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## **BIOLEACHING OF FLY AND BOTTOM ASHES FROM MUNICIPAL SOLID WASTE INCINERATORS: PRELIMINARY RESULTS FROM SIMP-2016 FELLOWSHIP**

VALERIO FUNARI

ISMAR-CNR Istituto di Scienze Marine, Consiglio Nazionale delle Ricerche, Via Gobetti 101, 40129 Bologna  
 Dipartimento BiGeA, Università di Bologna, Piazza di Porta San Donato 1, 40126 Bologna  
 BlueBiotech, Stazione Zoologica Anton Dohrn Napoli (SZN), Villa Comunale 1, 80121 Napoli

### INTRODUCTION

Massive amounts of municipal waste are generated every day, leaving lots of metals as landfilled waste and incineration slags. Despite the low absolute concentrations, substance flow analysis on selected Italian municipal solid waste incineration (MSWI) plants shows that fly ash (FA) and bottom ash (BA) can be low concentration streams of high-tech metals, with estimated annual flows of tens of kg and a total content comparable to low-grade active mines (Funari *et al.*, 2015). 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 (Halinen *et al.*, 2009; Rodrigues *et al.*, 2016; Lee & Pandey, 2012). Bioleaching can be a suitable and more sustainable alternative to chemical leaching for resource recovery from wastes. Bioleaching of Al, Cu, and Zn from MSWI ashes can be suitable for economic recovery using both fungi, mixed acidophilic bacteria (Lee & Pandey, 2012), and mixed alkaline bacteria (Ramanathan & Ting, 2016), but no upscaling of the technology has been developed. Funari *et al.* (2017) demonstrated the leaching behaviour of a wide range of metals that can be removed from MSWI FA using a mixed acidophilic culture in a one-step bioleaching process. The goal of this study is to investigate the feasibility of biotic leaching of metals from municipal incineration waste by using a mixed acidophilic culture from samples of the Libiola Fe-Cu mine area (Ligurian Apennines, Italy). The effect of different amounts of S<sup>0</sup> and Fe<sup>2+</sup> was evaluated at two pH setpoints to optimise metal recovery. Batch experiments with regenerating ion-exchange resins, Amberlite® IRA-400 vs. Chelex®100, were performed to assess the potential metal recovery from the leachate.

### MATERIALS AND METHODS

#### *MSWI samples*

The studied materials were collected from two Italian MSWI plants in 2013 following the sampling strategy adopted in Funari *et al.* (2015) for FA and BA samples. The selected incinerators use 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. The material pre-treatment included drying at low temperature (40°C) for one week, grinding, and milling (< 40 µm) with an agate vibratory mill disk. The milled BA and FA samples were analysed for the bulk chemical composition (Table 1) and used as the starting material throughout the experiments, except for “RN” BA in the reactor #2 (R2). The sample labelled “RN-R2” was used as raw bottom ash for the batch test to investigate a grain-size that would not require as much mechanical crushing before leaching.

Table 1- Chemical composition by ICP-OES of the starting materials.

		FE	FE7	RN	RN3
		MSWI-1 BA	MSWI-1 FA	MSWI-2 BA	MSWI-2 FA
<b>Si</b>	g/100g	12.2	7.6	15.1	6.6
<b>Ti</b>	“	0.6	0.5	0.7	0.9
<b>Al</b>	“	3.7	1.8	3.8	3.1
<b>Fe</b>	“	10.6	2.3	6.1	1.0
<b>Mn</b>	“	0.2	0.1	0.1	0.1
<b>Mg</b>	“	2.1	1.2	1.4	1.0
<b>Ca</b>	“	13.8	25.9	20.1	22.0
<b>Na</b>	“	2.4	4.1	2.5	2.0
<b>K</b>	“	0.5	3.4	0.7	1.9
<b>P</b>	“	0.3	0.3	0.5	0.7
<b>S</b>	“	0.5	3.0	0.6	2.9
<b>Cd</b>	mg/kg	4.6	177.5	<1	13.4
<b>Co</b>	“	167	27.1	119	28.9
<b>Cr</b>	“	602	313	492	659
<b>Cu</b>	“	13520	2679	3041	355
<b>Ni</b>	“	225	91.6	102	66.6
<b>Pb</b>	“	1136	8688	1475	515
<b>Sb</b>	“	283	1459	141	567
<b>Sn</b>	“	696	1951	498	554
<b>Zn</b>	“	5807	32744	3537	3869

