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Published Version:

The rare earth elements in municipal solid waste incinerators ash and promising tools for their prospecting / Funari, Valerio; Bokhari, Syed Nadeem Hussain; Vigliotti, Luigi; Meisel, Thomas; Braga, Roberto. - In: JOURNAL OF HAZARDOUS MATERIALS. - ISSN 0304-3894. - STAMPA. - 301:(2016), pp. 471-479. [10.1016/j.jhazmat.2015.09.015]

Availability:

This version is available at: <https://hdl.handle.net/11585/522338> since: 2021-12-06

Published:

DOI: <http://doi.org/10.1016/j.jhazmat.2015.09.015>

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FUNARI, VALERIO; Bokhari, Syed Nadeem Hussain; Vigliotti, Luigi; Meisel, Thomas; BRAGA, ROBERTO: The rare earth elements in municipal solid waste incinerators ash and promising tools for their prospecting. JOURNAL OF HAZARDOUS MATERIALS 301. 0304-3894

DOI: 10.1016/j.jhazmat.2015.09.015

The final published version is available online at:

<http://dx.doi.org/10.1016/j.jhazmat.2015.09.015>

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

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H I G H L I G H T S

- 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.

A R T I C L E I N F O

Keywords:

Bottom and fly ashes from incinerators
Rare earth elements
Mass specific magnetic susceptibility

A B S T R A C T

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 biohydrometallurgy [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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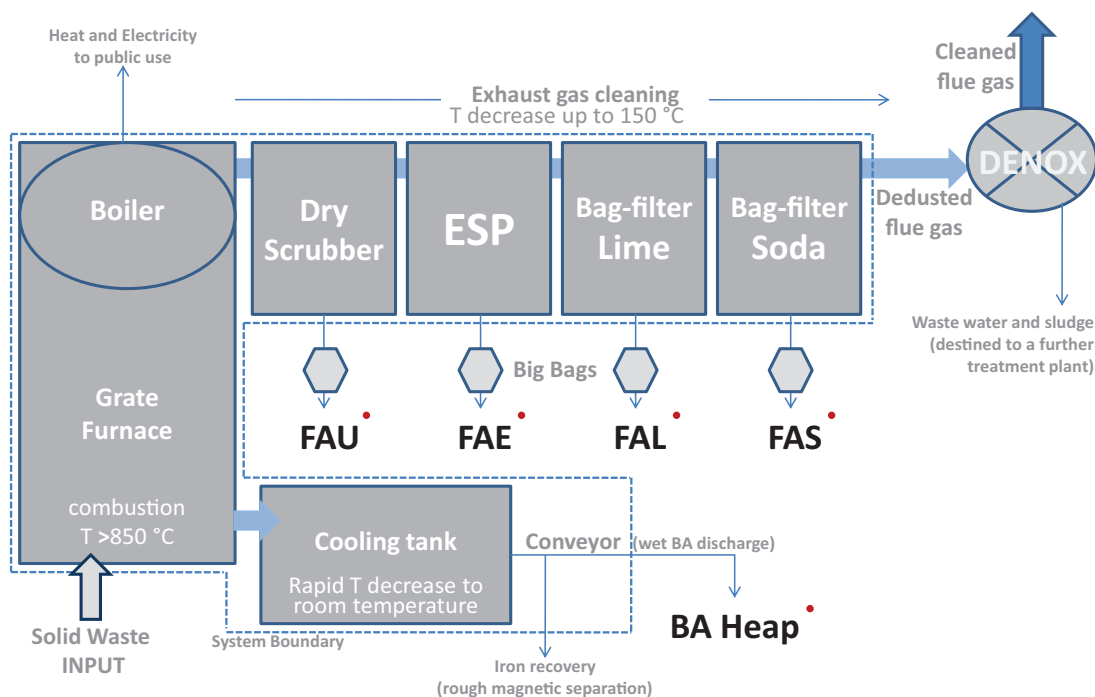


Fig. 1. Schematic picture of the incinerator system with its relevant processes, including sampling points (red dots) and temperature (T) profile. Acronyms used: BA = bottom ash; FAE = fly ash from ESP; FAL = fly ash from bag filter with lime additive; FAS = fly ash from bag filter with soda additive; 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 be 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 1.2×10^5 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 were 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

a large number of increments in order to reach representativeness. The primary sample of each FA was further subdivided by means of the quartering method in the laboratory. A total number of seven FA sample were collected.

According to the estimates provided by Morf et al. [6], the sample masses needed for reliable determination of low-concentration elements from BA and FA were in the range of hundreds of kilograms and tens of kilograms, respectively. In the present work, lower sample masses were used owing the capacity limitations of laboratory equipments.

Before being analysed, all the samples were milled ($<40\ \mu\text{m}$) with an agate vibratory disc mill and oven-dried (40°C) for one week. No separation procedures (e.g., magnetic extracts) have been undertaken and, hence, the samples can be considered as raw ashes.

