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Urban mining of municipal solid waste incineration (MSWI) residues with emphasis on bioleaching technologies: a critical review

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# 1 **Urban mining of Municipal Solid Waste Incineration (MSWI)** 2 **residues with emphasis on bioleaching technologies: A critical** 3 **review**

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13

## 14 **Abstract**

15 Metals are essential in our daily lives and have a finite supply, being simultaneously contaminants of concern.  
16 The current carbon emissions and environmental impact of mining are untenable. We need to reclaim metals  
17 sustainably from secondary resources, like waste. Biotechnology can be applied in metal recovery from waste  
18 streams like fly ashes and bottom ashes of municipal solid waste incineration (MSWI). They represent  
19 substantial substance flows, with roughly 46 million tons of MSWI ashes produced annually globally,  
20 equivalent in elemental richness to low-grade ores for metal recovery. Next-generation methods for resource  
21 recovery, as in particular bioleaching, gives the opportunity to recover critical materials and metals,  
22 appropriately purified for noble applications, in waste treatment chains inspired by circular economy  
23 thinking. In this critical review, we can identify three main lines of discussion: 1) MSWI material  
24 characterization and related environmental issues; 2) currently available processes for recycling and metal  
25 recovery; and 3) microbially-assisted processes for potential recycling and metal recovery. Research trends  
26 are chiefly oriented to the potential exploitation of bioprocesses in the industry. Biotechnology for resource  
27 recovery shows increasing effectiveness especially downstream the production chains, i.e. in the waste  
28 management sector. Therefore, this critical discussion will help assessing the industrial potential of  
29 biotechnology for urban mining of municipal, post-combustion waste.

30

31 **Key Words:** Circular economy; Waste-to-Energy (WtE) plants; Incineration wastes; Critical raw materials;

32 Secondary raw materials; Resource recovery

33

## 35 1. Introduction

36 Municipal Solid Waste Incineration (MSWI) is a predominant management practice in many  
37 countries, and it has been increasingly adopted in countries like China (Fan et al., 2021). According to the  
38 World Bank, 11% of the global MSW is incinerated, corresponding to an estimated 220 million tonnes (Kaza  
39 et al., 2018). In the European Union EU-27, in 2019, 60 million tonnes of municipal solid waste were  
40 incinerated (Eurostat, 2019). Despite reducing the waste volume and recovering energy, MSWI also produces  
41 two main kinds of residues, called bottom (BA) and fly ashes (FA), that must be sustainably managed. MSWI  
42 residues' features (chemical and mineralogical composition, grain size heterogeneity, etc.) and their disposal  
43 strategy influence their after-use in applications, for example, reuse its mineral fraction in the construction  
44 industry as secondary raw material. MSWI residues can be returned to secondary raw materials markets after  
45 appropriate treatment to enhance production cycles in urban mining actions, aiming to remove, recover and  
46 recycle the mineral resource that may be contained in anthropogenic materials with high economic potential  
47 (e.g. critical raw materials) or environmentally positive balance (e.g., producing acceptable secondary raw  
48 material with low environmental impacts). Copious research proposed innovative technologies with  
49 simultaneous improvements of environmental and financial drawbacks associated with MSWI residues, both  
50 BA and FA. BA and, to a lesser extent, FA can be recycled to produce concrete, soil improvers and fillers, glass  
51 and ceramics, or used to produce absorbents, stabilizing agents, and zeolites (Quina et al. 2018; Lam et al.  
52 2010). So far, urban mining attempts from MSWI residues are promising for application in integrated waste  
53 management to boost incomes and minimize environmental impacts, as demonstrated by Life cycle  
54 assessment (LCA) (Fellner et al., 2015). Combined separation, extraction, and recovery processes based on  
55 physical-mechanical methods, acid and alkaline leaching, biorecovery and electroplating, or  
56 bioelectrochemical systems seem particularly efficient for recovering metals from bottom ash and fly ash  
57 (Gomes et al., 2020).

58 New options to improve MSWI residues management are needed, especially those capable of the  
59 twofold benefit of metal recovery and quality enhancement of the post-treatment residue. Insights from  
60 chemical and mineralogical data on MSWI residues can inform recovery of secondary raw materials and  
61 marketable metals. For example, among metals of strategic interest and potentially mineable from MSWI  
62 residues, silver (Ag), antimony (Sb), cerium (Ce), lanthanum (La), niobium (Nb), nickel (Ni), vanadium (V) are  
63 enriched in the fine fractions, while gadolinium (Gd), chromium (Cr), scandium (Sc), tungsten (W), and yttrium  
64 (Y) partition in the coarse fractions (Mantovani et al., 2021).

65 MSWI residues are a potential low-grade urban mine of ore metals thanks to the significant flows of  
66 substance bearing metals downstream of the municipal waste incineration process (Funari et al., 2015). For  
67 MSWI-BA, Funari and co-workers estimated a total flow of more than 350 t/a magnesium (Mg), 8.5 t/a Cr,

68 4.3 t/a cobalt (Co), and nearly 3 t/a Sb. The overall annual flow of the light rare earth elements (LREE: La, Pr,  
69 Ce, Nd, Gd, Sm, Eu) and Sc and Y reach 2 t/a; while only the flow of heavy REE (HREE: Lu, Tb, Ho, Dy, Tm, Er,  
70 Yb) is about 0.1 t/a. The Substance Flow Analysis (SFA) also shows considerable amounts of gallium (Ga) and  
71 Nb (0.3 t/a) and the precious metals gold (Au) and silver (Ag) (0.01 t/a and 0.12 t/a, respectively). SFA analysis  
72 on MSWI-FA showed relatively high flows of Mg (79 t/a), Sb (2.4 t/a), Cr (1 t/a), Ce (0.05 t/a), Co (0.04 t/a),  
73 and also volatile elements such as Ag, Zn, and Sn have a considerable output retained in the solid FA. With  
74 further estimates coming from these figures, a total of 4500 tons Cu, 130 tons REEs, and 0.5 tons gold, are  
75 potentially recoverable from all MSWI-BA flowing on a national level. At the same time, the MSWI-FA output  
76 is a promising source of Zn, Sn, Sb, and Pb. Besides the relevance of metal recovery, successful urban mining  
77 strategies favour i) the reduction of the environmental impact, providing less dangerous leachates, ii) more  
78 control over nanoparticle pollution, and iii) high quality of post-treatment residues. In parallel, investigation  
79 of MSWI residues and related environmental media (e.g., topsoil nearby incinerators) would favour the  
80 development of finely tuned methods for urban mining with a close eye on sustainability. Looking ahead, the  
81 quality of MSWI feedstock materials and final solid residues, especially considering the 10-to-20-year life  
82 cycle of MSWI technology, needs continuous improvements from synergistic actions of both private and  
83 public stakeholders and the local communities.

