

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

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INTRODUCTION

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, and Platinum Group Elements), is of general concern (Fig. 1).

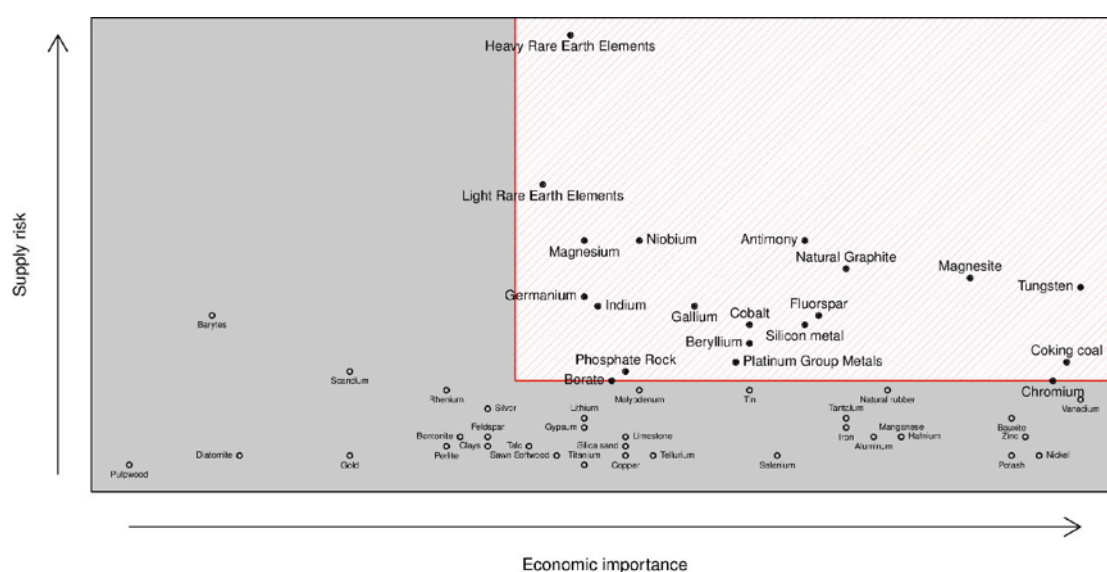


Fig. 1 - Critical raw materials for the EU according to their economic importance and supply risk (European Commission, 2014).

Industrial wastes have the potential to become an alternative source (flow) of strategic metals and, consequently, their valorization 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 addressed 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 tackled some environmental and economic issues.

Municipal solid waste incinerators (MSWI) and their solid residues

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, *i.e.*, grate-system and fluidized bed. Grate-furnaces are largely the most used. 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 (Fig. 2). 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, and scrubber residues; 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 represents about 2-6% of the initial mass of incinerated waste (Sabbas *et al.*, 2003). 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.

