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10-15-2013

# Comparative Study of Ageing, Heat Treatment and Accelerated Carbonation for Stabilization of Municipal Solid Waste Incineration Bottom Ash in View of Reducing Regulated Heavy Metal/metalloid Leaching

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Santos, Rafael M.; Mertens, Gilles; Salman, Muhammad; Cizer, Özlem; and Van Gerven, Tom, "Comparative Study of Ageing, Heat Treatment and Accelerated Carbonation for Stabilization of Municipal Solid Waste Incineration Bottom Ash in View of Reducing Regulated Heavy Metal/metalloid Leaching" (2013). *Faculty Publications and Scholarship*. 5.

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[DOI:10.1016/j.jenvman.2013.06.033](https://doi.org/10.1016/j.jenvman.2013.06.033)

Please cite this article as: Santos, R.M., Mertens, G., Salman, M., Cizer, Ö., Van Gerven, T. (2013). Comparative study of ageing, heat treatment and accelerated carbonation for stabilization of municipal solid waste incineration bottom ash in view of reducing regulated heavy metal/metalloid leaching. Journal of Environmental Management, DOI:10.1016/10.1016/j.jenvman.2013.06.033.

## **Comparative study of ageing, heat treatment and accelerated carbonation for stabilization of municipal solid waste incineration bottom ash in view of reducing regulated heavy metal/metalloid leaching**

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### **ABSTRACT**

This study compared the performance of four different approaches for stabilization of regulated heavy metal and metalloid leaching from municipal solid waste incineration bottom ash (MSWI-BA): (i) short term (three months) heap ageing, (ii) heat treatment, (iii) accelerated moist carbonation, and (iv) accelerated pressurized

slurry carbonation. Two distinct types of MSWI-BA were tested in this study: one originating from a moving-grate furnace incineration operation treating exclusively household refuse (sample B), and another originating from a fluid-bed furnace incineration operation that treats a mixture of household and light industrial wastes (sample F). The most abundant elements in the ashes were Si (20 to 27 wt.%) and Ca (16 to 19 wt.%), followed by significant quantities of Fe, Al, Na, S, K, Mg, Ti, and Cl. The main crystalline substances present in the fresh ashes were Quartz, Calcite, Apatite, Anhydrite and Gehlenite, while the amorphous fraction ranged from 56 to 73 wt.%. The leaching values of all samples were compared to the Flemish (NEN 7343) and the Walloon (DIN 38414) regulations from Belgium. Batch leaching of the fresh ashes at natural pH showed that seven elements exceeded at least one regulatory limit (Ba, Cr, Cu, Mo, Pb, Se and Zn), and that both ashes had excess basicity (pH > 12). Accelerated carbonation achieved significant reduction in ash basicity (9.3–9.9); lower than ageing (10.5–12.2) and heat treatment (11.1–12.1). For sample B, there was little distinction between the leaching results of ageing and accelerated carbonation with respect to regulatory limits; however carbonation achieved comparatively lower leaching levels. Heat treatment was especially detrimental to the leaching of Cr. For sample F, ageing was ineffective and heat treatment had marginally better results, while accelerated carbonation delivered the most effective performance, with slurry carbonation meeting all DIN limits. Slurry carbonation was deemed the most effective treatment process, achieving consistently significant leaching stabilization, while also effectively washing out Cl ions, a requirement for the utilization of the ashes in construction applications. The benefits of carbonation were linked to the formation of significant quantities of Ca-carbonates, including appreciable quantities of the Aragonite polymorph formed in the slurry carbonated samples.

Keywords: municipal solid waste incineration bottom ash; heavy metals; leaching; accelerated moist carbonation; accelerated pressurized slurry carbonation; ageing; heat treatment

## **1. Introduction**

Municipal solid waste incineration (MSWI) is a waste management technology that has increasingly been adopted around the world. It is particularly utilized in geopolitical regions where land availability is scarce, thereby limiting landfilling capacity, and where strict environmental regulations or tax incentives encourage incineration. The generation of energy from the combustion of the waste, termed waste-to-energy, is an additional incentive and in many cases a driver for the cost efficiency of the process (Fodor and Klemes, 2012).

The Flemish Public Waste Agency (OVAM, Belgium) conducted a study in 2007 on the final treatment of household wastes and household-like industrial wastes in the Low Countries. It showed an overall adoption rate of incineration of 68%, versus 32% for landfilling, for a total waste volume of 20 million tons (equivalent to 427 kg per capita for the region of 46.8 million inhabitants) (OVAM, 2007).

Although incineration enables reduction in waste volume by up to 90 vol.% (Aricckx et al., 2006), substantial amounts of residues are produced, including fly ashes and even greater amounts of bottom ashes (BA), which can reach 20–30 wt.% of the original waste mass (Van Gerven et al., 2005b). These solid residues are the final sinks for salts and numerous toxic and regulated heavy metals and metalloids, which severely limit the possibilities for valorisation of these materials. Tested applications of MSWI-BA, having sufficient volume demand to take up the substantial amounts of residue produced, include as a subbase material in road construction and as an aggregate in cement mortar and concrete. Dabo et al. (2009) found leaching of salts and heavy metals to occur in the first two years after construction of a pilot road tested over ten years in France, while François and Pierson (2009) detected the environmental impacts of MSWI-BA use in a French road even after 23 years of construction. Both studies identified carbonation as the main phenomenon responsible for the geochemical evolution of leaching over time. However, in the two test cases, carbonation was found to be slow and still in progress at the time of sampling (i.e. high basicity measured), likely as a consequence of the relative confinement of the material in the subbase of the roads. The formation of calcium carbonate (by reaction with atmospheric CO<sub>2</sub>) is the final step in the ageing progression undergone by MSWI-BA, which is characterized by a pH-buffering sequence that begins with Portlandite (Ca(OH)<sub>2</sub>), followed by Calcium Silicate Hydrate (C-S-H), pseudo-Wollastonite, and ceases with Calcite (CaCO<sub>3</sub>) (De Windt et al., 2011). Other important mineral components that play roles in the leaching chemistry include Al(OH)<sub>3</sub>, Barite, Ettringite and Monohydrocalcite, while Dissolved Organic Matter (DOM) is known to enhance the solubility of Cu over the solubility control of Tenorite (De Windt et al., 2011).

Alternatively, the utilization of MSWI-BA as a fine aggregate (0.1-2.0 mm) in cement mortars and concrete has been considered attractive, as the highly alkaline environment of cement (pH > 12) improves the leaching behaviour of the waste material over direct utilization of the untreated waste (Saikia et al., 2008; Ginés et al., 2009). However, this application route faces the challenge of the formation of expansive products (Ettringite, Al(OH)<sub>3</sub>, H<sub>2</sub>) upon reaction with alkali, which contribute to crack formation in the solid material, significantly lowering its compressive strength and limiting its marketability. Saikia et al. (2008) attributed these effects to

presence of metallic aluminium, sulphates, soluble salts and organic matter, which, as the study proposed, must be removed prior to application of the residue as an aggregate in construction materials.

In lack of suitable valorisation routes for MSWI-BA, the common industrial practice to date has been natural ageing of the material, with the aim of promoting weathering and thus reducing leaching to environmentally acceptable levels, prior to final disposal and storage in landfills. Natural ageing can be intensified by occasional turning of the heaps, exposing material that would otherwise have less contact with atmospheric agents (air and water) than the heap surface crust (Polettini and Pomi, 2004). Under aerobic conditions DOM can also play a role in the weathering of bottom ash, by sustaining microbial activity that can provide CO<sub>2</sub> via respiration for the carbonation reactions (Rendek et al., 2006a; Bayard et al., 2009). Ageing treatment has been shown successful in reducing to a certain extent the leaching of lead, molybdenum and zinc (Meima and Comans, 1997; Hyks and Astrup, 2009), however it has been reported inefficient or detrimental for the leaching of Cr, Cu and Sb (Cornelis et al., 2006; Hyks and Astrup, 2009; Gori et al., 2011). As such, ageing often falls short of meeting required environmental regulatory limits for safe storage or reutilization, and enhanced treatment methods are still desired.

Two approaches for accelerating the ageing mechanisms have been investigated in recent years: accelerated carbonation (reviewed by Costa et al. (2007)) and heat treatment. The former relies on the introduction of gases with higher than atmospheric concentrations of CO<sub>2</sub> (e.g. ~10% CO<sub>2</sub> in fossil fuel combustion flue gas compared to ~400 ppm in the atmosphere). It has been found that using high concentrations of CO<sub>2</sub>, coupled to introduction of an appropriate amount of moisture (to drive the aqueous carbonation reaction, more susceptible at low reaction temperatures and pressures than direct gas-solid carbonation), can improve carbonation kinetics and conversion considerably. Additionally, the utilization of flue gas-derived CO<sub>2</sub> for mineral carbonation can be a form of carbon capture and storage (as calcium and magnesium carbonates have high geochemical stability). This is only effective, however, if enough CO<sub>2</sub> can be made to react (high conversion), and if the amount of solids that act as the carbon sink can significantly abate the CO<sub>2</sub> emissions of a particular industrial facility. Rendek et al. (2006b) and Baciocchi et al. (2010) found that only 0.4–1 % of an incinerator's emissions (~4.7 tonne CO<sub>2</sub> per tonne bottom ash) could be captured by bottom ash carbonation (achieving 3–4 wt.% maximum differential CO<sub>2</sub> uptake). Hence the stabilization and valorisation of the waste material should be the main aim of applying this technology industrially.

Notable studies on accelerated carbonation of MSWI-BA include those of Van Gerven et al. (2005b), Arickx et al. (2006), Rendek et al. (2006a) and Baciocchi et al. (2010). The common process methodology has been

moist carbonation, whereby the solids are mixed with a limited amount of water (0.2–0.3 liquid-to-solid ratio (L/S) has been found ideal) and exposed to a CO<sub>2</sub>-rich atmosphere (10–100 vol.% CO<sub>2</sub>) at moderate temperatures (30–50 °C) for several hours to several days (up to 7 days being common) in static condition (e.g. thinly spread layer on Petri dish). The general precept is to maintain the temperature low enough to maximize CO<sub>2</sub> solubility in the water phase, but high enough to drive the carbonation reaction kinetics. Moreover, it is desirable to use a moisture content in the mixture that provides the water required for aqueous carbonation reaction (i.e. dissolved carbonates reacting with calcium and magnesium, leached from hydrated oxides and silicates, at the reacting zone near the particle surface), but that is thin enough to limit the diffusion distance the carbonate ion has to travel to reach the reaction zone (i.e. thin-film instead of flooded sample). Rendek et al. (2006b) found that pressurization of the gas aids carbonation kinetics (reducing time to reaction completion from 51 to 3.5 hours), but not having a significant effect on carbonation conversion/CO<sub>2</sub> uptake. These studies report improvement in the leaching behaviour of certain metals, especially Cu, Pb and Zn, but detrimental effect on the leaching of Cr, Mo and Sb.

Heat treatment has been tested as a means to reduce the amount of DOM in MSWI-BA, and thus reduce, in particular, the leaching of copper. Arickx et al. (2007) tested heat treatment in the range of 100–500 °C for 15–120 minutes duration; 30 minutes and 400 °C were sufficient to reduce leaching of Cu, Pb and Zn to below regulatory limits. Hyks et al. (2011) found detrimental effects for the leaching of Cr and Mo after heat treating MSWI-BA in a pilot-scale rotary kiln at temperatures in the range of 930–1080 °C for 40–70 minutes, likely as a result of changes in surface and mineralogical properties at these comparatively high temperatures.

