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# **Optimization routes for the bioleaching of MSWI fly and bottom ashes using microorganisms collected from a natural system**

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## ABSTRACT

This paper presents a route for the treatment of MSWI fly (FA) and bottom ashes (BA) using microorganisms to critically assess whether bioleaching is within reach of effective industrial application. The leaching of metals from BA and FA was investigated in a controlled laboratory environment using a culture isolated from a natural system where the dominant strains are acidophilic bacteria, mainly *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*. The community of microorganisms (mostly acidophilic, S- and Fe-oxidizing bacteria) was collected directly from overflows and ponds at the sediment-water interface of a natural system near a post-mining site. Pre-cultivation was done in 250 mL flasks followed by the adaptation to the different substrates (both FA and BA). The effect of different material pre-treatment and elemental sulphur concentrations were evaluated for both BA and FA, at a starting pH of 4. The bioleaching of BA and FA substrates experienced good yields of metal extraction with an optimum duration of two weeks. The results showed that more than 90% Zn, Cu, and 10% Pb are removed from FA; while 100% Cu, 80% Zn and 20% Pb are removed from BA samples. Batch experiments with regenerating ion-exchange resins did not perform well for metal recovery, but could serve as a valuable decontamination step. The techniques used here with FA and BA can be used for urban mining purposes (e.g. ashes and other meal-rich anthropogenic wastes), but also low-grade ores in the mining industry, contributing to resource recovery or decontamination agendas.

**Keywords:** Municipal Solid Waste Incineration (MSWI), MSWI bottom ash, MSWI fly ash, ion exchange resins, resource recovery, heterotrophic bacteria.

**Novelty statement:** We present and evaluate a novel process to demonstrate how naturally-occurring acidophilic bacteria can be cultured and deployed to leach metals from Municipal Solid Waste Incinerator ashes for both resource recovery and waste decontamination purposes. The experimental results provided here are useful to plan future investments on large scale post-treatment of incineration residues using microorganisms collected from an abandoned mine of sulphides. The different experimental setups were drawn on the basis of the chemical and mineralogical composition of the waste materials and moreover the different inocula were tailored to bottom ash and fly ash, respectively. This bottom-up approach helped to assess the effectiveness of the microorganisms' metabolic reactions on the waste treatment.

## 1. Introduction

The recently invoked concept of a circular economy relies on recycling and reuse of end-of-life products, to provide secondary raw materials in enhanced production chains [1-3]. It is therefore necessary to avoid landfill or consider it as the very last option. As such, the waste management sector suffers pressure from policy-makers and faces the lack of fine-tuned waste treatment routes from economic and environmental standpoints. It stands to reason that advancing waste stabilization and secondary raw materials recovery even from low-grade wastes is a priority for a more sustainable society. Millions of tons of municipal waste are generated every day, leaving significant quantities of metals in landfilled waste and incineration ashes that can both pose environmental risks in disposal settings while at the same time offering scope for resource recovery [2, 4]. Despite the low absolute concentrations, substance flow analysis on selected Italian municipal solid waste incineration (MSWI) plants showed that fly ash (FA) and bottom ash (BA) can be low concentration streams of critical raw materials and marketable metals, with estimated annual flows of tens of kg and a total content comparable to low-grade active mines [5]. The use of microorganisms to assist metal leaching can be a suitable and more sustainable alternative to leaching with refined industrial chemicals for resource recovery and recycling from wastes. Bioleaching is a reliable hydrometallurgical technology, based on the production of a mineral or organic acid by microorganisms to solubilise metals, and it is widely employed commercially for processing pyrite-rich, low-grade sulphide ores [6, 7]. Chemoautolithotrophic bacteria, like *Acidithiobacillus thiooxidans* (*At. thiooxidans*) and *Acidithiobacillus ferrooxidans* (*At. ferrooxidans*) are well known for their ability to oxidize reduced sulphur compounds or elemental sulphur to produce sulphuric acid. In addition, microorganisms like *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* are known to oxidize iron from a ferrous to ferric state leading to enhanced metal solubility. Accordingly, the bioleaching of sulphidic ore is believed to occur via direct or indirect mechanisms [8]. These bioleaching bacteria thrive in mineral rich, acid environments (pH 2 or lower) where the concentration of dissolved ferrous iron is about  $10^{16}$  times that found in circumneutral environments. They typically live in environments that have high concentrations of soluble metals (e.g., arsenic, mercury, and silver), as well as unusually high concentrations of potentially toxic metals (e.g., copper, iron, zinc). This has prompted numerous studies of nature-inspired bioleaching processes applied to metal recovery as well as decontamination of anthropogenic waste, coupling metal recovery with environmental remediation [9]. In general, the metabolic reactions of certain microorganisms, naturally present in the ecosystems, show some key capabilities that pertain to their use in industrial bioleaching, including the ability to oxidize both sulphur and iron, to resist low pH, varied pressure, and increased levels of potentially toxic organic and inorganic contaminants, and to selectively precipitate groups of metals from metal-loaded solutions.

