

STUDY OF MUNICIPAL SOLID WASTE BOTTOM ASH: CHEMICAL AND MINERALOGICAL CHARACTERIZATION

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INTRODUCTION

Municipal Solid Waste (MSW) Bottom Ashes (BAs) are solid residue products of incinerator combustion that consist mainly of polycrystalline fragments, such as glasses, silicate minerals and various waste metals. Many volatile metals (*e.g.*, zinc and lead) are incorporated in salts and in silicate glasses and their speciation in melts and crystals in MSW products are widely unknown.

In this PhD thesis I investigated two sets of bottom ash samples derived from two combustion facilities, one located in Rimini and the other in Piacenza. Both the incinerator systems work with rotary kilns, but in the incinerator plant of Piacenza the waste material treated is composed also of special hazardous waste, in particular hospital waste. The samples were mineralogically and chemically characterized by using X-ray Diffraction (XRD), X-ray Fluorescence (XRF), LA-ICP-MS and electron microprobe analyses.

The main goal of this work was to investigate the bottom ashes as starting combustion products and after vitrification treatments. The Fig. 1 compares the main oxide composition of BA samples of this study to literature data reported as minimum and maximum average values: except for the slightly higher SiO₂ content in these BA, all the other oxides concentrations were within the concentration ranges reported in the literature.

Thermal treatments on the BA samples were carried out at 1000-1300°C, with melting times from 1 h to 72 h. Vitrification of waste was useful to get more homogenous products and for volume reduction; moreover, it is considered a valuable technique to be used before possible re-utilization of the MSW.

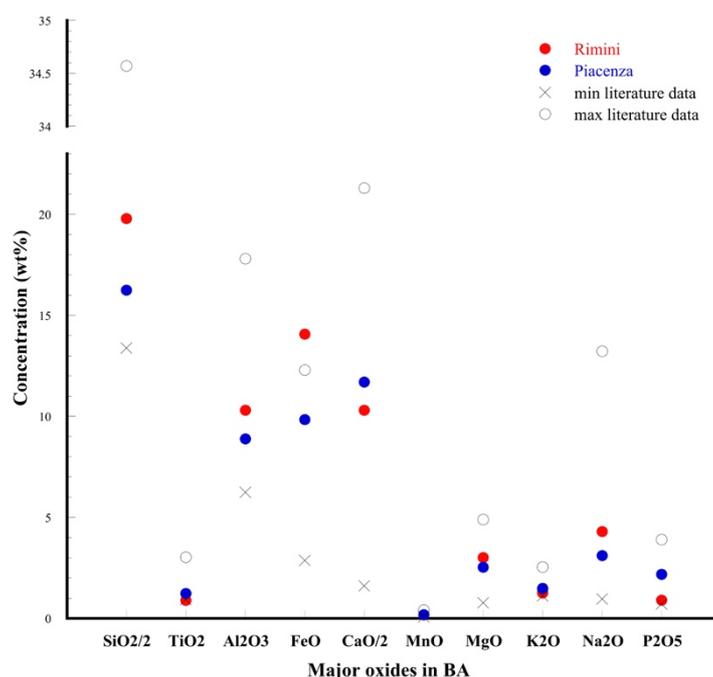


Fig. 1 - Bottom ash compositions, expressed as wt.% oxides for the bottom ashes from Rimini and Piacenza plants compared to various literature sources (min and max are the limits of literature range: Kirby & Rimstidt, 1993; Kida *et al.*, 1996; Barbieri *et al.*, 2000; Ferraris *et al.*, 2001; Appendino *et al.*, 2004; Forteza *et al.*, 2004; Fujimori *et al.*, 2004; Li *et al.*, 2004; Jung & Osako, 2007; Xiao *et al.*, 2007; Hyks *et al.*, 2009; Bayuseno & Schmahl, 2010; De Boom & Degrez, 2012)

The understanding of the behaviour of heavy metals during melting processes of MSW and Rare Earth Elements (REE) recovery was also of particular interest; for instance, light-REE (LREE) were enriched in the investigated bottom ash samples but their concentration was still below the economic feasibility limit of 0.2 wt.% determined by industries. Furthermore, the samples were classified by using the volcanic rock discrimination diagram (or TAS: total alkali vs. silica plot) and resulted to be similar to trachy-basaltic and basaltic compositions, but with a quite complex heterogeneous glass chemistry. Thus, they might be compared to natural rock systems and provided some parallels between the conditions and processes of combustion and melting in the facility and in natural magmatic system, which was a major interest concerning the behavior of volatile metal components (*e.g.*, Pb, Zn, As, Cd, *etc.*).

