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Title: Municipal solid waste incineration bottom ash as Alkali-Activated Cement precursor depending on particle size

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Abstract: Bottom Ash (BA) is the main by-product of municipal solid waste incineration (MSWI). It is stabilised outdoors to obtain weathered bottom ash (WBA) whose main application is in the construction sector as a secondary aggregate for road sub-base. Here, the aim of this work is to advance the study of the potential use of WBA as a precursor in the synthesis of new alkali-activated cements (AACs). An exhaustive physicochemical characterisation (X-ray fluorescence, X-ray diffraction, Fourier-transform infrared spectroscopy, inductively coupled plasma optical emission spectroscopy, and Inductively coupled plasma - mass spectroscopy) of WBA was provided depending on its particle size (<30, 30-16, 16-8, 8-4, 4-2 and 2-0 mm). The study reveals that WBA is composed mainly of the essential reactive phases to form AACs, which are SiO2, Al203, and CaO. It is demonstrated the larger the particle size, the higher the content of SiO2; and the smaller the particle size, the higher the heavy metal(loid) content. The availability of reactive phases was analysed through chemical attacks with HF and NaOH solutions of different concentrations (2M, 4M, and 8M). The results demonstrate the availability of reactive phases (including 150 to 250 g \cdot kg-1 of SiO2 and 50 to 65 $q \cdot kq - 1$ of Al2O3) in all the particle size fractions studied. WBA potential will be of considerable use to formulate AACs, depending on the particle size fraction and the Si/Al ratio, both as the sole precursor and mixed with others.

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The responses to editor suggestions are presented below. Hopefully, we answered all the questions and clarified all issues. Enclosed, please find the revised manuscript.

Answers to the Editor suggestions

Is it possible to remove 'as a function of particle size in the title? It will look better and looks like a title rather than a sentence.

Thank you for the suggestion. The authors think that the part 'as a function of particle size' provide relevant information for the potential readers. However, the title has been modified to looks like a title.

Please remove those redundant words, e.g. Additionally, etc.

The redundant words were removed.

Please make the Conclusions more concise, of about 1-2 paragraph to only underscore the key results and how it contributes to the future work.

The conclusions have been changed. Now, they are more concise underscore the key results and to emphasise the future work.

Municipal solid waste incineration bottom ash as Alkali-Activated Cement precursor depending on particle size

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Highlights

- Weathered bottom ash (WBA) potential as alkali-activation material has been evaluated.
- > SiO_2 , Al_2O_3 , and CaO are the main components of WBA.
- > The availability of SiO_2 and Al_2O_3 is high in the coarser fractions of WBA.
- > After NaOH 8M chemical attack, metal(loid)s content is high in the finest fractions.

Municipal solid waste incineration bottom ash as Alkali-Activated Cement precursor depending on particle size

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Abstract

Bottom Ash (BA) is the main by-product of municipal solid waste incineration (MSWI). It is stabilised outdoors to obtain weathered bottom ash (WBA) whose main application is in the construction sector as a secondary aggregate for road sub-base. Here, the aim of this work is to advance the study of the potential use of WBA as a precursor in the synthesis of new alkaliactivated cements (AACs). An exhaustive physicochemical characterisation (X-ray fluorescence, X-ray diffraction, Fourier-transform infrared spectroscopy, inductively coupled plasma – optical emission spectroscopy, and Inductively coupled plasma – mass spectroscopy) of WBA was provided depending on its particle size (<30, 30-16, 16-8, 8-4, 4-2 and 2-0 mm). The study reveals that WBA is composed mainly of the essential reactive phases to form AACs, which are SiO₂, Al₂O₃, and CaO. It is demonstrated the larger the particle size, the higher the content of SiO₂; and the smaller the particle size, the higher the heavy metal(loid) content. The availability of reactive phases was analysed through chemical attacks with HF and NaOH solutions of different concentrations (2M, 4M, and 8M). The results demonstrate the availability of reactive phases (including 150 to 250 g·kg⁻¹ of SiO₂ and 50 to 65 $g \cdot kg^{-1}$ of Al₂O₃) in all the particle size fractions studied. WBA potential will be of considerable use to formulate AACs, depending on the particle size fraction and the Si/Al ratio, both as the sole precursor and mixed with others.

Keywords: Bottom Ash, Waste Management, Alkali Activated Cement, Cement precursor

1. Introduction

The Waste Framework Directive (European Parliament and Council, 2008) of the European Parliament and the policies of the member states of the European Union (EU) focus on maintaining the value of products, materials and resources for as long as possible, moving towards a circular economy (European Commission, 2017). The priority of the member states is to continue promoting and developing systems and infrastructures that provide proper municipal solid waste (MSW) management. According to the EU waste management hierarchy (European Parliament and Council, 2008), landfilling is the least preferable option, and its use is expected to be limited to as little as 10% by the year 2030 (European Commision, 2015). The EU order of priority establishes prevention, reuse, and recycling as the main processes in MSW management. However, one of the most suitable alternatives to landfilling for MSW is energy recovery in waste-to-energy (WtE) plants, which contribute to reducing the volume (up to 90%) and weight (up to 75%) of municipal waste (MW) (Cheng and Hu, 2010).

