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Metal removal from Municipal Solid Waste Incineration fly ash: A comparison between chemical leaching and bioleaching

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ABSTRACT

Bio and hydrometallurgical experimental setups at 2 l reactor scale for the processing of fly ash from municipal waste incinerators were explored. We aimed to compare chemical H₂SO₄ leaching and bioleaching; the latter involved the use of H₂SO₄ 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 was effective 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 H₂SO₄, i.e., a part of agent costs, as a likely consequence of bio produced acid and improved metal solubility.

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 an aggregate in construction materials (Müller and 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 the atmosphere. Despite the mass of pollutants is lower in filtered fly ashes than in raw fly ashes due to the dilution with unreacted additives (e.g., lime and/or soda addition in bag filters) and their 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 (Funari et al., 2015, 2016b; Astrup et al., 2006) 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 the thousands of tonnes of MSWI fly ashes produced might contain 10³ kg Cu, Sn, and Sb, 10⁴ kg Al and Zn (Funari et al., 2015), 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 European Commission (2014)) (Funari et al., 2015; Morf et al., 2013). 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 stabilisation (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

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Nomenclature

| | | | |
|-----------------------------------|---------------------------------------------------|---------|---------------------------------------------------------|
| C | concentration of the treated sample (mass/mass) | FA WW | fly ash after water washing |
| CO | concentration of the untreated sample (mass/mass) | ICP AES | Inductively Coupled Plasma Atomic Emission Spectroscopy |
| i | index for element | L/S | liquid solid ratio |
| j | index for batch | LOI | loss on ignition |
| M | mass of the batch after treatment (mass) | MSWI | Municipal Solid Waste Incineration |
| M0 | mass of the batch before treatment (mass) | R% | removal rate (yield) |
| APC | Air Pollution Control | RSD | Relative Standard Deviation |
| BAFU | Federal Office for the Environment, Switzerland | SD | standard deviation |
| d | day | TCPL | Toxicity Characteristic Leaching Procedure |
| FA BIO | fly ash subjected to bioleaching | XRF | X ray fluorescence spectrometer |
| FA H ₂ SO ₄ | fly ash subjected to sulphuric acid leaching | | |
| FA RAW | untreated raw fly ash | | |

release. Various studies have investigated wet extraction processes by using chelating agents (Hasegawa et al., 2014; Hong et al., 2010), mineral or organic acids (Meawad et al., 2010 and reference therein) and bio produced acids (Lee and Pandey, 2012 and reference therein, Brombacher et al., 1998). However, 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), which can primarily endanger the environmental and human health, and outlines the influence of experimental parameters such as time, temperature, reagents used, and liquid solid ratio (Hong et al., 2010; Zhang and 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 in order to assess 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 and 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; Ishigaki et al., 2005) and, thereby, contributed to increase the interest on bio-assisted approach and its capabilities.

The present paper will help to figure out what procedure results in more enriched process solutions, where metals can be recovered by further treatment, and in 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% house hold waste and 10% of special waste. The latter input source consists of processing waste from ceramics and metallurgy, automobile shredder residues, hospital and pharmaceutical wastes. 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 3.2 10³ 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. (2015). 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 APC residues (e.g., fly ashes from chemical bag filters; for details, the reader can refer to a previous paper (Funari et al., 2016a).

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 analysed 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 and 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 and 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 through out the experiments. At the beginning of the experiments, the chemical parameters of FA WW were: 11.5 pH and 135 mV red ox potential.

2.2.2. Chemical leaching

The FA WW (10% v/v) and distilled water (90% v/v) were treated with H₂SO₄ in a 2 l glass reactor equipped with a top entered agitator and an aeration system, which supplied a continuous airflow from the bottom of the reactor (Fig. 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 and 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 min in which