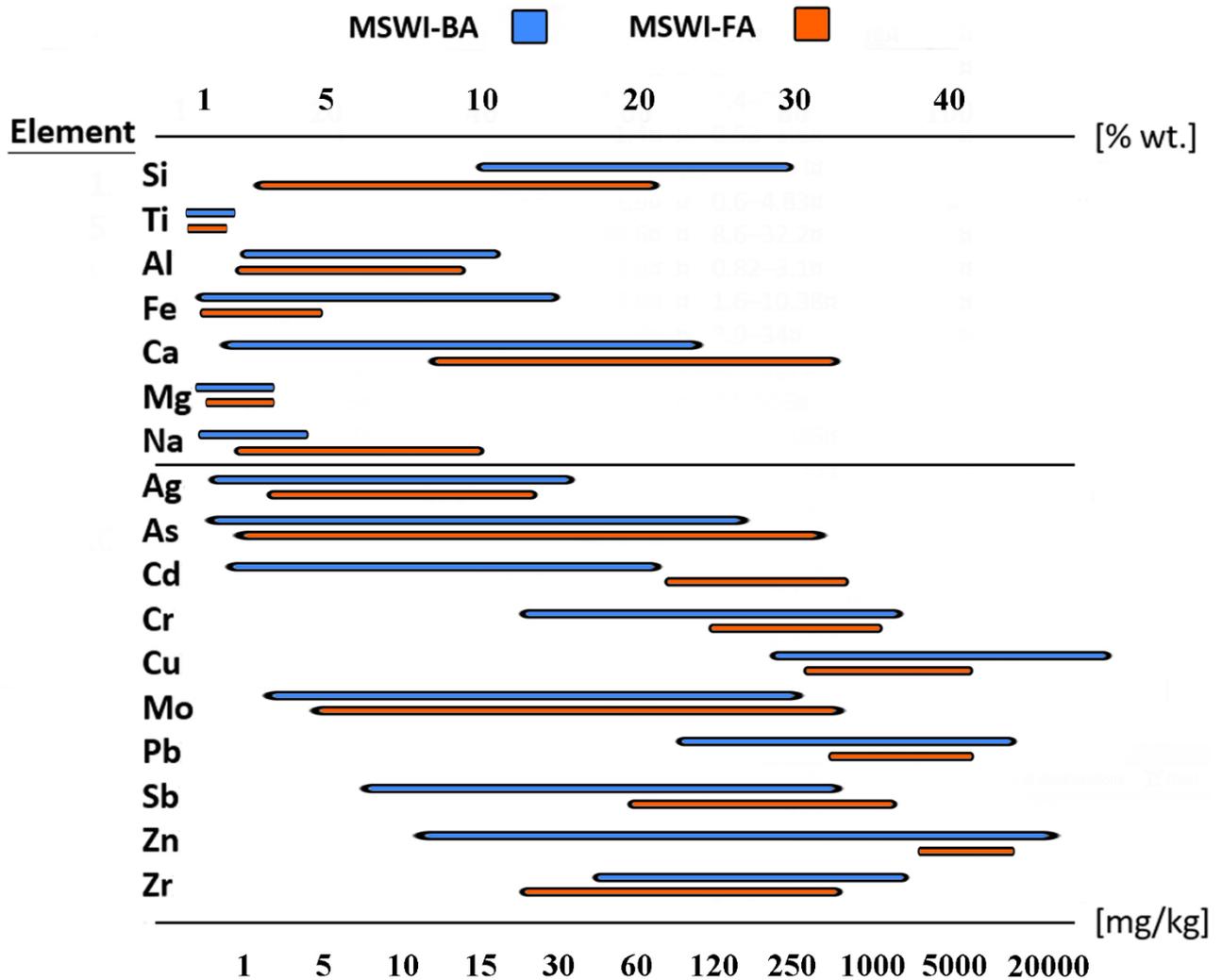
84 This paper aims to critically reflect on the application of biotechnologies for urban mining of waste  
85 streams in the context of the circular economy. Our objectives are to focus on: 1) MSWI material  
86 characterization and related environmental issues; 2) currently available processes for recycling and metal  
87 recovery; and 3) microbially-assisted processes for potential recycling and metal recovery.

## 88 2. Mineral resources and secondary raw materials from MSWI residues

### 89 2.1. Chemistry and Mineralogy of MSWI residues

90 MSWI residues can be thought of as a mineral matrix mixed with a small fraction of partly combusted  
91 organic matter and secondary organic by-products (approx. 4% by weight) resulting from temperature  
92 changes through the processing line of MSWI technology leading to the establishment of different  
93 thermodynamic equilibria (Guimaraes, et al. 2006). Eusden et al. (1999) described a detailed petrogenesis of  
94 the MSWI solid materials sent to incinerators. The major elements in MSWI residues are Ca, Si, Al, Fe, Mg,  
95 Na, K and Cl in the form of silicates, aluminosilicates, carbonates (e.g., calcite, trona), most of their oxides  
96 (e.g., calcium oxide, hematite, sodium oxide, titanium dioxide and potassium oxide) and alkaline salts (e.g.,  
97 halite, sylvite; preferably present in MSWI-FA). Usually, the most abundant components are Ca and Si oxides.  
98 Cu, Cr, Pb, Cd, Zn, Hg, Sb, and Ni metals are also found in these ashes as minor and trace elements potentially  
99 risky for the environment. Studies of element fractionation found that elements with high melting  
100 temperature tend to remain in the MSWI-BA, while the volatile ones tend to break down in the MSWI-FA

101 (Funari et al., 2015). The heterogeneity of the urban waste input feed directly influences the mineralogical  
 102 and chemical composition and the physical-mechanical properties of the incinerator ashes. Different  
 103 spectrometers are used to determine major, minor, and trace elements in MSWI residues together with other  
 104 analytical techniques depending on the analyte sought and, in general, from the purpose of the  
 105 characterization. Figure 1 shows the compositional range reported in the literature for measured analytes.  
 106 In MSWI-FA, the heavy metals content is generally higher than in BA due to the metal vaporization during  
 107 the combustion and adsorption on a higher specific surface area. Harmful compounds such as chlorides and  
 108 metal oxide nanoparticles from MSWI-FA are controlled by wet scrubbers in the Air Pollution Control (APC)  
 109 system, which primarily removes acid gases such as HCl and HF (Sabbas et al., 2003).