Bioleaching of metals from MSWI ashes using both fungi, mixed acidophilic bacteria [1], and mixed alkaline bacteria [10] was successful at the lab scale demonstrating potential for economic recovery, but no upscaling of the technology has been developed. Funari et al. [11] demonstrated the leaching behaviour of a wide range of metals that can be removed from MSWI FA using a mixed acidophilic culture in one-step bioleaching

process. The bioleaching procedure (acidic culture medium, 10% pulp density, 150 rpm, 30° C) yielded ~90% Al, Mg, Mn, Zn; ~80% Cu, P, Nd; ~60% Cr, Ga, Ni, Pb; ~50% Ce, Co; 30% La in the leachate solution. Compared to a traditional leaching route (H<sub>2</sub>SO<sub>4</sub>, 10% pulp density, 150 rpm, 30° C), bioleaching proved to be a viable and sustainable alternative [11]. Bioleaching showed low mobility of low-value bulk elements such as Ca, Si, Fe, and Ti, with highly selective removal of Co, Pb, and rare earth elements (REE), at low capital costs. However, there is considerable scope, that has hitherto been unexplored for optimisation of bioleaching processes to reduce process costs, e.g., by improving medium (S<sup>0</sup>, Fe<sup>2+</sup>, nutrients) and substrate quality, thermo-chemical conditions, or inoculum volume. Another important factor is the adaptation of microorganisms from natural systems to tolerate alkaline wastes such as MSWI ashes, which is challenging to upscale given the geochemical gradients from source to application scenarios.

The aim of this study is to investigate the feasibility of biotic leaching of the metals Al, Cu, Pb, and Zn from municipal waste incineration fly and bottom ashes by using a mixed acidophilic culture from samples of the Libiola Fe-Cu mine area (Ligurian Apennines, Italy) [12]. A preliminary genomic screening of the natural community was to inform a potential application in laboratory procedures, but a comprehensive microbiological study was not in the scope of this article. The effect of different experimental setups was evaluated to optimise the extraction. Batch experiments with regenerating ion-exchange resins, Amberlite® IRA-400 vs Chelex®100, were performed to assess potential metal recovery from the leachate.

## 2. Materials and Methods

### 2.1 MSWI samples and pre-treatment

The studied materials were collected from MSWI plants located in northern Italy following the sampling strategy adopted in Funari et al. [5] for FA and BA samples. The selected incinerator functions a thermo-recycling technology with grate-furnaces operating at 950-1050 °C. According to the company yearly report, the total processed waste includes 90% household and 10% special waste, and each incinerator produces around 4 · 10<sup>4</sup> ton/BA/year and 3 · 10<sup>3</sup> ton/FA/year as solid end-products. For the chemical analysis of bulk composition (Table 1), BA and FA material pre-treatment upon sampling included drying at low temperature (40 °C) for one week, grounding, and milling (<40 µm) with an agate vibratory mill disk. The starting material used throughout the experiments was dried at low temperature (40 °C) for one week, grounded and homogenised. An exception was for one BA sample (**Error! Reference source not found.**) that was finely milled to investigate a grain-size that differently from all test samples would require a further step of mechanical crushing before leaching.

**Table 1 – Chemical composition of the starting materials.**

	RN	RN3
	MSWI BA	MSWI FA

<b>Si</b>	<i>g/100g</i>	15.1	6.6
<b>Ti</b>	“	0.7	0.9
<b>Al</b>	“	3.8	3.1
<b>Fe</b>	“	6.1	1.0
<b>Mn</b>	“	0.1	0.1
<b>Mg</b>	“	1.4	1.0
<b>Ca</b>	“	20.1	22.0
<b>Na</b>	“	2.5	2.0
<b>K</b>	“	0.7	1.9
<b>P</b>	“	0.5	0.7
<b>S</b>	“	0.6	2.9
<b>Cd</b>	<i>mg/kg</i>	<1	13.4
<b>Co</b>	“	119	28.9
<b>Cr</b>	“	492	659
<b>Cu</b>	“	3041	355
<b>Ni</b>	“	102	66.6
<b>Pb</b>	“	1475	515
<b>Sb</b>	“	141	567
<b>Sn</b>	“	498	554
<b>Zn</b>	“	3537	3869

## 2.2 Microorganisms and culture media

A mixed culture of iron- and sulphur-oxidising microorganisms was obtained from a natural system by combining several samples from overflows and ponds of the Libiola Fe-Cu mine area (Ligurian Apennines, Italy), collected at the sediment-water interface. The characterisation of the original culture was performed at the FaBiT Department (University of Bologna) using the Terminal Restriction Fragment Length Polymorphism (T-RFLP) analysis that allows rapid profiling of complex microbial communities based on variation in the 16S rRNA gene. For the scope of this paper, accurate profiling of the culture was thought not to be critical because we aim to provide clues for the direct application of naturally available microbial communities in the industrial chain of alkaline waste management and, thereby, engineered bacterial strains tailored for the treatment of MSWI ashes. The pH of the liquid samples representing the original mixed culture varied between 1 and 3, and the samples contained red-brown iron(III) precipitates [12]. The composition of the nutrient growth medium (a modified 9K medium [11, 13]) was 3.0 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.5g K<sub>2</sub>HPO<sub>4</sub>, 0.5 g MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.1 g KCl, 0.014 g Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and 22.0 g FeSO<sub>4</sub>·7H<sub>2</sub>O per litre of deionised water. The modified 9 K medium was adjusted to pH 2.0 with concentrated H<sub>2</sub>SO<sub>4</sub>. All reagents used were of analytical grade. Initial conditioning of the original culture, which comprised a turbid suspension of water, minerals, and biomass, was performed in 250 mL Erlenmeyer flasks containing 90% (v/v) modified 9K medium on a shaker incubator (Infors HT Multitron Standard). The pH was maintained below 2.5 using concentrated H<sub>2</sub>SO<sub>4</sub>, as required, due to the fact that acidophilic bacteria like *At. ferrooxidans* and *At. thiooxidans* thrive at this pH level [9]. The culture was incubated at 150 rpm and 30 °C. To enhance the cell activity, the culture was renewed every 15 days, for three times in total, by inoculating 10% (v/v) of former cultivations and 90% (v/v) of the modified 9 K medium. Once activated, the acidophilic