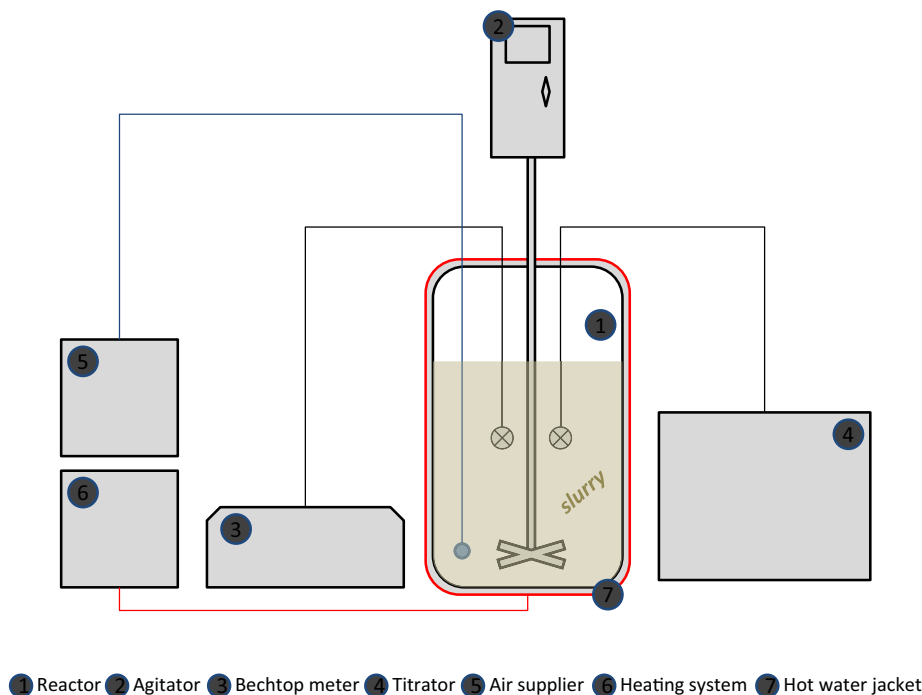
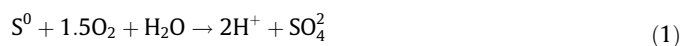


Fig. 1. Experimental setup of leaching procedure in a 2 l glass reactor, equipped with titration system and benchtop meter for the continuous monitor of pH, red-ox and temperature.

the pH level was maintained constant by 4M H₂SO₄ titration (T70, Mettler Toledo). A reaction time of 30 min was used because it is generally adequate to achieve good leaching performances (Nagib and 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 0.45 μm glass fibre filter. After vacuum filtration, several elements were determined in the leachate (Ca, Al, Fe, Cu, Cr, Sb, Sn, Zn) using 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; Rawlings, 2002; Sand et al., 2001) through the reaction:



Metal sulphides are found as minor phases within MSWI ashes (e.g., Bayuseno and Schmahl, 2011), therefore, when treating this 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 9 K medium (Silverman and Lundgren, 1959), containing (NH₄)₂SO₄ 3.0 g/l, K₂HPO₄ 0.5 g/l, MgSO₄ 7H₂O 0.5 g/l, KCl 0.1 g/l,

Ca(NO₃)₂ 0.01 g/l, FeSO₄ 7H₂O 22.5 g/l and also 10.0 g/l S⁰. The modified 9 K medium was adjusted to pH 2.0 with concentrated H₂SO₄. 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 9 K 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 9 K 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 H₂SO₄ and flasks were incubated in a rotary shaker (150 rpm, 30 °C). If a spontaneous decrease in pH was observed during 15 days, a new modified 9 K 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 l glass reactor with a similar setup as for chemical leaching (Fig. 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 9 K medium (without FeSO₄ 7H₂O) and the previously adapted acidophilic culture (10% v/v). The pH was fixed to 2.0 with concentrated H₂SO₄ 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 H₂SO₄, if necessary.

2.3. Analytical techniques

The total elemental chemistry of solid material was determined on pressed powder pellet (φ 37 mm) by a wavelength dispersive

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 is 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, 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 (see Supplementary materials). Total loss on ignition (LOI) was gravimetrically estimated after overnight heating at 950 °C.

The leachates were analysed by 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:

$$R_{ij} \% = \left(1 - \frac{C_{ij}M_j}{CO_{ij}MO_j}\right) \cdot 100 \quad (2)$$

where R_{ij} is the degree of removal of 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 , CO_{ij} is the concentration of the element i in the batch j in the untreated sample and MO_j is the mass of the untreated sample of batch j .