VITRIFICATION PRODUCTS

In the present study, the thermal behaviour and high temperature vitrification of MSW incineration bottom ashes were investigated under ambient pressure (air) at laboratory scale using a chamber furnace. Dried samples of bottom ashes were used for all melting experiments, and no other pre-treatment was conducted except for drying at 110°C for 24 hrs.

After treatments the samples resulted to be almost homogenous and glassy; some differences in elements abundance were be appreciated comparing these products to the starting samples (Fig. 2).

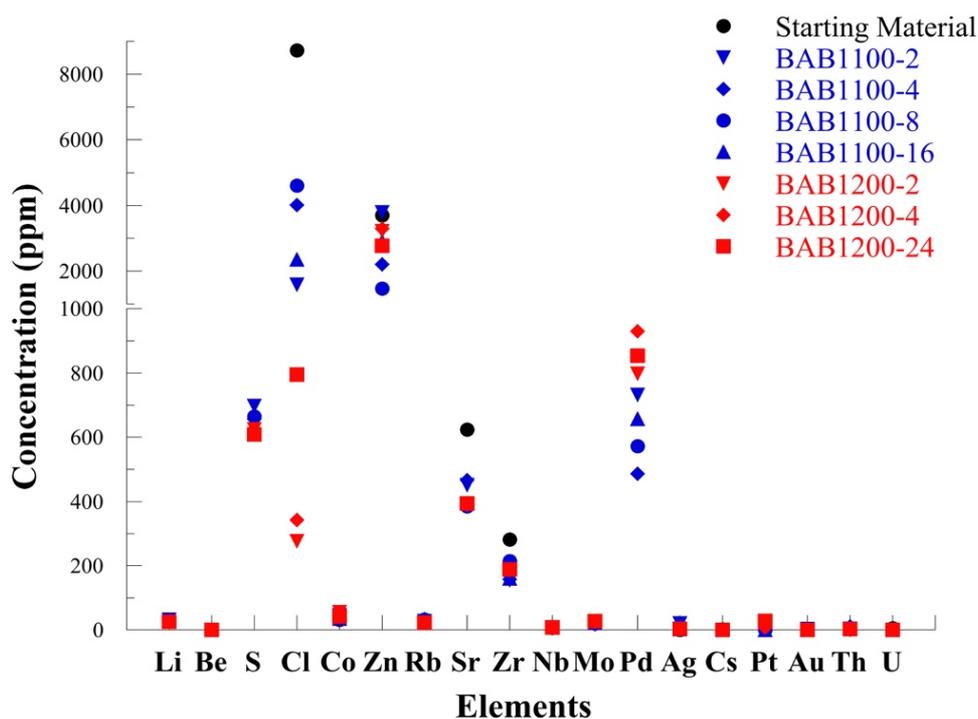


Fig. 2 - Abundance variation of minor elements in BAB samples (Rimini plant) at the two temperatures of 1100-1200°C (LA-ICP-MS analyses).

For instance, Cl and S evidenced high concentrations (exceeding 8000 ppm in the BA for Cl and 600-800 ppm for S) but comparable to the general concentrations found also in other studies (*e.g.*, Toshihisa *et al.*, 1998). The high Cl content can be generated from the plastic fraction, mainly PVC (Le Forestier & Libourel, 1998); in fact, even if both Cl and S are strongly volatile elements, they are usually present in higher concentration in the fly ashes rather than in the bottom ash residues. Cl is a serious issue for reutilization of solid residues (for example for Portland cement where Cl should be less than 200 ppm) and it needs to be removed and recovered

before any possible use; otherwise, if the facility does not consider the pre-treatment to remove some hazardous materials they will not be reused.

On the other hand, there were elements with moderate volatility, such as Zn, which were highly concentrated in both the starting and vitrified materials in the order of 4000 ppm. Generally, the volatility of heavy metals increases as the element boiling point decreases, but this relationship is not always observed (see also Jung & Osako, 2007). Furthermore, it was found that volatiles content in the glass was directly related to the elements abundance in the BA starting material, meaning that variations of these elements might result from variations of the same metals in the waste treated during combustion.

