

Proceedings of the  
4<sup>th</sup> International Symposium on  
**Enhanced Landfill Mining**

5 - 6 February 2018  
Mechelen, Belgium

**Editors**

Peter Tom Jones  
Lieven Machiels



# METALLURGICAL CONCEPTS FOR RECYCLING OF BOTTOM ASHES FROM MUNICIPAL WASTE INCINERATORS

Hugo LUCAS, Bernd FRIEDRICH

IME Process Metallurgy and Metal Recycling, RWTH Aachen University, 52056, Germany

*hlucas@ime-aachen.de, bfriedrich@ime-aachen.de*

## Abstract

In several European countries, incineration remains the main means of municipal solid waste (MSW) processing.<sup>1</sup> With pre-processing prior to incineration, inorganics and metal fractions are recovered by mechanical separation. However, there remains around 7% of metals mixed with inorganics and combustion residues which collect in the bottom of incineration furnaces. For Germany alone, bottom ash represents almost 4.8 million tonnes a year.<sup>9</sup> Currently, bottom ash is re-used in road works; however, the contained metals may cause damage to vehicles.<sup>8</sup> In recent years, scientists are looking at these materials as a precursor to produce Inorganic Polymers (IPs) that could be used to create eco-friendly and sustainable construction materials.<sup>7</sup> In this study, a robust characterisation analysis was undertaken with the objective of defining the most attractive strategies for pre-treating the ash fractions. Mechanical separation, leaching and pyrometallurgical treatment of the different ash fractions was also evaluated to maximise metal recovery. Finally, the inorganic phase produced as result of pyrometallurgical treatments was analysed and studied as a suitable inorganic polymer precursor.

## Introduction

Landfills are still the main disposal systems for Municipal Solid Waste (MSW). With more than 500,000 Landfills in Europe, this kind of disposal represents a serious environmental risk due to hazardous compounds. Several European countries turn to incineration as a way to valorise MSW as an energy source.<sup>1,3</sup> Incinerated residues represent 30% of the original MSW, where bottom ashes are the main residues.<sup>2,3</sup> Around 20 million tonnes of MSW incineration bottom ash (MSWI BA) is produced every year in Europe.<sup>1,3</sup> The use these ashes for construction materials after metal extraction becomes an economical route to exploit.<sup>4,5</sup> However, the presence of heavy metals and a wide range of complex compounds is the real limitation to use MSWI BA as a promising raw material.<sup>4,6</sup> This paper describes a combination of different approaches to recover almost all the valuable elements contained in MSWI Bottom ash as well as how to transform a complex and hazardous material into a safe

and stable vitrified slag that could be used as precursor for cements, inorganic polymers, ceramics, etc.<sup>7</sup>

## Methodology

In order to evaluate the quality and proportion of the metals inside MSWI BA, four different strategies were carried out (Figure 1). In all of them, an electrical arc furnace was used to melt the BA at the end. In strategies 2, 3 and 4, metals were recovered by mechanical separation. The last strategy introduces a second step of mechanical treatment to clean the metals, and a hydrometallurgical treatment to extract valuable metals from the finest BA fraction.