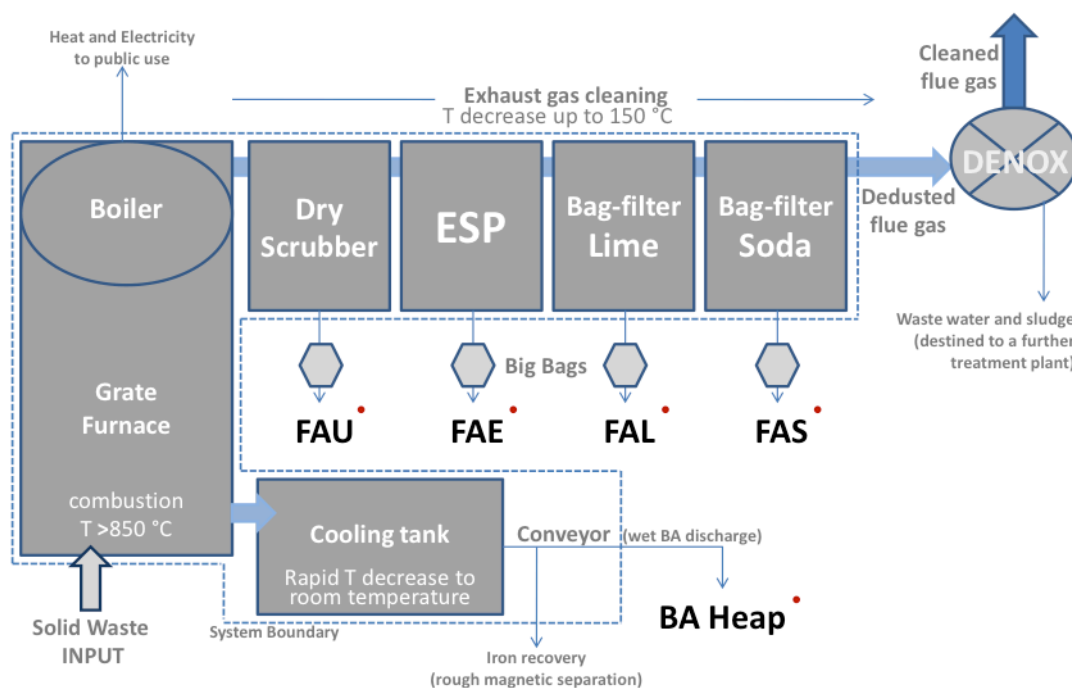


Fig. 2 - Schematic picture of the incinerator system (from Funari *et al.*, 2016a) with its relevant processes, including sampling points (red dots) and temperature (T) profile. Acronyms used: BA = bottom ash; FAE = fly ash from ESP; FAL = fly ash from bag filter with Ca-additive; FAS = fly ash from bag filter with Na-additive; FAU = untreated fly ash; ESP = electrostatic precipitator.

MATERIALS AND METHODS

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 the Emilia Romagna region, among the most industrialized areas of the Peninsula. All the investigated MSWI facilities are equipped with a grate-system furnace and allow the separate storage of BA and each different FA.

Wet BA (20-30% moisture content) from outdoor heaps were sampled and used throughout the present study. Several FA residues were sampled, depending on the available technology, and included: untreated fly ash from dry/semi-dry scrubbers (FAU), 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 can be found elsewhere (*e.g.*, Funari *et al.*, 2015, 2016a).

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), and Aalto University (School of Chemical Technology Dept., Finland).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), and X-Ray Fluorescence (XRF) were mainly used during the present work for the quantification of major (> 1% m/m) and trace elements (< 0.1% m/m).

After accurate analytes determination by ICP-MS, a Substance Flow Analysis (SFA) was also performed in order to assess the flows of elements hosted in the solid outputs of BA and FA.

Magnetic susceptibility measurement was carried out by using a MS2 Bartington meter and mass specific magnetic susceptibility (χ) was calculated with the following formula:

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

where χ is measured in m^3kg^{-1} and k is the volume susceptibility, dimensionless in SI units.

RESULTS AND DISCUSSION

Geochemical characterization

The concentrations of several critical raw materials hosted in MSWI by-products were determined (Funari *et al.*, 2015). The MSWI bottom and fly ashes resulted to contain 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, such as Al (> 50 g/kg), Cu and Zn (10 g/kg). Concerning the total content of rare earth elements (ΣREE), BA and FA had an average concentration of 104 and 54 mg/kg ΣREE , respectively. Volatile elements (*e.g.*, Sb, Zn, and Cd) concentrations are higher in FA rather than in BA, whereas other elements mass fractions preferably partitioned in BA. Elements like Ag, Sb, Ce, La, Nb, Ni, and V were enriched in the fine-grained fraction of the MSWI residues, whereas Gd, Cr, Sc, W and Y partitioned into the coarser fraction.

The analysis of Os concentrations and $^{187}\text{Os}/^{188}\text{Os}$ isotopic ratios of BA and FA from MSWI were reported for the first time (Funari *et al.*, 2016b). The Os concentrations of the investigated samples varied from 0.03 ng/g to 1.7 ng/g and were higher than expected considering literature data on other PGE concentrations from other industrial activities. Generally, the cycling of Os in the surface environments is limited in importance, but increased Os concentrations raise concern about the potential environmental risk. In the present study, the Os isotopic ratios (samples range from 0.24 to 0.70) and Os concentrations suggested that the Os signatures were a mixture of natural and anthropogenic contributions in the MSWI feedstock material. This, in turn, revealed that the MSWI can impact the natural geochemical Os cycle. The estimated Os annual flow from MSWI solid residues was 13.4 g/a for a single incinerator.

Resource evaluation and prospecting

The chemical characterization suggested that the concentrations of BA and FA, namely a MSWI urban ore, are comparable with a low-grade natural ore, indicating that the exploration and prospecting of anthropogenic waste should not be overlooked (Funari *et al.*, 2015). 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 SFA was used for the evaluation of critical and valuable elements flow within the MSWI output materials. The results

pointed out that the MSWI residues represented a low-concentration but high-flow streams of ore metals. According to the SFA applied to a MSWI plant (Table 1), the expected flows of Mg, Co, Cr, Sb (critical element), Al, Cu, Mn, Ni, V, Zn (elements of economic interest) were in the order of 10^4 - 10^3 kg/a, whereas in the order of 10^2 - 10^1 kg/a for the precious metals (Au and Ag) and the REE.

Table 1 - Estimated annual flow for BA and FA in kg/a (from Funari *et al.*, 2015). The average concentrations are calculated for n number of samples. KFA (%) is the relative recovery efficiency between BA and FA; KBAf (%) is the relative recovery efficiency in different granulometric fractions.