110  
 111 Figure 1. Chemical composition ranges of MSWI-BA and MSWI-FA for selected major, minor and trace elements (Izquierdo et al.,  
 112 2002; Sabbas et al., 2003; Bayuseno et al., 2010; Funari et al., 2015; Astrup et al., 2016; Xiaomin et al., 2017; Huber et al., 2019;  
 113 Wong et al., 2021; Maldonado-Alameda et al., 2021; Mantovani et al., 2021; Clavier 2021) in wt. % and mg/kg, respectively.

114 Numerous works elaborated the mineralogical composition of MSWI residues, e.g., by scanning  
 115 electron microscope defining morphology, single-point chemical composition and the interaction between  
 116 the different phases present inside the grains (Bayuseno and Schmahl, 2010; Bogush et al., 2015; Funari et

117 al., 2018; De Boom and Degrez, 2012). The thin sections show structural variability and complexity under the  
118 microscope. Moreover, it is possible to verify the presence of glassy and crystalline material together with  
119 metallic and empty parts (e.g., Mantovani et al., 2021). The presence of wollastonite ( $\text{CaSiO}_3$ ), with a dendritic  
120 crystallization in the glass matrix indicates a fast crystallization is frequent. There are also evident zoning and  
121 evidence of core recrystallization; sometimes, recrystallizations of fresh structures are observed within a  
122 metal matrix (Bogush et al., 2015). Iron, ubiquitous and present as a major element ( $> 0.1\%$  by weight),  
123 undergoes a complex petrogenesis and can form a series of oxides and hydroxides, but also remain as nuggets  
124 of metallic Fe, or Fe-phosphides (e.g., schreibersite, associated with reducing conditions) and -sulfides  
125 (pyrite, pyrrhotite, greigite among many) (Funari et al., 2018; 2020), making hard to determine minor iron-  
126 bearing phases. Mineralogical analysis on magnetic separates showed the presence of small ( $<5 \mu\text{m}$ )  
127 spherules containing Fe in the form of agglomerates of particles or loose particles that could be attributable  
128 to technogenic spheres (*sensu* Magiera et al., 2011) readily dispersible during handling, being generally  
129 MSWI-FA dustier than MSWI-BA. Despite the great uncertainty on the stoichiometry and quantification of  
130 the crystalline phases, the X-ray diffractograms readily detect various carbonates such as calcite, soluble salts  
131 such as halite, silicates such as quartz, solid solutions gehlenite-akermanite, pyroxenes and feldspars, sulfates  
132 and phosphates and oxides of iron. However, the origin of certain mineralogical phases, i.e., if the minerals  
133 observed in MSWI-BA or MSWI-FA are derived from the incoming waste or freshly formed remains puzzling.  
134 This is due to different processing technologies, chemical composition of the incoming waste and combustion  
135 temperatures reached, which, in turn, can depend on local policies and have seasonality effects. The  
136 commonly identified minerals from MSWI-BA and MSWI-FA by XRD are in Table 1.

137 The data reported in the literature also suggested the residues' particle size as a proxy of element  
138 enrichment or, in other words, a tool for mineral beneficiation. Carbonates and sulfatic phases typically occur  
139 in the finer fractions ( $<0.065 \text{ mm}$ ). Analytical determinations show a higher concentration of S, Cl and metals  
140 such as Zn, Pb, Cr, and Sr in fine particle sizes ( $<1 \text{ mm}$ ) (Speiser et al., 2000; Chimenos et al., 2003). In the  
141 finer fraction, there is a higher content of metals within mineralogical phases less resistant to weathering  
142 (carbonates and sulfates), that is, more available to environmental leaching. Analyzing the particle size's  
143 cumulative distribution, about 60% of total weight of MSWI-BA is composed of particles with a size between  
144 1 and 8 mm (belonging to the category coarse sand or gravel), while 20% has a particle size bigger than 10  
145 mm and the remaining 20% is made up of grains smaller than 1 mm. MSWI-FA is more homogeneous than  
146 MSWI-BA in its particle size, which results averagely silty. Both ashes show a minor but significant ultrafine  
147 fraction ( $<1 \mu\text{m}$ ). Overall, although not always agreeing on the identification of phases, the mineralogical  
148 data in the scientific literature confirms that the MSWI residues contain minerals of potential economic  
149 interest. However, the chemical composition can vary significantly according to the particle size, the quality  
150 of the incoming waste, the combustion process, and the type of residue.

151 Table 1 -Most common mineralogical phases detected by XRD from MSWI residues (Wan et al., 2006; Liu et al., 2009; Bayuseno and  
 152 Schmahl, 2010; De Boom and Degrez, 2012; Bogush et al., 2015; Funari et al., 2018; Mantovani et al., 2021). O: rare; X: common;  
 153 XX: very frequent; n.d.: not detected.