On the basis of the research reported to date, this study aimed at comparing the performance of different approaches for stabilization of regulated heavy metal and metalloid leaching from municipal solid waste incineration bottom ash, namely heap ageing, heat treatment and accelerated (moist) carbonation. Furthermore, an additional processing route was tested, which has been reported to intensify the carbonation reaction of other alkaline waste materials (Santos et al., 2013), but so far has not been reported for the treatment of MSWI-BA: pressurized slurry carbonation. Comparing four treatment methodologies on the same materials within the same study can enable a more precise assessment of the relative performances of each approach. In addition, two distinct types of MSWI-BA were tested in this study, one originating from a moving-grate furnace incineration operation treating exclusively household refuse, and another originating from a fluid-bed furnace incineration operation that treats a mixture of household and light industrial wastes. The use of these two types of materials

allows better insight into the effect of chemical, mineralogical and morphological properties on the leaching behaviour and stabilization performance.

## **2. Materials and Methods**

### *2.1 Materials sampling and pre-treatment*

Bottom ash samples were acquired from a major Belgian incineration operator, and originated from two distinct plants: one operating a moving-grate furnace and treating exclusively household waste (samples denominated B), and another operating a fluid-bed furnace and treating a mixture of household and light industrial wastes (samples denominated F), which processes greater amounts of construction material residues, impregnated wood, cardboard, PVC, sludge, shredder residues, etc. (Van Caneghem et al., 2012). The fresh bottom ash samples were taken directly from the incineration process, after quenching and magnetic separation. Three batches of fresh bottom ash were collected from each incineration plant at different time intervals within one week; these batches were blended to provide a single fresh sample from each plant. Aged samples were obtained from heap storage sites located at the incineration plants; sample batches were collected from heaps aged for three months, and coinciding with the timeframe the fresh samples were collected to ensure comparable composition.

Samples of about 1.5 kg were taken from each of the fresh and aged bottom ash batches and were dried in an oven at 60 °C for 48 hours prior to experimental testing. Dried samples were sieved to remove particles larger than 8 mm (mainly metallic, glass and ceramic pieces). Each sieved sample was split in a riffle-type sample splitter to obtain eight representative fractions of the same sample. Split fractions of each of the three fresh samples batches were mixed together, by passing simultaneously through the sample splitter, to obtain a mixed fresh sample from each incineration plant.

Samples used for treatment tests (carbonation and heat treatment) were carefully split from the prepared fresh mixtures to ensure homogeneity and reproducibility. After treatment, these samples were again carefully split to generate multiple representative fractions for the various leaching tests. Only for those analytical tests that use small sample amounts, namely XRF, XRD, LOI and TGA, representative split fractions of mixed fresh, aged and treated samples were milled in a ring mill to reduce the particle size to less than 125 µm prior to analysis.

## 2.2 Treatment experiments

Three laboratory-scale treatment options were assessed: heat treatment, moist carbonation, and slurry carbonation. Optimal operating conditions for these methods were chosen based on results reported in literature by our research group in recent years for dedicated research on each treatment route. Process conditions for heat treatment were obtained from the work of Arickx et al. (2007), for moist carbonation from the work of Van Gerven et al. (2005b) (in agreement with the more recent work of Baciocchi et al. (2010)), both of which were performed on MSWI-BA's, and for slurry carbonation from the work of Santos et al. (2013), which was performed on steel slags. The following are the experimental procedures used:

- Heat treatment: The samples were placed in ceramic crucibles, were heated to 425 °C in air atmosphere, and were maintained at that temperature for 45 min. The heating tests were performed in a W.C. Heraeus MR 260 muffle-furnace.
- Moist carbonation: The samples were initially wetted with MilliQ water to have a 25 wt.% moisture content, similar to the moisture content of the fresh as-received samples (due to in-plant quenching). The samples were thinly spread on trays and placed in a CO<sub>2</sub>-chamber (Sanyo CO<sub>2</sub> incubator MCO-17) at 30 °C and with a partial CO<sub>2</sub> pressure of 0.2 atm. The samples were rewetted during the experiment, at 48 h (addition of 2/5 of initial moisture content) and at 120 h (addition of 3/5 of initial moisture content), after manual de-agglomeration with a pestle of the hardened material, which is due to carbonate formation, leading to cementitious behaviour and drying out. Samples were removed from the CO<sub>2</sub>-chamber after 7 days of carbonation, and subsequently dried at 60 °C for 24 h.
- Slurry carbonation: The samples were put in a 1.1 L stirred batch autoclave reactor (Buchi Ecoclave 300 type 3E), in which they were heated to 90 °C, with 5 bar, gauge CO<sub>2</sub> partial pressure, at a liquid to solid ratio (L/S) of 2.6 (300 g sample in 800 ml MilliQ water), and stirred by a turbine impeller rotating at 600 rpm, for a duration of 24 h. The slurry was filtered (589/3 filter paper) and the recovered solids were oven dried at 105 °C for 4 h.

## 2.3. Materials characterization

The main elemental composition of fresh and aged bottom ashes was determined by X-ray Fluorescence (XRF, Panalytical PW2400) on the milled samples in duplicates; measurement uncertainty is approximately ± 2



units of the last significant figure reported, and verifiable detection limit is ~0.01 wt.%. The concentration of regulated and non-regulated heavy metals and metalloids in the bottom ash was determined by digesting in triplicates 0.1 g of milled material with concentrated HNO<sub>3</sub>, HClO<sub>4</sub> and HF consecutively; the samples were heated and the acids evaporated for three cycles. After digestion, the resulting liquid sample was diluted into 100 ml MilliQ water and measured for its elemental content by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Thermo Electron X Series).

To determine the Total Organic Carbon (TOC) content, the Loss On Ignition (LOI) of the samples was determined by heating about 10 g of milled sample to 440 °C, and maintaining at this temperature for 12 h. The samples were then cooled in a desiccator with silica-gel to avoid any hydration of the samples. From the weight loss, a weight percentage for the TOC could be determined.

The mineral composition of fresh, aged and treated bottom ashes was determined by X-ray Diffraction (XRD, Philips PW1830) on the milled samples. For the quantitative analysis measurements (QXRD), an internal standard (zincite; 15wt.%) was added to quantify the mineral content of the milled samples. Homogenizing and further milling was done by hand in an agate mortar. From the mixed powder, a scan was performed of the hkl-reflections (CuK $\alpha$  radiation / 5-75° 2 $\theta$  / step size 0.02° / 2s measuring time per step). The sample holder was filled by side-loading to obtain a random orientation of the particles. The quantification of crystalline mineral phases was done by Rietveld refinement technique (Topas Academic v4.1). Based on the amounts of the individual minerals determined by the Rietveld refinement, relative to that of the internal standard, the absolute weight-percentages of the minerals in the mixture were derived. The amount of amorphous/unidentified material was determined by subtracting the sum of crystalline phases from 100 wt.%. Mean quantification accuracy is approximately  $\pm 2$  wt.% of the quantified amount, based on replicate analyses.

The calcium carbonate content of the samples was also quantified by Thermogravimetric Analysis (TGA, Netzsch STA 409). An amount of 20–100 mg milled sample was weighed in a sample pan heated from 25 to 1000 °C under a nitrogen atmosphere at a heating rate of 10 °C/min. The weight loss was recorded by the TGA microbalance and the amount of CO<sub>2</sub> uptake (in wt.%) was quantified by the ratio of the weight loss between 500 and 800 °C (attributable to CaCO<sub>3</sub> decomposition to CaO<sub>(s)</sub> + CO<sub>2(g)</sub>), over the carbonated sample mass at 500 °C (to eliminate any mass gain due to hydration/hydroxylation). The method reproducibility, caused by sample size and inhomogeneity, and assessed by replicates, is  $\pm 2\%$ .

The particle size distribution was determined by sieving using eight standard sieves (0.0625, 0.25, 0.5, 1.0, 2.0, 4.0, 6.0, and 8.0 mm). To observe the particle morphology and distribution of main mineral phases in the

grains, unmilled fresh bottom ash samples were embedded in a resin and polished for their study by Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDX, FEI XL30 FEG-SEM). The samples were coated with carbon to ensure proper conduction of electrons in the SEM-chamber.

#### *2.4 Leaching tests*

Batch leaching tests were performed on unmilled fresh, aged and treated bottom ash samples to determine the effect of ageing and accelerated treatments on the solubility of heavy metals and metalloids and on the basicity of the ashes; triplicates were used to assess variability. Determination of aqueous elemental concentration was performed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Thermo Electron X Series). Solution matrix for ICP-MS measurement was 2 vol.% nitric acid. Measurement accuracy, determined using standard solutions (diluted from 1000 mg/L Merck CertiPUR elemental standards), is  $\pm 2\%$ . The following elements (in alphabetical order) were analyzed: As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, V and Zn.

To assess if the materials conformed to Belgian regulatory limits for valorisation of waste materials, batch leaching tests were conducted at natural pH according to standard procedure EN 12457-4/DIN 38414-S4 (Ministere de la Region Wallonne, 2001). For this leaching test, 10 g of sample was mixed with 100 ml of MilliQ water and shaken on a vibration table (Gerhardt Laboshake) at 160 rpm and 25 °C for 24 h. The solution was then filtered through a 0.45  $\mu\text{m}$  membrane filter, acidified with 2 vol.%  $\text{HNO}_3$ , and diluted 10 to 100 times (after which it was acidified again) before ICP-MS analysis. Filtrate solution from slurry carbonation experiments was tested by ion chromatography (IC, Dionex ICS 2000) for anion leaching ( $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ).

The leaching behaviour of the bottom ash samples as a function of pH were conducted in a similar manner to tests performed at natural pH, except for the addition of varying amounts of concentrated (70 wt.%) nitric acid (100, 200, 400, 800 and 1600  $\mu\text{l}$ ) to the 100 ml test solutions prior to shaking. The equilibrium pH of the solution was measured at the completion of the experiment, with no intermediate adjustment. These data are useful for understanding the chemical and mineralogical mechanisms that control leaching. In this study, select geochemical modelling results of the main compounds known to play a role in controlling leaching of heavy metals and metalloids from bottom ashes are reported, obtained with PHREEQC and Visual MINTEQ and with basis on the works of Fällman (2000), Cornelis et al. (2006), Cornelis et al. (2008), Zhang et al. (2008), Hyks et

al. (2011) and Cornelis et al. (2012). The pH-varying data are also useful for prediction of leaching behaviour if the material is exposed to an acidic environment during subsequent storage or re-use.

### 3. Results and discussion

#### 3.1. Material characterization results

The particle size distribution of collected bottom ashes (sieved, split and mixed fresh ashes, and sieved aged ashes) was determined by sieving. The particle size curves are shown in Fig. 1. Based on the weight contribution of each particle size fraction, the average particles sizes, calculated as the volume moment mean diameter ( $D[4,3]$ ) for B,fresh, F,fresh, B,aged, and F,aged samples are, respectively: 5.22, 3.88, 2.84 and 3.00 mm. Likewise, the average particles sizes calculated as the surface area moment mean diameter ( $D[3,2]$ ), in the same respective sample order, are: 1.31, 1.33, 0.62 and 0.82 mm. While the  $D[4,3]$  value better represents the morphology of the material (i.e. granular), the  $D[3,2]$  value better represents the surface area of the material, which controls its chemical behaviour, including basicity and leaching properties. It is believed that the aged samples are finer than the fresh samples due to segregation of larger particles in the storage heaps during turning over of the heaps for maturation.