Incineration bottom ash (IBA) is the main by-product of the combustion process in WtE plants (Chimenos et al., 1999). Around 18 $Mt \cdot y^{-1}$ of IBA is produced in the EU (CEWEP, 2016). This MSW incineration (MSWI) residue, which is approximately 85% of the solid resulting from combustion, can be considered as slag, granular material, and non-hazardous waste (Valle-zermeño et al., 2017). IBA is mainly composed of silicon, calcium, iron, aluminium, and sodium, although it also contains small amounts of several heavy metal(loid)s. For its subsequent reuse as a secondary material, a weathering (aging) process lasting 2-3 months is necessary, during which the IBA is stored outdoors. This procedure results in carbonation and oxidation of the IBA and its consequent pH stabilisation with

values between 8 to 10, as well as the neo-formation and hydration of mineral phases, among other consequences (Chimenos et al., 2000). The material resulting from the weathering process is known as weathered bottom ash (WBA). Approximately 85% of WBA is glass, ceramics, stone, brick, concrete, ash, and melting products, which has a grain size distribution and technical properties that are similar to those of natural sand and gravel (Zhang and Shimaoka, 2013). The potential applications of the WBA are plenty and assorted. In many countries like France, Italy, the Netherlands or China, there is a great interest in valorising WBA. During the last years several studies have been carried out in some sectors. In the field of civil engineering as secondary aggregate for road construction (Cioffi et al., 2011; Hjelmar et al., 2007), embankments (Pecqueur et al., 2001), and pavements (Toraldo et al., 2013), as well as concrete filling (Ginés et al., 2009). Regarding the building sector it is studied its application as ceramic material such as tiles, bricks and glass-ceramics (Lancellotti et al., 2014). In the chemical engineering field, studies have been carried out for its use as an absorbent for wastewater treatment processes (Shim et al., 2003) as well as co-disposal and biogas production (Silva et al., 2017).

Besides the concerns regarding waste management, the cement industry can also present a threat to the environment (Aljerf, 2015). Cement production is responsible for some 5%-7% of CO₂ emissions worldwide (McLellan et al., 2011) and it is estimated to consume 2% of global primary energy (Chen, 2009). The cement industry must face the challenge of finding new processes to manufacture in a more ecological and respectful way, reducing energy consumption and greenhouse gas emissions. The use of by-products such as WBA to manufacture cementitious materials could be one way to obtain eco-friendly cements. Full-scale demonstrations of the technical feasibility of unbound and cement-bound sub-base layers containing WBA, i.e. general ceramics, glass or glass-ceramics, have been successful (Arm, 2003; Magnusson, 2005). Alkali-activated cements (AACs) have become an ideal

alternative to ordinary Portland cement (OPC) because of their properties. AACs have good compression strength (Alonso et al., 2000), high resistance to chemical attack by aggressive aqueous and acid solutions (Bakharev, 2005), and resistance to fire and high temperature (Murri et al., 2013). However, the main benefit exhibited by AACs is their greater respect for the environment, compared to other cementitious materials. If AACs are compared to OPC, the former reduces the CO₂ emissions and the energy consumption associated with cement manufacture (Van Deventer et al., 2012). It is important to highlight that AACs, as most of the new cements produced using industrial by-products or waste (Bernal et al., 2016), follow the zero waste principle (Komnitsas, 2011). For this reason, AACs are considered new sustainable and eco-friendly cements (Phair, 2006). The alkaline activation reaction is a polycondensation which starts when a solid powder precursor (based on alumino-silicates) is dissolved in an alkaline medium. This reaction generates free silica tetrahedral and aluminium cations coordinated with oxygen, which will form a 3D structure (Duxson et al., 2007; Singh et al., 2015). The final AACs properties depend on the precursor, the relation between the proportions of SiO₂ and Al₂O₃, the CaO content, the alkali activator used, and the curing temperature (Aljerf, 2015).

Previous studies have revealed that WBA is mainly composed of SiO₂, Al₂O₃, and CaO (Valle-zermeño et al., 2017; Wei et al., 2011), which are the essential mineral phases required to formulate AACs. WBA contains enough glassy materials (primary or secondary glass) (Valle-zermeño et al., 2017), as well as important amounts of both sources of aluminium and calcium for its use as a precursor in the formulation of AACs. However, WBA presents a high heterogeneity and its composition varies depending on particle size fraction (Valle-zermeño et al., 2017). The availability of reactive phases (SiO₂ and Al₂O₃) in each fraction will vary as a function of the composition and the alkali activator concentration. Physicochemical characterisation and determination of SiO₂ and Al₂O₃ availability will allow to determine the

possibilities of using a specific WBA particle size as the sole precursor in the synthesis of AACs; or whether, additional sources (precursors) would be required to achieve an optimal SiO_2/Al_2O_3 ratio.(Aljerf, 2015).

In this research, the main goal is to determine the added value of WBA as precursor in AACs formulation to contribute to the EU's objectives in the waste management and valorisation fields. This work focuses on the determination of SiO_2 and Al_2O_3 available in WBA, as the reactive phases required to formulate new AACs, as a function of WBA particle size. The availability of these reactive phases in each fraction is analysed through chemical attacks, and it is related to the amorphous phases content, as well as with the material characterisation determined elsewhere (Chimenos et al., 1999; Valle-zermeño et al., 2017). For each particle size fraction of WBA under study, it is analysed the concentration of heavy metals and metal(loid)s leached during the alkaline activation of reactive phases to determine the potential release of WBA used as a precursor in the formulation of AACs.