2.3. Elemental chemistry determination

The complete sample digestion was obtained with the Na_2O_2 sintering technique [11], which has the capability to dissolve all the refractory materials known today, and the total elemental chemistry was determined by ICP-MS (7500ce Agilent Technologies). Analyses were performed at the Department of General

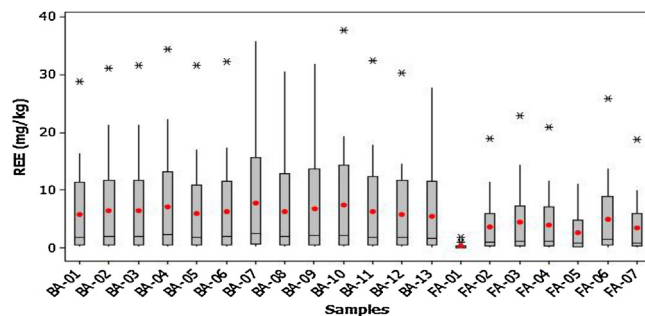


Fig. 2. The REE variability in the studied samples. The boundaries of the box indicate the 25th percentile and the 75th percentile, the continuous line within the box marks the median and the red dot marks the mean. Whiskers above and below the box indicate the 90th and 10th percentiles, whereas starred dots are the outliers (mainly Ce). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and Analytical Chemistry of Montanuniversität Leoben (Austria). The description of the analytical procedure followed for the analyses of MSWI samples can be found elsewhere [8]. Major and

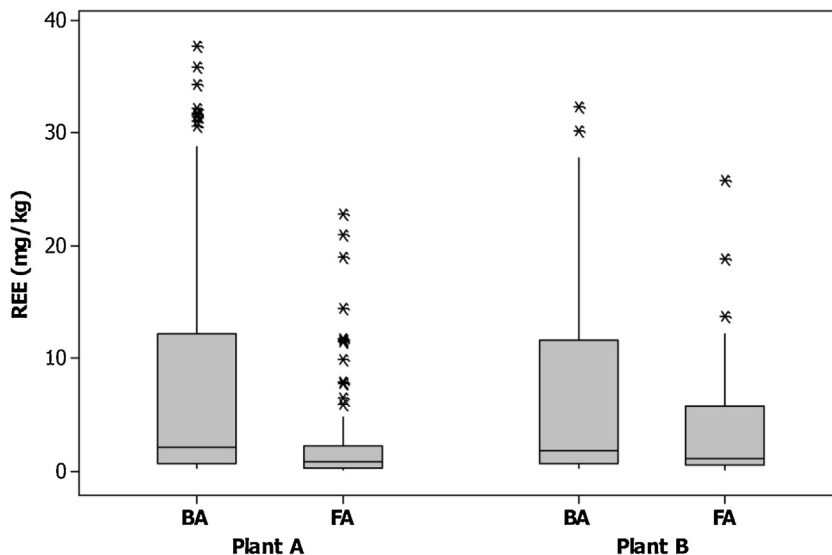


Fig. 3. The variability of REE in BA and FA samples, a comparison between incinerators A and B; outliers are mainly Ce and La. For the significance of box-plots see Fig. 1.

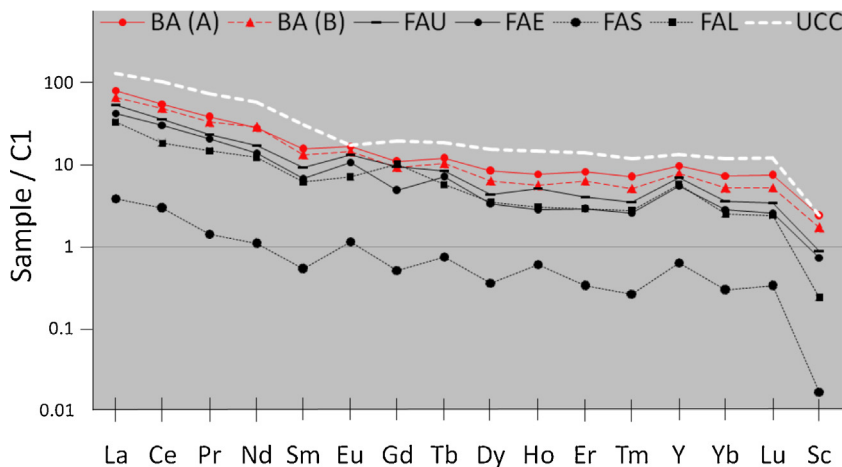


Fig. 4. Chondrite-normalised REE patterns for the MSWI ashes (C1 in the y-axis stands for type 1 of carbonaceous chondrite). The white dashed line represents the chondrite-normalised REE patterns of the Upper Continental Crust (UCC). Chondrite and UCC average values are from [23] and [24], respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