#### *Microorganisms and culture medium*

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 (Fig. 1). The characterisation of the original culture was performed by using Terminal Restriction Fragment Length Polymorphism (T-RFLP) analysis that allows rapid profiling of complex microbial communities based on variation in the 16S rRNA gene. According to the T-RFLP results, the mixed acidophilic culture contained members of *Acidovorax* genus, *At. thiooxidans*, *At. ferrooxidans*, *Chlorobium limicola*, and some species closely related to *Acidothiobacillus*. 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 (Dinelli *et al.*, 2001). The composition of the nutrient growth medium (a modified 9K medium [7,9]) 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 22.5 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>. The alkaline microbial community was sampled from natural waters close to neutrality (pH 6-7) and where a light-blue biofilm/colloidal precipitates occurred (Fig. 1). The T-RFLP identified actinobacteria, chlorobacteria, bacteria from the family of Nitrospiraceae and Flavobacteriaceae, able to thrive under alkaline conditions. The alkaline strains were cultivated in 90% (v/v) 9K medium supplemented with 10% (v/v) glucose (≥ 99.5%, Sigma-Aldrich). All reagents used were of analytical grade.

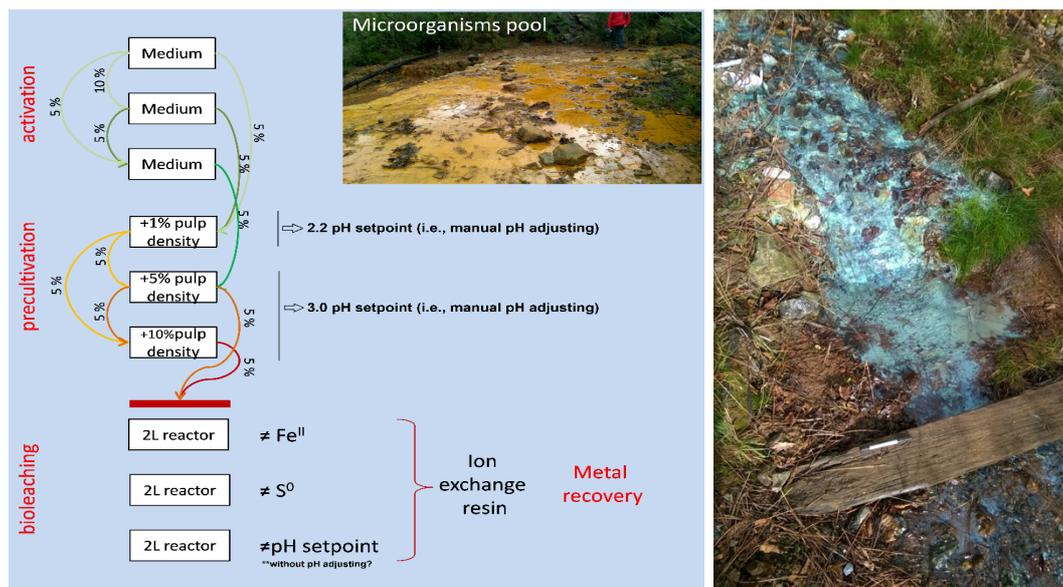


Fig. 1 - Graphical description of activation, cultivation, and bioleaching procedures with the photograph showing the ponds where bacterial cultures were collected (left, acidophilic 44°18'31.4"N 9°26'32.5"E; right, alkaline 44°17'59.9"N 9°26'42.4"E).

