.4%	49.3%	40.0%	54.9%
%Cl removed L/S = 4	39.1%	44.4%	44.4%	51.7%

shaking mechanism with air exhaust. By shaking, the light coal particles are lifted and removed using the air exhaust.

When well calibrated, the removal of fine light particles that are not coal should be limited.

5.3. Washing optimization

In order to investigate the quantity of chloride which is removed from solid boiler fly ash BF1 by distilled water, the chloride content of BF1 is determined as explained above. This is done for two pairs of measurements, a plain BF1 without any changes and a ground BF1. Furthermore, a sample has been sieved on a 500 μm and then the two subsequent fractions ground.

The plain BF1 samples were found to contain less chlorides than the ground samples (2882 ± 455 and 3714 ± 58 mg Cl/kg BF1 respectively), probably because not all chloride ions from the former were dissolved (some chloride ions contained in larger coal particles were not dissolved in water, which also explains the larger standard deviation for the samples which were not ground). The sample retained on the 500 μm sieve represents 13% by mass of the BF1 sample before sieving and was found to have the greatest chloride content (18,236 mg Cl/kg BF1 above 500 μm). The counterpart samples under 500 μm was measured to contain 3282 mg Cl/kg BF1 under 500 μm; it is believed that these two samples together give a good representation, giving a total chloride content of 5225 mg/kg BF1 which will be used further on as a base value. Moreover, this value is close to the results from the XRF analysis (5600 mg/kg BF1). These results show that coal particles have a large influence on the chloride content of a fly ash.

The same procedure was followed for the BF2 sample, analysing both plain and ground samples. However, this time the differences between the two samples were much lower (4061 ± 197 mg/kg BF2 for the plain samples and 4130 ± 35 mg/kg BF2 for the ground ones). This is probably due to smaller content of carbon particles (just 0.7% by mass over 500 μm) and the initial chloride content will be from now on considered to be 4131 mg Cl/kg BF2 fly ash.

Samples BF3 and BF4 are much finer (Table 3) and also have no apparent unburnt carbon content (Fig. 1), so their chloride content was also more stable and did not require grinding the samples in order to achieve the maximum chloride measurement. The initial chloride contents for these samples that will be used from now on are 19,526 mg/kg BF3 and 86,103 mg/kg BF4.

In order to optimize the washing process, different treatment parameters and their influence on the BF1 fly ash properties are investigated. In this case the fly ash is shaken for one hour with different water of different temperatures (20 and 60 °C), two different shaking speeds (120 and 240 rpm) and two different liquid to solid ratios (L/S = 2, L/S = 4 (Colangelo et al., 2012)). The remaining chlorides are measured by taking three ml of the leachate and measuring the chloride content by titration. The results are given in Table 6 and present an improvement by increasing the shaking speed compared to the original, especially for an L/S ratio of two.

5.4. Separation/grinding

This last treatment method is used to reduce the size of the particles using a ball mill (only for laboratory use), at the same time increasing the reactivity of the particles.

6. Chloride content

6.1. BF1 boiler fly ash

To ensure that the maximum chloride content will not exceed 1000 mg/kg as mentioned in Section 3 (according to EN 450 (EN 450, 2012)), the following treatment steps are carried out:

1. the biomass fly ash is sieved on a 500 μm sieve, to remove large coal particles (S);
2. The biomass fly ash is:
   a. air filtered removing fine coal particles (AF);
   b. thermally treated at 750 °C, to incinerate fine coal particles (H).
3. Each of the samples described under step two are then washed using the water treatment (W).

The results are illustrated in Fig. 3a.

The first step already reduced the available chloride content with 45%. This is due to absorbed chloride and chlorine in the carbon structure. Washing this fly ash will result in a total decrease of 51%. This is 6% lower than not washing, from which it can be concluded that washing has almost no effect as long as fine carbon particles are still present. The soluble chlorides are probably attached to the surface of the carbon particles and thus prevented to dissolve in water. Removing the fine carbon particles using Treatment 2a or 2b results in a reduction of 75% and 70%, respectively, compared to the original fly ash; washing these fly ashes results in a total chloride reduction of 93% and 82% respectively. This indicates that first removing the coal particles increases the removal of chlorides. Secondly, air filtering removes chlorides that are less soluble and with this decreases the remaining chloride content.

6.2. BF2 cyclone fly ash

Since this fly ash only has large carbon particles the following steps are performed:

1. the biomass fly ash is sieved on a 500 μm sieve, to remove large coal particles;
2. the biomass fly ash is washed using the water treatment.

Results are illustrated in Fig. 3b.

The chlorides in BF2 ash are easily soluble and after just the washing treatment the fly ash almost fulfils the maximum limit of 1000 mg/kg. When sieved on a 500 μm sieve, the chloride content is reduced by 12%. After sieving on a 500 μm sieve and water treatment only 9% of the chloride content remains, compared to 29% when washed without sieving. This means that by removing carbon the efficiency of the treatment increases by 8%, and as a result the chloride content fulfils the stated requirements.