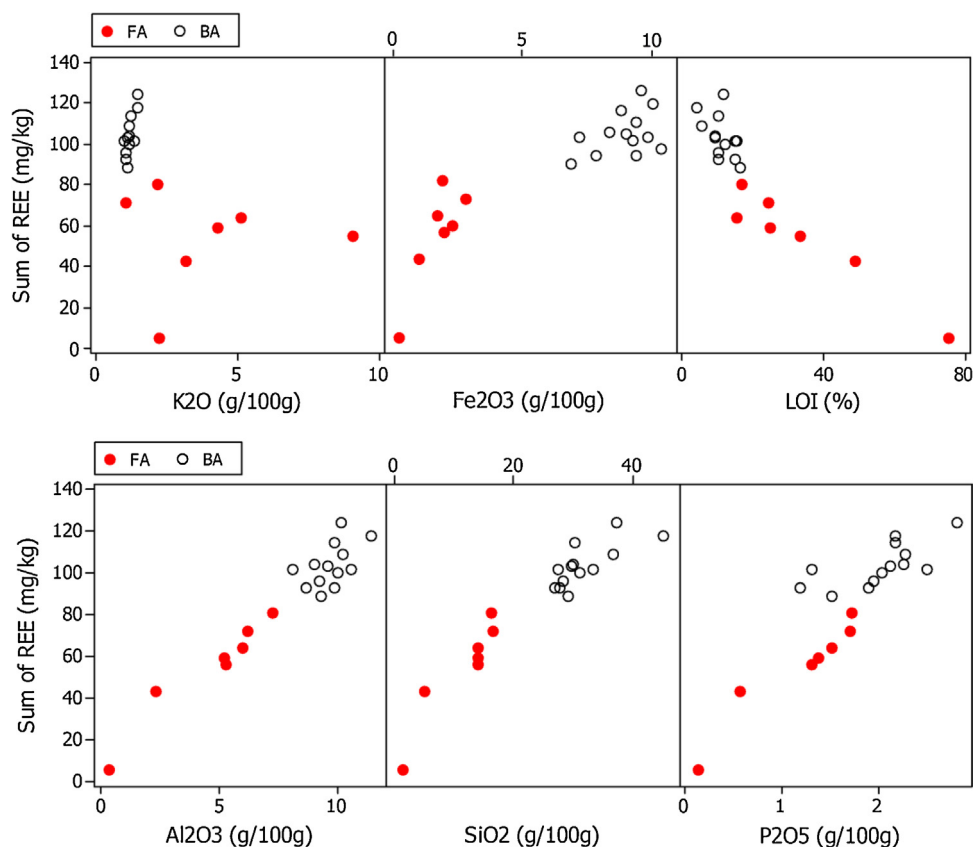


Fig. 5. Correlations of \sum REE and selected major elements. The REE vs. LOI scatter plot is also provided. The data set is grouped by kind (BA = bottom ash; FA = fly ash). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

trace elements were determined (Supplementary material S.1), but emphasis is given to all the Rare Earth Elements (REE), namely Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, and Yb plus Sc and Y which are the focus of this study.

2.4. Magnetic susceptibility measurement

Magnetic susceptibility is the most commonly measured magnetic parameter since the nature of its measurement is relatively easy and rapid [21]. Magnetic susceptibility can be roughly defined as a measure of the magnetisation capability of a given material. It is known to be a sensitive indicator of magnetic concentration and grain size. Initial magnetic susceptibility is defined to be the ratio of the induced magnetisation to the applied magnetic field. The volume susceptibility, κ , is dimensionless in SI units, while the mass specific susceptibility, χ , is measured in $\text{m}^3 \text{kg}^{-1}$. The latter is used throughout the present study.

Magnetic susceptibility was measured at two different frequencies (0.47 and 4.7 kHz) by using a dual frequency MS2B Bartington meter available at the Institute of Marine Sciences, National Research Council (Bologna). The difference between the two measurements was used to calculate the frequency dependence of susceptibility ($K_{fd}\%$). This parameter reflects the presence of very fine ($<0.03 \mu\text{m}$ for magnetite) ferromagnetic grains in the super paramagnetic (SP) state. The calibration of the instrument was checked using an alloy as a magnetic reference material. Dried and milled ($<40 \mu\text{m}$) samples of MSWI residues were laid down and gently compacted in cubic plastic boxes of 8 cm^3 volume. Mass specific magnetic susceptibility (χ) was calculated dividing κ , previously corrected for the drift, by the sample mass.

3. Results and discussion

3.1. The REE concentrations and distribution in MSWI ashes

The sum of REE (\sum REE) concentration ranges between 88 and 124 mg/kg within BA samples, whereas is 54 mg/kg on average within FA. The variation of REE in each sample, both for BA and FA, has been analysed using the box plots (Fig. 2). The general variability might reflect the heterogeneity of the samples, resulting from possible uncertainties associated to limitation of the primary sample size but also from different waste input, treatment steps and combustion condition between the two incineration facilities. However, the independent sample *t*-test conducted to assess the difference of REE concentration between plants A and B reveals the total of MSWI residues (BA + FA) are statistically equal for the two incinerators (Supplementary material Table T.2). Additional details regarding the test procedure and assumptions are provided in Supplementary material S.2.

Higher \sum REE is typically found in BA rather than in FA (Fig. 3) as a consequence of the high boiling points of REE (1194–3426 °C) [22]. In FA samples the majority of REE have concentration from around 0 mg/kg (25th percentile) to 7 mg/kg (75th percentile) while in BA from 0 (25th percentile) to 15 mg/kg (75th percentile). In this case, the independent sample *t*-test confirms what box plots show. The FA from plant A and B are statistically comparable despite the wide range of process treatments (e.g., different cooling conditions, chemical additives); on the other hand, the REE averages in the BA residues are significantly (at 0.05 significance level) different between plant A and B.

As can be seen from Fig. 4, both light REE (LREE: Sc, La, Ce, Pr, Nd, Sm, Eu, Gd) and heavy REE (HREE: Y, Tb, Dy, Ho, Er, Tm, Yb, Lu) normalised mass fractions are enriched in BA compared to FA, in

