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The critical raw materials potential of anthropogenic deposits

insights from solid residues of municipal waste incineration

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Preface

The present thesis is the result of a PhD project carried out at the Doctoral School on Earth Sciences of the University of Bologna. Dr. Roberto Braga (BiGeA Dept., University of Bologna) acted as supervisor of the PhD project titled "The critical raw materials potential of anthropogenic deposits: insights from solid residues of municipal waste incineration". Journal manuscripts prepared during this study are enclosed:

1. Funari V., Braga R., Bokhari N., Dinelli E., Meisel T. (2015). Solid residues from incinerators: a source for Critical Raw Materials. *Waste Management*, 45: 206-216.
2. Funari V., Bokhari N., Vigliotti L., Meisel T., Braga R (2016). The Rare Earth Elements in Municipal Solid Waste Incinerators ash and promising tools for their prospecting. *Journal of Hazardous Materials*, 301, p. 471-479.
3. Funari V., Mäkinen J., Salminen J., Braga R., Dinelli E., Revitzer H. Metal Recovery from Municipal Solid Waste Incinerators Fly Ash: a Preliminary Comparison between Chemical Leaching and Bioleaching. *Submitted to Waste Management*
4. Funari V., Meisel T., Braga R. (2015). The potential impact of municipal solid waste incinerators ashes on the anthropogenic osmium budget. *Science of the Total Environment*, 541: 1549-1555.

The above scientific articles, peer-reviewed or awaiting for decision, are reported as in their original version but with the text formatting of the present thesis. In addition, ten publications in proceedings have been accomplished during the study and their abstracts are enclosed in Appendix A.

Acknowledgements

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Furthermore, the PhD project benefited of visiting fellowships supported by the Marco Polo programme (University of Bologna) that allowed the following research visits: Montanuniversität Leoben (Austria, 4 months) and the VTT-Technical Research Centre (Finland, 3 months). Thomas Meisel (Chair at General and Analytical Chemistry, Montanuniversität Leoben) and Justin Salminen (Senior Researcher at Boliden, formerly at VTT), are warmly thanked for their support during these successful visiting periods.

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Abstract

Due to the current and foreseen global growth of raw material demand, the sustainable supply of minerals and metals for high-tech applications, the so-called *critical raw materials* (Co, Cr, Ga, Nb, Rare Earth Elements, Sb, W, Platinum Group Elements), is of general concern. Industrial wastes have the potential to become an alternative source (flow) of strategic metals and, consequently, their valorisation can be seen as a move towards resources efficiency and circular economy.

In this 3-years study I aimed to decipher the critical raw materials potential from solid residues produced by Municipal Solid Waste Incineration (MSWI), namely bottom and fly ashes. These solid residues, coming from different leading companies of MSWI in northern Italy, have been selected because they can be accounted for urban mining purposes and represent high elements flows, still poorly explored. In the present work I address the potential of MSWI solid residues as an alternative source of critical raw materials by studying the material chemistry, its resources flow and the evaluation of metals upgrading and recovery. Finally, I tackle some environmental and economic issues.

As a matter of fact, the concentrations of several critical raw materials hosted in MSWI stocks are provided and their estimated annual flow is significant (order of 10^3 kg/a Co, Cr, and Sb). Remarkably, MSWI fly ashes can be promising target for the recovery of rare earths such as Tb, Ho, and Eu. Therefore, MSWI end-products can represent an attractive low-concentration stream of valuable elements and the identification of added value anthropogenic materials, their upgrading and effective metal recovery processes are of crucial interest. The analysis of samples, collected by drawing a simple random stratified sampling, reveals that natural gravitational sorting of the bottom ash heaps might represent a preliminary upgrading process because of the higher contents of critical elements in the fine-

grained fractions (uppermost part of the heap) than others (heaps bottom). As a consequence, I suggested an easy way to manipulate solid residue stockpiles directly at the incinerator plant. The measures of major elements and mass specific magnetic susceptibility correlate with critical elements, especially rare earths, demonstrating beneficial for a cost- and time-effective prospection. Geochemical (major elements) and magnetic (susceptibility) measurements show potential for resources prospecting and they can be readily tested and used on-site through portable analysers. Last but not least, the PIF or Pricing Influence Factor based on the ratio between element price and the abundance of that element on the Earth's crust is introduced. The correlation between PIF and the widely employed (in ore geology) Enrichment Factor (EF) constitute a new empirical prospecting method that can be useful in decision-making strategies. The recovery potential of ore metals and critical elements by comparing sulphuric acid leaching and bio-assisted acid leaching is investigated. Both process resulted in satisfactory removal percentages (i.e., metal leached out from the solids) for Al, Cu, Mg, Mn, Ni, and Zn (>90%), Cr, Nd, and Sb (65%), Co, Ga, Nb and Ce (50-60%). Although chemical leaching still demonstrate higher yields than bioleaching, bio-assisted leaching resulted in low usage of mineral acid and low removal of unnecessary elements (Ca, Ti, Si, and Fe). Despite overall high metals leaching, the content of harmful substances of residual fractions after biohydrometallurgic treatments exceeds the guidance levels published by a Swiss public authority (BAFU) for solids landfilling. Also, liquids (leachates) are strongly acidic, requiring high-level control for wastewater. Thus there is still the aim to further processing each by-product. A schematic flow sheet of a hypothetical process chain for the treatment of MSWI fly ash is proposed. It involves the use of several processing steps, including optimised bioreactors, to recover critical elements from the ash and to reduce the

hazardous nature of both solid and liquid by-products for their safer and less expensive disposal.

This work also addresses two important environmental aspects. First, the magnetic behaviour of MSWI solid residues led to a preliminary assessment of harmful ultrafine particles: most of the samples have a high (>10%) super-paramagnetic fraction that can impact human and environmental health. Second, the determination of the rare chemical element osmium (Os) from MSWI samples demonstrates that point sources of Os contamination coming from waste incinerators should be acknowledged: hazardous volatile Os from MSWI smokestacks of a medium size country is predicted to be 16-38 ng Os/m^2/a, much higher than the naturally transported Os (about 1 pg Os/m^2/a).

The scaling up of the research findings to the industrial processes will be the final goal to reduce the loss of resources and to enhance the waste management system.

Keywords: Critical raw materials, Municipal solid waste incinerator residues, Urban mining, Resources prospecting, Bio-hydrometallurgy, Metal Recovery, Mass specific magnetic susceptibility, Anthropogenic Os cycle, Environmental risks.

Structure of the work

Chapter 1 frames the research problem, provides a brief description of constraints related to raw material supply, current strategies for solid waste treatment, and of materials and methods used throughout the subsequent chapters. Here the purpose is to give a comprehensive overview of objectives and the used approaches and adjunctive information that cannot be found elsewhere in the present manuscript.

Chapter 2 focuses on the critical elements occurrence in bottom and fly ash, produced by municipal solid waste incinerators. This work represents one of the first attempts in literature toward resources evaluation from Italian incinerator facilities by means of accurate material characterisation and mass flow analysis.

Chapter 3 deals with the Rare Earth Element contents of bottom and fly ashes produced by municipal solid waste incinerators. The results coming from the present study promote both the prospecting of rare metals and impact assessment through the application of alternative methodologies.

Chapter 4 shows a comparison of the performance characteristics of two leaching procedures for pre-treatment (prior to metal recovery) applied on a fly ash sample from a municipal solid waste incinerator. This work outlines two chief methods for metal leaching, sulphuric acid leaching and bio-assisted leaching.

Chapter 5 tackles the profound interactions between environment and humans' uses and needs. It focuses on the isotopic signature and concentration of Os within bottom and fly ashes produced by municipal solid waste incinerators. This first attempt in quantifying the impact related to Os contaminations contributes to stress the need to monitor Os pollution, generally overlooked, in areas close to incineration facilities and municipal waste landfill.

Chapter 6 reports an overview of the major conclusions drawn from this work and suggests possible research directions for the future.

Appendix A encloses conference proceedings and other research-related efforts, which have been accomplished during the 3-years PhD project.

Appendix B encloses the candidate's résumé, with last update February 2016.

List of Abbreviations

AES	Auger Electron Spectroscopy
APC	Air Pollution Control System (In: MSWI system)
B, M, T	Bottom, Intermediate, Top (referred to layers or strata in: Sampling)
BA	Bottom ash (MSWI by-product)
C	Concentration in mass/mass (in: SFA)
C&D	Construction and Demolition waste
C1	Carbonaceous chondrite (type 1)
CNR	National Research Council
CNR-ISMAR	National Research Council – Institute of Marine Sciences
CrE	Critical Elements (only chemical elements according EC, 2014)
CRM	Certified Reference Material
crm	Critical Raw Material (according EC, 2010; 2014)
CV	Certified Value
EC	European Commission
EF	Enrichment Factor
EIA	Environmental Impact Assessment
EMP	Electron Microprobe
EoL	End of Life
EPA	Environmental Protevtion Agengy
ESP	Electrostatic precipitator
EU	European Union
F	Flow in mass/time (in: SFA)
FA	Fly ash (MSWI by-product)
FAE	FA from electrostatic precipitator

FAL	Treated FA (from bag filter) with Lime-additive
FAS	Treated FA (from bag filter) with Soda-additive
FAU	Untreated FA (typically from dry scrubber)
FCA	Full Cost Accounting
GeoReM	Geological and Environmental Reference Materials (website)
GTK	Geological Survey of Finland
H	Magnetic field
HPA	High Pressure Asher (method of digestion)
HREE	Heavy Rare Earth Elements (Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu)
ICP	Inductively Coupled Plasma spectrometry
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ID	Isotope Dilution (analytical method)
ISPRA	Istituto Superiore per la Protezione e la Ricerca Ambientale
ISTAT	National Institute of Statistics
K(%)	Relative recovery efficiency (in: SFA)
K_{fd}%	Frequency dependence of susceptibility
LCA	Life Cycle Assessment
LOI	Loss on Ignition
LREE	Light Rare Earth Elements (Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd)
M	Magnetization
MFA	Material Flow Analysis
MSWI	Municipal Solid Waste Incineration
O	Output expressed in mass/time (in: SFA)
PGEs	Platinum Group Elements (Os, Ir, Ru, Rh, Pt, Pd)
PIF	Pricing Influence Factor

R^2	Coefficient of determination from regression curve
REE	Rare Earth Elements
REOs	Rare Earth Oxides
RM	Reference Material
RSD	Relative Standard Deviation
SCP	SCP Science, Canada (manufacturer)
SCR	Selective Catalytic Reduction of nitrogen oxides
SD	Standard Deviation
SEM	Scanning Electron Microscope
SEM/EDS	Scanning Electron Microscope/Energy Dispersive Spectroscopy
SFA	Substance Flow Analysis
SP	Super Paramagnetic (referred to grains or physical state)
SVDU	Syndicat national du traitement et de la Valorisation des Déchets Urbains
SWI	Solid Waste Incinerator (plant)
T	Transfer ratio or transfer coefficient (in: SFA)
TCLP	Toxicity Characteristic Leaching Procedure (1311 EPA)
TREO	Total of REOs
UCC	Upper Continental Crust
UNEP	United Nations Environment Programme
UNI	Italian technical standard
USGS	United States Geological Survey
VTT	Technical Research Centre of Finland
WDXRF	Wavelength-Dispersive X-ray spectroscopy
WEEE	Waste from Electric and Electronic Equipments
XRD	X-Ray Diffraction

XRF	X-Ray Fluorescence spectrometry
XRPD	X-Ray Powder Diffraction (poweder diffractometer)
ρ	Density
κ	Volume magnetic susceptibility
φ	Diameter (geometry)
χ	Mass specific magnetic susceptibility

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Chapter 1

Introduction to the thesis work

1. More than waste

During the Bronze and Iron Ages, human beings used a few metals (Fe, Ni, Cu, Ag, Au) and in small amounts. With time increasing amount of many other elements has been included in the anthroposphere, thus modifying their natural cycle. It has been recently estimated that we use 1.4 million kg of resources (metals, minerals and fuels) during our life (Kyser *et al.*, 2015) (Fig. §1-1).

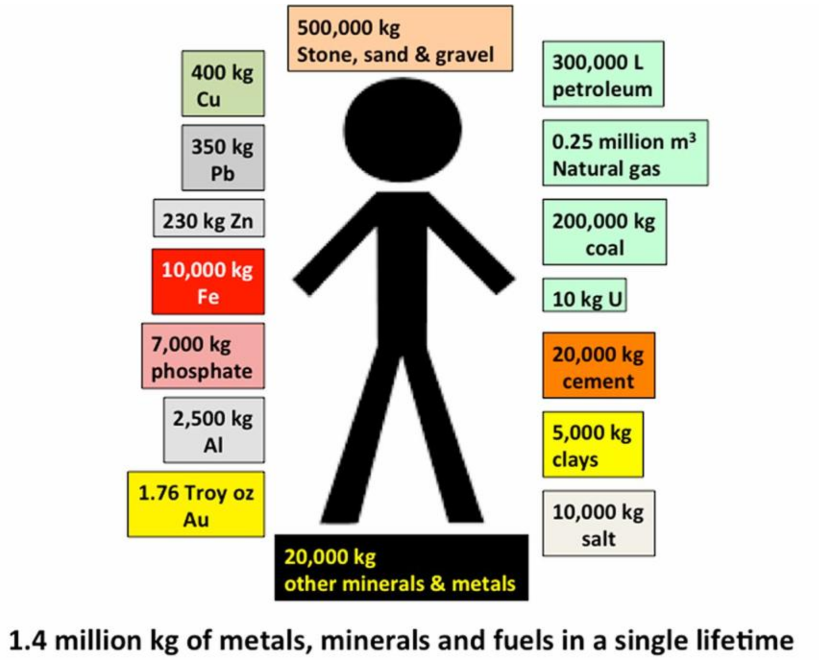


Fig. §1-1 Average lifetime consumption of resources for individuals (from Kyser *et al.*, 2015).

The increasing demand of raw materials for the global economic development has lead to move from limited and fixed stocks of primary ore deposits to the increasing anthropogenic stocks, which include notably high streams of waste. This creates the basis for the development of the *Urban Mining* concept, which represents actions and technologies for the recovery of secondary raw materials and energy from by-products of the urban catabolism (Baccini &

Brunner, 2012). Urban mining, therefore, provides systematic management of anthropogenic stocks and waste with long term benefits such as environmental protection, resource conservation, and eco-efficient technological development. Anthropogenic waste that can be potentially mined include, for example, waste from electric and electronic equipment (WEEE), end-of-life (EoL) vehicles, plastic residues, exhausted oils, construction and demolition waste (C&D), and combustion residues. The latter repository, in turn, includes bottom and fly ashes from municipal solid waste incinerators (MSWI), fly ash from sewage sludge treatment, coal ashes, industrial slag (e.g., foundry residues). Clearly, the closed loop of recycling and recovery of waste seems a promising option to meet the increased demand of critical metals and for the reduction in the consumption of primary raw materials. In practice this is highly challenging and requires high level of innovation and open-minded and multidisciplinary approach.

When moving towards sustainable use of Earth's resources through increased efficiency and improved material utilisation, the concept of urban mining becomes central for the assessment of the required tasks and strategies. After the exploration stage, namely the identification of potential alternative sources, the activities within a context of urban mining generally proceed with collection/sampling, material characterisation, evaluation of resources flow/stock, processing for upgrading and metal recovery, evaluation of recovery potential, environmental and economic assessment. In the present thesis I tried to address each of these steps, the MSWI solid residues will be the targets of the research. They are relatively unexplored anthropogenic deposits, but might represent high elements flows (see chapter 2), which can be recovered with high yields of extraction and with benefits for the environment (see chapter 4). The study of these residues requires the beneficial merging of a range of research aspects and stakeholders and, in long term view, can contribute to improve the status of resource management in Europe.

There are many alternatives for the management of solid waste including recycling, hydrometallurgical treatment, biological treatment, thermal treatment and landfill disposal. In general, solid waste management systems include the use of several of these processes. Highly selective separation methods, such as combined physical and bio-hydrometallurgical routes, might lead to recover elements of economic interest such as the critical raw materials for the EU, which are of particular interest throughout the present work but also they are present as minor species within MSWI. The incoming EU programs, in fact, highlight the need to increase recycling rates and recoveries of critical raw materials from waste streams when technically or economically possible, since they represent key elements and minerals for the technological development.

1.1 Critical Raw Material

The European Commission published a list of 14 raw materials regarded *critical*, including antimony, beryllium, cobalt, fluorspar, gallium, germanium, graphite, indium, magnesium, niobium, PGE (platinum group elements), LREE (light rare earth elements) and HREE (heavy rare earth elements), tantalum and tungsten (European Commission, 2014, 2010) (Fig. §1-2). This action wants to highlight the difficulty to supply these elements to industries, the dependence on imports and, hence, their strategic importance: each entry is selected according economic importance and supply risk. The list actually groups minerals and chemical elements. In the present thesis, the term "critical elements" refers to the chemical elements: Ge, Mg, HREE, LREE, Nb, In, Sb, Ga, Co, Be, PGE, W, Cr, whereas “elements of (high) economic importance” are V, Ni, Zn, Hf, Mn, Al, Ta, Sn, Mo (compare Fig. §1-2).

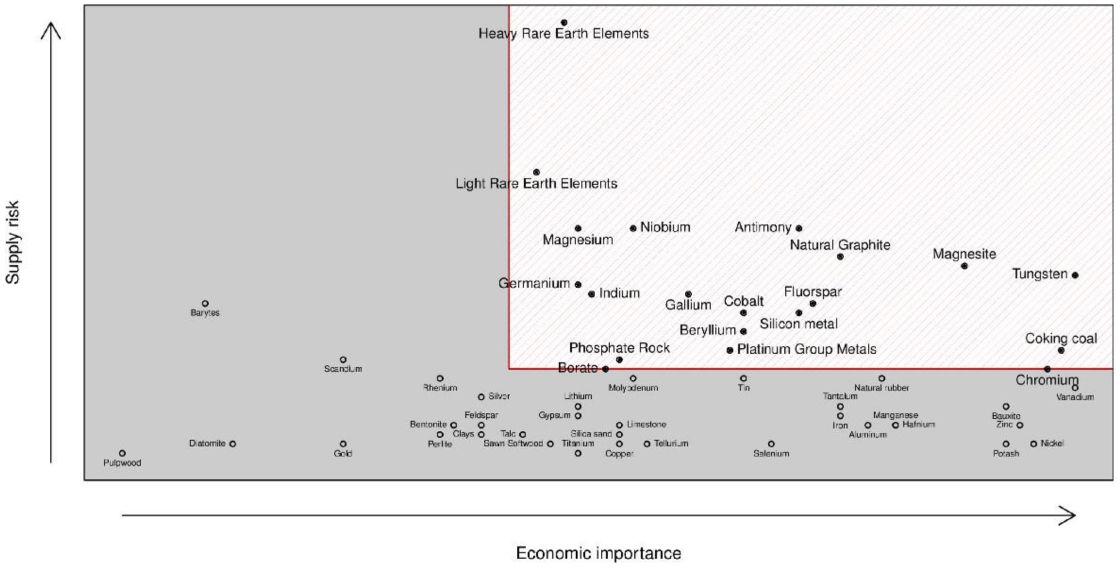


Fig. §1-2 Critical raw materials for the EU according their economic importance and supply risk (EC, 2014).

The increasing production and consumption of high-tech products to meet the burgeoning market demands is the result of a rapid technological progress. The critical elements play a significant role for a number of everyday products due to their unique physical and chemical properties. They usually meet specific requirements to perform essential functions in many industrial applications. Few or no satisfactory substitutes exist for critical elements (EC, 2010) contributing to stress their supply risk.

Striving for rapid and constant technological advances, critical elements are increasingly used and stored in different applications. As a consequence, rare metals are also contained within the waste stream of end-of-life products.

The rare earth elements (REE) and those of the platinum group (PGE), which are extensively used in modern applications, are particularly mentioned in the next chapters (3 and 5) and, thus, the following sections provide a general description of their properties and market conditions. Worth mentioning, the accurate quantification of PGE should have served for calculation of PGE flows in chapter 2, but low levels of concentration and isobaric interferences hampered reliable determinations. Only Os determinations, which relied on an *ad-hoc* analytical method, were found to be accurate enough and are discussed in chapter 5.

1.2 The rare earth elements

The rare earth elements (REE) are a moderately abundant group of 17 elements comprising the 15 lanthanides plus yttrium and scandium. The REEs shows similar physical and chemical properties. REEs ores are generally found in alkaline igneous rocks and also in sand or clay sediments as result of weathering processes of the source rock. There are about 200 known minerals containing light or heavy REE, six of those minerals are considered as primary sources: Bastnaesite (Ce, La, Y), Monazite (Ce, La, Pr, Nd Gd, Sm) Xenotime (Y, Dy, Er, Tb, Yb), Loparite (Ce), Apatite (Nd, Dy, Eu, Ce), Ion-adsorption clays (Y, Nd, La). The majority of REE ore deposits show grades that cannot be considered as economic, while other REE-rich deposits have a complex mineralogy requiring high level of processing for any mineral beneficiation. In addition, REE are usually associated with radioactive elements (uranium and thorium) and mining operations needs accurate safety controls. The REE recovery process requires high quantity of water, acids, and electricity, thus implying high costs and production of harmful by-products due to the potential release of hazardous and radioactive metals. The largest reserves are in China (60%, 110 million tonnes of REE oxides "REOs"), and this is also the largest producer with 97% of the total; follow this primacy India, Brazil and Malaysia. The larger consumers are USA, Europe, Japan, Korea and

China. The REE demand is continuously growing (10%-20% increase each year) (UNEP, 2009). They are used in a wide range of technological application as high purity metal or metal oxide. The REE represent key-elements in many modern fields such automotive catalytic converters, fluid cracking catalysts in petroleum refining, phosphors in colour television and flat panel displays (cell phones, portable DVDs, and laptops), permanent magnets and rechargeable batteries for hybrid and electric vehicles, generators for wind turbines, and numerous medical devices. Moreover REEs are essential in important defence applications, such as jet fighter engines, missile guidance systems, antimissile defence, space-based satellites and communication systems. Unfortunately the reserves of REEs are not equally distributed in the world: in Europe and many other countries no relevant sources are present, and moreover recently China's exportation of REE (major export country, about 97% of total export in the world) is dramatically decreased, for economic and environmental reasons (USGS, 2015). All these reasons push many countries to invest in mining the anthroposphere as solution for the industrial ecosystem, but this is not straightforward especially in presence of low grade ores. In general, promising waste streams for REE recovery (e.g., WEEE) contain relatively low concentrations of REE, typically well below 1%, whereas the present cut-off for extraction from primary ores is about 3% (Binnemans *et al.*, 2013).

1.3 The platinum group elements with emphasis on osmium

The Platinum Group Elements (PGE) are a group of six metals: ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt). The PGE mainly occur in the natural ore deposits of South Africa, Russia, Zimbabwe, Canada and United States. In 2012, world mining production of PGE was 451 tonnes. South Africa, Russia, Zimbabwe, Canada and United States accounted for 58%, 26%, 5%, 4%, and 4% of total global production in 2012, respectively. Their properties, such as good electrical conductivity, high melting point and corrosion resistance, make them indispensable for many industrial applications. To give two practical examples that show their high value for the social growth, PGE-bearing electronic components can increase the storage capacity in computer hard disk drives and powdered metals are used in automobile catalysts to reduce micro pollutants. The demand for PGE is leaded by the autocatalyst industry. PGE are also used in the glass industry, jewellery, chemical industry and electronics (USGS, 2015). Because of their unique physical and chemical properties, they cannot be effectively substituted by other materials so far. The consumption of PGE used in electronic products is decreasing due to the new substitutions with less PGE. Despite the limited PGE sources and their very low concentrations on the Earth's crust, reports on increasing PGE concentrations in the surface environment are raising concern on potential impact of contaminations. Anthropogenic PGE emission can derive from automobile catalysts, mining and metal production, from medical facilities, manufacture of PGE-bearing products, and use and disposal of these products.

Osmium was discovered in 1804 together with Ir. Like other PGE, Os occurs mainly in native alloys (e.g., osmiridium, iridosmine). Unlike other PGE, Os easily reacts with oxygen and may occur at various oxidation states, from +3 to +8, and also may have -1 oxidation state. Its abundance in the Earth's crust is calculated at 0.05 μg/kg. There are seven stable isotopes of Os. This metal is notable for its great density and the isotope ^{192}Os is even the most dense element. Os is used almost entirely as a hardening alloy with other precious metals, especially in the weapon industry. There is a small production of Os, estimated as 300 t/a (Reimann & De Caritat, 1998). During metal processing, various Os compounds are formed, such as OsF_6, $OsCl_4$ and volatile OsO_4. All the Os compounds are toxic to humans and animals. Longer exposure to increased levels of some Os compounds can cause lung congestion, skin and eye damages, and is hazardous to marrow, liver, and kidneys (Kabata-Pendias, 2010; Farago & Parsons, 1994). Anthropogenic Os emission is expected from the same sources of PGE emission, but there is not much information on Os contamination, even near potential sources of Os pollution (Kabata-Pendias, 2010; Rauch & Morrison, 2008). Os emission rates are reported from automobile catalysts, metal smelters, medical centres, but not from MSWI plants where end-of-life PGE-rich products, spent catalysts and metallurgical and medical waste might end up.

2. Driving-question and issues

The main driving -question of the PhD project is:

Can MSWI anthropogenic flows be considered as a dynamic "URBAN ORE"?

The main research problem embraces several specific questions that are addressed throughout the manuscript. These specific questions, divided according to the subject areas, are:

Characterisation of MSWI residues

Do MSWI solid residues contain significant amount of critical elements?

To what extent rare metals such as REE and PGE occur in MSWI residues?

Prospecting for resources in MSWI residues

What is the resulting magnitude of the critical elements flows?

Is this urban mine comparable with a low-grade ore deposit?

Do critical elements preferably partition into bottom ash or fly ash?

Where critical elements preferably partition in fine-grained or coarse-grained bottom ash?

Is there a simple and cost-effective method that can be used for any element prospecting?

Can correlation between major and critical elements, if any, help in prospecting?

What about magnetic signatures? Can magnetic measures help in prospecting?

Upgrading and metal recovery from MSWI residues

Is there a simple and cost-effective separation strategy that can be used for any mineral beneficiation?

Are the bio-hydrometallurgical procedures suitable for metal recovery?

What are the recovery performances of chemical leaching and bioleaching?

Are the proposed treatments affordable from economic and environmental point of view?

Environmental impact related to MSWI residues and their treatment

In addition to heavy metals contamination, are there any other sources of pollution related to MSWI residues?

Are there ultrafine magnetic particles within MSWI residues? Can magnetic susceptibility help assessing the extent of these harmful ultrafine particles?

Are Os levels significant into MSWI bottom and fly ashes? Is the Os release from MSWI bottom and fly ash, and MSWI smokestacks significant?

After bioleaching and chemical leaching, can fly ash be landfilled?

2.1 Main issues

To achieve the goals of the present work and answer the questions, several issues related to assessment methods, sampling and analytical quantification need to be addressed.

Best practise for sampling and chemical analyses of solid waste are not defined, and assessment methods concerning, for example, the environmental impact of MSWI residues or metal recovery, are not well ascertained.

Accurate sampling strategies and analytical methods are required for reliable mass flow analysis and evaluation of metal recovery. In order to avoid the domination of uncertainties introduced through sample heterogeneity, representative samples are needed. However, the composition of the MSWI feedstock, which can vary over time and between different incinerators, impacts the residues' homogeneity and representativeness. On the other hand, the main difficulty during the determination of MSWI residues chemical compositions resides in the complex matrix of anthropogenic waste that can affect the quality of analytical results. The following effects might produce bias of results in analytical measurements when using techniques such as X-Ray Fluorescence (XRF) or plasma-based (ICP) elemental analysis: nugget effect, introduction of error in sample preparation, spectral overlaps, lack of certified reference materials and efficient calibration. Effective digestion methods and low blanks are desirable for ICP-MS analysis, while the control of matrix effect is essential in XRF measurements. In addition, the determination of 1) non-routinely analysed critical metals, 2) metals at low concentrations (e.g., REE, PGE), 3) Os contents and isotopic ratios, and 4) magnetic properties (susceptibility) is highly challenging, given the above mentioned analytical difficulties and the lack of reference data from literature (especially for Os levels and magnetic susceptibility).

A few assumptions, therefore, have to be made for mass flow analysis, metal recovery, and environmental assessment purposes. In parallel, uncertainties continue to affect the analytical methods.

3. Municipal solid waste incinerators and their solid residues

Given the fluctuating markets of raw materials, reducing the loss of resources is needed and recycling becomes mandatory (Brunner, 2011) to provide alternative stable supplies. Worldwide the sharp technological advances favoured the increase of product consumption and wellness and, consequently, contributed to a significant stream of waste. The current strategies of waste management adopted in many industrialised countries for the unrecycled fractions (thus excluding separate collection) of municipal solid waste imply biological stabilisation of the biodegradable fraction and combustion with energy recovery of the un-biodegradable combustible part. Municipal solid waste incineration (MSWI) systems are actually widespread as they can reduce the volume of collected waste, destroy many toxic components and provide an alternative source of energy. Two main types of combustion chambers exist, grate-system and fluidised bed. Grate-furnaces are largely the most used (Fig. §1-3). Significant streams of incinerated residues are generated from the combustion chamber of MSWI plants and from the subsequent cleaning process of flue gas recovered by the air-pollution-control (APC) system (see 13-17, in Fig. §1-3). The first part includes bottom ash and grate siftings which are coarse-grained materials generally named as bottom ash (BA). The second part includes for instance boiler ash, ash collected from electrostatic precipitators, scrubber residues, etc and such very fine-grained materials from the APC system is referred as fly ash (FA). About 20-30 % of the initial mass of incinerated waste is converted into BA, whereas FA represent about 2-6 % of the initial mass of incinerated waste (Chandler *et al.*, 1997). The BA materials are separately stored from the FA almost everywhere. Conversely, in some cases the separate streams of FA are often mixed depending on further treatment options and/or current local legislation.

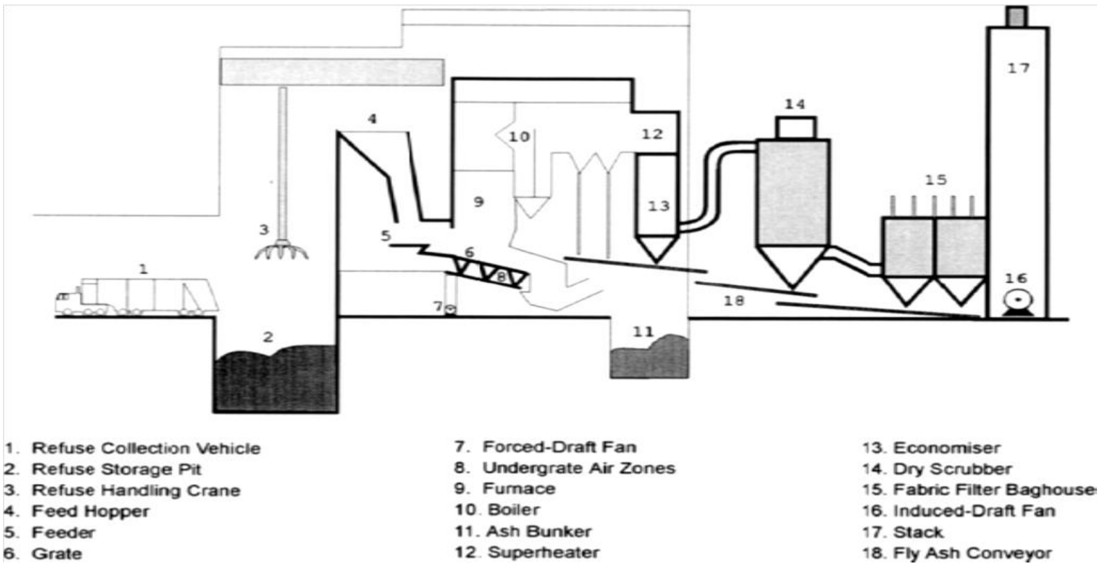


Fig. §1-3 Typical grate-furnace MSWI system (from Chandler *et al.*, 1997).

3.1 Bottom ash

The BA are the solid, sandy and pebbly materials deriving from the waste mass combustion into the furnace. After combustion (850-1100 °C), this residual material is quenched (i.e., cooled in water) and wet BA are typically stored in heaps falling from a conveyor belt line (see 11 in Fig. §1-3); some MSWI systems (e.g., Morf *et al.*, 2013) have a dry bottom ash discharger. As a result of similar operational conditions (e.g., allowed waste, temperature, residence time), BA generated in different incinerators are rather uniform in composition (Chandler *et al.*, 1997). Lower amount of potential pollutants than in FA and satisfactory mechanical properties make untreated BA a good binder for construction material. In addition, weathering of BA mostly through carbonation (i.e., taking up atmospheric CO_2 thereby changing mineralogy from hydroxides to carbonates) acts as a natural stabilisation process for many metals due to the fact that their carbonates have significantly lower solubility compared with the hydroxides. The release of pollutants from weathered BA is generally low and complies with Italian regulation that, in turn, follows the European guidance levels. As a consequence, a large fraction of the generated BA is reused or landfilled as an inert material in Italy.

3.2 Fly ash

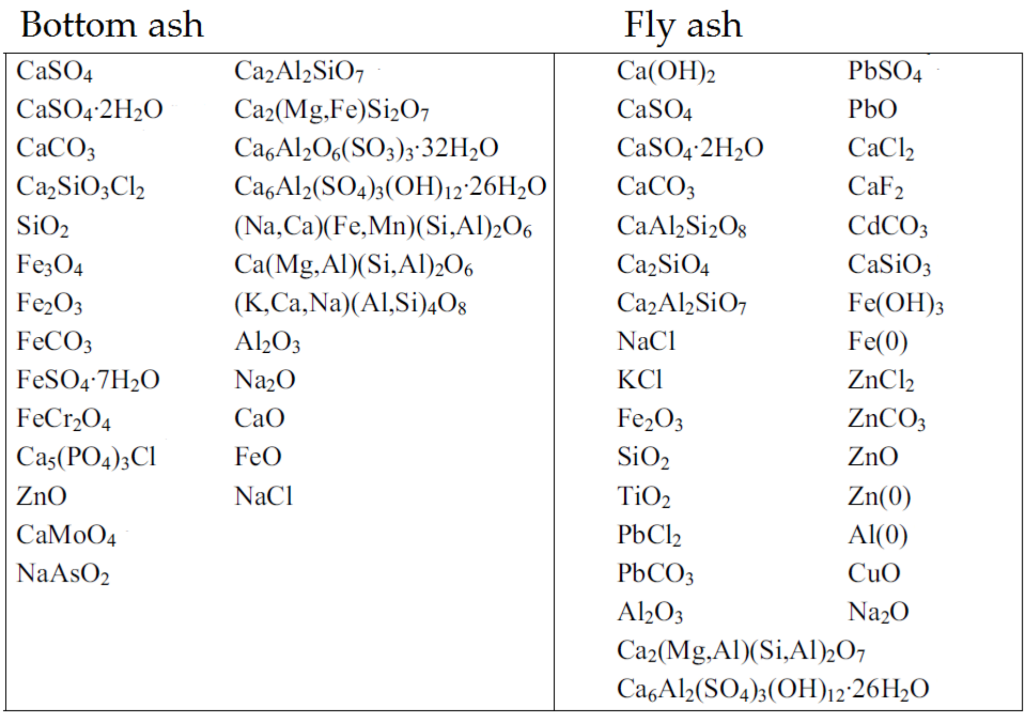
FA can be described as dust-like particles that are carried away from the combustion chamber with the flue-gas. The FA material is usually stored in *big bags* after each step of filtration (see 14, 15 in Fig. §1-3). Contrary to mass-combustion technology the APC systems is rather plant-specific, mostly reflecting legislative requirements and the currently available technologies. Therefore, FA produced in different incinerators vary in composition, water content, pH, etc.

Typically, the mass of pollutants is lower in treated FA than in "pure" FA due to the dilution with unreacted additives and the neutralization capacity. Nevertheless, both materials contain large quantities of readily soluble salts (e.g., Cl, Na) and hazardous metals (e.g., Pb, Sb, As). Consequently, FA residues should only be landfilled or stored underground after pre-treatment. As a matter fact, FA materials are classified as hazardous waste in Italy and landfilling is the main option for their management. However, in view of recent waste policy, there is interest to devise new solutions of treatment and disposal of MSWI FA. The new solutions for FA reuse have to meet the criteria of economic and environmental sustainability, and adequate performance characteristic of the final product. Possible new directions include FA reuse as additive in concrete, in ceramic and glass industries, as a fertiliser (thanks to the significant content of P and K), sorbent materials, as a filtrating agent in sewage sludge treatment.

3.3 Mineralogy of MSWI residues

Untreated BA is a heterogeneous material, the majority of which comprises of calcium-rich minerals and silicates potentially enriched in iron and sodium. Numerous studies concluded that a significant fraction of BA consists of melt products such as siliceous glass, spinel-group minerals (e.g., magnetite), and melitite-group minerals (e.g., gehlenite), calcite and many other minor phases (Kirby & Rimstidt, 1993, Bayuseno & Schmahl, 2010). Minerals commonly identified in bottom ash are in Tab. §1--1 The XRD patterns of BA samples from this study show a huge amount of peaks that correspond to numerous minerals of unreliable identification. Also FA show a complex mineralogy mainly due to processes occurring during the combustion and the subsequent flue-gas cleaning, i.e. vaporization, melting, crystallisation, vitrification, condensation and precipitation (Kirby & Rimstidt, 1993, Bayuseno & Schmahl, 2011). Consequently, sulphates, carbonates, silicates, phosphates, chlorides, (hydr)oxides, pure metals, and glass were identified in untreated FA (Tab. §1--1).

Tab. §1--1 Typical mineral phases experimentally detected in MSWI residues. Readapted from Kirby & Rimstidt (1993), Bayuseno & Schmah (2010, 2011).



Bottom ash		Fly ash	
$CaSO_4$	$Ca_2Al_2SiO_7$	$Ca(OH)_2$	$PbSO_4$
$CaSO_4 \cdot 2H_2O$	$Ca_2(Mg,Fe)Si_2O_7$	$CaSO_4$	PbO
$CaCO_3$	$Ca_6Al_2O_6(SO_3)_3 \cdot 32H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCl_2$
$Ca_2SiO_3Cl_2$	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	$CaCO_3$	CaF_2
SiO_2	$(Na,Ca)(Fe,Mn)(Si,Al)_2O_6$	$CaAl_2Si_2O_8$	$CdCO_3$
Fe_3O_4	$Ca(Mg,Al)(Si,Al)_2O_6$	Ca_2SiO_4	$CaSiO_3$
Fe_2O_3	$(K,Ca,Na)(Al,Si)_4O_8$	$Ca_2Al_2SiO_7$	$Fe(OH)_3$
$FeCO_3$	Al_2O_3	$NaCl$	$Fe(0)$
$FeSO_4 \cdot 7H_2O$	Na_2O	KCl	$ZnCl_2$
$FeCr_2O_4$	CaO	Fe_2O_3	$ZnCO_3$
$Ca_5(PO_4)_3Cl$	FeO	SiO_2	ZnO
ZnO	$NaCl$	TiO_2	$Zn(0)$
$CaMoO_4$		$PbCl_2$	$Al(0)$
$NaAsO_2$		$PbCO_3$	CuO
		Al_2O_3	Na_2O
		$Ca_2(Mg,Al)(Si,Al)_2O_7$	
		$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	

Generally, the identification of BA and FA minerals by means of, for example, XRD (X-Ray Diffraction) and AES (Auger Electron Spectroscopy) or by SEM (Scanning Electron Microscoopy) is challenging due to a high number phases produced under variable operating conditions of the MSWI system, combustion temperatures, variable chemical composition of the feedstock materials, which in turn control the minerals formation. The formation processes of minerals are still not well understood and such fact largely differentiates natural ores from anthropogenic stock. The determination of minerals where a certain metal partitions, is challenging and, especially, precise identification of minor compounds is often prevented. Large amounts of soluble salts (e.g. chlorides) occur in MSWI residues. As broadly ascertained, metals forming chloro-complexes such as Cd and Sb will be liberated emphasising the overall toxicity risk associated to these materials. Care should be paid when handling, management and landfilling of incineration waste are addressed and the environmental impact assessment is commonly carried out for both BA and FA to reduce contamination risk.

Preliminary attempts by XRD in identifying mineralogical phases have been made on selected BA samples during earlier stages of this work, but those results were not suitable to understand where the *crm* elements, occurring as minor phases, partitioned.

4. Samples collection

I organised the visit to the selected incinerators plants, in accordance with the MSWI managers who were previously contacted in order to grant permission to access to the plants. Thank to the logistic support of MSWI managers and operators, the visit allowed 1) to understand the system features and performances and 2) to sample the available BA and FA materials in the most effective way.

Samples repertory of this study derives from six MSWI facilities and includes original materials of BA and different FA types (according to the system technology). The selected MSWI plants are from northern Italy, mostly from Emilia Romagna region, among the most industrialised areas of the Peninsula. This translates in huge amounts of household waste and waste from industrial activities processed and impressive output flows of BA and FA, as detailed in chapter 2, supplementary material of chapter 3, and chapter 5.

All the investigated MSWI facilities are equipped with a grate-system furnace and allow the separate storage of BA and each different FA. Wet (20-30% moisture content) BA from outdoor heaps have been sampled and used throughout the present study. Several FA residues have been sampled, depending on the available technology, and include: untreated fly ash from dry/semi-dry scrubbers (FAU, also called FA-RAW in chapter 4), fly ash from electrostatic precipitator (FAE), and fly ash from bag filters treated with lime (FAL) or soda (FAS) additives. In each incinerator plant, the sampling was performed a few days before the residues' loading and subsequent relocation out of the storage site. The detailed sampling methodology is not addressed in this section because it is reported in the next chapters 2 and 3 and relative supplementary materials. Also, timeframe of residues' production and physical properties at the sampling site of BA and FA are outlined in chapter 2 and 3.

5. Methods

In this section I report the methods used following the order of their first appearance throughout the next chapters. Methods included geochemical and mineralogical characterisation, measures of magnetic and Os isotopic signature, other prospecting tools (e.g., mass flow analysis). Worth mentioning, the methods used for the purposes of the present research are typical of the *Solid Earth Science* and they were successfully applied to urban mining topics.

I performed samples preparation and measurements independently, in accordance with laboratories' supervisors. The analytical procedures and measurements were performed in the laboratories of the University of Bologna (BiGeA dept., Italy), University of Ferrara (Earth and Physical Science dept., Italy), Montanuniversität Leoben (General and Analytical Chemistry dept., Austria), CNR - National Research Council (Institute of Marine Sciences dept., Italy), VTT - Technical Research Centre (Material Recycling Reprocessing Recovery dept., Finland), Aalto University (School of Chemical Technology dept., Finland).

5.1 Geochemical methods

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and X-Ray Fluorescence (XRF) have been used during the present work for the quantification of major (>1% m/m) and trace elements (<0.1% m/m). Because of the considerable use of XRF and ICP-MS, the following sections describe the analytical procedures and address the possible issues related to these analytical methods. Each technique had advantages and limitations; they should be considered as complementary rather than competing techniques. The combination and comparison of the analytical techniques have lead to a reliable assessment of analytes concentrations.