6.3. BF3 cyclone fly ash

This fly ash has no carbon content issues and therefore the water treatment could immediately be applied to fulfil the chloride requirements (Fig. 4a). However, because of the observed reaction

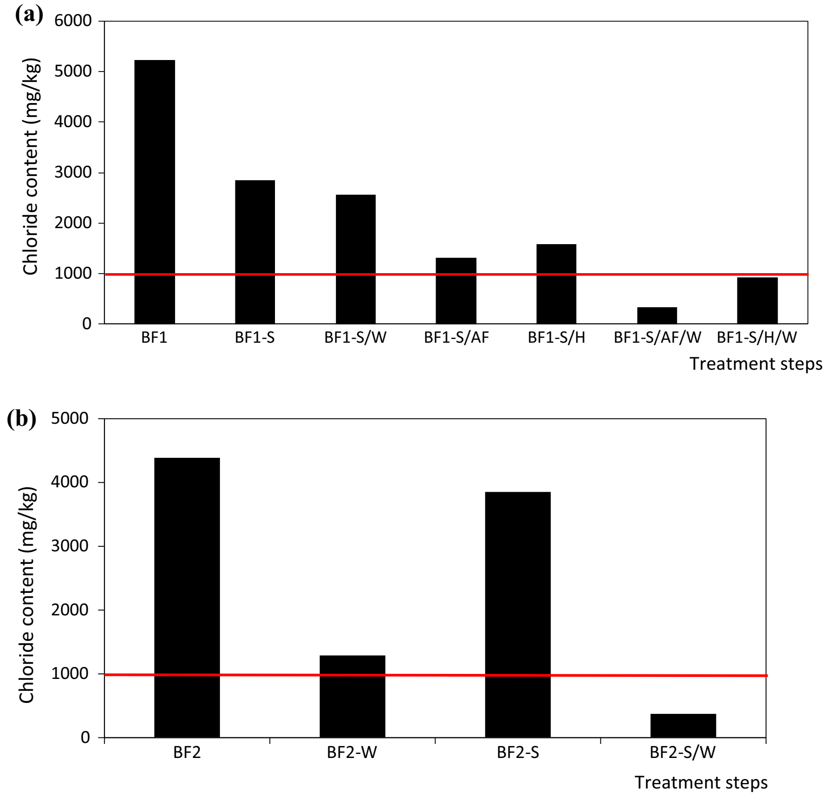

Fig. 3. Chloride ions in (a) BF1 boiler fly ash before and after different treatment steps (notations from Table 7) and (b) the BF2 cyclone fly ash before and after different treatment steps.

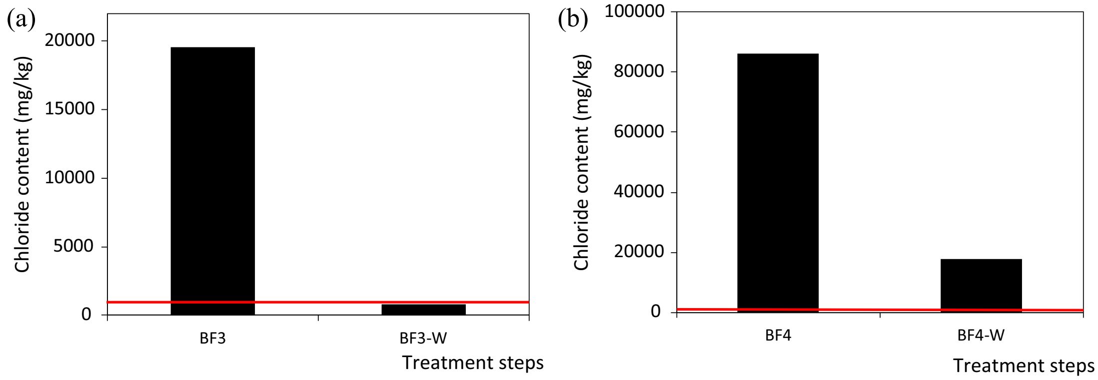

Fig. 4. Chloride ions in the (a) BF3 cyclone fly ash and (b) BF4 filter fly ash before and after treatment.

of metallic aluminium, the washing treatment was prolonged for 72 h, using an L/S = 4. After washing the chloride content is reduced by 96% and fulfils the stated requirements.

6.4. BF4 filter fly ash

This fly ash does not contain carbon particles (like BF3) and therefore can immediately be water-treated. It also contains metallic aluminium, but because the water treatment was not successful further research has not been performed. As it can be seen from Fig. 4b, the chloride content of this fly ash is 86 times more than allowed. After treatment this amount is reduced by ~80% but still it is too high to be used as cement replacement in concrete structures.

