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# The rare earth elements in municipal solid waste incinerators ash and promising tools for their prospecting

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## HIGHLIGHTS

- The REE concentrations of bottom and fly ashes from municipal incinerators are investigated.
- First attempt toward discriminating the magnetic signature (susceptibility) of ashes from incinerators.
- New methods and parameters for REE prospecting, which can be determined quickly and with limited costs, are provided.

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## ABSTRACT

Bottom and fly ashes from Municipal Solid Waste Incinerators (MSWI) are hazardous products that present concern for their safe management. An attractive option to reduce their impact both on the environment and the financial commitment is turning MSWI ashes into secondary raw materials. In this study we present the REE content and distribution of bottom and fly ashes from MSWI after a highly effective digestion method and samples analysis by ICP–MS. The chondrite-normalised REE patterns of MSWI bottom and fly ash are comparable with that of crustal averages, suggesting a main geogenic source. Deviations from typical crustal pattern (e.g., Eu, Tb) disclose a contribution of likely anthropogenic provenance. The correlation with major elements indicates possible sources for REE and facilitates a preliminary resource assessment. Moreover, magnetic susceptibility measurements can be a useful prospecting method in urban ores made of MSWI ashes. The relationship between REE and some influencing parameters (e.g., Pricing Influence Factor) emphasises the importance of MSWI ash as alternative source of REE and the need of further efforts for REE recovery and purification from low concentrations but high flows waste.



## 1. Introduction

Rare earth elements (REE) are among critical raw materials, as defined by the European Commission [1,2], because of their importance for new and green technologies. They are used as essential constituents in a wide range of technological application [3] and their low substitutability implies to secure a stable REE supply. The major REE ore deposits are located in a handful of countries [1,3]: restriction policies on the REE export from these countries may increase the supply risk for EU countries as occurred during the 2011 crisis. Therefore there is an increasing interest to evaluate other REE sources, as secondary raw materials.

Literature exists that investigated REE abundance and their recovery performances from exhaust phosphors or other waste from electric and electronic equipments (WEEE), e.g., [4,5]. Recently, it has been demonstrated that solid residues from municipal solid waste incinerators (MSWI) host significant amounts of critical elements [6–8] possibly due to a weak control over the collected waste and the separated collection upstream [9]. The REE within MSWI solid residues are not routinely analysed since their low concentrations suggest there would be only a small potential for economic and environmental benefits. However, the need to reduce hazardous waste and the advances of bio-hydrometallurgy [10] are adding new prospective for the metal recovery from waste streams. A better knowledge of REE within MSWI ashes and their

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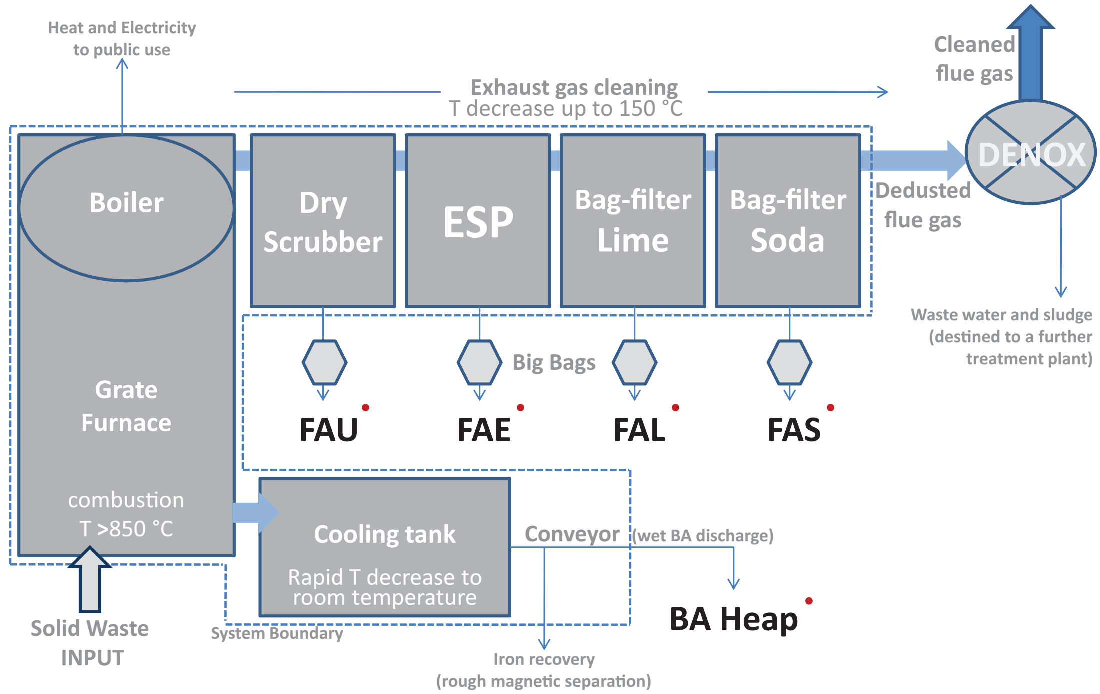