culture was adapted to increasing pulp density (1%, 5%, 10% v/v) of BA and FA sample materials for 15-day pre-cultivation tests [11, 14, 15]. Pulp density and pH setpoints were varied to inform upscaled bioleaching experiments.

### 2.3 Scaled-up bioleaching experiments

The experimental configurations used in the study were identical for BA and FA except for one parameter in order to assess the microbial response to a slightly different feed. Specifically, halved amounts of elemental sulphur (5 g/L vs 10 g/L) in FA experiments and raw or milled BA samples were used. Each inoculum tailored for BA and FA samples was used in one-litre flask containing the corresponding sample. The leaching experiments (one-step bioleaching) were carried out in triplicate using 10% (v/v) MSWI ash and 90% (v/v) bio-lixiviant (containing 10% (v/v) adapted inoculums in 9K medium) supplemented with 22 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  to promote the activity of iron oxidizers such as *At. ferrooxidans*. The flasks were shaken on an incubator shaker (Infors HT Multitron Standard) at 150 rpm at 30 °C for a total duration of 48 days. The bioleaching solution became alkaline after the addition of the solid materials due to the high buffering of the MSWI ashes. Bioreactors were titrated using concentrated  $\text{H}_2\text{SO}_4$  to a pH starting condition of 4 (pH setpoint) to evaluate a bioleaching process that would not require much chemical pretreatment. The pH and redox potential were measured daily; 10 mL of the slurry was sampled weekly for Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) analysis. Evaporation was corrected gravimetrically by the addition of distilled water. Control tests without inocula were performed in the same conditions.

### 2.4 Chemical analysis

The analytical determination was done using a Perkin Elmer Optima 5300 DV (ICP-OES). A certified reference material (CRM-ES AT-1529, lot number 1319108) was used for quality control. All aqueous samples (10 mL) were filtered (0.45  $\mu\text{m}$ , MCE Membrane Millex HA) with a vacuum pump and preserved with a few drops of  $\text{HNO}_3$  (Romil Trace Metal Super Purity Acid, Romil Ltd, Cambridge, UK). For the solid materials (i.e., the starting BA and FA materials), a representative sample of the dried and milled ash was weighed into an Xpress microwave digestion vessel (CEM MARS microwave digestion system, CEM Corporation, Milton Keynes, UK), and 5 mL nitric acid (Romil Trace Metal Super Purity Acid, Romil Ltd, Cambridge, UK) was added. The samples were left overnight to slowly digest at room temperature with the vessel sealed, and vented before microwave extraction. The microwave heating was programmed to heat to 200°C in 15 minutes, then held at that temperature for a further 15 minutes. When cooled to room temperature, the gaseous products from the vessels were vented into a fume cupboard, and then the digests were diluted by weight with pure water (Elga Purelab, 18 Megohm conductivity) into tared 50 mL sample vials. The clear solutions were analysed on the ICP-OES for 69 elements under high argon purge conditions, against a calibration of 10 ppm for all elements. In the batch reactors, pH, Eh, and temperature were also measured daily in a Jenway 3540 pH and conductivity meter.

## 2.5 Data analysis

Three different kinetic models were fitted to the data. The first one was the shrinking core model, where the reaction rate is controlled by solid product layer diffusion [16]. When the leaching rate is controlled by a chemical reaction at the particle's surface, the process can be represented by a first-order kinetic, a linear plot of gradient  $k$  (the first-order rate constant for the surface reaction). If the leaching process is not affected by a product layer, the amount of reacting material is proportional to the available surface of the unreacted core. When no product layer is formed on the solid phase, the reacting particle would be shrunk during the reaction, until the solid phase disappears. For a small particle, this can be explained by a Stokes regime [17].

