

Use of weathered and fresh bottom ash mix layers as a subbase in road constructions: Environmental behavior enhancement by means of a retaining barrier

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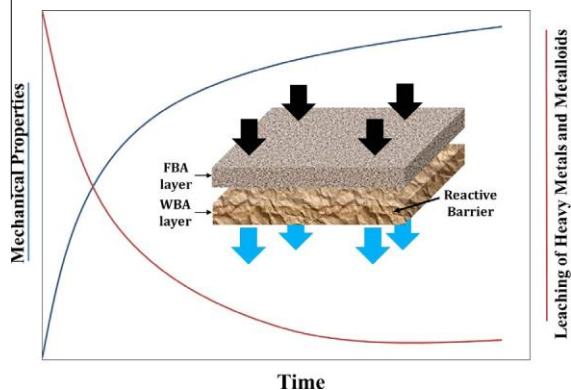
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h i g h l i g h t s

- Weathering of compacted freshly bottom (FBA) ash improves mechanical properties.
- FBA has a potential effect on the environment in the early stages of reutilisation.
- A WBA layer behaves as a reactive barrier for heavy metals and metalloids retention.
- WBA/FBA mix layers improve mechanical properties and reduce heavy metals release.

g r a p h i c a l a b s t r a c t



a r t i c l e i n f o

Article history:

Received 12 March 2014

Received in revised form 28 July 2014

Accepted 30 July 2014

Available online 1 September 2014

Handling Editor: O. Hao

Keywords:

Freshly bottom ash
Weathered bottom ash
Heavy metal retention
Road construction
Retaining barrier

a b s t r a c t

The presence of neoformed cement-like phases during the weathering of non-stabilized freshly quenched bottom ash favors the development of a bound pavement material with improved mechanical properties. Use of weathered and freshly quenched bottom ash mix layers placed one over the other allowed the retention of leached heavy metals and metalloids by means of a reactive percolation barrier. The addition of 50% of weathered bottom ash to the total subbase content diminished the release of toxic species to below environmental regulatory limits. The mechanisms of retention and the different processes and factors responsible of leaching strongly depended on the contaminant under concern as well as on the chemical and physical factors. Thus, the immediate reuse of freshly quenched bottom ash as a subbase material in road constructions is possible, as both the mechanical properties and long-term leachability are enhanced.

1. Introduction

Bottom ash (BA) from the incineration of municipal solid waste (MSW) is composed of grate ash and grate siftings. It is a highly

heterogeneous mixture of slag, ferrous and non-ferrous metals, ceramics, glass, other non-combustibles and residual organic matter (Chimenos et al., 1999). Unlike fly ash, BA is classified as non-hazardous waste by the European Waste Catalogue, as it is typically rich in calcium, aluminum, silicon and iron, resembling natural aggregate compounds but with different proportions (Chandler, 1997). However, chlorides, zinc, copper, lead and chromium are

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often present in high concentrations in BA, since they are widely used in the manufactured products that end up as waste. Consequently, a proper stabilisation process is needed in order to diminish the release of heavy metals and metalloids prior to reutilisation as secondary building material, either in road constructions or as concrete aggregate (Polettini et al., 2001; Chimenos et al., 2003; Fernández Bertos et al., 2004; Ginés et al., 2009). However, other alternatives for their recycling and reutilisation assuring environmental safety are a major concern in order to follow the path to sustainability.

Natural weathering is the most cost-effective stabilisation treatment method, since it results in the chemical stability of BA. The early stages are characterized by strong leaching of the heavy metal content, due to the reducing conditions that favor solubility and to the steep concentration gradients between phases (Sabbas et al., 2003; Grathwohl and Susset, 2009). After a one-to-three month period, natural weathering of freshly quenched BA (FBA) causes chemical and mineralogical changes that lead to neoformed phases and minerals that are thermodynamically more stable and less reactive.

Along with a change in heavy metal and metalloid solubility, the presence of neoformed cement-like phases during weathering also exerts a special influence in mechanical properties of FBA. Chimenos et al. (2005) found that the effect of the dissolution and precipitation of metastable phases, as well as hydration and oxidation, starts immediately after quenching and becomes greater after a short period of time. The neoformed phases, as well as the elevated water content, act as a binder layer among particles that exerts a curing process with time. Because of this, the mechanical parameters have a spectacular improvement during the short-term natural weathering process. As a consequence, the freshly compacted BA progresses from behaving as an unbound material into a bound pavement material with a better performance than compacted natural weathered BA (WBA). The short-term change in mechanical properties means that FBA can be used prior to weathering as a road subbase, since its stiffness and compressive strength gradually increase over time (Chimenos et al., 2005). Accordingly, the reutilisation of FBA becomes feasible, since good mechanical behavior is assured and furthermore improved after a short period of time.

Nevertheless, the high reactivity of non-stabilised FBA represents a disadvantage, because of its potential effect on the environment in the early stages of reutilisation. As it has been previously determined (Chimenos et al., 2000, 2003), the leaching of heavy metals and metalloids usually results in greater concentrations values than those established in the regulatory limits for the reuse of BA as secondary building material. However, the leached concentrations of some of these heavy metals and metalloids dramatically fall after a very short period of natural weathering. Taking into account all the above mentioned, the revalorisation of BA is only environmentally friendly once it has been stabilised by a natural weathering period. Alternatives for its immediate reuse have not yet been reported.

On the other hand, the potential environmental impact of the leachates generated by percolating water when BA is used as a secondary building material in soils and road constructions has been extensively assessed by numerous authors (Johnson et al., 1996; Kersten et al., 1998; Sabbas et al., 2003; Izquierdo et al., 2008; Olsson et al., 2009). In conclusion, it can be stated that leaching of heavy metals and metalloids is strongly controlled by pH and redox conditions, as well as by complexation effects and adsorption into neoformed phases and minerals (Chimenos et al., 2005; Grathwohl and Susset, 2009).