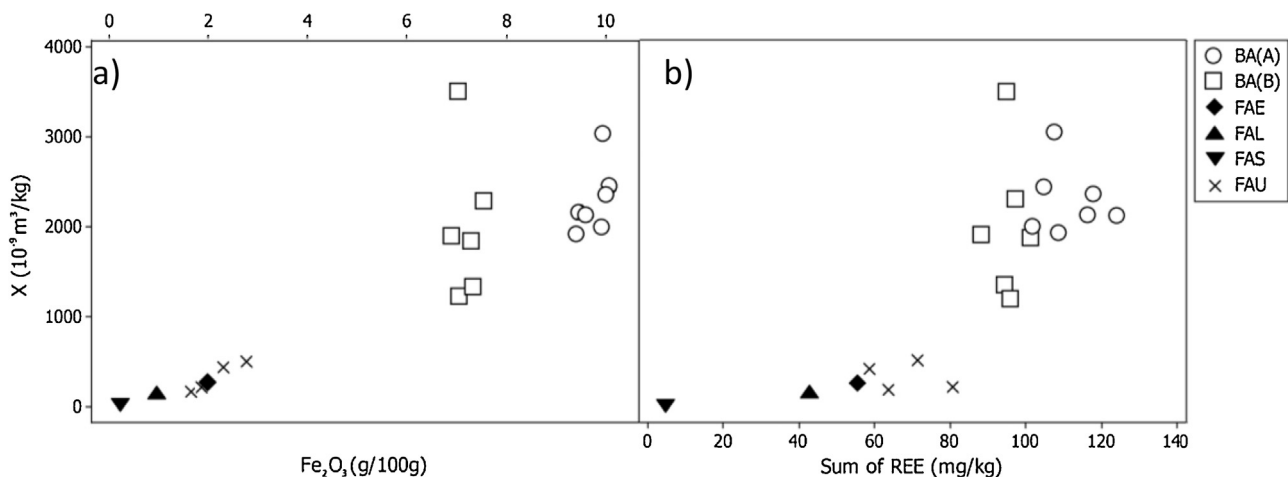


Fig. 6. Scatter plot of mass specific magnetic susceptibility (χ) vs. Fe_2O_3 (a) and ΣHREE (b). The data set is grouped by kind (BA = bottom ash; FAE = fly ash from ESP; FAL = lime-treated fly ash; FAS = soda-treated fly ash; FAU = untreated fly ash). The provenance of BA sample is also provided (A = plant A; B = plant B).

agreement with the partition coefficients calculated by Morf et al. [6] that revealed a significant mass flow of REE into BA rather than FA. The concentration of each element of the REE group is within the range quoted in literature [8 and reference therein] despite the wide range of investigated MSWI ashes from different places and times of sampling. As a matter of fact, the content of Gd, Nd, Sc, and Y within the MSWI input determined in [6] is consistent with elemental content into the MSWI output reported in the present work (see Supplementary material Table T.1), being in order of abundance $\text{Y} > \text{Nd} > \text{Sc} > \text{Gd}$.

Normalized REE pattern can be used to evaluate the relative enrichment of REE in studied materials, e.g. [25], and to highlight geochemical anomalies from typical crustal pattern, which might derive from anthropogenic contamination. The chondrite-normalised patterns of our MSWI samples (Fig. 4) resemble that of the Upper Continental Crust average (UCC, white dashed line), suggesting a principal geogenic source of REE. However, a few element anomalies are visible. All types of MSWI samples show enrichment in Eu and Tb over the adjacent elements. The BA patterns from both plants, moreover, have a weak Er enrichment with respect to the other HREE. The chondrite-normalised patterns of chemically treated FA (i.e., FAS and FAL) show differences with respect to the other patterns: FAL shows a significant enrichment in Gd, whereas FAS is the most REE-depleted sample but shows a relative enrichment in Ho compared to the other HREE. The overall sample set of MSWI ash normalised to the continental crust (data not shown) instead of the chondrite is enriched in Eu and Tb and depleted in La and Ce. Interestingly, similar observations were reported by Zhang et al. [25] who investigated MSWI ash from two Japanese incinerators. The normalised patterns of sampled MSWI ashes, however, differ from those reported by Zhao et al. [22] who investigated medical waste incinerator ashes. They found a remarkable Gd enrichment, possibly derived from medical wastes. Despite of the likelihood of some medical waste burned in the MSWI plants from this study, gadolinium is rather depleted in the sample set, with the exception of the FAL sample.

The LREE/HREE ratio ranges between 2.7–3.5 and 3.9–4.8 in FA and BA, respectively. The lowest LREE/HREE ratio is found in additives-treated FA, both FAS and FAL. The similar low LREE/HREE ratio of FAS and FAL might be explained by LREE retention during the early steps of the exhaust gas cleaning process (see Fig. 1) or by the introduction of HREE contained in lime- or soda-additives injected into the flue gas for acid gas control. However, the extent of additives' influence cannot be assessed since we were not allowed to sample and analyse these materials. When an effective method

for HREE recovery and purification from complex matrices will be devised, FA from bag filters could represent an added-value product or, at least, the most favourable product among MSWI ashes. This indication of HREE enrichments, which are the elements of REE group at the highest risk of supply according [2], could be critical in discussing the REE enrichment parameters in Section 3.4.