Rare Earth Elements (REEs) were typically found in higher concentrations in the BA than in the fly ashes because of their high boiling point (Funari *et al.*, 2016 and references therein), and our samples had typical REE concentrations between a few ppm to 80 ppm (Fig. 3).

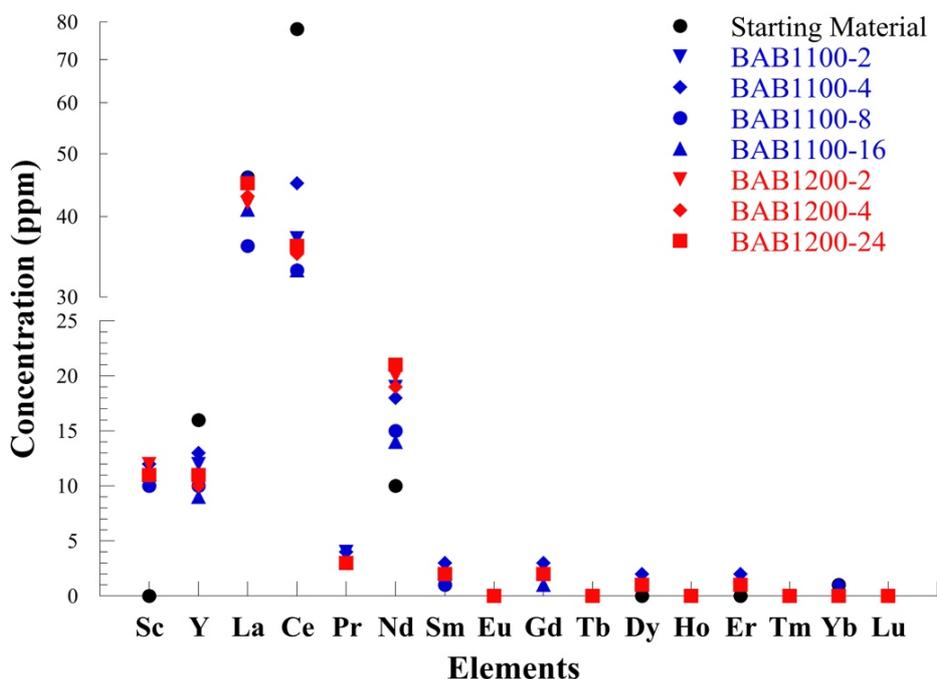


Fig. 3 - Abundance variation of REEs in BAB (Rimini plant) samples at different temperatures of 1100-1200°C.

The studied samples were mainly enriched in light REEs (LREE: Sc, La, Ce, Nd; Fig. 3), with the exception of Y, which is a heavy REE (HREE). Although the fact that REEs represent critical raw materials because of their important value in new technologies, recovery of REEs from MSWI is not of main concern for industries because of difficulties related to the low concentration and the way to process it. Moreover, the level of economical practicability of REEs, for example for the materials investigated in this study, was much lower than the one established by EREAN project (0.01 wt.% vs. 0.2 wt.%).

MINERALOGY

Mineralogy is the main way to investigate the possible host phases for potentially hazardous elements in ashes and, for this reason, a detailed mineralogical study of solid residue wastes is often useful. XRD analyses were carried out for all the starting BA compositions, but, for the sake of simplicity, we report here only the results for one sample. The figure 4 shows XRD spectra of the starting BAB sample (Piacenza plant) along with the glass sample treated at the highest temperature (1300°C) and longest duration (4 hrs; BAP-1300-4).

The diffraction pattern for the starting BA sample showed that the most abundant mineralogical phases were: quartz (1), gehlenite (2), calcite (3), magnesioferrite (4), ilmenite (5), and plagioclase (6), with the quartz peaks presenting the highest intensity compared to the other compounds. At the same time, XRD analyses confirmed that the thermally treated sample (BAP-1300-4) was largely glass (broad background bands from 17° to 38° of 2 θ ; *e.g.*, Post & Bish, 1989) and we observed only small peaks corresponding to trace amounts of the refractory magnesio-ferrite phase (4). This was the only resistant mineral with high stability temperature (stable to ~1665°C, Ambruz *et al.*, 1980) that may be found in the vitrification products.