## 2.6 Recovery with ion exchange resins

Ion exchange batch tests at pH 1 were performed with Amberlite®IRA-400 and Chelex® 100 (BIO-RAD) to assess the possibility of using the ion exchange resin for metal recovery. The first is a strong base anion exchange resin with quaternary ammonium functional groups ( $-N^+R_3$ ) in a polystyrene matrix, and particle sizes of 600-750  $\mu\text{m}$ . Before use, Amberlite®IRA-400 was converted to the hydroxide form according to Gomes et al. [18, 19]. Chelex® 100, classified as weakly acidic cation exchange resin, is a styrene divinylbenzene copolymer with paired iminodiacetate ions that act as chelating groups binding polyvalent metal ions. The hydrated Amberlite resin at a concentration of 50  $\text{g L}^{-1}$  was stirred at 150 rpm for 45 min with 100 ml of the leachate. Aqueous samples (10 ml) were taken at 1, 3, 5, 10, 15, 20 and 30 min. After 45 min, the solution was decanted off and sampled for elemental analysis. The resin was then mixed with 20 ml of NaOH 2M and stirred for 30 min to assess metal recovery. The NaOH was decanted off and analysed for elemental analysis. A similar procedure was followed with Chelex® 100, except that the metal recovery was made with 50 ml of 1 N HCl.

# 3. Results and Discussion

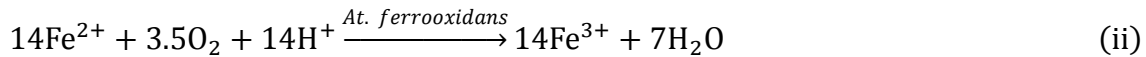
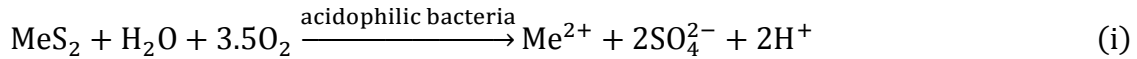
## 3.1 Rapid screening of the natural microbial community

The T-RFLP is a method for rapid profiling of complex microbial communities based on variation in the 16S rRNA gene. According to the T-RFLP results, the mixed acidophilic culture freshly sampled the mining area contained members of *Acidovorax* genus, *At. thiooxidans*, *At. ferrooxidans*, *Chlorobium limicola*, and some other species closely related to *Acidithiobacillus* (The different bacterial strains of the natural culture likely competed and struggled to adapt to the feed composition. Some microorganisms like *Acidovorax* genus and *Chlorobium limicola* possibly lived for a short time in the tested bioleaching systems mainly due to their optimum pH which is around the neutrality.

Table 2). The *Acidithiobacillus* sp. likely represents the dominant species in the culture. The water-sulphides interaction lowers the alkaline pH values of the natural waters up to strongly acidic levels (lower than pH



2.5) in the most polluted sites, leading to the formation of ochreous colloids, most likely enriched in microorganisms, and metal-loaded acid drainage with dissolved Fe, Al, Cu, Zn, Mn, and Ni [12]. In the aquatic environment, these bacteria use metal-sulphide mineral phases (and also elemental sulphur) as their substrate to produce sulphuric acid (e.g., pyrite oxidation), while the iron-oxidizing bacteria can enhance metal solubilisation producing ferric iron from Fe<sup>2+</sup>-bearing phases, according to the following equations [6, 8, 9]:



The different bacterial strains of the natural culture likely competed and struggled to adapt to the feed composition. Some microorganisms like *Acidovorax* genus and *Chlorobium limicola* possibly lived for a short time in the tested bioleaching systems mainly due to their optimum pH which is around the neutrality.

**Table 2 – Results of the T-RFLP analysis, reporting the relative abundance of main members of the bacterial community.**

<b>Taxonomy</b>	<b>Predicted peak</b>	<b>Observed peak</b>	<b>Relative Abundance</b>
proteobacteria	198	196.51	0.00814
<i>Acidovorax</i> sp. (assigned)			0.00110
proteobacteria	171	169.84	0.00756
<i>Acidithiobacillus thiooxidans</i> (assigned)			0.00158
<i>Acidithiobacillus</i> sp.	251	249.9	0.00456
<i>Acidithiobacillus ferrooxidans</i> (assigned)			0.00095
<i>Chlorobium limicola</i>	252	251.73	0.00435
uncultured bacteria	203	203.2	0.00334
uncultured bacteria	200	198.62	0.00107
uncultured actinobacteria	213	212.36	0.00074
<i>Acidiphilium</i> sp.	235	235.01	0.00071
<i>Acidiphilium</i> sp.	232	230.4	0.00016
uncultured <i>Acidisphaera</i> sp.	227	225.37	0.00004