3.2. Correlation between major elements and REE

Fig. 5 provides the correlation between Σ REE and selected major elements. Major elements like P_2O_5 (of likely anthropogenic introduction) and Al_2O_3 (both geogenic and anthropogenic component) show a positive correlation with Σ REE. The association of Al_2O_3 ($R^2 = 0.92$) with REE is the strongest amongst major elements, followed by SiO_2 ($R^2 = 0.87$) and P_2O_5 ($R^2 = 0.77$). The R^2 coefficients of other major ($>0.1 \text{ g}/100\text{g}$) and minor ($>0.01 \text{ g}/100\text{g}$) elements follow this sequence: Mn, Ba, Fe, Cu, Sn, Zn, Pb, and Ti. Aluminium and silicon (i.e., the BA and FA main components), and phosphorus oxides are chief indicators of REE occurrence in MSWI samples. The relative high variance of data in REE- Al_2O_3 and REE- SiO_2 scatter plots within BA samples, can be explained with the limitation of primary samples size which most likely affect BA material. Nevertheless, there is a clear positive correlation between the selected major elements and the REEs (Fig. 5). These trends suggest that the main sources of REE in solid residues from MSWI are aluminosilicates of perhaps primarily geogenic origin, as also corroborated by the normalized REE patterns (Fig. 4). However, manmade aluminosilicates that may give an anthropogenic REE contribution, e.g., polishing agents in ceramics, cannot be ruled out. The positive correlations of REE with P, Mn, Fe, Cu and Zn might be related to phosphates and hydroxides, which can contain REE difficult to mobilise [26]. Hydroxides minerals are used in various application fields and, moreover, they might be present within MSWI residues as newly-formed minerals (e.g., after quenching). Therefore, the identification of input sources that contain both hydroxides and REE is prevented. The inverse correlation between LOI and REE (Fig. 5) seems to preclude an effective contribution of hydrous phases over the REE occurrence, but the high LOI values are more likely related to the water absorption capacity of residues after their storage, especially of FA materials. The input sources of phosphates in the feedstock material can derive from technological applications such as fluorescent materials and phosphate binding agents used in the medical field, and from biogenic waste such as food waste, garden waste, road waste, fertilisers, and sewage sludge. There is the likelihood that the correlation between REE and P_2O_5 mass frac-

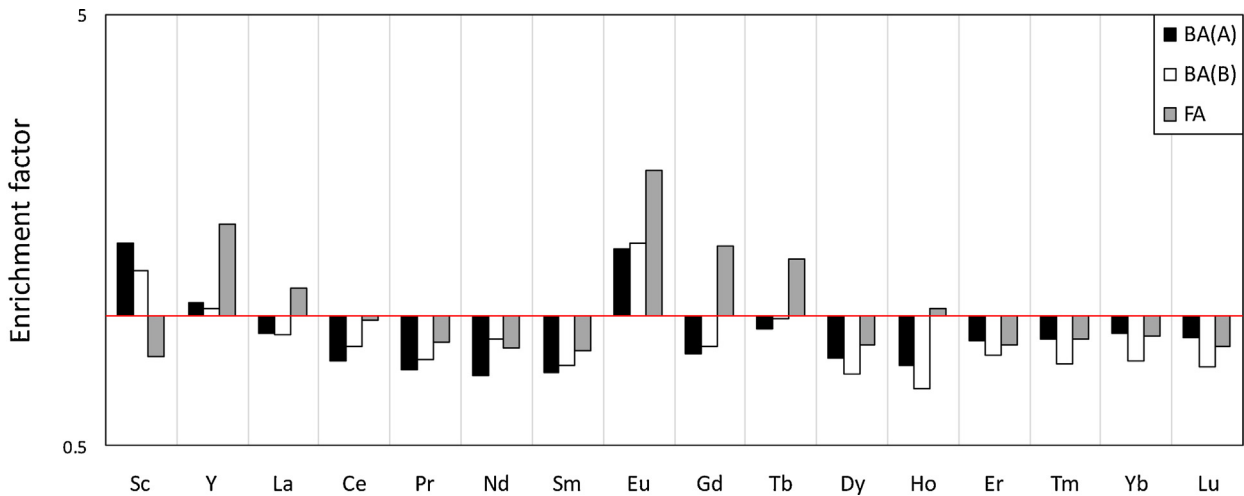


Fig. 7. Comparison of the enrichment factors for the REE in BA and FA from MSWI plants. The BA from MSWI plant A and B are reported separately. For the calculation of enrichment factors see Eq. (1).

tions derives from fluorescent materials and medical applications that host relevant amount of REE. Although the total REE content of biogenic waste is negligible compared to that of, e.g., fluorescent lamps, the amount of biogenic waste into the MSWI system is, however, more significant than any other P-rich fraction, revealing that the measured concentrations of REE include a contribution of anthropogenic origin.

3.3. Magnetic susceptibility and its potential correlation with REE

The investigated materials from MSWI show a wide range of mass specific magnetic susceptibility (χ) values varying between 2.3×10^{-8} and $304 \times 10^{-8} \text{ m}^3/\text{kg}$ (Table 1 Fig. 6), with a distinct magnetic signature for BA and FA samples. The BA samples show relatively high χ values ranging from $121 \times 10^{-8} \text{ m}^3/\text{kg}$ to $304 \times 10^{-8} \text{ m}^3/\text{kg}$, while FA samples show lower χ values of about one of order magnitude respect with BA. The FA samples (RSD% = 69) exhibit a larger variance of χ values than BA samples (RSD% = 28). The high χ values found in BA are clearly a response to high heavy metals loads [20] that partition in BA materials [7,8] and likely derive from metallic sheets, barrels and cans, remaining in the bottom materials.

These results lie within the wide range of χ values of urban sediments (e.g., $4\text{--}13000 \times 10^{-8} \text{ m}^3/\text{kg}$ [20]) and partly within the values range of other kinds of incineration residues such as coal ash, i.e., $306\text{--}1703 \times 10^{-8} \text{ m}^3/\text{kg}$ reported in [17]. Nevertheless, the χ measurements of MSWI ashes reported here are rather consistent with those of sediments near Fe-smelters ($200\text{--}600 \times 10^{-8} \text{ m}^3/\text{kg}$ [27]) and from MSW landfill ($64\text{--}970 \times 10^{-8} \text{ m}^3/\text{kg}$ [15]).