6.5. Final treated samples

After investigating the chloride content decrease of all the treatment options on all four bio fly-ashes, the final treatment method for each of these was selected. In the case of BF1, two treatment routes were chosen, both through air-filtering and heating; therefore, two treated samples will be investigated further, and termed BF1-T1 and BF1-T2. The BF2 and BF3 fly ashes each undergo only one treatment route and therefore the final treated samples will from here onwards be termed BF2-T and BF3-T. The BF4 sample will not be investigated further, as explained earlier.

Table 7 summarizes the treatment steps undergone by the BF1, BF2 and BF3 samples before being considered useable as non-shaped materials in concrete. Incompletely-treated samples (ones

Table 7
Treatment steps undergone by the BF1, BF2 and BF3 samples before being used as cement replacement.

Treatment	BF1-T1	BF1-T2	BF2-T	BF3-T
Sieving <500 μm (S)	X	X	X	
Air-filtering (AF)	X			
Heating (H)		X		
Washing (W)	X	X	X	X
Grinding (G)	X	X	X	

that underwent only some, but not all, of the treatment steps) will still be referred to using the abbreviation for the used treatments, as also mentioned in Table 7. For instance, a BF1 sample which has only been sieved will be termed BF1-S, while a BF1 sample which underwent sieving (S), heating (H) and washing (W), but not grinding (G), will be termed BF1-S/H/W.

7. Final properties

7.1. Composition and finess

In Fig. 5a the effect of both thermal treatment (BF1-S/H) and air filtering (BF1-S/AF) on the PSD of the fly ashes are illustrated, together with the original PSD of the BF1 boiler fly ash which was sieved to under 500 μm, BF1-S. Also ground BF1 (BF1-S/AF/G and BF1-S/H/G) which fulfil the EN 450 (EN 450, 2012) are presented and will be used for strength development in the following sections.

It can be seen that the thermal and the air filtering treatment yield almost the same PSD. Both PSDs are shifted to the right, indicating coarser particles due to the removal of the fine coal particles. Looking at the ground fly ash, 65% is smaller than 45 μm and 0.1% is larger than 212 μm, fulfilling the stated requirements concerning finess.

The effect of the water treatment on the PSD of this fly ash is illustrated in Fig. 5b. To obtain these results, the fly ash is first heated and ground (BF1-S/H/G) and afterwards separated into two groups where one is water treated for comparison (BF1-S/H/G/W). The effect of the water treatment is negligible and only the soluble materials that are removed provide a small change in the PSD.

Both BF2 and BF3 are water treated and ground. The results are presented in Fig. 6. Also these two biomass fly ashes are fulfilling the stated requirements after successfully being water treated and ground.

The data described in Table 3 indicates that even after grinding of the biomass fly ashes, the reference fly ash still has a smaller PSD and a larger SSA. However, there is a large improvement after treatment (all d_{10}, d_{50} and d_{90} decrease when compared to the original values).

Table 8 presents the oxide composition of the final treated samples, together with the LOI values. The reduction in Cl content is very clear, the final values detectable by XRF being extremely low in comparison to the ones presented in Table 4. The LOI of all samples is also reduced, as expected. Except for BF2-T, all other final treated biomass fly ashes do not comply with the requirement of LOI < 5% (Section 3). This is due to the formation of $Ca(OH)_2$ during washing, which is then decomposed at around 450 °C.