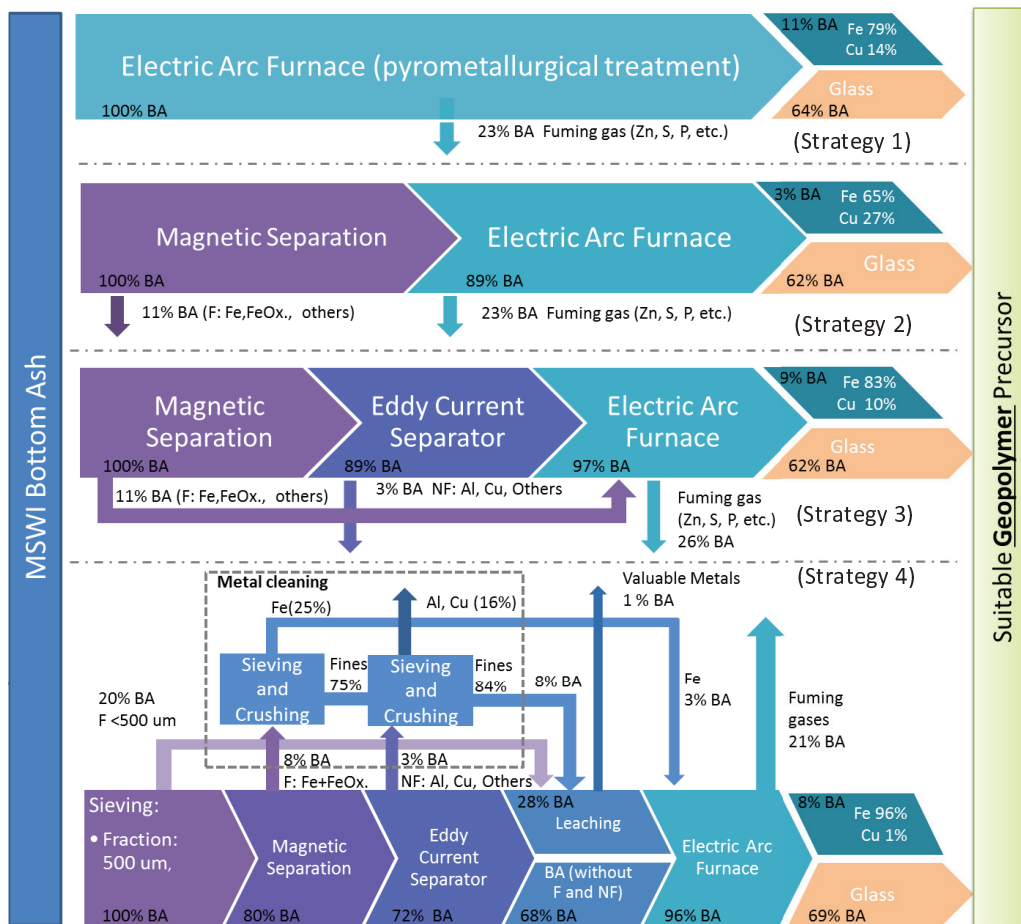


Figure 1: Strategies to valorise MSWI Bottom ash

## Sample preparation

For this study, 100 kg of wet MSWI BA with metals, provided by the company AVR in Netherlands, were consumed. BA was first dried at 200°C for 24 hours. Sieves between 45 µm and 10 mm, a jaw crusher and planetary ball mills were used to create

fractions for analysing. A magnet was used to hand-recover all BA magnetic particles. This method is more efficient than the traditional suspension-magnet-separator<sup>8</sup> used by industry. Non-ferrous-metals (NF-metals) were collected using an eddy-current-separator (ECS). A Jaw crusher was used to separate the fractions obtained by mechanical separation into metals and non-metals. Sifting these fractions, a clean stream of metal was obtained.

### **Chemical Analysis**

PANanalytical WDXRF spectrometer was used for the analysis of the final vitrified slag and bottom ash fractions; and a Portable XRF analyser (Thermo Fisher NITON XL3t 600) was used for metals and the fraction used for the leaching experiments. A PANanalytical X'Pert<sup>3</sup> x-ray diffractometer and HighScore software were employed for the mineralogical analyses. The mineralogical detection was made following the method of C. Kirby and J. Rimstidt.<sup>9</sup>

### **Leaching**

Three different solutions were performed to examine the yield of recovery of different elements present in the BA fraction < 500 µm. One using sulphuric acid with concentrations of 1 M, 2 M and 4 M; and the others with nitric and chlorhydric acid with a concentration 4 M in order to compare the performance of the acids. Tests were conducted at 50°C using a liquid-to-solid ratio (l/s) of 20 during 2 hours.

### **Pyrometallurgical treatment**

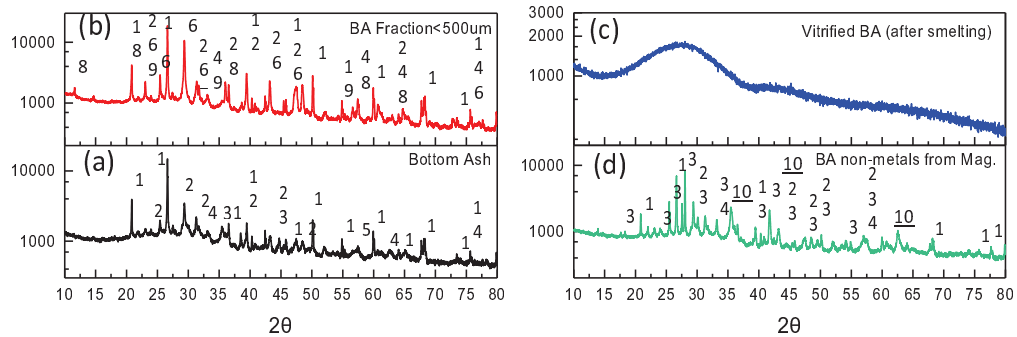
For this study a lab-scale electric arc furnace (EAF) operating in single-phase alternating current mode was used. This furnace uses a graphite electrode of 50 mm at the top and on the base the contra-electrode serving as a crucible. The graphite crucible with 150 mm diameter and 220 mm height could carry up to 3 kg of BA. The power of the furnace was set in order to maintain a temperature of around 1400-1500°C.