In the framework of this issue, the aim of this study was to carry out an environmental assessment of the use of WBA and FBA mix layers, placed one below the other, as a subbase material in road

constructions. A layer of WBA at the bottom would not only grant initial mechanical support but also enhance the environmental behavior of the leachates generated in the upper layer, as it would behave as a permeable reactive barrier (PRB) for heavy metals and metalloids retention. Moreover, the ageing processes would increase the mechanical properties of the top FBA layer over time, as a consequence of the presence of neoformed oxides, aluminosilicates, gypsum and ettringite, leading to the formation of the aforementioned cement-like phases that act as a binder material (Chimenos et al., 2005). Hence, a bound pavement material with enhanced environmental behavior can be gradually obtained.

For this purpose, layers with different proportions of WBA and FBA were prepared and studied. The potential environmental impact was evaluated using percolation leaching tests.

2. Materials and method

2.1. Bottom ash sampling

Both WBA and FBA were collected from a single MSW incinerator located in Tarragona (Spain). The feed stream is commonly composed of household waste with smaller proportions of waste from commercial vendors. The facility produces 35000 tonnes per year of BA, which is directly homogenized after quenching in a conditioned plant for the recovery of reusable metals. Afterwards, the BA is stabilised by natural weathering while stored in a stock pile in the open for up to 3 months. Sampling of both FBA and WBA was planned according to the schedule of the experiment. FBA was sampled by collecting approximately 25 kg directly from the drag conveyor following combustion and previous to the recovery of metals. The moisture content was measured immediately and then the sample was tested. Around 250 kg of WBA was taken from various stockpiles stored for at least 3 months in an open disposal environment. The characterization with respect to its moisture content was also measured. After homogenization, each sample of WBA and FBA was screened to a particle size below 25 mm and quartered by a riffle-type sample splitter.

In order to evaluate the leaching behavior and the potential impact of both types of BA, the batch leaching test was carried out according to EN 12457-4 (2004). In this test, representative samples of WBA and FBA were taken separately and reduced when necessary to a particle size below 10 mm and brought into contact with ten times the weight of water under continuous stirring for 24 h. The corresponding eluates were passed through 45 μ m polypropylene membrane filters, acidified by adding a few drops of HNO₃ and preserved in a fridge at 4 °C for subsequent analysis. Trace metal concentrations were determined by inductive coupled argon plasma mass spectrometry (ICP-MS). The results are shown in Table 1. The threshold established by the Catalan Government for landfill disposal and the regulatory limit values for reutilization of BA as secondary building material are also displayed for their corresponding classification (DOGC 2181 and 5370).

As it can be seen in Table 1, the concentration values for all the elements analyzed were below the values established by the Catalan Legislation for the revalorisation of WBA. As for the classification prior landfill, the majority of elements can be catalogued as inert with the exception of Cu, which fall in the concentration range of non-hazardous. In contrast, the concentration value of leached Pb for all samples of FBA studied were greater than the limit established and consequently this material should not be reused as secondary building material, requiring an adequate treatment before its final management. These results are in agreement with the values found in previous research works carried out with samples of FBA from the same facility (Chimenos et al., 2000).

Table 1
Results of the leaching test EN 12457-4 for both WBA and FBA. Threshold established by the Catalan Government for landfill disposal and the regulatory limit values for utilization of BA as secondary building materials.

Element	WBA	FBA	Limit values			Utilization ^a
			Landfill ^b			
			Inert	Non-hazardous	Hazardous	
As (mg kg ⁻¹)	<0.005	0.01–0.005	0.5	2	25	1
Ba (mg kg ⁻¹)	0.19	0.8–1.6	20	100	300	–
Cd (mg kg ⁻¹)	<0.005	<0.005	0.04	1	5	1
Cr (mg kg ⁻¹)	0.20	0.3–0.5	0.5	10	70	5 ^c
Cu (mg kg ⁻¹)	3.48	7.3–9.1	2	50	100	20
Hg (mg kg ⁻¹)	<0.01	<0.01	0.01	0.2	2.0	0.2
Mo (mg kg ⁻¹)	0.42	0.3–0.5	0.5	10	30	–
Ni (mg kg ⁻¹)	<0.03	0.1–0.2	0.4	10	40	5
Pb (mg kg ⁻¹)	0.20	5.3–9.7	0.5	10	50	5
Zn (mg kg ⁻¹)	0.16	3.2–5.8	4.0	50	200	20

^a Catalanian Order Number 2181/13.3.1996.

^b Catalanian Order Number 5370/30.4.2009.

^c Max. Cr(VI): 1 mg kg⁻¹.

2.2. Experimental

Percolation is known to be the major leaching mechanism for granular materials (Hage and Mulder, 2004). Therefore, column leaching tests are preferred because they are performed in more realistic conditions for the sake of field predictions (Kjeldsen and Christensen, 1990; Kalbe et al., 2007; Lopez Meza et al., 2008). The column leaching test is described in CEN 14405 and is generally characterized, among other factors, by the size of the column used, which is determined by the particle size, the leachant flow and the liquid to solid (L/S) ratio. The leachates are collected in several fractions according to different L/S ratios and the heavy metals and metalloids content is analyzed. Other measures such as pH, conductivity and the presence of some specific solutes (chlorides) are also carried out.