3. Results and discussion

3.1. Characterisation of the untreated raw fly ash

The Table 1 reports the bulk elemental content of the FA RAW as an average of three samples. 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. The concentrations of several elements such as Cr, Cu, Pb, Sb, and Zn are remarkably high: the FA RAW sample contains >1 wt.% of Zn, and about one order of magnitude less of Cr, Cu, Pb, and Sb. Despite a limited amount of primary sample (about 10 kg) was collected due to logistical reasons, the SD values for most of the major elements are within a narrow range, suggesting a relative homogeneity of the sampled material. The representativeness of fly ash material can be further assessed by comparing the analysis of FA RAW sample with concentrations range quoted in literature and recently outlined in Funari et al. (2015). The quality check of the XRF measurements showed good results for the most of critical elements in term of relative error (see Supplementary materials). Some discrepancies occurred for Al, Co, K, Mn, and Cl, and this might lead to an under estimation of their leaching yields and recovery potential, according to the relative error.

3.2. Effect of pre washing

High contents of Cl and mineral salts like 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. The fly ash pre washing removed most of water soluble salts (Fig. 2). More than 80% of Cl, K and Na were removed, in agreement with previous works (Nagib and Inoue, 2000; Wang et al., 2009).

Table 1

Chemical composition of the untreated raw fly ash, FA-RAW, by XRF. Elements are reported as wt.% of their major oxides, for simplicity.

| FA-RAW [wt.%] | | |
|--------------------------------|---------|------|
| | Average | SD |
| Al ₂ O ₃ | 3.65 | 0.28 |
| CaO | 19.9 | 0.82 |
| Fe ₂ O ₃ | 0.79 | 0.04 |
| K ₂ O | 3.76 | 0.34 |
| MgO | 1.70 | 0.11 |
| MnO | 0.05 | 0.00 |
| Na ₂ O | 5.09 | 0.64 |
| P ₂ O ₅ | 1.25 | 0.06 |
| SiO ₂ | 9.48 | 1.23 |
| TiO ₂ | 0.95 | 0.01 |
| CuO | 0.07 | 0.00 |
| ZnO | 1.14 | 0.04 |
| PbO | 0.35 | 0.03 |
| Cr ₂ O ₃ | 0.13 | 0.01 |
| Sb ₂ O ₃ | 0.10 | 0.00 |
| Cl | 12.8 | 1.39 |
| SO ₃ | 23.6 | 0.85 |
| LOI | 15.2 | |

3.3. Chemical leaching

The leaching behaviour of MSWI fly ash was investigated as a function of pH (e.g., Astrup et al., 2006) by testing the sample material subjected to several stages of pH and by analysing leaching solutions at specific pH intervals. At the end of the experiment (i.e., at 1 pH), the XRF analysis of solid by product allowed assessing metal removal rates (as R%, Table 2), which are calculated for each element according to the Eq. (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 H₂SO₄. 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%). The calculated yield for lanthanides is merely qualitative owing to their high values of SD. 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 environments, the overall Ca release was lower with respect to similar works reported in the literature (Huang et al., 2007; Zhang and Itoh, 2006; Nagib and Inoue, 2000).

The concentration of selected elements in leachates indicates that H₂SO₄ leaching performances change as a function of pH (Fig. 3). Elements such as Ca and Al show a good solubility even