<b>Mineral phase</b>	<b>Chemical formula</b>	<b>MSWI-FA</b>	<b>MSWI-BA</b>
<i>Silicates, aluminates, and aluminosilicates</i>			
Quartz	SiO <sub>2</sub>	<b>X</b>	<b>XX</b>
Cristobalite	SiO <sub>2</sub>	<i>n.d.</i>	<b>X</b>
Corundum	Al <sub>2</sub> O <sub>3</sub>	<b>X</b>	<b>XX</b>
Alkali Feldspars	(K,Na)(Al,Si) <sub>3</sub> O <sub>8</sub>	<i>n.d.</i>	<b>XX</b>
Plagioclase feldspars	NaAlSi <sub>3</sub> O <sub>8</sub> -CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<b>X</b>	<b>X</b>
	(K, Ca, Na)(Al,Si) <sub>4</sub> O <sub>8</sub>	<b>O</b>	<b>X</b>
Gehlenite	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>	<b>X</b>	<b>XX</b>
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>		
Akermanite	Ca <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	<b>X</b>	<b>XX</b>
	Ca <sub>2</sub> (Mg,Fe)Si <sub>2</sub> O <sub>7</sub>	<b>O</b>	<b>X</b>
	Ca(Mg,Fe)Si <sub>2</sub> O <sub>6</sub>	<i>n.d.</i>	<b>X</b>
Calcium Pyroxene	Ca(Mg, Al)(Si,Al) <sub>2</sub> O <sub>6</sub>	<b>O</b>	<b>X</b>
	(Na,Ca)(Fe,Mn)(Si,Al) <sub>2</sub> O <sub>6</sub>	<i>n.d.</i>	<b>X</b>
	CaSiO <sub>3</sub>	<b>X</b>	<b>X</b>
Wollastonite	Ca <sub>2</sub> SiO <sub>4</sub>	<b>X</b>	<b>X</b>
	Ca(OH) <sub>2</sub>	<b>X</b>	<b>X</b>
Portlandite	Ca(OH) <sub>2</sub>	<b>X</b>	<b>X</b>
Gibbsite	Al(OH) <sub>3</sub>	<b>O</b>	<b>XX</b>
Ettringite	Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> 26H <sub>2</sub> O	<b>X</b>	<b>X</b>
<i>Carbonates</i>			
Calcite	CaCO <sub>3</sub>	<b>XX</b>	<b>X</b>
Other	(Pb,Cd,Zn)CO <sub>3</sub>	<b>X</b>	<b>O</b>
<i>Fe-bearing phases</i>			
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	<b>O</b>	<b>XX</b>
Hematite	Fe <sub>2</sub> O <sub>3</sub>	<b>X</b>	<b>O</b>
Wüstite	FeO	<b>X</b>	<b>X</b>
Goethite	FeO(OH)	<i>n.d.</i>	<b>X</b>
	Fe(OH) <sub>3</sub>	<b>X</b>	<b>X</b>
	FeCO <sub>3</sub>	<b>O</b>	<b>O</b>
	Fe(Cr,Ti) <sub>2</sub> O <sub>4</sub>	<b>O</b>	<b>X</b>
	FeSO <sub>4</sub> 7H <sub>2</sub> O	<i>n.d.</i>	<b>X</b>
<i>S-based phases</i>			
Anhydrite	CaSO <sub>4</sub>	<b>XX</b>	<b>X</b>
Gypsum	CaSO <sub>4</sub> 2H <sub>2</sub> O	<b>X</b>	<b>XX</b>
	Ca <sub>6</sub> Al <sub>2</sub> O <sub>6</sub> (SO <sub>3</sub> ) <sub>3</sub> 32H <sub>2</sub> O	<i>n.d.</i>	<b>X</b>
	PbSO <sub>4</sub>	<b>X</b>	<i>n.d.</i>
<i>Other oxides</i>			
Lime	CaO	<b>XX</b>	<b>X</b>
	TiO <sub>2</sub>	<b>X</b>	<b>X</b>
	PbO	<b>X</b>	<b>O</b>
	ZnO	<b>X</b>	<b>X</b>
	Na <sub>2</sub> O	<b>XX</b>	<b>X</b>
	CuO	<b>X</b>	<b>XX</b>

	CaMoO <sub>4</sub>	<b>O</b>	<b>X</b>
	NaAsO <sub>2</sub>	<b>O</b>	<b>X</b>
<i>Cl-based phases</i>			
Friedel's salt	Ca <sub>2</sub> Al(OH) <sub>6</sub> Cl 2H <sub>2</sub> O	<i>n.d.</i>	<b>X</b>
Hydrocalumite	Ca <sub>2</sub> Al(OH)6Cl <sub>1-x</sub> (OH) <sub>x</sub> 3H <sub>2</sub> O	<i>n.d.</i>	<b>X</b>
	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	<b>O</b>	<b>X</b>
	Ca <sub>2</sub> SiO <sub>3</sub> Cl <sub>2</sub>	<b>O</b>	<b>X</b>
	CaCl <sub>2</sub>	<b>X</b>	<i>n.d.</i>
	KCaCl <sub>3</sub>	<b>X</b>	<i>n.d.</i>
	PbCl <sub>2</sub>	<b>X</b>	<i>n.d.</i>
	ZnCl <sub>2</sub>	<b>X</b>	<i>n.d.</i>
	NaCl	<b>XX</b>	<b>X</b>
	KCl	<b>X</b>	<i>n.d.</i>
<i>Other halides</i>			
fluorides	CaF <sub>2</sub>	<b>X</b>	<i>n.d.</i>
bromides	not specified	<b>O</b>	<b>O</b>
iodides	not specified	<i>n.d.</i>	<i>n.d.</i>
<i>Other compounds</i>			
organometallic compounds	organoarsenic compound	<i>n.d.</i>	<b>O</b>
<i>Native elements</i>			
zinc	Zn(0)	<b>X</b>	<b>X</b>
aluminium	Al(0)	<b>X</b>	<b>X</b>
copper	Cu(0)	<b>O</b>	<b>X</b>
gold	Au (0)	<i>n.d.</i>	<b>X</b>
other elements	Ti(0), Pb(0), Ag (0), Hg(0)	<b>X</b>	<b>O</b>

## 154 2.2. Hydrometallurgy for MSWI residues Urban Mining

155 Hydrometallurgical solutions in waste management typically involves the dissolution of the metals  
156 present in the mineralogical matrix in acids or bases. During the leaching procedures, minerals dissolve under  
157 varying thermodynamic conditions. Metals can be separated in the dissolution step when not soluble in the  
158 solvent used, producing a solid precipitate as a part of the process chain. Hydrometallurgical separation can  
159 rely on solvent extraction and solid ion exchangers and membranes, ionic liquids, and on adsorption capacity  
160 of other materials (e.g., carbon). Following the separation of the metals, the single metal can be purified, for  
161 instance, by sequential precipitation or electrowinning.

