THERMODYNAMICS OF CONDITIONING MSWI BOTTOM ASH USING SAF FOR USAGE IN MINERALS PRODUCTS

Hugo LUCAS, Bernd FRIEDRICH

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

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

Introduction

The incineration of municipal solid waste has become the most suitable solution to reduce by more than 80 percent the volume of waste disposed of on landfills.[1,2] Besides the energy generation; almost 30% of the mass input ends up as incineration bottom ash (IBA).[3] Depending on the local legislation, part or all of it is landfilled. Even if we tend to think that the composition of IBA is as diverse as the number of incinerator plants, the bulk composition is within one order of magnitude.[4]

Previous studies revealed that IBA is a heterogeneous material formed by carbonates, sulphates, chlorides, silicates, glasses and unburnt organics besides ferrous and nonferrous metals.[1,5] Most of the metals can be recovered by mechanical methods, nevertheless, the recovery efficiency is affected by the agglomeration of these with other elements.[1,2,5,6] That happens inside IBA which tend to a progressive solidification after the wet treatment of this ash, which in fact is related to the hydration of CaO into $Ca(OH)_2$, and then into $CaCO_3$ because of the absorption of atmospheric CO_2.[7]

The thermal treatment of IBA allows not only to recover metals but also conditioning the mineral phase into a clean and homogeneous vitrified slag that fulfils the standards for applications such as inorganic polymers, glass-ceramics or aggregates.[5,8,9] This work focused on the mechanisms of decomposition and homogenisation as a function of the temperature of the mineral fraction of IBA.

Materials and Methods

The IBA used in this study was provided by the company AVR in The Netherlands. The material was first dried at 200°C for 24 hours. Up to 3 kg of material was treated using a lab-scale *submerged arc furnace* (**SAF**). Once the material charged and smelted, the power was adjusted to keep it at 1500°C for a holding time of 1 hour. Physical changes for a temperature range comprised between 200°C and 1400°C were also studied. For this purpose, 7 graphite crucibles, protected by an alumina crucible from the outside, with 200 g of IBA inside were introduced at the same time in an *electric resistance furnace* (**ERF**), and heated up with a ramp of 400°C/h. One by one, the

crucibles were removed with a ΔT of 200°C until reaching 1400°C. Finally, all these results, including those in the SAF, were compared with thermal gravimetric analysis (TGA) and simultaneously with a differential thermal analysis (DTA) performed with a Netzsch thermobalance STA 409. Chemical reactions were confirmed using FactSage 7.0. Metals and slags were analysed using an XRF spectrometer, a sulphur/carbon analyser, and a PANanalytical X'Pert³ x-ray diffractometer.

Results and Discussion

IBA is a heterogeneous material which contains besides minerals, some unburnt organics (~ 3%) and metals (~ 10%) such as Fe, Al, Cu, and Zn.[5] There is a wide difference in term of composition (Table 1) and mineralogy (Figure 1a and 1c) between IBA and the produced slag at 1500°C. These composition changes in the mineral phase in function of the temperature are summarised in Figure 2b.

Table 1: Chemical composition of IBA (metals non-included), and the produced slag

wt%	SiO_2	CaO	Al_2O_3	Na_2O	Fe_2O_3	ZnO	CuO	PbO	SO_3	Cl	C
IBA	39.1	23.70	8.18	3.00	7.95	0.95	0.53	0.26	2.77	1.62	5.55
Slag	48.3	22.60	18.51	3.73	0.76	0.01	0.14	0.01	1.48	0.02	0.11

During the vitrification using the SAF at 1500°C, IBA lost around 21% of its weight. The final product is a homogeneous and amorphous slag, which represents 65% of the input, and a metal alloy composed mainly by Fe and Cu (~ 10% of IBA). Weight loss during heating in lab experiments follows a trend close to the TGA profile made on IBA samples using argon as a shield gas (Figure 2a).