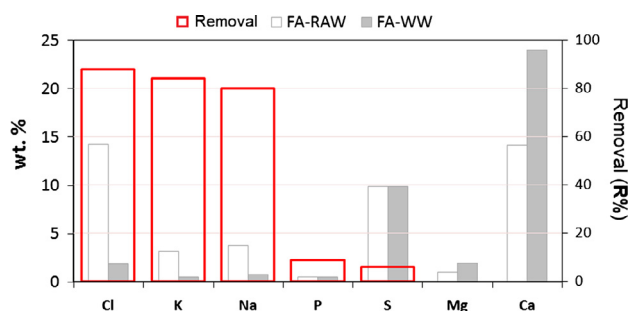
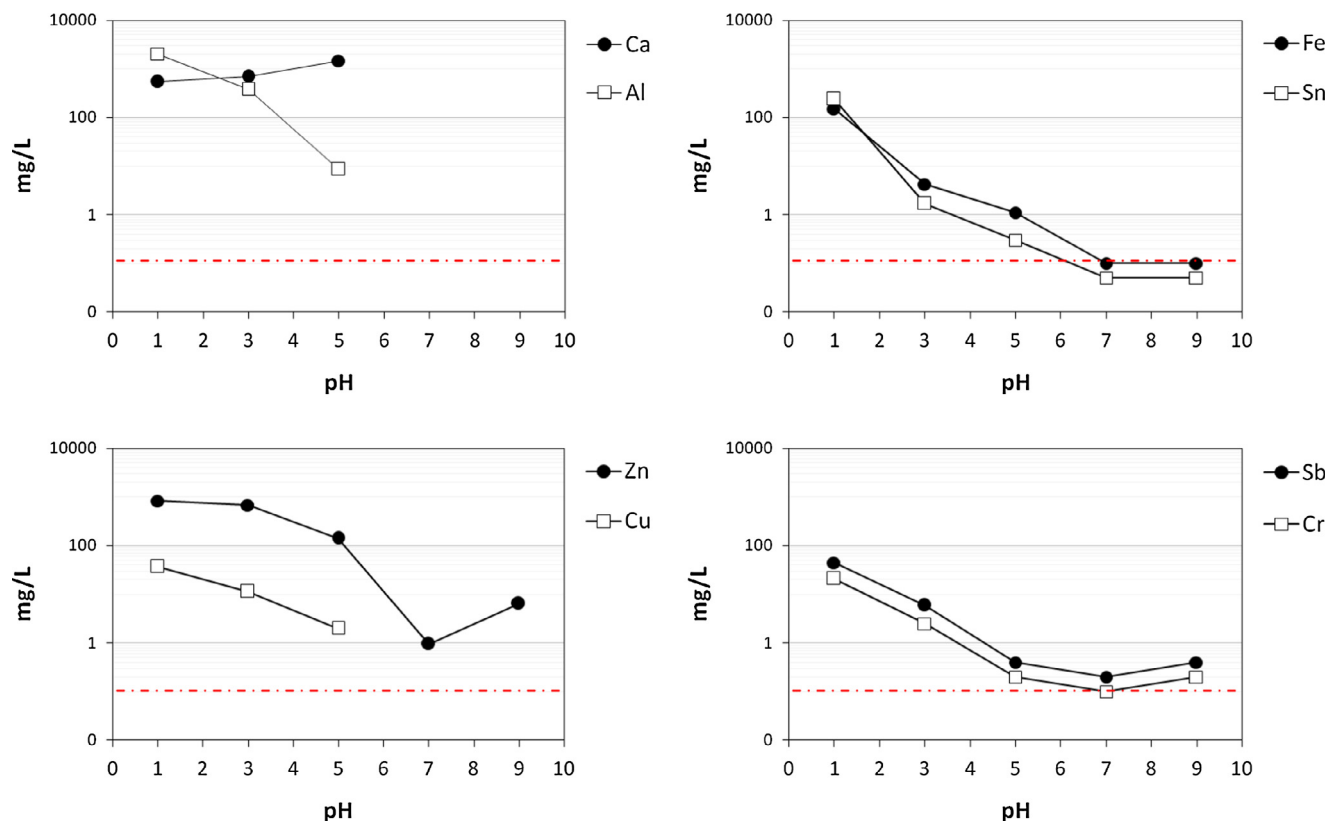


Fig. 2. Removal rates (R%) after water washing. Yields are calculated from the chemical composition (wt.%) of FA-RAW and FA-WW, by XRF. The most soluble elements, according to the R%, are shown.

Table 2Chemical composition of the FA-WW and samples after treatments (FA-H₂SO₄ and FA-BIO), by XRF. Calculated yield (R%) for FA-H₂SO₄ and FA-BIO is reported.

| | FA-WW [mg/kg] | | FA-H ₂ SO ₄ [mg/kg] | | R [%] | | FA-BIO [mg/kg] | | R [%] | |
|----|---------------|------|-------------------------------------------|------|-------|-----|----------------|--------|-------|-----|
| | ave. | SD | ave. | SD | ave. | SD | ave. | SD | ave. | SD |
| Al | 32,355 | 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 | 240,197 | 2192 | 166,301 | 1757 | 40 | 0.1 | 139,941 | 1757 | 45 | 2 |
| Ce | 31 | 6 | 18 | 3 | 49 | 1 | 17 | 1 | 48 | 8 |
| Cl | 18,509 | 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 | 11,296 | 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 | 19,373 | 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 | 53,399 | 8282 | 30,540 | 6441 | 50 | 4 | 34,886 | 12,241 | 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 | 10,474 | 207 | 3007 | 159 | 75 | 1 | 5543 | 330 | 50 | 3 |
| V | 102 | 3 | 35 | 2 | 70 | 1 | 52 | 6 | 52 | 6 |
| Zn | 14,400 | 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. The SD of R (%) was estimated on the basis of maximum and minimum removal for each element.