The total concentrations of the main elements and the regulated/non-regulated heavy metals and metalloids are shown in Table 1. Non-regulated elements are those for which Belgian legislation concerning leaching values has not yet been imposed, but are planned to be included in the regulations in the future (Van Gerven et al., 2005b). The most abundant elements are Si (concentrations ranging from about 20 to 27 wt.%), Ca (16 to 19 wt.%), Fe (3 to 11 wt.%) and Al (3 to 7 wt.%). Other less abundant elements are Na (1.6 to 2.5 wt.%), S (1.2 to 4.9 wt.%), K (0.9 to 1.3 wt.%), Mg (1.0 to 2.2 wt.%), Ti (0.6 to 0.9 wt.%), and Cl (0.5 to 1.7 wt.%). Of these main components, the most striking differences between samples B and F are the higher S and Si contents in samples F, and the higher Al and Fe contents in samples B. Na and Cl contents are higher in fresh samples compared to the aged samples (except for Cl in F,aged), which may be explained by washing out during maturation. The main regulated elements present in the ashes are Al and Ti, at 0.8 wt.% or over in most samples, followed by Cu and Zn, present at approximately 0.2 to 0.4 wt.%, and then followed by Ba and Pb, present at around 0.1 wt.% in all ashes. Nine other heavy metals and metalloids are present in ppm quantities in all ashes, while Se was not detected in any of the samples (i.e. <1 ppm). Aged samples appear to be enriched with several

metals compared to fresh samples (by 70–90% on average); no clear reason for this increase during maturation, other than waste heterogeneity, could be found.

The data for LOI at 440 °C are also reported in Table 1. These results can represent the TOC content of the ashes, but they should be considered with care. The weight loss in the range from ambient temperature to 440 °C cannot be uniquely assigned to the decomposition of organic matter. Other processes, such as the dehydration of minerals (e.g. Gypsum, Portlandite), or the loss of adsorbed water, may also be attributable to this weight loss. This may explain why aged samples have a higher LOI than fresh samples, since maturation can produce these hydrated minerals. The difference in LOI between B and F samples, however, is more likely due to organic content, as B ashes originate from exclusively household waste incineration, which are more likely to contain organic matter and produce ashes with residual (unburnt) organic matter.

The results for the QXRD analyses are shown in Table 2. The main crystalline substance present is Quartz ( $\text{SiO}_2$ ), at 8.5 to 23 wt.% (higher in F samples), followed by Calcite ( $\text{CaCO}_3$ ), Apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{Cl},\text{F},\text{OH})$ ), Anhydrite ( $\text{CaSO}_4$ ) and Gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) at up to 7.7 wt.%. Besides crystalline minerals, the samples consist of high amounts of amorphous material; the amounts range from 56 to 73 wt.% (B samples are more amorphous than F samples). These values are in agreement with a detailed study of MSWI-BA mineralogy conducted by Wei et al. (2011), who reported that bottom ashes consist mainly of assorted silicate-based glass phases (48–54 wt.%) with metallic inclusions (Fe, Cu, S, Sn, P, Pb and Zn dominated phases), as melt products formed during the incineration process. They also found that the compounds embedded in the glassy matrix play a dominant role in concentration of other minor heavy metals.

The differences in the amounts of minerals and the amounts of amorphous material between fresh and aged samples possibly reflect an evolution of the mineralogy due to maturation. For example, Calcite is a product of carbonation, which occurs during atmospheric weathering. Additionally, glassy phases can be subjected to secondary mineralization over time, which can act to retain heavy metals and improve leaching properties (Piantone et al., 2004). Moreover, it appears that part of the Anhydrite transforms into Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) during maturation.

Grains from fresh bottom ash samples B and F embedded in resin and polished were studied by SEM-EDX analysis to observe morphological aspects of the particles and distribution of the mineral phases. The Backscattered Electron (BSE) images as well as the selected areas and points for the EDX-analyses are given in Figs. 2 and 3 for B and F samples, respectively. The BSE gives a qualitative indication of the electron density (and hence the material density) of the phases. Bright areas are characterised by a higher density compared to

darker areas; black areas are the resin. The results of the semi-quantitative EDX-analyses are presented in Table SC-1 in the Supplementary Content. It should be noted that the carbon signal is at least partially attributable to the carbon-coating and/or the mounting resin.

The SEM-EDX results indicate that these bottom ashes are very heterogeneous; nearly all grains analysed have a distinct chemical composition. Nevertheless, the results confirm, at least partially, the results of the Quantitative XRD analyses. For instance, very Si-rich particles are detected (e.g. Fig. 2 – point A2, or Fig. 3 – point D1). These possibly correspond to Quartz/Cristobalite ( $\text{SiO}_2$ ), although amorphous glass phases could have a similar composition. Similarly, the presence of (nearly) pure Fe-particles and Fe-oxides (possibly Iron, Hematite, Magnetite or Wüstite) can be observed (e.g. Fig. 2 – points A1, B3 and D2). Fig. 2B possesses two regions rich in phosphorous that may correspond to the Apatite mineral phase. In some cases, rims covering the grains can be clearly identified in the images (e.g. Figs. 3A and 3B, where a Ca-rich rim surrounds a Si-rich core). Heavy metals and metalloids are barely detectable (only traces of V and Mo were found in the analyzed grains), which suggests that most are concentrated in particular grains or inclusions, as reported by Wei et al. (2011), rather than being dispersed throughout. After ageing, heavy metals can accumulate in secondary mineral phases formed over time such as Calcite and iron hydrates via adsorption mechanisms, in particular Cu, Ni, Pb and Zn (Piantone et al., 2004; Saffarzadeh et al., 2011).

### *3.2 Leaching results*

The results of the natural pH batch leaching tests on the collected materials (fresh and aged) are shown in Table 3. The leaching data are compared to the Belgian Flemish and Walloon regulatory limit values for waste reutilization in non-structural construction material applications. The leaching limits for non-regulated elements are informal and are obtained from Van Gerven et al. (2005b). Van Gerven et al. (2005a) compare Belgian leaching limits for waste reutilization with others in Europe, and show that those in Belgium are generally more complete. It should be noted that the current leaching tests were done by shaking (same procedure prescribed by Walloon regulations), whereas the Flemish regulation prescribes a column test (according to NEN 7343). Walloon limits are comparatively higher than Flemish limits because, in part, the shaking test is deemed harsher than the column test (i.e. leaching is magnified). It is possible, however, that batch leaching limits will be reduced in the future once trans-national regulations are erected, and hence the results in this study are compared with both sets of limit values. Leaching of Al and Ti are not reported as their limits are exceptionally high

(20,000 and 20 mg/kg, respectively, according to Walloon regulations) compared to their negligible leaching values.

### *3.2.1 Fresh bottom ashes*

Seven elements exceed at least one regulatory limit (Table 3): Ba, Cr, Cu, Mo, Pb, Se and Zn. The leaching of six out of these seven elements (with the exception of Se) were also exceedingly high from the bottom ashes studied by Van Gerven et al. (2005b), Arickx et al. (2006) and Arickx et al. (2007), which originated from another Belgian incinerator. However, only one element, Mo, exceeds limits for both fresh bottom ashes, an indication that the different waste compositions that these ashes originate from has an important effect on leaching properties of the ashes. Bottom ash sample B has a greater number of problematic elements, five (Ba, Cu, Mo, Pb, Zn), compared to three (Cr, Mo, Se) for sample F. The chemistry of these elements also varies greatly; four of the five elements of concern in sample B are cationic heavy metals, while those in sample F are oxyanionic metalloids. Leaching of Ba, Cu, Pb and Zn are greater from sample B, whereas Cr and Mo leaching are greater from sample F; dissimilar leaching mechanisms, ash mineralogy, or distribution of these elements in the ash grains may cause these differences. The basicity difference between these two ashes (sample B is 0.3 pH units more basic (Table 3)) could also play a role, as Ba, Cu, Pb and Zn are more mobile at higher pH (Dijkstra et al., 2008; Zhang et al., 2008; Santos et al., 2012b), whereas Cr and Mo are typically more mobile at lower pH (Cornelis et al., 2008; Santos et al., 2012b).

### *3.2.2 Ageing of bottom ashes*

Heap ageing results are also presented in Table 3. Maturation effectively lowered the basicity of sample B by nearly two pH units (from 12.4 to 10.5), an indication that weathering-induced carbonation occurred (as previously seen by the higher Calcite content of the aged ash and the absence of highly basic Portlandite (Table 2)). However, the pH value of sample F remained essentially unchanged, in agreement with the small Calcite content of this ash (Table 2). The nature of the waste from which sample F originates (light industrial) may make this ash more resilient to ageing. The lack of effect of ageing on sample F resonates on its leaching performance: not only is leaching of the three problematic elements (Cr, Mo and Se) in the aged ash unattenuated, but Cu and Pb leaching are now exceeding the regulatory limits. Higher leaching values in the aged ash could be caused by the apparent concentration of these elements in the aged ashes (Table 1), but given that leaching is normally a

solubility controlled process, rather than availability controlled (Santos et al., 2012b), changes in geochemical behaviour are more likely to be the cause of the greater leaching in the aged sample F ash.

The aforementioned interpretation is supported by the results of bottom ash sample B. Despite the aged ashes of sample B also being enriched in Cu and Pb compared to the fresh ash, leaching of both metals decreased substantially after ageing, with Pb leaching dropping well below the regulatory limits, and Cu leaching conforming to the Walloon limit. In addition, leaching of Ba and Zn also decreased substantially by ageing. The leaching of Mo remained above the Flemish limit, but below the Walloon limit. The most detrimental result was an increase in Sb leaching that surpassed the Flemish limit. The leaching of V increases for both samples B and F after ageing, but neither surpass the regulatory limits. The solids concentration of V in the aged ashes are one order of magnitude less than the Sb concentrations (Table 1), which may help limit its detrimental effect. Lastly, the heavy metals and metalloids As, Cd, Co and Ni do not appear to present a concern for the studied ashes before or after weathering.

### *3.2.3 Accelerated treatment of bottom ashes*

Comparison of the natural pH batch leaching test results of fresh ash samples with those treated by accelerated carbonation (moist and slurry methodologies) and heat treatment are shown in Fig. 6. These four sets of results originate from identical bottom ashes that were methodologically split to ensure identical chemical, mineralogical and morphological compositions. Therefore comparison of leaching values to each other can be presumed more accurate than comparison to the aged ashes, since these samples were recovered from large storage piles that, despite originating from the same plant and production period of the fresh ashes, could attain some unintended dissimilarities due to segregation or mixing with other stored ashes (such as particle size distribution and chemical composition, as already presented). The results show that the carbonation methods achieved significant reduction in ash basicity of both samples batches (to 9.3 for sample B and to 9.5–9.9 for sample F), significantly lower than the basicity of the aged samples (Table 3). Heat treatment had no effect on the basicity of sample F, but achieved a moderate effect on that of sample B (pH = 11.1); this was unexpected as the reduction of DOM is not intended to reduce basicity.

### *3.2.4 Compliance to regulatory limits*

Table 4 summarizes the compliance of all bottom ash samples to the regulatory limits. Heat treatment was the least effective process for reduction of leaching values. It reduced leaching of Cu from both ashes to below the

lower Flemish limit, and reduced the leaching of Ba and Pb from sample B below limits, but was highly ineffective for Cr leaching, which increased significantly in sample B (Fig. 6). Cr leaching was also magnified from sample F, while leaching of Mo only barely reduced below the Walloon limit. Mo and Se still exceeded the Flemish limits after heat treatment of sample F.