Generally, the variability of χ measurements of MSWI ashes might be ascribed to several factors: the initial composition and mineralogy, morphology and shape, technological conditions (e.g., combustion temperatures), solid-phase reactions, and stress levels within the particles. The latter factor is typically influenced by a very fast cooling, which can reasonably occur to BA materials (i.e., quenching). Moreover the presence of ultra fine grained superparamagnetic (SP) particles in our samples can increase the measured susceptibility. Frequency dependent susceptibility (K_{fd} %) values lower than 2 have little or no significance, as argued elsewhere [28]. However, Table 1 shows figures of K_{fd} up to 7.7% with an average of the whole sample set of 2.7%. According to the semi-quantitative model by Dearing et al. [29], the most of MSWI ashes have a SP fraction >10%. The SP fraction is even more significant for several FA samples. Quantify the extent of SP and multiple domain

grains in further works might have profound repercussions on the environmental risk associated to MSWI residues.

Correlations between magnetic data and heavy metals concentration have been observed, e.g., [16,30]; especially iron mass fraction and χ values typically show a good association in scatterplots since iron hosted in magnetic minerals (e.g., magnetite) led to an increase of magnetic susceptibility. The mass specific magnetic susceptibility of our set of samples is strongly related to iron oxide mass fraction (Fig. 6a), the R^2 coefficient equals to 0.90. Furthermore, magnetic susceptibility shows good to moderate association with other heavy metals (e.g., $R^2_{\chi\text{-Cu}} = 0.54$; $R^2_{\chi\text{-Co}} = 0.24$; $R^2_{\chi\text{-Mn}} = 0.46$). The mass specific magnetic susceptibility and its scattering with specific metals show that different kinds of MSWI ashes are readily distinguishable. The FA samples are characterised by χ values lower than $100 \times 10^{-8} \text{ m}^3/\text{kg}$ and they form a clearer trend compared with BA samples. The BA samples are scattered in two distinct groups, identifying the investigated MSWI plants (squares and circles in Fig. 6a). This scattering of BA samples might indicate the presence of variable amounts of magnetic minerals, which differentiate plant A and B.

There is a recent evidence that susceptibility measurements of topsoil from urban areas correlate with REE [19,20]. In MSWI samples, we found a direct correlation between χ values and REE (Fig. 6b), both LREE ($R^2 = 0.63$) and HREE ($R^2 = 0.51$), being the coefficients of determination to the stronger ($R^2=0.80$) to the poorer ($R^2 = 0.14$): Sc > Er > Dy > Tm > Sm > Lu > Yb > Ce > Pr > Ho > La > Nd > Y > Tb > Eu

> Gd. This positive correlation could be linked to a process of anthropogenic nature, for instance as a direct consequence of the presence of REE-bearing devices in waste input (mostly WEEE). Since the susceptibility correlates both with iron and REE mass fractions, there is the possibility that the presence of high Fe-REE products such as NdFeB magnets in the waste input controls the REE contents. However, the weak relative enrichment of Nd (see Fig. 4) rules out the presence of NdFeB magnets. The FA samples from bag filters, namely FAS and FAL, have the lowest REE contents, which usually correspond to lowest χ values. High magnetic values do not necessarily reflect a high REE content, with the highest density of samples high in REE around the χ value of $200 \times 10^{-8} \text{ m}^3/\text{kg}$.

This is a first attempt in order to discriminate magnetic signature of MSWI ash and, from the handful of data obtained so far, the mass specific magnetic susceptibility appears to be linked on the REE abundance.

Table 1

Mass specific magnetic susceptibility (χ) and frequency-dependent magnetic susceptibility in percent ($K_{fd}\%$) of MSWI ashes. Iron oxides mass fraction and the sum of REE are also reported. Samples are grouped by kind (BA = bottom ash; FAU = untreated fly ash; FAE = fly ash from ESP; FAL = lime-treated fly ash; FAS = soda-treated fly ash).

MSWI ash	Sample mass	χ (10^{-9} m ³ /kg)	K_{fd} (%)	Fe ₂ O ₃ (g/100g)	\sum REE (mg/kg)
BA(A)	8.8068	209.270	1.90	9.6	124
BA(A)	8.8266	236.898	3.44	10.1	118
BA(A)	6.9992	192.593	2.45	9.4	109
BA(A)	7.1343	200.020	2.73	9.9	101
BA(A)	8.2413	303.472	2.64	10.0	107
BA(A)	6.8589	212.570	2.54	9.5	116
BA(A)	6.0557	242.416	3.95	10.1	105
Average	BA(A)	228.177	2.80	9.8	111
BA(B)	9.3557	350.588	0.12	7.1	94.7
BA(B)	6.2748	132.339	0.02	7.4	94.1
BA(B)	8.1208	228.549	1.29	7.6	97.0
BA(B)	8.1468	186.945	2.10	7.2	101
BA(B)	6.4090	189.733	1.23	6.9	88.3
BA(B)	7.0321	121.440	1.87	7.1	94.7
Average	BA(B)	201.599	1.10	7.2	95.0
FAE(B)	6.0554	24.748	1.33	2.0	55.2
FAL(B)	5.7173	13.748	2.93	1.0	42.4
FAS(A)	5.2443	2.279	4.18	0.2	4.78
FAU(A)	8.5724	42.421	3.15	2.3	58.9
FAU(A)	3.1497	50.497	7.17	2.8	71.3
FAU(B)	7.8924	16.586	3.40	1.7	63.5
FAU(B)	6.9713	19.630	4.75	1.9	80.5
Average	FA	24.273	3.84	1.7	53.8

The letters A and B in parentheses indicate MSWI plant A and B, respectively.