### **Inorganic polymer preparation**

Vitrified slag after smelting was cooled down under air inside a metallic bucket coated with ZrO<sub>2</sub>. The slag was first milled for 10 hours in an Attritor mill to obtain a specific surface of 4200 g.cm<sup>-2</sup> (EN196-6) and then mixed with three different NaOH solutions using concentrations of 3 M, 6 M and 9 M. The liquid-to-solid ratio was 0.35. Finally, each mixture was poured into 2 x 2 x 8 cm<sup>3</sup> steel moulds, wrapped in plastic foil and then and then cured at 20°C for 45 days. Compressive strength tests were performed based on EN196-1.<sup>6</sup>

## Results

MSWI BA has a large amount of different compounds. XRD analyses reveal the presence of large quantities of carbonates and sulphates. Comparing XRF analysis (Table 1a) with these XRD profiles (Figure 2a and 2b), both elements represent 4.5 wt% and 2.2 wt%, respectively. The presence of these elements is higher in the finest fraction (BA < 500µm) where, for example, carbon represents 13 wt%, being present almost completely in Ca-carbonate. These phases are the most significant after amorphous phases and quartz (~65 wt%).



**Figure 2:** XRD profiles: (a) MSWI BA, (b) MSWI BA fraction <500µm, (c) Vitrified slag after MSWI BA smelting and (d) non-metallic fraction after cleaning metals. (1) quartz, (2) calcite, (3) magnetite, (4) hematite, (5) aluminium, (6) anhydrite, (7) halite, (8) gypsum, (9) perovskite, (10) cuprospinel

**Table 1:** XRF analysis of MSWI BA

(a) MSWI BA (wt%)									
Fraction	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	C	S
MSWI BA	39.7	16.1	8.6	4	9	1.8	0.8	4.7	0.8
BA<500 µm	19.4	26	7.3	0.6	5	1.7	1.1	13.1	1.3
(b) Trace element composition of MSWI BA fractions (ppm).									
Fractions	Zn	Cu	Pb	Cr	Sn	Co	Ag		
Non-metals from mag. sep.	5400	2090	930	1310	340	430	130		
Non-metals from ECS	3262	5986	842	382	319	0	20		
BA fraction<500µm	11670	2650	2340	550	290	0	0		
(c) Results of smelting MSWI BA in an EAF (wt%)									
Metal	Fe	Cu	Si	P	Cr	Mn	Ni	Co	Sn
Strategy 1	79.0	14.5	1.2	1.6	0.71	0.32	0.39	0.22	0.34
Strategy 2	65.10	26.70	1.30	1.90	1.50	0.92	0.70	0.50	0.27
Strategy 3	81.20	12.60	1.40	1.67	0.48	0.21	0.53	0.61	0.22
Vitrified slag	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>
Strategy 1	49.3	20.5	18.7	4.5	0.1	2.6	0.71	1.1	0.05

MSW is always first incinerated and then quenched in water.<sup>3</sup> These two processes have a strong influence on the metal quality. Ferrous metals are partially oxidised during the incineration and then corroded in contact with wet ashes (alkaline medium). Non-ferrous-metals such as aluminium, zinc, lead or tin are molten first and partially oxidised. Other metals such as copper do not suffer major changes in the BA.

The elements recovered by magnetic separation were between 8 and 10 wt% of the BA. Several reviews expose that ferrous metals represent between 7 and 10 wt% of BA<sup>3,10,11</sup> but no description is made about the quality of these metals. After mechanical cleaning of the magnetics, ferrous metals represent just 24 wt% of this fraction (3 wt% of BA). In the magnetic fraction there are almost 30 wt% of iron oxides (Figure 3b) nevertheless on average, there are 10 wt% of iron oxides spread in the ashes (Table 1a). XRD profile of Figure 2d shows that the half of these oxides are magnetite (created during the incineration) and the other part, hematite (produced by corrosion).

In the case of separation by eddy currents, recovered elements represent 3 wt% of BA but after mechanical cleaning, NF-metals depict 18 wt% of this fraction (0.6 wt% of BA). ECS works well for particles larger than 5 mm (Figure 3a). Aluminium represents 70% of metals separated by ECS but has a poor quality because it was molten and strongly polluted during the incineration.