### 3.2 Characterization of the initial MSWI ashes

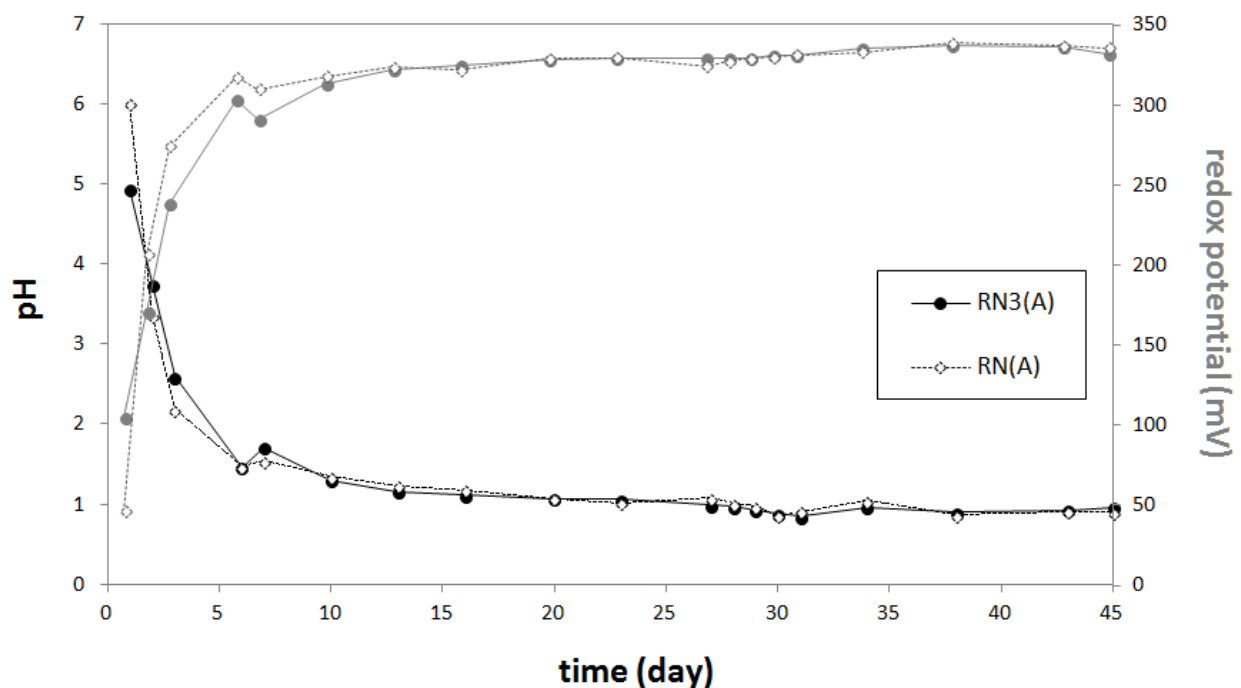
The selected BA and FA samples show a variable chemical composition (Table 1). The BA are Ca- and Si-rich materials with significant amounts of Fe and Al; other metals, such as Cu, Pb, and Zn are in the order of g/100g. The FA samples show a relatively less homogenous composition compared to BA. The FA samples are high in Ca and show variable concentrations of Si and alkaline metals; volatile elements, such as Sb, Sn,

and Zn are, at least, one order of magnitude higher than other trace elements. These compositional changes are consistent with those reported in scientific literature [5, 20]. With regard to metals that may favour the bioleaching process, we noted higher quantities of iron in BA than FA, whereas sulphur is more elevated in FA samples. MSWI ashes likely contain carbon, nutrients, and  $\text{Fe}^{2+}$  the microorganisms can easily source from organic matter partly combusted and soluble salts in the mineralogical assemblage of the ashes [21-23]. This is most pertinent to BA materials, suggesting favourable conditions for iron oxidizers like *A. thiooxidans*. The presence of sulphur species and nuggets of elemental sulphur in FA materials favours bioleaching via sulphur-oxidizers, however FA mineralogical phases are more prone to leaching of potentially inhibitory metals and more  $\text{H}^+$ -consuming in aqueous solution than BA [11, 15, 23]. Accordingly, the chemical analysis of the solid ash samples guided the experimental configuration from the pre-cultivation tests to the 1-L flasks experiments (see section 2.3).

### 3.3 Mixed acidophilic bacterial culture from natural to induced bioleaching system

#### 3.3.1 Activation and precultivation of the natural microbial community

The mixed culture sampled from the natural environment was successfully activated in the laboratory, as suggested by a spontaneous decrease in pH during each test. According to the precultivation tests, the culture tolerated the addition of up to 10% FA and BA samples (Fig. 1) despite their variable chemical composition and a significant presence of heavy metals (Table 1). The graphical comparison of pH and Eh trends in Fig. 1 is essential to monitor biogeochemical system as to follow the bacterial activity over time e.g., [15]. The pH curves show a steep decrease up to day 6; from day 6 (ca. 1.5 pH) onwards, the pH slightly decreases down to 1. The pH trends coupled with the increase in redox potential suggest a bacterial growth and activity during the experiment as evidenced by the acid production.



**Fig. 1 – pH (black) and redox potential (grey) as a function of time, measured during the precultivation phase (10% pulp density). Samples of BA (RN) and FA (RN3) are shown as triplicate average (A).**

### 3.3.2 Scaled-up bioleaching experiments

In BA experiments, the pH spontaneously decreases after day 15 demonstrating the culture growth and activity and, at the same time, most heavy metals start to be efficiently extracted (Fig. 2). The bioleaching of unmilled BA showed a slight pH increase after day 25 onward (RN-R2A in Fig. 2), possibly related to breaking of coarse-sized, acid consuming/buffering minerals at the later stage of the experiment. According to Fig. 2, the bioleaching performs better without BA milling except for the removal of aluminium whose solubility is inhibited after 20 days. The bioleaching yielded up to 100% Cu, 80% Zn and 20% Pb removal from the BA material (Fig. 2).