**Fig. 3.** 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. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 H₂SO₄ leaching are consistent with the outcomes of previous work (Astrup et al., 2006; Zhang and Itoh, 2006; Nagib and Inoue, 2000).

3.4. Bioleaching

Unlike the chemical leaching procedure, the sampling from the bioleaching reactor was performed over time at an initial pH of 1.8, maintained with H₂SO₄ addition. The buffer capacity of the MSWI fly ash sample was greater than biologically produced sulphuric acid and this made necessary a few manual additions of sulphuric acid during the experiment (see Section 3.5.2). Acid consumption significantly decreased after three days and a steady acid consumption was achieved (Fig. 4). 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.

The investigated elements show a high leachability already during the first days of the experiment (Fig. 5), and from the 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 days. 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 Table 2. 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.

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. 6. The error bars indicate the uncertainty associated with XRF measurements for each element. A larger standard deviation is frequently associated with

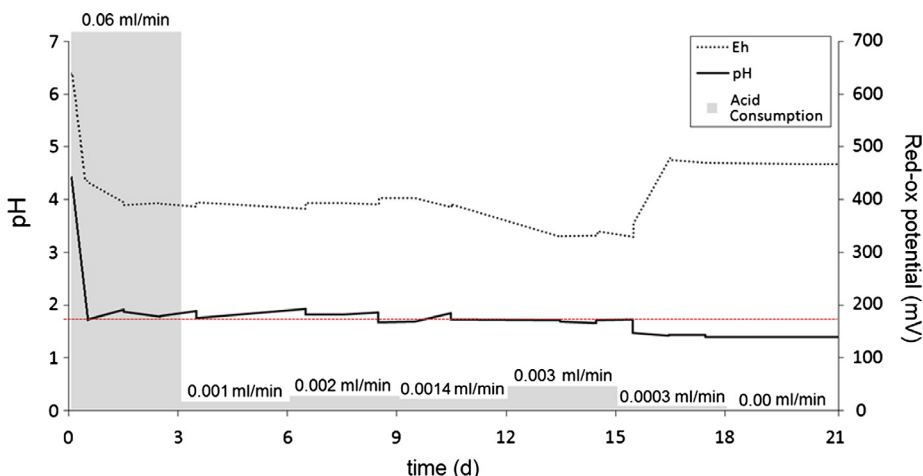


Fig. 4. Chemical parameters, pH and red-ox, of the bioreactor as a function of time. The cumulative acid consumption in ml/min is calculated over a period of three days (i.e., the histograms' height). The red dashed line is the pH 1.8 set point. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