*Scaled-up bioleaching experiments*

Each inoculum tailored for BA and FA samples was used in a 1-litre flask containing the corresponding sample (Fig. 1). The leaching experiments (one-step bioleaching) were carried out in triplicate using 10% (v/v) MSWI ash and 90% (v/v) bio-lixiviant (containing 90% (v/v) 9K medium and 10% (v/v) adapted inoculum). 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 H<sub>2</sub>SO<sub>4</sub> to different pH starting conditions (3 and 6 pH setpoint) to evaluate a bioleaching process that would not require much chemical pre-treatment. The pH and redox potential were measured daily; 10 mL of the slurry was sampled weekly for ICP-OES analysis. Evaporation was corrected gravimetrically by the addition of distilled water. Control tests without inocula were performed in the same conditions. Table 2 reports the experimental setup where different setpoints (*i.e.*, starting pH) and varied addition of S<sup>0</sup> and Fe<sup>2+</sup> (as FeSO<sub>4</sub>·7H<sub>2</sub>O) were used considering the chemical composition of the MSWI samples (Table 1).

Table 2 - Configuration of the different scaled-up bioleaching experiments.

	Type	S <sup>0</sup> [g]	Fe <sup>2+</sup> [g]	pH setpoint
<b>FE-R1</b>	BA	5.0	11.0	3.0 ± 0.5
<b>FE-R2</b>	BA	5.0	0.0	“
<b>RN3-R1</b>	FA	5.0	11.0	“
<b>RN3-R2</b>	FA	2.5	11.0	“
<b>RN-R1</b>	BA	5.0	11.0	6.0 ± 0.5
<b>RN-R2*</b>	BA	5.0	11.0	“
<b>FE7-R1</b>	FA	5.0	11.0	“
<b>FE7-R2**</b>	FA	5.0	22.0	“

\*raw bottom ash (unmilled), \*\*supplemented with 50% (v/v) alkaline inoculum.

### Chemical analysis

The analytical determination was done using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer (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) were 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.

### Recovery with ion exchange resins

Batch tests 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 ( $-\text{N}^+\text{R}_3$ ) 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.* (2016, 2017). 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 (Laboratories Bio-Rad, 2011). The hydrated Amberlite resin at a concentration of 50 g  $\text{L}^{-1}$  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.

## RESULTS AND DISCUSSION

### Scaled-up bioleaching experiments

#### pH SETPOINT: 3

For this run of bioleaching experiments, we opted for a relatively high starting pH (setpoint  $3.0 \pm 0.5$  pH) to lessen the environmental impacts and capital costs of the use of mineral acids and, in turn, to deliver a reproducible process. Most metals are efficiently leached out within 15 days for both BA (Fig. 2) and FA (Fig. 3). The leaching of Zn (and other elements like Sn, Cd, and Ni) from BA is not significantly affected by the experiment duration. The bioleaching results in 100% Cu, 80% Zn and 20% Pb removal from the BA material. Small changes in metal removals are observed during the BA bioleaching without  $\text{Fe}^{2+}$ . The results show that more than 90% Zn, Cu, and 10% Pb are removed from FA (Fig. 3), in an acidic medium supplemented with elemental sulphur and trivalent iron. Halved amounts of elemental sulphur in FA decrease the leaching efficiency of 5-15%. The solubility of Al is particularly enhanced using  $\text{S}^0$ . The improved performance of a bioreactor fed with elemental sulphur is clearly visible from the curves of pH variation.

#### pH SETPOINT: 6

We also tested a higher starting pH (setpoint  $6.0 \pm 0.5$  pH). The bioproducted metabolic substances greatly increase the acidity of the slurry in the BA bioleaching experiment (Fig. 4). This results in efficient removals of

Al, Cu and Zn. The latter solubilises mostly in a short period with the optimum efficiency reached in one week. The use of raw BA (RN-R2) produces similar or better yields compared to fine-grained BA (Fig. 4).

