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Solid residues from Italian municipal solid waste incinerators: A source for "critical" raw materials

Valerio Funari [a,*], Roberto Braga [a], Syed Nadeem Hussain Bokhari [b], Enrico Dinelli [a], Thomas Meisel [b]

[a] Dipartimento di Scienze Biologiche, Geologiche e Ambientali – Geology Division, University of Bologna, Piazza di Porta San Donato 1, 40126 Bologna, Italy
[b] General and Analytical Chemistry – Montanuniversität Leoben, Franz-Josef-Str. 18, 8700 Leoben, Austria

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ABSTRACT

The incineration of municipal solid wastes is an important part of the waste management system along with recycling and waste disposal, and the solid residues produced after the thermal process have received attention for environmental concerns and the recovery of valuable metals. This study focuses on the Critical Raw Materials (CRM) content in solid residues from two Italian municipal waste incinerator (MSWI) plants. We sampled untreated bottom ash and fly ash residues, i.e. the two main outputs of common grate-furnace incinerators, and determined their total elemental composition with sensitive analytical techniques such as XRF and ICP-MS. After the removal of a few coarse metallic objects from bottom ashes, the corresponding ICP solutions were obtained using strong digestion methods, to ensure the dissolution o
f the most refractory components that could host significant amounts of precious metals and CRM. The integration of accurate chemical data with a substance flow analysis, which takes into account the mass balance and uncertainties assessment, indicates that bottom and fly ashes can be considered as a low concentration stream of precious and high-tech metals. The magnesium, copper, antimony and zinc contents are close to the corresponding values of a low-grade ore. The distribution of the elements flow between bottom and fly ash, and within different grain size fractions of bottom ash, is appraised. Most elements are enriched in the bottom ash flow, especially in the fine grained fractions. However, the calculated transfer coefficients indicate that Sb and Zn strongly partition into the fly ashes. The comparison with available studies indicates that the CRM concentrations in the untreated solid residues are comparable with those residues that undergo post-treatment beneficiations, e.g. separation between ferrous and non-ferrous fractions. The suggested separate collection of "fresh" bottom ash, which could be processed for further mineral upgrading, can constitute an attractive option of the waste management system, when physical–mechanical devices are not available or could not be implemented in old MSWI systems. The suggested procedure may lead to the improvement of recovery efficiency up to 83% for CRM and 94% for other valuable metals.

1. Introduction

The European waste policy discourages waste landfill in favor of waste recycling, recovery and, finally, waste-to-energy processes (EC, 2008). Today, the waste incineration represents the mainstream method for the management of unsorted urban and industrial wastes in many industrialized countries. An integrated system of municipal solid waste incinerator (MSWI) reduces the volume of collected waste, destroys many toxic components and provides a source of alternative energy. Final solid residues are around 30% of the total mass input and their reuse, as additive for construction materials (e.g.: Bertolini et al., 2004; Izquierdo et al., 2001), or their disposal in landfills invariably requires the assessment of the amount of hazardous elements, which can endanger the environment and the human health (e.g.: Li et al., 2004; Pan et al., 2013). Efforts have been made to characterise the chemical and mineralogical composition of the residues, including the leachable fractions (e.g.: Hu et al., 2012; Pan et al., 2013; Zhang et al., 2008b).

The growing body of chemical (and mineralogical) data is adding a new perspective on solid waste as a secondary source of metals and other valuable chemical elements. During the last few years, several authors investigated on precious metals (mostly Ag, Au, Pt) in MSWI residues (Jung and Osako, 2009a; Muchova et al., 2009). Recently, the European Commission (2010, 2014)

* Corresponding author. Tel.: +39 051 20 94 959 (O), +39 389 68 35 032 (mobile).
E-mail address: valerio.funari@unibo.it (V. Funari).

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defined a list of "critical" raw materials on the basis of their relative economic importance and supply risk. Critical Raw Materials (CRM) are chemical elements and minerals such as Be, Co, Cr, Ga, Ge, In, Mg, Nb, Sb, W, Platinum Group Elements (PGEs), Rare Earth Elements (REE), borates, coking coal, fluorspar, graphite, magnesite, phosphate rock, silicon metal, which are important for the technological development. In this regard, recent works reported the total content of CRM in solid residues from incineration plants (Hasegawa et al., 2014), also inspecting the annual flow for several elements (Morf et al., 2013; Allegrini et al., 2014).

Although several studies dealt with the fractionation of potentially harmful elements in different grain size fractions of bottom and fly ashes (De Boom and Degrez, 2012; Yao et al., 2013; Zhang et al., 2008a), the distribution of CRM in such fractions has not been fully explored. Morf et al. (2013) and Allegrini et al. (2014) investigated the CRM content in treated bottom ashes (i.e., after magnetic separation or with automatic samplers of the MSWI system) and in grain size fraction of the treated residues (i.e., non-ferrous batches). However, the treatment after quenching of bottom ash (e.g. separation between magnetic and diamagnetic materials) might not be a common practice at the facility scale, especially when a 10–15 years old system is operating.