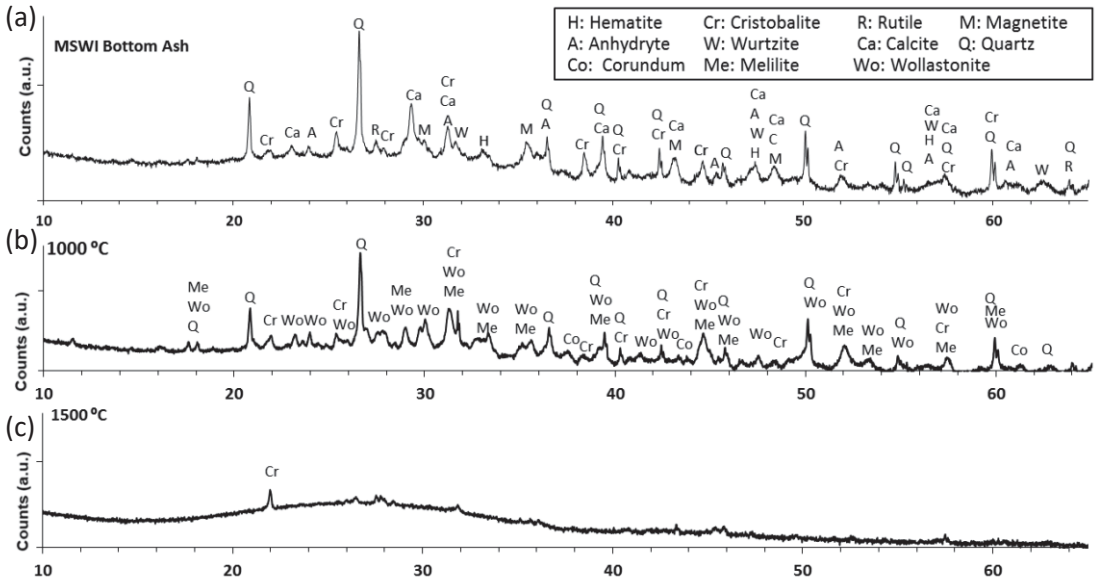

Figure 1: IBA XRD profiles: (a) before heating, (b) IBA at 1000°C and (c) 1500°C

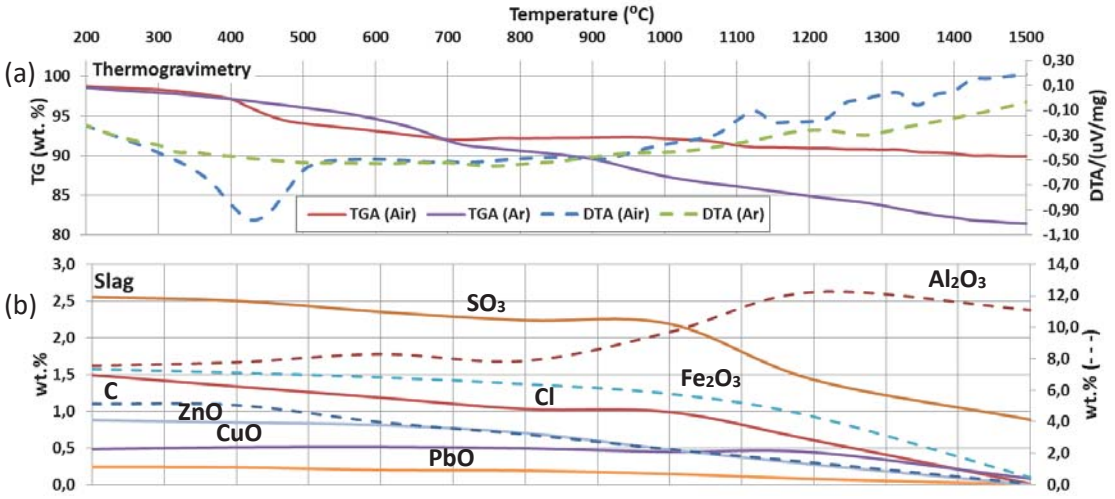

Figure 2: (a) TGA and DTA of IBA under Ar and Air atm.; (b) slag composition *vs.* temperature

The temperature range between 400°C and 700°C is driven by the decomposition of unburnt organics and carbonates (mostly $CaCO_3$) at the end. Part of this carbon leaves the system as CO_2 and CO, and the rest becomes char, which will serve as a reductant for metal oxides such as Fe, Cu or Zn. Between these temperatures, hematite (Fe_2O_3) decomposes into magnetite (Fe_3O_4); and the proportion of quartz (SiO_2) gradually begins to decompose to form new phases combined with Fe and Ca.

From 700°C to 1000°C, the commencement of chlorides, zinc and lead oxide vaporisation, as well as the decomposition of magnetite into wüstite (FeO) is seen. Apparently, main changes are led by the oxidation of Al (1.4% of IBA) which is reflected by the emergence of the corundum phase visible in the XRD profile of Figure 1b, and the increase of Al_2O_3 in the mineral phase (Figure 2b). Quartz dissolution in the mineral matrix becomes more important, aided by the reaction with CaO (from the decomposed carbonates), wüstite, and pieces of glass contained in IBA (~ 25%) to produce the crystalline phases of cristobalite (SiO_2), wollastonite ($CaSiO_3$) and melilite $(Ca,Na)_2(Al,Mg,Fe^{2+})[(Al,Si)SiO_7]$.

At 1130°C the first liquid phases appear and beyond this temperature, all the kinetics accelerate. The rest of chlorides, Zn, and PbO will rapidly leave the slag. FeO and CuO will be firstly reduced by C and Al (its influence ends at 1200°C), and then only by carbon. In the range of temperature of 1200 to 1300°C all the minerals in the slag, including sulphates, mainly combined with calcium, are dissolved. When the temperature reaches 1500°C, the slag liquefies completely, allowing a good separation of the metallic phase. After cooling, the produced slag shows an amorphous profile (Figure 1c) wherein only a small peak of cristobalite remains visible. Fe (79%), Cu (14%) and other elements such as Si, P, Ni, Cr with traces of Au and Ag, compose the metal tapped out from the furnace.

Conclusions

In general, the thermal conditioning of IBA does not need additional reductants or fluxing agents to decrease the melting point. High temperatures are only needed to homogenise and separate metals from the slag. The presence of commercial glass which has a matrix made of SiO_2-Na_2O-CaO together with the generation of CaO due to the decomposition of $CaCO_3$ have an important role in the dissolution of high melting point minerals such as quartz, rutile, and corundum. The dissolution of these is complete when the temperature exceeds 1400°C. The range of temperatures between 800 and 1300°C is crucial to cleaning IBA of the potentially contaminating bulk products such as heavy metals, chlorides, and phosphates.

There is no significant difference whether these slags are quenched in water or not after smelting; the high silica content makes them highly amorphous. For this reason, once these slags are re-melted and treated at high temperatures, they have, in term of composition and microstructure, excellent qualities to be used as precursors for elaborating glass-ceramics or inorganics polymers.[5,6,8]

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