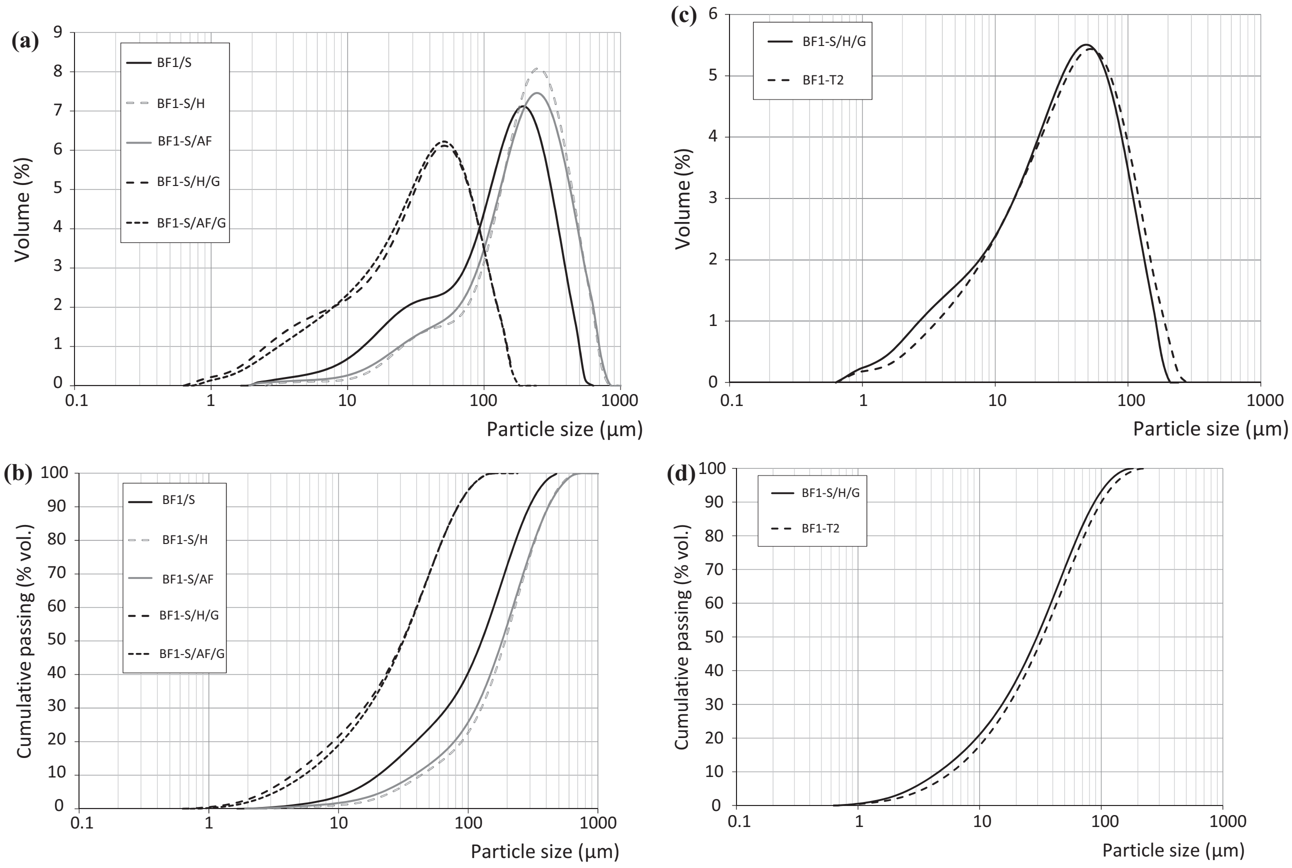

Fig. 5. PSDs of (a and b) BF1 and (c and d) of BF1-H boiler thermally treated before and after different treatment steps.