2. Experimental procedure

2.1. Materials

The WBA sample was supplied by the company Valorización de Escorias para la Construcción S.A. (VECSA), which is responsible for valorising and commercialising the IBA collected from the WtE plant located in Tarragona (Spain). The feed stream treated in the incineration plant (140 kt·y⁻¹) is mainly composed of household rubbish with a small input from commercial sources. The incineration temperature is around 950°C (Chimenos et al., 1999). Approximately, 32 kt·y⁻¹ of fresh IBA is produced by the incineration plant annually and treated to recover both ferrous and non-ferrous metals, as well as the lightweight materials that can be removed. After being conditioned, the resultant IBA is stockpiled outdoors for at least three months, to ensure immobilisation of heavy metal(loid)s by weathering and to obtain WBA. Due to the heterogeneity of IBA, for this study around 100 kg

 of WBA was collected from various stockpiles, homogenised, and stored in a 30 L plastic container.

2.2. Samples preparation

The samples preparation scheme is shown in Fig. 1. First, the WBA was dried overnight at 105°C in a stove. Then, the particle size distribution (PSD) was analysed by sieving the dried WBA through openings standards of 2, 4, 8 and 16 mm (Valle-zermeño et al., 2017). After sieving, around 100 g of each fraction (<30, 30-16, 16-8, 8-4, 4-2 and 2-0 mm) was initially quartered and crushed in a jaw crusher. The samples were milled in a vibratory disc mill, using a grinding set made of hardened steel. It is important to highlight that the <30 mm fraction corresponds to the bulk sample without being sieved. The milling continued until the whole sample passed through a sieve of 80 μ m mesh (except for the ferrous and non-ferrous metal particles which, due to their ductility, were retained in the sieves) resulting in a homogeneous powder. A magnet (Nd; 0.485 T) was passed over the sample to remove magnetic particles.



Fig. 1. Scheme of the preparation of samples.

2.2. WBA Characterization

2.2.1. Physicochemical characterization

For each powdered size fraction of the WBA, the chemical composition of the major and minor elements was determined by means of X-ray fluorescence spectroscopy (XRF) using a Panalytical Philips PW 2400 sequential X-ray spectrometer with UniQuant[®] V5.0 software.

The mineral and crystalline phases of the powdered WBA fractions were identified by Xray diffraction analysis (XRD) using a Bragg–Brentano Siemens D-500 powder diffractometer with CuK α radiation. The amorphous index for samples containing both amorphous and crystalline phases was quantified with the external standard method (Jansen et al., 2011; Snellings et al., 2014).

2.2.2. SiO_2 and Al_2O_3 availability

The availability of reactive phases (SiO₂ and Al₂O₃) was determined through chemical attacks with HF (1% v/v) and NaOH solutions (2M, 4M, and 8M) (Aljerf, 2015; Ruiz-Santaquiteria et al., 2011). For these experimental trials, one gram of WBA sample was mixed with 100 mL of each activating solution and stirred constantly for 5 h in a sealed plastic container, at 80°C for alkaline solutions, or at room temperature in the case of HF. The resulting solution was filtered and analysed by means of inductively coupled plasma optical emission spectrometry (ICP-OES) using Perkin Elmer Optima ICP-OES 3200 RL equipment to quantify the Si and Al leached (Ruiz-Santaquiteria et al., 2011). It was used Fourier-transform infrared spectroscopy by attenuated total reflection (FT-IR ATR) to evaluate the chemical structure and composition and compared both the initial and attacked WBA powders (with HF and the different NaOH solutions) using Spectrum TwoTM equipment from Perkin Elmer.

2.2.3. Heavy metals content

The potential environmental impact of the WBA was assessed by analysing the heavy metal(loid)s released in the filtered NaOH 8M solutions during the alkaline activation using a Perkin Elmer ELAN 6000 ICP mass spectrometry (ICP-MS) device.

3. Results and discussion

3.1. WBA Characterization

3.1.1. Physicochemical characterization

Fig. 2 shows the PSD of the WBA. Around 50% of the WBA corresponds to fractions below 4 mm (fine fraction), in agreement with previous findings (Chimenos et al., 1999; Valle-zermeño et al., 2017).



Fig. 2. Particle Size Distribution of Weathered Bottom Ash

The major and minor elemental composition, as elemental oxides and trace-elements in each size fraction of WBA analysed, are given in Table 1. As expected, the most abundant oxides were SiO₂, CaO, and Al₂O₃, which are the key compounds in cementitious materials

(Aljerf, 2015; Roy, 1999). As can be seen, the contents of these oxides varied, depending on the size fraction. The highest SiO₂ content was in coarse fractions (30-16, 16-8, and 8-4 mm) due to the primary and secondary glass present, as well as the synthetic ceramic materials present in these fractions (Chimenos et al., 2003; Valle-zermeño et al., 2017). As for Al₂O₃, its content trends to increase as the particle size decreases, except for the 30-16 mm fraction. This is due to the Eddy current device, because only recovers the non-ferrous fraction from the particle size fractions greater 10 mm. Moreover, the 30-16 mm size fraction contains a large amount of synthetic ceramics (Valle-zermeño et al., 2017). The high content of CaO in the finest fractions (4-2 and 2-0 mm) is due to the presence of large amounts of calcium carbonates that are neo-formed during the weathering process of portlandite (Chimenos et al., 2003). This CaO high amount is also because of the presence of cementitious materials, based on OPC, and synthetic ceramics from small domestic works. These materials are fragmented by mechanical attrition and thermal shock inside the combustion furnaces (Aljerf, 2015). It is important to note that the major and minor element contents of the <30 mm fraction agree with the contents calculated from the XRF results and the PSD weighting for each fraction (Fig. 2).