162 Water, mineral acids (i.e., sulfuric acid, aqua regia), bases (i.e., sodium hydroxide, ammonia), organic  
163 acids (such as maleic acid), salt solutions, and combinations of these are common leaching reagents. The  
164 process optimization can be achieved by playing with pressure, temperature, reaction time, but also by  
165 adding oxidizing (e.g., H<sub>2</sub>O<sub>2</sub>, Cl<sub>2</sub>, HClO, NaClO) or reducing (e.g., Fe<sup>2+</sup>, SO<sub>2</sub>) agents. The most used leaching  
166 methods include reactor leaching, heap leaching, vat leaching, dump leaching (heap without crushing), in-  
167 situ leaching (extractant pumped directly in the ore deposit) and autoclave leaching (high pressure and

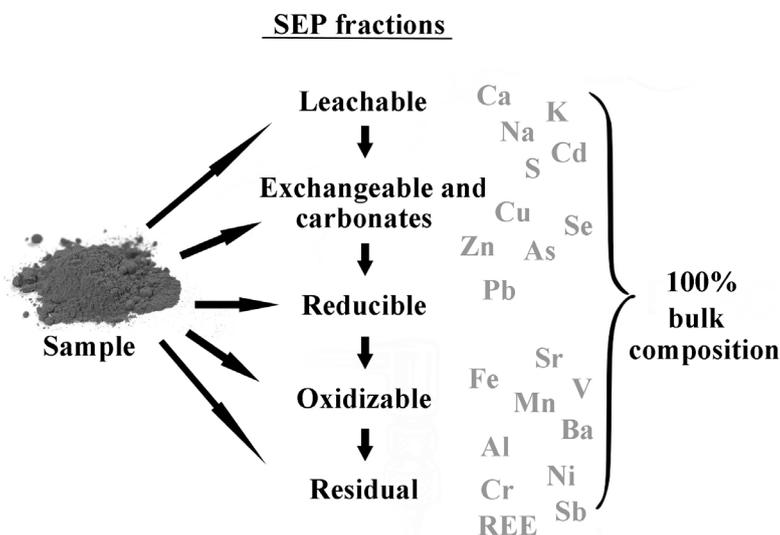
168 temperature). Galvanic, microwave, and ultrasound-assisted leaching are other methods investigated to  
169 enhance the efficiency of traditional leaching.

170 A technique mainly used to treat MSWI-BA before the process of metal recovery takes place or the  
171 residue is landfilled, is ageing (or natural weathering). It reduces the water content of the material up to an  
172 optimal humidity (10–15 wt. %) for metal recovery, improves environmental leaching properties and/or  
173 stabilizes the reactive matrix. Ageing occurs naturally during storage, which normally lasts from 4 to 12 weeks  
174 and sporadically up to one year. During ageing, the precipitation of carbonates, degradation of organic  
175 matter, and pH changes can occur (Nørgaard et al., 2019) as well as total or partial immobilization of Cu, Pb,  
176 Zn and chloride can be achieved. Conversely, oxyanion-forming elements (e.g., Cr, Mo, Sb and sulfate) may  
177 become more prone to mobilization (e.g., Arickx et al., 2006; Costa et al., 2007), likely impacting metal  
178 recovery.

179 Hydrometallurgical applications' primary purpose for managing MSWI residues is decontamination  
180 from harmful metals. In the earliest studies on pH-dependent leaching using HNO<sub>3</sub> (Eighmy et al., 1995), Ca,  
181 Cl, K, Na, and Zn dissolved easily, while other elements (Cr, Pb, Zn, Cu, and Al) exhibited amphoteric behavior  
182 with enhanced solubilization at low pH over a leaching period of 3h. Nagib and Inoue (2000) reported the  
183 recovery of different metals from MSWI-FA using acetic acid, sulfuric acid, sodium hydroxide, and  
184 hydrochloric acid, with a fixed L/S ratio of 7 ml/g. They found that most of Zn is dissolved quickly using sulfuric  
185 acid (10 wt. % H<sub>2</sub>SO<sub>4</sub>) leaching, while temperature was mainly affecting Fe and Mg solubility. Therefore, 30°C  
186 temperature and 5 min time were determined to be suitable for Zn acid leaching to suppress the solubility  
187 of Fe and Mg, which is significantly enhanced at 60°C (Nagib and Inoue, 2000). Hydrochloric acid (10 wt. %  
188 HCl) leaching dissolves 63% Zn and 40% Pb in 5 minutes, together with impurities such as Fe, Mg and Ca.  
189 Acetic acid (10 wt. % CH<sub>3</sub>COOH) leaching was effective, and most Pb and Zn were dissolved in 60 minutes  
190 (Nagib and Inoue, 2000). Acid leaching is efficient because it can dissolve nearly all Pb and Zn, but further  
191 separation and purification steps may be required since other potential impurities (e.g., Fe, Mg, Al, Ca) are  
192 acid soluble. Further implementation was applied to the recovery method of Al and Fe, combining physical  
193 and mechanical processes (e.g., Nayak and Panda, 2010). The use of thermal treatment combined with acidic  
194 leaching allows overcoming some limitations (with recovery efficiencies up to 86 % Al and 94 % Fe using  
195 sulfuric acid) and produced sintered pellets suitable as an inert and lightweight aggregate (Matjie et al., 2005;  
196 Li et al., 2007, 2009). However, the high costs for energy to reach the calcination temperatures (800-1200°C)  
197 and the time demand (up to 24h) make these processes uneconomic. The leaching behavior of antimony (Sb)  
198 is particularly chased because of its elevated concentrations in MSWI residues and environmental relevance  
199 tied to its speciation also during natural ageing. Cornelis et al. (2012) investigated the leaching of antimonate  
200 (Sb<sup>+5</sup>) and antimonite (Sb<sup>3+</sup>) in MSWI-BA as a function of degree of carbonation and pH. Results showed that  
201 acidification and carbonation increased Sb<sup>5+</sup> leaching and decreased Sb<sup>3+</sup> leaching, and pointed out that Sb

202 solubility depends on pH and calcium cations availability (romeite minerals are found to play an important  
 203 role in the antimonate leaching) (Cornelis et al., 2012). Alkaline leaching, on the other hand, is hampered by  
 204 the limited solubility of valuable metals (e.g., Zn), but can have the advantage of leaving a lesser amount of  
 205 impurities in the solid residue. Bipp et al. (1998) were among the first to suggest alkaline leaching for heavy  
 206 metals extraction. They tested gluconic acid and molasses hydrolysate leaching with sugar acid addition  
 207 (1.8%) in the typical pH range of MSWI residues, achieving good recovery performances for Zn, Pb, Cu, Cr,  
 208 and Cd with the molasses hydrolysate under weak alkaline condition. In general, alkaline leaching carried out  
 209 in pH conditions near the MSWI residue's starting pH showed limited performances (Lee and Pandey, 2012).