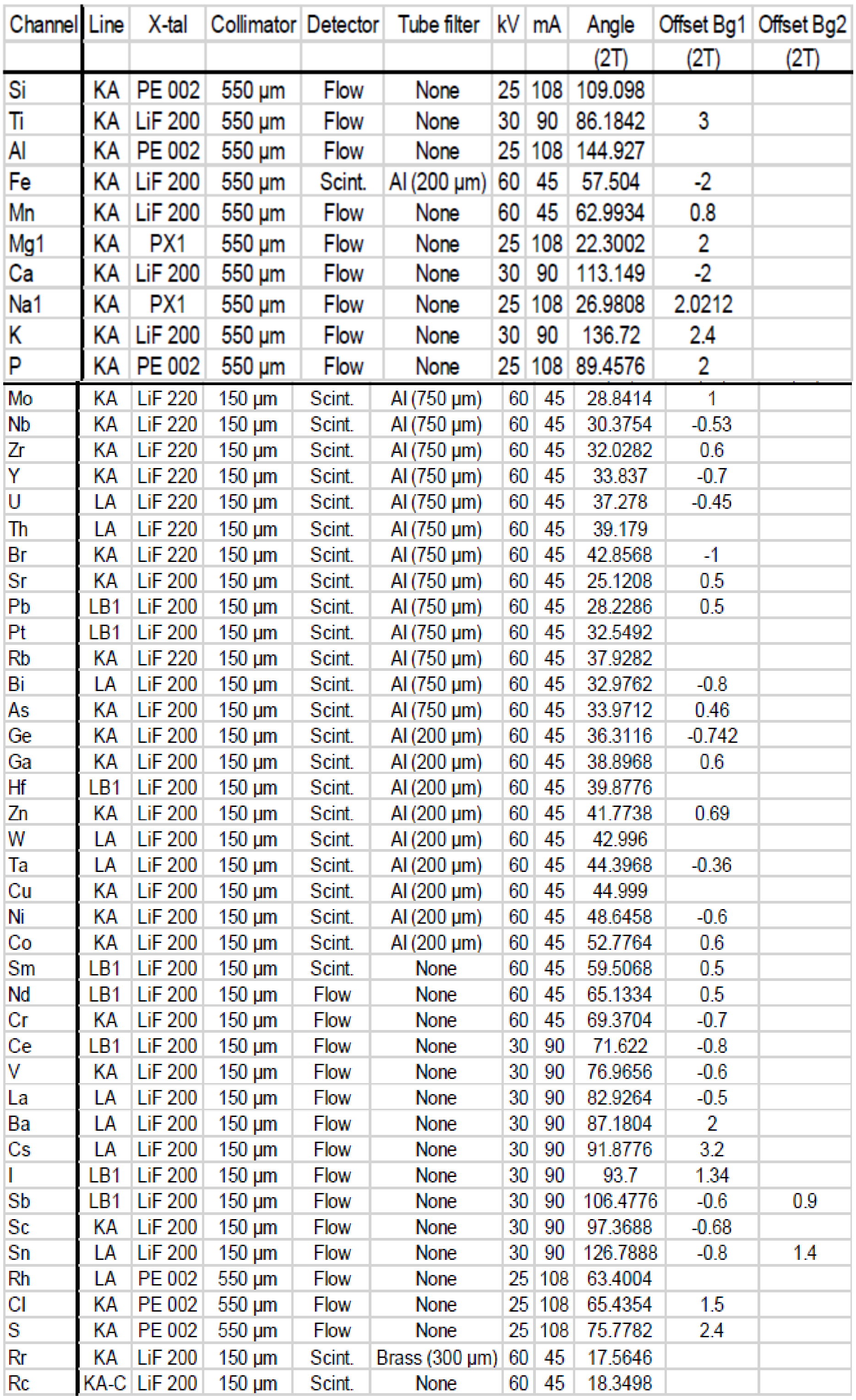
5.1.1 Sample preparation and efforts for reliable XRF measurements

The XRF is widely used for geochemical analysis, it has many advantages (inexpensive, simple sample preparation, reagents are not required) and disadvantages (high detection limit, usually narrow dynamic range, spectral overlaps, matrix effect, no isotopic information). Generally, the XRF analysis remains a reasonable choice when very low detection limits are not required. Detection limits for many trace elements lie in the range of 5-10 ppm under routine operating conditions.

I have undertaken the XRF analysis during different stages of this work at the BiGeA Department that is equipped with a PANalytical Axios wavelength dispersive X-ray fluorescence (WDXRF) spectrometer and all the facilities for samples preparation. About 5 g sample is grounded, dried (at 40°C), and accurately homogenised in an agate mortar until the powder is very fine milled (<40 μm). The powdered sample is then pressed (at 20 kPa) together with 10 g of boric acid, which acts as a “jacket”, by means of a hydraulic pressing machine.

The XRF is a comparative technique thus the calibration needs certified reference materials (CRM). During routine analysis, the calibration curves for elemental quantification are based on a number of CRM, which are included in the SuperQ software. An online correction procedure translates the detected counts into elemental concentrations. The calibration curves cover a wide range of concentration; thereby they can be used for a range of geological sample with variable composition. The SuperQ applications for major and trace elements determination follow the analytical conditions as in Tab. §1-2. Under these conditions, the estimated analytical precision by means of replicates analysis is as low as 4% for major elements and 10% for trace elements.

Tab. §1-2 Analytical condition of the XRF analysis for major and trace elements.



Channel	Line	X-tal	Collimator	Detector	Tube filter	kV	mA	Angle (2T)	Offset Bg1 (2T)	Offset Bg2 (2T)
Si	KA	PE 002	550 µm	Flow	None	25	108	109.098		
Ti	KA	LiF 200	550 µm	Flow	None	30	90	86.1842	3	
Al	KA	PE 002	550 µm	Flow	None	25	108	144.927		
Fe	KA	LiF 200	550 µm	Scint.	Al (200 µm)	60	45	57.504	-2	
Mn	KA	LiF 200	550 µm	Flow	None	60	45	62.9934	0.8	
Mg1	KA	PX1	550 µm	Flow	None	25	108	22.3002	2	
Ca	KA	LiF 200	550 µm	Flow	None	30	90	113.149	-2	
Na1	KA	PX1	550 µm	Flow	None	25	108	26.9808	2.0212	
K	KA	LiF 200	550 µm	Flow	None	30	90	136.72	2.4	
P	KA	PE 002	550 µm	Flow	None	25	108	89.4576	2	
Mo	KA	LiF 220	150 µm	Scint.	Al (750 µm)	60	45	28.8414	1	
Nb	KA	LiF 220	150 µm	Scint.	Al (750 µm)	60	45	30.3754	-0.53	
Zr	KA	LiF 220	150 µm	Scint.	Al (750 µm)	60	45	32.0282	0.6	
Y	KA	LiF 220	150 µm	Scint.	Al (750 µm)	60	45	33.837	-0.7	
U	LA	LiF 220	150 µm	Scint.	Al (750 µm)	60	45	37.278	-0.45	
Th	LA	LiF 220	150 µm	Scint.	Al (750 µm)	60	45	39.179		
Br	KA	LiF 220	150 µm	Scint.	Al (750 µm)	60	45	42.8568	-1	
Sr	KA	LiF 200	150 µm	Scint.	Al (750 µm)	60	45	25.1208	0.5	
Pb	LB1	LiF 200	150 µm	Scint.	Al (750 µm)	60	45	28.2286	0.5	
Pt	LB1	LiF 200	150 µm	Scint.	Al (750 µm)	60	45	32.5492		
Rb	KA	LiF 220	150 µm	Scint.	Al (750 µm)	60	45	37.9282		
Bi	LA	LiF 200	150 µm	Scint.	Al (750 µm)	60	45	32.9762	-0.8	
As	KA	LiF 200	150 µm	Scint.	Al (750 µm)	60	45	33.9712	0.46	
Ge	KA	LiF 200	150 µm	Scint.	Al (200 µm)	60	45	36.3116	-0.742	
Ga	KA	LiF 200	150 µm	Scint.	Al (200 µm)	60	45	38.8968	0.6	
Hf	LB1	LiF 200	150 µm	Scint.	Al (200 µm)	60	45	39.8776		
Zn	KA	LiF 200	150 µm	Scint.	Al (200 µm)	60	45	41.7738	0.69	
W	LA	LiF 200	150 µm	Scint.	Al (200 µm)	60	45	42.996		
Ta	LA	LiF 200	150 µm	Scint.	Al (200 µm)	60	45	44.3968	-0.36	
Cu	KA	LiF 200	150 µm	Scint.	Al (200 µm)	60	45	44.999		
Ni	KA	LiF 200	150 µm	Scint.	Al (200 µm)	60	45	48.6458	-0.6	
Co	KA	LiF 200	150 µm	Scint.	Al (200 µm)	60	45	52.7764	0.6	
Sm	LB1	LiF 200	150 µm	Scint.	None	60	45	59.5068	0.5	
Nd	LB1	LiF 200	150 µm	Flow	None	60	45	65.1334	0.5	
Cr	KA	LiF 200	150 µm	Flow	None	60	45	69.3704	-0.7	
Ce	LB1	LiF 200	150 µm	Flow	None	30	90	71.622	-0.8	
V	KA	LiF 200	150 µm	Flow	None	30	90	76.9656	-0.6	
La	LA	LiF 200	150 µm	Flow	None	30	90	82.9264	-0.5	
Ba	LA	LiF 200	150 µm	Flow	None	30	90	87.1804	2	
Cs	LA	LiF 200	150 µm	Flow	None	30	90	91.8776	3.2	
I	LB1	LiF 200	150 µm	Flow	None	30	90	93.7	1.34	
Sb	LB1	LiF 200	150 µm	Flow	None	30	90	106.4776	-0.6	0.9
Sc	KA	LiF 200	150 µm	Flow	None	30	90	97.3688	-0.68	
Sn	LA	LiF 200	150 µm	Flow	None	30	90	126.7888	-0.8	1.4
Rh	LA	PE 002	550 µm	Flow	None	25	108	63.4004		
Cl	KA	PE 002	550 µm	Flow	None	25	108	65.4354	1.5	
S	KA	PE 002	550 µm	Flow	None	25	108	75.7782	2.4	
Rr	KA	LiF 200	150 µm	Scint.	Brass (300 µm)	60	45	17.5646		
Rc	KA-C	LiF 200	150 µm	Scint.	None	60	45	18.3498		

The measured concentrations by XRF are also corrected by the value of loss of ignition (LOI), which is gravimetrically estimated after heating (for 12 hours, at 950 °C).

Anthropogenic samples have atypical composition compared to natural samples and, consequently, the matrix effects and spectral overlaps can be significant leading to unreliable quantification. As previously mentioned, suitable mathematical correction procedures are used to avoid discrepancies between the detected counts and final concentrations, mostly caused by absorption-enhancement effects. However, in some cases, the selection of CRM for calibration is a limiting factor of the x-ray spectrometry, especially for the analysis of industrial samples. Owing the analytical challenges on MSWI samples chemical characterisation by XRF, I developed an offline procedure for analytes determination in order to check and validate the quantification methods implemented in the SuperQ software. Selected CRM (JR-1 and TB), matrix matched CRM (BCR-176, BCR-176r, and NBS 1633a), and in-house reference materials (BCR-176* and NBS 1633a*) are used for calibration (Fig. §1-4). In-house reference materials represent the corresponding CRM diluted by a fixed factor with the CRM JGb-1 (gabbro powder, Geological Survey of Japan, 1984) in order to obtain calibration curves for suitable range of concentrations. Following elements were checked: Ca, Mg, As, Ba, Cl, Co, Ga, Cu, Cr, Ni, Sb, S, and Zn. According to the measures of selected CRM (i.e., UBN, NIM-D, MICA-Fe, BXN) as unknown samples, the estimated relative error is as low as 5% for Ca, Ba, Cr, Cu, Mg, Sb, and Zn, while around 10% for Co, Ga, Ni, As, Cl, and S. Certified values were derived from the GeoReM database (http://georem.mpch-mainz.gwdg.de/).

Samples measurements by XRF were done always in triplicate and the data quality were evaluated by means of statistical software (mostly, GCDkit and Minitab 16), following the recommendation outlined in Reimann *et al.* (2008).

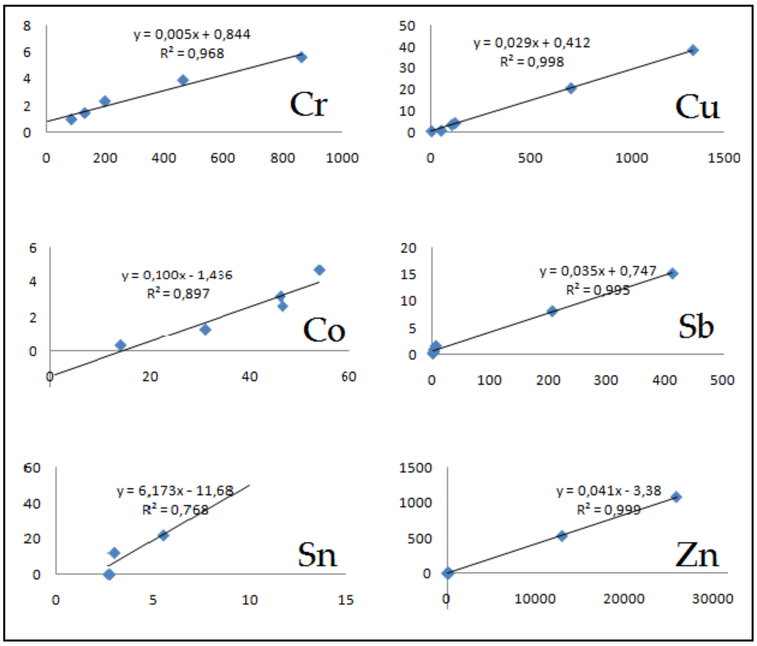


Fig. §1-4 Calibration curves for offline conversions of XRF counts.

5.1.2 The sodium peroxide sintering technique coupled with ICP-MS

Compared to XRF, ICP-MS has greater speed, precision and sensitivity but time-consuming sample digestion and/or pre-concentration steps are often required. An overview on published digestion and pre-concentration methods can be found elsewhere (Barefoot, 1997).

During the visiting period at the Montanuniversität Leoben, I analysed the MSWI samples using the sodium peroxide (Na_2O_2) sintering technique coupled with ICP-MS measurements. The Na_2O_2 sintering technique is an effective method of sample digestion for the most refractory material known today (Meisel *et al.*, 2002). The Na_2O_2 sintering is highly effective because Na_2O_2 can intimately attack minerals and the resulting sinter residue gets dissolved easily. The sodium peroxide decomposes to NaOH and O_2 and does not introduce elements that cause significant instrument memory. The present technique is simple, inexpensive and capable of digesting samples containing refractory minerals such as stable high melting temperature oxides, organic materials with high molecular mass, industrial magnesite, silicon carbide, etc. with highly reproducible and reliable results. In addition, the higher total dissolved solids compared to acid digestion techniques (e.g., $HNO_3/HClO_4/HF$ mixture) and higher blanks do not affect the quality of the result. It is, therefore, preferable over others due to its performance characteristics.

The procedure for Na_2O_2 sintering is hereafter outlined. About 0.1 g of dried and milled sample is exactly weighted into glassy carbon crucibles and each of them is thoroughly mixed with 0.6 g of fine powdered Na_2O_2 by a glass stirrer. The carbon crucibles are then heated in a muffle furnace at 480 °C for 30 minutes. Afterward, they sample crucibles are allowed to cool down to room temperature. The crucibles are washed from outside with Milli-Q water to remove any kind of possible exterior deposition due to heating. Carbon crucibles are kept in Teflon backers covered with glass lids and again heated on a hot plate (90 °C) along with magnetic stirrer stirring at 250 rpm for 30 minutes. Milli-Q water is added drop-wise in the crucibles till the reaction ceases and no more vapour is visible, which earlier is being accumulated on glass lids. The following reaction occurs:

$$2\ Na_2O_2 + 2\ H_2O \rightarrow 4\ NaOH + O_2$$

The solution is poured to the 50 ml PP centrifugation tubes and centrifuged at 4000 rpm for 5 minutes. The clear solution from centrifugation tubes is then poured into a 100 ml volumetric flask, while the solid residue from centrifugation is dissolved by 3 ml of 3M HCl. In parallel, 2 ml of conc. HCl (reagent grade) is added to all the crucibles to get sinter cake dissolved. All the solutions from the centrifuge tubes, Teflon backers and carbon crucibles are finally poured into 100 ml labelled flasks. The resulting solution is diluted to the mark with Milli-Q water after rinsing centrifuge tube, backer, and crucible. The flasks are closed with their stoppers, the solution mixed by gentle shaking and the final clear solution is poured into the tubes for further treatment (i.e., dilution, standard addition) required for ICP-MS analysis.

During our measures of incineration ash samples, exactly 1 ml of clear solution is used and further diluted up to 5 ml total with 1% HNO_3, while 100 µl In/Re (100 ppb) and 50 µl Ge (1 ppm) are added as internal standards. Blank solutions and selected reference materials (RM: MRH, SdAr-1) were also treated with the same procedure before final measurements by ICP-MS. The RMs allowed evaluating analytical uncertainties.

The analytes determination was satisfactory for most of the elements with excellent detection limits (at the ppb level), but the analysis of PGE mass fractions was challenging due to isobaric interferences. As a fact, the interferences of Ni, Cu, Cd, Cl, Sb, and Pb, typically hosted in high amounts within MSWI samples, hampered a reliable PGE quantification. Moreover, the lack of a comprehensive dataset of measurands in certified RM for MSWI ashes led to a weak determination. As a consequence, a comparison with a different technique might help assessing the integrity of PGE data from MSWI samples; isotope dilution (ID) with High Pressure Asher (HPA) acid digestion coupled with ICP-MS measurements is used. The following section provides essential information about this technique.

5.1.3 Isotope dilution with High Pressure Asher (HPA) acid digestion coupled with ICP-MS

As main advantages, the HPA-ID allows determining Re, has low level blanks, lower detection limits and, hence, better precision in low-level homogeneous samples (Savard *et al.*, 2010). We aimed to determine PGE concentrations by High Pressure Asher digestion (HPA-S; Anton Paar, Graz, Austria) followed by online separation and quantification by ID, as in Meisel *et al.* (2003). First, the production of a PGE-spiked solution is necessary. An ideal spike has the following characteristics: freedom of isobaric and molecular interference, highest possible enrichment of one isotope that has a low abundance in the natural element, and minimized total uncertainty of the concentration determination. The procedure of calibrated spike production can be found elsewhere (Savard *et al.*, 2010, Meisel *et al.*, 2001). Up to 2 g of finely powdered samples were weighed into 90 ml quartz glass vessels. There has been concern that OsO_4 could escape before the vials are sealed, thus it has been suggested pre-cooling acids in a regular refrigerator before adding them to the HPA-S vessels is sufficient (Meisel *et al.*, 2001). An appropriate amount of spike was added followed by 2 ml of cooled conc. HCl and 5 mL of conc. HNO_3 was added before closing the vials. After adding 2 ml of conc. HCl and 5 ml of conc. HNO_3 the vials were immediately sealed with Teflon tape and a glass lid and heated in the HPA-S, by following a setup of heating (at 300 °C and a pressure of ca. 125 bar during three hours) and slow cooling down (until room conditions). Soon after cooling, the samples were processed for Os immediately to avoid the dispersion of volatile Os. In fact, OsO_4 can be purged by directing the carrier gas of the ICP-MS through the vial filled with the solution recovered from the quartz glass vessels (Hassler *et al.*, 2000). Although dropping exponentially, the intensities remain sufficiently high to determine the Os concentration by determining the isotope ratios ($^{187}Os/^{188}Os$) that can be determined with adequate accuracy for geochemical purposes. The Os concentration of MSWI samples was immediately detected by direct OsO_4 sparging into the plasma torch with an argon gas flow. For Os measurements selected RMs and matrix matched RMs were used: BCR176, BCR176R, NIST1633a, and WPR-1.

On the other hand, the analysis by HPA-ID-ICP-MS of other PGE mass fractions from MSWI samples is still in progress. After Os measurements, the procedure continued by drying samples on a hot plate at 70–80 °C until the complete evaporation of the liquid phase. The residue was eluted with 2–10 ml of 0.1M HCl. After centrifugation, 0.2–1 ml of the solution was introduced into a 1-m long cation exchanged resin column previously washed with 6M HCl and equilibrated at 0.1 M HCl. The column was directly attached to the ICP-MS for online separation (Fig. §1-5). A multiple PGE-Au and Re stock solution (SCP Science, Canada) was used to monitor the mass drift. The isotopes used for quantification through ID were ^{101}Ru, ^{106}Pd, ^{186}Re, ^{188}Os, ^{193}Ir and ^{196}Pt.

The method limit of detection cannot readily be calculated for HPA-ID because the result is obtained by a summation of the signal integrated over a period of time that can vary. The uncertainty is dominated by sample inhomogeneity rather than that of the analytical technique. In general, limits of detection are about one order of magnitude lower than for nickel-sulphur fire assay technique, which is also widely used for PGE quantification.

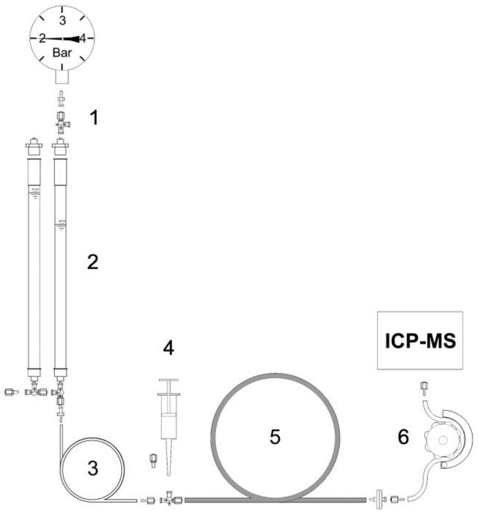


Fig. §1-5 Schematics of the on-line chromatographic set up from Meisel *et al.* (2003). (1) Application of 2 bar N_2 pressure, (2) 0.1M HCl reservoir (eluant), (3) sample loop ca. 2 ml, (4) sample introduction, (5) cation exchange column (1 m) and (6) peristaltic pump.

5.1.4 Chemical and mineralogical characterisation: other analytical methods

Other analytical results were used either for the preliminary characterisation or as complementary information, helped to drive and validate the main analytical work. For chemical characterisation Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and gas chromatography were used, whereas X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) allowed the identification of mineral phases and organic compounds. Moreover, I performed morphological observations by Electron Microprobe (EMP) and Scanning Electron Microscope (SEM) and semi-quantitative chemical analysis through Energy Dispersive Spectrometer (EDS) coupled to these analysers. Actually, the outcomes in Chapter 4 partly derive from ICP-AES and SEM analysis. Data from other analytical methods are not shown.

5.2 Strategic tools for prospecting: Substance flow analysis

Material flow analysis (MFA) is a systematic assessment of the flows and stocks of materials within a system defined in space and time (Brunner & Rechberger, 2004). It connects the sources, the pathways, and final sinks of a material. Because of the law of the conservation of matter, the results of an MFA can be controlled by a simple material balance comparing all inputs and outputs of a process. The input-output method has been recently incorporated into Life Cycle Assessment (LCA) to establish the economic input–output LCA method. In the last decades, solid waste LCA models or MFA are often used to evaluate the environmental and financial consequences of various waste management strategies (e.g., Brunner & Mönch, 1986; Fellner *et al.*, 2015).

In MFA, the term *Material* stands for both substances and goods. When using geochemical data and modelling flows of elements the term *Substance* is more appropriate, as broadly ascertained. Therefore, Substance Flow Analysis (SFA) has been used in the present study.

5.3 Magnetisation and magnetic methods

Magnetic susceptibility measurement issued in Chapter 3 was carried out at the Institute of Marine Sciences of the National Research Council (ISMAR-CNR) by using a MS2 Bartington meter. The exact sample mass was recorded and magnetic susceptibility values (k) on MS2 display were noted. Mass specific magnetic susceptibility (x) was calculated with the following formula:

$$X = (k \cdot 10)/(\text{mass of sample (g)})$$

Magnetisation which occurs as a response of an externally applied magnetic field M*i* is known as induced magnetization. The ratio between the induced magnetization, M*i*, and magnetic field, H*a*, is called magnetic volume susceptibility which is denoted with k.

$$\kappa = M_i/H_a$$

Dividing volume susceptibility by density gives specific susceptibility X.

$$X = k/\rho \ [m^3/kg]$$

In general, magnetic methods are widely used in geology for paleo-environmental reconstruction as the magnetisation is a sensitive tracer of the time when a rock formed. Magnetic measures are also sensitive to elements, especially heavy metals, and to grain size (e.g., ultra fine particles). It has been suggested to apply magnetic characterisation to environmental impact assessment. Heavy metals have affinity to form metallic bonding with ferrous material which leads to increase the magnetic susceptibility. Heavy metals are incorporated in ferromagnetic material during combustion process or they get adsorbed on the surface of ferrimagnetic materials already existing in the environment (Chaparro *et al.*, 2004). A correlation between magnetic data and concentrations of heavy metals is often observed (Maier & Scholger, 2004, Reyes *et al.*, 2011). Researchers have been trying to use magnetic susceptibility measurement as a tool to map areas with higher heavy metals contents and to study lithological and pedological impact on magnetic susceptibility (Hanesch & Scholger, 2002).

Interestingly, magnetic properties are very susceptible to specific minerals and elements (e.g., magnetite, Gd); fact that aimed to suggest the magnetic susceptibility correlates with metals of economic interest (such as REE) and can be helpful for quick mineral prospecting.

5.4 Methods for separation, upgrading and treatment of MSWI residues

In the present section I report an overview of potential methods for the treatment, metal separation and mineral beneficiation of MSWI residues. The detailed experimental procedures for metal upgrading/recovery is not addressed in this section because it is reported in the next chapters 2 and 4 and relative supplementary materials.

A number of processing techniques of BA and FA from MSWI have been proposed both to minimise harmful metals release (improve the environmental status of the residue) and recover metals of economic interest. MSWI residues are commonly treated with separation techniques, followed sometimes by thermal treatments or stabilisation/solidification (e.g., Adam *et al.*, 2009; Jakob *et al.*, 1996; Nowak *et al.*, 2010; 2012) (Tab. §1-3). Separation technologies consist of physical-mechanical separation and chemical processes.

Tab. §1-3 Main processing options for prior to utilisation of final disposal of MSWI residues (modified from Sabbas *et al.*, 2003).

Physical separation	Chemical separation	Stabilisation treatment	Thermal treatment
Size separation	Washing	Ageing/weathering	Sintering
Size reduction	Acid extraction	Carbonation	Vitrification
Magnetic separation	Alkaline extraction	Chemical stabilisation	Pyrolysis
Eddy current	Solvent extraction	Blending with cement	
	Combined extraction	Pelletizing	

5.4.1 Overview on physical-mechanical separation methods

Physical and mechanical treatments of MSWI residues are widely used 1) to recover scrap metals, 2) to improve the residual ash quality for its reuse as construction material or geopolymer, 3) to obtain any mineral beneficiation prior to hydrometallurgical processes. Iron, aluminium, copper and other base metals, with different grades of purity, can be obtained (especially from bottom ashes) by physical-mechanical separation incorporating drying, crushing, sieving, magnetic separation and eddy current separation. The magnetic separation methods are mainly used for separating metallic scraps, iron minerals from MSWI residues. Commonly used magnetic machines are cross-belt magnetic separator, drum magnetic separator and magnetic pulley separator. In the investigated MSWI facilities a drum magnetic separator recovers the biggest metallic scraps before the BA are piled up. Several systems divide ferromagnetic and non-ferromagnetic fractions of BA with relatively high efficiency. The former (almost iron) can be successfully recovered, while the non-ferrous fraction is further treated to recover, for example, Al and Zn. Ferrous and non ferrous metals are present in a range of 7-15% and 1-2%, respectively (Sabbas *et al.*, 2003). Further thermal treatments such as vitrification by re-melting (1200-1400°C) are suitable to destroy organic contaminants and stabilise inorganic compounds. However, thermal methods are rarely applied due to the high energy consumption.

5.4.2 Chemical separation: hydrometallurgy and bio-hydrometallurgy

Hydrometallurgical separation methods are those in which one, or more, of the phases related to the process is aqueous. The process chains of modern hydrometallurgy developed starting from the 19th century. Hydrometallurgical solutions are typically generated by dissolving metals present in the raw materials in acids or bases. Metals are separated in the dissolution step, the so-called *leaching*, when one or more of the metals are not soluble in the solvent used. Hydrometallurgical separation is also performed by solvent extraction or by means of solid ion exchangers, ionic liquids, membranes, and adsorption capacity of other materials. Once the metals have been separated from each other, pure metal can be produced for example by precipitation, cementation or electrowinning. Nevertheless, the reverse process of the leaching, i.e., production of a solid precipitate, is also widely used as a separation method and it can be part of the process chain. Biohydrometallurgy, i.e., a hydrometallurgical extraction enhanced by microorganism, is a widely studied (and with increasing interest) branch of hydrometallurgy and successfully employed in the treatment of mines and plants tailings, and in metal recovery from secondary sources. As a matter of fact, the industrial utilisation of bioleaching already started in the end of 19th century: Rio Tinto copper mine in South-Western Spain was considered the first large-scale biohydrometallurgical operation; during 1950-1980 bioleaching was utilized in heaps and from 1980 onwards in heaps and dumps (Bosecker, 1997). During the last decades, bio-mediated processes were progressively increased also for the treatment of by-products (e.g., for recovery of gold from tailings in Nerco Can Mine, Canada; Stefanski & Martin, 1992).

The falling grade of primary ores due to the intense exploitation has lead to develop fine-tuned bio- and hydrometallurgical methods, which are often more suitable than thermal treatments in terms of process economics and recovery performances. As the concentrations of ore metals in anthropogenic deposits such as MSWI waste streams are rather small, and also variable, hydrometallurgical methods are suitable for the treatment of such materials because they are more flexible than, for example, pyrolysis methods. Both bio-hydrometallurgical procedures can prove beneficial to decontamination of industrial waste and mine tailings, coupling metal recovery with environmental remediation. Commercial bio- and hydrometallurgical applications for secondary raw materials have been recently reviewed by Meawad *et al.* (2010) and Lee *et al.* (2012).

5.4.3 Leaching and leachability

During the leaching procedures, minerals or group of metals dissolve by varying thermodynamic conditions. Typical leaching reagents include water, mineral acids (H_2SO_4, HCl, etc.), bases (NaOH, NH_4OH), organic acids (e.g., maleic acid) salt solutions and combinations of these. Processes can be optimised by changing temperature, pressure, reaction time, but also by the addition of oxidizing (H_2O_2, Cl_2, HClO, NaClO) or reducing (Fe^{2+}, SO_2) agents. Equilibrium and kinetics of leaching are often favoured in aggressive conditions (e.g., elevated temperature and/or pressure, strongly acidic/alkaline environment). Among leaching methods, heap leaching, dump leaching (heap without crushing), reactor leaching, vat leaching, autoclave leaching (high pressure and temperature) and in-situ leaching (extractant pumped directly in the ore deposit) are the most used.

Also, microorganisms can enhance the leaching. An excellent overview on suitable microorganisms for metals recovery was provided by Rawlings (2002) and recent edited books cover a number of specific topics in biohydrometallurgy (Rehm and Reed, 2001; Donati and Sand, 2007; Rawlings, 1997; Rawlings and Johnson, 2007) to which the reader can refer for further information. Generally, bacteria can favour the metal solubility mostly by producing acid or by oxidisation mechanisms of Fe^{2+} to Fe^{3+}. As a consequence, bioleaching demonstrates potential to reduce operating costs compared to conventional leaching processes. It seems also an environmentally sustainable process, since the use of strong chemicals, energy and aggressive conditions are reduced.

Other methods that have been tested to improve the performance of conventional leaching are, for example, microwave- and ultrasound-assisted leaching.

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Chapter 2

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

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Highlights:

- The elements composition of bottom and fly ashes from 2 Italian MSWI is investigated.
- We conducted a substance flow analysis for critical elements and other metals.
- Many of critical elements are enriched in specific grain-size fractions.
- An onsite procedure to improve the relative recovery efficiency is suggested.
- Waste from MSWI might represent a low-concentration stream of valuable elements.

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 of 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.

Keywords: MSWI fly and bottom ash; Critical elements; Gravitational partitioning; Substance flow analysis.

1. Introduction

The European waste policy discourages waste landfill in favour 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 incineration (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 (Hu *et al.*, 2009; Jung and Osako 2009a; Muchova *et al.*, 2009). Recently, the European Commission (2010; 2014) 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 (PGE), 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 Moench, 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.*, 2015), 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 methods

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 85000 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 and 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 hours 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. Other outputs besides BA and FA, e.g., iron scrap from preliminary separation, off-gases, are accounted separately and do not affect the balance of the SFA for BA and FA.

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) and also successfully adopted for the management of incineration waste in France (SVDU, 1995). 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 grain-size analysis on primary samples conducted for the two plants (Fig. §2-1). 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 full big bags and blended from a large number of increments in order to reach representativeness. FA samples are very fine-grained with very low moisture content, i.e. < 1 wt. %. They were oven-dried at 40°C overnight.

For our study we did not average samples taken over a longer period. Although BA were collected about seven months earlier than FA, the latter were collected before the system cleaning and we assumed it is comparable to BA because of the low output flow rate of FA. The equipment of the selected MSWI plants did not allow to collect FA residues corresponding to the same BA mass burning.

The chosen samples of BA and FA were homogenized with an agate vibratory disk mill for 30 min and milled again with an agate mortar until the whole material had size <40 μm within one week after sampling. Only a few coarse metallic objects (>1 cm), which could not be size reduced, were removed from BA samples in order to pulverise the “fresh” BA materials, including the sub-centimetric fragments of metal.

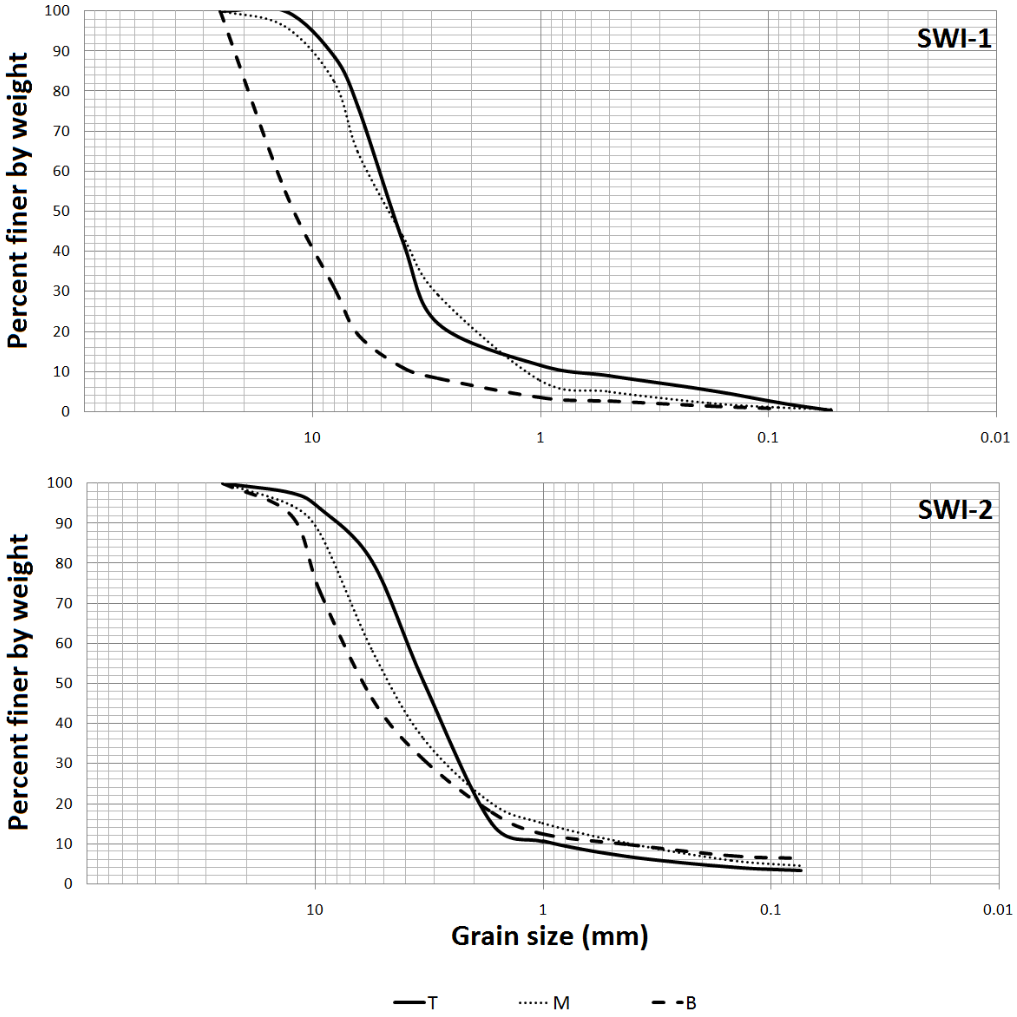


Fig. §2-1 Grain-size analysis of the sampled material in bottom (B), intermediate (M) and top (T) layers of the stratified simple random sampling method, for SWI-1 and SWI-2.

2.3 Analytical techniques

The bulk chemical composition of milled material was obtained by X-ray fluorescence spectrometry (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) techniques.

2.3.1 X-ray fluorescence spectrometry

Major (> 1 g/100g), minor (0.1 to 1.0 g/100g) and trace (< 0.1 g/100g) element analyses were performed on the bulk sample of each layer (B, M, T) for the two selected MSWI plants. The total number of analysed samples is 18, three samples for each layer. The total elemental chemistry was determined on thin layer pressed powder pellet (φ 37 mm) in boric acid binder, using three grams of the dried and milled sample. A sequential wavelength dispersive X-ray fluorescence (XRF) spectrometer (Axios-Panalytical), equipped with a 4 kW Rh tube and SuperQ 3.0 software, was used at the Department of Biological Geological and Environmental Sciences - Geology Division of the University of Bologna. The estimated precision for major and trace element determinations are better than 5% except for those elements ≤10 mg/kg (10–15%). Total loss on ignition (LOI) was gravimetrically estimated after overnight heating at 950°C. The following elements were analysed by XRF: Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, As, Ba, Ce, Co, Cr, Cu, Ga, La, Mo, Nb, Nd, Ni, Pb, Rb, Sc, Sm, Sn, Sr, V, Y, Zn and Zr.

2.3.2 Inductively coupled plasma spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) was used for the determination of the total elemental composition of FA samples (from both MSWI plants; 2 samples each) and BA samples (from SWI-1 layers; 3 samples each, 9 in total).

For BA analyses, 0.2 g dried and milled sample were totally digested with high purity grade HNO_3, $HClO_4$ and HF (Merck, Darmstadt, Germany) on a hot plate at 170°C until the digested solution was clear. Final H_2O_2 treatment followed the digestion procedure to dissolve the carbonic refractory fraction. Dissolved samples were dried out and then diluted to the mark in ultrapure water obtained from a Milli-Q purifier system (Millipore Corp., Bedford, MA, USA). The analyses were carried out using an X-Series Thermo-Scientific spectrometer at the Department of Physics and Earth Sciences of the University of Ferrara. Specific amounts of Rh, Re and In were added to the analysed solutions as an internal standard, in order to correct for instrument drift. The precision, based on replicated analyses of samples and standards, is estimated as better than 10% for all elements well above the detection limit.

FA samples were analysed at the department of General and Analytical Chemistry of Montanuniversität Leoben using the Na_2O_2 sintering technique (Meisel *et al.*, 2002) as a method of total digestion. For the digestion 0.1000 g of dried and milled samples were weighed into glassy carbon crucibles and each of them were mixed thoroughly with about 0.6 g of fine powered Na_2O_2 by a glass stirrer. The carbon crucibles were sintered in a muffle furnace at 480°C for 30 minutes, then they were allowed to cool down to room temperature. After cooling, crucibles were kept in Teflon beakers. Milli-Q water was added drop-wise in the crucibles till the reaction ceased. The Teflon beakers were heated again (90°C) along with magnetic stirrer stirring at 250 rpm for 30 minutes. The final solution was centrifuged at 4000 rpm for 5 minutes. The clear solution from centrifugation tubes was poured into a 100 ml volumetric flask, while 2 ml of concentrated HCl (reagent grade) and 3 ml of 3 mol/l HCl were added to the crucibles and the residues obtained after centrifugation, respectively, to dissolve the precipitates. All the solutions were poured from centrifuging tubes, Teflon beakers and crucibles into the respective labeled flasks and diluted to the mark (up to 100 ml). One ml of the final solution was taken for ICP-MS measurement and further diluted up to 5 ml total with 1% of HNO_3. 100 µl of In/Re (100 ppb) and 50 µl of Ge (1 ppm) were added as internal standard. Blank solution and reference materials were also treated similarly before final measurements with ICP-MS.

2.4 Substance flow analysis

An estimation of substance flow (Brunner and Rechberger, 2004) for SWI-1 BA and FA was carried out on single output products and their grain size fractions. The substance flow analysis allows to determine the annual flow of commodities within output products and the transfer coefficient from inputs to outputs. The spatial system boundary for the experiment was the MSWI process itself, from the waste collection to output products, and included the sampling and the preliminary samples clustering in grain size fractions. The temporal system boundary was defined as one year, assuming that the sampled material is representative for one year process activity (i.e., 2013).

For the calculation of total annual flow for BA and FA we used following simple equations:

$$F_{BA} = C_i \cdot O_{BA} \qquad [1]$$

$$F_{FA} = C_i \cdot O_{FA} \qquad [2]$$

Where: F is the annual flow in mass/time, C_i is the measured concentration of element *i* in mass/mass and O is the total output mass/time for the BA and FA.

The evaluation of the uncertainty propagation follows the Gauss' law of error propagation. Since only coarser fractions show strongly deviating data and skewed distribution, we decided to calculate means and error propagation assuming normal distribution. As the annual flow evaluation needs data of high precision in order to minimise the calculation bias, we have considered the ICP-MS results.

The following elements were selected for the annual flow analysis: the *crm* elements Be, Co, Cr, Ga, Mg, Nb, Sb, W, including the REE group (from La to Lu plus Sc and Y), the precious metals gold (Au) and silver (Ag), some metals of high economic importance, according the European Commission (2014), Al, Cu, Fe, Li, Mn, Mo, Ni, Sn, Ta, Ti, V and Zn and other metals, Ba, Bi, Hf, K, Pb, Rb, Sr, Tl and Zr.

Transfer ratios (*K*) of selected *crm* and other valuable metals were calculated by the following equations:

$$K_{FA} = \frac{\mathrm{FA(\%)}\times \mathrm{C}i_{\mathrm{FA}}\mathrm{(mg/kg)}}{\mathrm{BA(\%)}\times \mathrm{C}i_{\mathrm{BA}}\mathrm{(mg/kg)}+\mathrm{FA(\%)}\times \mathrm{C}i_{\mathrm{FA}}\mathrm{(mg/kg)}} \qquad [3]$$

$$K_{BA} = \frac{\mathrm{BA(\%)}\times \mathrm{C}i_{\mathrm{BA}}\mathrm{(mg/kg)}}{\mathrm{BA(\%)}\times \mathrm{C}i_{\mathrm{BA}}\mathrm{(mg/kg)}+\mathrm{FA(\%)}\times \mathrm{C}i_{\mathrm{FA}}\mathrm{(mg/kg)}} \qquad [4]$$

$$K_{BAf} = \frac{\mathrm{BA_f(\%)}\times \mathrm{C}i_{\mathrm{BAf}}\mathrm{(mg/kg)}}{\mathrm{BA(\%)}\times \mathrm{C}i_{\mathrm{BA}}\mathrm{(mg/kg)}} \qquad [5]$$

where: BA% and FA% are the mass flow in percent of the bottom and fly ash residues in the final solid output, respectively. $\mathrm{C}i_{\mathrm{FA}}$ and $\mathrm{C}i_{\mathrm{BA}}$ are the concentration of the element *i* in the respective residue. *K* from FA (K_{FA}) and BA (K_{BA}) final outputs were calculated, in a similar way adopted by Zhang *et al*. (2008a) for the evaluation of the distribution of heavy metals between different types of residues. The equation [5] allows us to calculate the *K* among different fractions of BA (K_{BAf}).