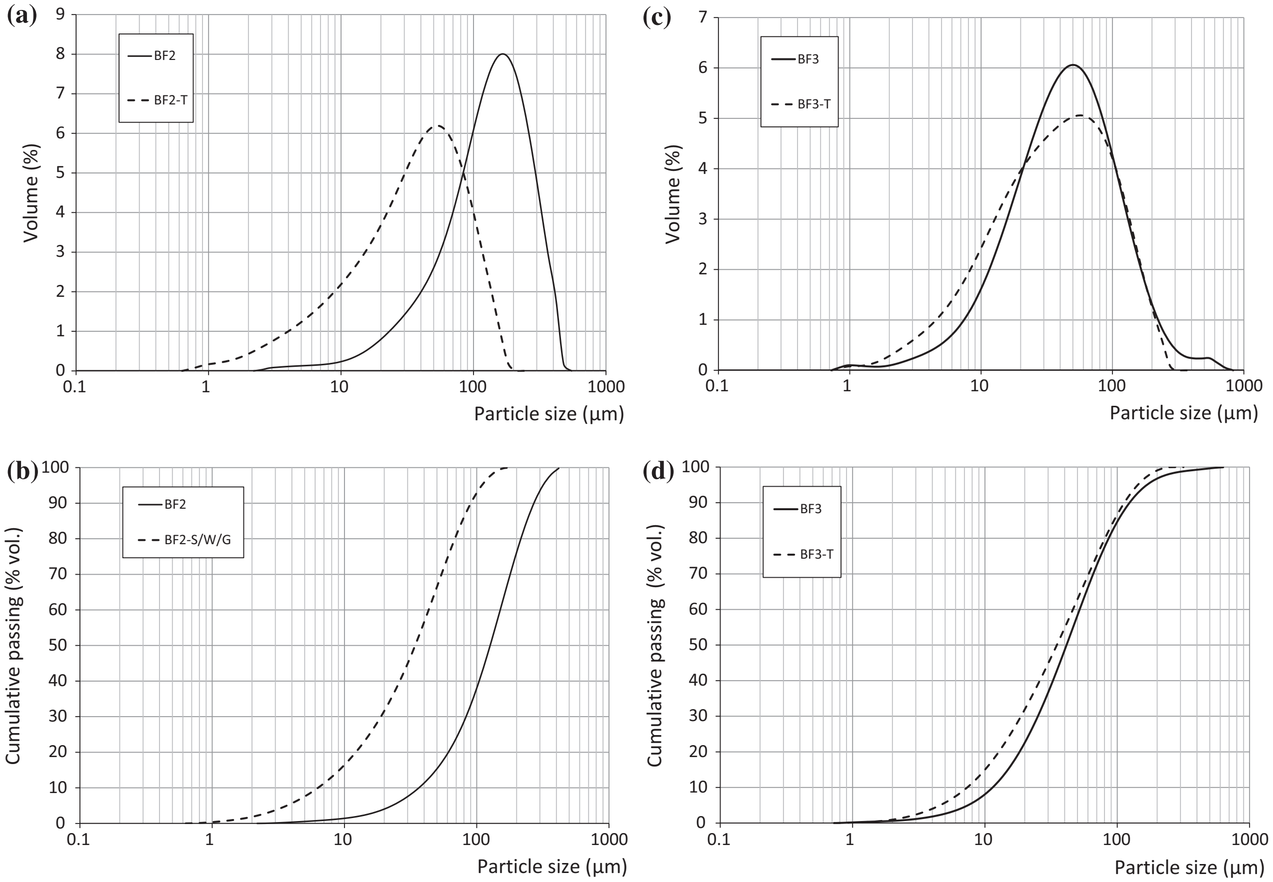

Fig. 6. PSD of (a and b) BF2 cyclone fly ash before and after the sieving, washing and grinding treatments and (c and d) BF3 fly ash before and after the washing treatment.

Table 8
Oxide composition of the final treated fly ash types obtained by XRF.

Oxide	BF1-T1	BF1-T2	BF2-T	BF3-T	BF4-T
CaO	29.1	28.2	27.1	31.0	48.9
SiO_2	28.5	29.3	33.3	18.9	8.1
Al_2O_3	4.2	4.6	4.7	5.8	3.3
Fe_2O_3	6.5	5.6	6.2	6.0	2.9
SO_3	6.7	6.2	4.7	11.7	12.4
Cl	0.05	0.14	0.04	0.04	0.97
Remaining oxides	18.2	18.2	15.3	16.9	12.7
LOI (oxidizing atmosphere)	6.7	7.7	8.7	9.7	10.7

However, this criterion was used in this study solely for comparison purposes, and the formed portlandite is not expected to be detrimental in the case of using these treated bio energy fly ashes as concrete ingredients.

X-ray diffraction was used to try to identify the chloride phases which can be removed through the washing process. For this purpose, the BF4 diffractograms of the original fly ash and the washed one (BF4-W) were subtracted, in order to highlight only certain changes. The BF4 sample was chosen for containing the largest amounts of chlorides both before and after washing (as shown in Fig. 7), therefore increasing the chance of observing the changes on a diffractogram more clearly.

BF4 contains phases like anhydrite ($CaSO_4$), portlandite ($Ca(OH)_2$), quartz (SiO_2), chlorides ($CaCl_2$ and NaCl) and calcite ($CaCO_3$), which were detailed in Section 4. After the water treatment the structure is similar and there is a visible increase in the height of the peaks of $Ca(OH)_2$ and a decrease of the height of the peaks of all the four investigated chlorides (NaCl, KCl, $CaCl_2$ and $MgCl_2$).

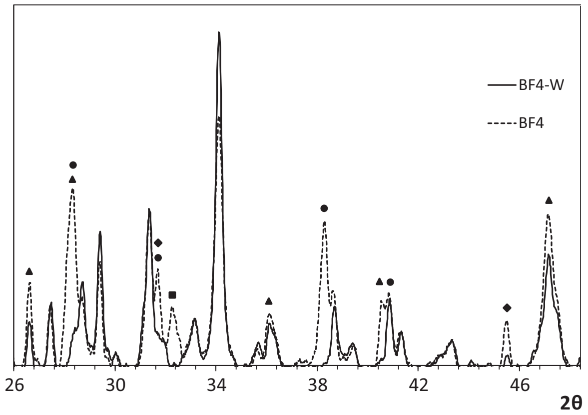

Fig. 7. XRD pattern of original BF-4 and water treated BF4-W highlighting just the chloride peaks: $MgCl_2$ (■), KCl (▲), NaCl (◆) and $CaCl_2$ (●).

7.2. Final leaching estimation of the treated bio fly ashes

The treated samples, BF1-T1, BF1-T2, BF2-T and BF3-T were tested for the leaching of contaminants, before attempting their

Table 9
Results of the 24 h leaching test on the final treated bio fly ashes (cascade test, EN 12457) and non-shaped building material requirements compared with the fly ash values (L/S = 10, column test EN 12457) according to the Soil Quality Regulation (2013).