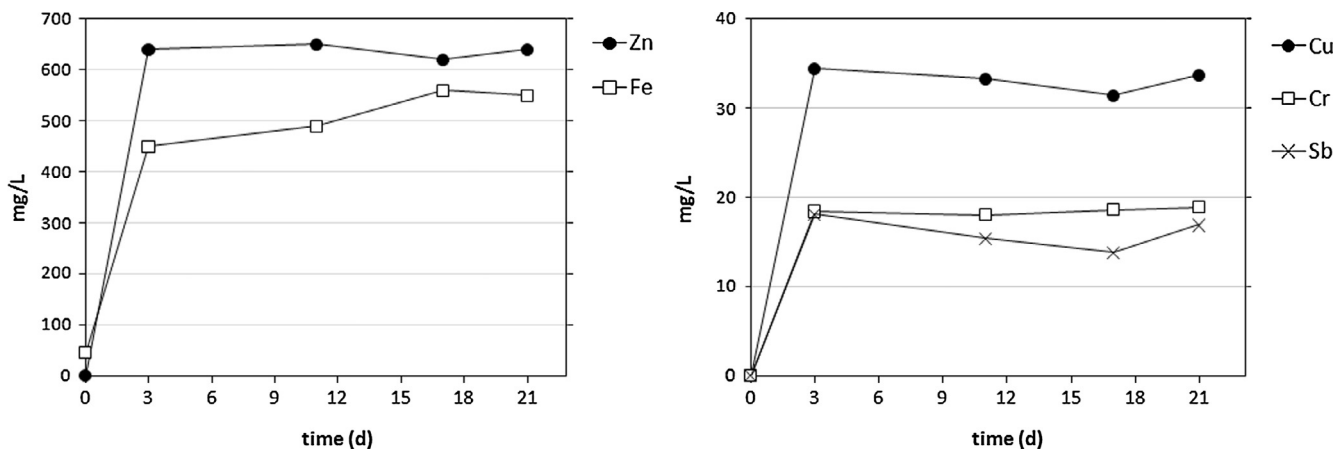


Fig. 5. Measured concentrations by ICP-AES of selected elements in leachates from bioleaching as a function of time.

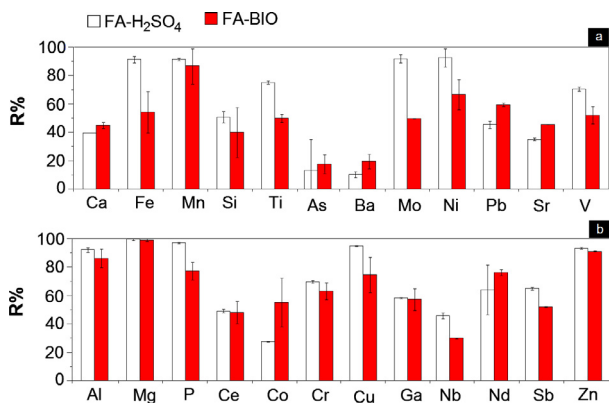


Fig. 6. Comparison of leaching yields (R%) between chemical leaching and bioleaching for selected unvalued/hazardous (a) and critical/marketable (b) elements. Error bars are the standard deviation of R%.

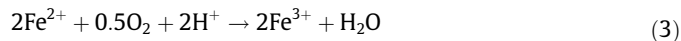
the bioleached rather than chemically leached residue. The reasons for this discrepancy are unclear. On the basis of morphological analysis of FA RAW, FA H₂SO₄ and FA BIO (see Supplementary materials) we suggest that the formation of coarse mineral grains may promote the nugget effect.

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. 6b), while a low mobilisation of Ca was noted. The presence of Ca could potentially inhibit the extraction of other elements (Kalmykova and 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 in the subsequent steps of filtration to remove SO₂ gas). 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 and Itoh, 2006).

Both procedures can be beneficial to the decontamination of MSWI fly ashes: the bioleaching enhanced the removal of several hazardous elements (Fig. 6a) 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. 6a). The removal rates of Co, Pb and Nd are enhanced by means of bioleaching. Although a similar acidic environment was reached at the end of both experiments (i.e., pH 1 for chemical leaching and pH 1.4 for bioleaching), a different mobilisation of metals was noted and this 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 other indirect activities of microorganisms (Brombacher et al., 1998). 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

Fe³⁺ 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 Fe²⁺ to Fe³⁺ during bioleaching:



On the other hand, lanthanides can accumulate on cell wall or bacteriogenic oxides (Moriwaki and Yamamoto, 2013). The effect of red ox reactions induced by bacteria, such as biotic oxidation of Fe²⁺ to Fe³⁺ 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 l of concentrated (96% purity) H₂SO₄ per kg of FA WW, while 0.810 l 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 H₂SO₄. According to the Eq. (1), biologic transformation of 1 ton of elemental sulphur produces approximately 3 tons of H₂SO₄. In U.S. (2013) the price of elemental sulphur and imported H₂SO₄ product was 69 and 63 \$/t, respectively (USGS, 2015). Therefore, chemical costs for bio based H₂SO₄ are three times lower than the price of imported sulphuric acid.