	(wt. %)							
	2-0 mm	4-2 mm	8-4 mm	16-8 mm	30-16 mm	<30 mm		
SiO ₂	25.11	39.02	54.45	59.3	50.23	45.44		
CaO	23.77	19.35	15.15	13.6	16.25	17.55		
Al ₂ O ₃	11.19	9.62	7.32	6.74	12.39	10.38		
Na ₂ O	2.78	4.93	8.14	7.77	3.11	5.04		
K ₂ O	1.11	1.41	1.25	1.61	1.95	1.54		
Fe ₂ O ₃	7.22	6.89	5.43	4.19	3.49	6.08		
MgO	2.88	3.24	1.99	2.30	2.74	2.66		
TiO ₂	0.82	0.67	0.44	0.37	0.56	0.65		
Cl	1.99	1.14	0.62	0.40	0.93	1.42		
SO ₃	3.57	1.59	0.96	0.63	2.27	2.57		
Mn	0.05	0.03	0.03	0.02	0.02	0.03		
Cu	0.18	0.13	0.10	0.04	0.04	0.13		
Zn	0.73	0.39	0.64	0.09	0.18	0.51		
Br	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01		

Table 1. Major-, minor- and trace-elements for each size fraction of WBA.

Rb	< 0.01	0.01	< 0.01	0.01	0.01	< 0.01
Sr	0.08	0.08	0.04	0.06	0.04	0.07
Y	< 0.01	< 0.01	< 0.01	n.d.	< 0.01	< 0.01
Zr	0.03	0.03	0.04	0.11	0.12	0.03
Nb	< 0.01	< 0.01	< 0.01	n.d.	< 0.01	< 0.01
Sn	0.03	0.02	0.01	0.01	0.02	0.02
Sb	0.02	0.01	0.01	< 0.01	0.01	0.01
Ba	0.15	0.10	0.07	0.04	0.05	0.07
Pb	0.15	0.34	0.13	0.05	0.04	0.11
LOI	18.13	10.98	3.17	2.65	5.54	5.78
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*Loss on ignition at 1,000 °C.

The XRD patterns of the <30, 30-16. 16-8 mm fractions shown in Fig. 3a demonstrates that the WBA is a heterogeneous material (Giro-Paloma et al., 2017b), which has low crystallinity and is mainly composed of amorphous phases, as shown between the angular range from 20° to 35° (2 θ). The Fig. 3b shows the dominant peaks in XRD patterns. The only crystalline phases present in all the fractions were quartz and calcite.



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3 3 3 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	078901234567890
3 3 3 4 4 4 4 4 4 4 4 4 4 4 5	078901234567890
33344444444455	0789012345678901
33344444444455	0789012345678901
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Fig. 3. (a) XRD patterns of <30, 30-16, and 16-8 mm fractions (b) Dominant peaks of XRD patterns of all samples

The main crystalline phases determined, depending on the size fraction, are shown in Table 2. The mineralogical compositions are similar, being the phases rich in Si, Al and Ca (quartz, calcite, albite, dolomite, etc.) more abundant. It is important to highlight the presence of metallic phases in the finest fractions (<30, 4-2 and 2-0 mm) and the great variety of silico-aluminate phases in all the fractions while being more abundant in coarse fractions.

Minoral Dhaga	Fraction									
winierai Filase	2-0 mm	4-2 mm	8-4 mm	16-8 mm	30-16 mm	<30 mm				
Albite (NaAlSi ₃ O ₈)			✓	\checkmark	\checkmark	√				
Akermanite (Ca ₂ MgSi ₂ O ₇)	\checkmark	✓	✓		\checkmark	✓				
Aluminium (Al)			\checkmark			\checkmark				
Anorthite (CaAl ₂ Si ₂ O ₈)		\checkmark								
Anorthoclase					\checkmark					

Т	al	blo	e 2	2.	M	ajor	cry	'stal	lline	p	hases	in	WB.	A	sampl	les.
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((Na,K)AlSi ₃ O ₈)						
Calcite (CaCO ₃)	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
Cesanite (Ca ₂ Na ₃ [(OH)(SO ₄) ₃])	\checkmark					
Cristobalite (SiO ₂)	\checkmark	\checkmark				\checkmark
Diopside (CaMgSi ₂ O ₆)				\checkmark		
Dolomite (CaMg(CO ₃) ₂)			✓	~	~	
Hematite (Fe ₂ O ₃)	\checkmark					\checkmark
Magnetite (Fe ₃ O ₄)	\checkmark	\checkmark				\checkmark
Mullite ($Al_6Si_2O_{13}$),					\checkmark	
Pseudowollastonite (Ca ₃ Si ₃ O ₉),			\checkmark			
Quartz (SiO ₂)	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark
Wustite (FeO)			\checkmark			
Xonotlite (Ca ₆ Si ₆ O ₁₇ (OH) ₂)	\checkmark					

From the XRD patterns of each size fraction, the amorphous phases of the samples were quantified (Jansen et al., 2011; Snellings et al., 2014). Due to their abundance, quartz and amorphous glass samples were used as external patterns for this quantification. First, the crystalline compound was determined and then the amorphous phases were derived by differences, in the main angular range from 5° to 80° (20). The results are shown in Table 3, where the amorphous index of the particle size fractions was 44%-70%. As expected, the 30-16, 4-2, and 2-0 mm size fractions presented the lowest amorphous index because of their high content in synthetic ceramics and metal compounds, in contrast to the rest of the fractions where the amorphous amount is around or above 60%. It is important to highlight that the amorphous index of the <30 mm is in agreement with that calculated using the external standard method and the PSD weighting of each fraction (Fig. 2).