Accelerated carbonation achieved comparable results to ageing for bottom ash sample B, that is, compliance to Walloon limits, but exceedance of Cu, Mo and Sb Flemish (column-test) limits. Still, Cu leaching was significantly reduced compared to the untreated ash, while Mo leaching was little changed. The leaching of Sb increased above the Flemish limit after carbonation, although the slurry carbonation leaching level of Sb is half that after ageing. For bottom ash sample F, accelerated carbonation yielded better results than the other two treatment techniques (ageing and heat treatment). It complied with nearly all Walloon limits (Mo marginally exceeded the limit for moist carbonation), with slurry carbonation performing generally better than moist carbonation. Slurry carbonation reduced leaching of Mo and Se more substantially than moist carbonation compared to the fresh F bottom ash, though not yet meeting the Flemish limits. Slurry carbonation also had a milder effect on V leaching, thereby not surpassing the Flemish limit, and it reduced the leaching of Ba farther below the Flemish limit. Leaching of As, Cd and Co, though apparently increasing more after slurry carbonation than moist carbonation, remained far below even the Flemish limits, and thus can be neglected. However, pH-varying results (Figs. 4 and 5) suggest that had the pH reduced beyond the obtained values after carbonation, these elements could become problematic. This indicates that more complete carbonation is not necessarily beneficial for leaching, and also means that if the treated ashes are exposed to long-term acidification (e.g. due to acid rain) this could induce undesired leaching (further discussion in Section 3.2.5).

To ease the comparison of the performance of each treatment methods towards leaching of all regulated heavy metals and metalloids, the results of a scoring and ranking scheme are also presented in Table 4. The score ( $S$ ) is calculated using Eq. 1, where ( $r_i$ ) is the relative ranking of a treatment method for the leaching of each heavy metal/metalloid or the pH value (fourteen parameters  $i$ ), which ranges from 1 (lowest leaching or pH) to 5 (highest leaching or pH); where leaching or pH values of two or more treatment methods differ by less than 0.01 mg/kg or 0.1 pH units, the rank is averaged. Each ranking value is multiplied by 1 or 100, depending whether the leaching limit (DIN or NEN) is exceeded (in which case the multiplier is 100) or not (then the multiplier is 1). The lowest the  $S$  score, the better the treatment method performs. The scores in Table 4 generally agree well with the previous data discussions. Fresh B bottom ash achieves the poorest scores, while fresh F bottom ash performed better than some treatment methods. Only slurry carbonation consistently



performed better than the fresh ashes, and generally performed better than other treatment methods, ranking first for three out of the four scores, being only marginally second to moist carbonation for the B sample NEN score.

$$S = \sum_{i=1}^{14} [r_i \{1,2,3,4,5\} \cdot (1 | 100)] \quad (1)$$

### 3.2.5 Additional treatment effects

A further benefit of slurry carbonation over the other treatment routes, including moist carbonation, is the extraction of soluble salts that limit the applicability of MSWI-BA as a construction material, most notable chloride (Saikia et al., 2008). Yang et al. (2012) verified that sufficient chloride can be extracted from MSWI-BA by water washing to render it usable as a fine aggregate material in concrete applications. Slurry carbonation thus combines the effect of water washing with that of accelerated weathering. Anion leaching during slurry carbonation was tested by ion chromatography. No phosphate leaching was detected, while 4.7 and 5.3 g/kg chloride was detected from B and F sample solutions, respectively. This represents roughly 30% extraction of the Cl content of the ashes (Table 1). More Cl is not extracted due to equilibrium limitations of the batch process and possibly the speciation of some Cl in insoluble compounds. A downside to slurry carbonation, however, is the generation of a salt-rich wastewater that must be treated for disposal, or used as process water within the incineration process, as is currently done with similar streams (e.g. quench water and scrubber solutions).

It is also important to note the effect of the accelerated treatment methods on the acid neutralization capacity (ANC) of the bottom ashes. Results are presented in Fig. SC-1 in the Supplementary Content. Carbonation lowers the initial buffering capacity of the ashes relative to the fresh ashes. For example, the carbonated B samples drop to pH 6 after addition of 1 mM HNO<sub>3</sub>, while the fresh ashes need nearly 2.5 mM to reach this same pH. Still, the carbonated samples remain at pH 6 until 2 mM HNO<sub>3</sub> is added. Similarly, for sample F, the carbonated and fresh samples reach the same pH of 6 just after 1 mM HNO<sub>3</sub> addition (this also means that fresh sample F has lower buffering capacity than sample B). For sample F the slurry carbonated sample pH is actually the highest after 2 mM HNO<sub>3</sub> addition. These results suggest that carbonation does not introduce added risk from the point of view of long-term storage in conditions where gradual acidification can occur, given that most heavy metals and metalloids only leach considerably once the pH drops below 6 (Figs. 4 and 5).

### 3.2.6 Leaching mechanisms

The pH-varying results presented in Figs. 4 and 5 can be used to understand the mechanisms that control leaching of the various heavy metals and metalloids. Three main mechanisms can be elucidated by this experimental test: (i) change in the solubility of the mineral compound that contains the element of interest due to shift in pH; (ii) change in speciation of the element of interest, resulting in a different leaching behaviour (curve) compared to that of the original sample; and (iii) adsorptive action of co-occurring mineral phases that reduce solubility below that of pure compounds. In order to understand which of these mechanisms controls leaching of particular elements, geochemical modelling is an important complementary technique, allowing the comparison of experimental data to the expected leaching behaviour of modelled compounds. Included on Figs. 4 and 5 are geochemical modelling results of the main compounds known to play a role in controlling leaching of heavy metals and metalloids from bottom ashes, as reported by Fällman (2000), Cornelis et al. (2006), Cornelis et al. (2008), Zhang et al. (2008), Hyks et al. (2011) and Cornelis et al. (2012). Next, the leaching results of the present study are discussed in the framework of established leaching mechanisms.

Cornelis et al. (2006) studied the mechanism of Sb leaching from carbonated MSWI-BA, and found a maximum mobility zone around pH 10 (similar to the pH of aged B ash). This behaviour was attributed to the dissolution of mineral phases to which Sb has good sorption affinity when the pH is lowered: Portlandite below pH 12, and Ettringite below pH 10.8. Calcite and Gypsum, stable at pH 10, were found to have low affinity for Sb. This behaviour was shown to be only reversible once the pH drops below 9, when Hydrous Ferric Oxides (HFO) and Amorphous Aluminium Minerals (AAM) develop enough positive charge to adsorb  $\text{Sb}(\text{OH})_6^-$ . The pH-varying results (Figs. 4 and 5) point to similar behaviour, though it appears that Sb leaching reversibility from the present samples occurs at slightly lower pH, around 7 to 8. More recently, Cornelis et al. (2012) have hypothesised that the dissolution of romeite (especially that of  $\text{Ca}_{1.13}\text{Sb}_2\text{O}_6(\text{OH})_{0.26}\cdot 0.74\text{H}_2\text{O}$ ) controls antimonate (Sb(V)) leaching from bottom ashes in the pH range of 8–11. They explain that the dissolution of romeites with relatively less vacancies (i.e. higher occupancy of Ca sites) results in lower dissolved Sb(V) concentrations at alkaline pH compared to the dissolution of romeites with more vacancies, such as  $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ . These findings agree with the pH-varying results herein obtained (Figs. 4 and 5).

Like Sb, V is also known to respond negatively to carbonation, and hence pH reduction (Cornelis et al., 2008; Santos et al., 2012b), and this effect is confirmed in the pH-varying tests (Figs. 4 and 5). Ca-, Ba- and Pb-vanadates ( $\text{Ca}_3(\text{VO}_4)_2$ ,  $\text{Ba}_3(\text{VO}_4)_2$ ,  $\text{Pb}_3(\text{VO}_4)_2$ ) are reported to control the solubility of V at alkaline pH (Cornelis et al., 2008), although the present results show an attenuated leaching behaviour relative to modelled  $\text{Ca}_3(\text{VO}_4)_2$ .

Competition of carbonate ions with vanadate ions for chemical bonding sites (i.e. carbonation of Ca, Ba and Pb oxides) can thus play a role in the mobility of V.

It does not appear that Cr leaching enhancement can be attributed solely to pH reduction, as was explained in the case of Sb and V leaching enhancement from aged ashes, since both B and F heat treated ashes suffered the same effect, while only the pH of B dropped after treatment. The pH-varying results (Figs. 4 and 5) also show that Cr leaching only becomes significant below pH 5. Hyks et al. (2011) observed a similar effect of heat treatment on Cr leaching, and linked the phenomenon to the oxidation of Al(0), which controls Cr leaching in untreated MSWI-BA by reducing the more mobile form of chromium, Cr(VI), to its immobile form, Cr(III). In the absence of Al(0), they propose, based on geochemical modelling, that Cr leaching from the treated bottom ash becomes controlled by  $\text{BaS}_{0.77}\text{Cr}_{0.23}\text{O}_4$ . The present pH-varying results (Figs. 4 and 5), however, appear to follow the solubility curve of  $\text{Cr}_2\text{O}_3$  more closely, as was used by Zhang et al. (2008).

Molybdenum leaching appears to be little affected by pH change in the approximate range of 6 to 12, according to pH-varying results (Figs. 4 and 5). Molybdenum is characteristically redox insensitive, and its leaching has been reported to be controlled by powellite ( $\text{CaMoO}_4$ ) over this pH range (Cornelis et al., 2008), although Mo leaching from the present materials appears attenuated (Figs. 4 and 5) compared the theoretical solubility of this compound (also seen in Cornelis et al. (2008)). Therefore it does not seem possible to control its leaching behaviour by ageing or carbonation.

Several elements appear to follow the solubility curve of the untreated sample after treatment, except being shifted towards lower pH values, where leaching is attenuated (Figs. 4 and 5). This is the case for Cd, Co, Ni, Pb and Zn. As such, these elements do not seem to undergo significant speciation changes, and their leaching control mechanism is dominated by reduction in basicity. Barium leaching appears to behave in two different ways from the treated samples; for heat treated samples the leaching follows the fresh sample trend well, while for carbonated samples a clear shift in the curve is seen. This suggests that Ba leaching is controlled by  $\text{BaCO}_3$ . Lead and zinc are also known to undergo carbonation (Freyssinet et al., 2002), thus it is possible that their leaching mechanism from carbonated samples also changes, but since their leaching from both fresh and treated bottom ashes in the pH range of the treated samples is minute, it is difficult to use the pH-varying results to confirm this mechanism. Similar deviations as those of Ba are also seen for As, Se and V, but the controlling mechanisms of these elements in bottom ashes is less well understood (hence reference compounds are absent in Figs. 4 and 5), as they are present in small amounts in these waste materials and thus have not been studied in detail.

Recent geochemical studies of fundamental nature suggest that carbonation can play a role in the solubility control of As and Se. Román-Ross et al. (2006) showed that As(III) can be taken up by pure calcite through co-precipitation (up to  $30 \pm 6$  mmol/kg) as well as adsorption mechanisms. More recently, however, Yokoyama et al. (2012) verified the speciation of As in both the liquid (using HPLC-ICP-MS) and solid (using K-edge XANES) phases, and found that, in the pH range 7–12, As(V) is preferentially incorporated into calcite over As(III), even when only As(III) is present in solution. They suggest that in the presence of the  $\text{Ca}^{2+}$ , the oxidation of As(III) to As(V) and the stabilization of As(V) occurs due to the formation of calcium arsenate complexes in the aqueous phase. A similar case has been reported by Aurelio et al. (2010) for Se(IV). They were able to estimate by neutron diffraction study combined with *ab initio* simulation that Se(IV) can co-precipitate with calcite, by selenite ( $\text{SeO}_3^{2-}$ ) substitution of the carbonate anion, leading to solid phase uptakes of 30–75 mmol/kg. On the other hand, the selenate oxyanion ( $\text{SeO}_4^{2-}$ ) was found by Renard et al. (2013) to have insignificant physicochemical affinity during calcite formation. Since both selenium oxyanions have the same electronic charge (-2), this behaviour was attributed to the different geometry and bond valence of selenate, which when substituting for the carbonate anion distorts to a greater extent the calcite crystal structure compared to selenite.