210 Significant impact on leaching of MSWI residues comes from selective extractions used in typical  
 211 geochemical investigation to understand metal behaviours under different environmental conditions.  
 212 Although it is not possible to reach complete selectivity in each step, a sequential extraction procedure is  
 213 applied to MSWI residues (Figure 2) and corroborated by experimental and theoretical models (Kirby and  
 214 Rimstidt, 1993; Van Herck and Vandecasteele 2001; Chou et al., 2009; Funatsuki et al., 2012). The sequential  
 215 extraction procedures highlight that metals like Zn, Cu, Pb, and Cd are soluble at low pH (>3.5), but oxidizing  
 216 conditions are necessary to leach additional Zn. While Ca, K, Na, chlorides, and sulfates exhibit high solubility  
 217 in water (step 1), Al and, to a lesser degree, Fe remain in the residual fraction. Most trace elements including  
 218 REE tend to endure in the residue. The desired pH of the extractions and the sample matrix influence the  
 219 chemical species found in the fractions.



220  
 221 Figure 2. Generalization and summary of the fractions and analytes interested by Sequential Extraction Procedure (SEP) after Van  
 222 Herck et al., 2000; Wan et al., 2006; Huang et al., 2007; Zhao et al., 2008; Chou et al., 2009; Chang et al., 2009.

223 Several authors investigated metal extraction using various aminopolycarboxylic acids such as DTPA,  
 224 EDTA, NTA (Hong et al. 2000). Hong et al., 2000 underlined that the efficiency is not pH-dependent and  
 225 solvent demanding (reagents concentration ranging between 0.5 wt. % and 1.0 wt. %); the extraction  
 226 performed well for Pb (80 % recovery) in moderate alkaline condition with EDTA and DTPA, but the

227 application of such chelating agents is uneconomic at the full scale for their high selling costs. Finally,  
228 experiments using batch extraction under similar conditions have shown that applying electric current can  
229 improve the solubility of some metals. Pedersen et al. (2005) evaluated different assisting agents for  
230 electro-dialytic removals: the best aid in the removal of Cd was an NH<sub>3</sub> solution, perhaps because it helped  
231 build stable tetraamine complexes, while the best aid in the removal of Pb was Na-citrate. The optimum for  
232 removing a group of metals (up to 86% Cd, 81% Cu, 62% Zn, 44% Cr and 20% Pb) used 0.25 M ammonium  
233 citrate/1.25 % NH<sub>3</sub> solution (Pedersen et al., 2005).

### 234 2.3. Current Options for Resource/Material Recovery from MSWI 235 residues

236 Since the early 1990s through the research programs known as NITEP (National Incinerator Testing  
237 and Evaluation Program) and WASTE (Waste Analysis, Sampling, Testing, and Evaluation) which were  
238 pioneered by Canada and the USA, MSWI-BA and MSWI-FA have been the focus of years of research efforts  
239 (Chandler et al. 1997). Several processing techniques for MSWI residues have been proposed to recover  
240 metals of economic interest and secondary raw materials, minimize harmful metals releases, and improve  
241 the final residue environmental status. Commonly, MSWI residues are treated initially with separation  
242 techniques, sometimes tailed by thermal treatments or stabilization or solidification processes (Kuboňová et  
243 al. 2013; Sabbas et al. 2003). Separation technologies consisting of physical-mechanical separation have been  
244 the most popular options because of their relative technical and economic feasibility compared to advanced  
245 treatment processes. Physical and mechanical treatments of MSWI residues aim primarily at:

- 246 i. Recovering concentrated stream fractions (e.g., ferrous- and non-ferrous metals)
- 247 ii. Improving the final residue quality for its reuse or inert landfilling
- 248 iii. Achieving mineral beneficiation before hydrometallurgical processes (as a pre-treatment)

249 A plethora of metals, notably aluminum, iron, copper and other base metals, can be obtained at  
250 different purity levels by simple physical/mechanical separation. Before the MSWI-BA are piled up, a drum  
251 magnetic separator often recovers the biggest magnetic bars/alloys that can be sold to metal refiners.  
252 Various systems can further divide non-ferrous and ferrous fractions of MSWI-BA with rather high efficiency  
253 during the processing of these stockpiles. The non-ferrous part is rich in Au, Ag, Cu, Al, Pb, Zn and Sn and is  
254 commonly preferred for their recovery (Muchova et al., 2009; Biganzoli and Grosso, 2013). To optimize the  
255 recovery of Cu, Ag, Pb, Sn, and Zn from a heavy fraction and an Al-rich product from the light fraction,  
256 separation techniques such as magnetic density separation, kinetic gravity separation, and Eddy current  
257 separation are frequently employed. A final thermal treatment step to stabilize inorganic compounds and  
258 destroy organic contaminants could be suitable. However, due to high costs, such as in the case of vitrification  
259 by re-melting (1200-1400°C), they are hardly applied, although they can suite in post-processing of mineral  
260 concentrates or stabilization in dedicated plants.

261 The recovery efficiency likely increases after size reduction steps and washing with water is suitable  
262 for removing unwanted compounds such as easily soluble salts and sulfates. In fact, natural or accelerated  
263 ageing and water washing are the most adopted treatment for MSWI residues.

#### 264 2.3.1. Bottom ashes

265 MSWI-BA depending on the type of discharge system can usually be treated by wet or dry processing.  
266 While the wet discharge is most adopted, leading to the production of typical quench products of MSWI-BA,  
267 dry discharge systems are rare and technically demanding despite demonstrating some advantages like a  
268 minor number of mineralogical phases formed and the low levels of corrosions and inter-mineral reaction  
269 edges, thus higher recovery potential (Chandler et al., 1997; Eusden et al., 1999; Šyc et al., 2020). In the late  
270 90's dry discharge technology raised limited interest likely because the recovery of secondary resources from  
271 waste was believed to be a less critical issue.