During bioleaching of FA in one-litre flask experiments (Fig. 2), the bioproducted metabolic substances contribute to increase the acidity of the slurry from the pH 4 setpoint down to pH 2. The improved performance of a bioreactor provided with elemental sulphur is clearly visible from the curves of pH variation (Fig. 2). It can be estimated that when elemental sulphur concentrations in FA are halved, there is a subsequent decline in leaching efficiency of 5-15%. The solubility of Al is noticeably enhanced when using doubled  $S^0$  quantities. The results show that more than 90% Zn, Cu, and 10% Pb are removed from FA (Fig. 3), in acidic solution supplemented with elemental sulphur and divalent iron. Overall, copper and zinc were efficiently leached in the early days of bioleaching. The remarkable Cu and Zn leaching from BA and FA samples demonstrated the positive effect of high initial  $Fe^{2+}$  concentrations (22 g/L) from the activation step to bioreactor experiments. The amount divalent iron in solution supported the bacterial iron oxidation providing abundant  $Fe^{3+}$ , which is, in turn, a strong oxidising agent for elemental copper and zinc [15]. The spread of error bars highlights the analytical uncertainty related to ‘nugget effects’ effects in triplicate samples. In BA bioleaching (Fig. 2), the coarse-grained BA shows a significant nugget effect for copper likely due to instantaneous breaking of aggregate particles containing pure metals (or alloys). Solution pH also has a role in copper dissolution. Excessive  $Fe^{2+}$  concentration consumes more acid and oxygen, possibly affecting sulphur oxidation and driving a pH decrease. The accumulation of ferrous ions on the surface results in a diffusion barrier to the ferric attack, producing an increase of the ferric ion concentration in the bulk solution that inhibits the microbial oxidation capacity for concentrations higher than a specific value [24]. This has a negative effect also on iron oxidation, and therefore copper yields may decrease [3].

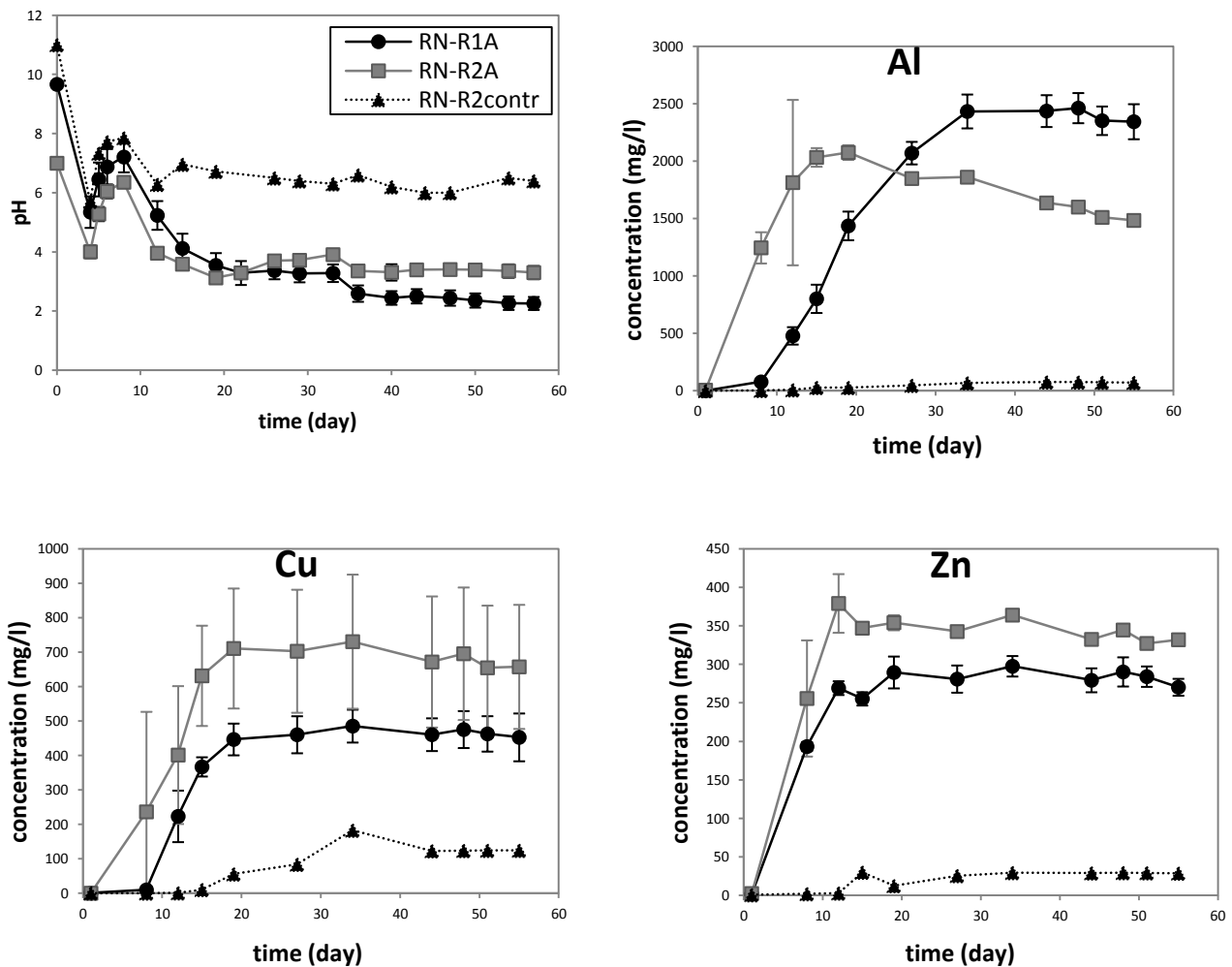


Fig. 2 – Variation of pH (top left) and removal of selected metals as a function of time, during bioleaching of MSWI BA sample from a pH 4 setpoint. Error bars may be smaller than symbols.