### 3.3 Treated solids analysis

The collected samples and the samples subjected to the different treatments were analysed by TGA to evaluate differences in the presence of thermally sensitive components in the materials, such as the formation of Ca-carbonates during the ageing and carbonation, the decomposition of dissolved organic matter (DOM) during heat treatment, as well as the changes in the amounts of hydrated Ca- and  $\text{SO}_3$ -bearing compounds. The weight loss curves (TG) and their derivatives (DTG) for B and F bottom ash samples are shown in Fig. 7. The weight loss in the range from 50 to 200 °C can be attributed, at least partially, to the decomposition of Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and Hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) (Lager et al., 1984). Organic matter, such as humic substances, is expected to decompose at temperatures up to 450 °C (Giovanela et al., 2004). The weight loss around 500–800 °C corresponds predominantly to the decomposition of  $\text{CaCO}_3$  (i.e. release of  $\text{CO}_{2(g)}$ ) (Santos et al., 2012b).

From these TGA data, several effects of the treatments can be observed. Heat treatment results in a reduction in weight loss up to 450°C, confirming that it serves to decompose DOM present in the material, as well as

decomposition of hydrated compounds. This effect was much greater for sample B than for sample F, which suggests that sample B contained greater amounts of organic matter due to its household waste origin. The amounts of hydrated compounds that decompose at temperatures up to 200 °C increased markedly for aged and moist carbonated samples. The lower temperature and CO<sub>2</sub> partial pressures in these processes compared to slurry carbonation likely plays a role in the final mineralogy, promoting the formation of hydrated compounds.

The decomposition extent of Ca-carbonates is proportional to the intensity of the carbonation process. This is particularly clear in the case of sample F ashes, where the slurry carbonated sample had greater weight loss above 500 °C compared to moist carbonation, which in turn had greater weight loss than the aged sample. For sample B ashes, accelerated carbonation also produced the largest weight losses at the high temperature range, though the difference between moist and slurry carbonation was smaller. It is also observed that the CaCO<sub>3</sub> decomposition temperature for slurry carbonation, indicated by the peak minimum in the DTG plot, is higher than for moist carbonation, which in turn is slightly higher than for ageing; greater carbonate content, varying levels of crystallinity or polymorph ratios can account for this shift. Table 5 presents the calculated amounts of CaCO<sub>3</sub> based on thermogravimetric analysis. The greatest amounts of inferred CaCO<sub>3</sub> content are present in the slurry carbonated specimens (9.8–14.8 wt.%), followed by those treated by moist carbonation (5.3–12.6 wt.%). Fresh, aged and heat treated samples had similar carbonate amounts. The finding that fresh and aged samples contain similar quantities of CaCO<sub>3</sub> is in agreement with the work of Rocca et al. (2013), who suggest that the presence of carbonate in bottom ash is not necessarily indicative of weathering, but can result from in-situ carbonation in the incinerator outlet, when the material temperature may fall to between 450 and 650 °C while it is still in contact with CO<sub>2</sub>-rich combustion gases.

The samples subjected to the different treatments were also analysed by Quantitative X-Ray Diffraction (QXRD) to evaluate changes in the amounts of neo-formed minerals, in particular the formation of Calcite, Aragonite and Vaterite (polymorphs of CaCO<sub>3</sub>) from the carbonation processes, and Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), a hydration product. The XRD diffractograms and the full QXRD results are provided, respectively, in Fig. SC-2 and Table SC-2 in the Supplementary Content. The diffractograms show little crystallographic changes after treatment; the only visibly clear peak change (growth) is that of Calcite. This is confirmed in QXRD results, which show significant changes only in the carbonate phases (also presented in Table 5). Similarly, it is not possible to clearly discern morphological changes to the bottom ashes after treatment by SEM-EDX analysis. Comparing the particles shown in Figs. 2 and 3 (fresh ashes) with those in Figs. SC-3 and SC-4 (treated ashes) it is difficult to attribute with certainty any observable distinction to the effect of ash treatment. Bottom ashes are

very heterogeneous, and therefore differences in morphology of single particles can be due to treatment but also to innate heterogeneity.

The sums of CaCO<sub>3</sub> polymorph values determined by QXRD are generally smaller than the calculated values from TGA analyses. The TGA analysis may overestimate the amount of crystalline Ca-carbonates as some other mineral phases also undergo decomposition in the same temperature range. For instance, the presence of amorphous calcium carbonate, undetectable by XRD, is possible (Cizer et al., 2012b). Upon heating during TGA, this amorphous phase transforms into a more stable form of calcium carbonate which will count for the weight loss in the carbonate decomposition region (Cizer et al., 2012a). Nevertheless, the trends in Ca-carbonates from QXRD analysis agree with the trends observed by TGA, in that accelerated carbonation resulted in greater quantities of Ca-carbonates than the other samples. Slurry carbonation resulted in greater amounts of Ca-carbonates than moist carbonation due to faster dissolution and precipitation kinetics in the aqueous solution under elevated temperature and pressure. This implies highest capture and hydration rate of carbon dioxide among the three treatment methods. Interestingly, a newly formed phase of Aragonite appears in low amounts after slurry carbonation of both B and F samples, while the metastable phase of Vaterite precipitates in low amounts only from sample B exposed to moist and slurry carbonation. Aragonite is a meta-stable polymorph of CaCO<sub>3</sub> whose formation is promoted at higher carbonation temperatures and in the presence of magnesium ions (Santos et al., 2012a); hence its presence in the slurry carbonated samples that were prepared at 90 °C. Vaterite is known to form from amorphous calcium carbonate and eventually transform to calcite via dissolution/precipitation process (Sawada, 1997). The reason for this metastable phase precipitating only in sample B is not straightforward due to the compositional complexity of the sample, although the presence of Portlandite could be a possibility. Another interesting result is that gypsum production was accentuated in the moist carbonation process, over slurry carbonation and ageing (Table 5).

Some of the leaching characteristics of the treated samples can be related to their mineralogy. The Ba-leaching of the slurry carbonation samples is much lower compared to other samples, including moist carbonated ones (Fig. 6). A possible explanation is that Aragonite can accommodate large cations such as Ba and Pb in its crystal lattice through replacement of Ca atoms, thereby increasing the stability of the ninefold coordination of the orthorhombic crystal structure (Dietzel et al., 2004). On the other hand, Zn, a smaller cation, is more readily taken up by the crystal structure of Calcite (Reeder, 1996). Therefore, the leaching of Zn is reduced effectively by the formation of Calcite during accelerated carbonation as well as ageing (Fig. 6).

#### 4. Conclusions

This study compared the performance of four different approaches for stabilization of regulated heavy metal and metalloid leaching from municipal solid waste incineration bottom ash (MSWI-BA), the last of which is reported herein for the first time: (i) short term (three months) heap ageing, (ii) heat treatment, (iii) accelerated moist carbonation, and (iv) accelerated pressurized slurry carbonation. These treatments were performed on identical materials, methodologically sampled and split to ensure similarity of material properties. This makes the comparison of treatment performance more reliable than comparing studies available in literature performed by different research groups on differing materials. To better elucidate the effect of material characteristics and the geochemical effects of the treatment methods on the treated ash properties, two distinct types of MSWI-BA were tested in this study: one originating from a moving-grate furnace incineration operation treating exclusively household refuse (sample B), and another originating from a fluid-bed furnace incineration operation that treats a mixture of household and light industrial wastes (sample F). The leaching values of all samples were compared to the Flemish (NEN 7343) and the Walloon (EN 12457-4/DIN 38414-S4) Belgian regulations.

Pressurized slurry carbonation was deemed the most effective treatment process, ranking best for stabilization of the ashes in three of four cases, being only marginally second to moist carbonation for the B sample NEN score. Slurry carbonated bottom ashes met all DIN limits; for NEN limits, Mo and Sb consistently exceeded the leaching limits. Tests conducted with varying pH, by acid addition, point to the leaching enhancement of these elements at lower pH (< approx. 11). For the present samples, Sb is the only element present in sufficient quantities to pose a risk, but this is an issue that should not be overlooked when it comes to the effect of carbonation. For heavy metals and metalloids that cannot be stabilized by accelerated treatment processes or short term ageing, it appears that only long-term (order of decades) mineral alterations, such as the formation of Al- and Fe-hydrates that permanently bind such elements, as described by Saffarzadeh et al. (2011), can provide definitive stability.

Lowered basicity due to mineral carbonation of alkaline oxides was deemed the dominant stabilization mechanism. Slurry carbonation is able to reach greater carbonation conversion due to its intense mixing, which improves mass and heat transfer and increases the homogeneity of the treatment compared to the stationary and hardening solids in moist carbonation. The higher temperature of the treatment is also useful for enhancing carbonation kinetics (leaching and CaCO<sub>3</sub> precipitation), and pressurization assists in maintaining sufficient CO<sub>2</sub> solubility. Furthermore, appreciable quantities of Aragonite, a polymorph of CaCO<sub>3</sub> that is beneficial to Ba and

Pb uptake, were detected in the slurry carbonated samples due to the higher temperature carbonation conditions (90 °C). Slurry carbonation is also effective in washing out Cl ions, which may permit utilization of the treated samples in construction applications that required low chloride leaching.

From a practical application point of view, slurry carbonation also avoids two limitations of the other two accelerated treatment methods. For instance, the heat treatment process would require holding the incinerated material in the primary furnace for longer periods, to ensure complete combustion, or introducing a secondary heating step after the primary process (e.g. rotary kiln (Hyks et al., 2011)). In either case, this type of processing would inherently introduce additional expenses and inefficiencies in the incineration process, and are thus less preferable than accelerated ageing/carbonation. Moist carbonation, on the other hand, requires substantially longer treatment times (7 days used in this study) to achieve satisfactory carbonation conversion and hence leaching stabilization; from an industrial perspective, holding and processing 7 days worth of bottom ashes, which must be spread thinly, regularly turned over, and kept moist, would require large processing facilities and extensive energy expenditure. Slurry carbonation also poses some uncertainties of its own, such as determining if flue gases could be directly used as a CO<sub>2</sub> source, or if purification or concentration of the gases (to reduce compression costs) would be required.

It would be ideal to develop treatment technologies for particular MSWI-BA compositions, since it would likely achieve better results (e.g. lower leaching) than methods developed more generally (i.e. for an array of composition ranges). The preference of the industry, however, is for the development of treatment technologies that can be applied ‘off-the-shelf’, that is, that can be adapted to a variety of plants and that will work with a wide range of feed inputs into the incinerator. In this manner, detailed monitoring of feed input and excessively burdensome process control can be avoided, thus allowing incinerators the flexibility to change feed as the market or process economics dictate. A necessary next step in developing bottom ash treatment technologies should be the investigation of process design options and the determination of processing costs.

### **Acknowledgements**

The KU Leuven Industrial Research Fund (IOF) is gratefully acknowledged for funding the Knowledge Platform on Sustainable Materialization of Residues from Thermal Processes into Products (SMaRT-Pro<sup>2</sup>) in which this work was performed. R.M.S. is thankful for the PGS-D support from the Natural Sciences and Engineering Research Council of Canada (NSERC). The KU Leuven Department of Metallurgy and Materials



Engineering is acknowledged for the use of XRF and SEM-EDX equipment. Special thanks to Michèle Vanroelen for assistance with leaching tests, solids digestion, IC and ICP-MS measurements, and to Gerda Hechtermans for assistance with sample milling.