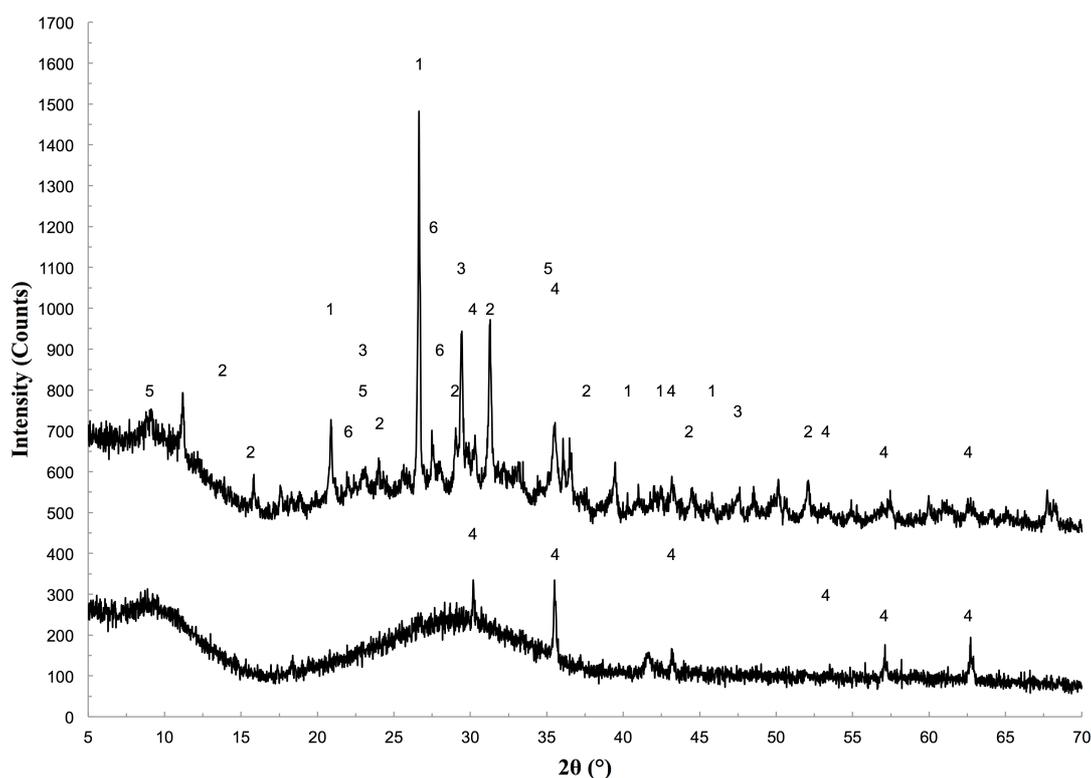


Fig. 4 - XRD scan of the untreated starting sample and of the sample after vitrification at the highest temperature and longest duration of the thermal treatment (BAP-1300-4).

GEOCHEMICAL RESULTS AND IMPLICATIONS

Major oxide crystal-chemistry (Fig. 5) obtained by Electron Microprobe (EMP) analyses revealed that bottom ashes had a bulk composition similar to basic rocks (*e.g.*, trachybasalts, basalts). They differ from acid rocks (*e.g.*, rhyolite with a silica concentration higher than 66 wt.%) because of the lower SiO₂ content and the higher CaO concentrations (with the exception of only few samples for the Piacenza incinerator). EMP results are reported as variation diagrams of major elements *vs.* wt.% of CaO in figure 5. Basaltic to trachy-basaltic compositions from literature studies are also reported together with BAs (see references in the figure caption) in order to create a parallelism between the synthetic and the natural compositions.

It is clear that BA samples show rough positive correlations of CaO *vs.* MgO and alkali and negative correlations for SiO₂, Al₂O₃ and FeO, whereas basalts show poorly defined negative trends also for SiO₂, Al₂O₃ and FeO, being comparable to the BA but with higher contents of SiO₂ and FeO. In this way, it is possible to correlate the combustion systems to magmatic ones and infer the behaviour of major oxides and volatile metals of major interest for melted products in natural samples.