For this reason we focus on the characterisation and the CRM potential evaluation of the main outputs of common incineration systems: (1) the whole and "fresh" (=after quenching) bottom ash residues and (2) the untreated (=prior to any filtration) fly ashes. We provide the elements mass fraction by XRF and ICP-MS and the estimated element flows (kg/a) of some CRM and other valuable metals through a substance flow analysis, as carried out in other works (Astrup et al., 2011; Belevi and Moench, 2000; Brunner and Ernst, 1986; Brunner and Mönch, 1986; Morf et al., 2013; Zhang et al., 2008a). In general, the annual flow evaluation lack in balanced mass account and in a clear description of uncertainty assessment (Astrup et al., in press), but in this contribution we provide the necessary information for the substance flow calculation to prove its integrity and to facilitate the inter-comparison with existing works.

Applying the same methods of analysis and elements flow evaluation, we further explore the different grain sizes of "fresh" bottom ash stocks by means of a visual-aided separation, easy for unskilled operators, in order to understand if the recovery potential of bottom ashes can be improved immediately after the incineration process and with low costs for the plant managers. In addition, the separate collection of fresh untreated bottom ash may constitute a good choice when physical–mechanical devices are not available or could not be implemented in old MSWI systems.

The CRM elements Be, Co, Cr, Ga, Mg, Nb, Sb, REE, W and Y are investigated in this study and hereafter called CRM for simplicity reason.

2. Materials and method

2.1. Bottom and fly ash samples

We collected the final solid residues from two waste incinerator plants from Northern Italy, named SWI-1 and SWI-2. The selected incinerators have similar thermo-recycling technology, with two boiler systems that produce an average electricity of 85,000 MW/h per year. The incineration systems consist of two lines that drive the collected waste, about 0.13 Mt/a (this value refers to the mean of the two plants), in the furnace that operates at temperatures between 850 and 1100 °C. More than 90% of the solid waste input is made of unsorted municipal solid waste while the remaining consists of special waste derived from pre-processing of the former. Moreover, the input to the SWI-1 also includes pharmaceutical/hospital waste.

The main outputs of the incineration process are slag, bottom and fly ashes. Hot slag and bottom ashes (hereafter called BA) are quenched in cooling tanks. The residence time of the residue in the water varies between 4 and 8 h depending on the throughput of waste and on its calorific value. At this stage, a broad magnetic separation removes the coarse ferric scrap; since this residue is completely recycled, it is not considered in our investigation. Belt conveyors transport the remaining wet residues (depurated only by the largest ferric objects, which is not considered in the final mass-weighted for the calculation of elements flow) to a temporary outdoor storage site where the BA are piled up. There is no further post-combustion treatment (e.g., trammel screening, magnetic separation). The total annual output of BA is about 0.023 Mt/a and 0.032 Mt/a for SWI-1 and SWI-2, respectively.

Untreated fly ashes from the furnace (hereafter, FA) are among the first residues produced during the incineration in both plants. These residues derive from mechanical waggle of the FA evacuation systems and are separately collected in big bags. Such kind of ash is typical of many conventional MSWI systems. Fly ashes undergo further steps of physical and chemical treatment (ESP, scrubber and bag filter with chemical additives) but these treated fly ashes are not the object of the present work. The total annual output of FA is about 2400 t/a and 3200 t/a for SWI-1 and SWI-2, respectively.

The overall process ensures that there is no mixing between FA and BA.

2.2. Sampling and sample preparation

The BA sampling from the two plants (SWI-1 and SWI-2) was carried out in a typical day of the process activity in May 2013, directly from the outdoor storage site. Each sampled stockpile was 3–4 meters high and representative of two-month deposition in total, since the last loading took place in early March 2013.

The samples collection followed the "stratified simple random sampling", a method outlined in the Italian technical standard UNI 10802 (2013). The method is suitable in case of solid waste forming an accumulation, which contains separate units or "strata" with vertical or horizontal direction. The strata should be readily distinguishable by specific features (e.g., colour, grain size, etc.) and are followed by drawing a simple random sample from each stratum. Generally, the stratified simple random sampling is more representative of the population than the simple random sampling (Kaur et al., 1996 and reference therein).

As the hill-shaped pile was clearly influenced by gravitational sorting, the variable that allows to stratify the BA stockpile is the gravity, which affects the grain size distribution of the solid material. Although the high deposition rate of materials, a visual inspection of the BA pile revealed coarser BA at the bottom of the pile and fine-grained BA at the top. This visual inspection allowed us to identify three layers (strata) based on their prevalent grain-size. Layers are named B, M, T respectively for bottom, intermediate and top. The influence of the gravity in grain size sorting is appraised by a granulometric analysis on primary samples conducted for the two plants (Fig. 1). Directly from fresh BA stock, 7–8 kg primary sample was taken from each layer. Each batch was split in four portions, the opposite portions were mixed together and again split for three times, to ensure homogeneity and representativeness. Three subsamples were taken from primary samples (i.e. each layer), nine in total from each incinerator plant. BA have 5–10 wt.% moisture content and show cm-sized fragments of metals, glassware and ceramics. All samples were oven-dried at 40 °C for one week under continuous air flow.

FA were collected in December 2013 from "big bags" with a random sampling method (UNI 10802, 2013). In both incinerator plants, about 5 kg FA primary sample was collected from almost