## **Appendix A. Supplementary Content**

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## List of Tables

Table 1

Total elemental composition and loss on ignition of fresh and aged B and F bottom ash samples (in wt.% for average of XRF results in duplicate; in mg/kg for average of ICP-MS results in triplicate).

	Fresh samples		Aged samples		Fresh samples		Aged samples			
	B	F	B	F	B	F	B	F		
XRF (wt.%)					ICP-MS (mg/kg)					
Al <sup>°</sup>	4.8 ±0.2	2.8 ±0.2	7.3 ±0.4	3.6 ±0.2	As <sup>‡°</sup>	94 ±64	50 ±17	47 ±32	41 ±14	
Ca	19.4 ±3.6	15.8 ±4.1	16.6 ±3.6	18.7 ±4.9	Ba <sup>†</sup>	1,508 ±391	1,517 ±262	1,314 ±340	1,904 ±329	
Cl	1.5 ±0.2	1.5 ±0.3	0.47 ±0.08	1.7 ±0.4	Cd <sup>‡°</sup>	9 ±11	2 ±1	165 ±195	5 ±3	
Fe	9.4 ±2.6	3.2 ±1.2	10.9 ±3.4	5.9 ±2.1	Co <sup>†°</sup>	31 ±1	28 ±3	41 ±2	27 ±3	
K	1.3 ±0.2	1.0 ±0.2	1.1 ±0.2	0.94 ±0.22	Cr <sup>†°</sup>	238 ±11	199 ±18	367 ±16	535 ±48	
Mg	2.2 ±0.2	1.0 ±0.2	1.8 ±0.2	1.0 ±0.2	Cu <sup>‡°</sup>	3,116 ±135	2,130 ±184	4,394 ±190	3,037 ±263	
Mn	0.11 ±0.03	0.14 ±0.05	0.16 ±0.05	0.17 ±0.06	Mo <sup>†°</sup>	11 ±2	24 ±1	18 ±3	43 ±2	
Na	2.1 ±0.2	2.5 ±0.2	1.6 ±0.2	1.7 ±0.2	Ni <sup>‡°</sup>	238 ±14	182 ±10	242 ±14	354 ±19	
S	1.2 ±0.2	4.0 ±0.7	1.3 ±0.2	4.9 ±0.9	Pb <sup>‡°</sup>	698 ±49	741 ±83	1,325 ±93	1,116 ±125	
Si	20.1 ±1.0	26.8 ±1.3	20.9 ±1.9	22.9 ±2.1	Sb <sup>†°</sup>	51 ±3	341 ±20	154 ±10	887 ±53	
Sr	0.06 ±0.02	0.09 ±0.04	0.06 ±0.02	0.10 ±0.04	Se <sup>†</sup>	<	<	<	<	
Ti <sup>°</sup>	0.83 ±0.21	0.59 ±0.20	0.85 ±0.24	0.78 ±0.26	Sn	158 ±2	99 ±12	466 ±5	302 ±36	
Zr	0.03 ±0.02	0.06 ±0.02	0.03 ±0.02	0.08 ±0.03	V <sup>†</sup>	41 ±16	26 ±3	67 ±26	86 ±11	
Balance (H,C,O...)	33.8 ±8.7	39.9 ±8.7	31.6 ±10.5	35.7 ±11.6	Zn <sup>‡°</sup>	4,370 ±421	1,673 ±113	4,146 ±400	1,915 ±130	
LOI (wt.%)	3.1 ±0.2	0.7 ±0.1	5.3 ±0.4	1.8 ±0.2						

< : below detection limit (1 ppm)

‡ : regulated metal(loid) in Flanders; † : non-regulated metal(loid) in Flanders; ° : regulated metal(loid) in Wallonia.

**Table 2**

Mineralogical composition of fresh and aged B and F bottom ash samples determined by quantitative X-ray diffraction analysis (in wt.%); there are no indications for the presence of unidentified minerals.

Mineral phase	Chemical formula	Fresh samples		Aged samples	
		B	F	B	F
Calcite	CaCO <sub>3</sub>	3.6	3.5	7.5	1.9
Quartz	SiO <sub>2</sub>	8.5	23	12	21
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	n/d	n/d	0.7	0.4
Aluminium	Al	0.3	n/d	1.1	n/d
Magnetite <sup>1</sup>	Fe <sub>3</sub> O <sub>4</sub>	2.3	0.5	2.5	0.8
Hematite	Fe <sub>2</sub> O <sub>3</sub>	1.2	1.9	1.0	2.4
Gehlenite	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>	4.0	0.9	4.5	0.7
Pyroxene <sup>2</sup>	XYZ <sub>2</sub> O <sub>6</sub>	1.3	n/d	1.0	n/d
Wüstite	FeO	0.8	n/d	0.6	n/d
Wollastonite	CaSiO <sub>3</sub>	1.7	0.5	1.8	1.6
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (Cl,F,OH)	1.4	5.5	n/d	7.7
Feldspar_Alkali	(Na,K)Si <sub>3</sub> AlO <sub>8</sub>	0.4	4.1	1.8	2.2
Cristobalite	SiO <sub>2</sub>	0.7	0.5	0.6	1.1
Anhydrite	CaSO <sub>4</sub>	0.3	3.9	0.3	4.1
Ettringite	Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26(H <sub>2</sub> O)	0.1	n/d	n/d	n/d
Portlandite	Ca(OH) <sub>2</sub>	1.2	n/d	n/d	n/d
Others/Amorphous		73	56	65	56

<sup>1</sup> Or Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) which has a defect spinel structure with a hematite stoichiometry. Magnetite (Fe<sub>3</sub>O<sub>4</sub>) also has the spinel structure, as well as several other minerals; they cannot always be distinguished unambiguously from the XRD-spectra.

<sup>2</sup> X : Ca<sup>2+</sup>, Na<sup>+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, Li<sup>+</sup>; Y : Mn<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Ti<sup>4+</sup>; Z : Si<sup>4+</sup>, Al<sup>3+</sup>.

n/d : not detected.

**Table 3**

Results of the batch leaching test (performed according to EN 12457-4/DIN 38414-S4) of fresh and aged samples (in mg contaminant per kg ash) compared to the Walloon (Ministere De La Region Wallonne, 2001) and Flemish (Van Gerven et al., 2005b) limit values. The bolded figures indicate values that exceed at least one regulated limit. Error values correspond to standard deviation of triplicates.

Sample	pH	As <sup>1</sup>	Ba	Cd	Co	Cr <sup>2</sup>	Cu	Mo	Ni	Pb	Sb	Se	V	Zn
B,fresh	<b>12.4</b> ±0.2	<	<b>17.4</b> ±5.2	<	0.01 ±0.001	0.27 ±0.05	<b>9.9</b> ±1.0	<b>0.57</b> ±0.02	0.12 ±0.01	<b>33.9</b> ±10.3	0.07 ±0.01	<	0.03 ±0.004	<b>5.1</b> ±0.6
B,aged	10.5 ±0.2	0.03 ±0.01	<	<	0.01 ±0.001	0.36 ±0.06	<b>3.8</b> ±0.4	<b>0.64</b> ±0.03	0.08 ±0.005	0.04 ±0.01	<b>0.97</b> ±0.2	0.04 ±0.01	0.30 ±0.04	<
F,fresh	<b>12.1</b> ±0.2	0.01 ±0.003	1.3 ±0.4	0.01 ±0.003	0.01 ±0.001	<b>2.9</b> ±0.5	0.40 ±0.04	<b>1.6</b> ±0.07	0.12 ±0.01	0.23 ±0.07	0.05 ±0.01	<b>0.15</b> ±0.04	0.04 ±0.01	0.28 ±0.03
F,aged	<b>12.2</b> ±0.2	0.02 ±0.01	<	<	0.02 ±0.001	<b>3.1</b> ±0.5	<b>1.8</b> ±0.2	<b>1.9</b> ±0.08	0.14 ±0.01	<b>2.0</b> ±0.6	0.01 ±0.002	<b>0.14</b> ±0.04	0.18 ±0.03	0.40 ±0.05
Walloon limits <sup>3</sup>	7-12	1.00	n/a	1.00	1.00	1.00	20.00	1.50	2.00	2.00	2.00	n/a	n/a	9.00
Flemish limits <sup>4</sup>	n/a	0.80	1.60 <sup>5</sup>	0.03	0.25 <sup>5</sup>	0.50	0.50	0.20 <sup>5</sup>	0.75	1.30	0.10 <sup>5</sup>	0.04 <sup>5</sup>	0.80 <sup>5</sup>	2.80

n/a: not applicable (not regulated, no suggested value available).

<: below detection limit (0.01 mg/kg).

<sup>1</sup> Limits prescribed for total As, as measured.

<sup>2</sup> Limits prescribed for Cr(VI), whereas total Cr leaching values were measured.

<sup>3</sup> Limits applicable to the EN 12457-4/DIN 38414-S4 24 hour batch shaking leaching test.

<sup>4</sup> Limits applicable to the NEN 7343 column leaching test (note: this study uses batch leaching tests only).

<sup>5</sup> Non-regulated limit values.

**Table 4**

Summary of compliance to Walloon (DIN) and Flemish (NEN) leaching limits and calculated performance scores (*S*) for fresh, aged, heat treated, moist carbonated and slurry carbonated bottom ash samples.

	Exceeds DIN limits	Score (rank) DIN	Exceeds NEN limits	Score (rank) NEN
B,fresh	pH, Pb	1036.5 (5 <sup>th</sup> )	Ba, Cu, Mo, Pb, Zn	2719.5 (5 <sup>th</sup> )
B,aged	–	51.0 (3 <sup>rd</sup> )	Cu, Mo, Sb	1239.0 (4 <sup>th</sup> )
B, 'heat treat'	Cr	533.5 (4 <sup>th</sup> )	Cr, Mo, Sb	1226.5 (3 <sup>rd</sup> )
B, 'CO <sub>2</sub> moist'	–	38.5 (2 <sup>nd</sup> )	Cu, Mo, Sb	830.5 (1 <sup>st</sup> )
B, 'CO <sub>2</sub> slurry'	–	35.5 (1 <sup>st</sup> )	Cu, Mo, Sb	926.5 (2 <sup>nd</sup> )
F,fresh	pH, Cr, Mo	1235.5 (5 <sup>th</sup> )	Cr, Mo, Se	1582.0 (2 <sup>nd</sup> )
F,aged	pH, Cr, Mo	1234.5 (4 <sup>th</sup> )	Cr, Cu, Mo, Pb, Se	2373.0 (5 <sup>th</sup> )
F, 'heat treat'	Cr	936.0 (3 <sup>rd</sup> )	Cr, Mo, Se	1629.0 (4 <sup>th</sup> )
F, 'CO <sub>2</sub> moist'	Mo	330.5 (2 <sup>nd</sup> )	Mo, Sb, Se, V	1617.5 (3 <sup>rd</sup> )
F, 'CO <sub>2</sub> slurry'	–	37.5 (1 <sup>st</sup> )	Mo, Sb, Se	829.5 (1 <sup>st</sup> )



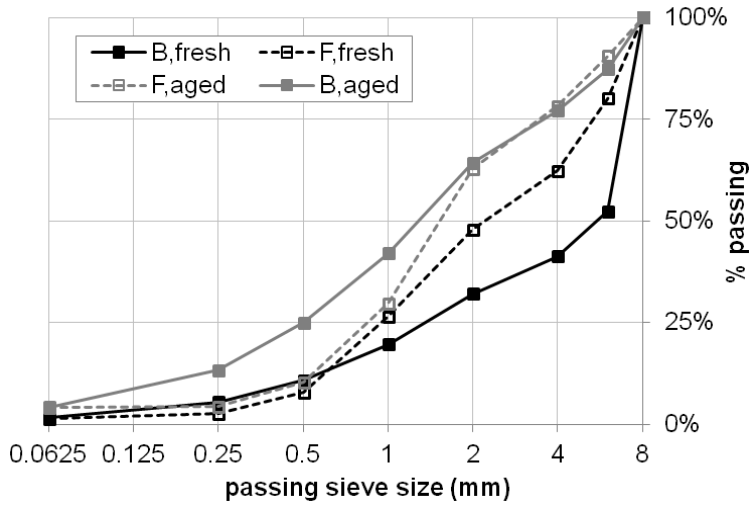
**Table 5:**

Determination of calcium carbonate and Gypsum contents of fresh, aged and treated B and F bottom ash samples by thermogravimetric analysis (TGA) and quantitative X-ray diffraction analysis (QXRD); results expressed in wt.%.