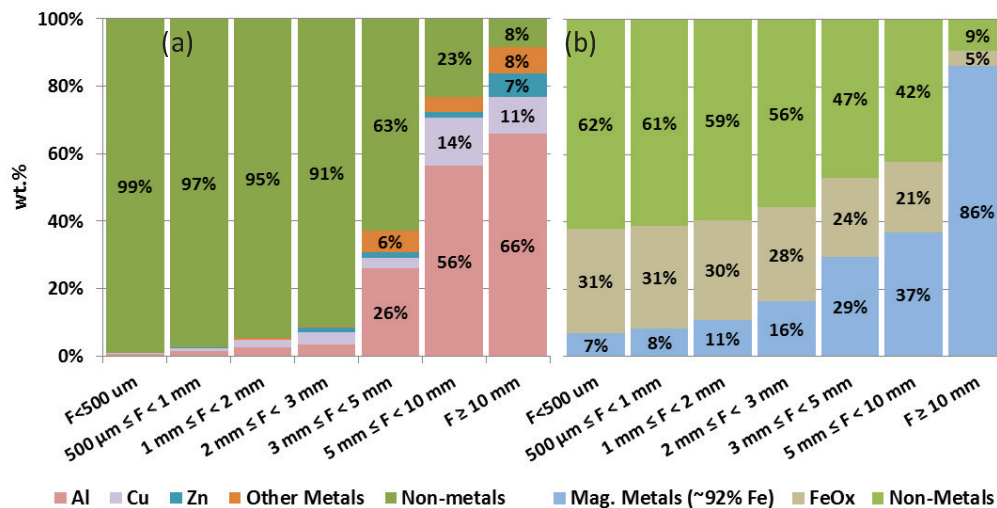
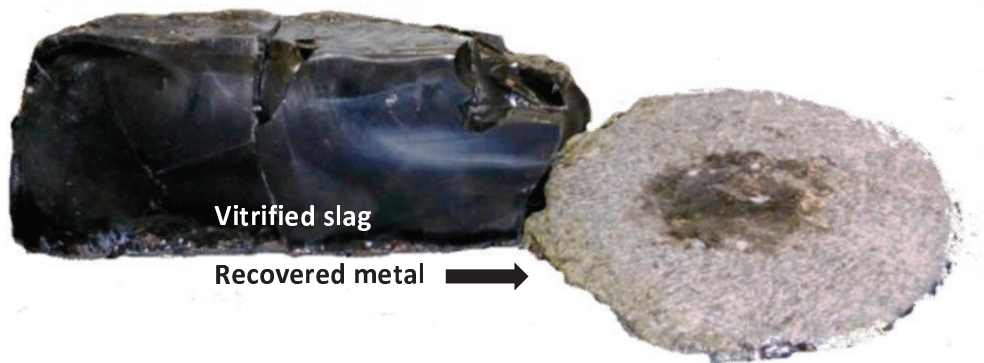


Figure 3: Mechanical separation: (a) eddy-current-separator and (b) magnetic separation

### Pyrometallurgical treatment

Smelting BA has several advantages, such as the reduction of all iron oxides using the carbon present in these ashes (~ 5 wt%), re-melting the metals and transforming all the inorganic compounds into a vitrified slag (see Figure 5). After smelting, the iron

recovered was 9 wt% of BA against 3 wt% obtained after mechanical cleaning (Figure 1-strategy 4). At high temperature, almost all heavy metals leave the slag and can be recovered in the fly ash.