3.4. The REE enrichment and Pricing Influence Factor

In order to evaluate the abundance of REE within MSWI ash samples the Enrichment Factors (EFs) are calculated. Element EFs are widely used in environmental sciences to speculate on the origin and fate of elements among a variety of environmental records. To calculate the EF for a given element, the measured concentration of that element in the sampling medium is divided by the concentration of the same element in the Earth's crust and possibly normalised to a "conservative" element [31]. For the normalisation purpose, we used aluminium oxide mass fraction as adopted in [32] for MSWI bottom ashes and in [33] for sewage sludge. The EF is expressed according to the equation:

$$EF = \frac{(X_{\text{sample}}/Al_{\text{sample}})}{(X_{\text{crust}}/Al_{\text{crust}})} \quad (1)$$

where X_{sample} and Al_{sample} are the measured mass fraction of the element of REE group and Al_2O_3 in the sample, and X_{crust} and Al_{crust} are their mass fraction in the continental crust reported in literature [24].

Fig. 7 shows the calculated EFs as the degree of REE enrichments of BA samples from plant A and B and the average of FA samples. Yttrium, La, Eu, Gd, Tb, and Ho are significantly enriched in FA samples compared to BA samples. Conversely, scandium is enriched in BA samples. These observations are consistent with EFs calculated using data in [6] with the exception of Sc that is slightly enriched in FA (EF = 0.68 in FA, EF = 0.31 BA). Seven over sixteen of REE show enrichment, while the most of REE are rather depleted in MSWI ashes with respect to upper continental crust concentration. The EFs for the enriched elements of REE are lower than 10. Fujimori et al. [32] reported EFs of MSWI bottom ashes over 100 for Cu, Mo, Pb, Sb, and Zn that were characterised by a relatively low variability among the investigated MSWI plants (up to one order of magnitude). The EFs of REE of BA samples are even more similar for the two MSWI plants, despite these samples were collected from different incinerators with likely diverse kinds and proportions of input waste materials, revealing a substantial homogeneity concerning the REE occurrence within BA. The calculated EFs from data by [6] for Y, Sc, Nd, and Gd within BA further confirm this hypothesis, being in a range of 1.32–0.31. The differences of EF values of BA are within

a very narrow range, with the exception of Nd. The differences of EF values between BA and FA samples are relatively high especially for Y, Eu, Gd, Tb, and Ho.

Although our results represent a first estimate and more data are needed, the overall EFs of REE are near the unit in agreement with the normalised patterns of MSWI ashes (see Fig. 4) and recent out-comes [32,33] as well as the calculated EFs using data from [6]. This indicates a poor REE enrichment within MSWI ashes and highlights a geogenic provenance rather than anthropogenic.

To take insight of the elements enrichment, the EF values can be compared to the mining influence factors as defined in [31], which is calculated as the ratios of annual human use of the elements to their crustal reserves. However, the literature data about the mined tonnage only available for a limited group of REE so far has followed to suggest a modified procedure which takes into account the price of each REE (as 99.9% purity metals). The Pricing Influence Factor (PIF) can be defined as follow:

$$PIF = \frac{X_{\text{price}}}{X_{\text{crust}}} \quad (2)$$

where X_{price} is the price of the element, from [34], and X_{crust} is its abundance in the upper continental crust, from [24]. The price of the element can be considered as an indicator of its human use and priority of supply, while the abundance on the upper continental crust might give a rough estimate of its availability. For example Ce and Nd pure metals are sold for 30 US\$/kg, but Nd is rarer than Ce, being their mean content in the upper continental crust 27 mg/kg and 63 mg/kg, respectively. Therefore, the PIF of Nd is more than two times higher than that of Ce, being their PIF value 1.1 and 0.48, respectively. The correlation between EF and PIF is shown in Fig. 8, both for BA and FA. There is a positive correlation between the EF and PIF values for REE with PIF values larger than 100 and lower than 1800, indicating that these elements are enriched in MSWI ash and virtually marketable. The higher the slope of the tendency line (red lines in Fig. 8) relatively more advantageous can be the considered source. Considering their market price and their EF within MSWI ashes, europium and some HREE (i.e., Tb, Ho and Yb) can be the potential targets for the development of new recovery strategies. Fig. 8 also discloses that Sc, Y, La, and other LREE are relatively enriched in MSWI ashes but current (as for 2015) market price of