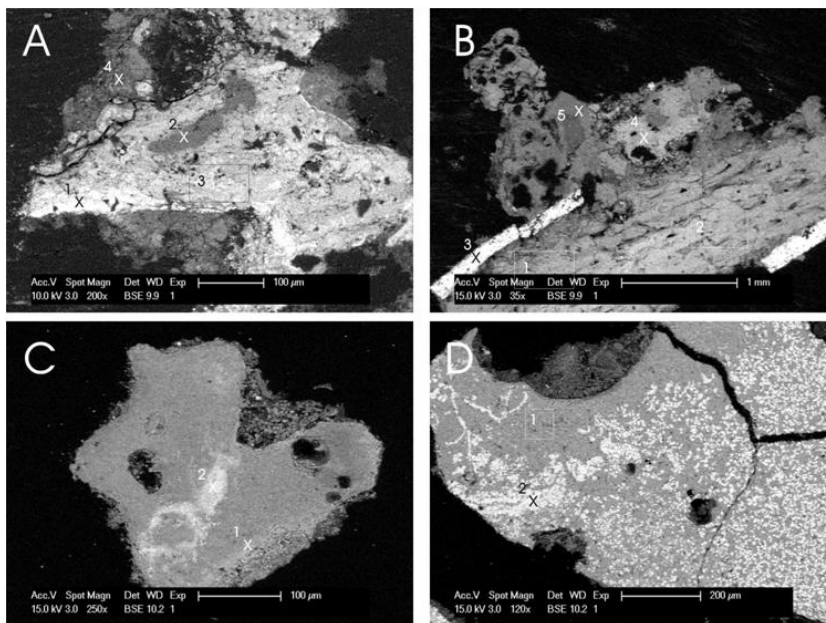
Mineral phase	Chemical formula	Method	B,fresh	B,aged	B,'heat treat'	B,'moist CO <sub>2</sub> '	B,'slurry CO <sub>2</sub> '
Calcium carbonate	CaCO <sub>3</sub>	TGA <sup>1</sup>	8.2	9.7	8.9	12.6	14.8
Calcite	CaCO <sub>3</sub>	QXRD	3.6	7.5	8.0	9.8	9.4
Aragonite	CaCO <sub>3</sub>	QXRD	-	-	-	-	0.7
Vaterite	CaCO <sub>3</sub>	QXRD	-	-	-	0.8	0.5
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	QXRD	-	0.7	-	0.8	0.2
Mineral phase	Chemical formula	Method	F,fresh	F,aged	F,'heat treat'	F,'moist CO <sub>2</sub> '	F,'slurry CO <sub>2</sub> '
Calcium carbonate	CaCO <sub>3</sub>	TGA <sup>1</sup>	2.6	2.0	2.8	5.3	9.8
Calcite	CaCO <sub>3</sub>	QXRD	3.5	1.9	2.2	4.8	5.0
Aragonite	CaCO <sub>3</sub>	QXRD	-	-	-	-	1.2
Vaterite	CaCO <sub>3</sub>	QXRD	-	-	-	-	-
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	QXRD	-	0.4	-	1.1	0.5

<sup>1</sup> TGA results based on mass loss between 500 and 800 °C, which can be largely attributed, though not exclusively, to the decomposition of CaCO<sub>3(s)</sub> to CaO<sub>(s)</sub> and CO<sub>2(g)</sub>.

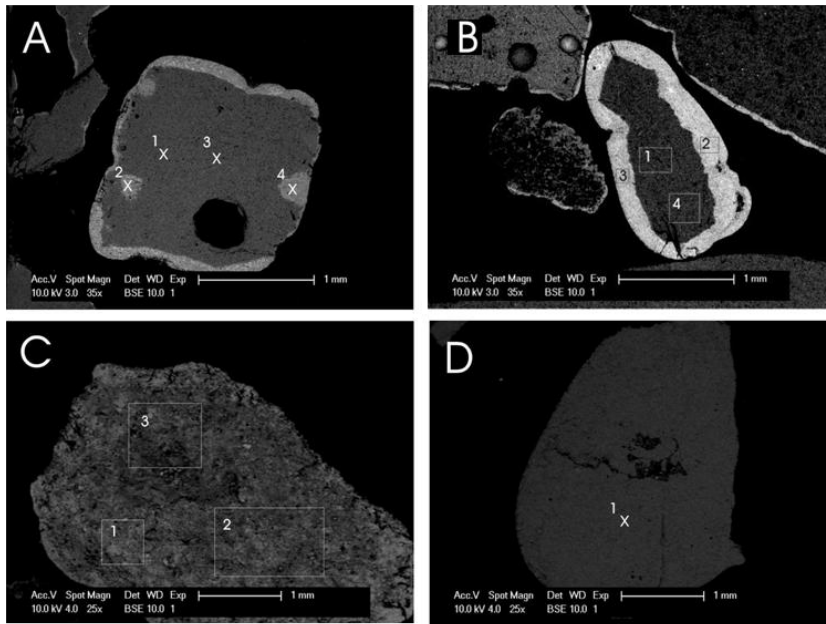
## List of Figures



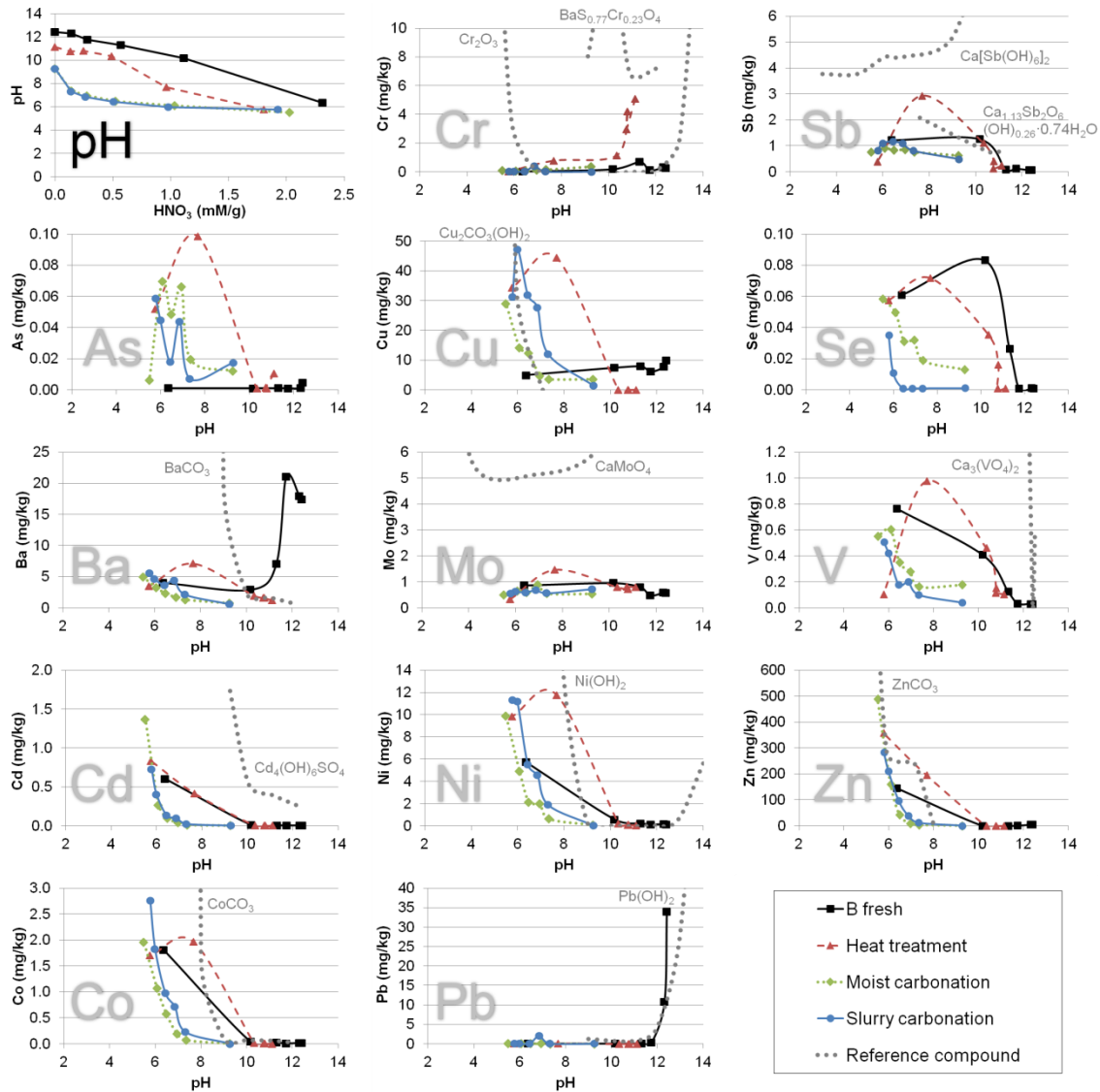
**Fig. 1.** Grain size distribution curves of the fresh and aged B and F bottom ash samples, determined by sieving; greater than 8 mm fraction was removed and not used in testing.