**Fig. 1.** Schematic picture of the incinerator system with its relevant processes, including sampling points (red dots) and temperature (T) profile. Acronyms used: BA = bottom ash; FAE = fly ash from ESP; FAL = fly ash from bag filter with lime additive; FAS = fly ash from bag filter with soda additive; FAU = untreated fly ash; ESP = electrostatic precipitator. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

availability is therefore required. Novel and cost-effective methods for REE prospecting from waste streams will ultimately provide a twofold benefit: improving hazardous materials management and creating potential economic value.

We aim to test the hypothesis that correlations with either major elements or magnetic measurements are an alternative way for the evaluation of REE potential in MSWI ashes. For that purpose chemical analyses of bottom and fly ashes from two incineration plants were performed, with emphasis on REE, and the accurate analytes determination was achieved by the $Na_2O_2$ sintering technique [11] coupled with ICP–MS. Simultaneously, the magnetic susceptibility measurement of MSWI ash samples was adopted as complementary or alternative tool for geochemical prospecting of REE in urban mines. As a fact, magnetic analyses have been correlated with heavy metal contents in a range of materials [12–16], including coal fly ashes [17,18], and discriminating plots derived from magnetic susceptibility measurements have a great potential to determine the source of magnetic minerals as well as the environmental impact. Remarkably, correlations between the magnetic susceptibility and REE were observed within samples from urban areas [19,20], which, in turn, suggested the need to measure such parameter in the current study. The magnetic behaviour of incinerated ashes assessed by analysing different magnetic properties will not the object of this study, but the attention is focused on the mass specific magnetic susceptibility, which can be determined quickly and with a very limited cost. To the best of our knowledge, the magnetic susceptibility measurements of raw MSWI ash are reported here for the first time.

## 2. Materials and methods

### 2.1. Investigated incinerators

Solid residues from two MSWI plants from Northern Italy, named plant A and B were collected. The selected incinerators consist of two lines that drive the collected waste, about $1.2 \times 10^5$ t/a, in the grate-furnace that operates at temperatures between 850 and 1100 °C. Both plants are Waste-To-Energy systems that burn unsorted waste (more than 90% of solid waste input is household waste and around 10% special waste such as shredder automobile residues, industrial, and hospital waste).

### 2.2. Sampling of bottom and fly ash

The main outputs of the incineration process are bottom and fly ashes. The concept design of the MSWI system is reported in Fig. 1 to which the reader can refer to identify main processes, sampling points and temperature profiles.

Belt conveyors transport the bottom ashes (BA) to a temporary outdoor storage site where they are piled up. Directly from the BA storage site, the heap of several tons of BA material was first sampled following the approach as in [8]. Three subsamples from the heap were blended from a large number of increments and roughly divided on site by the quartering method through a loader machine. From the last batch (order of hundreds of kilograms), 7–8 kg primary sample was taken by a simple random sampling. In the lab, the primary samples was thoroughly mixed on a hard, clean surface and split in four portions, the opposite portions were mixed together and again split for three times, to ensure representative sampling. Seven BA samples from incinerator A and six BA samples from incinerator B were collected. Furnace and boiler fly ash (FA) are recovered through the air pollution control system, undergoing further treatment steps (Fig. 1) before being released in the atmosphere. Specific devices/filters retain the residual FA fraction during each treatment step. The FA samples have been separately sampled at the different devices from the two incinerators. Where it was possible, untreated FA (FAU) were collected from dry scrubbers, after the electrostatic precipitation system (FAE) and after bag filters. Bag filters involve the use of soda (FAS) or lime (FAL) additives. In both incinerator plants, about 5 kg FA primary sample was collected with a random sampling method from the FA material stored in big bags (approximately 1 ton), previously blended from