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

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

The study of transfer coefficients from SFA revealed that MSWI fly ashes could be a promising target for the recovery of metals (*e.g.*, Sb and Zn), whereas MSWI bottom ashes can be treated for the recovery of the critical elements Mg, Co, and Cr. Moreover, the finest fraction of MSWI bottom ashes could be a good choice for critical elements recovery.

Other strategic tools (correlations between REE and major elements or magnetic susceptibility, pricing influence/enrichment factor) that might help during prospecting of MSWI residues were used (Funari *et al.*, 2016a). 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 showed a distinct magnetic susceptibility signature, different from any geological materials. The investigated magnetic parameter helped to distinguish BA from FA, and even among different kinds of treated FA. Both chemical (major elements) and magnetic measurements can be performed quickly, with low costs and on-site by means of portable analyzers. An empirical model 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 (Fig. 3). This, in turn, might help the decision-making authorities regarding the management of these residues.

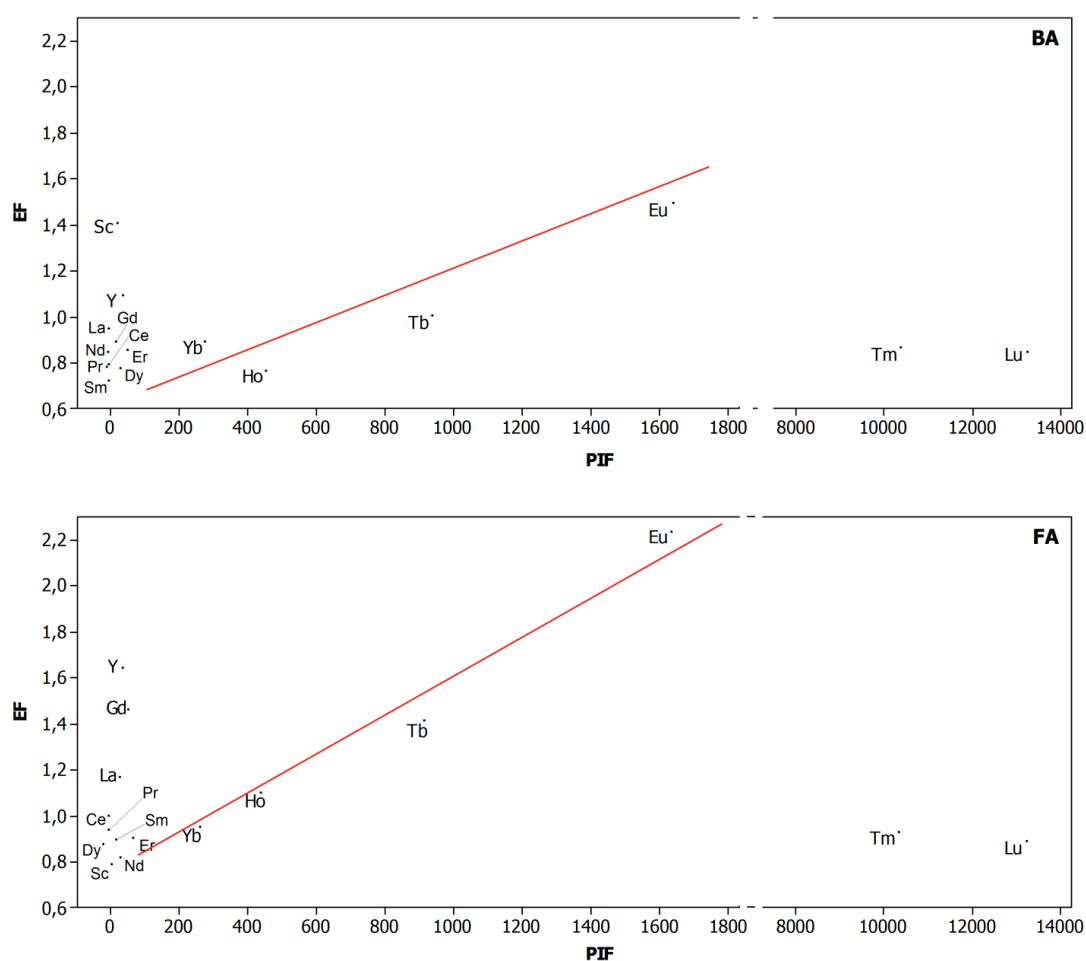


Fig. 3 - Bi-plot of Enrichment Factor (EF) and Pricing Influence Factor (PIF) of REE in BA (above) and FA (below) sampled materials. The red line represents the trend line of observations within a selected range of PIF values (100-1800). For EF and PIF calculation the reader can refer to Funari *et al.* (2016a).