3.5.3. Potential environmental implication

According to the European regulation (European Union, 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, Table 3 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 (Table 3). Harmful elements such as Zn, Cr, Pb, and Sb were significantly removed, but they still keep high concentrations and prevent the residues' landfilling. The solid by products have potential for re use after further removal of these elements, especially Pb and Sb.

3.6. The management of MSWI fly ash

The management of fly ashes represents a significant cost for the incineration plants. In particular, an evident new route in fly ash management is the recovery of secondary raw material from this type of solid residue. If successful, the recovery of valuable metals will have a twofold aim: environmental stabilisation of this hazardous waste and revenues from the recovered metals. These will certainly impact on the economics of an incineration plant.

Table 3
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.

| | FA-RAW | | FA-WW | | FA-H ₂ SO ₄ | | FA-BIO | | Guidance levels | | |
|---------|--------------|----|--------------|----|-----------------------------------|-----|--------------|----|-----------------|------|------|
| | Average RSD% | | Average RSD% | | Average RSD% | | Average RSD% | | TCPL | Coal | Slag |
| (mg/kg) | | | | | | | | | | | |
| Ca | 142,000 | 4 | 240,200 | 1 | 166,300 | 1 | 139,900 | 3 | – | – | – |
| Cl | 142,000 | 10 | 18,500 | 3 | 130 | 17 | 300 | 3 | 25,000 | – | – |
| S | 105,700 | 3 | 106,200 | 4 | 232,000 | 1 | 177,500 | 4 | 50,000 | – | – |
| Si | 44,300 | 12 | 53,400 | 17 | 30,500 | 19 | 34,900 | 28 | – | – | – |
| Na | 37,700 | 11 | 8000 | 2 | 1700 | 2 | 1100 | 55 | – | – | – |
| K | 31,200 | 8 | 5300 | 15 | 3300 | 8 | 1500 | 8 | – | – | – |
| Al | 19,300 | 7 | 32,400 | 2 | 2900 | 15 | 4800 | 27 | – | – | – |
| Mg | 10,300 | 11 | 19,400 | 6 | 80 | 173 | 200 | 52 | – | – | – |
| Zn | 10,200 | 3 | 14,400 | 3 | 1400 | 4 | 1600 | 2 | 250 | 1000 | 400 |
| Ti | 5700 | 1 | 10,500 | 2 | 3000 | 5 | 5500 | 5 | – | – | – |
| Fe | 5500 | 5 | 11,300 | 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 |

However, there is no a unique solution for the treatment of MSWI fly ash. The current technologies involve physical and chemical treatments such as eddy current separators, thermal treatments, electrochemical processes, and hydrometallurgy. These routes of treatment, which often consist of step wise treatments (e.g., washing, milling, sieving, and subsequent thermal or hydrometallurgical processes), produce physical and chemical state changes to stabilise hazardous compounds and enhance the mechanical properties of the final product. One of the main advantages of these approaches is a fast reaction kinetic. Nevertheless, such process chains are costly because they require a high consumption of energy and/or chemicals, producing an adverse effect on the process economics. Despite some treatment strategies have been proposed and commercialised, the experimental results don't suffice to validate a more widespread implementation. For example, treatment options for the production of glass ceramic, cement clinkers, geo polymers, synthetic zeolites or other adsorbents from MSWI fly ashes were found to be inefficient for the complete stabilisation of hazardous compounds and/or for the conversion of raw fly ashes into a material with good mechanical characteristics (e.g., De Casa et al., 2007); hydrometallurgical methods for metals recovery have the disadvantage of a massive use of mineral acid and still lack in well targeted techniques for the (re)precipitation of metals from the enriched solutions. Due to these technology gaps the management of fly ash still represents a huge cost for MSWI companies. A successful technology to be applied in the field of waste management relies on process sustainability and has to meet a market demand. The main economic motivation for the treatment of MSWI fly ash is Zn and Al recovery and the loss of these metals can be reduced using an integrated strategy. The separation of the non ferrous fraction for the recovery of Al is a quite common practice, even if is mainly applied for bottom ash, because it combines metal recovery and enhanced mechanical properties of by products in a relatively cost effective manner. However, the mechanical separation requires further steps to obtain metals of adequate quality for the re introduction into the raw material market (Biganzoli et al., 2012). Because of the lower Al contents in MSWI fly ashes with respect to bottom ashes (Funari et al., 2015), any investment in this

sense is virtually uneconomic. Similar is the case of Zn. Fellner et al. (2015) indicated that the most of Zn from MSWI fly ashes is hardly extractable because the production costs would be at least 10 times higher than current Zn market price. Significant amount of Zn can be extracted at low pH values, requiring huge amounts of acid. This prevents a positive balance between the agent costs of a hypothetical treatment process and the economic gains.