Element/ion	Non-shaped building materials (mg/kg)	BF1-T1 (mg/kg)	BF1-T2 (mg/kg)	BF2-T (mg/kg)	BF3-T (mg/kg)
Antimony (Sb)	0.32	**0.94**	0.044	**1**	**0.46**
Arsenic (As)	0.9	0.1	0.1	0.45	0.1
Barium (Ba)	22	2.7	1.2	2.7	2.3
Cadmium (Cd)	0.04	0.01	0.01	0.01	0.01
Chromium (Cr)	0.63	**3.3**	**3.5**	**1.9**	**7.5**
Cobalt (Co)	0.54	0.1	0.1	0.1	0.1
Copper (Cu)	0.9	0.1	0.1	0.1	0.1
Mercury (Hg)	0.02	0.005	0.005	0.005	0.005
Lead (Pb)	2.3	0.1	0.1	0.1	0.1
Molybdenum (Mo)	1	0.2	0.7	0.22	0.36
Nickel (Ni)	0.44	0.1	0.1	0.1	0.1
Selenium (Se)	0.15	0.039	0.04	0.039	0.08
Tin (Sn)	0.4	0.1	0.1	0.1	0.1
Vanadium (V)	1.8	0.36	0.12	0.29	0.18
Zink (Zn)	4.5	0.2	0.2	0.2	0.2
Bromide (Br^-)	20	2	2	2	2.1
Chloride (Cl^-)	616	38	84	56	180
Fluoride (F^-)	55	3.2	2	12	4.6
Sulphate (SO_4^{2-})	2430	**4200**	**5900**	**5700**	**14,000**

use as cement replacement. However, because the official leaching test (Soil Quality Regulation, 2013) is time-consuming, an accelerated test was performed. The four treated samples were leached for 24 h with water, with an L/S ratio of 10 and a shaking speed of 240 rpm. The leachate was then analysed and the results are presented in Table 9.

The results of this cascade leaching test (EN 12457) are expected to be higher than the usual column leaching test, due to the shaking of the samples for 24 h at high rotational speed. Therefore, the values are not directly comparable to the ones presented in Table 2. However, these values will be compared with the non-shaped building materials requirements according to the Soil Quality Regulation (2013), trusting that these values will be lower than the column test ones.

It can be observed from Table 9 that only the antimony, chromium and sulphate levels are still over the legal limit (values in **bold**). In all cases, the leached chlorides are well under the legal limit. In the case of both antimony and chromium, the leaching values were under or very close to the legal limits even before the treatment steps (see Table 2), so it is assumed that this will continue to be the case with the final treated samples. The very much decreased chloride leaching levels achieved using the above-described method prove promising that all the rest of the maximum contaminant leaching values will also be met.

8. Pilot test

8.1. Combined treatment

In addition to the previous laboratory-scale experiments, a larger scale washing experiment was performed. This pilot scale experiment was designed to simulate a real life industrial washing process, such as the industrial mineral washing plant of Van Gansewinkel Minerals. This experimental approach provides vital information on the feasibility and boundary conditions needed, putting this scientific washing approach in practice (Pociecha and Lestan, 2012; Rajamma et al., 2009; Sheets and Bergquist, 1999; Xu et al., 2014; Zhang et al., 2007). The main goals within this pilot were: firstly, to get better visual and technical indications of a washing process and secondly, to obtain more know-how on the effects of the treatment on the environmental properties of the fly ashes.

The experiments were conducted on two of types of biomass fly ash, a fine (BF3) and coarse particle size distributed ash (BF2). By testing both types, a broader range of technical treatment properties related to various ash types was conducted. In addition, the individual performance of various treatment steps was analysed, simulating a step-wise real life treatment process. The ashes were treated using various steps:

8.1.1. Step 1: Cycloning

Around 5 kg dry fly ash is mixed for 10 min with 50 l tap water and further treated with a hydrocyclone, with a size separation dimension of 63 µm. In one session both cyclonated fractions were sampled (top and bottom flow). The top fraction ⩽63 µm contained the very fine particles and the overall initial organic carbon fraction. The bottom fraction ⩾63 µm is the inorganic content (78% dry matter) and was used as input for the flotation step; the two biomass fly ashes obtained are termed BF2-C and BF3-C.

8.1.2. Step 2: Flotation

The input cycloned fraction ⩾63 µm BF2-C was diluted with tap water up to 35% dry matter, in a total volume of 1 l. Firstly, for 10 min. the mixture was conditioned (slowly mixed) with a small addition (drops) of collector (liquid soap), which acts as complexion polymer toward potential contaminates like heavy metals, mineral oil and polyaromatic hydrocarbons. The mechanism behind complexion is based on a reactive negatively charged hydroxyl group, which forms a complex with cationic species (Fig. 8). In addition, this contaminant-complex also contains hydrophobic properties. Secondly, a foaming agent (1 drop), which introduces stable air bubbles in the mixture is added and flotation is started (Fig. 9). The hydrophobic state contaminant-complex is

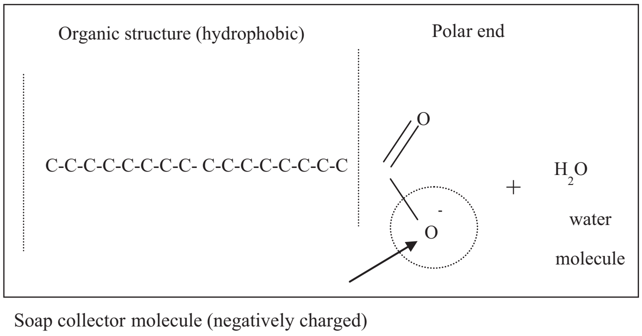

Fig. 8. Complexation mechanism during the cycloning stage of the pilot treatment.