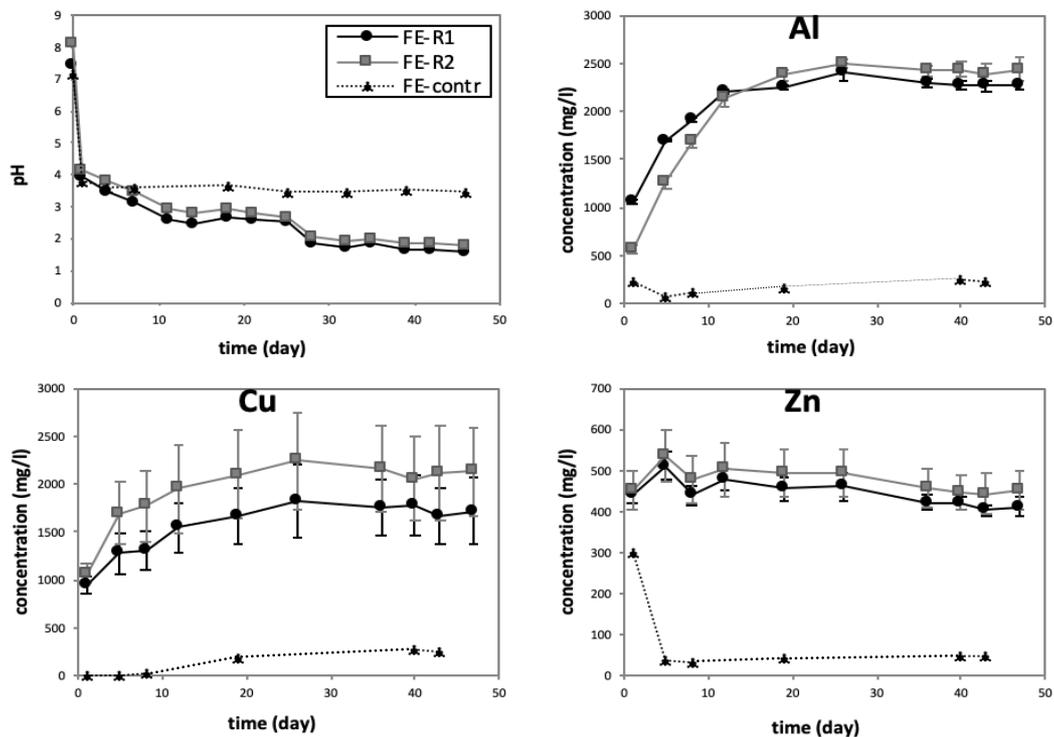


Fig. 2 - Variation of pH (top left) and removals of selected metals as a function of time, during bioleaching of MSWI BA sample from a 3 pH setpoint. Error bars may be smaller than symbols.