Both leaching methods tested here sufficiently extract marketable metals including Al and Zn, and the outcomes deriving from this comparison can act as a testing ground for future fine tuned experiments in view of widespread implementation of a new MSWI fly ashes value chain for the recovery of certain metals from this low grade high flow waste stream.

Future experiments should be addressed to improve stabilisation of solid by products and metal recovery from process solutions: they might include leaching at elevated temperatures, high acid composition and combined bioleaching and chemical leaching to utilise 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 out by water (see Fig. 2) and the pre washing treatment might be further optimised towards improved removal amounts. Other impurities such as Fe and Mn can be removed by drop wise adding NaOH and KMnO₄, 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 (e.g., Tang and Steenari, 2015). Well known methods such as thermal treatments and carbonation (e.g., Nowak et al., 2010; De Casa et al., 2007) might lead to inert solid by products in a closed loop strategy.

3.6.1. The route of bioleaching for potential industrial application

Developing new and less costly methods is extremely important to provide recycling alternatives and, in this view, the bioleaching offers an opportunity for a potential industrial roll out. Although the H₂SO₄ leaching is still not affordable for industrial application

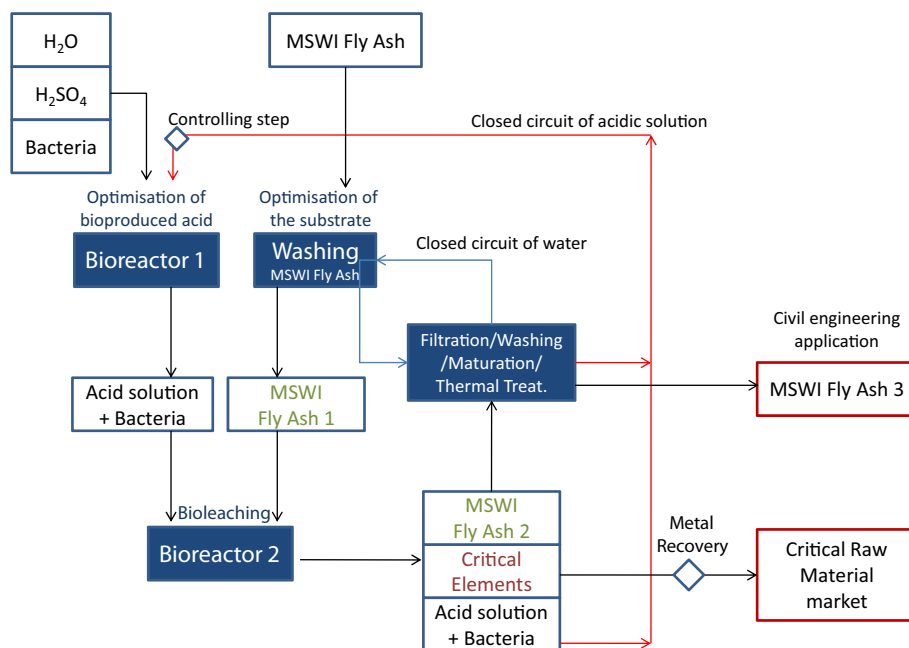


Fig. 7. Flow sheet of a hypothetical process chain for the treatment of MSWI fly ash.

(Meawad et al., 2010; Okada et al., 2007), 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) and transportation (the process can be implemented on site). As a consequence of this resource saving approach, enhancing the leaching yields with pre treatment steps will moderately impact on the process economic. The bioleaching procedure has a great (and relatively unexplored) potential for optimisation with limited additional costs, 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 at pH 1.0 removes some elements (e.g., Cu, Fe, Ni, P, and Sb) better than bioleaching at 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 (Bosecker, 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. 7 we report the conceptual 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.

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 unnecessary 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 land filling 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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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.wasman.2016.07.025>.

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