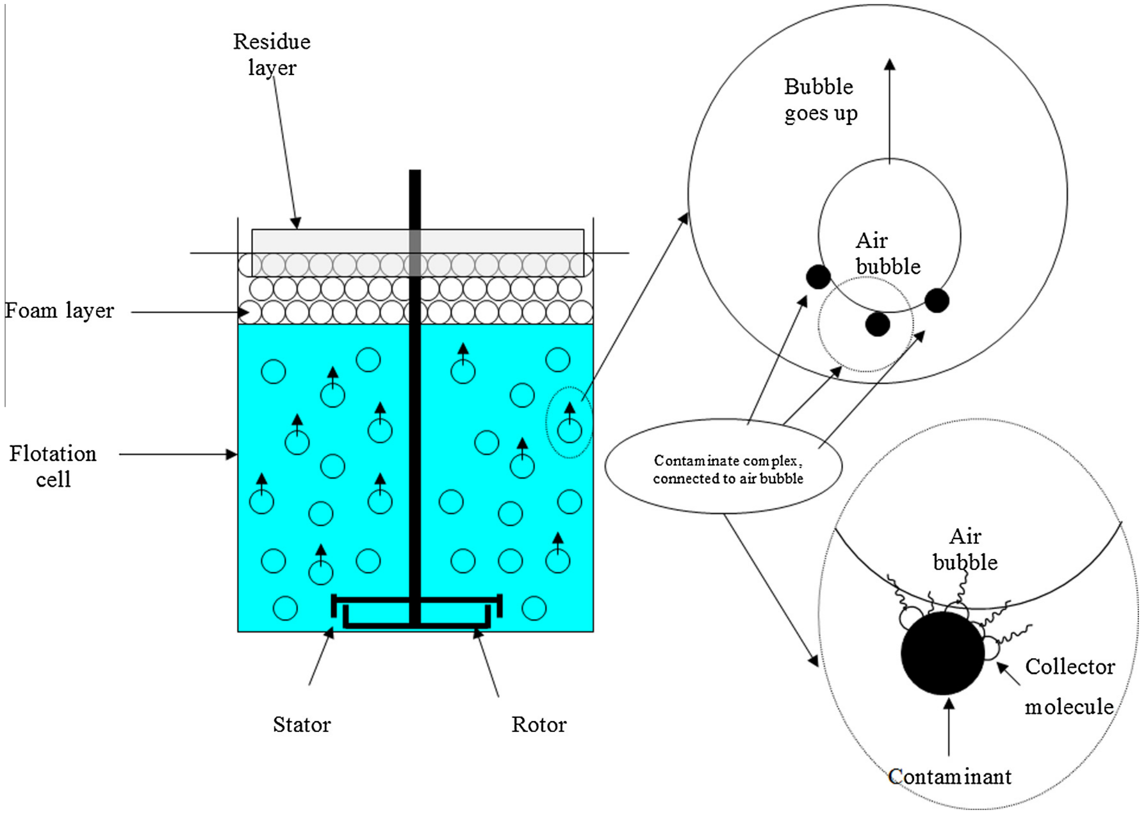

Fig. 9. Flotation scheme (Step 2 of the pilot treatment for BF2).

Table 10
Results of the column leaching test on the treated bio fly ashes after the pilot treatment (L/S = 10, cascade test EN 12457); bold values exceed the limits set by the Soil Quality Regulation (2013).

Element/ion	BF2-C (mg/kg)	BF2-C/F (mg/kg)	BF2-C/F/W (mg/kg)	BF3-C (mg/kg)
Antimony (Sb)	0.04	0.04	0.04	0.04
Arsenic (As)	0.1	0.1	0.1	0.1
Barium (Ba)	5.5	5.6	6.1	1.2
Cadmium (Cd)	0.01	0.01	0.01	0.01
Chromium (Cr)	**4.8**	**4.4**	**4.3**	**1.5**
Cobalt (Co)	0.1	0.1	0.1	0.1
Copper (Cu)	0.1	0.1	0.1	0.1
Mercury (Hg)	0	0	0	0
Lead (Pb)	**5.2**	2.2	1.3	0.26
Molybdenum (Mo)	0.29	0.28	0.25	0.64
Nickel (Ni)	0.1	0.1	0.1	0.1
Selenium (Se)	0.04	0.04	0.04	0.04
Tin (Sn)	0.1	0.1	0.1	0.1
Vanadium (V)	0.1	0.1	0.1	0.1
Zink (Zn)	1.4	0.52	0.34	0.2
Bromide (Br^-)	2	2	2	2
Chloride (Cl^-)	110	56	39	400
Fluoride (F^-)	7	5.6	4.5	4
Sulphate (SO_4^{2-})	**2220**	**2180**	**1970**	**13,000**

connected to air bubbles and rises in the mixture (together with the leftover organic carbon particles), forming a debris layer which can be extracted and thus creating a contaminant-free mineral fraction. Only the fine bio-fly ash was used for this step and termed BF2-C/F.