This type of test is highly valuable, as a large amount of information is generated, since leaching behavior changes with L/S ratio. However, it is time consuming as the total time of the experiment might exceed 21 d (Hage and Mulder, 2004). In order to exclusively focus on the effect of FBA layers placed in different proportions along with WBA, some modifications were made to the cited standardized test so that it resembled natural conditions and a real scenario. First, the size of the samples was not reduced, and therefore a particular column was selected for all experimental trials ($d = 150$ mm; $h = 400$ mm). Fig. 1 shows the column dimensions as well as the accompanying equipment. On this matter, it has been reported elsewhere that different column dimensions do not show any substantial influence on the percolation test results (Grathwohl and Susset, 2009).

Demineralized water was used as a leachant and was pumped from the bottom of the column. The column was prepared, filled and packed according to standard procedure. The proper mass of material to be packed in was calculated according to the proportion of each layer, the thickness of a subbase layer in real road construction (200 mm), the column dimensions and the optimal dry density (1690 ± 20 kg m⁻³) and humidity (an average of 17.1%) of processed BA, the two latter determined by means of the standard Proctor compaction test (UNE 103500:1994). The moisture content measured immediately after sampling was taken into account and the Proctor humidity was reached by adding demineralised water. Five mix layers were considered in the study (% height of FBA (l_f) to % height of WBA (l_w) ratio): 0/100, 25/75, 50/50, 75/25 and 100/0. Each FBA layer was placed at the bottom as the column works in an up-flow regime, simulating real conditions where it would be on the top (Fig. 1). An inert and compacted material was used between support filters and tested material at the top

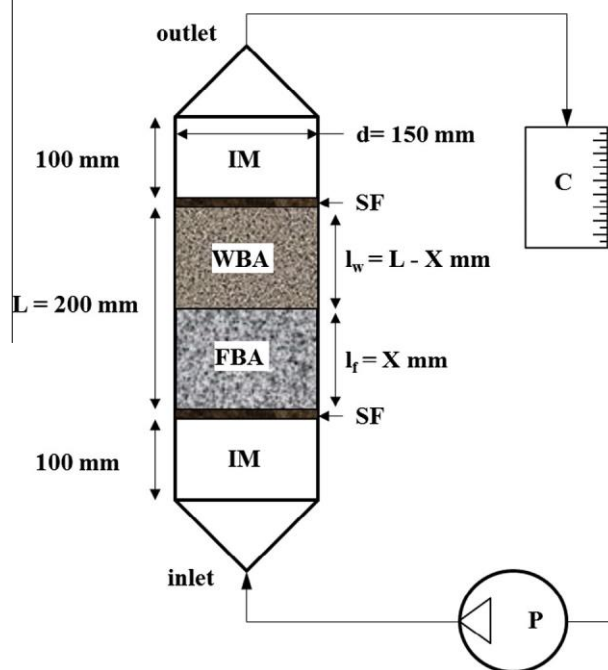


Fig. 1. Column dimensions and the accompanying equipment. IM: inert material; WBA: weathered bottom ash; FBA: fresh bottom ash; SF: support filters; P: pump; C: collector; l_w : height of the WBA layer; l_f : height of the FBA layer.

and at the bottom for mechanical assistance and to avoid filter obstruction. Furthermore, no saturation or equilibration period was considered appropriate as the objective was to evaluate differences in the leaching potential of the five mix layers to be tested as a function of both the FBA and WBA percentage. In this context, the L/S ratio was not considered as the main variable, and time progression was selected instead. A constant flow rate of 6 ± 0.5 mL min⁻¹ was chosen to favor the undesired equilibrium conditions (Quina et al., 2011). Different times were fixed for collecting eluate fractions (10–2880 min). Hence, as water percolated through the column the L/S ratio increased.

The eluate fractions were analyzed to determine pH and conductivity and the chloride concentration was measured by ion selective electrode. Finally, eluate fractions were properly stored in acid medium at 4 °C for subsequent analysis of the heavy metals and metalloids by inductively coupled plasma mass spectrometry (ICP-MS). Likewise, in order to avoid the chloride interference,

arsenic was reduced before analysis using a potassium iodide solution and determined by ICP-MS using hydride generation. Experimental trials for each mix layer considered in the study were performed in duplicate. Therefore, the results are presented as the average value.

Representation of cumulative concentrations loads of the different elements studied were calculated by summing the concentrations corresponding to each time of collection and taking into account both the amount of leachate involved in the time interval and the dry sample weight. Thus, concentration values are presented in mg kg^{-1} dried matter.

3. Results and discussion

The cumulative L/S ratio was consistent among all the experimental trials. It started at 0.01 L kg^{-1} at the beginning of the experiment and reached an average of 2 L kg^{-1} after 48 h. For subsequent evaluations of environmental limits, this cumulative L/S ratio interval is very representative of field applications such as road constructions (Grathwohl and Susset, 2009; Quina et al., 2011).

The pH measures were as expected, given the nature of WBA and FBA (Fig. 2). The 100% WBA (0/100) had a lower pH range between 10.4 and 10.6, mainly as a consequence of carbonation by the uptake of atmospheric CO_2 during natural weathering, which leads to the formation of pH-controlling phases such as calcite, ettringite, gibbsite and gypsum (De Windt et al., 2011). The pH range of 100% FBA (100/0) was 12.3–12.6, and was mainly controlled by the equilibrium solubility of portlandite. There were no major differences between the pH determined for trials of 100/0 and 75/25, with little effect from the barrier layer of WBA. In contrast, trials 50/50 and 75/25 showed a decrease of pH between 0.8 and 1.3 units after 48 h respectively, with a remarkable neutralizing effect of WBA layer. When pH decreases close to 11 its value is controlled by the formation of aluminum sulphates (Meima and Comans, 1997) and aluminum hydroxides. In this stage, ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$), gibbsite ($\text{Al}(\text{OH})_3$) and gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) have been recognized to be some of the dominant secondary mineral phases. While ettringite is formed under equilibrium conditions from oversaturated leachates, which can be hardly obtained with such a short contact time in the column leaching test, the kinetics of gypsum precipitation and gibbsite formation are very fast and both reactions can be