3. Results and discussion

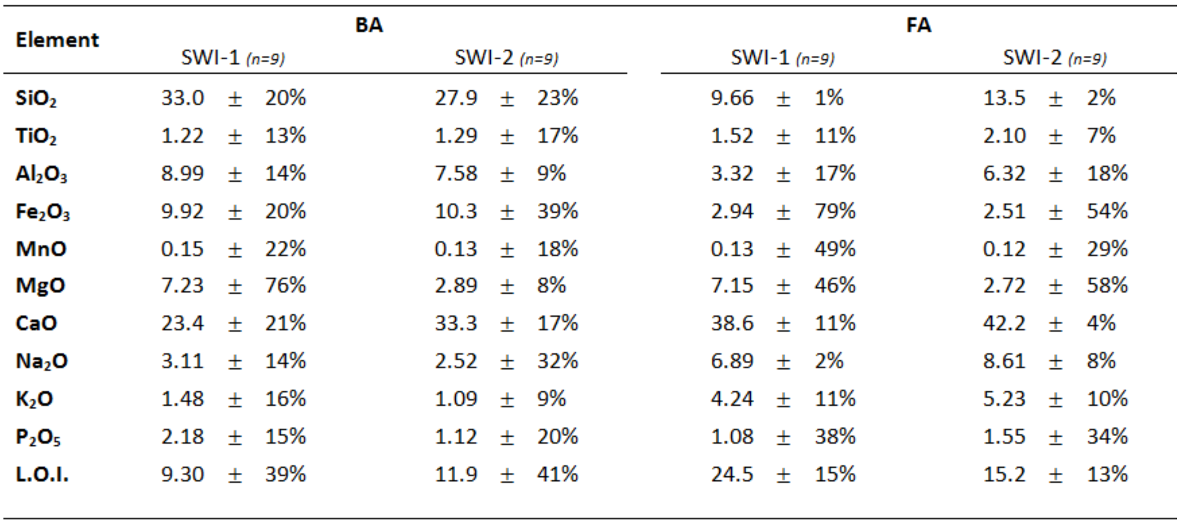
3.1 Bottom ash

SiO_2 and CaO are the main oxides in BA (Tab. §2-1), with concentrations higher than 30 g/100g and 20 g/100g, respectively. The BA contain about 10 g/100g of iron (expressed as Fe_2O_3), about 8 g/100g of Al_2O_3. The contribution of titanium, aluminium, iron and manganese oxides is similar between SWI-1 and SWI-2. The mean values are quite similar and the relative standard deviation ranges between 10 and 40 %, pointing that the material is rather homogeneous. This is probably due to similar waste input and combustion conditions (De Boom & Degrez, 2012). The amount of MgO is higher in SWI-1 rather than SWI-2, with a large variance calculated for the former. Magnesium could derive from metallurgical processes, electronic devices, agricultural fertilizer, chemicals and pharmaceuticals. Therefore it is worthy to note that the waste input to SWI-1 comprises also pharmaceutical/hospital waste.

XRF trace elements analyses of BA samples from SWI-1 and SWI-2 (Tab. §2-2) show high concentrations of the following heavy metals (in decreasing order of abundance): Zn, Cu, Ba, Cr, Pb, Sn and V. Each sample contains more than 2 g/kg of Zn and Cu, over 1 g/kg Ba. Many trace elements show high standard deviation probably due to a random error during sampling operations, e.g. the presence of sub millimeter metallic scraps can affect lead, tin and zinc concentrations. However trace elements concentration are quite similar in SWI-1 and SWI-2 BA residues, only V, Ni and La, show higher values in SWI-1 relative to SWI-2.

ICP-MS data for SWI-1 BA (Tab. §2-3) show a silver mean concentration of 5.5 mg/kg, 0.4 mg/kg Au, 0.6 g/kg as sum of selected *crm* (Be, Co, Cr, Ga, Nb, Sb, W), over 0.1 g/kg ΣREY (REE + Sc + Y), 7.7 g/kg other metals with high economic importance (Cu, Li, Mo, Ni, Sn, Ta, V and Zn - according to EC, 2014). Cerium is the prevailing element of the REE group (31.8 mg/kg), chromium and antimony are the most abundant amongst *crm* elements (0.37 and 0.12 g/kg, respectively). For most of trace elements ICP-MS measured concentrations are in good agreement with XRF data of this study (see Tab. §2-2) and within the ranges quoted in the literature (Tab. §2-3). Moreover, the untreated samples composition is comparable to the Danish and Swiss treated residues, analysed by Allegrini *et al*. (2014) and Morf *et al*. (2013), revealing that the post-treatment (i.e., separation between ferrous and non-ferrous material) of BA leads to a weak mineral beneficiation.

Tab. §2-1 *Major elements concentration of bottom (BA) and fly ash (FA) samples from the selected incinerators (SWI-1 and SWI-2) by XRF. Average values are reported in g/100g of oxides with relative standard deviation (%) for n number of samples. Loss of ignition (L.O.I.) value is also provided.*



Element	**BA**		**FA**	
	SWI-1 *(n=9)*	SWI-2 *(n=9)*	SWI-1 *(n=9)*	SWI-2 *(n=9)*
SiO_2	33.0 ± 20%	27.9 ± 23%	9.66 ± 1%	13.5 ± 2%
TiO_2	1.22 ± 13%	1.29 ± 17%	1.52 ± 11%	2.10 ± 7%
Al_2O_3	8.99 ± 14%	7.58 ± 9%	3.32 ± 17%	6.32 ± 18%
Fe_2O_3	9.92 ± 20%	10.3 ± 39%	2.94 ± 79%	2.51 ± 54%
MnO	0.15 ± 22%	0.13 ± 18%	0.13 ± 49%	0.12 ± 29%
MgO	7.23 ± 76%	2.89 ± 8%	7.15 ± 46%	2.72 ± 58%
CaO	23.4 ± 21%	33.3 ± 17%	38.6 ± 11%	42.2 ± 4%
Na_2O	3.11 ± 14%	2.52 ± 32%	6.89 ± 2%	8.61 ± 8%
K_2O	1.48 ± 16%	1.09 ± 9%	4.24 ± 11%	5.23 ± 10%
P_2O_5	2.18 ± 15%	1.12 ± 20%	1.08 ± 38%	1.55 ± 34%
L.O.I.	9.30 ± 39%	11.9 ± 41%	24.5 ± 15%	15.2 ± 13%

Tab. §2-2 Trace elements concentration of bottom ash (BA) samples (from SWI-1 and SWI-2) by XRF. Average values reported in mg/kg with relative standard deviation (%) for 3 samples each sampled layer.

Element	Sampled layers of BA (SWI-1)			Sampled layers of BA (SWI-2)		
	B	M	T	B	M	T
As	9.4 ± 67%	4.2 ± 24%	6.2 ± 25%	3.3 ± 17%	2.9 ± 10%	11.0 ± 24%
Ba	1122 ± 14%	1110 ± 22%	1042 ± 16%	666 ± 17%	1232 ± 65%	583 ± 4%
Ce	23.7 ± 51%	25.8 ± 49%	35.6 ± 38%	19.7 ± 11%	32.3 ± 57%	30.1 ± 13%
Co	22.7 ± 61%	26.6 ± 16%	24.7 ± 20%	25.7 ± 66%	25.3 ± 45%	31.0 ± 14%
Cr	606 ± 31%	590 ± 16%	426 ± 34%	568 ± 11%	695 ± 14%	640 ± 12%
Cu	2459 ± 30%	2549 ± 29%	2452 ± 30%	3068 ± 91%	1907 ± 55%	2599 ± 27%
Ga	9.4 ± 25%	9.7 ± 38%	9.0 ± 35%	6.7 ± 35%	6.7 ± 9%	14.3 ± 12%
La	14.1 ± 42%	16.5 ± 36%	17.1 ± 33%	6.3 ± 18%	8.3 ± 45%	12.7 ± 30%
Mo	15.2 ± 29%	20.0 ± 12%	20.6 ± 25%	8.7 ± 13%	8.7 ± 18%	10.1 ± 34%
Nb	12.4 ± 31%	15.8 ± 34%	16.3 ± 27%	6.7 ± 9%	6.0 ± 33%	12.6 ± 8%
Nd	8.7 ± 37%	9.8 ± 24%	11.2 ± 36%	8.3 ± 7%	10.0 ± 30%	22.8 ± 9%
Ni	163 ± 28%	184 ± 17%	233 ± 23%	98.3 ± 23%	103 ± 36%	139 ± 12%
Pb	354 ± 30%	611 ± 13%	452 ± 23%	543 ± 46%	820 ± 17%	1026 ± 39%
Rb	25.5 ± 20%	33.0 ± 15%	32.0 ± 17%	22.3 ± 3%	19.7 ± 13%	44.3 ± 17%
Sc	14.3 ± 17%	8.8 ± 8%	13.5 ± 4%	9.1 ± 11%	7.5 ± 9%	9.7 ± 4%
Sm	1.8 ± 6%	1.6 ± 4%	2.5 ± 5%	1.5 ± 47%	2.0 ± 1%	7.0 ± 11%
Sn	358 ± 81%	157 ± 12%	184 ± 27%	183 ± 32%	224 ± 32%	128 ± 24%
Sr	356 ± 16%	392 ± 5%	402 ± 4%	376 ± 20%	857 ± 92%	469 ± 13%
V	132 ± 23%	222 ± 3%	254 ± 6%	30.7 ± 9%	31.7 ± 10%	52.7 ± 12%
Y	15.0 ± 5%	13.0 ± 12%	16.8 ± 10%	13.3 ± 9%	13.3 ± 9%	10.3 ± 31%
Zn	3443 ± 27%	2912 ± 32%	2971 ± 24%	3748 ± 53%	3303 ± 42%	2259 ± 26%
Zr	165 ± 32%	210 ± 42%	232 ± 27%	140 ± 41%	204 ± 53%	205 ± 12%

Tab. §2-3 Average content of bottom (BA) and fly ash (FA) samples from SWI-1 plant by ICP-MS compared with literature ranges, upper continental crust (UCC) mean values and typical ore concentrations. Major elements (from SiO_2 to P_2O_5) are reported in g/100g of oxides, minors and traces (from Ag to Zr) in mg/kg.

	MSWI, Italy		Literature data (BA) [a]	Literature data (FA) [a]	UCC [b]	Ore concentration [d]	Active mines (2013) in Fennoscandia [e]
Element	*This study*		*min-max*	*min-max*	*Average*	*min-max*	*min-max*
	BA	*FA*					
SiO_2	32.5	13.9	9.1-30.8 (10)	2.4-23.6 (9)	66.6	-	-
TiO_2	1.24	1.42	0.3-1.8 (10)	0.53-1.5 (8)	0.64	-	1.67-11
Al_2O_3	8.89	5.58	1.9-11.0 (11)	1.8-8.18 (9)	15.4	-	-
FeO	9.84	1.99	0.4-15.0 (11)	0.6-4.83 (9)	5.04	-	27.2-53.9
CaO	23.4	38.6	1.2-24.0 (11)	8.6-32.2 (9)	3.59	-	-
MnO	0.19	0.11	0.001-0.41 (11)	0.02-0.27 (9)	0.10	-	0.03-1.98
MgO	2.53	3.66	0.04-3.1 (11)	0.82-3.1 (8)	2.48	10-40	-
K_2O	1.49	4.72	0.08-1.6 (11)	1.3-10.0 (9)	2.80	-	-
Na_2O	3.11	6.89	0.3-4.2 (11)	1.6-10.38 (9)	3.27	-	-
P_2O_5	2.18	1.45	0.1-2.4 (9)	0.4-2.49 (8)	0.15	-	1.15-17.63
Ag	5.51	19.3	<0.29-36.9 (3)	3.9-34 (3)	0.05	-	1.3-151
As	11.9	21.1	0.12-189 (12)	0.7-307 (4)	4.80	1000-40000	-
Au	0.44	0.58	<0.11-2.2 (4)	<1-2.2 (2)	0.002	<5-30	0.008-5.2
Ba	1404	970	69-3990 (12)	12-1870 (8)	628	590000	-
Be	0.56	-	1.2-6 (2)	2.4-7.6 (1)	2.10	3000-50000	-
Bi	2.28	51.2	0.35-57 (2)	6-150 (3)	0.16	-	-
Cd	5.62	114	0.35-70.5 (11)	72-456 (5)	0.09	1000-10000	-
Ce	31.8	20.0	15.1-51.0 (10)	2.85-18 (5)	63.0	18000-300000	-
Co	35.4	21.0	6-350 (10)	6.7-262 (4)	17.3	500-3000	150-2300
Cr	367	635	20.4-3170 (11)	120-2026 (5)	92.0	310000	200000
Cs	1.51	4.80	0.78-15.3 (3)	9.0-110 (1)	4.90	-	-
Cu	3490	952	190-25100 (12)	330-5530 (9)	28.0	5000-20000	1000-26700
Dy	1.87	0.96	0.79-3 (3)	0.16 (1)	3.90	430-47000	-
Er	1.26	0.60	0.72-2 (3)	0.39 (1)	2.30	13-29000	-
Eu	0.92	0.71	0.25-1 (5)	0.06-2 (2)	1.00	220-1100	-
Ga	14.5	7.88	7.84-24 (4)	3-18 (3)	17.5	100-1000	-
Gd	2.43	1.29	1.7-5.03 (3)	0.59-2.6 (2)	4.00	650-21000	-
Hf	2.70	1.44	2.33-42.0 (2)	-	5.30	-	-
Ho	0.39	0.26	0.30-0.43 (2)	0.18 (1)	0.83	16-11000	-
La	18.8	11.6	2-30.5 (5)	1.76-6.6 (2)	31.0	2600-180000	-
Li	26.6	23.7	-	40-110 (1)	24.0	-	-
Lu	0.17	0.08	0.02-0.17 (2)	<1 (1)	0.31	<2200	-
Mo	16.5	20.4	2.5-280 (3)	4.6-489 (4)	1.10	<10000	26-70
Nb	14.8	10.5	2-12 (2)	12-16 (1)	12.0	4100-21000	3400-3800
Nd	12.1	7.15	6.4-20 (4)	1.35-7 (2)	27.0	6000-98000	-
Ni	224	85.9	7-4280 (12)	17-614 (6)	47.0	15000-30000	700-73300
Pb	1517	2987	74.7-13700 (12)	640-5500 (9)	17.0	300000-400000	4000-70000
Pr	3.35	1.95	1.78-5.5 (3)	0.53 (1)	7.10	1600-33000	-
Sb	119	1022	7.6-432 (7)	59-2107 (6)	0.40	27000	1000-25000
Sc	10.2	4.59	1.3-22 (4)	0.6-4 (2)	14.0	20-130000	-
Sm	2.26	1.29	1.32-5 (4)	<0.1-1 (2)	4.70	690-16000	-
Sn	201	713	2-470 (6)	240-5880 (7)	2.10	4000	-
Sr	440	429	85-1000 (9)	150-740 (7)	320	-	-
Ta	1.12	1.19	2.47-14.2 (4)	1.2-43 (1)	0.90	<410	260-310
Tb	0.41	0.29	0.18-3 (4)	0.07-2 (2)	0.70	45-53000	-
Tm	0.16	0.08	0.01-0.18 (2)	-	0.30	3-4900	-
U	1.45	0.91	0.75-1.97 (2)	-	2.70	-	17
V	196	19.7	20-122 (6)	<10-86 (4)	97.0	500-13000	-
W	20.8	8.77	9.7-40.4 (6)	6.2-629 (3)	1.90	<15000	-
Y	14.3	9.88	2.0-79 (5)	0.9-14 (3)	21.0	-	-
Yb	1.10	0.52	0.55-5 (3)	0.20-2 (3)	1.96	3-34000	-
Zn	3562	13417	10-20000 (11)	3800-16800 (8)	67.0	50000-150000	4400-110000
Zr	108	71.4	41-1200 (9)	20-480 (4)	193	-	1600

a: the number of literature sources used to define the range in the tables is reported in parentheses. The sources were: Allegrini et al. (2014), Hasegawa et al. (2014), Sekito et al. (2014), De Boom and Degrez (2012), Bayuseno and Schmahl (2010), Muchova et al. (2009), Hyks (2008), Zhao et al. (2008), Chung et al. (2007), Jung and Osako (2007), Wan et al. (2006), Fujimori et al. (2004), Chandler et al. (1997), Kida et al. (1996).

b: the upper continental crust (UCC) mean values are from Rudnick & Gao (2014).

c: ore concentrations are from Allegrini et al. (2014) and reference therein.

d: concentration reference of active mines (2013) in Fennoscandia from Geological Survey of Finland (GTK-website: http://en.gtk.fi/).

The "-" means data not available.

3.1.1 Gravitative selection control on partitioning of critical elements

The simple gravitative selection of the stockpile drives the distribution of the elements. The total content of Zn, Cu and Ba is more abundant in the B layer as far over 1 g/kg. Ni, V and Zr concentrations range between 0.10 and 0.25 g/kg, with the T layer enriched compared to the others.

Fig. §2-2 shows the elements distribution within the sampled layers of SWI-1: Ag, Ce, La, Nb, Sb and Mo preferentially partition in the finer fractions, as the most of REE, whereas Cr and Gd are relatively enriched into the coarser fraction of the bottom layer. About 0.5 mg/kg gold and 7 mg/kg silver are found in the top layer, as well around 15 mg/kg La, Nb and Nd. Conversely, Au, Co, Ga, Sc, Ta and Y seem to be less influenced by grain size.

These results suggest that the potential recovery of some elements could be simplified by treating specific grain size fractions, readily distinguishable on the storage piles. XRF analyses on sieved samples are provided in the Supplementary Materials of Chapter 2 to further confirm the hypothesis of the grain size control on the distribution of some *crm*. Therefore, the visual aid sampling may represent a good choice when any mineral beneficiation is required before the elements recovery is planned from low concentration streams. Moreover this primary separation onsite, which could be performed by unskilled operators, is cost-effective because require no further devices, whose implementation could be expensive especially for old MSWI systems. In section *3.3 Estimated annual flow of SWI-1 residues* we report an estimation of annual substance flow for BA sampled fractions.

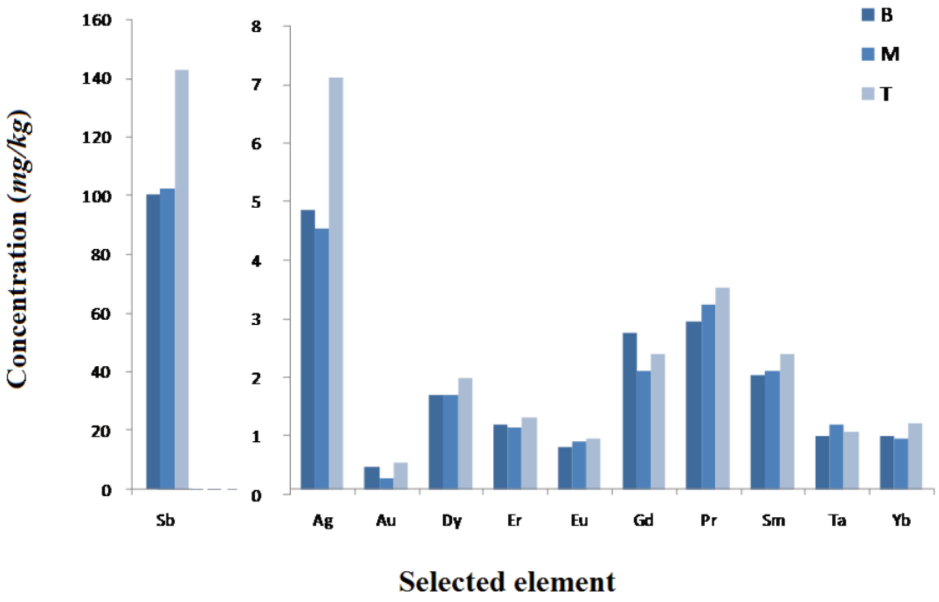


Fig. §2-2 *The distribution of selected crm (including REE) and precious metals in B, M and T layers of the stratified simple random method, by ICP-MS. Concentrations are in mg/kg.*

3.2 Fly ash

The major constituents of FA samples (Tab. §2-1) are CaO (>30 g/100g), SiO_2 (>10 g/100g), Al_2O_3, MgO and K_2O (around 5 g/100g), Fe_2O_3, TiO_2 and P_2O_5 (< 3 g/100g). Lithophile elements such as silicon, aluminum and calcium, which form very stable oxides and anions and have high boiling point are more concentrated in BA rather than in FA (see Tab. §2-1).

FA contain a high amount of the *crm* elements Sb (around 0.1 g/kg) and Cr (around 0.6 g/kg), as well as the base metals Zn (> 10 g/kg) and Pb (> 2 g/kg), in both incinerator plants (Tab. §2-4). Such values are one to two orders of magnitude higher than those of others *crm* and valuable metals. Elements like Bi, Cd and Rb range between 0.04 and 0.12 g/kg, Cu and Sn from 0.7 to 0.9 g/kg.

FA residues from the two MSWI facilities show a silver mean concentration of 19.3 mg/kg, 48 mg/kg as the sum of selected *crm* (Co, Ga, Nb, W), 62 mg/kg ΣREY (REE + Sc + Y), 150 mg/kg other metals with high economic importance (Li, Mo, Ni, Ta and V - according to EC, 2014). FA present very similar concentrations between SWI-1 and SWI-2; the MgO exception is probably due to the different waste input composition, as suggested for BA (see Tab. §2-1).

Results are in good agreement with the available data from literature on furnace ashes from Belgian MSWI plants (De Boom & Degrez, 2012) and are within the compositional ranges of the overall fly ash data, which are provided in Tab. §2-3.

Tab. §2-4 Trace elements concentration (averages) of FA from SWI-1 and SWI-2, by ICP-MS. Values are reported in mg/kg.

Element	FA SWI-1	FA SWI-2
Ag	22.5	16.1
As	21.2	21.0
Au	0.71	0.45
Ba	1088	852
Bi	63.4	39.0
Cd	121	107
Ce	19.0	20.9
Co	21.3	20.7
Cr	328	941
Cs	4.81	4.80
Cu	993	910
Dy	0.83	1.10
Er	0.59	0.61
Eu	0.72	0.70
Ga	7.98	7.77
Gd	1.24	1.33
Hf	1.69	1.19
Hg	0.01	0.00
Ho	0.30	0.21
La	11.5	11.7
Li	24.0	23.3
Lu	0.07	0.09
Mo	23.1	17.8
Nb	10.0	10.9
Nd	6.39	7.91
Ni	95.2	76.4
Pb	2388	3586
Pr	1.70	2.21
Rb	95.8	106
Sb	994	1050
Sc	4.74	4.44
Se	15.1	11.0
Sm	1.17	1.42
Sn	760	665
Sr	394	463
Ta	1.28	1.09
Tb	0.27	0.31
Th	2.33	2.77
Tl	1.08	0.93
Tm	0.07	0.09
U	0.83	0.99
V	17.2	20.1
W	9.40	8.14
Y	9.87	9.89
Yb	0.43	0.60
Zn	14837	11998
Zr	76.4	66.5

3.3 Estimated annual flow of SWI-1 residues

With the simple mass balance given by the equations [1] and [2] we estimated the yearly flows of selected metals, in kg/a, for the SWI-1 (Tab. §2-5). Only ICP-MS data was used for calculations. The estimated annual flows are reported both for BA and FA, which are separately stored and managed in common incinerator plants, in order to determine the most useful residue for the recovery of certain *crm*. The owners of the incinerator plant provided the total BA and FA output, as reported in section 2.1.

For BA residues we determined a total flow of more than 350 t/a Mg, 8.5 t/a Cr, 4.3 t/a Co, nearly 3 t/a Sb. The overall annual flow of the light REE (La, Ce, Pr, Nd, Sm, Eu, Gd) plus Sc and Y exceeds 2 t/a; whereas the flow of heavy REE (Tb, Dy, Ho, Er, Tm, Yb and Lu) is around 0.1 t/a, being Yb the most significant flow. The annual flow analysis even shows considerable amount of other *crm*: W (0.5 t/a), Ga and Nb (0.3 t/a). The flow for precious metals is approximately 0.01 t/a gold and 0.12 t/a silver. Because of the small amount of the BA test portions (tens of kilograms), the contribution of "nuggets" to the total elements content cannot be evaluated and the average value of the real flows could be underestimated.

Tab. §2-5 shows a flow of 79 t/a Mg, 2.4 t/a Sb, around 1 t/a Cr, 0.05 t/a Ce, 0.04 t/a Co for FA residues. Other metals have relatively high flows, in decreasing order: Bi, Tl, Zn, Sn, Ag, Au, Mo and Ta. In the FA the contribution of nuggets on the total content of precious and valuable metals could be negligible due to the sample and grain size homogeneity. The FA annual flows are about one order of magnitude lower than BA flows because of the difference between the total mass output of fly ashes and bottom ashes. The origins in the input sources of the elements were not evaluated in this study. The separate collection of waste from electrical and electronic equipment (WEEE), among the others, is adopted in the region, but the presence of REE and other specific elements might reveal a poor upstream separation. The evaluation of elemental flows in final waste outputs discloses deficiency in the separate collection system. The overall flows data presented in this study are in good agreement with the results of Morf *et al*. (2013), although the latter report an estimated annual flow for the total waste input of a Swiss incinerator plant. By multiplying their measured concentrations with the inferred output flow of the Swiss facility (40-60 k ton per year), the flows of elements range in the same order of magnitude than the output flows of the Italian incinerator plant. As an example, flows from 0.01 to 0.03 t/a Au, 0.45-0.65 t/a Co, 0.28-0.43 t/a Nd can be found in the output materials and these figures are comparable with values reported in Tab. §2-5. Considering 46 active MSWI plants in Italy during 2013 (ISPRA, 2013), the total solid waste output in Italy is approximately 1.8 million tons and the national substance flow of selected precious metals, *crm* and other elements can be estimated. 4500 ton Cu, 130 ton of total REE and 0.5 ton Au might be potentially recovered from BA, near the projected values reported in Swiss and Denmark by Morf *et al*. (2013) and Allegrini *et al*. (2014), respectively; while huge amounts of Zn (6700 t) and Sb (500 t) are in the FA output.

Tab. §2-5 Estimated annual flow for BA and FA in kg/a by the equations 1 and 2. The average concentrations are calculated for n number of samples. K_{FA} (%) is the relative recovery efficiency between BA and FA; K_{BAf} (%) is the relative recovery efficiency in different granulometric fractions. Percentages are calculated on the basis of transfer coefficients (equation 3, 4 and 5).

		Flow (kg/a) **Bulk BA** (n=9)*	K_{BAf} (%)			Flow (kg/a) **Bulk FA** (n=2)*	K_{FA}(%)	
			B	**M**	**T**		O_{FA}	$O_{FA} = O_{BA}$
CRM	**Mg**	354,000 ± 5,600	0	-6	+7	78,500 ± 350	-78	+113
	Cr	8,500 ± 400	+16	-4	-13	800 ± 53	-92	-10
	Co	4,300 ± 3,000	-43	-40	+83	42 ± 11	-98	-90
	Sb	266 ± 440	-13	-11	+24	2401 ± 60	+3	+767
	Ce	730 ± 53	-1	+0	+3	46 ± 7.0	-94	-40
	W	483 ± 13	-1	+4	-4	22 ± 4.1	-95	-57
	La	430 ± 38	-2	-9	+14	27 ± 0.1	-94	-40
	Ga	330 ± 22	-6	+0	+6	19 ± 0.2	-94	-45
	Nb	330 ± 49	-3	+9	-6	24 ± 0.2	-93	-30
	Y	321 ± 33	-7	-8	+15	23 ± 1.0	-92	-31
	Nd	270 ± 35	-11	-4	+11	15 ± 1.0	-94	-48
	Sc	230 ± 11	+4	-4	+4	11 ± 0.5	-96	-57
	Pr	70 ± 10	-14	+0	+14	3.1 ± 0.2	-95	-57
	Gd	50 ± 11	+20	-20	0	2.1 ± 0.4	-97	-60
	Sm	50 ± 6	-6	-4	+10	2.1 ± 0.1	-96	-60
	Dy	40 ± 7	-25	-25	0	1.0 ± 0.1	-97	-75
	Yb	24 ± 3.3	-4	-8	+17	1.0 ± 0.1	-95	-58
	Er	20 ± 3.7	0	0	+50	1.0 ± 0.2	-95	-50
	Eu	20 ± 2.6	-50	0	0	1.0 ± 0.1	-90	-50
	Be	11 ± 1.0	-27	-9	+36	-	-	-
	Tb	9.0 ± 1.0	-11	-11	+11	0.6 ± 0.02	-92	-33
	Ho	8.0 ± 1.3	0	-13	+13	0.6 ± 0.03	-97	-67
	Lu	3.7 ± 0.5	-5	-8	+16	0.1 ± 0.001	-97	-67
	Tm	3.6 ± 0.4	-6	-6	+17	0.2 ± 0.01	-97	-67
Valuable Metals	**Fe**	1,500,000 ± 31,700	-2	+9	-7	39,000 ± 1,300	-97	-76
	Al	1,200,000 ± 26,400	+5	-6	+1	66,500 ± 2,100	-95	-47
	Ti	145,000 ± 5,170	+6	-6	0	19,000 ± 440	-88	+26
	Cu	81,000 ± 7,350	-11	+12	-2	2,400 ± 50	-97	-72
	Zn	69,500 ± 3,920	+7	-4	-4	36,000 ± 200	-52	+396
	Mn	24,000 ± 495	-3	-3	+5	1,650 ± 23	-93	-34
	Ni	5,200 ± 346	-4	-6	+10	230 ± 9.2	-95	-58
	V	4,200 ± 570	-50	-44	+94	41 ± 3.5	-98	-91
	Sn	3,680 ± 140	+16	-18	+2	1,840 ± 14	-57	+379
	Li	610 ± 38	+2	-7	+7	57 ± 0.7	-91	-10
	Mo	380 ± 22	-5	-8	+13	55 ± 1.6	-85	+39
	Ag	120 ± 41	-8	-17	+33	54 ± 0.3	-51	+333
	Ta	25 ± 5.5	-8	+8	-4	3.0 ± 0.1	-87	+16
	Au	10 ± 3.7	+10	-40	+20	1.7 ± 0.2	-85	+60
Other Metals	**K**	220,000 ± 17,400	+2	-8	+7	86,500 ± 600	-62	+276
	Pb	34,600 ± 7,120	-2	-1	+2	5,770 ± 52	-83	+60
	Ba	32,400 ± 1,050	-2	-1	+3	2,630 ± 332	-92	-22
	Sr	10,200 ± 700	-7	-1	+2	950 ± 14	-90	-10
	Zr	2,630 ± 1,200	-19	+2	+18	184 ± 38	-91	-33
	Rb	790 ± 65	-13	-9	+6	230 ± 2.2	-66	+181
	Cd	122 ± 24	-16	-4	+19	291 ± 6.1	+139	+2209
	Hf	60 ± 24	-17	0	+17	4.0 ± 0.8	-94	-50
	Bi	50 ± 15	+40	-40	-40	150 ± 9.5	+119	+2840
	Tl	3.0 ± 1.5	0	0	+33	2.6 ± 0.07	-13	+733

* *Estimated average annual flow and uncertainty are calculated also with replicates measurement.*

3.4 Transfer coefficients of SWI-1 residues

Transfer coefficients were used to determine the distribution of specific elements between BA and FA output fractions (B, M, T), which are shown in Tab. §2-5 as relative percentage. These data may provide information on which grain size fraction is more promising for the eventual element recovery.

The calculated transfer coefficients (see Tab. S.2 in Supplementary Materials of Chapter 2) by equations [3] and [4] reveal that Cr, Co, Cu, Mn, Zr and other base metals are found primarily in the BA, whereas the volatile elements (e.g.: Zn, Sb, Cd and Bi) are more distributed between BA and FA, as observed by others (e.g.: Morf *et al.*, 2013; Astrup *et al.*, 2011; Zhang *et al.*, 2008a).

The recovery efficiency of FA on the basis of the relative mass output flows (O_{FA}) seems to be very low, with almost all negative values. However, FA residues are enriched in volatile elements such as Bi, Cd and Sb despite the mass output difference. Most of the *crm*, but Sb, preferentially partitions into the BA (Fig. §2-3).

Silver, gold and other valuable metals (i.e., Bi, Mo, Sn, Ta, Zn) have rather high transfer coefficients to FA. Furthermore, hypothesizing a recovery process with the same mass volume of BA and FA ($O_{FA} = O_{BA}$ in Tab. §2-5), the relative efficiency from FA residues is significantly higher for Bi, Cd and Sb than the same elements from BA; moreover, for elements like Zn, Sn, Ag, Mg and Au the recovery performance is improved (396%, 379%, 333%, 113% and 60%, respectively).

We determined the transfer coefficients for BA in different granulomentric fractions (T_{BAf}) following the equation [5]. The percentage represents the enrichment or the depletion of the concentration with respect to the bulk BA content. The *crm* show a relative enrichment in the top layer, except for chromium, niobium and tungsten.

Precious and other valuable elements (Ag, Be, Co, Sb and V) are more abundant in the finest fraction of BA, while Bi, Cr and Zn are enriched in the coarser BA. REE are preferentially portioned in the finer BA, except for Gd that it is enriched in the coarser BA. Europium, dysprosium and scandium are dispersed between fractions. Similar percentages or positive values both for B and T layers indicate the absence of a granulometric control for Au, Sc and Sn. The results indicate that a simple separation procedure of the fresh and untreated BA may lead to an increase of the relative recovery efficiency up to 94% for certain elements. It is important to highlight that the accumulation and concentration of elements in output fractions are not due to the different ageing of sampled materials. The sampled stockpile was representative of two-months deposition with high deposition rate. Several authors (e.g.: Meima & Comans, 1998; Cornelis *et al*., 2008; Santos *et al*., 2013) investigated bottom and fly ashes in different stage of ageing in order to assess the environmental risk and leaching properties. They pointed out that aged bottom and fly ashes always show an enrichment of heavy metals, such as Be, Co, Mo, Sb, V, W and Zn. In this study we found higher content of these metals preferentially in finer fractions or T layers, which would be rather younger levels.

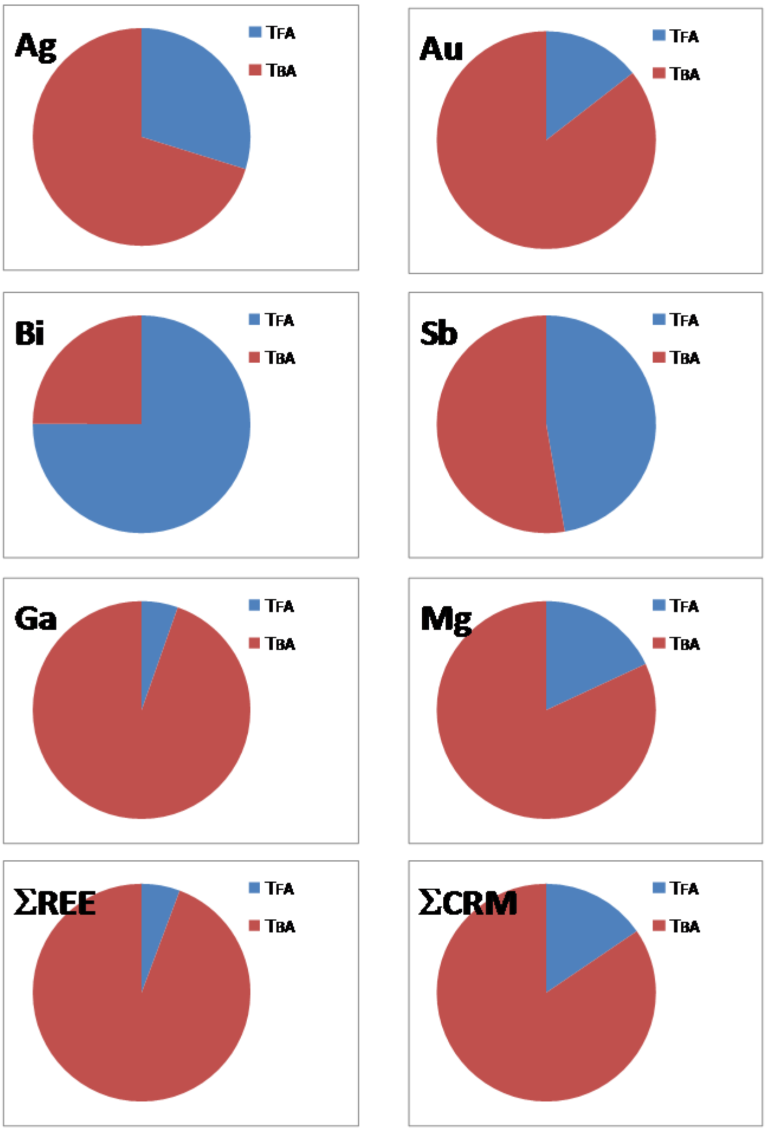


Fig. §2-3 *Distribution of selected crm between BA and FA final outputs calculated following equations 3 and 4.*

3.5 "Urban" ore deposits as a potential target for raw materials supply

The EU policies encourage reducing the waste of waste and lead to consider MSWI residues as anthropogenic flows of resource. Since those flows can change in composition, size and, additionally, the knowledge on the size varies, they are dynamic "urban" ore deposits. Bearing in mind boundaries and assumptions of the

SFA, we discuss the potential on raw material of the investigated MSWI flows. In Tab. §2-3 the average values of SWI-1 BA and FA ("urban" ore), by ICP-MS, are compared with the average upper continental crust (UCC) values (from Rudnick and Gao, 2014) and with typical values of concentrated ores (from Allegrini *et al.*, 2014 and reference therein). Most of analysed *crm*, including REE, show concentrations in the "urban ore" comparable with UCC values. Zinc, tin, antimony, sulfur, lead, copper, cadmium, bismuth, gold, silver concentrations are one order of magnitude higher than the UCC. Compared with UCC, interesting amount of vanadium and strontium are found in BA; chromium, silver and tin in FA. However, the concentration levels are by far lower than typical levels in concentrated ores, with the exception of copper (whose concentration is close to the concentrated ore values) and magnesium (only one order of magnitude lower than the low-grade concentration).

As a qualitative index to evaluate economic feasibility of urban ore deposits as an alternative source of supply for Europe, we compare the MSWI residues concentrations with reference values from the Geological Survey of Finland (GTK) reports of active mines in Fennoscandia during 2013. The minimum concentration for naturally occurring silver is 1.3 g/t (in the Aitik-Nautanen metallogenic area), while this study shows a silver grade of 5.5 g/t in the urban ore. Likewise, copper and zinc oxides have a minimum concentration of 0.01 g/100g and 0.4 g/100g, respectively; the concentrations resulted from this study indicate occurrences of 0.03 g/100g Cu in BA residues and 1.3 g/100g Zn in FA residues. Lead, molybdenum and nickel are also close to the reported values for active mines in Fennoscandia; the concentration of some *crm* and other base metals in MSWI outputs can be compared to a depleted ore in Europe and to polymetallic deposits (e.g., Cu, Cr, Co, Sn, Ni and Zn) in China and India (Dachang, Zhaokalong and Koira-Noamundi metallogenic areas; Li *et al.*, 2013; Mohapatra *et al.*, 2009; Jiang *et* *al*., 1999). REE concentrations appear too low in the "urban ore" to be considered as a potential target for the recovery. The total content of rare earths as oxides (TREO) has to be in the range of 0.5% to 3% today to allow an economic exploitation. For example, the Kvanefjeld mining field contains 1.35% of TREO (www.ggg.gl), which is higher than the TREO content of the MSWI residues (about 0.01 %). Although the urban mining as a source of critical elements is gaining increasing interest, at present the recovery of these materials does not seem feasible (Morf *et al*., 2013). Furthermore, applying the existing technologies for metal recovery would be not economic, especially when a large amounts of impure metals and strong alkaline conditions are found, such as in MSWI residues. However, the urban ore deposit has the advantage of being already in granular form and leads to a limited environmental impact (or perhaps reduces it), in contrast with the natural ore deposit that may require lengthy and expensive operations: i.e., obtain concessions, remove the overburden, concentrate the mineral ore and restore the natural area. From this point of view, the efforts in the development of urban mine plans in order to recover valuable metals have to be increased. The concentration of metals of environmental concern, e.g. Ba, Cd, Pb, Mo and the antimony itself, is over the minimum range of concentration of active mines (Tab. §2-3). This may represent an advantage for their recovery, but leaching properties of solid residues and, consequently, the risk for contamination should be accounted.

4. Conclusions

In the near future incineration processes will continue to be an important part of the waste management system along with recycling and waste disposal. As a consequence, the governance of the solid residues will remain a general concern. Our working hypothesis considers the solid residues as an unconventional source of *crm*. The recovery of precious metals from MSWI residues might be an attractive option if the growing demand for raw materials will confront with their supply risk related to the instability of international markets. The main results of this study are:

The analysed bottom and fly ashes from two grate furnace incinerators confirm the presence of *crm* and other valuable elements in concentration comparable with a low-grade ore deposit (e.g.: magnesium and copper).

A simple mass balance for untreated bottom and fly ash residues indicates significant amounts per year of critical elements and other metals of economic interest, such as antimony, cobalt, copper, magnesium and zinc. Furthermore, the transfer coefficients allow to identify added-value products, which could be processed for further mineral upgrading and recovery with the existing technologies.

There is a grain size control over the distribution of Ag, Sb, Ce, La, Nb, Ni, V which are enriched in the fine-grained portion, whereas Gd, Cr, Sc, W and Y preferentially partition into the coarser fraction of the residues.

The grain size fractions of bottom ash, commonly stored in stockpiles, are readily distinguishable at the storage site. This evidence permits a simple and cost-effective separation strategy easy to implement at the plant scale. Such operation can be performed by less trained operators and may lead to an increase of the relative recovery efficiency up to 83% for *crm* elements.

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Supplementary Materials of Chapter 2

S.1 Effectiveness of a stratified random method

One of the aims of the present study is defining a simple and cost-effective strategy to manage solid wastes after incineration. A careful collection of the output waste allows to improve the relative recovery efficiency of some elements. The separate collection of fresh bottom ash (BA) stockpiles shows potential in the defining added-value products, which could be processed for further mineral upgrading and recovery with the existing technologies. Therefore, waste processors may benefit from a separation strategy with no or very low modification of the operations of the current system.

The sampling of BA residues from the selected incineration plants followed the "stratified random sampling" mainly after the protocol UNI 10802. The analytical results indicated higher relative recovery efficiency in the uppermost strata (likely of finer grain size) rather than in the bottom ones. The hypothesis is consequently supported by XRF data on sieved fractions from bulk BA batches (Supplementary Materials of Chapter 2). The XRF data are consistent with data provided in the paper, with some exceptions e.g., Cr, Zr; this is probably due to nugget effects highlighted by relatively high RSD in the coarser fractions. These are supplementary information to sections 2.2 *Sampling and sample preparation* and *3.1.1 Gravitative selection control on partitioning of critical elements*.