8.1.3. Step 3: Water rinsing

The fly ash BF2-C/F obtained after flotation was rinsed using tap water, flushing the remaining contaminates out. Within this treatment easy soluble salts (bromide, fluoride, chloride and sulphate) and potential cationic heavy metals were removed (copper, lead, zinc and chromium). The obtained fly ash is termed BF2-C/F/W.

8.2. Leaching results

All fractions created within the 3 treatment steps were analysed using a cascade test (L/S 10, EN 12457). The leaching results of all obtained treated fly ashes can be seen in Table 10. Just as with the results from the lab-scale tests (Table 9), all obtained fractions have a higher Cr leaching level than accepted; the same is true for sulphates, but these were reduced in the case of the BF2 treatments. Moreover, antimony has been successfully removed with the pilot treatment steps. In the case of BF2-C the lead leaching is above the limit, but after the following treatment steps this is no longer the case.

8.3. Economic feasibility

In case a non-hazardous biomass fly ash fulfils the Landfill Ban Decree (2012), the price for landfilling is approximately 40 €/ton; this is exclusive tax of the country (e.g. for the Netherlands this would amount to ±13 €/ton) (Wiebes, 2014). A more favourable situation would be the application of biomass fly ashes in the concrete industry. In case additional treatment is required, like washing and separation, the price will increase with approx. 20 €/ton. If the material is too coarse and requires milling, the cost increase would be approx. 10–15 €/ton (+1 €/% moisture content for drying if it cannot be used wet, all costs without tax). Additional costs like storage and analyses will be ±3 €/ton, while the residue (sludge) will be sent to a landfill, at a cost of approx. 30 €/ton of sludge excluding tax, which represents approx. 8 €/ton of biomass fly ash. This residue (accumulated with metals and salts) needs to go to landfill and depending on the type of fly ash e.g. the carbon content and fine fraction ($\leqslant$10–20 μm) will be approximately 15–20% per ton of the initial input material. In this mass percentage the ±50% water absorption/content by the material is included.

Finally, two scenarios are possible, namely fly ash treatment (a) without grinding and (b) with grinding which will yield in the following costs:

(a) 31 €/ton treatment costs. Indicative market cost is −5 to −10 €/ton (yielding to +4 to −1 €).
(b) 41–46 €/ton treatment costs. Indicative market price is 5 €/ton (yielding to +4 to −1 €).

Hence, the approach mentioned in this paper is applicable in practice, allowing biomass fly ashes to enter the market, while having environmentally but also cost technically an advantage compared to landfilling.

9. Conclusions

Four types of biomass fly ashes were studied: a boiler and a cyclone ash from a grill-oven incinerator and a cyclone and a filter ash from a circulating fluidized bed. Complex treatments were performed on both lab-scale and pilot scale, and analysis was done before and after treatment. The following conclusions can be drawn:

- The main oxides found in all four fly ashes are CaO, SiO_2, Al_2O_3, Fe_2O_3, and SO_3; from a mineralogical point of view, the fly ashes were found to consist of mainly quartz and Ca-containing phases ($CaSO_4$, $CaCO_3$, CaO and $Ca(OH)_2$ in various combinations).
- Chlorides were found to be the main contaminant from leaching tests, together with sulphates, antimony, chromium and lead. A washing treatment was designed and optimized in terms of duration and L/S ratio in order to remove chlorides efficiently. Besides removing these soluble chlorides, the unburnt carbon content in the grill oven biomass fly ashes was found to be related to their chloride content; a treatment that removes most of the unburnt coal (such as sieving, air filtering and thermal treatments) also lowers significantly the chloride leaching of these fly ashes.
- A pilot test employing cycloning and flotation steps was successfully designed for the upscaling of the proposed treatment. This industrial scale treatment was found to be very efficient for the removal of chlorides, sulphates and chromium (by 99.5%, 90.1% and 72% respectively in the case of BF2).
- The filter ash from a CFB was found to have the highest chloride content; despite the efficiency of the treatments, which lowered the chloride content with ~80%, this particular fly ash is deemed unsuitable for reuse due to its high remaining chloride content. All other fly ashes, either through laboratory treatments or pilot scale treatment were rendered non-hazardous.
- The treatment toward application of the biomass fly ashes, even when milling and washing are required, is environmentally and cost favourable compared to landfilling the material.

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