regarded as the most important pH controllers. In terms of conductivity, this parameter ranged from 5 to 13 mS cm^{-1} , for lower L/S ratios, to $1\text{--}3 \text{ mS cm}^{-1}$ for L/S ratios close to 2 after 48 h. The trend in conductivity was similar to that of chloride concentration in the leachates, where any significant differences were observed between all experimental trials. This fact might be the expected given the nature of the main contributors to conductivity: sulphates and chlorides. These ions are balanced by Na, K and Mg except at high concentration values (the corresponding to the lowest L/S ratios), where Ca is also involved in compensating chlorides (Meima and Comans, 1997; Freyssinet et al., 2002). The conductivity values rose quickly from smaller L/S ratios to up to a maximum after 45–60 min. After reaching this maximum, they decreased steadily, indicating that the highest release of the major elements occurred during the first moments.

Ito et al. (2008) determined that S and Cl are the elements that are dissolved the most in a water washing process (51% and 39%, respectively, at a L/S ratio of 10), indicating that the main soluble compounds in BA are comprised of these two elements (Ito et al., 2008). As previously mentioned, the release of chlorides (Fig. 3) took place mainly at lower L/S ratios. In other words, a high percentage of easily water-soluble chloride was leached out in the first volumes of washing water. According to that, the great solubility of chlorides is characteristic of availability-controlled leaching, as depletion and rapid wash out occur when the L/S ratio is increased (Kosson et al., 1996; Sabbas et al., 2003). As it can be seen in Fig. 3, the release of chlorides from all mix layers is practically exhausted for L/S ratios close to 2 (48 h), especially for the 0/100, 25/75 and 75/25 samples. Furthermore, it also can be observed that the leaching concentration of chlorides from the column formulated only with FBA (100/0) is lower than any layer containing WBA, with the 0/100 layer showing the greater chloride release. When the pH is controlled by the solubility of portlandite, e.g. 100% FBA layer (100/0), the high concentration of calcium can influence the release of chlorides by means of the precipitation of calcium chloride. The concentration of calcium is controlled by the formation of more soluble compounds such as gypsum, ettringite or calcite and as it decreases the release of the pH-dependent chlorides increases. According to that, the concentration of chlorides should increase as the height of WBA does.

Fig. 4 shows the cumulative concentration of sulphate from column leaching trials. As it can be seen, its release had a similar behavior to chlorides. In contrast, after 48 h, the release kept

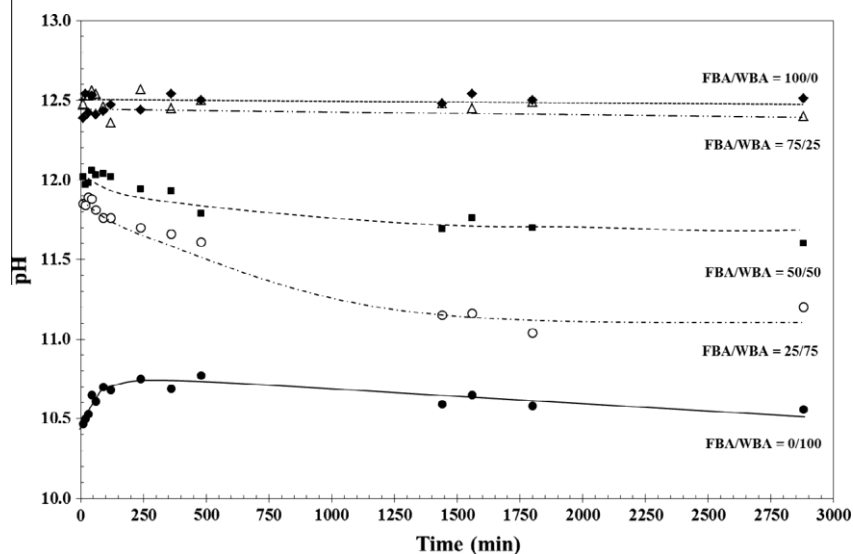


Fig. 2. pH as a function of time.

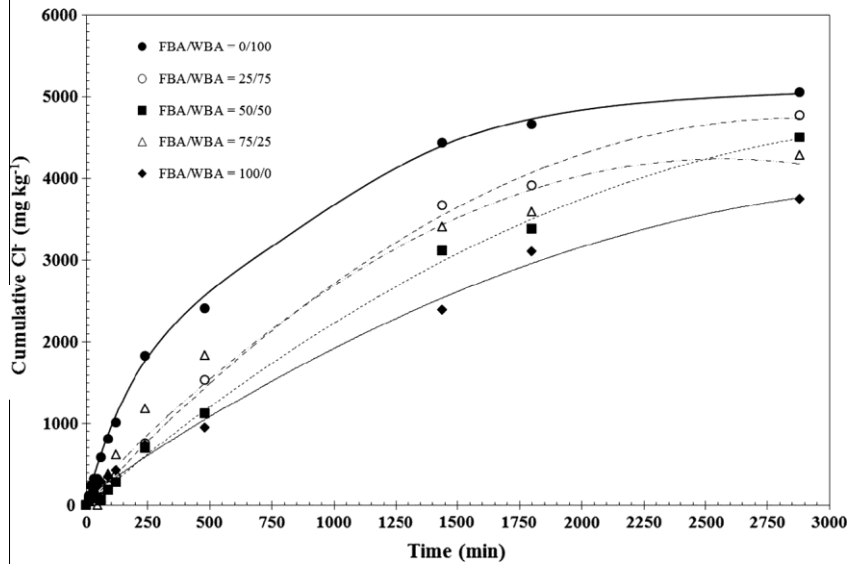


Fig. 3. Cumulative chloride concentration as a function of time for the column leaching trials.