Tab. S.1. *Trace elements concentration of sieved BA samples (from SWI-1 and SWI-2) by XRF. Average values each 3 samples (sieved fraction) are reported in mg kg*$^{-1}$ *with relative standard deviation (%).*

Element	**Sieved samples of SWI-1**		**Sieved samples of SWI-2**	
	< 1 mm BA	> 1 mm BA	< 1 mm BA	> 1 mm BA
As	6.22 ± 28%	16.4 ± 30%	5.65 ± 10%	14.0 ± 34%
Ba	922 ± 19%	1395 ± 5%	1104 ± 79%	786 ± 13%
Ce	16.7 ± 57%	46.6 ± 19%	35.3 ± 50%	29.4 ± 17%
Co	17.1 ± 66%	34.1 ± 13%	23.2 ± 27%	45.0 ± 27%
Cr	415 ± 33%	745 ± 7%	617 ± 25%	690 ± 6%
Cu	2031 ± 22%	3225 ± 13%	1330 ± 69%	6290 ± 26%
Ga	7.44 ± 22%	10.2 ± 8%	7.77 ± 20%	15.7 ± 27%
La	9.56 ± 48%	22.5 ± 11%	8.43 ± 25%	15.5 ± 31%
Mo	14.4 ± 41%	25.3 ± 13%	7.07 ± 22%	12.4 ± 13%
Nb	10.4 ± 57%	20.4 ± 17%	7.13 ± 28%	13.3 ± 25%
Nd	6.33 ± 56%	13.0 ± 9%	15.3 ± 16%	22.9 ± 31%
Ni	147 ± 34%	286 ± 14%	108 ± 22%	155 ± 22%
Pb	398 ± 61%	690 ± 15%	594 ± 59%	1337 ± 21%
Rb	25.7 ± 28%	37.6 ± 15%	30.9 ± 10%	40.4 ± 24%
Sc	13.5 ± 34%	17.0 ± 20%	8.78 ± 9%	10.0 ± 14%
Sm	1.75 ± 0.5%	6.51 ± 37%	3.30 ± 17%	6.80 ± 40%
Sn	371 ± 83%	192 ± 12%	178 ± 53%	231 ± 18%
Sr	383 ± 3%	419 ± 11%	824 ± 99%	505 ± 12%
V	185 ± 39%	270 ± 20%	41.2 ± 8%	49.9 ± 20%
Y	15.0 ± 8%	17.0 ± 13%	12.5 ± 9%	14.0 ± 21%
Zn	2137 ± 43%	4207 ± 8%	3137 ± 67%	4565 ± 18%
Zr	145 ± 70%	309 ± 21%	218 ± 58%	204 ± 18%

S.2 The calculation of transfer coefficients (TC)

The distribution of inert mass flows and the partitioning of selected metals between BA and FA have been calculated (as transfer coefficients) by mean of the Eqs. 3-4 and the output mass of solid waste. SWI-1 had an annual waste input of 120000 t a^{-1} (as referred in 2013) resulting in 29900 t a^{-1} of total solid waste output. The incineration system produced 23200 t a^{-1} and 2400 t a^{-1} BA and FA residues, respectively (sewage sludge and recovered metallic scrap are the remaining). The transfer coefficients among different sampled strata of BA (i.e.: B, M, T) have been also reported, assuming 50%, 30% and 20% of total mass residues as fraction mass for B, M and T, respectively. In the S.2 *The calculation of transfer coefficients (TC)* the transfer coefficients are reported (with the sum of output = 1). These are supplementary information to sections 2.4 *Substance flow analysis* and 3.4 *Transfer coefficients of SWI-1 residues*.

Tab. S.2. *Transfer coefficient among different residues (FA vs. BA) and BA fractions (B, M, and T).*

	FA vs. BA		**BA Fractions (B, M, T)**		
Element	K_{FA}	K_{BA}	K_{BAB}	K_{BAM}	K_{BAT}
Ag	0.298	0.702	0.441	0.248	0.258
Al	0.052	0.948	0.523	0.283	0.202
Au	0.145	0.855	0.554	0.192	0.250
Ba	0.075	0.925	0.490	0.296	0.207
Bi	0.751	0.249	0.734	0.230	0.153
Cd	0.678	0.322	0.410	0.257	0.192
Ce	0.058	0.942	0.491	0.297	0.205
Co	0.012	0.988	0.292	0.179	0.364
Cr	0.085	0.915	0.581	0.290	0.175
Cu	0.029	0.971	0.447	0.337	0.196
Dy	0.046	0.954	0.476	0.283	0.221
Er	0.048	0.952	0.490	0.281	0.217

Eu	0.077	0.923	0.454	0.307	0.214
Fe	0.025	0.975	0.488	0.328	0.186
Ga	0.054	0.946	0.467	0.301	0.213
Gd	0.050	0.950	0.569	0.261	0.198
Hf	0.061	0.939	0.414	0.304	0.232
Ho	0.076	0.924	0.504	0.268	0.220
La	0.060	0.940	0.488	0.270	0.225
Li	0.086	0.914	0.505	0.281	0.212
Lu	0.041	0.959	0.470	0.275	0.229
Mg	0.181	0.819	0.498	0.281	0.213
Mn	0.064	0.936	0.488	0.293	0.210
Mo	0.127	0.873	0.474	0.278	0.225
Nb	0.067	0.933	0.484	0.327	0.188
Nd	0.053	0.947	0.458	0.290	0.223
Ni	0.042	0.958	0.479	0.282	0.221
Pb	0.142	0.858	0.492	0.298	0.204
Pr	0.052	0.948	0.455	0.301	0.217
Sb	0.473	0.527	0.436	0.267	0.248
Sc	0.046	0.954	0.512	0.284	0.206
Se	0.263	0.737	0.390	0.251	0.277
Sm	0.053	0.947	0.468	0.290	0.220
Sn	0.332	0.668	0.578	0.246	0.205
Ta	0.108	0.892	0.462	0.329	0.196
Tb	0.065	0.935	0.474	0.281	0.223
Ti	0.115	0.885	0.529	0.283	0.200
Tl	0.396	0.604	0.489	0.264	0.229
Tm	0.045	0.955	0.460	0.283	0.228
V	0.010	0.990	0.248	0.168	0.389
W	0.045	0.955	0.497	0.313	0.193
Y	0.069	0.931	0.463	0.276	0.231
Yb	0.041	0.959	0.477	0.273	0.227
Zn	0.340	0.660	0.536	0.289	0.193
Zr	0.065	0.935	0.405	0.304	0.235
∑REE	0.057	0.943	0.488	0.296	0.208
∑crm	0.180	0.820	0.468	0.274	0.230

REE: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y, Yb.
***crm*:** Co, Cr, Ga, Mg, Nb, Sb, W.

Chapter 3

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 ash from municipal incinerators are investigated.
- First attempt to discriminate the magnetic signature (susceptibility) of incineration ash.
- New methods and parameters for REE prospecting, which can be used quickly and with limited costs, are provided.

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.

Keywords: MSWI fly and bottom ash; Rare Earth Elements, Mass specific magnetic susceptibility.

1. Introduction

Rare Earth Elements (REE) are among critical raw materials, as defined by the European Commission (EC, 2010; 2014), because of their importance for new and green technologies. They are used as essential constituents in a wide range of technological application (Chakhmouradian & Wall, 2015) and their low substitutability implies to secure a stable REE supply. The major REE ore deposits are located in a handful of countries (EC, 2010; Chakhmouradian & Wall, 2015): 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., Binnemans & Jones, 2014; Innocenzi *et al*., 2014). Recently, it has been demonstrated that solid residues from municipal solid waste incinerators (MSWI) host significant amounts of critical elements (Morf *et al*., 2013; Allegrini *et al*., 2014; Funari *et al*., 2015) possibly due to a weak control over the collected waste and the separated collection upstream (Singh *et al*., 2014). 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 (Lee & Pandey, 2012) are adding new prospective for the metal recovery from waste streams. A better knowledge of REE within MSWI ashes and their 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 (Meisel *et al.*, 2002) 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 (Lecoanet *et al*., 2003; Jordanova *et al*., 2004; Fialová *et al*., 2006; Sagnotti *et al*., 2009; Huliselan *et al*., 2010), including coal fly ashes (Veneva *et al*., 2004; Lu *et al*., 2009), 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 (Wang & Qin, 2005; Zhang *et al*., 2012), 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 $1.2\cdot10^5$ 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. §3-1 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 Funari *et al.* (2015). 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. §3-1) 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.* (2013), 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 μm) 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.

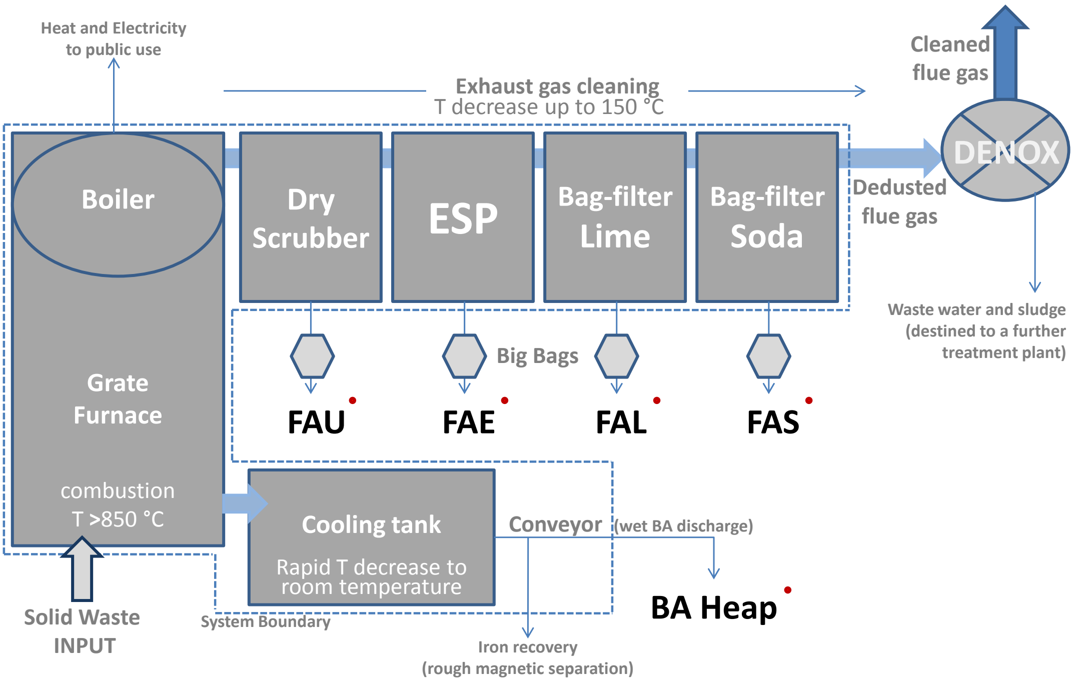

Fig. §3-1 Schematic picture of the incinerator system with its relevant processes, including sampling points (red dots) and temperature (T) profile. Acronyms used: BA=bottom ash; FAE=fly ash from ESP; FAL=fly ash from bag filter with Ca-additive; FAS=fly ash from bag filter with Na-additive; FAU=untreated fly ash; ESP=electrostatic precipitator.

2.3 Elemental chemistry determination

The complete sample digestion was obtained with the Na_2O_2 sintering technique (Meisel *et al.*, 2002), 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 and Analytical Chemistry of Montanuniversität Leoben (Austria). The description of the analytical procedure followed for the analyses of MSWI samples can be found elsewhere (Funari *et al.*, 2015). Major and trace elements were determined (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 (Peters & Thompson, 1998). 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 m^3kg^{-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 μm 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 μm) 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 (∑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. §3-2). 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 (Tab. T.2, Supplementary Materials of Chapter 3). Additional details regarding the test procedure and assumptions are provided in S.2 *Independent sample t-test*.

Higher ∑REE is typically found in BA rather than in FA (Fig. §3-3) as a consequence of the high boiling points of REE (1194-3426 °C) (Zhao *et al.*, 2008). 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. §3-4, 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 agreement with the partition coefficients calculated by Morf *et al*. (2013) 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 (Funari *et al*., 2015 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 Morf *et al*. (2013) is consistent with elemental content into the MSWI output reported in the present work (see Tab. T.1, Supplementary Materials of Chapter 3), being in order of abundance Y>Nd>Sc>Gd.

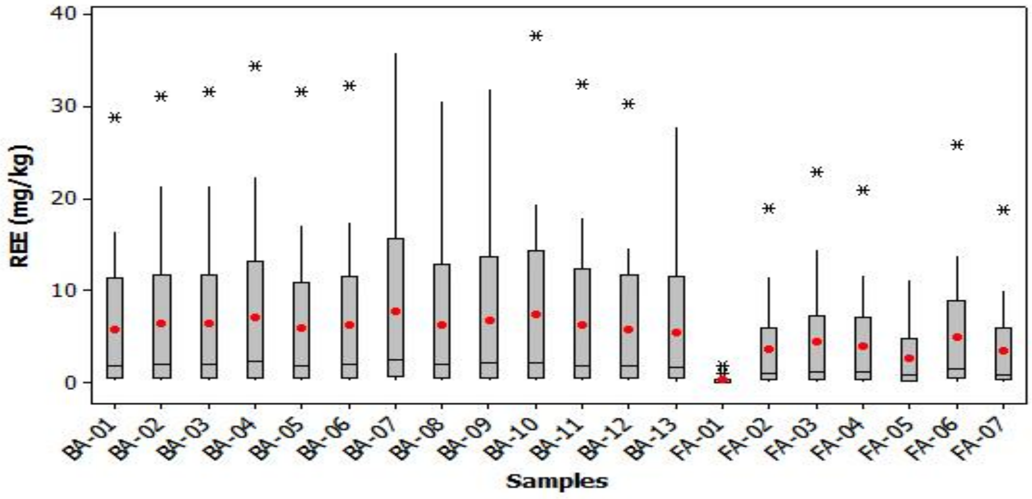

Fig. §3-2 The REE variability in the studied samples. The boundaries of the box indicate the 25th percentile and the 75th percentile, the continuous line within the box marks the median and the red dot marks the mean. Whiskers above and below the box indicate the 90th and 10th percentiles, whereas starred dots are the outliers (mainly Ce).

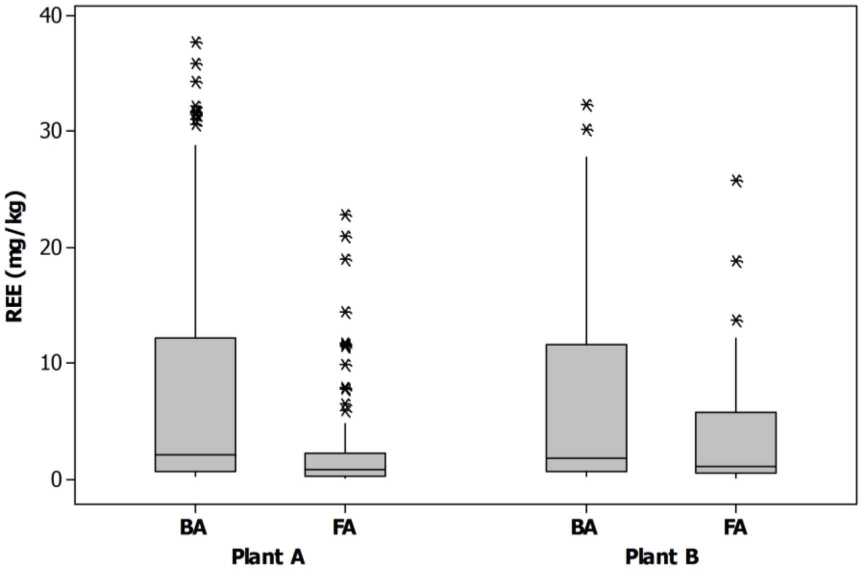

Fig. §3-3 The variability of REE in BA and FA samples, a comparison between incinerators A and B; outliers are mainly Ce and La. For the significance of box-plots see **Fig. §3-2**.

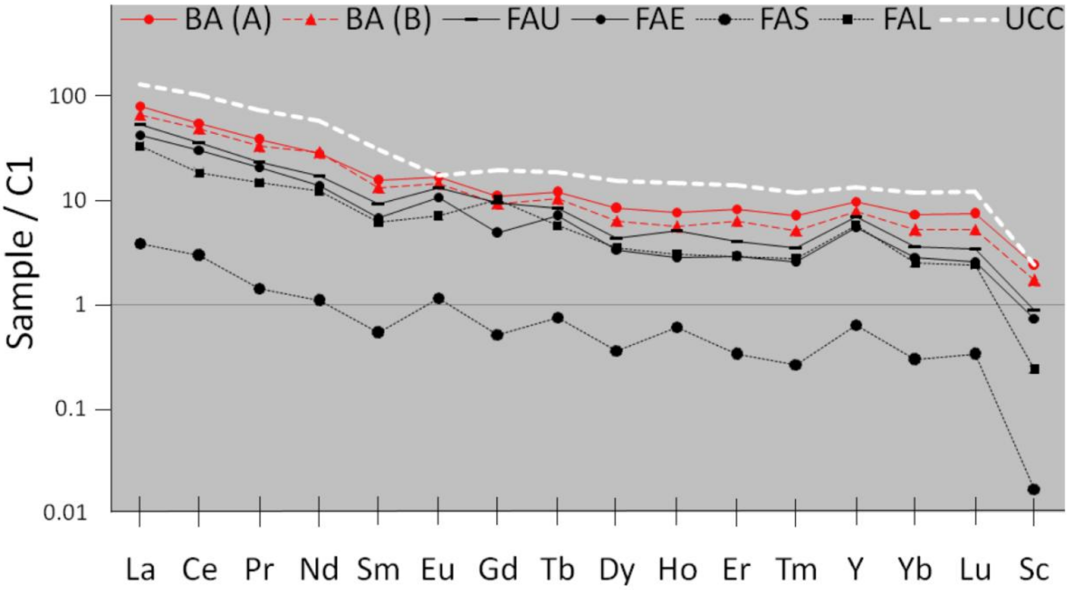

Fig. §3-4 Chondrite-normalised REE patterns for the MSWI ashes (C1 in the y-axis stands for type 1 of carbonaceous chondrite). The white dashed line represents the chondrite-normalised REE patterns of the Upper Continental Crust (UCC). Chondrite and UCC average values are from McDonough & Sun (1995) and Rudnick & Gao (2014), respectively.

Normalized REE pattern can be used to evaluate the relative enrichment of REE in studied materials (e.g., Zhang et al., 2002), and to highlight geochemical anomalies from typical crustal pattern, which might derive from anthropogenic contamination. The chondrite-normalised patterns of our MSWI samples (Fig. §3-4) resemble that of the Upper Continental Crust average (UCC, white dashed line), suggesting a principal geogenic source of REE. As a fact, when there are no clear anomalies for an element, it might likely derive from natural rocks, geologic processes, and from its use into goods and products without the need of an enrichment of that element (e.g., no typical REE enrichment in construction materials). However, a few element anomalies are visible and they might be related to manmade processes, which had lead to an enrichment of specific elements in certain everyday products (e.g., magnets, fluorescent lights). 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 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*. (2001) who investigated MSWI ash from two Japanese incinerators. The normalised patterns of sampled MSWI ashes, however, differ from those reported by Zhao *et al*. (2008) 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. §3-1) 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 EC (2014), could be critical in discussing the REE enrichment parameters in section 3.4 *The REE enrichment and Pricing Influence Factor*.

3.2 Correlation between major elements and REE

Fig. §3-5 provides the correlation between ∑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 ∑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 g/100g) and minor (>0.01 g/100g) 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. §3-5). 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. §3-4). 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 (Pang *et al*., 2002). 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. §3-5) 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 fractions 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.

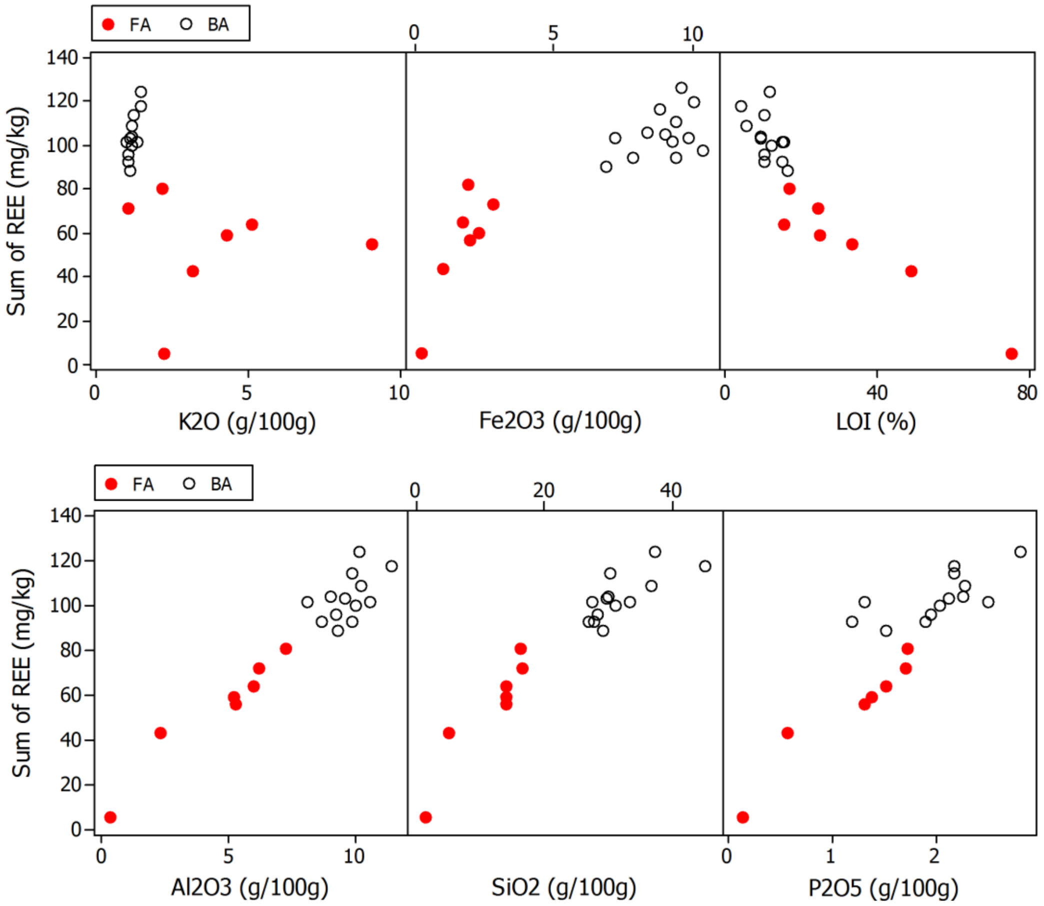

Fig. §3-5 Correlations of ∑REE and selected major elements. The REE vs. LOI scatter plot is also provided. The data set is grouped by kind (BA=bottom ash; FA=fly ash).

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 $2.3 \cdot 10^{-8}$ and $304 \cdot 10^{-8}$ m^3/kg (Tab. §3-1, Fig. §3-6), with a distinct magnetic signature for BA and FA samples. The BA samples show relatively high χ values ranging from $121 \cdot 10^{-8}$ m^3/kg to $304 \cdot 10^{-8}$ m^3/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 (Zhang *et al.*, 2012) that partition in BA materials (Allegrini *et al.*, 2014; Funari *et al.*, 2015) 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., 4-13000 · 10^{-8} m^3/kg as in Zhang *et al.*, 2012) and partly within the values range of other kinds of incineration residues such as coal ash, i.e., 306-1703 · 10^{-8} m^3/kg reported in Lu *et al.* (2009). Nevertheless, the χ measurements of MSWI ashes reported here are rather consistent with those of sediments near Fe-smelters (200-600 · 10^{-8} m^3/kg as in Zhang *et al.* 2011) and from MSW landfill (64-970 · 10^{-8} m^3/kg as in Huliselan *et al.* 2010).

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 super-paramagnetic (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 (Oldfield, 1991). However, Tab. §3-1 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.* (1997), 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.

Tab. §3-1 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 electrostatic precipitator; FAS = Soda-treated fly ash; FAL = Lime-treated fly ash). The letters A and B in parentheses indicate MSWI plant A and B, respectively.

MSWI ash	**Sample mass**	**χ** (10^{-9} m^3/kg)	**K_{fd}** (%)	**Fe_2O_3** (g/100g)	**∑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*

Correlations between magnetic data and heavy metals concentration have been observed (e.g. Lecoanet *et al.*, 2003; Maier & Scholger, 2004); especially iron mass fraction and χ values typically show a good association in scatter-plots 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. §3-6a), being 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 $100 \cdot 10^{-8}$ m^3/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. §3-6a). This scattering of BA samples might indicate the presence of variable amounts of magnetic minerals, which differentiate plant A and B.

There is recent evidence that susceptibility measurements of topsoil from urban areas correlate with REE (Wang & Qin, 2005; Zhang et al., 2012). In MSWI samples, we found a direct correlation between χ values and REE (Fig. §3-6b), both LREE (R^2=0.63) and HREE (R^2=0.51), being the coefficients of determination from 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. §3-4) 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 $200 \cdot 10^{-8}$ m^3/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.

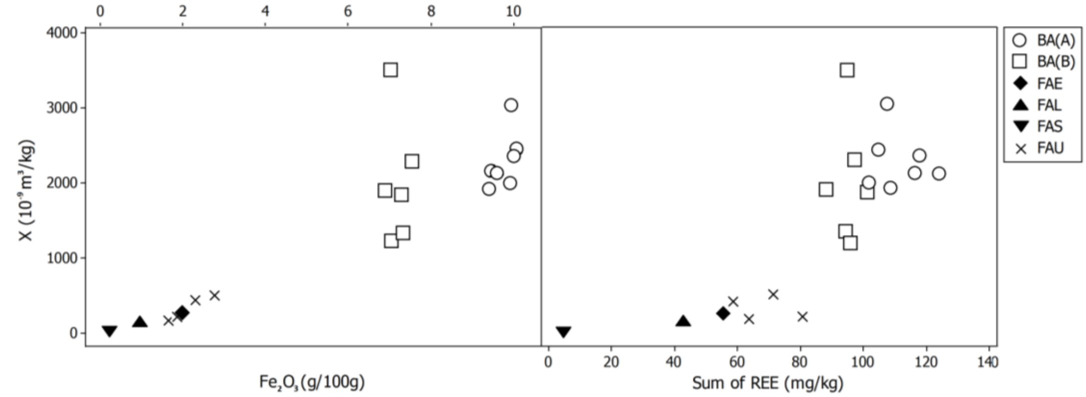

Fig. §3-6 Scatter plot of mass specific magnetic susceptibility (χ) vs. Fe_2O_3 (a) and ΣHREE (b). The data set is grouped by kind (BA=bottom ash; FAE=fly ash from ESP; FAL=fly ash from bag filter with Ca-additive; FAS=fly ash from bag filter with Na-additive; FAU=untreated fly ash). The provenance of BA sample is also provided (A=plant A; B=plant B).

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 (Reimann & De Caritat, 2000). For the normalisation purpose, we used aluminium oxide mass fraction as adopted in Fujimori *et al*. (2004) for MSWI bottom ashes and in Westerhoff *et al*. (2015) for sewage sludge. The EF is expressed according the equation:

$$EF= (X_{sample} / Al_{sample}) / (X_{crust} / Al_{crust}) \qquad [Eq.\ 1]$$

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 (Rudnick & Gao, 2014).

Fig. §3-7 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 Morf *et al*. (2013) 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*. (2004) 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 Morf *et al*. (2013) 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.

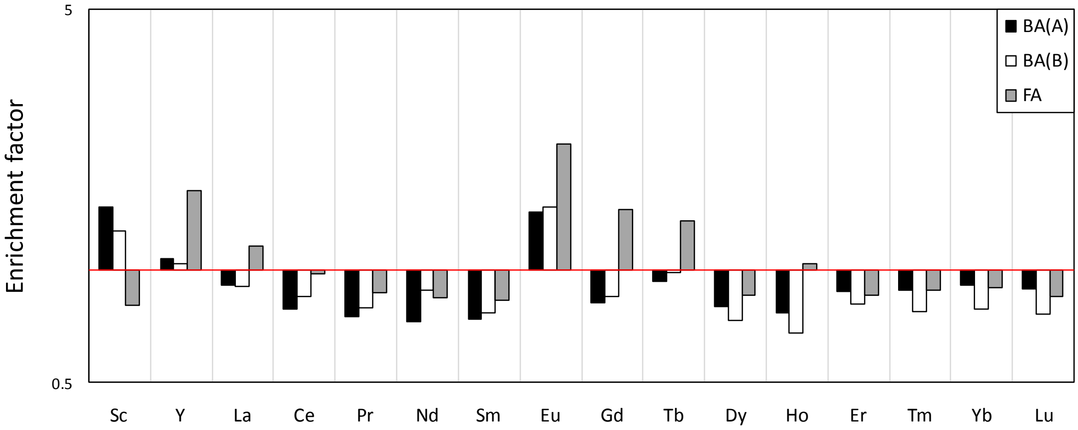

Fig. §3-7 Comparison of the enrichment factors for the REE in BA and FA from MSWI plants. The BA from MSWI plant A and B are reported separately. For the calculation of enrichment factors see Eq. 1.

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. §3-4) and recent outcomes (Fujimori *et al.*, 2004; Westerhoff *et al.*, 2015) as well as the calculated EFs using data from Morf *et al.* (2013). 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 Reimann & De Caritat (2000), 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:

$$PIF= X_{price} / X_{crust} \qquad \textit{[Eq. 2]}$$

where X_{price} is the price of the element, from Kogel (2006), and X_{crust} is its abundance in the upper continental crust, from Rudnick & Gao (2014). 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. §3-8, 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. §3-8) 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. §3-8 also discloses that Sc, Y, La, and other LREE are relatively enriched in MSWI ashes but current (as for 2015) market price of 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 Fig. §3-7 and Fig. §3-8) 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 S.3 *REE flows of MSWI output*).

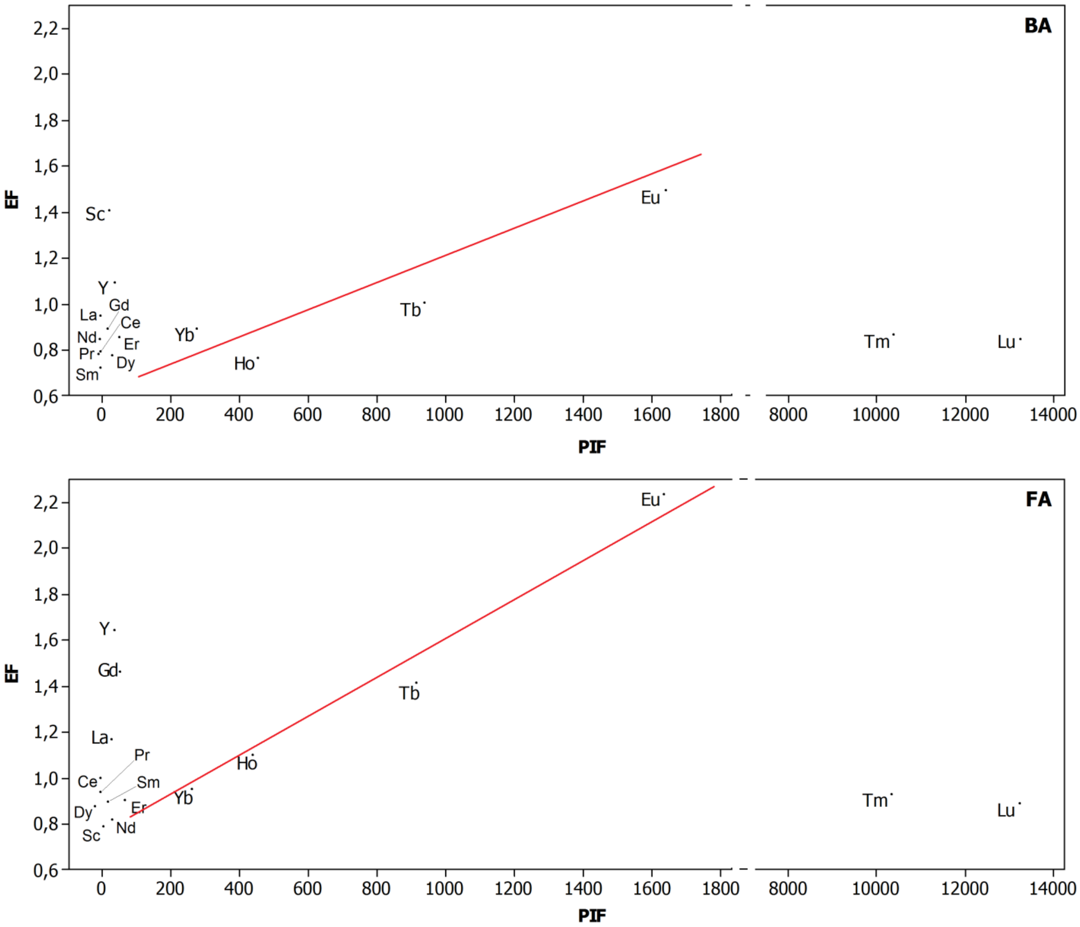

Fig. §3-8 Bi-plot of Enrichment Factor (EF) and Pricing Influence Factor (PIF) of REE in BA (above) and FA (below) sampled materials. The red line represents the trendline of observations within a selected range of PIF values (100-1800). The EF and PIF were calculated by the Equations 1 and 2, respectively.

4. Conclusions and outlook

Bottom and fly ashes have an average concentration of 104 and 54 mg/kg ∑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., Lecoanet *et al.*, 2003) or of harmful ultrafine SP particles (e.g., Fialová *et al.*, 2006), and for the appraisal of best substrates for the synthesis of magnetic geo-polymers (e.g., Belviso *et al.*, 2015). 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.

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Supplementary Materials of Chapter 3

S.1 Total elemental chemistry of MSWI ashes

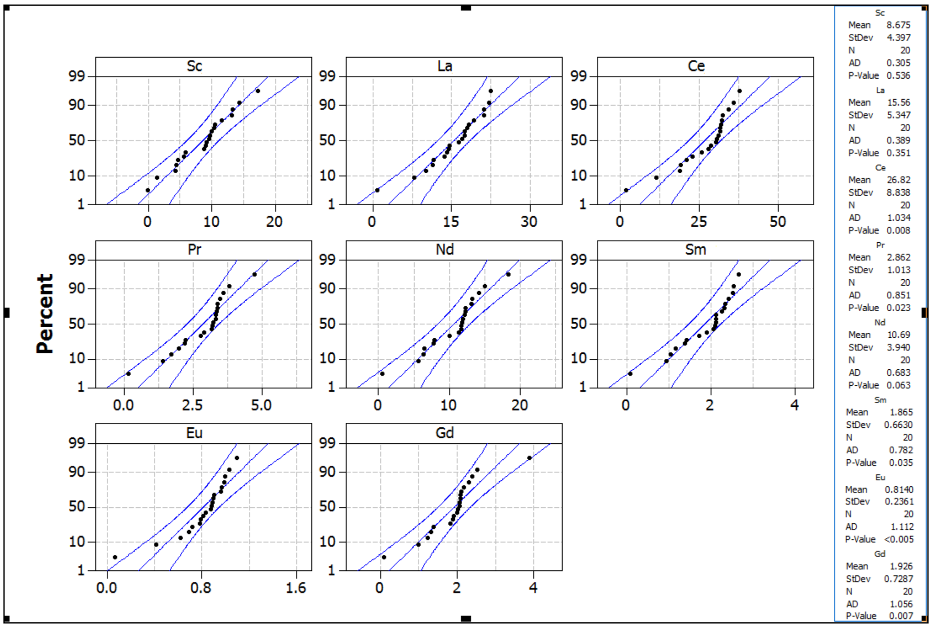
Tab. T.1 Major and trace elements concentration of MSWI samples (Plant A and B).

	BA(A)	BA(A)	BA(A)	BA(A)	BA(A)	BA(A)	BA(A)	BA(B)	BA(B)	BA(B)	BA(B)	BA(B)	BA(B)	FAE(B)	FAL(B)	FAS(A)	FAU(A)	FAU(A)	FAU(B)	FAU(B)
g/100g																				
Al2O3	10.2	11.0	10.2	10.6	10.0	10.2	10.4	9.0	8.7	8.4	8.1	9.3	8.7	5.2	2.3	0.3	5.2	6.2	6.0	7.3
CaO	20.7	17.8	19.2	19.0	18.9	19.9	17.5	23.6	23.0	21.6	22.0	26.0	24.0	18.5	30.5	1.9	24.9	27.8	27.0	29.9
Fe2O3	9.6	10.0	9.4	9.9	10.0	9.5	10.1	7.4	7.4	7.6	7.2	6.9	7.1	2.0	1.0	0.2	2.3	2.8	1.7	1.9
K2O	1.5	1.4	1.2	1.4	1.3	1.4	1.3	1.1	1.1	1.0	1.0	1.1	1.1	9.1	3.2	2.3	4.3	1.1	5.1	2.2
MgO	3.1	2.7	3.0	2.7	2.7	3.1	2.6	2.0	2.0	1.9	2.0	2.0	2.0	1.4	1.0	0.6	5.4	6.3	1.9	2.1
P2O5	2.8	2.3	2.3	2.5	2.4	2.5	2.2	1.4	1.3	1.2	1.3	1.5	1.4	1.3	0.6	0.1	1.4	1.7	1.5	1.7
SiO2	37.3	39.2	36.7	33.3	33.0	37.0	35.6	28.5	28.2	27.6	27.6	29.3	28.4	14.0	5.1	1.4	13.9	16.6	14.0	16.3
TiO2	1.2	1.4	1.0	1.1	1.1	1.1	1.3	1.1	1.1	1.0	1.1	1.2	1.1	1.2	0.6	0.1	1.3	1.6	1.5	1.7
mg/kg																				
As	7.6	7.0	8.8	7.8	8.1	8.2	7.6	6.9	6.9	6.5	6.9	7.7	7.3	34.4	11.4	9.8	21.2	24.0	21.0	9.5
Ba	1478	1377	1272	1402	1418	1375	1376	1029	1055	1028	1108	1109	1108	855	476	116	1088	1167	852	1064
Cd	9.9	8.4	7.5	14.1	9.8	8.7	7.5	5.6	4.7	4.0	2.8	6.1	4.4	307	104	134	121	162	107	19.6
Ce	35.9	34.1	31.8	30.6	32.7	33.8	33.3	29.0	30.2	31.3	32.4	27.8	30.1	18.8	11.2	1.8	19.0	22.8	20.9	25.9
Co	38.8	32.2	23.7	46.3	37.8	31.3	30.9	25.5	27.8	30.4	32.4	22.6	27.5	23.2	9.3	2.2	21.3	34.6	20.7	17.1
Cr	703	637	557	598	636	630	627	741	751	671	770	910	840	590	238	53	328	383	941	989
Dy	2.44	2.09	2.06	2.04	2.08	2.25	1.98	1.61	1.63	1.69	1.67	1.51	1.59	0.84	0.90	0.09	0.83	1.09	1.10	1.36
Er	1.44	1.36	1.44	1.21	1.27	1.44	1.30	1.04	1.07	1.15	1.13	0.90	1.01	0.48	0.48	0.05	0.59	0.70	0.61	0.76
Eu	1.10	0.92	1.00	0.96	0.99	1.05	0.92	0.80	0.83	0.85	0.89	0.80	0.84	0.62	0.41	0.07	0.72	0.78	0.70	0.84
Ga	11.2	10.5	10.6	10.2	10.2	10.9	10.1	8.6	8.3	8.1	7.8	8.7	8.3	10.8	4.0	3.3	8.0	9.3	7.8	7.3
Gd	2.54	2.17	2.17	2.03	2.19	2.35	2.12	1.95	1.94	2.00	1.93	1.84	1.88	0.99	2.10	0.11	1.24	1.39	1.33	3.88
Ho	0.47	0.44	0.43	0.41	0.41	0.45	0.41	0.31	0.32	0.33	0.33	0.29	0.31	0.16	0.17	0.03	0.30	0.37	0.21	0.27
La	22.63	18.51	18.34	17.61	19.11	20.49	18.03	14.47	15.64	16.33	17.98	14.26	16.12	10.14	7.85	0.92	11.51	14.44	11.68	13.75
Lu	0.19	0.18	0.24	0.16	0.17	0.21	0.17	0.13	0.13	0.14	0.14	0.13	0.13	0.07	0.06	0.01	0.07	0.09	0.09	0.10
Mn	1283	1080	1112	1162	1151	1197	1056	790	784	794	772	764	768	519	293	61	682	798	605	754
Mo	21	21	22	21	20	21	20	13	12	10	9	15	12	45	37	10	23	26	18	22
Nb	14.1	18.0	14.9	16.8	15.1	14.5	16.8	8.8	8.9	8.9	9.2	9.0	9.1	22.4	3.8	0.8	10.0	12.8	10.9	13.5
Nd	18.28	12.41	11.68	11.66	13.78	14.98	12.07	12.56	13.39	14.13	15.03	11.91	13.47	6.45	5.72	0.51	6.39	7.78	7.91	10.09
Ni	306	202	246	274	263	276	205	185	162	127	117	233	175	292	56	18	95	139	76	81
Pb	1066	927	3881	1419	1238	2474	1028	1543	1389	1260	1080	1645	1363	5066	2982	2585	2388	2759	3586	573
Pr	4.74	3.40	3.17	3.19	3.77	3.96	3.39	3.09	3.19	3.34	3.37	2.88	3.12	1.97	1.41	0.13	1.70	2.18	2.21	2.76
Rb	40	38	36	35	35	38	36	30	30	31	30	28	29	177	68	54	96	30	106	44
Sb	111	83	183	106	105	147	88	117	106	91	86	137	111	1289	575	754	994	1123	1050	427
Sc	13.30	15.28	14.32	13.22	12.05	13.81	13.40	10.36	9.97	9.14	9.17	11.62	10.40	4.34	1.42	0.00	4.74	5.87	4.44	5.66
Sm	2.667	2.321	2.322	2.117	2.304	2.495	2.256	1.999	2.042	2.113	2.127	1.898	2.013	1.050	0.948	0.081	1.169	1.395	1.420	1.728
Sn	232	178	171	210	203	201	174	218	206	192	181	233	207	1476	506	588	760	906	665	262
Sr	475	403	523	449	462	499	423	445	456	457	478	454	466	316	234	37	394	420	463	553
Tb	0.492	0.439	0.457	0.462	0.437	0.475	0.412	0.358	0.383	0.394	0.432	0.360	0.396	0.265	0.214	0.028	0.267	0.305	0.312	0.381
Tm	0.20	0.17	0.20	0.16	0.17	0.20	0.16	0.13	0.13	0.14	0.14	0.12	0.13	0.07	0.07	0.01	0.07	0.09	0.09	0.11
U	1.74	1.71	1.93	1.54	1.51	1.84	1.56	1.32	1.28	1.22	1.20	1.39	1.29	0.76	0.74	0.08	0.83	1.04	0.99	1.12
Y	16.40	14.55	17.41	14.49	14.56	16.91	13.97	11.85	12.37	12.98	13.42	11.15	12.28	8.53	9.04	1.00	9.87	11.41	9.89	12.13
Yb	1.28	1.18	1.48	1.11	1.13	1.38	1.12	0.87	0.89	0.93	0.93	0.83	0.88	0.48	0.43	0.05	0.43	0.61	0.60	0.79
Zn	3158	2668	2162	3672	3224	2660	2726	2933	3081	2809	3378	3626	3502	24510	8198	9786	14835	17958	11995	4323
Zr	67.6	87.1	491	91.5	87.3	279	92.3	71.7	70.5	65.3	68.2	80.9	74.6	67.3	45.6	22.5	76.4	54.3	66.5	54.1

S.2 Independent sample t-test

The *independent sample t-test* was used in order to compare the means of independent observations between two unrelated groups, namely the concentration of each element of the REE between the two unrelated groups of measurements from MSWI plant A and MSWI plant B.

a



b

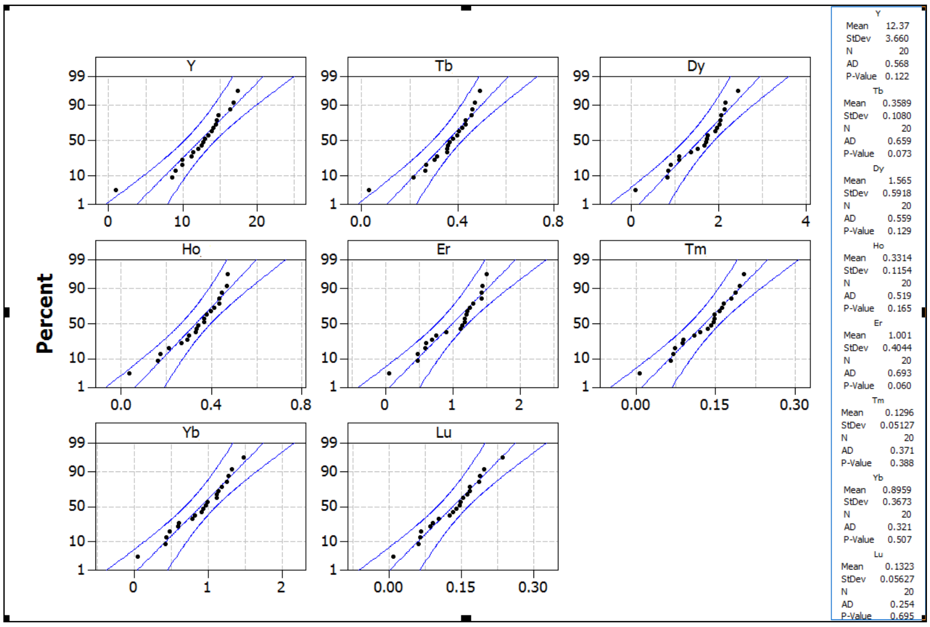


Fig. S.1 Probability plots of standard normal distribution of LREE (a) and HREE (b). The blue lines show the hypothetical normal distribution and the 95% confidence interval. On the picture's side, the statistical parameters and the p-values are reported for each element.