Table 3. Amorphous content (wt.%) in the size fractions of WBA.

Size Fractions	Amorphous content (wt.%)
<30 mm	60
30-16	14
mm	++

16-8 mm	66
8-4 mm	70
4-2 mm	53
2-0 mm	49

3.1.2. SiO_2 and Al_2O_3 availability

XRF and XRD results show a large content of silico-aluminate phases and amorphous phases, but not all of these are available to react with the activating solution and form AACs. In fact, although thermodynamics allows certain reaction mechanisms, the chemical kinetics shows that some of these require very long reaction times that cannot be assumed. It is known that the crystalline phases are far less reactive than the amorphous phases, and that the active surface of the particles and their size. The reaction temperature and the concentration of the activators, are some of the important parameters for activation of the reactive phases (Ruiz-Santaquiteria et al., 2011). Accordingly, for each WBA particle size fraction, a chemical attack test was performed to determine the real amount (g·kg⁻¹ of WBA) of SiO₂ and Al₂O₃ available to form AACs. It is expected that most of the SiO₂ and Al₂O₃ available come from the amorphous phases. To a greater or lesser extent, all the particle size fractions contain SiO₂ and Al₂O₃ amorphous phases, as shown in Figs. 4 to 6.

Focusing on the NaOH chemical attacks as a function of WBA particle size fraction, Fig. 4 shows that there is a broad trend (except for 8-4 and 16-8 mm) to increase SiO_2 availability as the NaOH concentration increases. This tendency is due to the highly aggressive chemical attack (from 2M to 8M). Moreover, if it is compared the trend for all the fractions as a function of chemical attack, the same curve results in all cases and the maximum value was for the 16-8 mm fraction. Analysing the SiO_2 availability of each fraction with the primary and secondary glass results obtained in a previous study (Valle-zermeño et al., 2017), validates this trend, except for the results in the 30-16 mm fraction. In this last case, the SiO_2 extracted with chemical attacks comes from the synthetic ceramics. It is important to highlight

that the HF attack indicated the existence of a large amount of available SiO_2 amorphous phases that were not extracted with the NaOH chemical attacks, since they are less aggressive.



Fig. 4. SiO₂ availability of WBA as a function of particle size fraction and chemical attack solution.

Fig. 5 shows the percentage of SiO_2 extracted from the NaOH chemical attacks as a function of the SiO_2 extracted from HF chemical attack (thereby assuming that the amount extracted with the HF attack is 100% of the SiO_2 available in the WBA samples). The results show that it is not possible to extract the same amount of SiO_2 with NaOH as with HF chemical attacks, at least not under the experimental conditions of this study (particle size, NaOH concentration, agitation, and temperature).



Fig. 5. SiO₂ percentage extracted from NaOH attacks as a function of HF attack.

The Al₂O₃ availability in Fig. 6 shows the same broad trends as in Fig. 4. Considering each particle size fraction, as the NaOH concentration increases, the Al₂O₃ availability also increases (except for the 8-4, and 16-8 mm fractions). Regarding the trend for all the fractions as a function of the chemical attack, an inverse curve to that observed in Fig. 4 is the result, with the minimum value for the 16-8 mm fraction. Considering each fraction, as NaOH concentration increases, it is also increasing the Al₂O₃ availability (except for the <30 and 8-4 mm fractions). The main reason for the high Al₂O₃ availability in the finest fractions is that the Eddy current equipment only separates fractions above 10 mm, as mentioned previously. Hence, the aluminium content in fractions below 10 mm is high. The low Al₂O₃ availability in coarse fractions is due to the high content of synthetic ceramics, which implies more Al₂O₃ crystalline phases. The results obtained with the HF chemical attack are not shown, since this solution does not contribute to the extraction of the reactive Al₂O₃ phases.



Fig. 6. Al₂O₃ availability of WBA as a function of particle size fraction and chemical attack solution.

Considering the SiO₂ and Al₂O₃ availability the SiO₂/Al₂O₃ ratio was obtained, as shown in Fig. 7. Taking into account that several authors consider the optimal SiO₂/Al₂O₃ ratio for AACs to be around 2 (Duxson et al., 2005), this matches with the <30 mm fraction (for all the NaOH chemical attacks), the 4-2 mm fraction (for NaOH 8M), the 8-4 mm fraction (for NaOH 8M), and the 2-0 mm fraction (for NaOH 4M). It should be emphasised that the other fractions need an additional source of Al₂O₃ or SiO₂, depending on their content of SiO₂ or Al₂O₃, respectively. Considering the high Al₂O₃ availability in the finest fractions and the high SiO₂ availability in coarser fractions, it is expected the best results for the <30 mm fraction. This fraction presents the required ratio between the available SiO₂ and Al₂O₃ content.



Fig. 7. Si/Al ratio of WBA as a function of particle size fraction and chemical attack solution.

The initial WBA FT-IR spectra for each fraction were compared to the FT-IR spectra of the attacked WBA in order to evaluate changes in its structure and composition after the chemical attacks. Fig. 8 depicts the FT-IR spectra of the initial WBA samples, according to particle size fraction. The predominant peaks observed in the spectra are typical of carbonate and silicate compounds (Criado et al., 2005). On the one hand, there is a strong band at 1429 cm⁻¹, assigned to the stretching mode of carbonates, as well as sharp peaks at 875 cm⁻¹ and 714 cm⁻¹ related to the bending mode of carbonates. On the other hand, there is a broad band at 1000 cm⁻¹ associated with Si-O-Si bridging bonds in quartz (SiO₂) (Criado et al., 2005). It can be observed a broad shoulder around 980 cm⁻¹ related to Si(Al)-O asymmetrical vibrations. The FT-IR results validate those of the XRF and XRD analysis, where Si and Al

were determined as major elements and some alumino-silicate compounds were also identified.