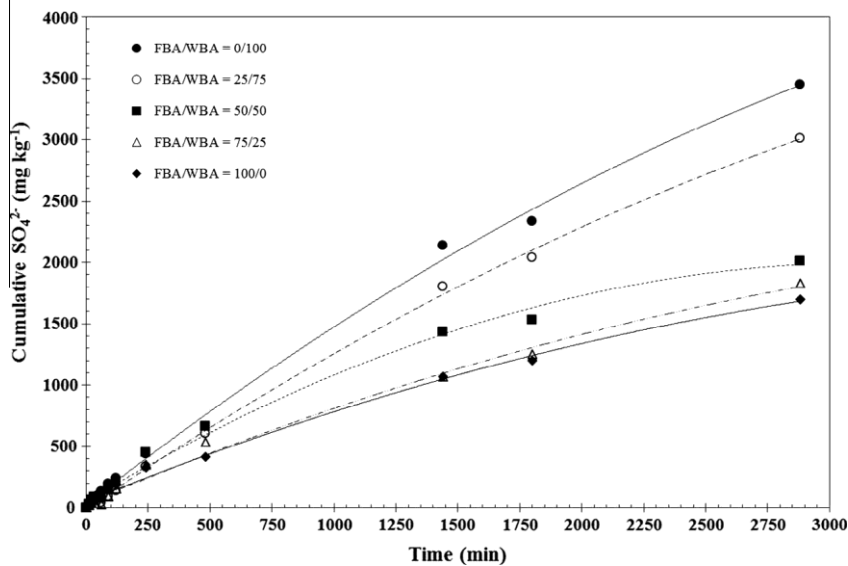


Fig. 4. Cumulative sulphates concentration as a function of time for the column leaching trials.

increasing and did not show any signs of depletion. It was also observed that the release of sulphates increased while the increased thickness of WBA increased too, being the 0/100 experimental trial the mix layer that showed the greatest concentration release. The leaches from FBA show a high $\text{Ca}/\text{SO}_4^{2-}$ molar ratio with respect to gypsum and ettringite, the controlling phases of the release of sulphates (Freyssinet et al., 2002). Moreover, during the weathering process, the oxidation of organic matter and metallic sulphurs takes place, increasing the content of sulphates while decreasing the release of calcium. Consequently, as the thickness of the WBA layer increased, the concentration of sulphates in the leachates also increased.

The results of the leaching experiments for the selected heavy metals and metalloids are shown in Figs. 5–7. The species considered were those included in the Catalan environmental legislation for the revalorisation of BA (DOGC 2181): As, Cd, Cu, Cr (VI), Cr (total), Hg, Ni, Pb and Zn (Table 1). However, Catalan legislation is based on a batch leaching test with an L/S ratio

of 10. Nevertheless, according to Quina et al. (2011), batch and column leaching tests can be compared for the majority of metals and metalloids when the results of both are expressed for the same L/S ratio (Quina et al., 2011). Therefore, the regulatory threshold for an L/S ratio of 2 described in European Council Directive 1999/31/ECC (Table 2) was taken for comparison.

As it can be seen in the above mentioned figures, all the heavy metals and metalloids studied followed a similar range pattern, showing the highest cumulative release for 100% FBA (100/0) layer and gradually decreasing as the WBA percentage increased. Likewise, the release of all heavy metals and metalloids mainly took place at lower L/S ratios, where the cumulative concentration rose very quickly until reaching an interval where the release is very small or almost negligible. The factors responsible of leaching strongly depended on the element under study as well as on the chemical and physical factors of both layers.

The results of the column leaching test revealed two different patterns in the release of the studied heavy metals and metalloids.