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, was suggested and resulted to increase the relative recovery up to 83% for critical elements (Funari *et al.*, 2015). Moreover, bio-hydrometallurgical

routes considered to be highly suitable for the treatment of complex and/or low grade ores, such as waste streams, were tested. Both sulphuric acid leaching and bioleaching of FA sample from MSWI resulted in good recovery performances. Comparable removals were 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 had 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 bioleaching halved the use of H₂SO₄ with respect to the “pure” sulphuric acid leaching while achieving similar yields. This could favorably impact on the process economics. Bioleaching of valuable metals could be further improved by physical-mechanical pre-treatment (*e.g.*, crushing, size separation) and by varying bioleaching parameters such as iron concentration, pH, T, and duration of the experiment. A schematic flow sheet of a hypothetical process chain for the treatment of MSWI fly ash was proposed (Fig. 4). It involved the use of several processing steps, including optimized 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.

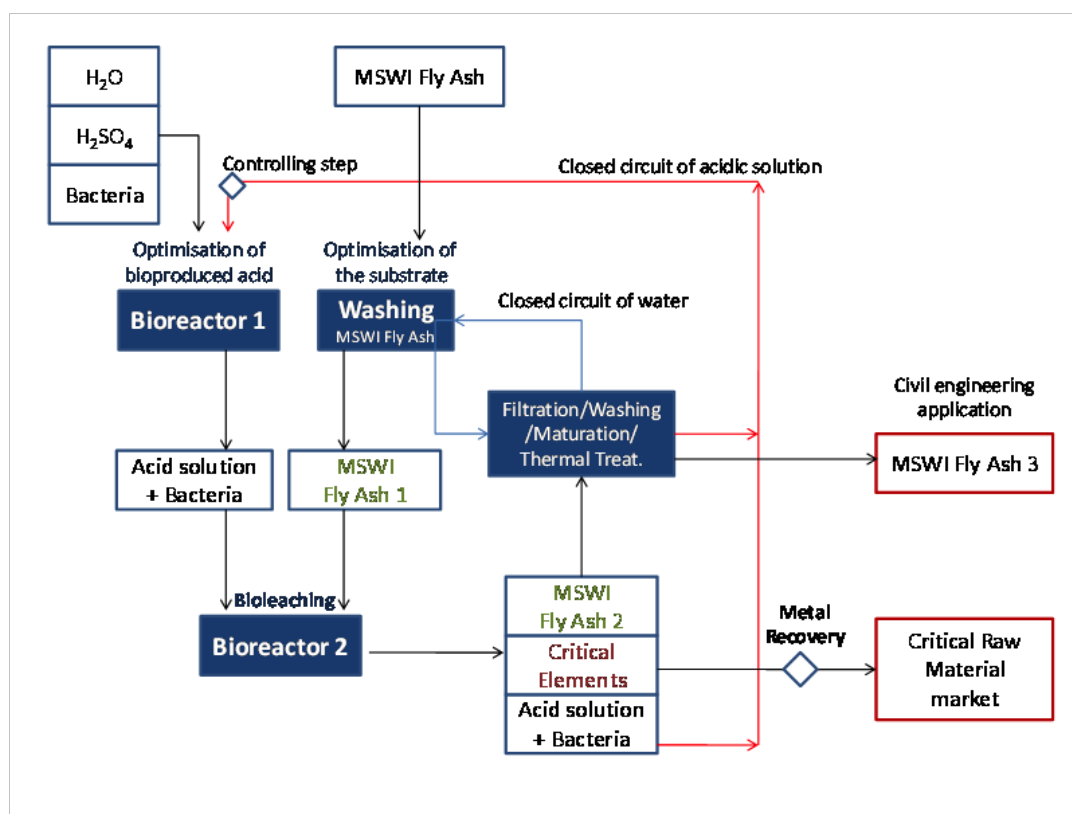


Fig. 4 - Flow sheet of a hypothetical process chain for the treatment of MSWI fly ash.

Environmental issues

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 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 (Funari *et al.*, 2016b). 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). 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 estimation of Os release from MSWI smokestacks was predicted to be from 16 to 38 ng Os/m²/a, much higher than the naturally transported osmium in the atmosphere of about 0.001 ng Os/m²/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 suggested the presence of ultrafine super-paramagnetic fractions (> 10%; Funari *et al.*, 2016a), which could represent matter of concern for humans and animals health.

CONCLUSIONS AND OUTLOOK

Basic principles of the Earth Sciences have been applied in order to assess the geochemical characteristics, resources potential, and environmental impact of municipal solid waste incinerators (MSWI) residues, with the final aim of understanding their potential as urban ore deposit.

There is interest in shifting the research findings to the industrial processes with the final goal of reducing the loss of resources and improving the waste management system.

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