272 Ageing, washing, and limited crushing are the key process for re-using MSWI-BA in the construction  
273 industry. To further promote residue stabilization and reduce leaching, the addition of Al(+3) and Fe(+3) salts,  
274 cement or other bonding agents during ageing is also used. The MSWI-BA treatment trains rely on physical-  
275 mechanical treatments including density separation, sieving, sensor-based sorting, Eddy current separation,  
276 and even hand-picking. The recovery of ferrous (FeF) and non-ferrous (n-FeF) metal fractions by Eddy current  
277 separators is widespread (Smith et al., 2019), favoring the marketability of added-value streams as well as  
278 BA acceptance at smelters or refiners. Dry technologies are more efficient than wet processes regarding  
279 water consumption and, to some extent, reduced transport costs (due to reduced weight and volume).  
280 However, the main drawback of dry processing is abundant dust formation (Šyc et al., 2020).

281 The first installation of MSWI-BA treatment plant came in 1995. Only two sieved fractions, fine  
282 (<4mm) and coarse (4–45 mm), were designed to undergo stepwise magnetic and Eddy current separators  
283 achieving average outputs of 36 wt. % FeF and 1.9 wt. % n-FeF (Chandler et al., 1997; Sabbas et al., 2003).  
284 However, the total Fe content in FeF was only 20–30 wt. % due to agglomeration with other minerals. Similar  
285 treatment trains built after the 2000s suited medium- to low-capacity MSWI plants and showed recovery  
286 efficiency of around 80 wt. % FeF and 9-48 wt. % n-FeF with enhanced Fe concentrations and aluminium  
287 products recovery (Grosso et al., 2011; Šyc et al., 2020). In countries like Switzerland and The Netherlands,  
288 implementing the best available practices is mandatory by legislation (e.g., The Netherlands' Green Deal).

289 Regarding commercially available treatment methods, MSWI-BA are usually sieved using bar seizers,  
290 trommel, vibrating screens, and flip flow screens (the latter only for wet treatments). In advanced plants,  
291 tens of fractions can be sorted for enhanced metal recovery. However, sieving can be expensive with a water  
292 content < 10 % because appropriate dust control during the handling of the material must be assured, and  
293 the crushing changes the size distribution likely precluding residual fraction utilization where well-sorted  
294 materials are required (Hyks and Hjelm, 2018). Density separation is another effective method for the

295 recovery of different components, such as copper, gold, and brass showing a significant density contrast  
296 compared to MSWI-BA matrix ( $2700 \text{ kg/m}^3$ ). Density separation does not apply for Al recovery because its  
297 density resembles that of bulk MSWI-BA, so it is preferably recovered using magnetic methods. Belt and drum  
298 are the two main devices commercially available. Multi-step magnetic separation is typically used for sieved  
299 fractions in advanced treatment plants before the Eddy current separation stage. Ballistic separation (patent  
300 WO 2009/123452 A1) is a cutting-edge technology used in advanced dry recovery processes that  
301 mechanically separates the fine particles ( $< 2 \text{ mm}$ ) associated with the moisture content. This device can  
302 couple with conventional dry separation processes, improving performance. Sensors-based separation  
303 technologies in MSWI residues processing are quite innovative and mainly used for separating glass and  
304 metal particles (Bunge, 2018). Among these, magnetic induction separation based on electromagnetic  
305 sensors is capable of identifying types of metals and alloys in the fraction coarser than  $4 \text{ mm}$ . Other types of  
306 sensors include X-ray fluorescence to detect different metals, optical sensors for distinguishing shapes,  
307 colored or transparent materials. Still, they are rarely applied to MSWI residues processing.

308         The most used processing options are dry technologies tailored for wet discharged MSWI-BA (e.g.,  
309 Holm and Simon, 2017), even though dry discharge is experiencing a renaissance tied to its ability to avoid or  
310 minimise the negative effects of the formation of reaction by-products after quenching, mainly credited by  
311  $\text{Ca(OH)}_2$ ,  $\text{CaCO}_3$ , Friedel's salt and hydrocalumite (Inkaew et al., 2016). The KEZO MSWI plant in Switzerland  
312 is one example of dry treatment of dry discharged MSWI-BA that yields around  $10 \%$  FeF,  $4.5 \%$  n-FeF, and  
313  $1.1 \%$  glass, generating a total revenue of  $95 \text{ CHF/t}$  of dry MSWI-BA with a total consumption of about  $16$   
314  $\text{kWh/t}$  of treated waste (Böni and Morf, 2018). However, efficient recovery of the heavy n-FeF can increase  
315 the revenues due to its precious metals content. Notably, the fraction with particles  $< 0.3 \text{ mm}$  is sold without  
316 treatment at a likely depreciated value despite a potentially significant content of marketable metals.

317         On the other hand, fervor is on the development of wet technologies for the treatment of MSWI-BA  
318 that, however, implies a massive use of water as a primary limiting factor. Ageing is typically not included in  
319 the treatment to avoid a detrimental effect from the formation of mineral coatings. The first wet technology  
320 pilot plant for metal recovery came in 2005 in Amsterdam, The Netherlands. The treatment plant allows to  
321 recover inert granulates for building materials and marketable metal fractions of different levels of purity,  
322 equipped with several wet processing stages such as wet gravity separator, the wet eddy current separator,  
323 and the wet magnetic separator (Muchova et al., 2009). Although a recovery efficiency up to  $83 \%$  FeF and  
324  $73 \%$  n-FeF, the plant never went to full scale, mainly due to the high water-demand and costs for water  
325 treatment. Another example is the Brantner&Co. plant in operation since 2013, located on an Austrian landfill  
326 site (Stockinger, 2018). With a treatment capacity of about  $40,000 \text{ Mg/year}$  of MSWI-BA, it counts on two-  
327 step magnetic separation, including overbelt magnets, separating iron scraps, and fine ( $>50\text{mm}$ ) and large  
328 ( $<50 \text{ mm}$ ) fractions. A wet jig further separates material streams by density: a fraction of carbon-based

329 materials and floating plastics, the heavy (density < 4,000 kg/m<sup>3</sup>) n-FeF containing copper, brass, stainless  
330 steel, and precious metals, and the light n-FeF mainly composed of Al-bearing materials. One wet technology,  
331 installed in 2016 in Alkmaar, The Netherlands, and first developed by the Boskalis Company in response to  
332 the Netherlands' Green Deal, has a treatment capacity of about 240,000 Mg/year of MSWI-BA. This  
333 technology separates different fractions using dry sieving instead of a wet drum sieve, and then each fraction  
334 is washed to remove soluble salts and metals. A bar sizer separates fine (>40mm) and large (<40mm)  
335 particles, followed by magnetic separation for large particles, which, in turn, removes iron scrap and stainless  
336 steel as a first value-added material. The fine particles fraction undergoes a wet drum sieve and a vibrating  
337 screen. However, the main drawback is the production of large amounts of sludge with a high concentration  
338 of heavy metals according to the mass balance of the Alkmaar plant (Born, 2018).