Several assumptions are required for an independent t-test to obtain a valid result: 1) the variables should be measured on a continuous scale; 2) the independent variable should consist of two categorical, independent groups; 3) independence of observations, i.e. no relationship between the observations in each group or between the groups themselves; 4) the dependent variable should be normally distributed; 5) the homogeneity of variances should be acknowledged. Assumptions 1 to 3 are fulfilled because of the nature of data: they are elemental concentrations, in mg/kg, of samples collected from two different MSWI plants. Considering the whole sample set, the assumption of population normality is fulfilled with the exception of europium (Fig. S.1). Conversely, the data set of the two independent groups (i.e., plant A and plant B, taken individually) approximately follows a normal distribution. As a fact, all the selected elements satisfy the normality assumption with the exception of Dy, Eu, Gd, Ho, La, Sc, Sm, Tb and Y of the "plant A" group. However, t-tests are quite robust to violations of normality and even valid when the samples come from non-normal populations (Reimann *et al.*, 2008). This property makes them one of the most useful procedures for making inferences about population means.

The homogeneity of variances was tested by means of Bartlett's test and has been reported in Tab. T.2 together with the results of the independent sample t-test.

Tab. T.2 The independent sample t-test, performed for bulk MSWI (BA+FA), BA and FA. Comparison of the REE mean content in MSWI residues from plants A and B.

	Bartlett's test for homogeneity of variance			t-Test for equality of the mean				95% confidence interval	
REE	Equal variance	k-squared	p-value	t	p-value (two-tailed)	Mean A	Mean B	Lower	Upper
	BA + FA								
Ce	Equal variance not assumed	1.77	0.18	0.30	0.77	28.59	27.73	-5.04	6.76
Dy	Equal variance assumed	8.66	0.00	1.11	0.28	1.72	1.50	-0.19	0.63
Er	Equal variance assumed	4.41	0.04	1.16	0.25	1.11	0.95	-0.12	0.43
Eu	Equal variance assumed	4.31	0.04	0.88	0.39	0.86	0.79	-0.09	0.23
Gd	Equal variance not assumed	0.02	0.89	-0.79	0.44	1.87	2.05	-0.67	0.30
Ho	Equal variance assumed	6.69	0.01	2.09	**0.05**	0.37	0.29	0.00	0.15
La	Equal variance assumed	4.52	0.03	1.11	0.28	16.79	14.89	-1.63	5.45
Lu	Equal variance assumed	7.98	0.00	1.48	0.15	0.15	0.12	-0.01	0.07
Nd	Equal variance not assumed	1.38	0.24	-0.84	0.41	11.12	12.23	-3.84	1.62
Pr	Equal variance assumed	4.10	0.04	0.34	0.74	3.05	2.93	-0.59	0.83
Sc	Equal variance not assumed	2.42	0.12	1.50	0.15	10.62	8.41	-0.82	5.24
Sm	Equal variance assumed	4.85	0.03	0.50	0.62	1.99	1.88	-0.34	0.57
Tb	Equal variance assumed	4.90	0.03	0.22	0.83	0.38	0.37	-0.07	0.08
Tm	Equal variance assumed	8.85	0.00	1.36	0.18	0.14	0.12	-0.01	0.06
Y	Equal variance assumed	11.17	0.00	0.97	0.34	13.15	11.98	-1.32	3.66
Yb	Equal variance assumed	8.67	0.00	1.48	0.15	1.00	0.82	-0.07	0.43
	BA								
Ce	Equal variance not assumed	1.75	0.19	2.80	**0.01**	32.93	30.53	0.60	4.19
Dy	Equal variance assumed	8.34	0.00	7.11	**0.00**	2.06	1.63	0.30	0.56
Er	Equal variance not assumed	0.84	0.36	6.12	**0.00**	1.33	1.07	0.17	0.35
Eu	Equal variance assumed	3.98	0.05	5.31	**0.00**	0.97	0.84	0.08	0.17
Gd	Equal variance assumed	8.22	0.00	4.43	**0.00**	2.18	1.93	0.13	0.37
Ho	Equal variance assumed	5.24	0.02	8.76	**0.00**	0.42	0.32	0.08	0.13
La	Equal variance not assumed	0.91	0.34	4.68	**0.00**	19.30	16.13	1.75	4.58
Lu	Equal variance assumed	16.00	0.00	5.25	**0.00**	0.18	0.13	0.03	0.06
Nd	Equal variance not assumed	2.86	0.09	-0.93	0.36	13.07	13.68	-1.97	0.76
Pr	Equal variance assumed	6.54	0.01	2.39	**0.03**	3.57	3.20	0.05	0.68
Sc	Equal variance assumed	7.55	0.01	3.50	**0.00**	12.92	9.93	1.20	4.78
Sm	Equal variance assumed	4.38	0.04	4.91	**0.00**	2.35	2.05	0.17	0.42
Tb	Equal variance not assumed	0.69	0.41	2.94	**0.01**	0.43	0.39	0.01	0.07
Tm	Equal variance assumed	8.82	0.00	6.38	**0.00**	0.17	0.13	0.03	0.05
Y	Equal variance not assumed	2.35	0.13	5.44	**0.00**	14.97	12.53	1.50	3.38
Yb	Equal variance assumed	10.90	0.00	6.69	**0.00**	1.21	0.90	0.21	0.41
	FA								
Ce	Equal variance not assumed	0.10	0.75	-0.59	0.58	15.58	19.33	-20.17	12.66
Dy	Equal variance not assumed	0.64	0.43	-1.60	0.17	0.71	1.12	-1.07	0.26
Er	Equal variance not assumed	0.85	0.36	-1.01	0.36	0.45	0.62	-0.59	0.27
Eu	Equal variance not assumed	0.32	0.57	-0.49	0.65	0.55	0.65	-0.63	0.43
Gd	Equal variance not assumed	1.34	0.25	-1.86	0.17	0.93	2.44	-4.32	1.32
Ho	Equal variance not assumed	1.95	0.16	-0.01	0.99	0.22	0.22	-0.23	0.23
La	Equal variance not assumed	0.76	0.38	-0.54	0.61	9.25	11.09	-10.78	7.10
Lu	Equal variance not assumed	0.42	0.52	-1.20	0.28	0.06	0.08	-0.08	0.03
Nd	Equal variance not assumed	0.29	0.59	-1.28	0.26	5.28	7.90	-0.79	2.67
Pr	Equal variance not assumed	0.18	0.67	-1.03	0.35	1.50	2.13	-2.20	0.94
Sc	Equal variance not assumed	0.07	0.80	-0.07	0.95	3.71	3.84	-4.84	4.59
Sm	Equal variance not assumed	0.28	0.60	-1.20	0.28	0.92	1.37	-1.39	0.50
Tb	Equal variance not assumed	0.31	0.58	-1.08	0.33	0.22	0.30	-0.29	0.12
Tm	Equal variance not assumed	0.61	0.43	-1.44	0.21	0.06	0.09	-0.09	0.02
Y	Equal variance not assumed	1.72	0.19	-0.11	0.35	7.70	10.35	-9.63	4.34
Yb	Equal variance not assumed	0.14	0.71	-1.33	0.24	0.39	0.61	-0.62	0.20

[Numbers smaller than 0.05, significance level, are in bold character]

S.3 REE flows of MSWI output

An estimation of substance flow for BA and FA residues was carried out to determine the REE annual flow within output products, following the method and recommendations outlined in literature (Brunner & Rechberger, 2004; Astrup *et al.*, 2015). The spatial system boundary for the experiment was the MSWI process itself (see Fig. §3-1 in main text), from the waste collection to outputs products, and included the sampling. The temporal system boundary was defined as 1 year, assuming that the sampled material is representative for one year process activity (i.e., 2013). For the calculation of total annual flow, F in kg/a, we used the following equation:

$$F = C_i \cdot O_r \qquad [Eq.\ E.1]$$

Where: C_i is the measured concentration of element *i*, expressed in mass/mass, and O_r is the total output, in mass/time, of the final solid residue, *r*, i.e. BA or FA. The measured concentrations are provided by ICP-MS analyses. The owners of the incinerator plant provided the total BA and FA output in mass per year. According to the national recommendation, these figures are known with good accuracy. The output flow of BA materials is $2.8 \cdot 10^4$ t/a (average value of two plants), while the FA output is $2.7 \cdot 10^3$ t/a (average value of different kinds of FA). It is essential to keep in mind that the overall process ensures no mixing between FA and BA but disallows the FA sampling of the same BA burning mass, in reason of the significantly different output flow rate. However we assumed that the collected input waste was rather homogeneous within region during time in order to consider FA representative of the BA stockpile. We are moderately confident about our hypothesis because a substantial homogeneity in the municipal waste has been found among different municipalities in the region (Regione Emilia Romagna, 2009). The evaluation of the uncertainty propagation follows the Gauss' law of error propagation. Even if Ce, Gd, and Nd show a non-normal distribution, we decided to calculate means and error propagation assuming normal distribution for the whole sample set. With the simple mass balance given by the Equation E.1, we estimated the yearly flows of REE, in kg/a, for the incinerators A and B (Tab. T.3).

Tab. T.3 The estimated annual flow (kg/a) of selected residues. Mean and standard deviation (SD) are calculated on seven samples for FA and BA(A) and on six samples for BA(B). For FA samples the range of flows is also reported.

	BulkFA (A, B)			***BA (A)***		***BA (B)***	
	range	*mean*	*SD*	*mean*	*SD*	*mean*	*SD*
Ce	5 - 83	47	±21	760	*±60*	1020	*±50*
Dy	0.2 - 4.4	2.3	±1.4	45	*±4.9*	55	*±1.0*
Er	0.1 - 2.4	1.4	±0.8	30	*±2.9*	37	*±1.3*
Eu	0.1 - 2.6	1.5	±0.8	22	*±1.9*	28	*±1.7*
Gd	0.2 - 12.5	4.3	±4.2	50	*±4.7*	65	*±3.3*
Ho	0.1 - 1	0.5	±0.3	9.4	*±1.0*	11	*±0.2*
La	2.1 - 44	27	±14	440	*±5.5*	530	*±76*
Lu	0.1 - 0.4	0.2	±0.1	4	*±0.7*	4.4	*±0.2*
Nd	1.2 - 33	18	±10	290	*±5.7*	458	*±42*
Pr	0.3 - 9	5	±2.9	81	*±1.3*	110	*±1.3*
Sc	0.1 - 18	10	±6.8	240	*±6.3*	296	*±1.6*
Sm	0.1 - 5.5	3	±1.8	54	*±5.0*	68	*±1.0*
Tb	0.1 - 1.2	0.6	±0.4	10	*±1.1*	13	*±1.8*
Tm	0.1 - 0.3	0.1	±0.1	4	*±0.5*	4.4	*±0.2*
Y	2.4 - 40	24	±12	340	*±3.9*	421	*±20*
Yb	0.1 - 2.5	1.3	±0.8	27	*±3.8*	30	*±3.5*
LREE	9 - 207	115	±67	1930	*±205*	2570	*±170*
HREE	3 - 51	31	±16	470	*±51*	580	*±20*
∑REE	11 - 258	148	±83	2400	*±240*	3140	*±190*

[bulkFA=mean flow of fly ashes; BA=Bottom ash; A and B are the selected MSWI plants]

The REE mean concentrations are *quasi*-equally distributed between the different kinds of MSWI residues but the estimated yearly mean flows are higher in BA than FA (Fig. S.2), as a consequence of the higher BA output-flow rate with respect to that of FA. The comparison of wedges of pies (from concentrations to flows) in Fig. S.2 gives an indication of the REE partitioning and transferring into the output streams. A separate estimate of BA flows is needed for each incinerator as indicated by the *t-test* results (see Tab. T.2), and actually it would be a wise choice because of the heterogeneity of sample materials and possible sampling bias. In Tab. T.3 we reported BA flows for plants A and B with their standard deviation values (on the basis of the samples batch) and the mean flow of FA residues from the two plants, i.e., BulkFA (A,B). Considering to Fig. S.2 and Tab. T.3, the FA residues from bag filters with soda additive (FAS) have the lowest potential of REE flow. Bottom and fly ashes have an average concentration of 104 and 54 mg/kg ΣREE, respectively. For FA the expected annual flow is 115 kg/a LREE and 31 kg/a HREE, whereas for BA is 2250 kg/a LREE and 525 kg/a HREE. The REE flow from BA(B) is slightly higher than that deriving from BA(A). The annual flows of REE are in good agreement with recent works (Morf *et al*., 2013; Allegrini *et al*., 2014; Funari *et al*., 2015).

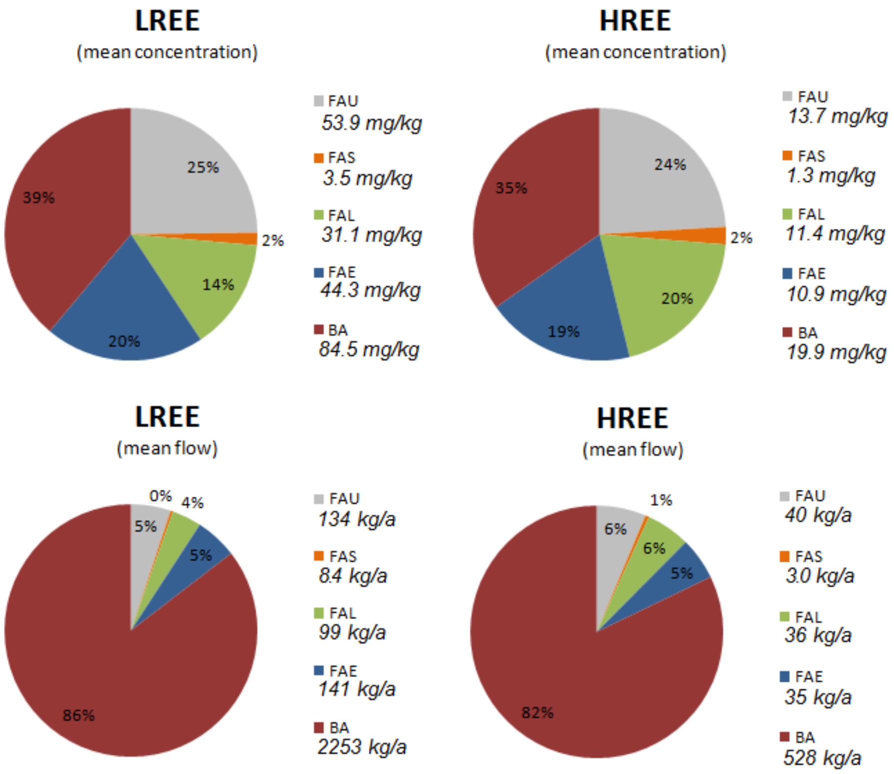


Fig. S.2 Pie charts of LREE and HREE; the partitioning of mean concentrations and mean flows between the different outputs are reported (BA = bottom ash; FAU = untreated fly ash; FAE = fly ash from electrostatic precipitator; FAS = Soda-treated fly ash; FAL = Lime-treated fly ash).

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Chapter 4

Metal recovery from municipal solid waste incinerators fly ash: a preliminary comparison between chemical leaching and bioleaching

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Highlights:

- Bio-hydrometallurgical treatments are carried out on incineration fly ash sample.
- The performance characteristics of H_2SO_4 leaching and bioleaching are compared.
- Processes economics and environmental sustainability are discussed.

Abstract

Bio- and hydrometallurgical experimental setups at 2-litre reactor scale for the processing of fly ash from municipal waste incinerators were explored. We aimed to compare chemical H_2SO_4 leaching and bioleaching; the latter involved the use of H_2SO_4 and a mixed culture of acidophilic bacteria. The leaching yields of several elements, including some of those considered as critical (Mg, Co, Ce, Cr, Ga, Nb, Nd, Sb and Sm), are provided. At the end of the experiments, both leaching methods resulted in comparable yields for Mg and Zn (>90%), Al and Mn (>85%), Cr (~65%), Ga (~60%), and Ce (~50%). Chemical leaching showed the best yields for Cu (95%), Fe (91%), and Ni (93%), whereas bioleaching for Nd (76%), Pb (59%), and Co (55%). The two leaching methods generated solids of different quality with respect to the original material as we removed and significantly reduced the metals amounts, and enriched solutions where metals can be recovered for example as mixed salts for further treatment. Compared to chemical leaching the bioleaching halved the use of H_2SO_4, i.e., a part of agent costs, as a likely consequence of bio-produced acid and improved metal solubility.

Keywords: MSWI fly ash; H_2SO_4 leaching; bioleaching, critical elements, metal removal.

1. Introduction

Municipal Solid Waste Incineration (MSWI) systems can reduce waste volume up to 90% (of the input mass) and simultaneously produce energy for public use (Sabbas *et al*., 2003). However, the management and recycling of solid by-products deriving from MSWI, namely bottom ashes and fly ashes, are of general concern. While the bottom ash is rarely classified as hazardous waste and is typically reused as aggregate in construction materials (Müller & Rübner, 2006), fly ashes pose the most severe environmental problems. The fly ashes are dust-like particles carried away from the combustion chamber with the flue-gas that undergo several steps of filtration (e.g., dry/wet scrubber, electrostatic precipitator, chemical bag filter) through the Air Pollution Control (APC) system, before being released into atmosphere. Despite the mass of pollutants is lower in filtered fly ashes than in raw fly ashes due to the dilution with unreacted additives and the neutralization capacity, both materials contain large quantities of soluble salts (e.g., Cl, Na) and hazardous metals (e.g., As, Cd, Pb) that are easily volatilised after burning (Eighmy *et al*., 1995; Astrup *et al*., 2006; Pan *et al*., 2013; Funari *et al*., 2015a,b) and readily accessible to weathering and transport into the environmental sinks. Consequently, the fly ash material is considered as hazardous waste and is landfilled or stored underground after pre-treatment.

Every year thousands of tonnes of MSWI fly ashes might contain 10^3 kg Cu, Sn, and Sb, 10^4 kg Al and Zn (Funari *et al*., 2015a), but their landfilling results in a loss of marketable metals such as Al, Cu, Sn, Zn, and critical raw materials (e.g., Cr, Co, Ga, Mg, Nb, Sb, and lanthanides; according to the EC, 2014) (Morf *et al*., 2013; Funari *et al*., 2015a). There is, therefore, interest in turning MSWI fly ashes into a secondary resource. Enhancing metal removal and recovery from these alternative sources requires accurate investigations and new technologies need to be compared and combined in order to meet specific aims of treatment.

Desirable approaches are always those capable of both metal recovery and environmental stabilization (Meawad *et al.*, 2010). Main technologies of MSWI fly ash pre-treatment are thermal or hydrometallurgical processes. The hydrometallurgical approach may lead to a safe disposal of precipitates and eluates and to the recovery of valuable metals (by means of subsequent reprecipitation from solutions) with relatively low energy demand and toxins release. Various studies have investigated wet extraction processes by using chelating agents (Hong *et al.*, 2000; Hasegawa *et al.*, 2014), mineral or organic acids (Bipp *et al.*, 1998; Meawad *et al.*, 2010 and reference therein) and bio-produced acids (Brombacher *et al.*, 1998; Lee & Pandey, 2012 and reference therein; Xu *et al.*, 2014).Since there has long been interest in assessing the environmental impact of MSWI ashes and developing new technologies for decontamination or immobilisation of harmful elements, the majority of literature works focuses on the leaching behaviour of toxic metals and a handful of other elements (Astrup *et al.*, 2006; Huang *et al.*, 2007; Pan *et al.*, 2013; Funari *et al.*, 2015a) and on evaluating the influence of experimental parameters such as time, temperature, reagents used, and liquid solid ratio (Hong *et al.*, 2000; Zhang & Itoh, 2006).

In this work we focus on two leaching methods for subsequent metals recovery from MSWI fly ash, namely chemical leaching and bioleaching, in acid solution. A comparison of their leaching yields is provided to help assessing an affordable pre-treatment strategy prior to metal recovery. Leaching behaviour and recovery potential of Mg, Co, Cr, Ga, Nb, Sb, La, Ce, Nd, and Sm (hereafter critical elements), Al, Cu, Mn, Sn, and Zn (hereafter marketable elements), Ca, Fe, and Ti (unvalued elements), As, Ba, Mo, Ni, Pb, Sr and V (hazardous elements) are discussed. Chemical leaching by means of sulphuric acid was used because it is found to be effective in metal removal (Nagib & Inoue, 2000) and relatively less expensive than other strong acids (Meawad *et al.*, 2010). Conversely, in the bioleaching procedure we employed a mixed culture with sulphur- and iron-oxidizing bacteria that are commonly used at industrial scale for the bioleaching of sulphide ores (Bosecker, 1997; Rawlings, 2002). Recent works demonstrated these bacteria are adaptable to MSWI substrate (Brombacher *et al.*, 1998; Krebs *et al.*, 2001; Ishigaki *et al.*, 2005) and, thereby, contributed to increase the interest on bio-assisted approach and its capabilities.

The outcomes of the present paper will help to figure out which procedure results in more enriched process solutions, where metals can be recovered by further treatment, and more stable solids. Emphasis is given on the bioleaching method, which is relatively unexplored for the treatment of MSWI fly ashes and shows major potential for improvements.

2. Experimental Section

2.1 Materials

The studied fly ash comes from an Italian grate-furnace incinerator with thermo-recycling technology, which burns 90% household waste and 10% of special waste. The latter input source consists of processing waste from ceramics and metallurgy, automobile shredder residues, hospital and pharmaceutical waste. The main output products of the MSWI are bottom and fly ashes.

The investigated fly ash material derives from the dry scrubber located after the combustion chamber and prior to the chemical bag filters within the APC system. This fly ash can be defined as untreated raw fly ash (hereafter FA-RAW) and represents the most undiluted, hence hazardous, residue deriving from the

APC. The output flow of the FA-RAW is $3.2 \cdot 10^3$ t/a at the year of the sampling, according to the facility report.

The samples were collected in May 2013 from a big bag (order of hundreds of kilograms) after blending a large number of increments, as in Funari *et al.* (2015a). Colour and grain size of the collected samples were homogeneous upon visual inspection. The FA-RAW was recovered into the big bag during normal and stable operation of the combustor. The MSWI system allowed the separate recovery of the FA-RAW and other kind of APC residues (e.g., treated fly ashes), following the system steps described elsewhere (Funari *et al.*, 2016).

2.2 Leaching procedure

2.2.1 Pre-treatment of fly ash material

The collected primary sample (approximately 10 kg) was oven dried at low temperature (40°C) for one week, grounded, homogenised and very fine milled (< 40 μm) with an agate vibratory mill disk, before being used in the experiments. The milled material of FA-RAW was firstly analyzed and then used as starting material before bio-hydrometallurgical treatments.

In order to remove water-soluble salts the FA-RAW was washed with distilled water prior to the leaching step. The washing treatment promotes leaching efficiency during both chemical leaching (Zhang & Itoh, 2006) and bioleaching methods (Wang *et al.*, 2009). A 10:1 liquid-solid ratio (L/S) and three steps of washing were used, since they have been found to be enough to dissolve the most of water soluble salts (Nagib & Inoue, 2000). The solid residue and the liquid were separated using a centrifuge (Allegra X-15R, Beckman Coulter). After separation, the washed residue (hereafter FA-WW) was dried at 105 °C for 24 h and used throughout the experiments. The chemical parameters of FA-WW were pH 11.5 and red-ox potential of 135 mV at the beginning of the experiments.

2.2.2 Chemical leaching

The FA-WW (10% v/v) and distilled water (90% v/v) were treated with H_2SO_4 in a 2 litre glass reactor equipped with a top-entered agitator and an aeration system, which supplied a continuous airflow from the bottom of the reactor (Fig. §4-1). Rotation speed of 320 rpm and airflow rate of 1.0 l/min were used. As high temperatures do not improve remarkably leaching kinetics and yields in sulphuric acid leaching of MSWI fly ashes (Nagib & Inoue, 2000), the reactor operated at room temperature. In order to investigate leaching as a function of pH, several pH intervals (i.e., pH 1.0, 3.0, 5.0, 7.0, 9.0) have been sampled, after a leaching time of 30 minutes in which the pH level was maintained constant by 4M H_2SO_4 titration (T70, Mettler-Toledo). Reaction time of 30 minutes was used because it is generally adequate to achieve good leaching performances (Nagib & Inoue, 2000). The overall duration of the leaching experiment was six hours. A benchtop meter (Consort C3040) was used in order to monitor pH, red-ox (Ag/AgCl in 3M KCl) potential and temperature values. The liquid solution was collected using a vacuum filtration system and a 45 μm glass-fibre filter. After vacuum filtration, several elements were determined in the leachate (Ca, Al, Fe, Cu, Cr, Sb, Sn, Zn) using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), while the solid precipitate was poured again into reactors in order to avoid weight loss and dilution effects during the experiments. Only the final solid precipitate was analysed for total elemental chemistry by XRF, after being washed using two times of its volume of distilled water in order to remove the water soluble materials (mainly salts), oven-dried, and exactly weighted for further mass balance assessment.

2.2.3 Bioleaching: preliminary adaptation of the bacteria mixture and experimental setup

For bioleaching a mixed acidophilic culture, enriched from a sulphide ore mine site (Halinen *et al*., 2009), containing *At. ferrooxidans*, *At. thiooxidans*, *At. caldus*, *L. ferrooxidans*, *Sb. thermosulfidooxidans*, *Sb. thermotolerans* and some members of *Alicyclobacillus* genus was used. These bacteria use metal-sulphide phases and also elemental sulphur as their substrate to produce sulphuric acid (Bosecker, 1997; Sand *et al*., 2001; Rawlings, 2002) through the reaction:

$$S^0 + 1.5\ O_2 + H_2O \rightarrow 2\ H^+ + SO_4^{2-} \quad [1]$$

Metal-sulphides are found as minor phases within MSWI ashes (Bayuseno & Schmahl, 2011); therefore, when treating these kind of unconventional materials, sulphur-oxidizing bacteria must be fed with elemental sulphur to achieve sulphuric acid production and promote leaching. The culture was cultivated in a modified Silverman 9K medium (Silverman & Lundgren, 1959) containing $(NH_4)_2SO_4$ 3.0 g/l, K_2HPO_4 0.5 g/l, $MgSO_4 \cdot 7H_2O$ 0.5 g/l, KCl 0.1 g/l, $Ca(NO_3)_2$ 0.01 g/l, $FeSO_4 \cdot 7H_2O$ 22.5 g/l and also 10.0 g/l S^0. The modified 9K medium was adjusted to pH 2.0 with concentrated H_2SO_4. The culture was incubated in a rotary shaker (150 rpm) and the temperature was set to 30°C due to mesophilic *At. thiooxidans* (Rawlings, 2002). The culture was renewed every 15 days by inoculating 10% (v/v) of former cultivation and 90% (v/v) of the modified 9K medium.

The original acidophilic culture was adapted to tolerate the presence of MSWI fly ash and the adaptation experiment was conducted in 250 ml Erlenmeyer flasks containing 90 ml of the modified 9K medium. Flasks were inoculated with the acidophilic culture (10% v/v) followed by the addition of the FA-WW. The pH was adjusted to 2.0 with concentrated H_2SO_4 and flasks were incubated in a rotary shaker (150 rpm, 30°C). If a spontaneous decrease in pH was observed during 15 day, a new modified 9K medium with an increased amount of FA-WW was prepared and inoculated with the former solution (10% v/v) of the adaptation experiment. The amounts of solid FA-WW were increased three times (1, 2, and 5%) of L/S ratio, respectively.

After the adaptation experiment, a scaled-up experiment was conducted in a 2 litre glass reactor with a similar setup as for chemical leaching (Fig. §4-1) by using the same sample mass of FA-WW (100 g) to obtain more representative results. Rotation speed of 320 rpm and airflow rate of 1.0 l/min were used. The reactor temperature was maintained at 30°C using a heated water jacket. The reactor contained 90% (v/v) modified 9K medium (without $FeSO_4 \cdot 7H_2O$) and the previously adapted acidophilic culture (10 % v/v). The pH was fixed to 2.0 with concentrated H_2SO_4 and precultivation of microorganisms was conducted for 4 days without FA-WW sample. Then, 5 % (v/v) of FA-WW sample was introduced and bioleaching continued for 21 days with pH fixing to pH 1.8 (i.e., set point) with concentrated H_2SO_4, if necessary.

Fig. §4-1 Experimental setup of leaching procedure in a 2 litre glass reactor, equipped with titration system and benchtop meters for continuous monitor of pH, red-ox and temperature.

2.3 Analytical techniques

The total elemental chemistry of solid material was determined on pressed powder pellet (ϕ 37 mm) by a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF), PANalytical Axios, equipped with a 4 kW Rh tube. The SuperQ 3.0 software was used for online correction and analytes quantification. The estimated precision for trace element (<0.01 *wt.* %) determinations are better than 5% except for those elements at 10 mg/kg and lower (10–15%). Triplicate samples analysis was carried out in order to assess the precision of measurements by means of standard deviation (SD) and relative standard deviation (RSD). In addition, a MSWI fly ash reference material (BCR-CRM 176) was analysed as unknown sample to evaluate precision and accuracy of the analytical method. Total loss on ignition (LOI) was gravimetrically estimated after overnight heating at 950°C.

The leachates were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Perkin-Elmer). The solutions were completely dissolved with aqua *regia* in closed alumina bombs at 170°C until the digested solution was clear. Element quantification employed calibration curves prepared with diluted standard solutions.

2.4 Metal removal

The measured concentrations of solid residues and leached solution obtained by XRF and ICP-AES, respectively, are used to evaluate the percentage of metal removal (yield), R%, which is defined as

$$R_{ij}\,\% = (1 - C_{ij}\,M_j / C0_{ij}\,M0_j) \cdot 100 \qquad [2]$$

where R_{ij} is the degree of removal for the element *i* in the batch *j*, C_{ij} is the concentration of the element *i* in the batch *j* in the treated sample, M_j is the mass of the treated sample of batch *j*, $C0_{ij}$ is the concentration of the element *i* in the batch *j* in the untreated sample and $M0_j$ is the mass of the untreated sample of batch *j*.

3. Results and Discussion

3.1 Characterisation of original MSWI ash sample

The bulk elemental content of the FA-RAW is given as averages of three FA-RAW samples in order to test sample homogeneity and representativeness (Tab. §4-1). Despite a low amount of primary sample (about 10 kg) was collected due to logistical reasons, the representativeness of fly ash material can be assessed by comparing the analysis of FA-RAW sample with concentrations range quoted in literature and recently outlined in *Funari et al*. (2015a). Comparing the values of the matrix-matched reference material with the certified values (CV) served for a quality check. Good results in term of relative error (when applicable) were obtained for the most of critical elements, even if some discrepancies occur due to spectral overlaps and/or matrix effect. This might lead to underestimation of leaching yields and recovery potential for elements like Al, Co, K, Mn, and Cl, according to Tab. §4-1. The FA-RAW is characterised by high amounts of Ca, S, Cl, and Si, being their oxides weight fractions of about 20, 24, 13, and 9 *wt*. %, respectively. SD values for most of major elements are within a narrow range, suggesting a relative homogeneity of the sampled material.

There are high concentrations of several elements such as Cr, Cu, Pb, Sb, and Zn. The FA-RAW sample contains more than 1 *wt*. % of Zn, and about one order of magnitude less of Cr, Cu, Pb, and Sb. A number of trace elements show high SD probably due to characteristic fragments ending up into sample: for example the presence of metallic scraps can influence Pb concentrations, plastics might affect Sb and Cl, ceramic waste Ce, Co, Nb, and Nd.

Tab. §4-1 Major and trace elements composition of the reference material (BCR-CRM 176) and the untreated raw fly ash, FA-RAW.

	BCR-CRM 176					**FA-RAW**		
	CV	average	SD	%RSD	RelErr	average	SD	%RSD
Major element (wt. %)								
Al_2O_3	19.20	16.74	0.13	0.75	13	6.11	0.10	1.76
CaO	8.80	8.42	0.01	0.08	4	33.61	0.31	0.98
Fe_2O_3	3.05	2.72	0.01	0.51	11	1.62	0.02	1.01
K_2O	5.42	3.99	0.01	0.26	26	0.64	0.09	14.9
MgO	-	3.10	0.02	0.64	-	3.21	0.17	5.56
MnO	0.19	0.13	0.00	0.00	32	0.09	0.01	6.93
Na_2O	4.04	6.20	0.06	0.90	53	1.09	0.02	1.51
P_2O_5	-	1.58	0.04	2.22	-	1.21	0.05	4.17

SiO_2	-	25.22	0.25	1.00	-	11.42	1.77	16.6
TiO_2	-	1.30	0.00	0.00	-	1.75	0.03	2.13
CuO	0.16	0.16	0.00	1.79	2	0.11	0.00	1.91
ZnO	3.21	3.26	0.02	0.56	2	1.92	0.05	3.01
PbO	1.25	1.27	0.03	2.15	1	0.63	0.04	7.41
Cr_2O_3	0.13	0.14	0.00	2.11	8	0.22	0.01	2.53
Sb_2O_3	0.05	0.05	0.00	1.45	2	0.16	0.00	3.28
Cl	4.00	3.46	0.02	0.69	13	1.98	0.06	3.34
SO_3	8.74	8.82	0.09	0.98	1	28.42	0.96	3.62
LOI		13.44				5.81		
Trace element (mg/kg)								
As	95	92	0.1	0.08	3	31	4	12.6
Ba	5000	5004	73	1.47	0	879	37	4.18
Ce	-	76	14	18.49	-	22	3	12.6
Co	31	26	1	3.61	14	8	1	11.2
Cs	-	43	8	18.05	-	13	2	18.9
Ga	-	33	1	1.42	-	29	2	6.07
La	-	32	2	7.63	-	11	5	49.6
Mo	-	30	0.3	0.96	-	21	1	6.38
Nb	-	21	1	2.76	-	15	0.3	2.01
Nd	-	42	9	20.39	-	13	5	38.3
Ni	124	131	6	4.43	6	53	7	13.9
Sm	-	3	0.07	2.24	-	3	0	4.00
Sr	462	411	10.2	2.48	11	510	19	3.68
V	100	108	8.91	8.26	8	81	2	2.73
Zr	-	160	5.37	3.37	-	151	6	3.98

Average, standard deviation (SD) and relative standard deviation (RSD) values of triplicate samples are reported. Certified values (CV) of reference material allowed the calculation of the relative error (RelErr). Certified values of the BCR-CRM 176 are taken from the GeoReM database (http://georem.mpch-mainz.gwdg.de/).

3.2 Effect of pre-washing

High contents of Cl and mineral salts as those of Na, Ca, K typically hamper an efficient recovery of metals from MSWI fly ashes (Okada *et al.*, 2007). Alkali salts consume large amounts of acid during the leaching and they may also complicate the separation of valuable metals bonded with them. Our fly ash pre-washing removes most of water soluble salts (Tab. §4-2). More than 80% of Cl, K and Na were removed, in agreement with previous works (Nagib & Inoue, 2000; Wang *et al.*, 2009).

Tab. §4-2 Chemical composition of FA-RAW and FA-WW by XRF, and calculated yield (R%). Elements are listed from highest to lowest R%.

	FA-RAW		**FA-WW**		**R**	
	average	SD	average	SD	average	SD
	(mg/kg)		(mg/kg)		(%)	
Cl	142830	*13942*	18509	*618*	88	*1*
K	31246	*2847*	5315	*742*	84	*1*
Na	37767	*4767*	8058	*113*	80	*3*
P	5476	*243*	5301	*206*	9	*1*
Sm	3	*0.1*	3	*0.3*	7	*11*
Cr	1456	*50*	1459	*62*	6	*1*
S	105656	*3397*	106156	*3846*	6	*1*
Sr	510	*19*	556	*13*	1	*2*
Mo	21	*1*	24	*1*	1	*6*
Nb	15	*0.3*	17	*0.5*	<1	*1*
Zr	151	*6*	180	*3*	<1	*4*
Si	44301	*5763*	53399	*8282*	<1	*4*
Ba	879	*37*	1084	*11*	<1	*5*
V	81	*2*	102	*3*	<1	*0*
Nd	13	*5*	17	*7*	<1	*7*
As	31	*4*	41	*8*	<1	*11*
Sb	925	*3*	1232	*40*	<1	*5*
Ga	29	*2*	40	*1*	<1	*6*
Ce	22	*3*	31	*6*	<1	*11*
Cs	13	*2*	19	*7*	<1	*33*
La	11	*5*	14	*4*	<1	*54*
Cu	591	*13*	881	*20*	<1	*2*
Co	8	*1*	12	*1*	<1	*7*
Ni	53	*7*	88	*2*	<1	*30*
Al	19322	*1463*	32355	*530*	<1	*13*
Zn	10182	*291*	14400	*433*	<1	*1*
Ca	142037	*5894*	240197	*2192*	<1	*7*
Pb	3365	*280*	5076	*376*	<1	*6*
Ti	5713	*69*	10474	*207*	<1	*2*
Mn	370	*44*	692	*45*	<1	*14*
Mg	10260	*1258*	19373	*1005*	<1	*18*
Fe	5538	*283*	11296	*107*	<1	*11*

Average and standard deviation (SD) values of triplicate samples are reported. SD of the R (%) was estimated on the basis of maximum and minimum removal for each element.

3.3 Chemical leaching

The leaching behaviour of MSWI fly ash was investigated as a function of pH (Eighmy *et al*., 1995; Astrup *et al*., 2006) by testing the sample material subjected to several stages of pH and analysing leaching solutions at specific pH intervals. At the end of the experiment (i.e., at pH 1), the XRF analysis of solid by-product allowed assessing metal removal rates (as R%, Tab. §4-3), which are calculated for each element according the equation 2 and the mass balance of the experiment. Chemical leaching effectively removes elements such as Al, Cu, Fe, Mg, Ni, P, and Zn, showing > 90% yields. The leaching efficiency coupled with the relatively high concentrations of these elements within initial MSWI fly ash show significant recovery potential. Other elements such as Cl, Mo, Na, are almost totally recovered by H_2SO_4. Among critical elements, Cr, Sb and Nd show a better leaching yield (nearly 70%) than Ga (58%), Ce (49%), Nb (46%), Sm (31%), and Co (28%). However, high values of SD for lanthanides emphasise a limited confidence on their calculated yield. It was also found that 40% Ca, 50% Si, and 45% Pb were mobilised. Despite Ca can be present as easily soluble compounds in acidic environment, the overall Ca release was lower with respect to similar work reported in literature (Nagib & Inoue, 2000; Zhang & Itoh, 2006; Huang et al., 2007).

Tab. §4-3 Chemical composition of the FA-WW and samples after treatments (FA-H_2SO_4, and FA-BIO), by XRF. Calculated yield (R%) for FA-H_2SO_4 and FA-BIO is reported.

	FA-WW		**FA-H_2SO_4**		**R**		**FA-BIO**		**R**	
	average	**SD**	**average**	**SD**	**average**	**SD**	**average**	**SD**	**average**	**SD**
	(mg/kg)		**(mg/kg)**		**(%)**		**(mg/kg)**		**(%)**	
Al	32355	*530*	2923	*480*	92	*2*	4768	*1659*	86	*7*
As	41	*8*	41	*1*	13	*22*	35	*5*	18	*7*
Ba	1084	*11*	1115	*29*	10	*2*	920	*50*	19	*5*
Ca	240197	*2192*	166301	*1757*	40	*0.1*	139941	*1757*	45	*2*
Ce	31	*6*	18	*3*	49	*1*	17	*1*	48	*8*
Cl	18509	*618*	133	*25*	99	*1*	319	*12*	98	*0.4*
Co	12	*1*	10	*1*	28	*0.3*	6	*2*	55	*17*
Cr	1459	*62*	620	*10*	70	*1*	721	*50*	63	*6*
Cs	19	*7*	4	*4*	80	*23*	4	*2.7*	84	*11*
Cu	881	*20*	51	*4*	95	*0.5*	239	*87*	74	*12*
Fe	11296	*107*	1149	*214*	91	*2*	5475	*1283*	54	*15*
Ga	40	*1*	19	*1*	58	*0.4*	18	*3*	57	*8*
K	5315	*742*	3262	*293*	46	*4*	1524	*155*	73	*1*
La	14	*4*	16	*2*	<1	*24*	10	*2*	30	*11*
Mg	19373	*1005*	84	*160*	100	*1*	201	*133*	99	*1*
Mn	692	*45*	69	*1*	91	*1*	102	*89*	87	*16*
Mo	24	*1*	2	*1*	92	*3*	12	*0.3*	50	*0.2*
Na	8058	*113*	1683	*43*	82	*0.3*	1111	*771*	87	*13*
Nb	17	*0.5*	11	*0.6*	46	*2*	13	*0.4*	30	*0.3*
Nd	17	*7*	7	*1*	64	*17*	4	*2*	76	*2*
Ni	88	*2*	8	*2*	93	*7*	31	*7*	66	*11*
P	5301	*206*	182	*25*	97	*0.4*	1284	*297*	77	*6*
Pb	5076	*376*	3792	*120*	45	*3*	2963	*211*	59	*1*
Sb	1232	*40*	496	*13*	65	*1*	856	*17*	52	*0.4*
Si	53399	*8282*	30540	*6441*	50	*4*	34886	*12241*	40	*18*
Sm	3	*0.3*	2	*0.2*	31	*4*	2	*0.1*	9	*9*
Sr	556	*13*	414	*5*	35	*1*	319	*8*	45	*0.1*
Ti	10474	*207*	3007	*159*	75	*1*	5543	*330*	50	*3*
V	102	*3*	35	*2*	70	*1*	52	*6*	52	*6*
Zn	14400	*433*	1449	*56*	93	*1*	2069	*47*	91	*0.2*
Zr	180	*3*	106	*4*	49	*2*	120	*4*	36	*2*

Average and standard deviation (SD) values of triplicate samples are reported. SD of the R (%) was estimated on the basis of maximum and minimum removal for each element.