Fig. 8. FT-IR spectrum of the particle size fractions of WBA.

Fig. 9 shows the FT-IR spectra for all the samples as a function of the chemical attack solution, with remarkable differences between them. If the spectra of the WBA samples attacked by HF and NaOH 8M solutions are compared with the FT-IR spectrum of the initial WBA samples, a great reduction (slightly pronounced in HF) of the Si-O-Si peak can be observed. The spectra of the WBA samples attacked with NaOH 2M and NaOH 4M presents a morphological variation in the Si-O-Si peak compared with the spectrum of the initial WBA samples (a sharpening of the peak at 1000 cm⁻¹). These results agree with those obtained in the chemical attacks, where more SiO₂ with the HF and NaOH 8M attacks were extracted than with the NaOH 2M and NaOH 4M attacks, due to the greater aggressiveness of the formers. It also can be observed that the initial carbonate broad band and sharp peaks

disappear in the HF chemical attack, in contrast with the NaOH 4M and NaOH 8M solutions, where there is an increase in the intensity of the peaks. As for NaOH 2M, both the broad band and sharp peak are slightly reduced in comparison with the initial WBA. This is all consistent with the aggressiveness of the reactive solutions. When a slightly aggressive reactive solution was used (i.e. NaOH 2M), the solubility in aqueous media of some alkali-carbonates, mainly sodium and potassium carbonates was strongly affected. However, the solubility of alkaline-earth carbonates (e.g. calcium carbonate) and SiO₂-based vitreous compounds was hardly affected. The aggressiveness of the reactive solution (i.e. NaOH 4M and 8M) increases the solubility of the SiO₂, mainly the vitreous materials. When the solubility of alkaline-earth carbonates decreases, the relative content of the carbonates in the attacked residues increases.



Fig. 9. FT-IR spectra of attacked WBA samples as a function of chemical attack solution (a) HF (b) NaOH 2M (c) NaOH 4M (d) NaOH 8M

An environmental characterisation of the WBA was performed to evaluate the potential release of metal(loid)s. The study was only conducted for the worst-case scenario, corresponding to the use of the most aggressive reactive alkaline solution (i.e. NaOH 8M). The heavy metal(loid)s content (mg·kg⁻¹) is shown in Table 4. The results demonstrate that the WBA samples release more metal(loid)s with an excess of NaOH 8M. This means that the alkaline nature of NaOH 8M caused a severe activation of heavy metal(loid)s, because of the high pH value obtained, since the initial WBA is considered a non-hazardous material (Giro-Paloma et al., 2017a; Valle-zermeño et al., 2017). However, it is expected that with the formulation of AAC using WBA as precursor, most of the activated metalloids will remain encapsulated (Kupwade-Patil et al., 2014).

Table 4. Metal(loid)s content of WBA ($mg \cdot kg^{-1}$) samples.

Fraction	As	Ва	Cr	Cu	Hg	Mo	Ni	Pb	Zn
<30 mm	6.06	294.58	23.39	23.87	0.05	14.84	8.04	133.30	896.00
>16 mm	16.77	196.98	35.65	13.44	0.16	16.72	8.24	582.07	454.70
16-8 mm	12.71	385.89	10.31	18.95	0.28	16.59	8.99	477.00	325.18
8-4 mm	8.80	536.79	19.98	26.79	-	16.90	6.58	156.68	2209.05
4-2 mm	16.05	474.21	16.43	48.17	-	18.60	9.13	736.89	1710.49
2-0 mm	8.82	408.09	18.41	77.63	0.07	17.72	8.48	433.43	4187.92

4. Conclusions

It is necessary to find a solution to valorise the large amount of MSWI bottom ash produced around the world and especially in Europe, to promote the new environmental policies of the EU. The research reported herein demonstrates the potential of WBA for use as a precursor in the alkali-activation of cements. Physicochemical characterisation determined the composition based on aluminosilicates and the amorphous nature of WBA samples. The chemical attacks results showed that the SiO₂ and Al₂O₃ reactive phases are available in each particle size fraction of the WBA. The calculated Si/Al ratio of each WBA sample suggests the possibility of formulating AACs using WBA as sole precursor, or mixed with others, in order to adjust the Si/Al ratio to around 2. The environmental characterisation of WBA

samples showed a high activation of heavy metal(loid)s, due to the redissolution of the pHdependent metal(loid)s in high pH media, generated by the alkaline reactive solutions.

The investigation future line will be based on the formulation of AACs using WBA as only precursor. The main goal must be valorising the maximum amount of WBA (using >30 mm sample or mixing some fractions) without affecting to the AACs environmental properties. It will certainly be necessary to study the release of heavy metals and metal(loid)s from new AACs developed using WBA as a precursor to elucidate if it means a limitation on the final environmental properties of the materials. It is expected that to obtain AACs, there will be less release due to the encapsulation of metal(loid)s in the binder matrix and a decrease of the permeability of leaching solutions. Otherwise, WBA will be mixed with other more noble precursors in order to dilute the concentration of the heavy metal(loid)s content.