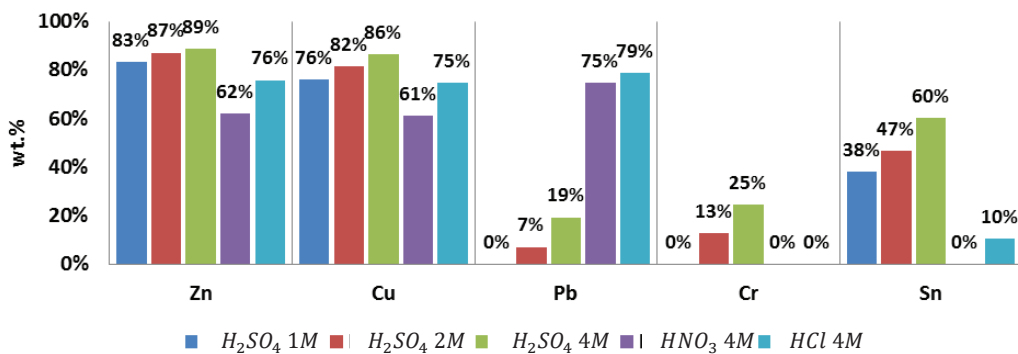


**Figure 4:** Final products after pyrometallurgical treatment of MSWI BA

Copper is one the most difficult elements to extract from bottom ash. Regarding the result of strategy 1 (Figure 1) there is between 1 and 1.5 wt% of copper in the bottom ash. By ECS only a fifth part was extracted. The magnetic and the finest fraction of bottom ash also contain copper (Table 1b and Figure 1 - strategy 2/3). Except for the proportion of aluminium oxide that is reduced by 10 percent in vitrified slag produced in the strategies 3 and 4 (aluminium recovered with ECS), the slag composition remains practically unchanged.

### Leaching experiments

The non-metallic-fractions recovered after mechanical cleaning show the presence of copper, zinc, lead and silver. The elements in Table 1b represent a potential source of valuable metals that can be recovered by hydrometallurgy.



**Figure 5:** Extraction Yield for of valuable elements present in the MSWI BA

Results of leaching experiment for the finest BA fraction are shown in Figure 5. Solutions containing sulphuric acid seem to be effective to extract the majority of

valuable elements from BA, except lead where nitric acid was more effective. No major differences were observed between sulphuric acid concentrations of 2 M and 4 M.

### Inorganic polymers

The XRD profile in Figure 2c revealed that vitrified slags had a fully amorphous structure. During the preparation of inorganic polymer pastes, the mixing glass/alkali-solution produced gas bubbles altering the quality. Small metallic particles at the interface metal/slag are the origin of this defect. The results are exposed in Figure 6. Inorganic polymer pastes produced from vitrified slags (Figure 4), carried out with very slow cooling, solidified well after 45 days. Even if the quality was not excellent due to the pollution with metals and alkali solutions still need to be optimised, these IPs produced from MSWI BA are a promising solution to recycle MSWI.

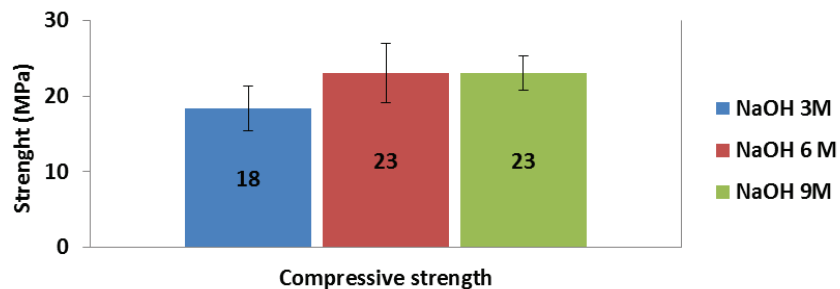


Figure 6: Mechanical properties of inorganic polymers produced from MSWI BA

### Conclusions

MSWI Bottom ash produced in moving grate incinerators contains a wide amount of species that could be avoided using other technologies such as gasifiers.<sup>3</sup> For this reason, it is usual to find unburned plastics, papers, textile, but also hazardous compounds such as asbestos or fiberglass which only can be destroyed at high temperatures. The finest BA fraction also contains large amounts of heavy metals. These metals could be extracted using strong leaching solution, nevertheless always a small amount of these remain in the ashes.

Eddy current separators are efficient to extract metals larger than 5 mm but below this size the efficiency falls.<sup>10</sup> The proportion of elements extracted using magnets and ECS are in the same order that those reported in other reviews.<sup>8,9,11</sup> However, after a second step of mechanical cleaning, the metals recovered were a quarter of these fractions. Examining the mass balance of the different processes carried out, it can be concluded that less than 20 wt% of non-ferrous metals are extracted by traditional separation technics.



It was demonstrated that pyrometallurgical treatments effectively upgrade BA. In addition, the large content of commercial glass inside BA allows an amorphous structure after smelting. The composition and structure of the vitrified slag can be employed to produce inorganic polymers and some types of glass-ceramics. For these applications, it will be decisive to avoid any trace of metals, and if it is desired to increase reactivity, and thus the conversion of BA to slags followed by quenching is favoured.

## Acknowledgments

The authors would like to acknowledge the financial support of the European Union with the Programme Horizon 2020 under Grant Agreement No 721185 (ETN New-MINE). We are thankful for the support given by Georgia Flesoura, Yiannis Pontikes and Remus Iacobescu from the Department of Material Engineering KU Leuven. A special gratitude goes to Cristina Garcia of I.A.R. RWTH-Aachen for her assistance in Mechanical Separation.

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