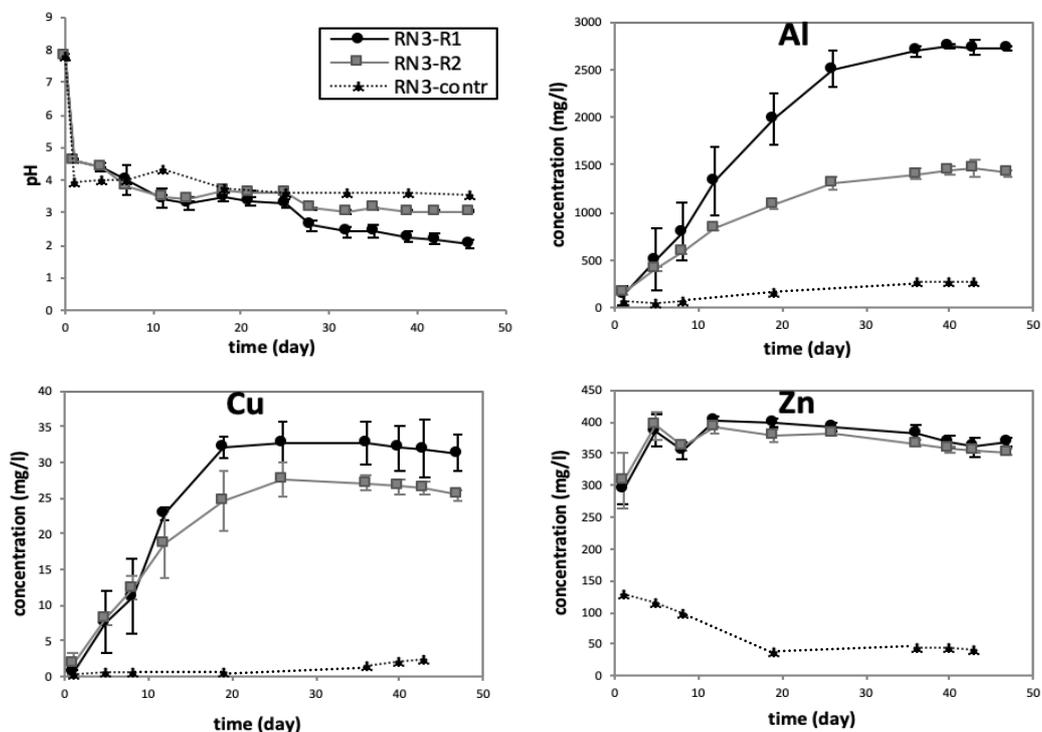


Fig. 3 - Variation of pH (top left) and removals of selected metals as a function of time, during bioleaching of MSWI FA sample from a 3 pH setpoint. Error bars may be smaller than symbols.

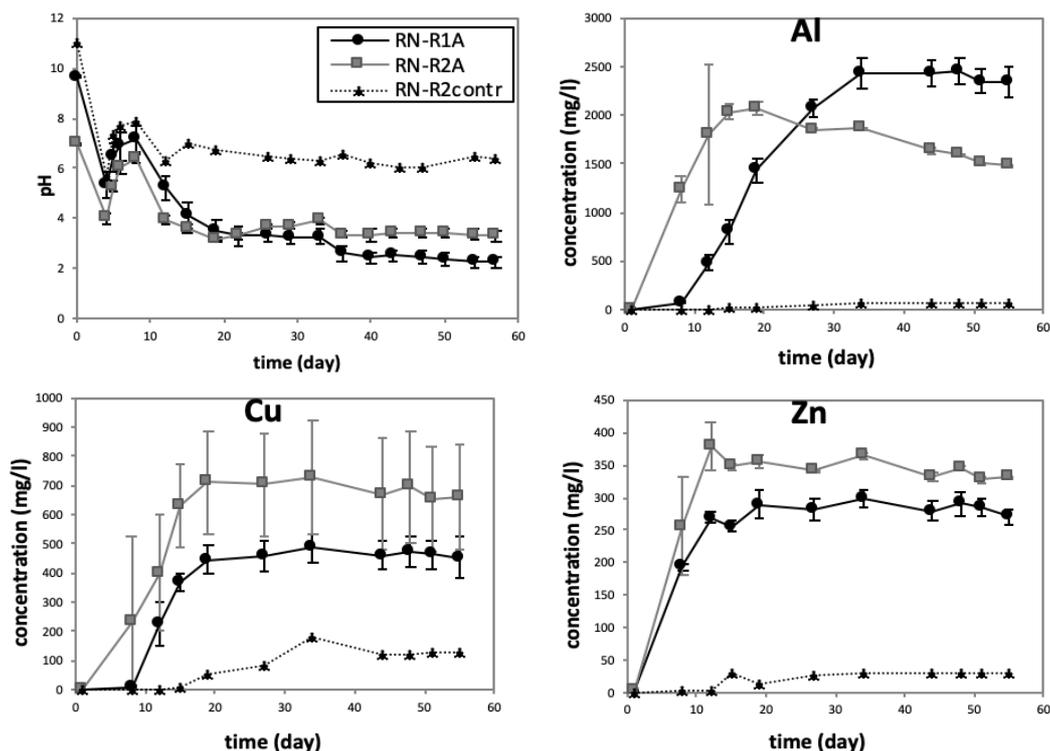


Fig. 4 - Funari *et al.* (2019) variation of pH (top left) and removals of selected metals as a function of time, during bioleaching of MSWI BA sample from a 6 pH setpoint. Error bars may be smaller than symbols.

*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. The Fig. 5 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 (Funari *et al.*, 2015). 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.