The experimental results demonstrated that Al removal from FA requires elemental sulphur during bioleaching (RN3-R2 in Fig. 3). BA bioleaching showed that aluminium yields in fine-grained BA samples slowly increased over time and yielded a maximum plateau in a later stage of the experiment (day 33). On the contrary, the coarse-grained BA materials experienced a peak of Al extraction after ten days, and then clogged at a certain point. This corresponds to the slight rise in pH observed from the second week of reaction onwards. The reaction was inhibited likely due to dissolving of acid-consuming mineral phases e.g., calcite, magnesite, plagioclase [25]. The bioleaching of MSWI BA and FA in one-litre flasks experienced good metal yields starting from a relatively high pH level (setpoint  $4.0 \pm 0.5$  pH). It stands to reason that this use of naturally-available acid-producing microbial consortia would help to lessen environmental and economic drawbacks of the use of mineral acids during the treatment of alkaline MSWI ashes. Commercially available technologies tied to chemical acid leaching are much more costly [2]. Time is the controlling factor that primarily drives the potential industrial rollout. Based on the experimental timeframe investigated, an optimum duration of 15 days bioleaching for BA and FA under the same condition can provide satisfactory performances for simultaneous removal of Al, Cu, Pb, and Zn. In addition, the use of MSWI ashes without

pre-milling is a viable choice for BA (Fig. 2) that might generate savings because there would be no need for mechanical pretreatment.

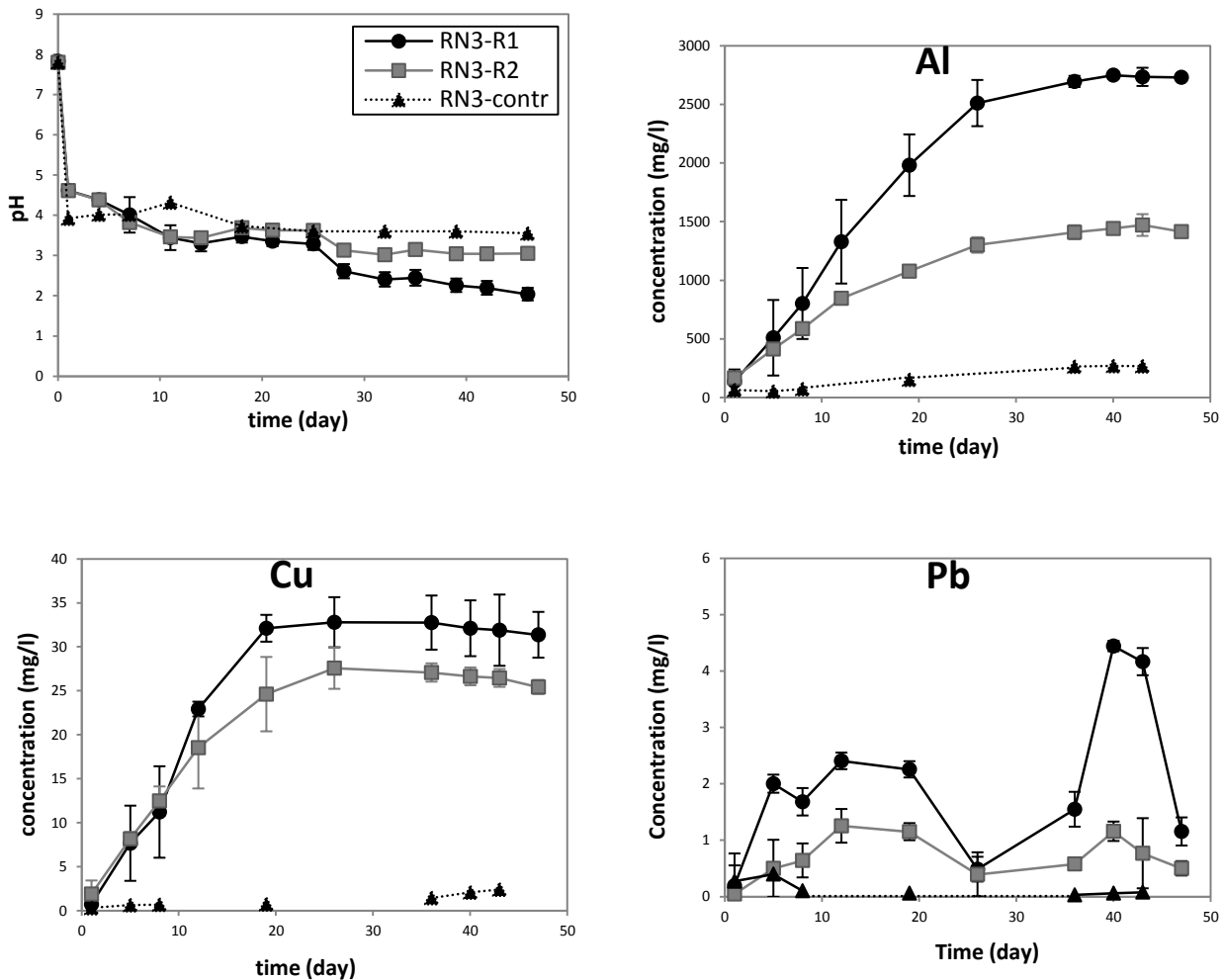


Fig. 3 – Variation of pH (top left) and removal of selected metals as a function of time, during bioleaching of MSWI FA sample from a pH 4 setpoint. Error bars may be smaller than symbols.