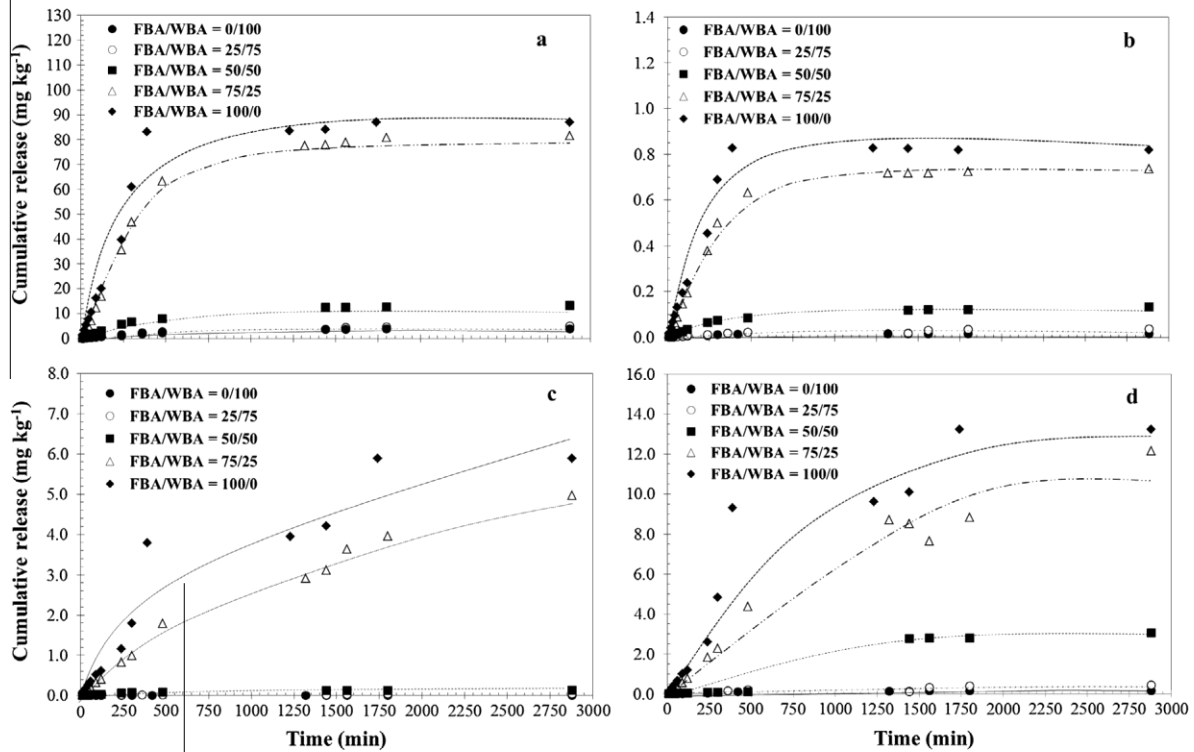


Fig. 5. Cumulative concentration values (mg kg^{-1}) as a function of time (a) Cu; (b) Ni; (c) Pb; and (d) Zn.

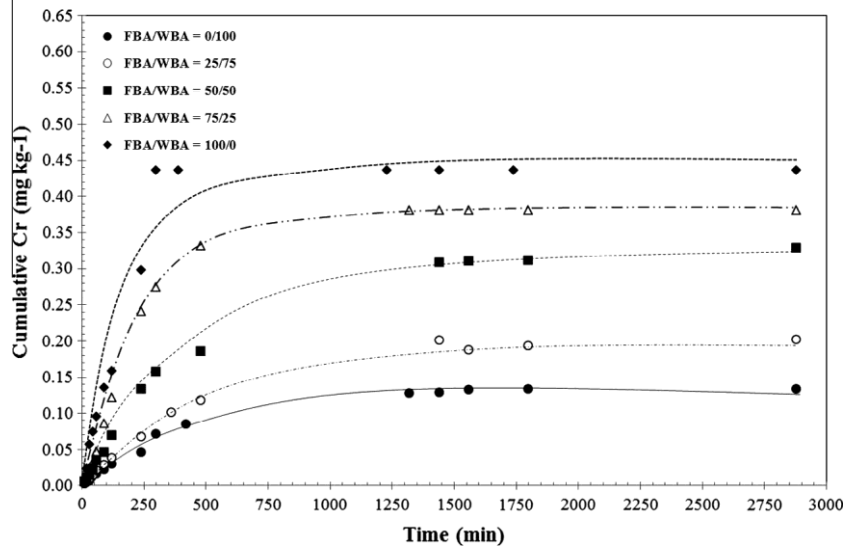


Fig. 6. Cumulative chromium concentration as a function of time for the column leaching trials.

A first pattern shown by Cu, Ni, Pb and Zn (see Fig. 5), in which the decrease in the release of these heavy metals was strongly influenced by the PRB generated by the WBA layer. In these trials, a significant drop in the release of these metals was observed when the thickness of the WBA layer was higher than 50% (i.e. 50/50, 25/75 and 0/100). However, the release of Cr showed a particular behavior in which a dilution effect was attributed as the main mechanism in the concentration decrease. In this case, the release of Cr proportionally decreased while decreasing the FBA percentage (see Fig. 6).

The cumulative concentration of Cu, Ni, Pb and Zn as a function of time is shown in Fig. 5. In the case of Cu (Fig. 5a), a high content of metal and electrical devices is considered to be responsible for

the high leaching observed (Sabbas et al., 2003). Moreover, this element is commonly linked to the release of dissolved organic carbon, as it usually forms strong complexes with organic substances such as hydrophilic and hydrophobic acids (Johnson et al., 1996; Meima et al., 1999; Yao et al., 2010; De Windt et al., 2011). Hence, given the high content of unburned organic matter in FBA, Cu is likely to dissolve and form corresponding ligands. As it can be observed, a substantial decrease in the release of this metal to below regulatory limits was attained when 50% of WBA was added. This was not just driven by dilution effects, as the decrease was not proportional. Therefore, the formation of a less soluble phase of copper (hydr)oxides when exposed to lower pH or the sorption into amorphous Fe/Al-(hydr)oxides formed in the

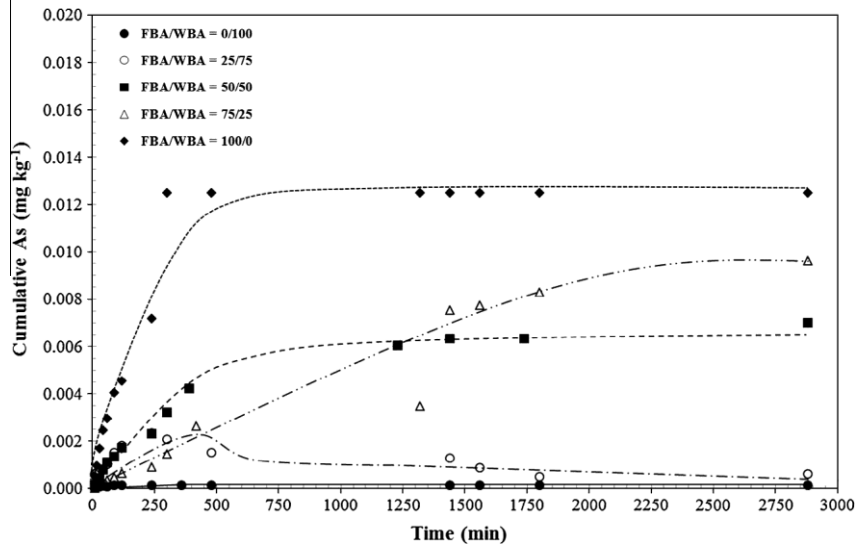


Fig. 7. Cumulative arsenium concentration as a function of time for the column leaching trials.