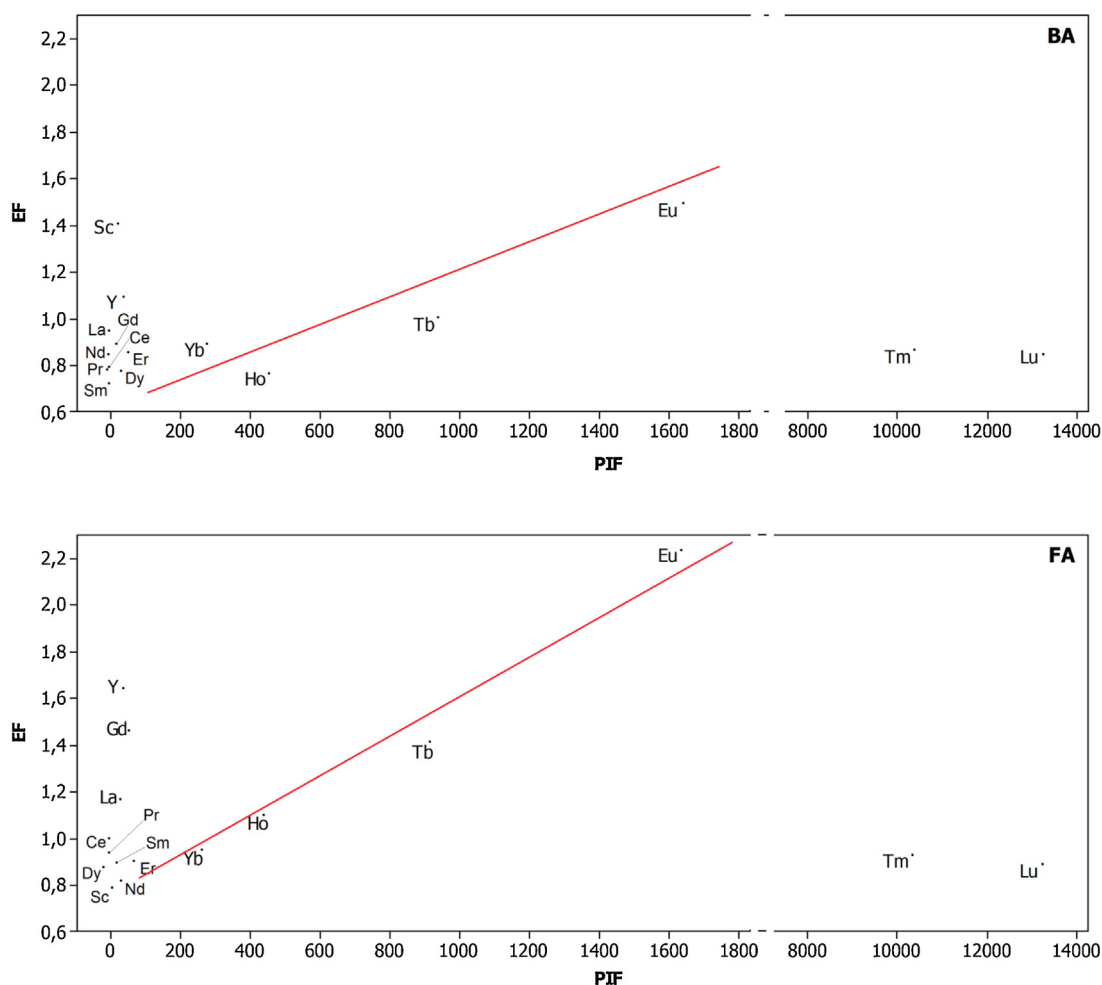


Fig. 8. Bi-plot of Enrichment Factor (EF) and Pricing Influence Factor (PIF) of REE in BA (above) and FA (below) sampled materials. The red line represents the trendline of observations within a selected range of PIF values (100–1800). The EF and PIF were calculated by the Eqs. (1) and (2), respectively.

these elements most likely disallow any planning for their recovery and, hence, their exploitation from MSWI sources. Thulium and Lu show a different behaviour: they are slightly enriched in MSWI ashes but have a great economic importance. The efforts in the development of new techniques in order to recover these valuable metals, and to secure them also from urban mines, might be profitable in any case.

The above outcomes deriving from EF and PIF (provided in Figs. 7 and 8) highlight that FA materials are promising targets for future recovery of Eu and some HREE with respect to BA materials, even though both EF and PIF parameters do not consider the output flows (reported in Supplementary material S.3).

4. Conclusions and outlook

Bottom and fly ashes have an average concentration of 104 and 54 mg/kg Σ REE, respectively, which translate in a low stream of REE from MSWI plants. In this study some useful tools for REE prospecting were recognised, which give indications on where the REE recovery strategies have to focus, if the supply risk will further decrease and new market condition will enable the metals recovery from urban mines.

Major elements/compound mass fractions like P_2O_5 and Al_2O_3 show a positive correlation with REE concentrations and also magnetic susceptibility values can be used as proxies for REE. Moreover, the susceptibility measurement has produced some intriguing results which can be used as information for further purposes such

as the assessment of heavy metals contamination e.g., [16] or of harmful ultrafine SP particles e.g., [13], and for the appraisal of best substrates for the synthesis of magnetic geo-polymers e.g., [35]. Interestingly, both chemical (major elements) and magnetic measurements can be performed quickly, with low costs and on-site. Magnetic susceptibility analysers are small and light equipments and portable XRF is a reliable alternative for major elements analysis in the field. Even if they cannot provide the accuracy of laboratory measurements and testing, the quality is adequate to identify valuable ores from waste heaps. Finally, some parameters such as the enrichment factor and the pricing influence factor are suggested as valuable indicators of potential urban mines and decision-making strategies.

In order to plan investments regarding REE recovery from MSWI residues, these first results need to be corroborated by new data based on accurate sampling strategies. Nonetheless, the integration of magnetic, chemical, and statistical methods demonstrated potential to a better assessment of secondary raw materials from hazardous substances. Still, there is scope to test the limits of these preliminary efforts and new attempts have to be made to establish a general work practice for REE prospecting in MSWI residues.

Acknowledgement

V.F. acknowledges the scholarship grant from the SPINNER consortium (<http://www.spinner.it>) and extramural funds by Giovanni Gabbianelli (University of Bologna). The authors acknowledge the

financial support granted by Montanuniversität Leoben, ISMAR-CNR (u.o.s. Bologna) and RFO-Unibo during various stages of this work. Comments from Jim Hower and an anonymous reviewer helped to improve the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2015.09.015>.

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