### 3.3.3 Kinetics of the bioleaching

Three different kinetic models were fitted to the results of the experiments (Table 3). RN3-R1 and RN3-R2 data better fitted the models. Elements like Al, (Cr), and Pb had high coefficient of determination ( $R^2 > 0.95$ ) for the shrinking core model theory (Table 3), which assumes that bioleaching kinetics is controlled by a solid product layer diffusion, and it is usually the best model to explain bioleaching of metals [16, 17]. Copper and zinc had the lowest  $R^2$  values, suggesting that none of the models is appropriate to describe the concentrations found in solution. The bacterial production of sulphuric acid and iron bio-oxidation likely contributed to enhance metal solubility during the experiment.

Table 3 - Kinetic models applied to the experiments. Equations used for modelling are from Chen et al. [17].

Model	Equation	Sample	Coefficient of determination ( $R^2$ )
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			Al	Cu	Pb	Zn
Shrinking core theory	$k_t = 1 - \frac{2}{3}F_t - (1 - F_t)^{2/3}$	RN3-R1	0.878	0.661	0.914	0.433
		RN3-R2	0.861	0.692	0.962	0.052
		RN-R1	0.864	0.606	0.955	0.451
		RN-R2	0.007	0.130	0.960	0.322
First order kinetics	$k_t = 1 - (1 - F_t)^{1/3}$	RN3-R1	0.904	0.654	0.940	0.026
		RN3-R2	0.871	0.697	0.957	0.134
		RN-R1	0.864	0.797	0.979	0.419
		RN-R2	0.068	0.465	0.942	0.008
Stokes regime	$k_t = 1 - (1 - F_t)^{2/3}$	RN3-R1	0.912	0.638	0.779	0.056
		RN3-R2	0.910	0.693	0.959	0.023
		RN-R1	0.857	0.635	0.985	0.399
		RN-R2	0.082	0.130	0.963	0.316

$F_t$  represents the fraction of metal mobilised;  $t$  is the leaching time, and  $k$  the rate constant

### 3.4 Metal recovery with ion exchange resins

The metal-rich leaching solutions were subjected to batch experiments with regenerating ion-exchange resins, Amberlite® IRA-400 vs Chelex®100, to assess the potential metal recovery. Fig. 4 shows the metal recovery for the selected resins. The performances of the two resins were not so encouraging likely due to the presence of competing ions. Nonetheless, around 10% Cu and Pb are recovered by Amberlite® IRA-400. This can be nearly economic considering the substance flow of copper from BA [5]. Alternatively, the use of Amberlite® IRA-400 or another low-priced resin can serve as a decontamination step of the leaching liquor before being recirculated in a closed bioleaching system pushed to the maximum efficiency. The removal of the possible interference anions through selective precipitation could improve the performance of the resin. So further research is needed to minimise interferences and maximise metal recovery.

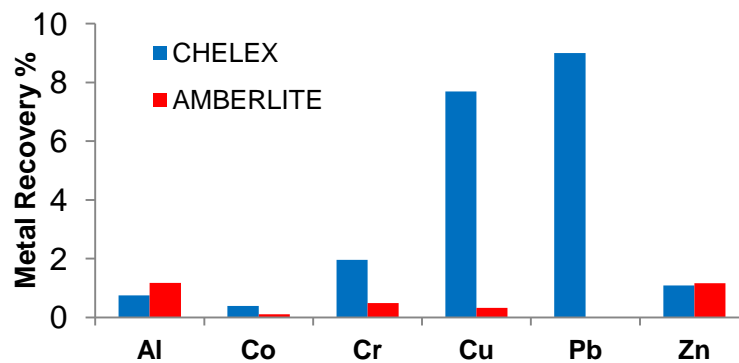


Fig. 4 - Comparison of the ion exchange resins for metal recovery from BA leachate.

## 4. Conclusion

The work presented here demonstrates a potentially eco-friendly means of recovering metals from MSWI ashes with green lixivants as an alternative to landfilling, which is the predominant destination of MSWI ashes in Europe. Scaled-up bioleaching experiments had the treatment capacity of 1 tonne per cubic meter of bio-lixiviant and demonstrated effectiveness in decreasing the pH from 4 or more to well below 2, significantly contributing to metal removal. The proposed process removed 90% Zn, Cu, and 10% Pb from FA and 100% Cu, 80% Zn and 20% Pb from BA. The results show the potential of bioleaching for mining metals from FA and BA and for environmental stabilization of ever-increasing waste flows. However, the recovery percentage of metals from the leachate using the tested ion exchange resins was not very encouraging, so further developments are needed to separate the metals for recovery and recycling.

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