Table 2
Regulatory threshold non-hazardous materials limits. L/S: 2L
kg⁻¹. European Council Directive 1999/31/ECC.

Element	mg kg ⁻¹
As	0.4
Cd	0.6
Cr (total)	4
Cu	25
Hg	0.05
Ni	5
Pb	5
Zn	25
Cl ⁻	10 000

WBA layer might explain the considerable decrease in the concentration release (Meima et al., 1999; Quina et al., 2011).

In all experimental trials, Ni release was below the threshold limits (Fig. 5b). Like Cu, the addition of 50% WBA substantially reduced the leaching values. Nickel, like other divalent metals, is pH-dependent and its release is mainly attributed to the low solubility of Ni(OH)₂ in the weathered layer, which is reported to be the main equilibrium controlling phase (Quina et al., 2011). Furthermore, as the pH decreased in the weathered layer, sorption onto neofomed iron (hydr)oxides also took place.

Zn and Pb have amphoteric characteristics and therefore presented a high solubility in both acidic and alkaline conditions. Both metals showed the same range pattern as Cu and Ni (Fig. 5c and d respectively). In the case of Pb, the concentration values for those mix layers with 100% and 75% FBA almost reached regulatory limits, whilst the other experimental trials showed steady values under 1 mg kg⁻¹. The low Pb mobility in higher WBA proportions can be attributed to its precipitation as lead hydroxide, whose solubility in the pH range of 9–10 is low (Chandler, 1997). In addition, as the leachate passes through the weathered layer, adsorption mechanisms over Al and Fe (hydr)oxides act as well (Meima and Comans, 1997; Åberg et al., 2006; Hyks et al., 2011). The release of Zn was below regulatory limits for all experimental trials. In alkaline conditions, Zn solubility is mainly controlled by calcium zincate while the more stable zincite dominates at lower pH values (Meima and Comans, 1997).

Cumulative concentration of chromium as a function of time is showed in Fig. 6. Chromium is an oxyanion-forming metal and therefore deserves special attention due to its high toxicity. High

values of redox potential and alkaline conditions in FBA favor the oxidation of Cr(III) to the more mobile Cr(VI) (Kersten et al., 1998). All the experimental trials showed concentration values below the regulatory threshold and presented a range pattern in which the release of Cr decreased while the WBA percentage increased. In this case, depletion was directly related to the WBA percentage. The incorporation of Cr(VI) into low solubility minerals like ettringite during the formation of new phases has been described elsewhere (Quina et al., 2011). However, this process only takes place during the first stages of natural weathering. Sorption onto the already formed Fe/Al (hydr)oxides is excluded. Thus, a dilution effect may be attributed as the main mechanism in the decrease of Cr release.

Like Cr, As is an oxyanion-forming metal and therefore deserves special attention due to its toxicity. A special sampling method for its analysis using ICP-MS had to be used due to the possible interference of chlorides. This alternative method entailed hydrides generation and the elimination of interferences. However, major errors are associated if the concentration values are low or very close to detection limit. Taking this into account, the release of As (Fig. 7) in all experimental trials was below legislation limits and the same range pattern as in the other elements was again observed. Pronounced speciation at the beginning may be provoked by the Cl⁻ ions (Olsson et al., 2009). Lower As concentrations when the percentage of WBA is higher can be attributed to the adsorption of arsenates over Fe (hydr)oxide surfaces when the percolation water passed through the weathered layer.

The Cd and Hg concentration values were below the detection limit (<0.10 mg L⁻¹) in all experimental trials.

To sum up, the processes and factors responsible for leaching strongly depend on the contaminant under concern, as well as on the chemical and physical factors. The physical factors were the same for all experimental trials and therefore the retention barrier for the immobilisation of harmful substances is chemically-controlled. The main factor responsible is the pH gradient created between layers. Moreover, the presence of new sorption sites such as Fe and Al (hydr)oxides in the weathered layer also contribute to immobilisation.

4. Conclusions

The reuse of FBA as a subbase material in road constructions is very attractive from a mechanical point of view, since a bound

pavement material can be obtained after a certain period of time. This mechanical enhancement can be explained by the presence of neoformed cement-like phases during weathering. However, the high reactivity of FBA could lead to a potential environmental impact, due to the release of the heavy metals and metalloids that are not yet stabilised by weathering. In this study, the feasibility of using FBA as an environmentally safe subbase material has been proven.

The combination with different amounts of WBA, in the form of layers placed under the FBA, allows the retention of leached heavy metals and metalloids by means of a reactive barrier. The percolation water passing through the upper FBA layer sweeps trace metals and metalloids into the WBA layer, where retention takes place. This reactive barrier can be depicted as a zone in which retention mechanisms such as pH solubility and adsorption or surface complexation achieve immobilisation of heavy metals and metalloids. The addition of 50% of WBA to the total subbase content reduces toxic species release to below environmental regulatory limits. Thus, the immediate reuse of FBA as a subbase material in road constructions is possible, as both the mechanical properties and long-term leachability are enhanced.

Acknowledgements

The authors would like to thank the SIRUSA and VECSA companies for their financial support and for providing access to sampling sites. Thanks are also given to Mrs. Judit Gómez for her assistance with chemical analysis and data management.