As expected, the concentration of selected elements in leachates (Fig. §4-2) indicates that H_2SO_4 leaching performances change as a function of pH. Elements such as Ca and Al show a good solubility even at pH intervals close to neutrality, whereas Zn, Cr, and Sb demonstrate a slight amphoteric behaviour where removal rates fall at 7 pH and start rising again in alkaline conditions. Overall, removal rates and potential recovery of marketable elements (especially Al, Cu, and Zn) from MSWI fly ash after H_2SO_4 leaching are consistent with the outcomes of previous work (Nagib & Inoue, 2000; Astrup *et al.*, 2006; Zhang & Itoh, 2006).

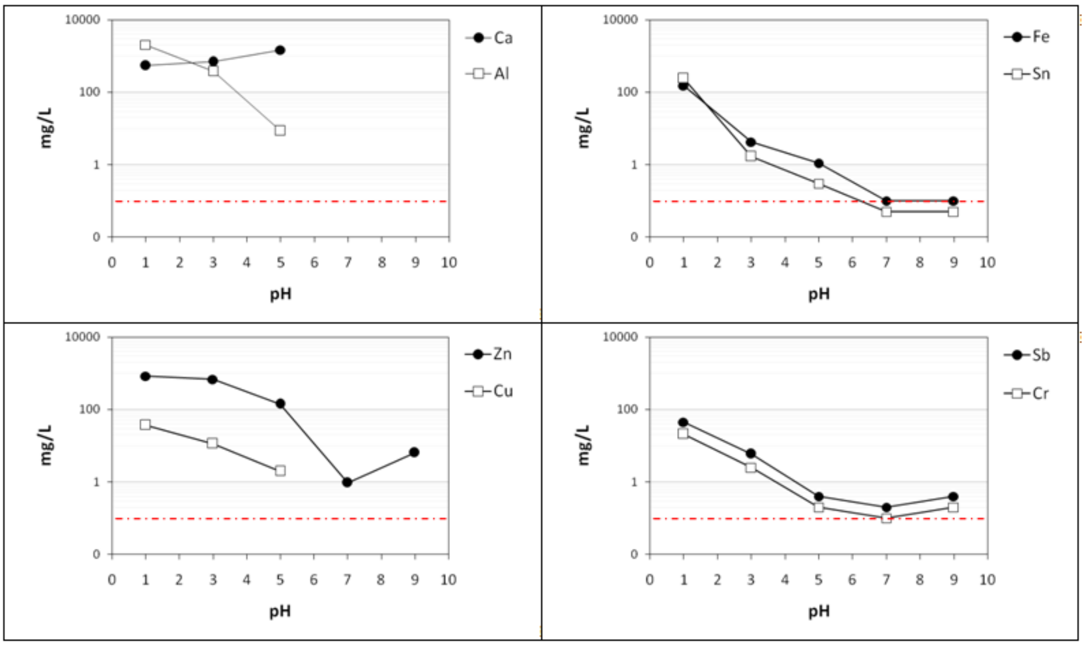

Fig. §4-2 Measured concentrations by ICP-AES of selected elements in leachates from H2SO4 leaching as a function of pH. Red dashed line is the detection limit.

3.4 Bioleaching

Unlike the chemical leaching procedure, the sampling from bioleaching reactor was performed over time at an initial pH of 1.8, maintained with H_2SO_4 addition. The buffer capacity of MSWI fly ash sample was greater than biologically produced sulphuric acid and this made necessary a few manual addition of sulphuric acid during the experiment (see 3.5.2 *Effect of pH and acid consumption/production*). Acid consumption significantly decreased after three days and a steady acid consumption was achieved (Fig. §4-3). The sampling started on the third day and carried out each day for ten days, then three days before the end of the experiment, and at the end of the experiment (after three weeks in total). At the end of the experiment, pH had decreased to 1.4, clearly below the pH 1.8 set point, showing the activity of sulphur-oxidizing bacteria and production of sulphuric acid from elemental sulphur.

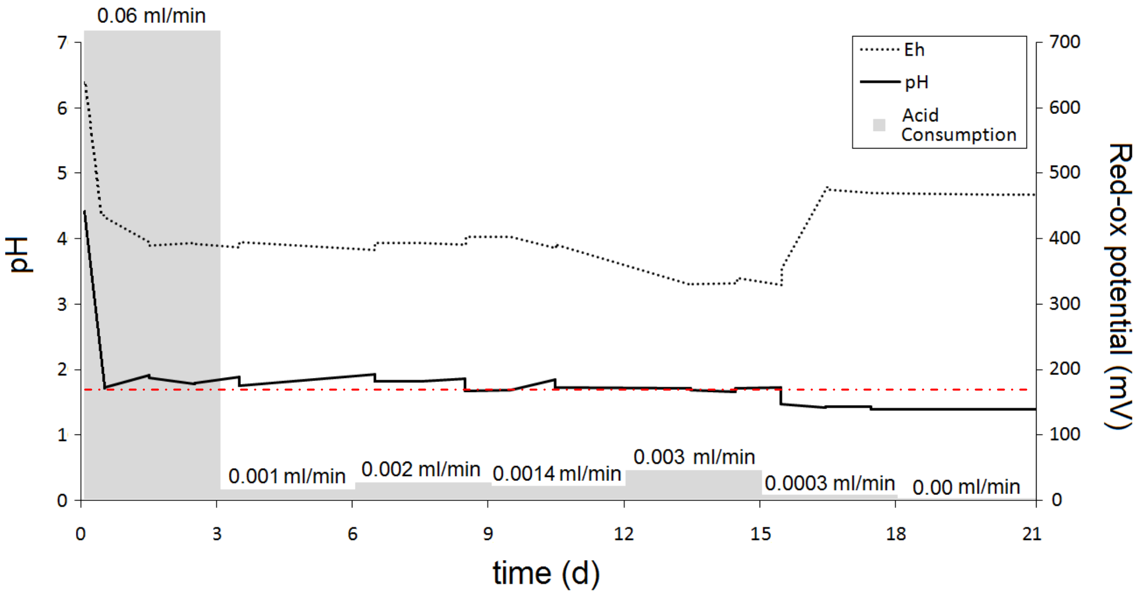

Fig. §4-3 Chemical parameters, pH and red-ox, of the bioreactor as a function of time. The cumulative acid consumption in ml/min is calculated over a period of three days (i.e., the histograms' height). Red dashed line is the pH 1.8 set point.

The investigated elements show a high leachability already during the first days of the experiment (Fig. §4-4), and from third day onwards the bioleaching reactor was close to equilibrium. The bioleaching system does not show a clear time-dependence and the majority of leaching most likely occurs within 0-3 day. From day-3 sample to day-21 sample, data disclose a slight increase of Fe, Cr, and Zn concentrations in leachates and a slight decrease of Cu and Sb.

The recovery performances of the bioleaching procedure, based on the XRF analysis of FA-BIO solid sample, can be evaluated in Tab. §4-3. Critical and marketable elements such as Mg, Zn, Mn, Al, Nd, and Cu show removal percentages of 99, 91, 87, 86, 76, and 74, respectively. Moreover, toxic elements such as Ni and Pb, and the critical elements Cr, Co, and Ga were efficiently solubilised with removal close to 60%. Other critical elements were moderately leached out from the solids, for example 52% Sb, 48% Ce and 30% Nb were removed. The mobility of the unvalued Si, Ca, Ti and the harmful As from solid to solution after bioleaching is relatively low.

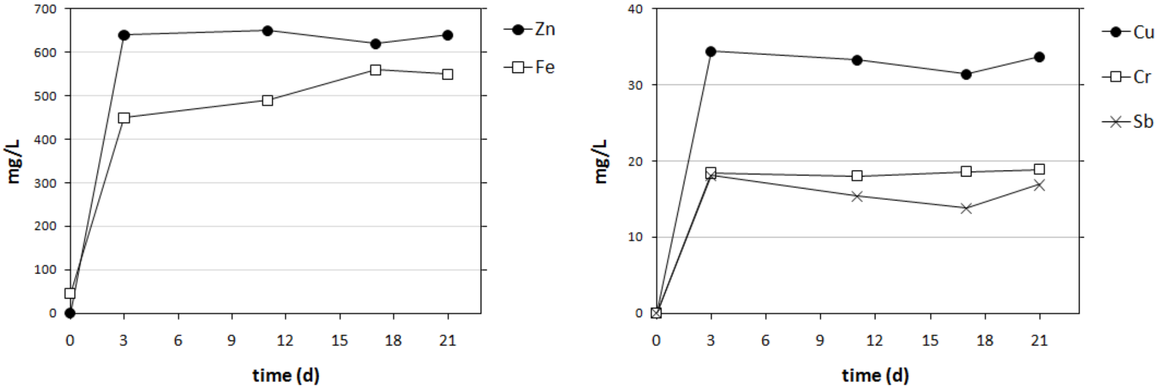

Fig. §4-4 Measured concentrations by ICP-AES of selected elements in leachates from bioleaching as a function of time.

3.5 Comparison of chemical leaching vs. bioleaching

3.5.1 Speciation of elements within solid residues of MSWI fly ash after chemical leaching and bioleaching

A comparison of the performance (yields) between chemical leaching and bioleaching is shown in Fig. §4-5. The error bars indicate the uncertainty associated to XRF measurements for each element. A larger standard deviation is frequently associated with the bioleached rather than chemically leached residue. The reasons of this discrepancy are unclear. On the basis of morphological analysis of FA-RAW, FA-H_2SO_4 and FA-BIO (see Supplementary Materials of Chapter 4) we suggest that the formation of coarse mineral grains may promote the nugget effect.

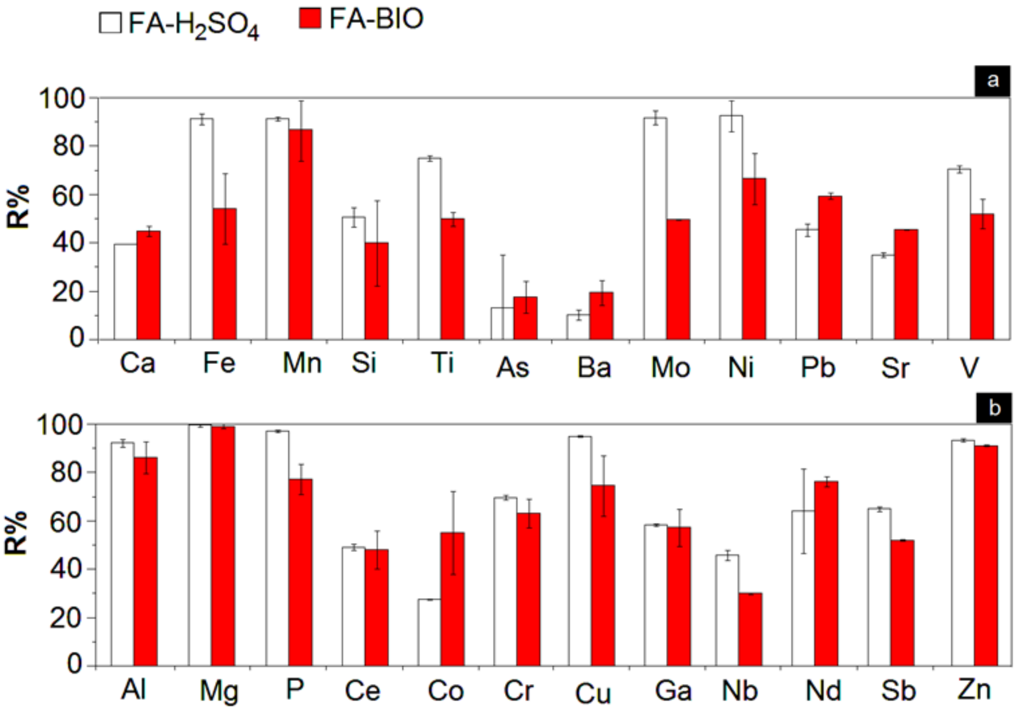

Fig. §4-5 Comparison of leaching yields (R%) between chemical leaching and bioleaching for selected unvalued/hazardous (a) and critical/marketable (b) elements. Error bars are the standard deviation of R%.

Chemical leaching and bioleaching showed comparable yields for easily soluble elements such as Al, Cl, Cs, Mg, and Na, but larger differences in Ba, K, Mo, Co, and Fe. The element Sm showed unreliable differences in leaching yield due to the analytical sensitivity, therefore Sm is not reported. Both procedures are efficient in the removal of critical/marketable metals such as Al, Ce, Cr, Ga, Mg, and Zn (Fig. §4-5b), while a low mobilisation of Ca was noted. The presence of Ca could potentially inhibit the extraction of other elements (Kalmykova & Fedje, 2013), thus low Ca yields might be of beneficial for the quality of the final product and the overall recovery potential. The reason of low Ca release after both treatments may relate to the untreated fly ash used in the present study, which had not lime addition (typically employed to remove SO_2 gas from APC systems). In fact, Ca-bearing compounds within untreated fly ashes can occur in form of low soluble amorphous silicates, oxides or sulphides rather than gypsum and calcium carbonate minerals, which are instead more mobile (Zhang & Itoh, 2006).

Both procedures can be beneficial to the decontamination of MSWI fly ashes: the bioleaching enhanced the removal of several hazardous elements (Fig. §4-5a) such as As, Ba, Pb, and Sr while chemical leaching is an option for the removal of Mo, Ni, and V. Overall, As was slightly mobilised from the solid material probably due to its low concentration in the FA-RAW or bonding with refractory silicates.

The chemical leaching resulted in higher leaching yields for Cu, Fe, Ni, P, and Sb with respect to bioleaching, but the removal of unvalued elements such as Si and Ti is even high (Fig. §4-5a). The removal rates of Co, Pb and Nd are definitely enhanced by means of bioleaching. Generally, similar leaching (acidic solutions at pH 1-1.4) of metals should result in similar levels of total acid consumption (either with mineral or bio-produced H_2SO_4); a different mobilisation of metals could be related to a different reaction time (a few hours for the chemical leaching; several days for the bioleaching) but also to mechanisms of direct enzymatic reduction or any other indirect activities of microorganisms (Brombacher *et al.*, 1998). Although a detailed investigation of bacteria activity and growth is not the aim of this paper, the unbalanced yields especially for Co, Pb, and Nd suggest that the bio-produced sulphuric acid is not the sole agent of metals mobilisation. Several mechanisms might compete during leaching which, in turn, might selectively enhance or inhibit the solubilisation of some metals. The improved solubilisation of Co and Pb, which partly occur in sulphide minerals within MSWI ashes, might be enhanced by Fe^{3+} produced by iron-oxidizing bacteria (Sand *et al.*, 2001). These bacteria (*At. ferrooxidans* and *L. ferrooxidans*) were found from the mixed acidophilic culture and were most likely oxidizing acid-dissolved Fe^{2+} to Fe^{3+} during bioleaching:

$$2\ Fe^{2+} + 0.5\ O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + H_2O \qquad [3]$$

On the other hand, lanthanides can accumulate on cell wall or bacteriogenic oxides (Moriwaki & Yamamoto, 2013). The effect of red-ox reactions induced by bacteria, such as biotic oxidation of Fe^{2+} to Fe^{3+} that catalyses metals solubilisation, might play an important role on leaching efficiency and will be the object of a forthcoming paper.

3.5.2 Effect of pH and acid consumption/production

The overall acid consumption during chemical leaching was 2.014 litre of concentrated (96% purity) H_2SO_4 per kg of FA-WW, while 0.810 litre during bioleaching. The added value for bioleaching is the limited consumption of sulphuric acid, two times less than chemical leaching, illustrating the activity of sulphur-oxidizing bacteria and their capability to produce remarkable amounts of H_2SO_4. According to the equation 1, biologic transformation of 1 ton of elemental sulphur produces approximately 3 tons of H_2SO_4. In U.S. (2013) the price of elemental sulphur and imported H_2SO_4 product was 69 and 63 $/t, respectively (USGS, 2013). Therefore, chemical costs for bio-based H_2SO_4 are three times lower than the price of imported sulphuric acid.

3.5.3 Potential environmental implication

According to the European regulation (EU, 2002), the limit values for waste acceptance at landfills are based on a leaching procedure (TCPL, Toxicity Characteristic Leaching Procedure), which have to follow Technical Specification of the European Committee for Standardization. Although our experiments do not comply with the standard procedures for TCLP as it was not in the scope of the present work, Tab. §4-4 shows that the composition of treated MSWI ashes are below the European guidance levels (for leachates) for several regulated chemical elements such as Cl, Cu, Mo, Ni, and V. Other harmful elements within solid by-products largely exceed the TCPL limits and likely have an impact on the environment.

Limit values for waste acceptance in landfill or for waste reuse as construction material are not available for solids. Data of solid residues after chemical leaching and bioleaching treatments can be compared with guidance levels published by BAFU (Federal Office for the Environment, Switzerland) as suggested elsewhere for other incineration ashes (Nowak *et al.*, 2010). The comparison helps assessing whether treated residues can be reused and, thus, can constitute an added value product rather than a secondary waste. The solid residues produced at the end of bio-hydrometallurgical treatments do not meet the guidance levels of BAFU for a number of elements (Tab. §4-4). Harmful elements such as Zn, Cr, Pb, and Sb were significantly removed, but their still high concentrations prevent the residues' landfilling. The solid by-products have potential for re-use after further removal of these elements, especially Pb and Sb.

Tab. §4-4 Chemical composition of the FA-RAW and process solids (FA-WW, FA-H2SO4, and FA-BIO). The TCLP limits and BAFU criteria for waste acceptance at landfill of pulverised coal ash and blast furnace slag are also reported.

Element	**FA-RAW**		**FA-WW**		**FA-H_2SO_4**		**FA-BIO**		**Guidance levels**		
	average	RSD	average	RSD	average	RSD	average	RSD	**TCPL**	**Coal**	**Slag**
(mg/kg)											
Ca	142000	*4*	240200	*1*	166300	*1*	139900	*3*	-	-	-
Cl	142000	*10*	18500	*3*	130	*17*	300	*3*	25000	-	-
S	105700	*3*	106200	*4*	232000	*1*	177500	*4*	50000	-	-
Si	44300	*12*	53400	*17*	30500	*19*	34900	*28*	-	-	-

Na	37700	*11*	8000	*2*	1700	*2*	1100	*55*	-	-	-
K	31200	*8*	5300	*15*	3300	*8*	1500	*8*	-	-	-
Al	19300	*7*	32400	*2*	2900	*15*	4800	*27*	-	-	-
Mg	10300	*11*	19400	*6*	80	*173*	200	*52*	-	-	-
Zn	10200	*3*	14400	*3*	1400	*4*	1600	*2*	250	1000	400
Ti	5700	*1*	10500	*2*	3000	*5*	5500	*5*	-	-	-
Fe	5500	*5*	11300	*1*	1100	*17*	5400	*18*	-	-	-
P	5500	*4*	5300	*4*	180	*12*	1200	*18*	-	-	-
Pb	3400	*8*	5100	*7*	3800	*3*	3000	*7*	5	300	75
Cr	1500	*4*	1500	*3*	600	*3*	700	*11*	5	300	200
Ba	900	*4*	1080	*1*	1100	*3*	900	*5*	100	1500	1000
Sb	900	*1*	1300	*3*	500	*3*	860	*2*	150	10	5
Cu	600	*2*	900	*2*	50	*7*	200	*36*	250	200	200
Sr	500	*4*	560	*2*	400	*1*	300	*3*	1	-	-
Mn	370	*1*	690	*7*	70	*0*	100	*69*	-	-	-
V	80	*3*	100	*3*	30	*6*	50	*12*	250	300	300
Ni	50	*14*	90	*1*	10	*63*	30	*23*	250	200	200
As	30	*13*	40	*19*	40	*2*	30	*13*	5	40	30
Mo	20	*6*	20	*2*	2	*26*	10	*3*	30	-	-
Co	8	*14*	12	*11*	10	*4*	6	*28*	-	100	100

Relative standard deviation (RSD) in percent is reported.

3.5 Limits and potential improvements toward industrial application

Both leaching methods could sufficiently extract marketable metals and serve as a pre-treatment step toward factual metals recovery from urban waste streams like MSWI fly ashes. However, wastewater and solid by-products require further control and processing. Future experiments to improve stabilisation of solid by-products and metal recovery from process solutions could include leaching at elevated temperatures, high acid composition and combined bioleaching and chemical leaching to utilize the selectivity differences and maximise recoveries and environmental status of the residue. Chlorides and alkali salts, which are substantially unvalued/hazardous compounds and may hinder the recovery of marketable metals, can be leached by water (see Tab. §4-2) and the pre-washing treatment might be further optimised toward improved removal amounts. Other impurities such as Fe and Mn can be removed by drop-wise adding NaOH and

$KMnO_4$, respectively, to the leaching liquor at room temperature, as in Chen *et al.* (2015). Marketable elements can be recovered from process solutions by solvent extraction or ion exchange experiments (Nguyen & Lee, 2014; Chen *et al.*, 2015; Tang & Steenari, 2015). Well known methods such as thermal treatments and carbonation (Nowak *et al.*, 2010; Liu *et al.*, 2015) might lead to inert solid by-products in a closed-loop strategy.

Although the H_2SO_4 leaching is still not affordable for industrial application (Okada *et al.*, 2007; Meawad *et al.*, 2010), the bioleaching in sulphuric acid solution, under our experimental conditions, resulted in satisfactory removals, low amount of unvalued elements in the leachate, and low agent costs for H_2SO_4 (due to bio-produced acid). Moreover, the bioleaching procedure has great (and relatively unexplored) potential for optimisation, e.g., by improving medium (S^0, Fe^{2+}, nutrients) and substrate quality, thermo-chemical conditions, inoculum volume and fraction of bacterial strains. Chemical leaching in pH 1.0 removes some elements (e.g., Cu, Fe, Ni, P, and Sb) better than bioleaching in pH 1.4. The possible requirement for a low pH is not a process-limiting factor in bioleaching as, for example, the well-known sulphur-oxidizing bacterium, *At. thiooxidans*, can thrive even in pH 0.5 (Bosecher, 1997). Therefore, the pH can be adjusted to the desired level also in bioprocess, but this tends to be relatively far away from their pH optimum (between pH 1.0 and 2.5) and can have an effect on the bioprocess performance that should be tested before implementation. The production rate of the H_2SO_4 is clearly the limiting factor, as bioleaching required additions of sulphuric acid during the main leaching period (days 0-3). Therefore, the potential industrial application for fly ash bioleaching would consist of two reactors, the first one optimised for biologic H_2SO_4 production from elemental sulphur (in the absence of fly ash) and the second reactor utilizing this bio-based lixiviant for fly ash chemical leaching. In Fig. §4-6 we report the concept design of a hypothetical treatment strategy for MSWI fly ash. It involves two optimised bioreactors ensuring closed circuits of washing water and acidic solution, and suggests industrial uses of process by-products.

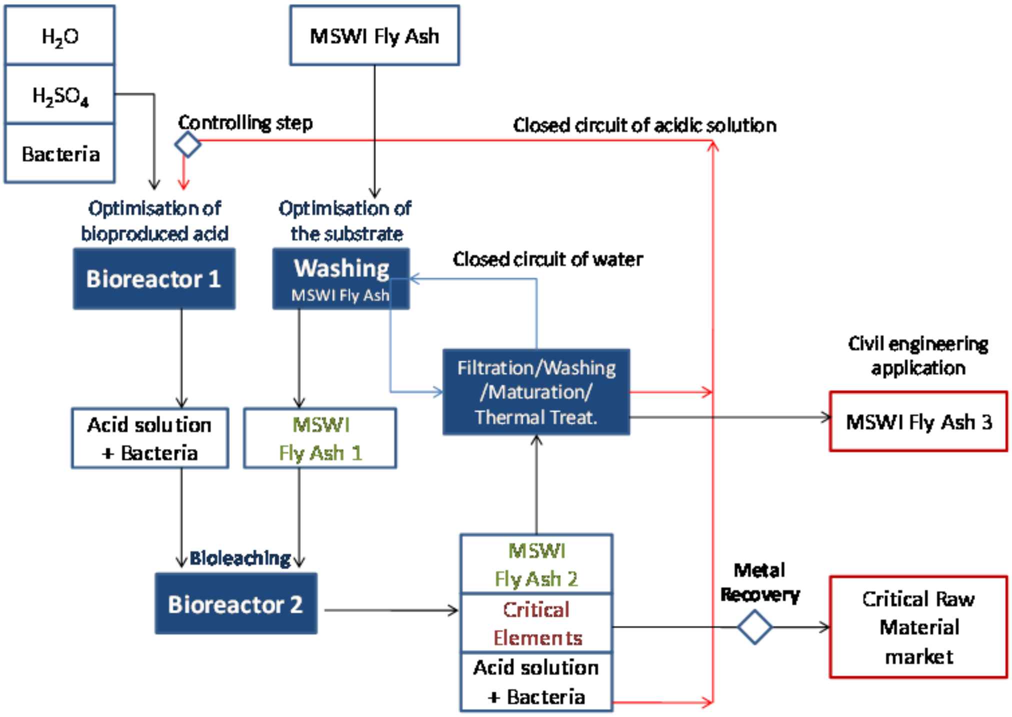

Fig. §4-6 Flow sheet of a hypothetical process chain for the treatment of MSWI fly ash.

4. Conclusions

Fly ash samples from an Italian incinerator of municipal solid waste were treated by chemical leaching and bioleaching in glass reactors after a pre-washing treatment. The results can be summarised as following:

1. Both processes resulted in good leaching yields (>85%) for a number of elements, especially for Al, Cu, Mg, Mn, and Zn, which can be potentially recovered from solutions by known methods, and low removals for Ca (~ 40%) and As (~10%).
2. Chemical leaching still demonstrated higher yields than bioleaching for elements such as Al, Mg, Zn, Cu, Ni, Sb, and Sn.
3. Bioleaching showed good yields also for Pb, Ce, Co, La, Nd and Sb with the advantage of significant selectivity (especially for toxic elements) and lower removal of un-necessary elements (e.g., Si and Ti) compared to chemical leaching. In addition, the bio-produced H_2SO_4 favourably impacts on agent costs for reagents.
4. Final residues deriving from the two methods under the experimental conditions used in this work (leaching time, temperature, and acid composition) cannot be reused as construction material and need further processing for landfilling as non-hazardous or inert waste status. A process chain for MSWI fly ash treatment, which includes optimised bioreactors and suggests the final destination of by-products, could be tested for industrial application.

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Supplementary Materials of Chapter 4

S.1 Morphological characterisation of solids pre- and post-treatment

Morphological images of MSWI fly ash particles were obtained by Scanning Electron Microscopy (SEM), Philips 515B, working at 15 kV electron accelerating voltage and with a beam current of about 1 nA at the specimen level. For these observations, disaggregated loose particles with different sizes below 40 μm were embedded in stubs and sputtered with gold. Semi-quantitative chemical analysis on spot superficial point was also performed using an energy dispersive X-ray spectrometer (EDS) coupled to the SEM. Morphology and compositional analysis by SEM-EDS were employed as complementary information to evaluate differences between raw fly ashes and treated ones.

Morphological images by scanning electron microscopy (SEM) were taken on the FA-RAW sample and on the solid residues after the leaching procedures (Fig. S.1). The fly ash sample before leaching (Fig. S.1 a) shows particles with a wide range of shapes. Highly agglomerated fragments, in which smaller particles amalgamate forming irregular clusters greater than 100 μm, with a rough surface, are the main feature of the FA-RAW, in line with the majority of observations reported by others (Huang *et al*., 2007; Fedje *et al*., 2010). Due to the small size of the ash particles and their tendency to agglomerate into clusters, a detailed study by EDS on the distribution of specific elements within the particles was not possible. Generally, these agglomerated bodies contain Si-Ca compounds plus variable amounts of Al, Fe, S, and alkali (Fig. S.1, inset A1). A very limited presence of euhedral crystals and of gypsum/anhydrite minerals suggests that most of Ca occur in form of amorphous silicates, oxides and sulphides. In FA-RAW, rare spherules are present, even though spherical morphologies of complex aluminosilicates have been documented in MSWI fly ashes from electrostatic precipitators (Eighmy *et al*., 1995; Zhang *et al*., 2007). The SEM images of FA-RAW shows, moreover, equant and columnar fragments (A2 in Fig. S.1) that are characterised by a flat morphology and contain sulphur and chloride salts and minor elements such as Pb and Zn. Micrographs b and c of Fig. S.1 reveal that agglomerated particles, as those observed in micrograph a, partly disappeared due to the formation of secondary compounds and minerals with near euhedral shapes. In the treated fly ashes, both FA-H2SO4 and FA-BIO, morphological images and EDS analysis showed the presence of Ca-sulphate precipitates (inset B1). The occurrence of coarser gypsum crystals in the FA-BIO rather than in FA-H_2SO_4 can be simply related to a longer leaching time. The presence of spherules up to 40 μm diameter containing S, Ti and Fe (inset C1) might be linked either to the activity of microorganisms, which enhance Ti substitution in sulphur rich systems, as occurs in marine environments (e.g., Botsou *et al*., 2015), or to typical magnetic spherules generated by industrial processes at specific thermo-chemical conditions (e.g., Blaha *et al*., 2008). These hypotheses, however, need to be confirmed by means of further investigation. The reason of a nearly absence of spherules in the FA-RAW sample still remains doubtful, but may occur that the relative abundance of S-Ti-Fe-bearing spheres increased in the bioleached residue due to their low solubility, as suggested by Eighmy *et al*. (1995). The S-Ti-Fe spherules occurrence and coarse-grained fragments in the solid residue after bioleaching could favour a further selective removal of metals by means of subsequent physical-mechanical techniques such as sieving, density or magnetic separation. If this can serve to improve future bioleaching process chains, clear advantages given by later treatments after the chemical leaching cannot be assessed by SEM observation of the solid residue.

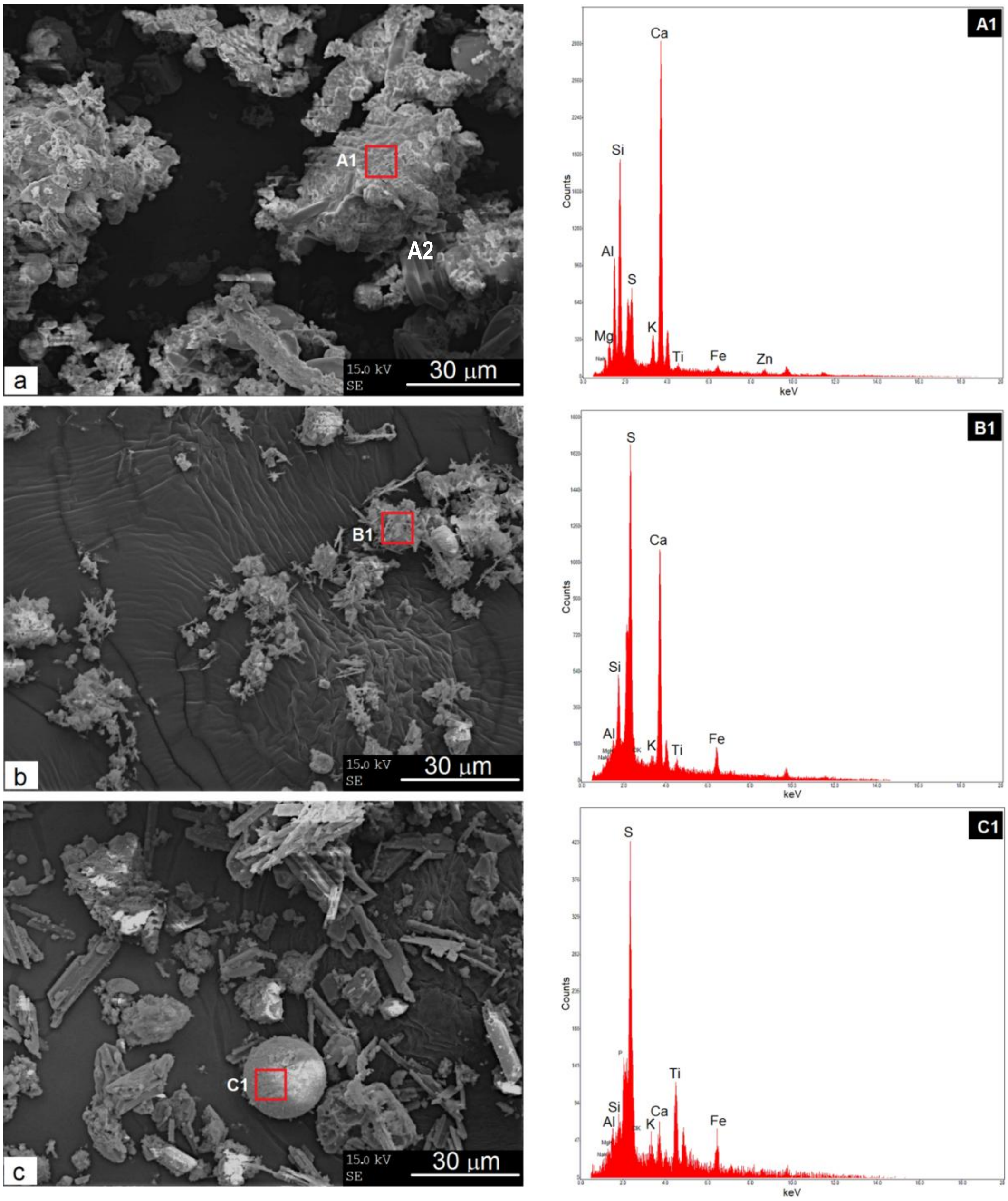

Fig. S.1 SEM micrographs of FA-RAW (a), FA-H2SO4 (b), and FA-BIO (c). Images A1, B1, and C1 are EDS spectra of red squares drawn in micrographs a, b, and c, respectively. For A2 see description in the text.

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Chapter 5

The Potential Impact of Municipal Solid Waste Incinerators Ashes on the Anthropogenic Osmium Budget

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Highlights:

- Bottom and fly ashes from municipal solid waste incinerators are investigated
- Their Os levels and Os isotopic signatures are discussed
- An estimate of Os release from incinerators and incinerated ashes is given
- Os contamination from incineration plants impacts the geochemical Os cycle.

Abstract

Osmium release from Municipal Solid Waste Incinerators (MSWI), even if acknowledged to occur at least over the last fifteen years, remains overlooked in the majority of recent studies. We present the osmium concentration and $^{187}Os/^{188}Os$ isotopic measurements of different kinds of bottom and fly ash samples from MSWI plants and reference materials of incinerator fly ash (BCR176 and BCR176R). The analysis of the unknown ash samples shows a relatively wide range of $^{187}Os/^{188}Os$ ratios (0.24-0.70) and Os concentrations (from 0.026 ng/g to 1.65 ng/g). Osmium concentrations and isotopic signatures differ from those of other known Os sources, either natural or manmade, suggesting a mixture of both contributions in the MSWI feedstock material. Furthermore, the comparison between the BCR176 and the renewed BCR176R indicates a decrease in Os concentration of one order of magnitude over the years (from 1 to 0.1 ng/g) due to improved recycling efficiency of Os-bearing waste. The estimated annual amount of Os from a typical incinerator (using average Os values and MSWI mass balance) is 13.4 g/a. The osmium potentially released from MSWI smokestacks is predicted to be from 16 to 38 ng Os/m^2/a, considering a medium size country having 50 MSWI facilities; therefore much higher than the naturally transported osmium from continental dust in the atmosphere (about 1 pg Os/m^2/a). MSWI systems are considered one of the best options for municipal solid waste management in industrialised countries, but their contribution to the Os budget can be significant.

Keywords: Osmium, Incinerators, Bottom and Fly ashes

1. Introduction

The Platinum Group Elements (PGE: Pt, Pd, Rh, Ru, Os and Ir) are among the rarest elements in the Earth crust, but increasing PGE levels have been noted in many environmental compartments (Lattermoser, 1994; Barefoot, 1997; Barbate *et al.*, 2001; de Vos *et al.*, 2002; Whiteley & Murray, 2003; Fritsche & Meisel, 2004; Rauch *et al.*, 2005). The study of PGE isotopic compositions allows distinguishing the sources of pollution either natural or anthropogenic and indicates that unexpected concentrations found in the environmental records are a likely consequence of PGE's massive use in industrial applications during the last century. The chemical element osmium (Os, atomic number 76) that like other PGE occurs in native alloys of variable composition has a small production (estimated as 300 tons/year in 1995) and a limited number of anthropogenic uses (Kabata-Pendias, 2010). Its industrial application as a main component is still limited to specialty alloys and microelectronics and it can occur as impurity in other high-PGE products. Several studies reported anthropogenic Os in estuarine samples and coastal sediments (Williams & Turekian, 2002; Turekian *et al.*, 2007), lakes (Rauch *et al.*, 2004), atmospheric precipitation (Chen *et al.*, 2009) and urban airborne particles (Rauch *et al.*, 2005). The Os isotopic composition is a tracer of crustal and mantle inputs to seawater and sediments and the distinctive characteristics of the Re-Os isotopic system can lead to decipher the principal sources of anthropogenic Os contamination (Esser & Turekian, 1993; Sharma *et al.*, 1997; Meisel *et al.*, 2001; Reisberg & Meisel, 2002). In fact, the radiogenic part of Os isotope 187 is derived from radioactive decay of ^{187}Re ($t_{1/2}$ ca 42 billion years). As Os is highly siderophile and chalcophile and compatible element it is associated with metal and sulphide minerals. Also, during melting processes involving the Earth's mantle Os hardly partitions into the melt (e.g., basalts) and remains in the mantle. As such, the Re/Os ratio is highly variable with high values in crustal rocks leading also to highly variable radiogenic ^{187}Os contributions. This information can be used to identify sources contributing to the total Os budget of samples. The ^{187}Os/^{188}Os of the primitive upper mantle, i.e. a hypothetical upper mantle that has never experienced a melt enrichment or depletion, is estimated to be 0.1296 (Meisel *et al.*, 2001) while sediments derived from continental crust have average ^{187}Os/^{188}Os ratios roughly around unity with exceptions having ratios higher than 10. Most samples taken from anthropogenic sources are expected to reveal ^{187}Os/^{188}Os somewhere in between the two end-members. Natural sources of Os to the atmosphere include continental mineral aerosols (^{187}Os/^{188}Os = 1.26), cosmic dust (^{187}Os/^{188}Os = 0.13) and volcanic aerosols (^{187}Os/^{188}Os = 0.14), while potential anthropogenic sources are combustion of fossil fuels (^{187}Os/^{188}Os = 1.2-13.7), smelting of PGE, chromium and base metals sulphide ores (^{187}Os/^{188}Os = 0.12-0.20), and automobile catalytic converters (^{187}Os/^{188}Os = 0.1-0.2) (McCandless & Ruiz, 1991; Esser & Turekian, 1993; Sharma *et al.*, 1997; Poirier & Gariépy, 2005; Chen *et al.*, 2009). Isotopic ratios of ^{187}Os/^{188}Os close to 1 are considered as “radiogenic”, whereas those near 0.1 as “unradiogenic” and, generally, higher Os concentrations and lower ^{187}Os/^{188}Os ratios have been linked to anthropogenic sources in urban areas. It has been supposed that the usage of automobile catalytic converters could provide the principal source of globally dispersed Os (Chen *et al.*, 2009). Moreover, processing waste from industrial activities (Williams & Turekian, 2002) and metallurgical smelters (Rodushkin *et al.*, 2007; Gogot *et al.*, 2015) are considered as additional sources of anthropogenic Os. Since Os is widely used as fixative and stain in the preparation of tissue thin sections for optical and electron microscopy (Esser & Turekian, 1993) and high Os levels near hospital and medical research centres are reported, several authors infer the Os contamination is strongly linked to the discharge and incineration of biomedical waste (Helz *et al.*, 2000; Williams &

Turekian, 2002; Turekian *et al*., 2007). The waste incineration process, which typically works at temperature higher than 850 °C, might enhance Os contamination, like other PGE (Lattermoser, 1994; Jackson *et al*., 2010), and can be effective in promoting Os oxidation into its volatile form (boiling point of OsO_4 ca.110 °C).

The Os easily reacts with oxygen gaining various oxidation states and, as a consequence, it may pollute any environmental sink. However, there is not much information on Os contamination mainly due to analytical difficulties even in the vicinity of expected sources of Os pollution. Given this fact and also the toxicity risk for humans and animals associated to all Os compounds (Farago & Parsons, 1994; Kabata-Pendias, 2010), a better knowledge of Os signature and OsO_4 release from incineration facilities is required. The present study aims to 1) analyse samples of Municipal Solid Waste Incineration (MSWI) solid by-products and 2) evaluate the potential Os release associated to MSWI plants. The MSWI system is one of the main options for the management and minimisation of a wide range of waste materials, from household and gully waste to industrial and hospital waste (Chandler *et al*., 1997). Waste incinerators are common in industrialised countries and generate huge amounts of solid and gaseous output flows, which represent concern as they contain heavy metals such as Cr, Pb, Mo and Sb (Lam *et al*., 2010; Funari *et al*., 2015; 2016), and also release dust pollutants into the atmosphere. Atmospheric pollution is directly associated with the emission of fine particulate matter via roof vents, whereas the storage of solid materials (namely fly ash and bottom ash materials) are mainly in charge of heavy metals contamination. Bag filters, chemical additives and specific devices for air pollution control such as SCR (Selective Catalytic Reduction) are addressed toward reduction of environmental issues related to MSWI outputs. The Os concentrations have never been detected neither in solids nor in gases and also its isotopic signatures in MSWI residues are virtually unknown. As a fact, end-of-life products that contain Os in variable amount such as specialty alloys, medical waste and the unrecycled fraction of spent car catalysts, might be processed into incinerators and intimately modified by combustion. This in turn might lead to an increased bioavailability of elemental Os and also its volatile form. The capability of OsO_4 to be reduced quickly once released in atmosphere rules out a very disperse contamination, but the toxicity of exposure, which causes lung congestion, skin and eye damage, and chronic diseases to marrow, liver and kidneys (Farago & Parsons, 1994; Kabata-Pendias, 2010), might be locally intensified. To the best of our knowledge, this study is the first attempt in quantifying the impact of MSWI plants and their solid by-products on the anthropogenic Os budget.

2. Experimental

2.1 Materials

Bottom ashes and fly ashes from four MSWI plants were collected; the selected incinerators, named A, B, C and D, are situated in four different municipalities of northern Italy. The municipalities where the MSWI plants are located have a population size ranging from 3 to 7 10^5 inhabitants, distributed in a similar area of about 2,500 square kilometres with the exception of MSWI-D area that is three times smaller than others. According to the population density, the investigated MSWI plants can be listed in increasing order as MSWI-C, MSWI-A, MSWI-B and MSWI-D. The MSWI thermo-recycling technology, which is adopted in all the four incinerators, produces an average electricity of 85,000 MW/h per year and the overall process complies the local regulation for final waste production. Each MSWI system consists of two lines that drive the collected waste into a grate-furnace that operates at temperatures between 850 and 1100 °C. The solid waste input consists of 90% household waste and 10% of special waste, i.e. processing waste from ceramics and metallurgy, automobile shredder residues, hospital and pharmaceutical waste. Incinerator C collects also hospital and pharmaceutical waste, representing 1% of the total waste input. For other incinerators this is not declared, but there is the possibility that hospital and pharmaceutical waste end up in the category of special waste. The amount of sewage sludge fraction within the feedstock material is nearly negligible as all the municipalities refer to other facilities for the treatment of sewage sludge. The separate collection of waste from electric and electronic equipments (WEEE) and spent catalysts, among the others, is adopted in the region. However, we cannot exclude any contamination from such kinds of waste because of the likelihood of a weak upstream separation.