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References

- Aljerf, L., 2015. Effect of Thermal-cured Hydraulic Cement Admixtures on the Mechanical Properties of Concrete. Interceram - Int. Ceram. Rev. 64, 346–356. https://doi.org/10.1007/BF03401142
- Alonso, S., Vázquez, T., Puertas, F., Martínez-Ramírez, S., 2000. Alkali-activated fly ash / slag cement Strength behaviour and hydration products. Cem. Concr. Res. 30, 1625–1632. https://doi.org/10.1016/S0008-8846(00)00298-2

Arm, M., 2003. Mechanical properties of residues as unbound road materials - experimental

tests on MSWI bottom ash, crushed concrete and blast furnace slag.

- Bakharev, T., 2005. Resistance of geopolymer materials to acid attack. Cem. Concr. Res. 35, 658–670. https://doi.org/10.1016/j.cemconres.2004.06.005
- Bernal, S.A., Rodríguez, E.D., Kirchheim, A.P., Provis, J.L., 2016. Management and valorisation of wastes through use in producing alkali-activated cement materials. J. Chem. Technol. Biotechnol. 91, 2365–2388. https://doi.org/10.1002/jctb.4927

CEWEP, 2016. Bottom ash fact sheet.

- Chen, I.A., 2009. Synthesis of Portland Cement and Calcium Sulfoaluminate-Belite Cement for Sustainable Development and Performance. PCA R&D Ser. No. SN3130 1–216.
- Cheng, H., Hu, Y., 2010. Municipal solid waste (MSW) as a renewable source of energy: Current and future practices in China. Bioresour. Technol. 101, 3816–3824. https://doi.org/10.1016/j.biortech.2010.01.040
- Chimenos, J., Segarra, M., Fernández, M., Espiell, F., 1999. Characterization of the bottom ash in municipal solid waste incinerator. J. Hazard. Mater. 64, 211–222. https://doi.org/10.1016/S0304-3894(98)00246-5
- Chimenos, J.M., Fernández, A.I., Miralles, L., Segarra, M., Espiell, F., 2003. Short-term natural weathering of MSWI bottom ash as a function of particle size. Waste Manag. 23, 887–895. https://doi.org/10.1016/S0956-053X(03)00074-6
- Chimenos, J.M., Fernandez, A.I., Nadal, R., Espiell, F., 2000. Short term natural weathering of MSWI bottom ash. J. Hazard. Mater. B79 79, 287–299.

Cioffi, R., Colangelo, F., Montagnaro, F., Santoro, L., 2011. Manufacture of artificial aggregate using MSWI bottom ash. Waste Manag. 31, 281–288. https://doi.org/10.1016/j.wasman.2010.05.020

Criado, M., Palomo, A., Fernández-Jiménez, A., 2005. Alkali activation of fly ashes. Part 1: Effect of curing conditions on the carbonation of the reaction products. Fuel 84, 2048– 2054. https://doi.org/10.1016/j.fuel.2005.03.030

- Duxson, P., Fernández-Jiménez, A., Provis, J.L., Lukey, G.C., Palomo, A., Van Deventer, J.S.J., 2007. Geopolymer technology: The current state of the art. J. Mater. Sci. 42, 2917–2933. https://doi.org/10.1007/s10853-006-0637-z
- Duxson, P., Provis, J.L., Lukey, G.C., Mallicoat, S.W., Kriven, W.M., Van Deventer, J.S.J., 2005. Understanding the relationship between geopolymer composition, microstructure and mechanical properties. Colloids Surfaces A Physicochem. Eng. Asp. 269, 47–58. https://doi.org/10.1016/j.colsurfa.2005.06.060

European Commision, 2015. Directive of the European Parlament and of the Council amending Directive 94/62/EC on packaging and packaging waste. https://doi.org/10.1007/s13398-014-0173-7.2

- European Commission, 2017. Report from the commission to the european parliament, the council, the european economic and social committee and the committee of the regions. Off. J. Eur. Union COM(2017), 1–14.
- European Parliament and Council, 2008. Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain directives. Off. J. Eur. Union 3–30. https://doi.org/2008/98/EC.; 32008L0098

Ginés, O., Chimenos, J.M., Vizcarro, A., Formosa, J., Rosell, J.R., 2009. Combined use of MSWI bottom ash and fly ash as aggregate in concrete formulation: Environmental and mechanical considerations. J. Hazard. Mater. 169, 643–650. https://doi.org/10.1016/j.jhazmat.2009.03.141

Giro-Paloma, J., Maldonado-Alameda, A., Formosa, J., Barbieri, L., Chimenos, J.M.,
Lancellotti, I., 2017a. Geopolymers based on the valorization of Municipal Solid Waste
Incineration residues, in: IOP Conference Series: Materials Science and Engineering.
https://doi.org/10.1088/1757-899X/251/1/012125

Giro-Paloma, J., Ribas-Manero, V., Maldonado-Alameda, A., Formosa, J., Chimenos, J.M., 2017b. Use of municipal solid waste incineration bottom ash and crop by-product for producing lightweight aggregate, in: IOP Conference Series: Materials Science and Engineering. https://doi.org/10.1088/1757-899X/251/1/012126