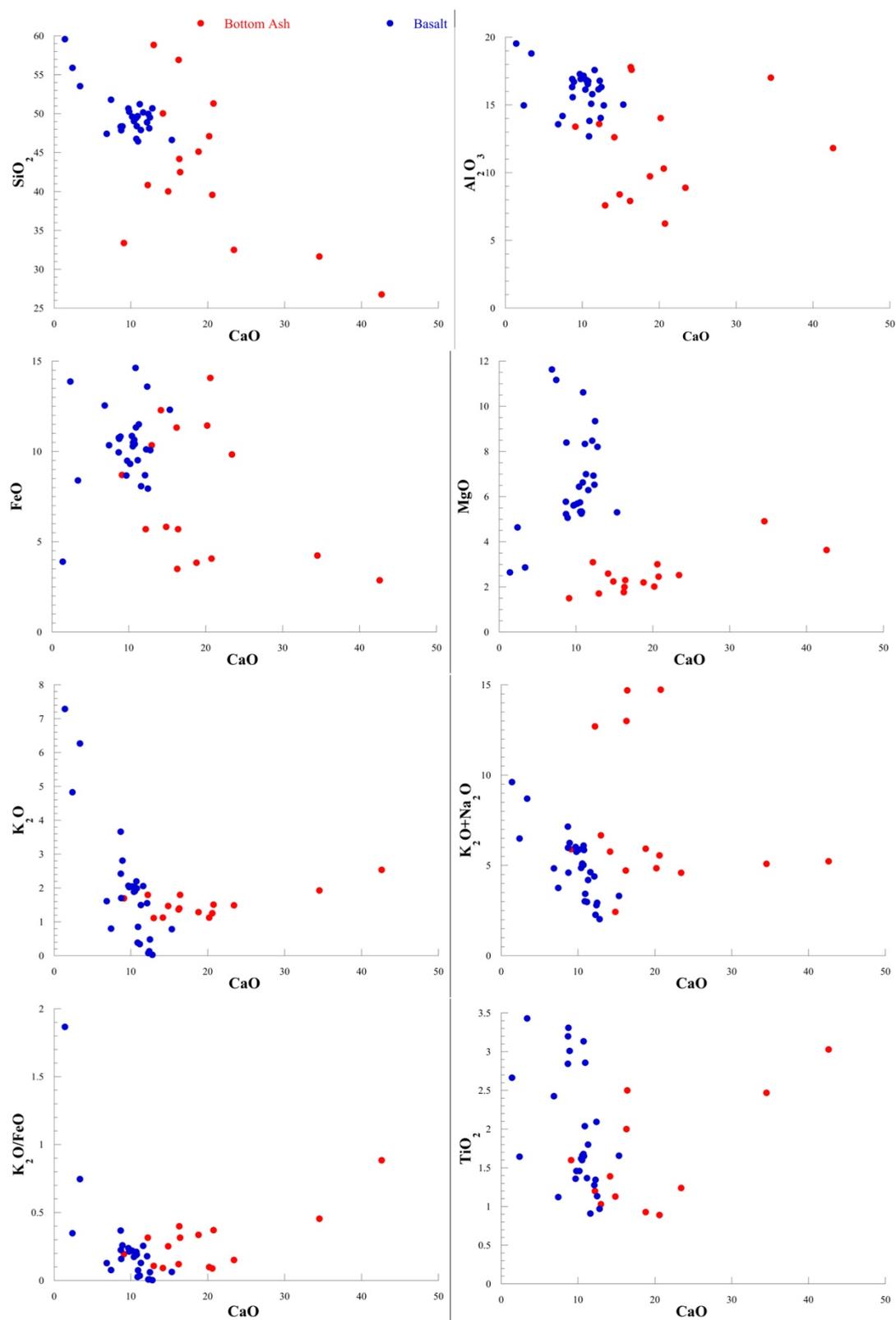


Fig. 5 - Variation diagrams of major elements vs. CaO (wt.%) of bottom ash from this study compared with literature data on selected natural basalts (Hofmann & White, 1982; Alt & Honnorez, 1984; Alt *et al.* 1986; Sun & McDonough, 1989; Staudigel *et al.*, 1996; Kelley *et al.*, 2003; Viccaro *et al.*, 2006; Misiti *et al.*, 2009; Fanara *et al.*, 2015).

Finally, the same vitrified samples offer high resource potential for MSW in the way to be recycled and reused as inerts in different civil engineering applications, because vitrification treatments ensure homogeneity and strong depletion of hazardous elements in such products. In particular, vitrification processes immobilize harmful elements (e.g., Cr, Ni), reduce Cl and S contents, yield a material more resistant to alteration/leaching compared with untreated bottom ash samples, and restrain negative environmental effects like unvitrified waste is prone to do.

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