The main output products of MSWI facilities are bottom ashes (BA) and fly ashes (FA). After burning and quenching, the BA are a sandy and pebbly material stored in outdoor heaps. The BA samples were collected in all the investigated MSWI. Conversely, the FA are the finest material from burner and boiler and undergo several treatment steps, e.g. dry/wet scrubbers are used to spray fine dispersed slurry or lime powder in order to neutralise the acid gases (Chandler *et al.*, 1997), within the air pollution control (APC) system before being released in the atmosphere. Each specific device/filter retains a residual FA fraction producing different kinds of FA. Where it was possible, FA were collected at a first step without any treatment (untreated, FAU), after the electrostatic precipitation system (FAE) and after chemical bag filters, which involve the use of soda (FAS) or lime (FAL) additives. As a matter of fact, the MSWI system consists of a typical sequence of treatments for FA which produce in the following order FAU, FAE, FAL and FAS (Lam *et al.*, 2010; Funari *et al.*, 2016). However in some case one or two treatment steps are missing, as it is in our investigated plants. Generally, the

FAS is the last residue before the flux of residual FA (i.e., the fraction not retained by filtration) undergoes to the SCR treatment and then to the atmosphere. The reader can refer to Figure 1 in Funari *et al*. (2016), which is also reported in the Supplementary Material of Chapter 5, in order to examine concept design, steps of processing, temperature profiles and potential sampling points of a fully-equipped MSWI system. The BA and FA have been sampled directly to their temporary storage site during process activity (in mid-2013). The samples from this study are representative of the solid residues produced during the first-half 2013 (see S.1 *Bottom and fly ashes sampling*). From each MSWI facility, one or two FA output materials were sampled depending on their availability and assuming them representative of the corresponding BA output materials. The materials (order of tonnes) were blended from a large number of increments and followed by drawing a simple random sampling; approximately 7 kg of primary sample taken from each sampling point. The sampling procedure for BA and FA followed the approach as in Funari *et al*. (2016) and a detailed description is also reported in the supplementary material. All the collected material was oven dried at low temperature (40°C) for one week, grounded, homogenised and very fine milled (less than 40 μm) with an agate vibratory mill disk. A second drying before the measurement procedure was accomplished, being the samples highly sensitive to the moisture adsorption.

Two fly ash reference materials (RM) namely BCR-CRM176 and BCR-CRM176R, obtained from the Community Bureau of Reference, were also analysed with the aim of comparing Os content and $^{187}Os/^{188}Os$ ratios of more representative samples, since large batch of those reference materials have been tested for homogeneity (within 5% for certified analytes) by the above mentioned institute. These reference materials come from fly ash collected in the electrostatic filter of the same Dutch MSWI facility and they represent an aliquot from a 195 kg batch of grinded and homogenised (<105 μm) material. Moreover, the measurements of reference materials can prove the variation, if it does exist, of the isotopic signature over a 20 years period because in 2007 the BCR-CRM176R has replaced the year 1987 BCR-CRM176.

2.2 Methods

The digestion procedure and the Os determinations of the mass fractions and the isotopic composition through isotope dilutions isotope ratio measurements (ID-ICP-MS) were accomplished at the General and Analytical Chemistry laboratories of the Montanuniversität Leoben (Austria) following the procedure outlined in Meisel *et al.* (2001) and using a High Pressure Asher, HPA-S (Anton Paar Instruments, Graz), with 7 X 50 ml quartz glass vessels and a single quadrupole ICP-MS in standard configuration (7500 Agilent Technologies). About two grams of sample powder mass was exactly weighted in a glass vials and spiked with an Os spike solution enriched in ^{190}Os. The spike preparation and calibration procedure can be found in Meisel *et al.* (2001). After adding 2 ml of conc. HCl and 5 ml of conc. HNO_3 the vials were immediately sealed with Teflon tape and a glass lid and heated in the HPA-S, by following a setup of heating (at 300 °C and a pressure of ca. 125 bar during three hours) and slow cooling down (until room conditions). Upon cooling, the volatile OsO_4 was sparged directly into the plasma torch with an argon gas flow (Hassler *et al.*, 2000). Rinsing in-between each sample was adopted in order to reduce uncertainties introduced through instrumental memory. The measurement uncertainty, as relative standard deviation (RSD), of the isotope ratio results was assessed by replicate determinations of the in house Os isotope standard solution (LOsST) and is estimated to be 2 %RSD for 1 ng and up to 10% for 100 pg and less. Considering the range of isotopic compositions of the samples this is considered to be fit for the purpose. The acquisition of isotopic species' counts was followed by de-convolutions and corrections off-line. The long term total analytical blanks were 1 pg and does not contribute significantly to the measurement uncertainty budget. After HPA acid digestion some un-dissolved phases are found in the vessels, reasonably made of amorphous silicates, hematite or other strongly refractory minerals. However, the PGM and associated Os are found in sulphides or sulphates either as native form which can be easily dissolved with the aid of HPA acid digestion thus making accessible the noble metals chemical reactions and dissolution. Moreover, in the case scenario of incomplete Os liberation from the residual fraction, the released Os calculated here would be underestimated rather than overestimated and the insights from this study would then be even more significant.

The chemical composition was also determined using the Na_2O_2 sintering technique, a method of digestion considered to be capable of complete dissolution of the most refractory components known today, coupled with ICP-MS (Meisel *et al.*, 2002). Moreover, the major elements composition of unknown samples was previously obtained on thin-layer pressed powder pellets in a boric acid binder by an X-ray fluorescence spectrometer (XRF, PANalytical), equipped with SuperQ software, at the BiGeA department (Geology Division), University of Bologna. The accuracy of data was assessed by analysing both industrial and matrix matched geological reference materials; uncertainties were as low as 5%. The chemical composition of selected MSWI samples can be found in the S.2 *The chemical composition of selected MSWI samples*.

Tab. §5-1 The Os content (ng/g) and isotopic ratios of MSWI ashes and fly ashes RM. Where: BA = bottom ash; FAU = untreated fly ash; FAE = fly ash from electrostatic precipitator; FAL = lime-treated fly ash; FAS = soda-treated fly ash.

	Os [ng/g]	$^{187}Os/^{188}Os$	RSD
MSWI-A			
FAU	0.03	0.489	4.1%
BA	0.26	0.241	2.7%
MSWI-B			
FAE	0.10	0.374	5.4%
BA	0.11	0.663	2.3%
MSWI-C			
FAS	1.65	0.299	0.9%
FAU	0.18	0.391	13%
BA	0.56	0.322	1.0%
MSWI-D			
FAL	0.08	0.704	6.4%
FAU	0.03	0.433	4.8%
BA	0.12	0.372	3.0%
Reference Materials			
BCR176	1.04	0.206	0.8%
BCR176R	0.11	0.504	2.7%

The relative precision of $^{187}Os/^{188}Os$ ratios is presented at the 95% confidence level.

3. Results and discussion

3.1 Unknown MSWI ashes

In this section we will focus on the unknown MSWI ashes coming from the four investigated incinerators. The XRF and ICP-MS analyses of unknown MSWI ashes indicate that all samples consist of silicates, calcium silicates and alumina-silicates. The MSWI BA contains significant amount of iron and aluminium oxides mass fraction due to metallic scraps and metal sheets, while MSWI FA has variable Ca-, Na-, K-, Mg-oxides mass fraction likely due to variable composition of the carrier gas and chemical additives of the bag filters. Generally, major and trace elements composition are within the range of values quoted in literature (Funari *et al.*, 2015). The PGE contents are below the μg/g level. Reliable PGE determinations of MSWI solid matrices are hampered by isobaric interferences (e.g. those of Cu, Mo, Sn, etc.) and require detailed investigation by means of a comparison between different independent techniques.

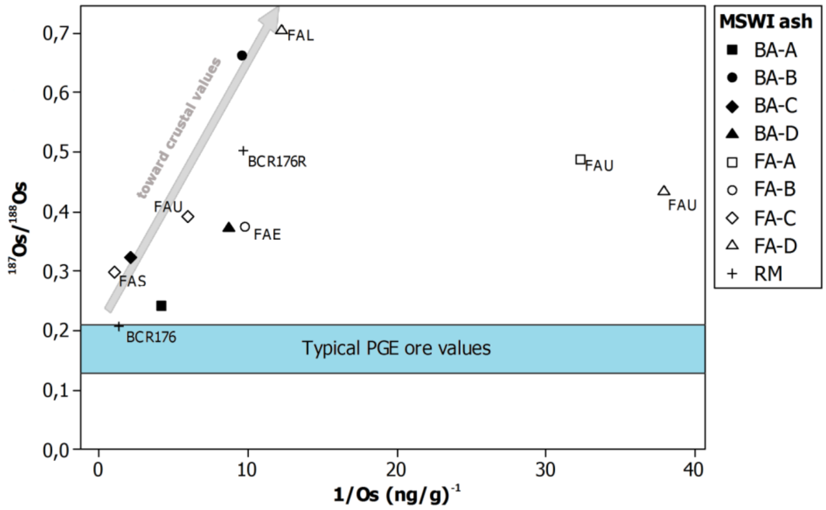

Fig. §5-1 Inverse of Os content (expressed in ng/g) and isotopic signature of BA and FA from MSWI plants A, B, C and D. Fly ash RM are also reported. Abbreviations for the FA types are: FAU = untreated fly ash; FAE = fly ash from electrostatic precipitator; FAL = lime-treated fly ash; FAS = soda-treated fly ash. Gray arrow points to crustal values.

Replicates of Os isotopic ratios differ by up 13% and exceed the measurement uncertainty of a single measurement, possibly indicating the heterogeneity of investigated MSWI ashes linked to the variable input of feedstock materials and a random error during sampling from the heaps. The Os isotopic signatures of unknown MSWI ashes range from 0.24 to 0.70 (Tab. §5-1; Fig. §5-1) and actually both BA and FA ^{187}Os/^{188}Os ratios ranges are similar (between 0.24 - 0.66 and 0.30 - 0.70, respectively). These figures are inconsistent with ^{187}Os/^{188}Os ratios of typical PGE ore deposits (e.g., 0.15 - 0.20 for ultramafic PGE-bearing rocks in Bushveld Complex; McCandles & Ruiz, 1991), while they fall within the widest range of natural signatures (from 0.1 to 2.6; Esser & Turekian, 1993). The ^{187}Os/^{188}Os ratios range of MSWI ashes is wider than those of PGE ore deposits, disclosing a significant variability of Os sources (Fig. §5-2). However, the measured ratio of FAL lies out the 95% confidence interval of the cumulative probability plot of

$^{187}Os/^{188}Os$ data and if we exclude the measured values of FAL the Os isotopic signature of the other samples shows a standard deviation (SD) of 0.12. The relatively smaller variation of Os isotopic composition of FA (SD=0.14) with respect to BA (SD=0.18) might indicate a similar process of fractionation and mass transfer from BA to FA during combustion.

The Os concentrations vary from 0.03 ng/g to 1.7 ng/g and are higher than expected considering that MSWI residues are found to contain very low amounts of other PGE (e.g., 60 ng/g Pt and 0.09 ng/g Rh in Morf *et al.*, 2013). Generally, the Os contents of unknown ash samples from the selected MSWI are dissimilar reasonably due to a variable feedstock input. The highest overall Os concentrations of MSWI-C products might derive from the hospital wastes that are clearly acknowledged in the owners' report of that incinerator, unlike the others. According to the national recommendation, the input and output mass fractions have to be known with good accuracy but a quality control on feedstock materials is not required. Therefore we cannot exclude that the large category of special waste, declared to be burned in the other incinerators, includes a fraction of hospital/pharmaceutical waste. Generally, the proportion of each subcategory of special waste collected in MSWI plants is unknown.

Bottom ash samples (including BA from MSWI-C) have an Os mass fraction that ranges almost in the same order of magnitude whereas FA samples show a pronounced variability of Os mass fraction between each other (Tab. §5-1, Fig. §5-1). Such variability is likely ascribable to different treatments that the FA undergoes. Two samples of untreated FA from selected MSWI facilities, i.e. FAU from MSWI-A and MSWI-D, are strongly depleted in Os concentration respect with the others. While the most of the samples follow a mantle-crust mixing trend, the FAUs lie outside of such distinct range. This evidence contradicts the notion that higher Os concentrations and lower $^{187}Os/^{188}Os$ ratios are linked to anthropogenic Os sources. The combustion and filtration processes might conceal the original Os yields through leaching of Os during transport of particles or dilution with low-Os material.

Presumably the use of specific devices for the FA purification influences the Os yields. The processes of filtration with chemical additives or electrostatic precipitator seem to inhibit the Os volatility as one could argue by comparing Os yields of FAE, FAL and FAS with those of FAU. We suspect that Os can condensate in sulphur-complexes or alkali-salts within the APC system while the temperature is lowered (from 1000°C of the furnace to 150°C in the APC; Chandler *et al.*, 1997) and the content of chlorides and sulphides relatively increases. This hypothesis seems reasonable since the Os mass fraction shows a good negative correlation with CaO mass fraction (R^2= 0.79; the most significant among major elements) and a positive correlation with Na_2O (R^2= 0.71). The lower the Os mass fraction the higher the calcium oxides mass fractions might indicate that in a high-Ca system the available sulphur will form bonds with calcium to the detriment of Os content. The measured concentration from FAS is up to two orders of magnitude higher than the other samples. These preliminary results should trigger matter of concern when any recovery and recycling strategies from FAS residues are planned. The FAS solid fraction is recovered after Na-treatment and prior to the final selective catalytic reduction (SCR system) of nitrogen oxides. It is well known that the free OsO_4 can be dissolved at this stage in aqueous alkali to give $Na_2[OsO_2(OH)_4]$ but also can be reduced to H_2OsCl_6 or $OsCl_2O_2(NH_3)_4$ in presence of hydrochloric acid or NH_4Cl, respectively. Both these options for Os precipitation might be fulfilled in the APC system at this stage and might explain the relatively high concentration of Os found in the FAS residue.

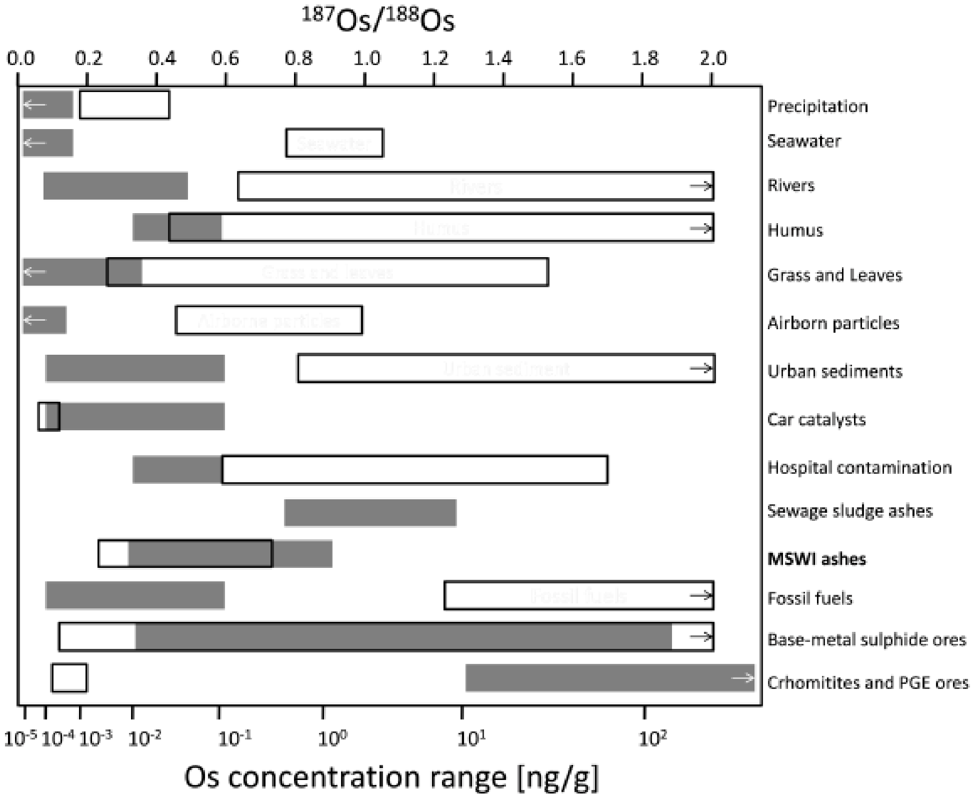

Fig. §5-2 Comparison of Os concentration and Os isotope ratios ranges between MSWI ashes and other recognised sources, both natural and manmade. The grey boxes are concentrations range, whereas the outlined boxes show isotopic variations. Black and white arrows mean that values exceed the limit of representation for isotopic and concentration ranges, respectively. Data references are: precipitation, seawater, rivers, fossil fuels, base-metal sulphide ores, chromites and PGE ores (Chen *et al*., 2009 and references therein), airborne particles (Rauch *et al*., 2005), urban sediments (Rauch *et al*., 2004), car catalysts (Poirier & Gariépy, 2005), hospital contamination (inferred contamination of sediments by biomedical activities; Helz *et al*., 2000), sewage sludge ash (Jackson *et al*., 2010).

To date, the overall range of Os composition and isotopic ratios determined in MSWI ash samples do not resemble any other known source, either natural or anthropogenic, but rather look like a mixture of carbon-related products (i.e. fossil fuels, humus, and leaves), spent automobile catalysts, biomedical waste and smelting of PGE-bearing ores (Fig. §5-2), readily burned in incinerator systems. Car catalysts, possibly one of the most important Os sources to end up into incinerator as unsorted waste, show a composition range from 0.006 to 0.2 ng/g and isotopic ratios close to 0.1-0.2 (Poirier & Gariépy, 2005). Conversely, since high $^{187}Os/^{188}Os$ ratios coupled with low Os concentrations are found in several samples, medical/hospital waste might be one of the chief Os sources, as Helz *et al*. (2000) suggested. Jackson *et al*. (2010), in their paper on the PGE determination in incinerated sewage sludge from UK, report Os concentrations from 5 to 12 ng/g, being 2 ng/g the lower detection limit, and they pointed out that the overall PGE abundance is higher in incinerated ash than in the original waste. This may implicate that the burning process can play an important role in Os concentrations upgrading.

3.2 MSWI ashes reference materials

The analysis of BCR-CRM reference materials shows relatively high Os concentrations and radiogenic $^{187}Os/^{188}Os$ ratios (Tab. §5-1). The results are consistent with those of unknown MSWI ashes. Although the BCR-CRM reference materials are fly ashes from electrostatic precipitator of the same MSWI facility, they are notably different from each other. This might indicate that the feedstock material has changed considerably over time; in fact the old and new BCR-CRM reference materials were produced in 1987 and 2007, respectively. The BCR-CRM176 is the only material that lies within the area of typical PGE ore values (Fig. §5-1). Conversely, the source material of the BCR-CRM176R is characterised by higher $^{187}Os/^{188}Os$ ratio than the material used to produce BCR-CRM176. The reasons for such difference between the two RM can be, for example: 1) a poor recycling efficiency of PGE in the past, 2) the earlier high-PGE products such as bio-medical applications and car catalysts (from 1986 in Europe) were more Os-rich because of an inferior purification/refinement of the raw material, and 3) the processing techniques of PGE-bearing ores were probably less efficient.

The Os concentration and isotopic signature of the new reference material, BCR-CRM176R, are similar to those of the unknown FA sample from the electrostatic precipitator (FAE). A comprehensive dataset of observation is needed to assess the spatial independence of the Os envelope among different MSWI ashes of today, but the similarity between BCR-CRM176R and FAE might suggest that the feedstock material is rather uniform, as a consequence of massive technological advances on PGE production and refinement.

Since the geochemical behaviour of Os can be chalcophile and strongly associated with organic-rich systems (Reisberg & Meisel, 2002), we have further undertaken the Os measurements of NIST1633a reference material to assess whether coal fly ashes host significant amounts of Os and distinct isotopic signatures. The Os concentrations of the coal ash RM are below the detection limit (as low as 20 pg) under our instrument condition. This agrees with the available data for the coal fly ash reference material NIST-SRM1633b (Os=0.005-0.02 ng/g and $^{187}Os/^{188}Os=5.018$; Rodushkin *et al.*, 2007).

4. Environmental Impact Assessment of MSWI

4.1 Assessment of osmium volatility and partitioning

Modern MSWI grate-furnaces approximately operate at temperature higher than 850 °C and the combustion under these conditions would reasonably enhance the oxidation of Os, of indistinct natural and anthropogenic origin, into its gaseous form. The origin of volatile Os coming from natural sources cannot be positively assessed, but for its industrial applications, e.g. in staining tissues or carbon materials for optical and electron microscopy, chemical syntheses, etc., Os is typically employed as powered or spongy Os tetraoxide, which is known to have a slow volatility even at room temperatures. In addition, a 75-95% depletion in the initial Os yield of car catalysts is observed after heating at 400°C (Poirier & Gariépy, 2005). Thus we suspect that significant amounts of Os would be lost from the PGE- or Os-bearing waste and partitioned into MSWI outputs. The Os contents resulted in BA samples can be due to one of following factors or a combination of them: 1) refractory Os-alloys or some natural Os sources are hardly volatilised, 2) unburnt materials (low temperature areas within the furnace may lead to incomplete combustion), and 3) the volatilised Os is not completely transferred into the FA because of the turbulent air flow, which is sparged to allow the complete burning of lightest particles (i.e. paper, wood and plastic), and some Os condensed in BA. The volatile Os that flows through the tubing of the APC system is transferred in different FA residues. A good understanding of the Os transferring and stabilising among the FA kinds is hampered by several factors, e.g. the carrier gas composition, the inner working of filtering devices and the cooling at each stage (ca 150 °C average temperature within the APC system).

The results here produced allow pointing out that MSWI ashes host considerable amount of Os and its release and the kinetics of its oxidation/volatilisation should be carefully taken into account when further treatments of incinerated ashes are planned. The majority of post-treatment procedures for stabilisation, recycling or metal recovery require temperature higher than 110°C and over that temperature OsO_4 becomes gaseous.

4.2 MSWI ashes, landfill and smokestacks

The above results (Tab. §5-1), which provide the whole spectra of potential MSWI outputs but refer to representative samples of the first-half year of waste production, and the mass balance of investigated MSWI systems (Tab. §5-2) allow us to estimate the annual quantity of Os in solid residues from each MSWI plant. The annual amount of Os in BA outputs is 8.3, 5.1, 13, and 4.1 grams per year for incinerator A, B, C and D, respectively, while that in FA outputs range between a minimum of 0.08 g/a in FAU from MSWI-D and a maximum of 3.0 g/a in FAS from MSWI-C. These figures reveal that the size of the facility and the relative population density is not directly related to Os outputs, being the MSWI-C residues the highest in Os yields but the lowest in final solid outputs. Taking the average of MSWI total output ($4.32 \cdot 10^4$ t/a) and the average Os concentration of 0.31 ng/g, we obtain 13.4 g/a Os that can be indicative of Os annual flow from solid ashes of a typical MSWI system.

Tab. §5-2 Mass balance of the selected MSWI systems. Figures refer to the owners' report and are expressed in kilo tonnes per year. The hyphen means residue not produced or unworkable sampling. It can be noted that the sum of BA and FA output is not equal to total output and the lack in balance represents the mass fraction of the recovered iron from BA (low field magnetic separation after quenching) and sewage sludge.

	Pop. Density[a]	Total input	Total output	BA output	FA output			
					FAU	*FAE*	*FAL*	*FAS*
MSWI-A	166	140	41	32	3.2	-	-	-
MSWI-B	259	200	60	48	-	3.8	-	-
MSWI-C	116	110	30	23	2.5	-	-	1.8
MSWI-D	393	140	42	35	3.0	-	2.0	-

a: Data from National Institute of Statistics (ISTAT)

This translates approximately in 675 g of relatively non volatile Os discharged every year in the environment by a medium size country running 50 MSWI plants. The four selected incinerators are assumed to be representative of an average plant in order to give an order of magnitude of the expected Os yield and release, but Os concentrations and behaviour are influenced by several variables and further studies are needed in order to compare different regions.

The Os loss from MSWI landfill by evaporation in tetraoxides species or mobilisation after weathering would be expected. Considering that the natural Os input from continental erosion (using Os continental crust average value of 0.030 ng/g) is estimated to be ~800 pg/m^2/a (Poirier & Gariépy, 2005) and the Os average concentration in MSWI landfill is potentially ten times higher than in continental crust, the Os derived from MSWI landfill would have a significant impact in urban areas. Os in landfill waste is probably more accessible to leaching, transport etc. than Os in the crustal material where it is bound to refractory minerals and alloys.

Moreover, a fraction of volatile Os can directly spread from MSWI plants hot spot. Although further studies in MSWI facility areas are required, some volatilised Os is likely introduced to the atmosphere by smokestacks or can be lost due to an irregular insulation of the system itself.

Bearing in mind the processing steps of the MSWI system (see S.1 *Bottom and fly ashes sampling*), we assume all the Os fluxing through the APC system is retained within the FAS residues and the Os yields of each MSWI final product maintains the same proportion of those of MSWI-C, i.e. the only plant having FAS. Therefore we estimate the Os loss from MSWI systems lacking in Na-additive bag filter, further assuming a 100% Os loss in the OsO_4 species. These hypotheses would represent a compromise between the inferred and the real Os loss because it has to be considered that unlikely all the Os fixates on FAS residues and there is no release through the tubing of the whole system. Being Os from (MSWI-C)FAS three times higher than Os from (MSWI-C)BA, the potential Os yields in the other MSWI plants (without the last-step of filtration) will range from 0.31 ng/g to 0.77 ng/g. Generally, MSWI plants produce 0.7 t of gases and particulate vapour per tonne of input waste (Committee for Prevention and Precaution, 2004), which translate, using an average of $1.47 \cdot 10^5$ t/a, in $1.03 \cdot 10^5$ t/a of gas and particulate vapour. Then we obtain a range of between 33 and 78 g of volatile Os per year fluxing from the smokestack of a typical MSWI plant, i.e. from 16 to 38 ng Os/m^2/a will be distributed in a medium size country (using an average area of 360000 km^2, calculated by dividing the European surface area over the number of EU countries) having 50 MSWI facilities.

The above estimates are based on a 100% volatility of the Os contained within the APC system and are thus a maximum range value. However, they provide an order of magnitude for emissions from MSWI systems and show how significant the impact of their smokestacks and residues on the Os geochemical cycle. This line of argument, similar to that undertaken by Poirier and Gariépy (2005), facilitates a comparison with the emissions of Os from catalytic converters (up to 120 pg Os/m^2/a in highly urbanised areas), which are considered one of the chief sources of liberated Os. Nevertheless, the predicted Os emissions reported in the present work are consistent with recent values calculated by Gogot *et al*. (2015) for an aluminium smelter. It has been suggested that the residence time of OsO_4 in the atmosphere can be very short and volatile Os might have only a local impact. The Os is probably reduced to non-volatile or metal form that can subsequently be mobilized by weathering and accumulated into the environmental records. This consequently would add with the Os yields from MSWI landfill. Therefore, MSWI outputs are strong candidates to account for the higher Os concentrations coupled with variable $^{187}Os/^{188}Os$ ratios encountered in urban sedimentary records and the potential Os release from MSWI landfill and smokestack can adulterate the measured values in urban areas.

5. Conclusion

We measured osmium concentrations and isotopic composition of MSWI solid by-products, namely bottom and fly ashes. The study of isotopic signatures suggested a mixture of natural and anthropogenic contribution on the MSWI feedstock material. The assessment of Os-related impact, though the estimate is based on the first-half year of waste production for northern Italy, revealed up to 13.4 g/a Os within the stream of final by-products and up to 78 g/a of volatile Os emitted from the smokestack of a sole MSWI plant. Therefore, the incineration of unsorted waste and the landfill and reuse of MSWI residues might be a significant source of anthropogenic Os on the continental scale, considering that on average a MSWI plant burns thousands of tonnes of waste per year and MSWI facilities are actually widespread in industrialised and developing countries. Despite the analytical challenges in Os determination and the lack of accurate information about the input waste fractions, this work demonstrates the MSWI contribution to the anthropogenic Os budget should not be overlooked. This work provides a first attempt on the impact assessment of MSWI output products to the Os budget and highlights the need of further investigations on areas close to MSWI plants and MSWI ashes as well as more efforts from the companies and local communities to improve the quality on feedstock material. Future research directions could include the study of seasonal and geographical variations of Os levels and potential epidemiologic implications.

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Supplementary Material of Chapter 5

S.1 Bottom and fly ashes sampling

The main outputs of the incineration process are bottom (BA) and fly ashes (FA). The concept design of a typical fully-equipped MSWI system is reported in **Fig. S.1** to which the reader can refer to identify main processes, temperature profiles and all the potential sampling points.

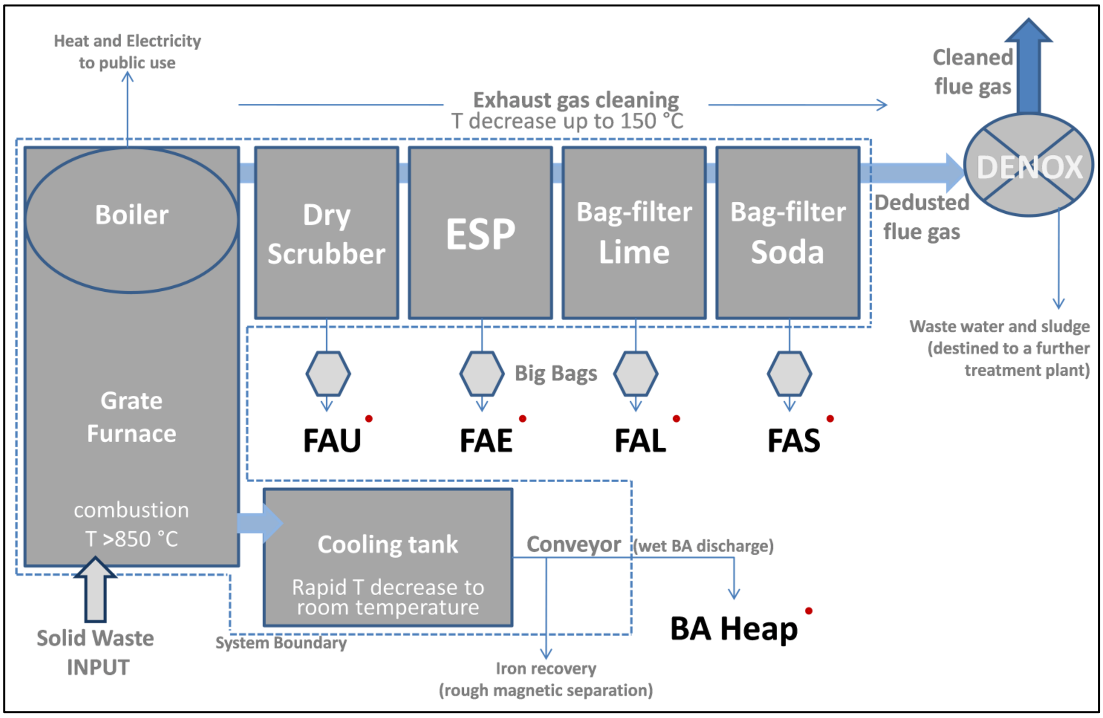

Fig. S.1 Schematic picture of the incinerator system with its relevant processes, including sampling points (red dots) and temperature (T) profile (Funari *et al*. 2016). Acronyms used: BA=bottom ash; FAE=fly ash from ESP; FAL=fly ash from bag filter with Ca-additive; FAS=fly ash from bag filter with Na-additive; FAU=untreated fly ash; ESP=electrostatic precipitator.

We arranged the sampling in end-May during a typical working day of MSWI system just before the end-products were about to leave the plant for the first time of the year 2013. As a fact, the maintenance service of MSWI plants is regularly carried out during last two weeks of December, whereas from January to May and from June to December there are the first and second rounds of end-products production, respectively. Therefore, the samples from this study are representative of the end-products production of first-half year 2013. The sampling strategy followed a stratified/simple random sampling as outlined in the Italian technical standard (UNI 10802, 2013) and two steps of quartering on site and in the laboratory, respectively. The procedure was slightly different for the sampling of BA and FA materials due to their different storage status:

BA) Belt conveyors transport the BA to a temporary outdoor storage site where they are piled up. We sampled the BA heap when the capacity limit of the storage site was reached. Directly from the BA storage site, the heap of several tons of BA material was first sampled following the stratified simple random sampling method as used in Funari *et al*. (2015). 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), about 10 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. We collected three BA samples from each incinerator. These three samples, to be intended as exclusive of a MSWI plant, have been exactly portioned to achieve the needed sample mass for Os measurements. Such mass, in turn, is the representative sample of BA from one MSWI plant.

FA) In each incinerator plants, FA from different devices as in Fig. S.1 are stored in big bags, which contain approximately 1 tonne of material when completely filled. The sampling took place when the big bags were full and about to leave the plant. Approximately 5 kg FA primary sample was collected with a simple random sampling from the FA material stored in big bags, previously blended from a large number of increments and quartered on site in order to reach representativeness. The primary sample of each FA was further subdivided by means of the quartering method in the laboratory. One sample of FA was collected from each available sample point and was used for Os measurements.

S.2 The chemical composition of selected MSWI samples

Tab. T.1 Major and trace elements composition of MSWI ashes, by XRF. The percentages of loss on ignition (LOI) are also reported.

Sample	FAU-A	BA-A	FAE-B	BA-B	FAS-C	FAU-C	BA-C	FAL-D	FAU-D	BA-D
(g/100g)										
Al_2O_3	5.96	9.31	5.24	6.82	0.34	5.20	10.2	2.28	7.25	9.63
CaO	27.0	26.0	18.5	35.8	1.92	24.9	20.7	30.5	29.9	27.9
Fe_2O_3	1.68	6.91	1.98	4.77	0.23	2.30	9.64	0.97	1.87	5.89
K_2O	5.13	1.11	9.12	0.84	2.28	4.31	1.50	3.21	2.19	0.43
MgO	1.92	2.02	1.40	2.91	0.56	5.39	3.11	0.98	2.08	1.47
MnO	0.06	0.08	0.05	0.12	0.01	0.07	0.13	0.03	0.08	0.08
P_2O_5	1.52	1.53	1.31	1.43	0.14	1.38	2.81	0.57	1.73	1.59
SiO_2	14.0	29.3	14.0	21.1	1.40	13.9	37.3	5.06	16.3	19.4
TiO_2	1.53	1.19	1.17	1.14	0.09	1.31	1.21	0.57	1.70	0.84
Na_2O	5.83	1.70	23.9	1.72	53.7	7.27	2.37	4.07	3.81	1.64
Cl	12.5	5.20	1.11	11.0	9.90	8.87	3.01	3.56	14.1	13.6
LOI %	22.7	15.3	23.6	11.7	30.3	25.0	10.6	48.9	18.6	17.8
(mg/kg)										
As	21	8	34	3	10	21	8	11	9	3
Ba	852	1109	855	707	116	1088	1478	476	1064	721
Co	21	23	23	20	2	21	39	9	17	13
Cr	941	910	590	324	53	328	703	238	989	163
Cu	910	3904	1286	1740	670	993	3222	824	499	1477
Ga	8	9	11	8	3	8	11	4	7	3
Mo	18	15	45	9	10	23	21	37	22	8
Nb	11	9	22	7	1	10	14	4	13	4
Ni	76	233	292	81	18	95	306	56	81	59
Rb	106	28	177	23	54	96	40	68	44	11
Sn	665	233	1476	198	588	760	232	506	262	135
Sr	463	454	316	419	37	394	475	234	553	327
Y	10	11	9	14	1	10	16	9	12	8
Zn	11991	3642	24281	2251	9756	14834	3183	8193	4341	1582

BA = bottom ash; FAU = untreated fly ash; FAE = fly ash from electrostatic precipitator; FAL = lime-treated fly ash; FAS = soda-treated fly ash. After the descriptive acronyms of MSWI ashes, letters A, B, C and D represent the investigated MSWI plants, as used in the text.

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Chapter 6

Conclusions and future research directions

1. Conclusions

Both pure and applied research ventures play fundamental roles in providing the techniques to manage raw material production in sustainable manner. This approach can lead towards efficient ore mining also from anthropogenic waste streams. The growing demand and increasing market prices of critical raw materials (i.e., those of crucial importance for the technological development) pushes to invest in anthroposphere mining.

In the present thesis I applied basic principles of the Earth Sciences in order to assess the geochemical characteristics, resources potential and environmental impact of municipal solid waste incinerators (MSWI) residues, with final aim of understanding their potential as urban ore deposit. Such urban repository is generally poorly explored for critical raw materials, despite MSWI residues represent one of the fastest growing waste streams. This drove the research project to explore a range of residues from Italian MSWI facilities.

The main conclusions of the present thesis are hereafter listed according the theoretical stages of the urban mining approach: geochemical characterisation, evaluation/prospecting, upgrading/recovery, environmental issues.

1.2 Geochemical characterisation

The MSWI bottom and fly ashes contains significant amount of critical raw materials and other ore metals such as the critical elements Mg (30 g/kg), Cr and Sb (1-2 g/kg), and the other elements of economic interest Al (>50 g/kg), Cu and Zn (10 g/kg). Concerning the total content of rare earth elements (∑REE), bottom and fly ashes have an average concentration of 104 and 54 mg/kg ∑REE, respectively. Volatile elements (e.g., Sb, Zn, Cd) concentrations are higher in MSWI fly ash rather than in bottom ash, whereas other elements mass fractions preferably partition in MSWI bottom ash. Elements like Ag, Sb, Ce, La, Nb, Ni, and V are enriched in the fine-grained fraction of the MSWI residues, whereas Gd, Cr, Sc, W and Y partition into the coarser fraction.

To the best of our knowledge, other characterisation analyses are performed for the first time during this work: the analysis of Os concentrations and $^{187}Os/^{188}Os$ isotopic ratios.

The Os concentrations of the investigated samples vary from 0.03 ng/g to 1.7 ng/g and are higher than expected considering literature data on other PGE concentrations from MSWI. The cycling of Os in the surface environments is limited in importance, but increased Os concentrations raise concern about the potential environmental risk. The study of Os isotopic ratios (samples range from 0.24 to 0.70) and Os concentrations suggested the resulting Os signatures are a mixture of natural and anthropogenic contributions in the MSWI feedstock material. The estimated Os annual flow from MSWI solid residues is 13.4 g/a for a single incinerator.

1.3 Resource evaluation and prospecting

The present work suggests MSWI urban ore are comparable with a low-grade natural ore, indicating that the exploration and prospecting of anthropogenic waste should not be overlooked. In addition, the MSWI urban ores have many advantages: 1) they are already in granular form that allows overcoming constraints of expensive drilling/crushing operations; 2) they represent a continuous flow of material rather than the limited volumes of natural ores; 3) the hypothetical treatment of these materials can reduce their environmental impact rather than produce new impacts (e.g., the associated gangue material can be used in civil engineering applications). In this study, useful tools for MSWI residues prospecting were successfully used/devised. The mass flow analysis has been used for the evaluation of critical and valuable elements flow within the MSWI output materials. The results pointed out that the MSWI residues represent a low-concentration but high-flow streams of ore metals. According to the mass flow analysis applied to a MSWI plant, the expected flows of Mg, Co, Cr, Sb (critical element), Al, Cu, Mn, Ni, V, Zn (elements of economic interest) are, conservatively, in the order of 10^4-10^3 kg/a, while 10^2-10^1 kg/a for the precious metals, Au and Ag, and the REE. The study of transfer coefficients revealed MSWI fly ashes can be a promising target for the recovery of, for example, Sb and Zn, while MSWI bottom ashes can be treated for the recovery of the critical elements Mg, Co, and Cr. Also, the finest fraction of MSWI bottom ashes can be a good choice for critical elements recovery. I suggested other strategic tools (correlations between REE and major elements or magnetic susceptibility, pricing influence/enrichment factor) that might help during prospecting of MSWI residues. The P_2O_5 and Al_2O_3 mass fractions and the mass specific magnetic susceptibility are reliable indicators of the REE occurrence within MSWI residues. In particular, the MSWI residues show a distinct magnetic susceptibility signature, different from any geological materials. The investigated magnetic parameter helps distinguishing bottom from fly ash, and even among different kinds of treated fly ash. Both chemical (major elements) and magnetic measurements can be performed quickly, with low costs and on-site by means of portable analyzers. An empirical parameter that considers both element partitioning and relative abundance in ores (enrichment factor, EF) and market price (pricing influence factor, PIF), pointed out that MSWI fly ashes represent the most promising target for future recovery of the REE, especially Tb, Ho, Yb, and Eu. This, in turn, might help the decision-making authorities regarding the management of these residues.

Overall, the prospecting stage benefited from the integration of magnetic, chemical, and statistical methods, leading to a better assessment of secondary raw materials and also of hazardous substances.

1.4 Upgrading and recovery

The study of upgrading/recovery efficiency was accomplished by applying and testing several strategies. A separation strategy, deriving from natural sorting of bottom ash heaps, can increase the relative recovery efficiency up to 83% for critical elements. It is simple, cost-effective and easy to implement at the plant scale. This separation process can be actually assimilated to a sampling strategy that might lead to the identification an upgraded starting material for later treatments.

This work confirms that bio-hydrometallurgical routes are highly suitable for the treatment of complex and/or low grade ores, such as waste streams. Both sulphuric acid leaching and bioleaching of fly ash sample from MSWI resulted in good recovery performances. Comparable removals are calculated for Mg and Zn (>90%), Al and Mn (>85%), Cr (~65%), Ga (~60%), and Ce (~50%). On average, the chemical leaching performed better than bioleaching with the highest removals for Cu (95%), Fe (91%), and Ni (93%). Bioleaching showed satisfactory yields for the critical elements Ce, Co, La, Nd, Sb and for the ore metals, Zn and Pb. Bioleaching has the advantage of an improved selectivity especially for toxic elements and low removal of un-necessary element (e.g., Si and Ti). In addition, the bio-produced H_2SO_4 favourably impacts on the process economics. Valuable metals yields can be improved by controlled physical-mechanical methods (e.g., crushing, size separation) and finally utilising fine-tuned hydrometallurgical processes.

1.5 Environmental issues

In the next years growing MSWI streams will continue to flow and cause severe pollution into environmental sinks. MSWI bottom and fly ashes contain high levels of hazardous substances; especially the latter are enriched with mobile harmful elements such as Pb, Cd, and Mo. The MSWI bottom and fly ashes constitute an environmental problem that can be faced by the urban mining concept. Our point of view is that the environmental sustainability matches the urban mining concept and turning waste into resources means also decontamination. Bio-hydrometallurgical processes are most affordable as they often show high efficiency with low energy consumption with respect to physical methods. However, final residues deriving from the two methods under the experimental conditions used in this work (leaching time, temperature, and acid composition) cannot be reused as construction material and need further processing for landfilling as non-hazardous or inert waste status. According to the guidance levels published by BAFU (Federal Office for the Environment, Switzerland) for pulverised coal ash and blast furnace ash, a further removal of Zn, Cr, Pb, and Sb is needed prior to final disposal of the studied treated residues. Nonetheless, during bioleaching the selected bacteria mixture allowed to halve the use of manually added acid (through the bio-production of sulphuric acid from sulphur) and demonstrated potential for improvements. Highly selective metal-microbe interactions offer the possibility to combine decontamination with enhanced resource recovery.