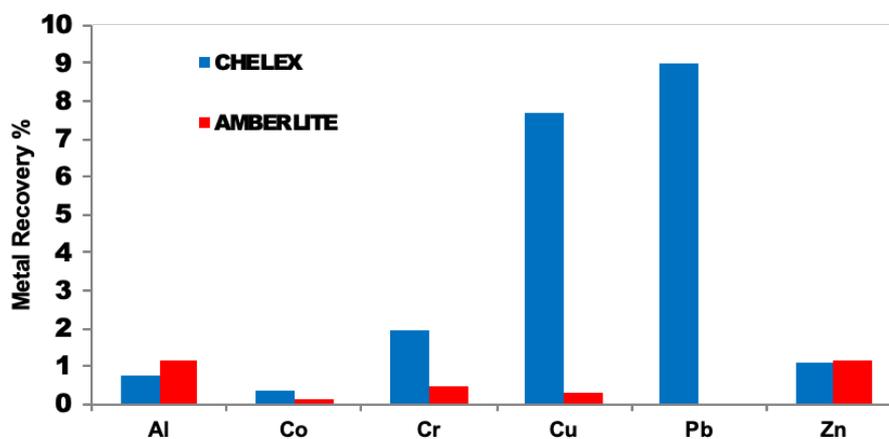


Fig. 5 - Funari *et al.* (2019) comparison of the ion exchange resins for metal recovery.

## CONCLUSION

The results show the potential of bioleaching for mining metals for fly and bottom ashes from municipal solid waste incinerators. The recovery percentage of metals from the leachate using ion exchange resins was not very encouraging, so further developments are needed to separate the metals for recovery and recycling. Leaching data on MSWI ashes tend to be collected before landfilling (e.g. leaching test) rather than for resource recovery (e.g. total extractable metals), thus a lot of data already collected is of little use for the latter. Nonetheless, MSWI ashes can be a valuable secondary resource if processed in an eco-friendly manner. As such, we reported the results of a bioleaching process with modified experimental setups ( $\text{Fe}^{2+}$ ,  $\text{S}^0$ , inoculum). The process has the potential to be easily scaled-up and transferred to the waste management industrial chains. Building-up a knowledge network for the recovery of metals and secondary raw materials from MSWI ashes would be beneficial to make much better use of these anthropogenic resources and thereby to achieve a more circular economy.

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Funari, V., Gomes, H.I., Cappelletti, M., Fedi, S., Braga, R., Dinelli, E., Mayes, W.M., Rogerson, M. (2017): Metal recovery from MSWI fly ash and bottom ash by bioleaching and ion exchange resin. AIV-SGI-SIMP-SoGel Meeting - Geosciences: a tool in a changing world, Pisa, Italy, 4-6 September 2017;

Funari, V., Gomes, H.I., Cappelletti, M., Fedi, S., Dinelli, E., Rogerson, M., Mayes, W.M. (2018): Bioleaching of fly ash and bottom ash from Municipal Solid Waste Incineration for metal recovery. 6<sup>th</sup> International Conference on Sustainable Solid Waste Management, 13-16 June 2018, Naxos Island, Greece;

Funari, V., Gomes, H.I., Cappelletti, M., Fedi, S., Dinelli, E., Rogerson, M., Mayes, W.M., Rovere, M. (2018): Bioleaching of Municipal Solid Waste Incineration residues by S- and Fe-oxidizing bacteria. RFG2018 - Resources for Future Generations, Vancouver, Canada, 16-21 June 2018;

Funari, V., Gomes, H.I., Mayes, W.M., Rogerson, M., Cappelletti, M., Fedi, S., Dinelli, E., Rovere, M. (2018): Bioleaching of alkaline wastes using mixed bacterial culture sourced from a natural system. SGI-SIMP Meeting - Geosciences for the environment, natural hazard and cultural heritage, Catania, Italy, 12-14 September 2018.

Afterwards, bioleaching data was further elaborated and discussed in:

Funari, V., Gomes, H.I., Cappelletti, M., Fedi, S., Dinelli, E., Rogerson, M., Mayes, W.M., Rovere, M. (2019): Optimisation Routes for the Bioleaching of MSWI Fly and Bottom Ashes Using Microorganisms Collected from a Natural System. *Waste Biomass Valor.*, **10**, 3833-3842;

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