References

- Åberg, A., Kumpiene, J., Ecke, H., 2006. Evaluation and prediction of emissions from a road built with bottom ash from municipal solid waste incineration (MSWI). *Sci. Total Environ.* 355, 1–12.
- Chandler, A.J., 1997. *Municipal Solid Waste Incinerator Residues Studies in Environmental Sciences*. Elsevier Science Publishers B.V., Amsterdam, Netherlands.
- Chimenes, J.M., Segarra, M., Fernández, M.A., Espiell, F., 1999. Characterization of the bottom ash in municipal solid waste incinerator. *J. Hazard. Mater.* 64, 211–222.
- Chimenes, J.M., Fernández, A.I., Nadal, R., Espiell, F., 2000. Short-term natural weathering of MSWI bottom ash. *J. Hazard. Mater.* 79, 287–299.
- Chimenes, 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 Manage.* 23, 887–895.
- Chimenes, J.M., Fernandez, A.I., Miralles, L., Rosell, J.R., Ezquerro, A.N., 2005. Change of mechanical properties during short-term natural weathering of MSWI bottom ash. *Environ. Sci. Technol.* 39, 7725–7730.
- De Windt, L., Dabo, D., Lidelöw, S., Badreddine, R., Lagerkvist, A., 2011. MSWI bottom ash used as basement at two pilot-scale roads: comparison of leachate chemistry and reactive transport modeling. *Waste Manage.* 31, 267–280.
- Diari Oficial de la Generalitat de Catalunya (DOGC) 2181, 1996.
- Diari Oficial de la Generalitat de Catalunya (DOGC) 5370, 2009.
- EN 12457-4, 2004.
- Fernández Bertos, M., Li, X., Simons, S.J.R., Hills, C.D., Carey, P.J., 2004. Investigation of accelerated carbonation for the stabilisation of MSWI incinerator ashes and the sequestration of CO₂. *Green Chem.* 6, 428–436.
- Freyssinet, P., Piantone, P., Azaroual, M., Itard, Y., Clozel-Leloup, B., Guyonnet, D., Baubron, J.C., 2002. Chemical changes and leachate mass balance of municipal solid waste bottom ash submitted to weathering. *Waste Manage.* 22, 159–172.
- Ginés, O., Chimenes, 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.
- Grathwohl, P., Susset, B., 2009. Comparison of percolation to batch and sequential leaching tests: theory and data. *Waste Manage.* 29, 2681–2688.
- Hage, J.L.T., Mulder, E., 2004. Preliminary assessment of three new European leaching tests. *Waste Manage.* 24, 165–172.
- Hyks, J., Nesterov, I., Mogensen, E., Jensen, P.A., Astrup, T., 2011. Leaching from waste incineration bottom ashes treated in a rotary kiln. *Waste Manage. Res.* 29, 995–1007.
- Ito, R., Dodbiba, G., Fujita, T., Ahn, J.W., 2008. Removal of insoluble chloride from bottom ash for recycling. *Waste Manage.* 28, 1317–1323.
- Izquierdo, M., Querol, X., Josa, A., Vazquez, E., López-Soler, A., 2008. Comparison between laboratory and field leachability of MSWI bottom ash as a road material. *Sci. Total Environ.* 389, 10–19.
- Johnson, C.A., Kersten, M., Ziegler, F., Moor, H.C., 1996. Leaching behaviour and solubility – controlling solid phases of heavy metals in municipal solid waste incinerator ash. *Waste Manage.* 16, 129–134.
- Kalbe, U., Berger, W., Simon, F.-G., Eckardt, J., Christoph, G., 2007. Results of interlaboratory comparisons of column percolation tests. *J. Hazard. Mater.* 148, 714–720.
- Kersten, M., Schulz-Dobrick, B., Lichtensteiger, T., Johnson, C.A., 1998. Speciation of Cr in leachates of a MSWI bottom ash landfill. *Environ. Sci. Technol.* 32, 1398–1403.
- Kjeldsen, P., Christensen, T.H., 1990. Leaching tests to evaluate pollution potential of combustion residues from an iron recycling industry. *Waste Manage. Res.* 8, 277–292.
- Kosson, D.S., van der Sloot, H.A., Eighmy, T.T., 1996. An approach for estimation of contaminant release during utilization and disposal of municipal waste combustion residues. *J. Hazard. Mater.*
- Lopez Meza, S., Garrabrants, A.C., van der Sloot, H., Kosson, D.S., 2008. Comparison of the release of constituents from granular materials under batch and column testing. *Waste Manage.* 28, 1853–1867.
- Meima, J.A., Comans, R.N.J., 1997. Geochemical modeling of weathering reactions in municipal solid waste incinerator bottom ash. *Environ. Sci. Technol.* 31, 1269–1276.
- Meima, J.A., Van Zomeren, A., Comans, R.N.J., 1999. Complexation of Cu with dissolved organic carbon in municipal solid waste incinerator bottom ash leachates. *Environ. Sci. Technol.* 33, 1424–1429.
- Olsson, S., Gustafsson, J.P., Berggren Kleja, D., Bendz, D., Persson, I., 2009. Metal leaching from MSWI bottom ash as affected by salt or dissolved organic matter. *Waste Manage.* 29, 506–512.
- Polettini, A., Pomi, R., Sirini, P., Testa, F., 2001. Properties of Portland cement – stabilised MSWI fly ashes. *J. Hazard. Mater.* 88, 123–138.
- Quina, M.J., Bordado, J.C.M., Quinta-Ferreira, R.M., 2011. Percolation and batch leaching tests to assess release of inorganic pollutants from municipal solid waste incinerator residues. *Waste Manage.* 31, 236–245.
- Sabbas, T., Polettini, A., Pomi, R., Astrup, T., Hjelmar, O., Mostbauer, P., Cappai, G., Magel, G., Salhofer, S., Speiser, C., Heuss-Assbichler, S., Klein, R., Lechner, P., 2003. Management of municipal solid waste incineration residues. *Waste Manage.* 23, 61–88.
- Yao, J., Li, W.-B., Tang, M., Fang, C.-R., Feng, H.-J., Shen, D.-S., 2010. Effect of weathering treatment on the fractionation and leaching behavior of copper in municipal solid waste incinerator bottom ash. *Chemosphere* 81, 571–576.