Osmium measurements, which were not straightforward due to analytical challenges, showed increased Os levels in MSWI residues. The assessment of Os-related impact revealed up to 13.4 g/a Os within the stream of MSWI final by-products. These Os quantities get lost in landfill where anthropogenic Os (e.g., from end-of-life PGE applications) is probably more accessible to weathering and transport than Os in the geological records (e.g., refractory minerals and alloys).

Furthermore, we estimated up to 78 g/a of volatile Os emitted from the smokestack of a sole MSWI plant. Considering a medium size country having 50 MSWI facilities, the estimate of Os release from MSWI smokestacks is predicted to be from 16 to 38 ng Os/m^2/a, much higher than the naturally transported osmium in the atmosphere of about 0.001 ng Os/m^2/a. The Os contamination from MSWI should be acknowledged as a strong candidate to account for the geochemical Os cycle.

The magnetic susceptibility data for MSWI residues suggest the presence of ultrafine superparamagnetic fractions (>10%), which could represent matter of concern for humans and animals health.

2. Way forward

The following aspects would need further researches:

Sampling and characterisation. Best practices in waste management have to be defined to secure methods homogenisation, inter-comparison and, consequently, enhanced know-how. Public authorities, industrial managers and the research community would benefit from appropriate sampling strategies. There is the lack of a proper classification of MSWI and their end-products that prevents any accurate comparison. Furthermore, waste input collection needs to be improved. The Italian case study pointed out that MSWI inputs are not accurately managed. The different fractions are not separately weighed; the upstream separate collection (glass, metallic scrap) still not reaches high levels of efficiency. The WEE separate collection also seems to be somehow lacking, as corroborated by the presence of REE and other specific elements. The correlations between major elements/magnetic susceptibility vs. REE (and other correlations, e.g., Ni-Ga) highlighted that some indicators of substances typically contained in WEEE does exist; thus a few properties (and their relationships) of by-products can serve as a monitoring tool for WEEE separate collection efficiency. Finally, seasonal and spatial variations concerning MSWI input and output materials should be accounted. Upcoming researches will include the accurate PGE determination (data evaluation is in progress) and a comprehensive magnetic characterisation of MSWI residues in order to increase the number of reference data and, consequently, for improving the methods of prospecting and environmental assessment. In general, more and accurate chemical data are needed in order to perform massive and reliable SFA for national flows and stocks of marketable and hazardous (including Os) elements. This would definitely help assessing the relevance of MSWI systems on potential economic losses and environmental impact (with subsequent FCA and EIA, respectively). Further improvement of the work (especially, that deriving from chapter 2 and 3) concerns the possible integration of chemical data with detailed microstructural and mineralogical analytical characterisation. These efforts may provide some useful indications about the mineralogical incorporation of trace elements in specific mineral phases and, in turn, provide valuable information for the optimisation bio-hydrometallurgical process (see chapter 4).

Resources evaluation and prospecting. This work demonstrates that MSWI output residues represent low grade, but high flows ores. They could represent the future of raw material supply if recovery strategies will focus on separation, processing and recycling of minor species. Improving the selectivity characteristics of, for example, bio-hydrometallurgical processes, is therefore of crucial importance. In order to plan investments regarding critical elements/ore metals recovery from MSWI residues, the proposed prospecting methods such as mass flow analysis, geochemical/magnetic correlations need to be corroborated by new data based on accurate sampling strategies. The magnetic parameter can be used to identify minor magnetic phases (when otherwise is not possible by XRD analysis) where critical elements may concentrate. This could be highly desirable for resource prospecting and environmental assessment.

Metal recovery. There is no single solution for the processing of waste streams and metal recovery from them due to varying conditions even at local scale, thus more efforts have to be made to solve real-life situations. To enhance the recovery of critical elements from low concentrations complex wastes the proposed process chains must be optimised. There is still the aim to further treat each by-product from the bio-hydrometallurgical processes, by testing precipitation from solutions and physical post-treatment of solids and, finally, assess the environmental stability of the final solids and liquids. In addition, future experiments could include leaching at elevated temperatures, the use of other catalysing agents, and combined bioleaching and chemical leaching to utilise the selectivity differences and maximise recoveries and environmental status of the residue. In order to exploit the intrinsic capability of some microorganisms for metal recovery, more efforts are needed to understand the behaviour of microorganism during leaching and to identify new promising species or association of bacterial strains. Biotechnologies will continue to play a crucial role for the supply with critical raw materials, because they offer eco-efficient alternatives. For proper assessment of a suitable treatment strategy, the performance characteristics of the bioleaching need to be compared with other leaching procedures from economical and ecological point of view, by using evaluation tools such as: Full Cost Accounting (FCA), Life Cycle Assessment (LCA), and Environmental Impact Assessment (EIA).

APPENDIX A.

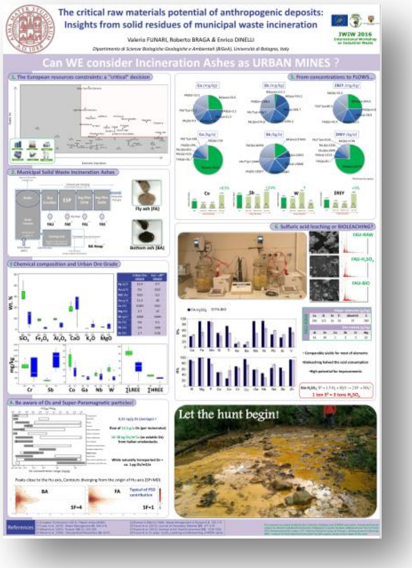
This section reports the contributions (abstracts) to national and international conferences to which I participated during different stages of the PhD work. Each speech or poster presentation has been of great help for exchange knowledge and for networking.

Conference: IWIW 2016 (Feb. 2016, Genova, IT)

THE CRITICAL RAW MATERIALS POTENTIAL OF ANTHROPOGENIC DEPOSITS: INSIGHTS FROM SOLID RESIDUES OF MUNICIPAL WASTE INCINERATION

Valerio Funari · Roberto Braga · Enrico Dinelli

In the present work we address the potential of MSWI solid residues as an alternative source of critical raw materials by studying the material chemistry, its resources flow and the evaluation of metals upgrading and recovery. The recovery potential of ore metals and critical elements from MSWI fly ashes is investigated by comparing sulphuric acid leaching and bio-assisted leaching.



The critical raw materials potential of anthropogenic deposits: Insights from solid residues of municipal waste incineration

Valerio FUNARI, Roberto BRAGA & Enrico DINELLI

Dipartimento di Scienze Biologiche Geologiche e Ambientali (BiGeA), Università di Bologna, Italy

Can WE consider Incineration Ashes as URBAN MINES ?

1. The European resources constraints: a "critical" decision

2. Municipal Solid Waste Incineration Ashes

3. Chemical composition and Urban Ore Grade

4. Be aware of Os and Super-Paramagnetic particles!

5. From concentrations to FLOWS…

6. Sulfuric acid leaching or BIOLEACHING?

Let the hunt begin!

References

Conference: SARDINIA 2015 (Oct. 2015, S. Margherita di Pula, IT)

METAL RECOVERY FROM MUNICIPAL SOLID WASTE INCINERATORS FLY ASH BY SULPHURIC ACID LEACHING AND BIOLEACHING

Valerio Funari · Justin Salminen · Jarno Mäkinen · Hannu Revitzer · Roberto Braga

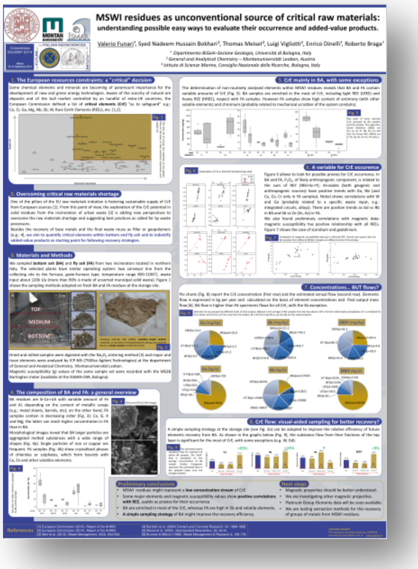
Municipal solid waste incinerators (MSWI) ashes are being investigated in order to understand recovery opportunities with the final aim of diversifying sourcing and partly overcoming raw materials shortage. Turning waste into resource in the most efficient way is challenging, especially when secondary critical raw materials are the final objectives of recovery. The advances on bio- and hydrometallurgy are crucial for enhanced metals recovery and mitigation of environmental risks directly associated with the treatment of solid waste. Here we present preliminary results of bio- and hydrometallurgical experiments for critical metals recovery from MSWI fly ash and a comparison of the performance characteristics between acid leaching and acid bioleaching. Sulphuric acid leaching showed the advantage of reduction and mobilisation of Ca, thus improving the quality of the final product. Conversely, bioleaching experiments were performed in a mixed culture of *T. ferrooxidans* and *T. thiooxidans* and their efficiency was evaluated over a period of several weeks; reagents involved are lower than those needed for acid leaching thus making the process economically feasible and more environmental friendly. The influence of the experimental parameters will be discussed for both acid leaching and acid bioleaching procedures.

Conference: SGI-SIMP 2014 (Sept. 2014, Milano, IT)

MSWI RESIDUES AS UNCONVENTIONAL SOURCE OF CRITICAL RAW MATERIALS: UNDERSTANDING POSSIBLE EASY WAYS TO EVALUATE THEIR OCCURRENCE AND ADDED-VALUE PRODUCTS.

Valerio Funari · Syed Nadeem Hussain Bokhari · Thomas Meisel · Luigi Vigliotti · Enrico Dinelli · Roberto Braga

Critical raw materials (CM) are chemical elements and minerals such as Be, Co, Ga, Ge, In, Mg, Nb, Sb, Ta, W, Platinum Group Elements (PGE), Rare Earth Elements and Y (REY), fluorite, graphite, which are important for the technological development (European Commission, 2010) needed to achieve a low-carbon society. Solid residues from Municipal Solid Waste Incinerators (MSWI) may represent an unconventional source of valuable chemical elements, as a continue flow stream (e.g.: Morf et al., 2012). In this contribution we will show that the CM content in bottom and fly ashes, which are the common MSWI outputs, and their estimated annual flow (t/a) are significant. Analyses were carried out by ICP-MS and XRF, reaching very low detection limits in order to evaluate the CM potential. Total CM (Ce, Co, Nb, Sb, Ta, W) in bottom ashes is 380 mg/kg; fly ashes contain 1022 mg/kg Sb, 49 mg/kg total other CM (Ce, Co, Nb, Ta, W). Bottom and fly ashes have an average concentration higher than 60 mg/kg SREY. The estimated substance flow shows that a hypothetical recovery is advantageous in bottom ashes for the most of the elements. To further explore the CM potential of bottom ashes, we have considered the different granulometric fractions produced by simple gravitational sorting during their temporary storage as stockpiles. The substance flow analysis reveals that the bottom ash finer fraction (which forms the top layer) shows an overall enrichment in CM compared to the other coarser layers. The finer bottom ashes residing on the top of stockpiles, which can be sampled by simple visual inspection at the plant storage facility, seem to represent the most promising target for future recovery strategies. We are also investigating whether correlations with the mass specific magnetic susceptibility of the MSWI solid residues can be used as proxies for CM occurrence (and, hence, as a fast indicator of CM's relative availability). First results show that this parameter is related to the REE distribution. On


MSWI residues as unconventional source of critical raw materials: understanding possible easy ways to evaluate their occurrence and added-value products.

Valerio Funari[1], Syed Nadeem Hussain Bokhari[2], Thomas Meisel[2], Luigi Vigliotti[3], Enrico Dinelli[1], Roberto Braga[1]

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the short term, our data will help to bolster the attention on incinerated waste as an unconventional solution for raw materials supply. A comprehensive strategy has to be implemented to address the quantitative availability of CM through new prospecting technologies, as called for by the European Commission in its European Innovation Partnership in Raw Materials (EIP).

Conference: SGI-SIMP 2014 (Sept. 2014, Milano, IT)

MARINE GEORESOURCES OF THE SOUTHERN TYRRHENIAN SEA: CRITICAL ELEMENTS POTENTIAL ASSESSED BY GEOCHEMICAL DATA

Valerio Funari · Marzia Rovere · Fabiano Gamberi · Michael Marani · Enrico Dinelli · Roberto Braga

Critical Elements (CrE), i.e. Be, Co, Ga, Ge, In, Mg, Nb, Sb, Ta, W, the Platinum Group Elements (PGE) and the Rare Earth Elements (REE), have been identified to be essential for Europe due to their high relative economic importance concurrent with their high supply risk. The highest production of CrE is based in non-EU countries and in China in particular (European Commission, 2010). Their availability is increasingly under pressure because of their strategic importance for emerging new and green-energy technologies, such as hybrid cars, energy saving LEDs, electronic devices memories, wind power generators, medical applications. In the past few years, the development of seafloor exploration technology and novel geochemical and mineralogical results are adding new perspectives to the economic potential of marine georesources. Several submarine geological processes are suggested to be capable of depositing CrE (e.g. Kato et al., 2011). Here we present the preliminary results of XRF and ICP-MS analyses performed on a number of sub-surface (depth < 1 m) seafloor samples collected in the southern Tyrrhenian Sea from different provinces associated with cold seeps and hydrothermal vents at the seabed. We focus on: 1) the determination of geochemical proxies for the CrE occurrence in specific deep-sea settings and 2) the prediction of CrE's potential in the seafloor sediments through colour-shaded concentration maps. The southern Tyrrhenian seabed shows up to 47 g/kg total CrE. By clustering samples on the basis of the average bulk concentration of the main oxide, we found that Co content is high in iron oxy-hydroxides, while REE are enriched in Al-Si-rich samples. The Ca- and Mn-rich samples appear to be depleted in CrE. Interpolated maps of CrE concentration indicate that the Paola Basin and the Eastern Aeolian Arc show relatively high content of Co and REE, the Palinuro area is high in Mg and precious metals (both with local hot spots of highest concentration). Seabed mining is still in its infancy with a few companies at present fully engaged in exploring the potential of deep sea resources worldwide, while general skepticism about the real potential of the seabed CrE deposits, coupled with the growing sensibility to environmental protection issues, are increasing. Yet, the global demand could drive further expansion of seabed mining in the near future and any efforts to develop innovative and sustainable exploration and exploitation techniques have to be encouraged among both the scientific community and the industry.

Conference: SGI-SIMP 2014 (Sept. 2014, Milano, IT)

URBAN ORE DEPOSITS: MSWI SOLID OUTPUTS, A SOLID PERSPECTIVE

Valerio Funari

Invited speaker

W2 pre-conference workshop: *Georesources in Horizon 2020. Perspectives of deep sea and continent exploration/exploitation and recycling of non-energy raw materials*.

This workshop will cover topics on exploration and sustainable supply of raw materials from on-land and deep-sea environments, in the framework of the

Horizon 2020 Societal Challenge "Climate, Environment, Resource Efficiency and Raw Materials". The programme includes talks and discussions on:

1. Technology development and innovation in deep sea prospecting
2. Supply of georesources and economic aspects for the EU
3. Re-cycling and re-use of waste
4. Ocean governance and the protection of the Marine Environment
5. Mineral deposits in Italy

Discussions will focus on how to foster relations between the research community and industry within the European Innovation Partnership (EIP) on Raw Materials.

Conference: ERES 2014 (Sept. 2014, Milos Island, GR)

THE REE POTENTIAL IN "URBAN" ORE DEPOSITS: AN EVALUATION ON CONTENTS AND PROSPECTING TOOLS FROM ITALIAN MUNICIPAL SOLID WASTE INCINERATORS.

Valerio Funari · Syed Nadeem Hussain Bokhari · Thomas Meisel · Luigi Vigliotti · Roberto Braga

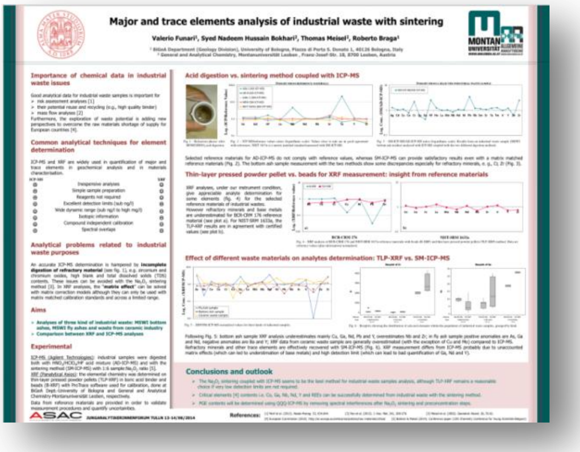
Solid residues from Municipal Solid Waste Incinerators (MSWI) may represent an unconventional source of REE and other critical raw materials as defined by the European Commission. In this contribution we present the total REE content in bottom and fly ashes, which are the common MSWI outputs, and their estimated annual flow are significant. Samples were digested with sodium peroxide sintering which is highly effective analytical technique and the analysis was performed with ICP-MS. Bottom and fly ashes have an average concentration of 103 and 54 mg/kg ΣREY, respectively. For fly ashes the expected annual flow is 1.1 t/a LREE and 0.3 t/a HREE, whereas for bottom ashes is 22.5 t/a LREE and 5.2 t/a HREE. Moreover, we show that simple magnetic susceptibility measurements can be a promising prospecting method when exploring for REE in urban ores is concerned.

Conference: ASAC 2014 (Jun. 2014, Tulln, AT)

MAJOR AND TRACE ELEMENTS ANALYSIS OF INDUSTRIAL WASTES WITH SINTERING

Valerio Funari · Syed Nadeem Hussain Bokhari · Thomas Meisel · Roberto Braga

Knowledge about the chemical composition of industrial waste is important for: i) risk assessment analysis, ii) understanding economic potential of residue for raw material supply and iii) mass flow analysis. Accurate analyte determination from industrial waste is hampered by incomplete digestion of refractory material e.g. industrial magnesite, chrome-bearing materials (e.g. chromite), refractory materials from pyrometallurgical processes (containing MgO, Al_2O_3, CaO), stable high melting temperature oxides, silicon carbide, zirconium and chromium oxides, organic materials with high molecular mass, noble metals, ceramics scrap, etc. Effective measurement procedures are required for a complete digestion of these refractory materials. Dissolution by wet acid digestions is often incomplete and high blank and total dissolved solids (TDS) contents with alkali fusions can lead to an underestimation of analyte concentrations. Hence an effective analytical procedure that successfully dissolves refractory material is needed to be employed for reliable analytical results. The Na_2O_2 sintering combined with solution ICP-MS has the capability of complete digestion of all the refractory material known today. We have undertaken the study of three kinds of industrial wastes i.e. fly ashes, bottom ashes and waste from processing ceramics. Sintering was performed to achieve total digestion and the quantification was done with ICP-MS (Agilent 7500ce). A comprehensive data set of



Major and trace elements analysis of industrial waste with sintering

Valerio Funari[1], Syed Nadeem Hussain Bokhari[2], Thomas Meisel[2], Roberto Braga[1]

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[2] General and Analytical Chemistry, Montanuniversität Leoben, Franz-Josef-Str. 18, 8700 Leoben, Austria

Importance of chemical data in industrial waste issues

Common analytical techniques for element determination

Analytical problems related to industrial waste purposes

Aims

- Analyses of three kind of industrial waste: MSWI bottom ashes, MSWI fly ashes and waste from ceramic industry
- Comparison between XRF and ICP-MS analyses

Experimental

Acid digestion vs. sintering method coupled with ICP-MS

Thin-layer pressed powder pellet vs. beads for XRF measurement: insight from reference materials

Effect of different waste materials on analytes determination: TLP-XRF vs. SM-ICP-MS

Conclusions and outlook

References:

measurands, e.g., of As, Ba, Ce, Co, Cr, Cu, Ga, La, Mo, Nb, Nd, Ni, Pb, Rb, Sr, V, Y, Zn, Zr was obtained with sintering and ICP-MS. In comparison XRF data were unreliable due to higher detection limits and unaccounted matrix effects. For example, XRF analysis in bottom ash residues underestimates mainly lead, yttrium, and gallium and overestimates niobium, molybdenum, chromium, and zirconium mass fractions. Moreover, critical element contents i.e. Ce, Co, Cr, La, Ga, Nb, Nd, Y, Zn, can be successfully determined (and cost effectively recovered) from industrial waste with the sintering method. As a next step PGE contents of the industrial waste will be determined using QQQ-ICP-MS by removing spectral interferences after Na_2O_2 sintering and preconcentrations steps.

Conference: SUM 2014 (May 2014, Bergamo, IT)

SOLID RESIDUES FROM INCINERATORS: A SOURCE FOR CRITICAL RAW MATERIALS?

Valerio Funari · Enrico Dinelli · Syed Nadeem Hussain Bokhari · Thomas C. Meisel · Roberto Braga

The European Commission (2010) 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, Ga, Ge, In, Mg, Nb, Sb, Ta, W, Platinum Group Elements (PGE such as Ag, Au, Pd, Pt, Rh etc.), Rare Earth Elements and Y (REY), fluorite, graphite, which are important for the technological development needed to achieve a low-carbon society. We focus our research on the content of these CRM in solid residues from municipal waste incinerator plants. In previous works, solid residues from incinerator were studied in order to reduce their impact on the environment and human health, to assess their potential reuses, e.g. as road construction materials or concrete additives, and/or to look for significant concentrations of precious metals. The solid residue from incinerators as potential source of CRM has not yet been fully understood.

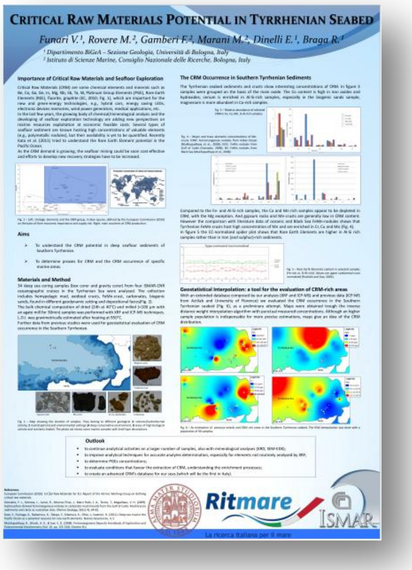
We sampled slags, bottom and fly ashes from two grate-furnace incinerators and determined their total elemental composition with sensitive analytical techniques such as X-ray fluorescence spectrometry (XRF) and inductively coupled plasma mass spectrometry (ICP-MS). Bottom ash analyses show a silver mean concentration of 5.5 mg/kg, 0.4 wt. % CuO, whereas other base metals oxides are up to 0.7 wt. %, 380 mg/kg total CRM (Be, Ce, Co, Nb, Sb, Ta, W), 69 mg/kg ∑REY (REE + Y), 697 mg/kg other metals with high economic importance (Cr, V, Ni, Mo, Tl - according to EC, 2010). For investigated fly ashes we determined a silver mean mass fraction of 19.3 mg/kg, 1022 mg/kg Sb, 49 mg/kg total other CRM (Ce, Co, Nb, Ta, W), 62 mg/kg ∑REY (REE + Y) and 776 mg/kg other metals with high economic importance (Cr, V, Ni, Mo, Tl - according to EC, 2010). Grain-size distribution and gravitational sorting in stockpiles (only for bottom ashes and slags) seems to affect the distributions of some CRM in different granulometric fractions, e.g.: the fine-grained fraction is enriched in Sb, Ce and La relative to the coarse grained fraction, whereas there is no granulometric control over Co, Ga and Ta. Therefore a substance flow analysis for CRM, including REE, and other valuable metals has been conducted in order to evaluate the relative efficiency of a hypothetical recovery from the total residues and investigated granulometric fractions of bottom ashes. Our data will help to focus the attention on incinerated waste as an unconventional solution for raw materials supply.

Conference: RITMARE (Apr. 2014, Bologna, IT)

CRITICAL RAW MATERIALS IN TYRRHENIAN SEABED

Valerio Funari · Marzia Rovere · Fabiano Gamberi · Michael Marani · Enrico Dinelli · Roberto Braga

Critical Raw Materials (CRM) are some chemical elements and minerals such as Be, Co, Ga, Ge, In, Mg, Nb, Sb, Ta, W, Platinum Group Elements (PGE), Rare Earth Elements (REE), fluorite, graphite (EC, 2010; Fig. 1), which are important for the new and green-energy technologies, e.g., hybrid cars, energy saving LEDs, electronic devices memories, wind power generators, medical applications, etc. In the last few years, the growing body of chemical/mineralogical analysis and the developing of seafloor exploration technology are adding new perspectives on marine resources exploitation at economic feasible costs. Several types of seafloor sediment are known hosting high concentrations of valuable elements (e.g., polymetallic nodules), but their availability is yet to be quantified. Recently Kato et al. (2011) tried to understand the Rare Earth Element potential in the Pacific Ocean. As the CRM demand is growing, the seafloor mining could be soon cost-effective and efforts to develop new recovery strategies have to be increased. In order to understand the CRM potential in deep seafloor sediments of Southern Tyrrhenian we aim to 1) determine proxies for CRM occurrence, 2) produce preliminary interpolation maps of CRM by using Surfer® 13 - Golden Software – and the kriging method of interpolation.



CRITICAL RAW MATERIALS POTENTIAL IN TYRRHENIAN SEABED

Funari V.[1], Rovere M.[2], Gamberi F.[2], Marani M.[2], Dinelli E.[1], Braga R.[1]

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Importance of Critical Raw Materials and Seafloor Exploration

The CRM Occurrence in Southern Tyrrhenian Sediments

Aims

Materials and Method

Geostatistical Interpolation: a tool for the evaluation of CRM-rich areas

Outlook

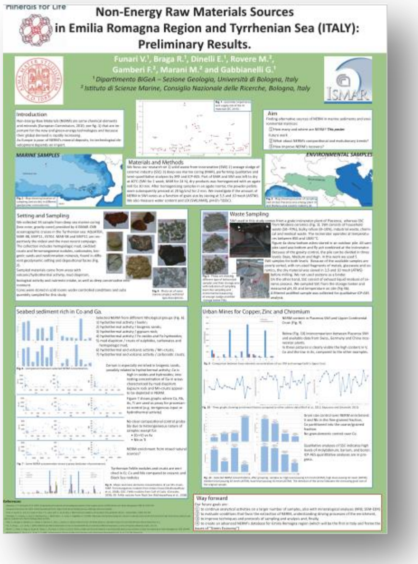
La ricerca italiana per il mare

Conference: MINERALS FOR LIFE (Jun. 2013, Edinburgh, GB)

NON-ENERGY RAW MATERIALS SOURCES IN EMILIA ROMAGNA REGION AND TYRRHENIAN SEA (ITALY): PRELIMINARY RESULTS.

Valerio Funari · Roberto Braga · Enrico Dinelli · Marzia Rovere · Fabiano Gamberi · Michael Marani · Giovanni Gabbianelli

Non-Energy Raw Materials (NERM) are some chemical elements and minerals, defined by the European Commission (2010), such as Sb, Ge, In, Ga, Nb, Ta, W, Mg, Be, Platinum Group Metals (PGM), Rare Earth Elements (REE), fluorite, graphite that are important for the new and green-energy technologies and because their global demand is rapidly increasing. As Europe is poor of NERM's mineral deposits, NERM supply is critical for Italy and Emilia-Romagna region which supports our research through the SPINNER consortium funds (www.spinner.it). We aimed to quantify NERM from alternative sources: 1) ash from waste incineration (IWA), 2) processing waste and sewage sludge from ceramic industry (WSC), 3) deep-sea sediment from the southern Tyrrhenian Sea (MAR) that include samples from cores and dredged sediments. This study will allow to evaluate compositional and evolutionary trends of specific environmental matrices in order to identify conditions that favour significant concentrations of NERM and, consequently, improve their recovery. For example, knowing the mineral/vitreous phases in which NERM are concentrated can facilitate their extraction through bio-metallurgical techniques. Preliminary qualitative and semi-quantitative analyses by XRF and ICP-AES shows interesting concentrations of Mn, Ti, Ni, Co, Cr, V, Ga, As, Br, Mo (in marine samples) and Ni, Cu, Ga, Ce (in IWA), Mo, B, W (in "ceramic" sludge). The available IWA samples are poorly sorted, with 5-10 wt% moisture content and showing cm-sized fragments of metals, glassware and ceramics. Currently we are investigating if the amount of NERM varies as a function of IWA grain-size. Finally, our data will be used to improve analytical protocols and create an advanced NERM database for Emilia Romagna region.



Minerals for Life

Non-Energy Raw Materials Sources in Emilia Romagna Region and Tyrrhenian Sea (ITALY): Preliminary Results.

Funari V.[1], Braga R.[1], Dinelli E.[1], Rovere M.[2], Gamberi F.[2], Marani M.[2] and Gabbianelli G.[1]

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APPENDIX B.

Valerio Funari
Research Scientist

BiGeA Department (Geology Division)
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PERSONAL INFORMATION

Birth on the **19/02/1987** in San Benedetto del Tronto (ITALY)

Home address via Giorgio Perlasca, 14 – 40137 BOLOGNA (ITALY)

Italian car driving license

Nationality and mother tongue: **Italian** - Other languages: **English**, fluent; **French**, notions

PRESENT OCCUPATION AND RESEARCHES

02.2016 →present **Post-doctoral associate** at the University of Bologna, Department of Biological Geological and Environmental Sciences (BiGeA). Chemical and mineralogical characterisation of natural and anthropogenic materials, soils and water; bio-hydrometallurgy; sustainable production of secondary raw materials; environmental impact assessment and environmental remediation. Collaboration with IREN S.p.A and Herambiente S.p.A (fly and bottom ash samples from Municipal Solid Waste Incinerator), Gruppo Concorde S.p.A. (ceramics scraps), MontanUniversität Leoben and University of Ferrara (ICP-MS, Isotope geochemistry, Microprobe analysis), ISMAR-CNR National Research Council (Magnetic characterisation, Marine georesources), VTT oy-Finland and University of Padua (Metal recovery)

08.2012 →present **Engineering geologist** (licensed to practise: 22/07/2012), main activities include geotechnical/geophysical surveys (MASW, HVSR, GPR) and environmental assessment reports. Past experiences: traineeship at the "Mancini geotechnical surveys s.r.l." (3 months), contract job as consultant at "ENVIA-Environmental Geology/Geophysics s.r.l" (8 months).

EDUCATION AND ACADEMIC CAREER

02.2016 →present **Post-Doc**, University of Bologna, Department of Biological Geological and Environmental Sciences (BiGeA). Project title: "*Bio-hydrometallurgic development for critical raw materials exploitation*". Keywords: Applied Geochemistry, Bio-hydrometallurgy, ICP-MS, Environmental Geology, Ore mines, Waste Management. Supervisor: Prof. E. Dinelli.

01.2013 - 12.2015 **PhD student** in Earth Science, University of Bologna, Italy. Project title: "*The critical raw materials potential of anthropogenic deposits: insights from solid residues of municipal waste incineration*". Keywords: Applied Geochemistry, Mineralogy, Environmental Geology, Waste Management, Bio-hydrometallurgy, and Mining. Supervisor: Prof. R. Braga.

09.2006 – 03.2012 **MSc with honours**, in Geology, University of Bologna,

Thesis title (2nd cycle): "Structural and geological study of mud diapirs in the Southern Tyrrhenian", supervisors: Prof. G. A. Pini, Dr. F. Gamberi, Dr. M. Rovere;

Thesis title (1st cycle): "Structural analysis of Mt. Giovo (N-Apennines)", supervisor: Prof. G. A. Pini.

09.2001– 06.2006 **College diploma** at the Liceo Scientifico Statale B. Rosetti (Science-oriented topics)

VISITING SCIENTIST

- Institute for Rock Magnetism (IRM), University of Minnesota (1 month). Project title: "*Magnetic characterization of solid by-products from Municipal Solid Waste Incinerators for simultaneous evaluation of environmental hazard and recovery of valuable elements*", supervisor: Dr. Mike Jackson.
- VTT-Technical Research Centre of Finland (3 months). Project title: "*Research on Critical Metals: recycling and hydrometallurgical recovery from alternative sources*", supervisor: Dr. Justin Salminen.
- Montanuniversität Leoben, General and Analytical Chemistry (1 month). Project title: "*Evaluation o PGEs content from industrial samples by HPA-ID-ICP-MS*", supervisor: Prof. Thomas Meisel.
- Montanuniversität Leoben, General and Analytical Chemistry (3 months). Project title: "*Accurate analytes determination by ICP-MS of industrial waste samples with emphasis on PGEs*", supervisor: Prof. Thomas Meisel.

FELLOWSHIPS, CRUISES AND RESEARCH PROJECTS

- IRM Visiting Fellowship – Travel Award for research on rock magnetism (1 month, Minnesota)
- COST action: Mining the Anthroposphere (MINEA). European funds *(partner)*
- Marco Polo Project – Young researchers fellowship for research abroad (3 months, Finland)
- Marco Polo Project – Young researchers fellowship for research abroad (3 months, Austria)
- PhD Fellowship – University of Bologna (3 years research project)
- RITMARE: Ricerca Italiana per il Mare. National funds *(partner)*
- MAPPER: Critical Raw Material. Regional funds for PhD project.
- MAGIC: Marine geo-hazard along Italian coasts. National funds *(partner)*
    - Oceanographic Cruise MAGIC ISMAR 08/11 – 15 days in southern Tyrrhenian
    - Oceanographic Cruise MAGIC ISMAR 09/11 – 7 days in southern Tyrrhenian

INTERNATIONAL CONGRESSES AND SCHOOLS

- IWIW 2016. International Workshop on Industrial Waste – Workshop
- Sardinia_2015. International symposium on waste management and landfill – Conference
- Waste Management: Environmental Compliance and Regulatory Requirements - Short Course
- SGI-SIMP 2014. The Italian Geosciences of the Future – Conference
- Georesources in Horizon 2020. Perspectives of deep sea and continent exploration/exploitation and recycling of non-energy raw materials – SGI-SIMP 2014 conference workshop
- ERES 2014. International Conference on European Rare Earth Resources. – Conference
- 3D Raman Imaging and Correlative Scanning Microscopy Techniques - Short Course
- ASAC- 2014. Young scientists conference on geoanalysis and analytical techniques – Conference
- SUM 2014. International symposium on Urban Mining – Conference
- PGE exploration and their mineral ore deposits – SEG Workshop
- The Rietveld method for XRPD analysis purposes – Short Course
- MINERAL FOR LIFE: Overcoming resource constraints – Conference

- Artificial recharge of aquifer, salt intrusion and hydrogeochemistry in coastal areas – Short Course

INVITED SPEAKER

- “Urban Ore Deposits: MSWI solid outputs, a solid perspective”, SGI-SIMP 2014 The Future of Italian Geosciences The Italian Geosciences of The Future, pre-conference workshop. 09/09/2014, Milan (IT)

FUNDING

University of Bologna	Marco Polo Project, grant for research abroad (3 months, Finland)
University of Bologna	Marco Polo Project, grant for research abroad (3 months, Austria)
SPINNER Consortium	MAPPER, grant for PhD innovative project
University of Bologna	PhD Fellowship
ErGo Consortium	Performance ranking in support of MSc. and BSc. degree courses

TEACHING EXPERIENCES

ASSISTANT

- 1h lecture (cycle of seminars for doctoral students): *Isotopic signature and environmental impact o osmium* at the School of Sciences, BiGeA department (Geology Division) – University of Bologna.
- 4h lecture (as a part of the 72755 - Natural and Artificial Stone Laboratory): *GIS software for cultura heritage studies* at the school of “Science for the Conservation-Restoration of Cultural Heritage” (Second cycle degree/Two year Master - 120 ECTS) - Campus of Ravenna.
- 01.2013 →present: Laboratory instructor (Sample preparation, XRF, XRD, SEM, ICP-MS).

CO-SUPERVISOR

- BSc. thesis (**1-** *WDXRF analysis of deep-sea sediment samples from the southern Tyrrhenian an interpolation maps of “critical” elements: a preliminary resources assessment*; **2-** *WDXRF analysis o deep-sea sediment samples from the southern Tyrrhenian and statistical analysis on “critical’ elements: a preliminary resources assessment*; **3-** *WDXRF, SEM-EDX and XRD analyses of deep-sea sediment samples from the southern Tyrrhenian: understanding the resources potential o (ox)hydroxides;* **4-** *Analysis of solid residue of MSWI ashes after acid leaching and its safe disposal;* **5**- *Analysis of industrial waste leachates after hydrometallurgical treatment for metal recovery;* **6**- *Metals extraction from MSWI fly ashes using EDTA: performance evaluation as a function of pH and time*)

LIST OF PUBLICATION

PAPERS

- Funari V., Mäkinen J., Salminen J., Braga R., Dinelli E., Revitzer H. *Metal Recovery from Municipa Solid Waste Incinerators Fly Ash: a Preliminary Comparison between Chemical Leaching an Bioleaching.* **Submitted to** Journal of Hazardous Materials
- Funari V., Meisel T., Braga R. *Isotopic Signature and Impact of European MSWI Ashes on the Anthropogenic Osmium Budget.* Science of the Total Environment, 541: 1549-1555. DOI: 10.1016/j.scitotenv.2015.10.014

- Funari V., Bokhari N., Vigliotti L., Meisel T., Braga R (**2015**). *The Rare Earth Elements in Municipa Solid Waste Incinerators ash and promising tools for their prospecting*. Journal of Hazardous Materials, 301: 471-479. DOI: 10.1016/j.jhazmat.2015.09.015
- Funari V., Braga R., Bokhari N., Dinelli E., Meisel T. (**2015**). *Solid residues from incinerators: a source for Critical Raw Materials.* Waste Management, 45: 206-216. DOI: 10.1016/j.wasman.2014.11.005
- Rovere M., Gamberi F., Funari V., Pini G.A., Mercorella A., Marani M., Gallerani A., Leidi E. (**2013**); *Venting and seepage systems associated with mud volcanoes and mud diapirs in the southern Tyrrhenian Sea*. Marine Geology, 347:153-171. DOI: 10.1016/j.margeo.2013.11.013
- Pini G.A., Funari V. (**2009**). Mt. Giovo thrust system: 2D reconstruction and shortening computation and 3D geological model. 2D and 3D Computer Models and Report.

Conference Abstracts

- Funari V., Braga R., Dinelli, E. (**2016**). *The critical raw materials potential of anthropogenic deposits*. IWIW 2016, Workshop on Industrial Waste, 02/2016, Genova (Italy)
- Funari V., Mäkinen J., Salminen J., Braga R., Revitzer H. (**2015**). *Metal Recovery from Municipal Solid Waste Incinerators Fly Ash: a Comparison between Acid Leaching and Bioleaching.* SARDINIA 2015, International symposium on waste management and landfill; 09/2015, S. Margerita di Pula (IT).
- Funari V. (**2015**). *Bio-hydrometallurgic development for Critical Raw Materials Exploitation*. SARDINIA 2015, workshop on EU project ideas; 09/2015, S. Margerita di Pula (IT).
- Bokhari N., Meisel T., Walkner C., Funari V. (**2015**). *Determination of Ru, Pd, Rh and Au in MUH-1 reference material with sintering-Te-co-precipitation.* GEOANALYSIS 2015, The 9th international conference on the analysis of geological and environmental materials; 08/2015, Leoben (AT).
- Bokhari N., Meisel T., Walkner C., Braga R., Funari V. (**2015**). *Determination of Rh, Ir and Ag in Platinum Group Elements reference materials for industrial analytics.* ANACON 2015, International conference on analytical chemistry and related fields; 03/2015, Graz (AT).
- Funari V., Bokhari N., Meisel T., Vigliotti L., Dinelli E., Braga R. (**2014**). *MSWI residues as unconventional source of critical raw materials: understanding easy ways to evaluate their occurrence and possible added-value products*. SGI-SIMP 2014 Conference, ISSN 2035-8008; 09/2014, Milan (IT).
- Funari V., Rovere M., Gamberi F., Marani M., Dinelli E., Braga R. (**2014**). *Marine Georesources of the southern Tyrrhenian Sea: Critical Elements potential assessed by geochemical data*. SGI-SIMP 2014 Conference, ISSN 2035-8008; 09/2014, Milan (IT).
- Funari V., Bokhari N., Meisel T., Vigliotti V., Braga R. (**2014**). *The REE potential in “urban” ore deposits: evaluation on contents and prospecting tools from Italian municipal solid waste incinerators*. ERES 2014 Conference, ISBN: 978-960-6746-15-4; 09/2014, Milos Island (GR).
- Funari V., Bokhari N., Meisel T., Braga R. (**2014**). *Major and trace elements analysis of industria wastes with sintering.* ASAC-Junganalytikerinnenforum; 06/2014, Tulln (AT).
- Funari V., Dinelli E., Bokhari N., Meisel T., Braga R. (**2014**). *Solid residues from incinerators: a source for Critical Raw Materials?* SUM 2014, Symposium on Urban Mining; 05/2014, Bergamo (IT).
- Funari V., Rovere M., Gamberi F., Marani M., Dinelli E., Braga R. (**2014**). *Critical Raw Materials in Tyrrhenian Seabed.* Ritmare - CNR meeting; 04/2014, Bologna (IT).

- Funari V., Braga R., Dinelli E., Rovere M., Gamberi F., Marani M. and Gabbianelli G. (**2013**); *Non-energy raw materials sources in Emilia Romagna region and Tyrrhenian sea (Italy): Preliminary results.* Minerals for Life: overcoming resource constraints; 05/2013, Edinburgh (GB).

OUTREACH

- Martinucci M., Amanti S., Funari V., Poli G., Pompei M., Staglianò A. (**2010**); *Il ruolo del geologo nella direzione dei lavori.* Il Geologo dell'Emilia-Romagna *O.G.E.R.* journal.
- *GeoDay* and *OpenDay.* Educational events organised by the BiGeA dept. (Geology Division)
- 40h course: Scientific English.
- 17h course: German Language (Level A1.1).
- ECDL full– European Computer Driving Licence.

OTHER RESEARCH-RELATED EFFORTS

Participation in several seminars (1-2h lectures), including:

- *A taste of Python and its capabilities.* Emily Wolin
- *The challenge of capturing Carbon Dioxide from Air.* Stefano Brandani
- *Complex ridge-transform evolution at the St. Paul fracture zone system.* Marcia Maia
- *Nano-technology for clean water*. Christopher James Durning
- *OneGeology-standardizing geological data globally with the purpose of its wide usage.* Marko Komac
- *Dense sampling method for satellite observations of urban changes and impacts.* Son Nghiem
- *Distinguished Lectures - "The Oceanic Crust".* Marco Ligi, Stefano Poli
- *Cascadia and St. Andreas turbidite paleoseismology and earthquake hazards.* C. Hans Nelson
- *Analisi spettrale e dinamica di serie temporali.* Roberto Carniel
- *Accretionary wedges in the Nankai area.* Michey Strasser

AFFILIATIONS

Since 2013: International Waste Working Group (IWWG), Geochemical Society, Società Italiana di Mineralogia e Petrologia (SIMP), Gruppo Nazionale di Petrografia (GNP-SIMP), Gruppo Italiano di Geologia Strutturale (GIGS); ***Since 2015***: member of MINEA (http://www.cost.eu/COST_Actions/ca/CA15115), member of ProSUM information network (http://www.prosumproject.eu/)

REVIEWER FOR:

Elsevier, book proposal "Solid and Hazardous Waste Management".
Waste Management (Journal, Elsevier).

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Last update, February 2016.

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