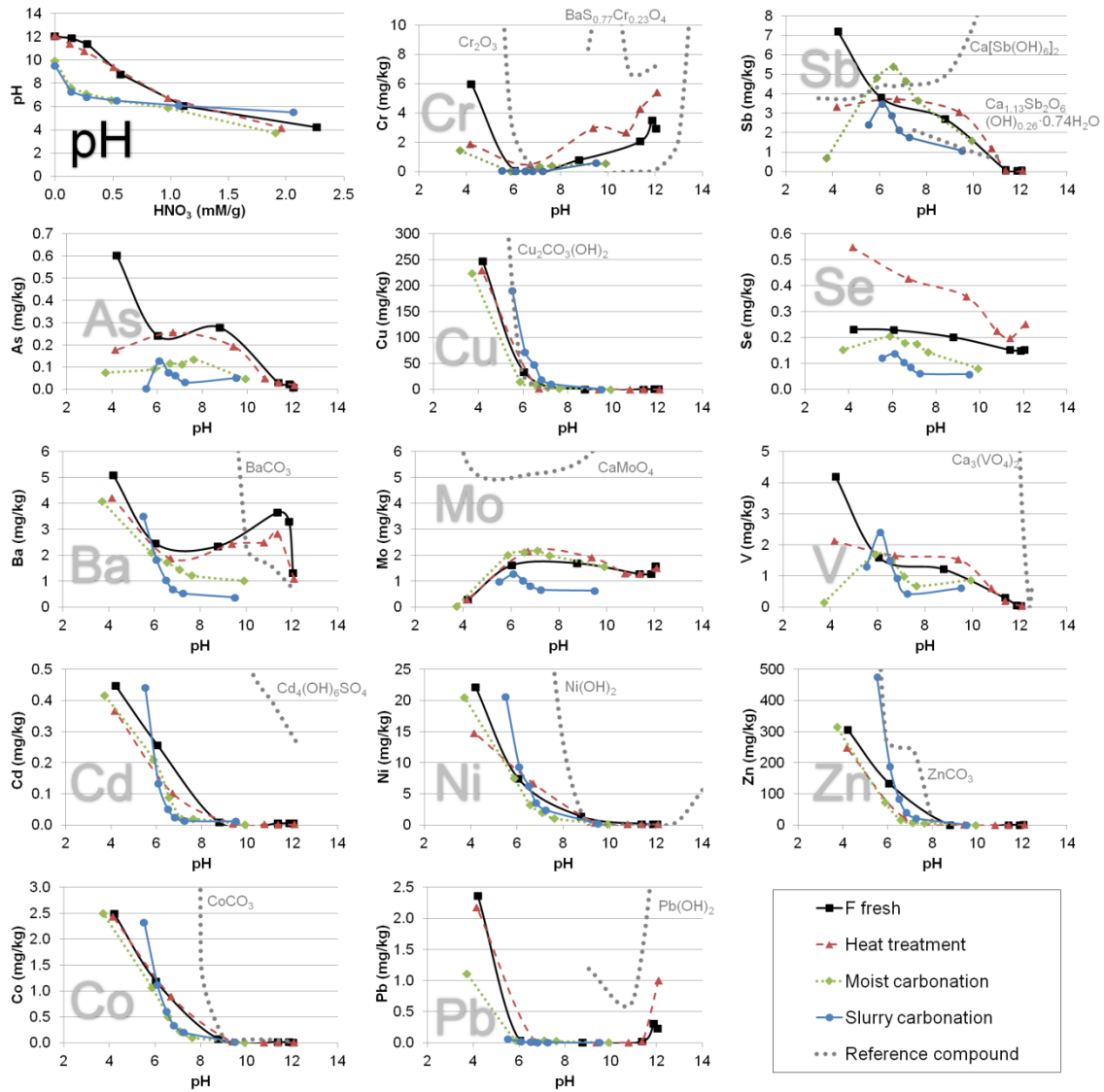
**Fig. 2.** BSE images of the polished sections of fresh bottom ash sample B. The areas and crosses indicate the positions where EDX-analyses were performed: see Table SC-1 for the analysis results.



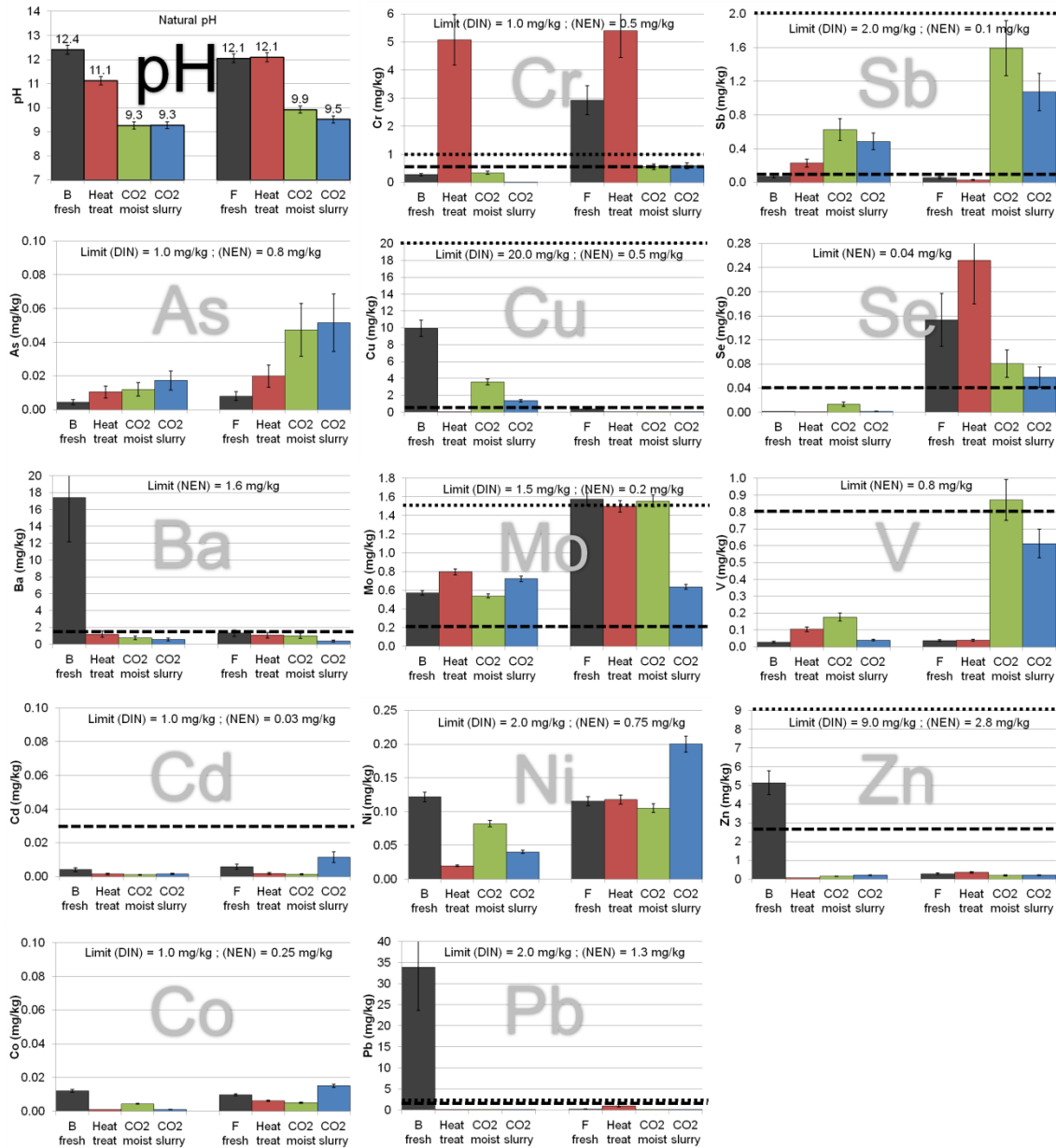
**Fig. 3.** BSE images of the polished sections of fresh bottom ash sample F. The areas and crosses indicate the positions where EDX-analyses were performed: see Table SC-1 for the analysis results.



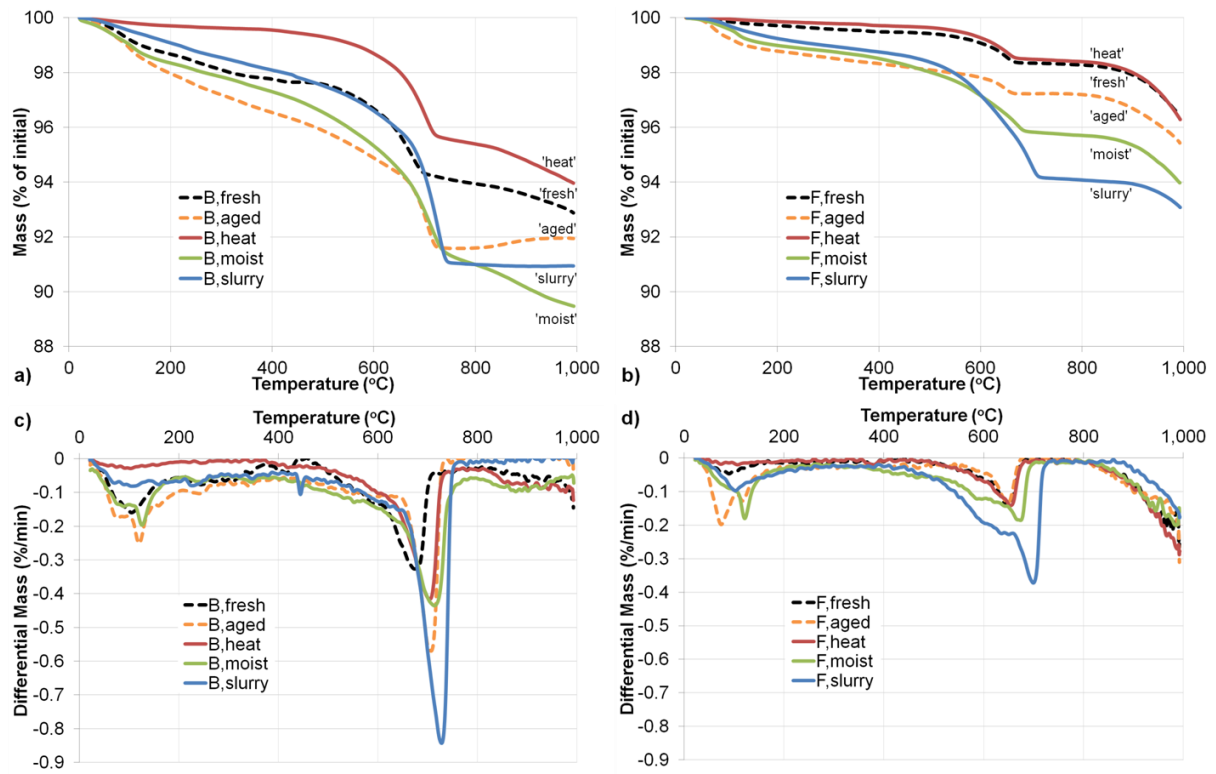
**Fig. 4.** Results of batch leaching tests performed at varying pH (adjusted by  $\text{HNO}_3$ ) and  $L/S = 10$  of bottom ash sample 'B fresh' and of the same sample after three different treatments: heat treatment, moist carbonation and slurry carbonation. Dotted curves indicate theoretical leaching of reference compounds obtained by geochemical modelling (PHREEQC and Visual MINTEQ), on the basis of the work of Fällman (2000), Cornelis et al. (2006), Cornelis et al. (2008), Zhang et al. (2008), Hyks et al. (2011) and Cornelis et al. (2012).



**Fig. 5.** Results of batch leaching tests performed at varying pH (adjusted by  $\text{HNO}_3$ ) and  $L/S = 10$  of bottom ash sample 'F fresh' and of the same sample after three different treatments: heat treatment, moist carbonation and slurry carbonation. Dotted curves indicate theoretical leaching of reference compounds obtained by geochemical modelling (PHREEQC and Visual MINTEQ), on the basis of the work of Fällman (2000), Cornelis et al. (2006), Cornelis et al. (2008), Zhang et al. (2008), Hyks et al. (2011) and Cornelis et al. (2012).



**Fig. 6.** Results of leaching tests at natural pH (performed according to EN 12457-4) of bottom ash samples ‘B fresh’ and ‘F fresh’ and of the same samples after three different treatments: heat treatment (‘Heat treat’), moist carbonation (‘CO<sub>2</sub> moist’) and slurry carbonation (‘CO<sub>2</sub> slurry’). The leaching limits of the Walloon (DIN) and Flemish (NEN) regulations are also indicated where applicable; dashed lines (DIN: fine dash; NEN: coarse dash) mark the limits where they are within the y-axes ranges. Error bars correspond to standard deviation of triplicates.



**Fig. 7.** TG (top row) and DTG (bottom row) diagrams of fresh, aged and treated ('heat' treatment, 'moist' carbonation, 'slurry' carbonation) B and F bottom ash samples.