- Hjelmar, O., Holm, J., Crillesen, K., 2007. Utilisation of MSWI bottom ash as sub-base in road construction: First results from a large-scale test site. J. Hazard. Mater. 139, 471–480. https://doi.org/10.1016/j.jhazmat.2006.02.059
- Jansen, D., Stabler, C., Goetz-Neunhoeffer, F., Dittrich, S., Neubauer, J., 2011. Does Ordinary Portland Cement contain amorphous phase? A quantitative study using an external standard method. Powder Diffr. 26, 31–38. https://doi.org/10.1154/1.3549186
- Johansson, I., Bavel, B. Van, 2003. Polycyclic aromatic hydrocarbons in weathered bottom ash from incineration of municipal solid waste. Chemosphere 53, 123–128. https://doi.org/10.1016/S0045-6535(03)00299-6
- Komnitsas, K.A., 2011. Potential of geopolymer technology towards green buildings and sustainable cities. Procedia Eng. 21, 1023–1032.

https://doi.org/10.1016/j.proeng.2011.11.2108

- Kupwade-Patil, K., Allouche, E.N., Islam, R., Gunasekaran, A., 2014. Encapsulation of solid waste incinerator ash in geopolymer concretes and its applications. ACI Mater. J. 111, 691–700. https://doi.org/10.14359/51686834
- Lancellotti, I., Ponzoni, C., Bignozzi, M.C., Barbieri, L., Leonelli, C., 2014. Incinerator bottom ash and ladle slag for geopolymers preparation. Waste and Biomass Valorization 5, 393–401. https://doi.org/10.1007/s12649-014-9299-2
- Magnusson, Y., 2005. Environmental Systems Analysis for utilisation of bottom ash in ground constructions. Trita-KET-IM.

McLellan, B.C., Williams, R.P., Lay, J., Van Riessen, A., Corder, G.D., 2011. Costs and

carbon emissions for geopolymer pastes in comparison to ordinary portland cement. J. Clean. Prod. 19, 1080–1090. https://doi.org/10.1016/j.jclepro.2011.02.010

- Murri, A.N., Rickard, W.D.A., Bignozzi, M.C., Riessen, A. Van, 2013. High temperature behaviour of ambient cured alkali-activated materials based on ladle slag. Cem. Concr. Res. 43, 51–61. https://doi.org/10.1016/j.cemconres.2012.09.011
- Pecqueur, G., Crignon, C., Que, B., 2001. Behaviour of cement-treated MSWI bottom ash 21, 229–233.

Pérez-Martínez, S., Giro-paloma, J., Maldonado-alameda, A., Formosa, J., Queralt, I., 2019. Characterisation and partition of valuable metals from WEEE in weathered municipal solid waste incineration bottom ash , with a view to recovering 218, 61–68. https://doi.org/10.1016/j.jclepro.2019.01.313

- Phair, J.W., 2006. Green chemistry for sustainable cement production and use. Green Chem.8, 763–780. https://doi.org/10.1039/b603997a
- Roy, D.M., 1999. Alkali-activated cements: Opportunities and challenges. Cem. Concr. Res. 29, 249–254. https://doi.org/10.1016/S0008-8846(98)00093-3
- Ruiz-Santaquiteria, C., Fernándes-Jiménez, a, Palomo, a, 2011. Quantitative determination of reactive SiO2 and Al2O3 in aluminosilicate materials. 13th Int. Congr. Chem. Cem. 1–7.
- Shim, Y., Kim, Y., Kong, S., Rhee, S., Lee, W., 2003. The adsorption characteristics of heavy metals by various particle sizes of MSWI bottom ash. Waste Manag. 23, 851–857. https://doi.org/10.1016/S0956-053X(02)00163-0
- Silva, R. V., de Brito, J., Lynn, C.J., Dhir, R.K., 2017. Use of municipal solid waste incineration bottom ashes in alkali-activated materials, ceramics and granular applications: A review. Waste Manag. 68, 207–220.

https://doi.org/10.1016/j.wasman.2017.06.043

- Singh, B., G., I., Gupta, M., Buattacharyya, S.K., 2015. Geopolymer Concrete : A Review of some recent developments. Constr. Build. Mater. 85, 78–90.
- Snellings, R., Salze, A., Scrivener, K.L., 2014. Use of X-ray diffraction to quantify amorphous supplementary cementitious materials in anhydrous and hydrated blended cements. Cem. Concr. Res. 64, 89–98. https://doi.org/10.1016/j.cemconres.2014.06.011
- Toraldo, E., Saponaro, S., Careghini, A., Mariani, E., 2013. Use of stabilized bottom ash for bound layers of road pavements. J. Environ. Manage. 121. https://doi.org/10.1016/j.jenvman.2013.02.037
- Valle-zermeño, R., Formosa, J., Chimenos, J.M., 2017. Material characterization of the MSWI bottom ash as a function of particle size . Effects of glass recycling over time. Sci. Total Environ. 581–582, 897–905. https://doi.org/10.1016/j.scitotenv.2017.01.047
- Van Deventer, J.S.J., Provis, J.L., Duxson, P., 2012. Technical and commercial progress in the adoption of geopolymer cement. Miner. Eng. 29, 89–104. https://doi.org/10.1016/j.mineng.2011.09.009
- Wei, Y., Shimaoka, T., Saffarzadeh, A., Takahashi, F., 2011. Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metalbearing phases. J. Hazard. Mater. 187, 534–543. https://doi.org/10.1016/j.jhazmat.2011.01.070
- Yao, W.J., Fan, L., Liu, G.Y., 2018. Properties of Alkali-Activated Waste Glass-Cement Cementitious Materials. Mater. Sci. Forum 926, 134–139. https://doi.org/10.4028/www.scientific.net/MSF.926.134
- Zhang, H., Shimaoka, T., 2013. Formation of Humic Substances in Weathered MSWI Bottom Ash. Sci. World J. 2013.