339 Metal recovery can occur on-site, preferably at big MSWI plants where the flow of residues can justify  
340 the investment leveraging on transportation costs. Another option is to establish centralized or mobile  
341 treatment plants serving several MSWI plants, but they usually demonstrate lower efficiency than on-site  
342 plants (Šyc et al., 2020). Nowadays, seven MSWI plants implemented with dry extraction system for MSWI-  
343 BA are operational in Europe (5 plants in Switzerland and 2 plants in Italy). The main drawbacks of this  
344 technology are tied to the need for further treatments to allow afteruse of MSWI-BA in the construction  
345 industry and control or better recover the finest fractions that must be safely managed (Böni and Morf, 2018).  
346 Especially the numerous stages of crushing lead to abundant dust formation and unfavorable grain-size  
347 distribution curve for residue's reuse in the production of building materials. The high investment required  
348 for upgraded treatment plants stems from the demanding crushing stages, the presence of multi-step  
349 magnetic separation, and sensor-based sorting systems.

350 Each treatment plant is unique, although the processing methods can be the same. The recovery rate  
351 increases with the number of recovery devices: more than ten eddy-current separators can be used in series,  
352 still influencing the capital costs. According to the 2018 technical report of European Integrated Pollution  
353 Prevention and Control Bureau, the electricity consumption of MSWI treatment plants averages 3 kWh/t of  
354 treated waste, sometimes reaching up to 15 kWh/t (EIPPCB, 2018).

### 355 2.3.2. Fly ashes

356 Disposal of MSWI-FA through backfilling also after packaging in "big bags" made of a resistant  
357 material is viable underground in natural cavities such as salt mines. The most used option is landfilling after  
358 an appropriate treatment such as stabilization or solidification using other types of wastes (e.g., co-landfilling  
359 with red mud) or binders (Quina et al., 2018; 2008). The stabilization processes suffer, however, some  
360 limitations such as increased mass and volumes that may result in unsustainable space demand. Landfilling  
361 after thermal stabilization (vitrification, sintering, thermal treatment with mixed wastes) is widely used as it  
362 can reduce leaching of inorganic pollutants and destroy toxic organic components. However, LCA analysis

363 demonstrated that thermal treatments of MSWI-FA are uneconomic due to the high energy demand to  
364 achieve suitable treatment temperatures (Fruegaard et al., 2010). The poor magnetic susceptibility of MSWI-  
365 FA compared to MSWI-BA, due to lower concentration of Fe and magnetic minerals (Funari et al., 2020),  
366 prevents the use and scalability of magnetic separation methods for material upgrading and FeF and n-FeF  
367 recovery that is rarely attempted.

368 Decontamination/detoxification is the first pathway towards recovery and recycling of MSWI-FA as  
369 secondary raw material for other applications avoiding landfilling (e.g., reuse for preparation of geopolymers;  
370 Sun et al., 2013). Different methods can be performed, such as carbonation (Costa et al., 2007; Wang et al.,  
371 2010), washing, leaching or bioleaching (Benassi et al., 2016; Funari et al., 2017), electrodialysis (Parés Viader  
372 et al., 2017), and mechanical methods, e.g., ball milling (Chen et al., 2016). MSWI-FA for the production of  
373 secondary raw materials is well suited for ceramic materials, epoxy composites, glass-ceramics, zeolite-like  
374 materials, low-cost stabilizers and buffering agents, lightweight aggregates and secondary building materials  
375 for geotechnical applications, adsorbents including high capacity materials for energy storage (Quina *et al.*,  
376 2018 and reference therein). Other practical applications include biogas production, CO<sub>2</sub> sequestration  
377 (Bacocchi et al., 2010), filler for embankment and landfill top cover (Brännvall and Kumpiene, 2016). The  
378 primary aim of MSWI-FA washing is the removal of easily soluble salts to improve  
379 decontamination/detoxification treatments. The Solvay Process developed during the 1860s is extensively  
380 used to recycle sodium chloride from MSWI-FA produced by wet or semi-dry APC system (Chandler et al.,  
381 1997), especially from FA collected at the sodic bag filters. Recently, Stena Recycling A/S developed the  
382 HALOSEP® process to remove and recover chlorine salts (mostly CaCl<sub>2</sub>) and a concentrate metal cake from  
383 MSWI-FA. The key application for these salt products is road de-icing in compliance with the criteria CEN TC  
384 337 WG1. The metal filter cake shows an average concentration of around 38-40 wt. % Zn, so it is particularly  
385 suited for Zn recovery at the smelter.

386 Several efforts have been made in recent years for metal recovery from MSWI-FA with commercial  
387 potential, such as Zn (Fellner et al., 2015), P (Kalmykova et al., 2013), Cu, and other precious and rare metals  
388 (Morf et al., 2013; Allegrini et al., 2014; Funari et al., 2016). The removal or stabilization of hazardous  
389 substances using traditional robust means such as water washing or co-landfilling is preferred over methods  
390 aiming at metal recovery so that, for example, bioleaching and electrocoagulation or eventual landfill mining  
391 strategies are still far from industrial rollout. However, some successful examples exist at the demonstration  
392 scale such as co-mixing with rice husks (Benassi et al. 2016) to recover an environmentally compatible  
393 secondary raw material. The FLUWA process dedicated to recovering Cu and volatile toxic metals such as Zn,  
394 Pb, Cd, and organic substances started in 1997 in Switzerland (Bühler and Schlumberger, 2010). It further  
395 allows metal separation and recovery through multistep acidic and neutral scrubbing and oxidation,  
396 providing a residual MSW-FA less prone to environmental leaching. Organic substances remaining in the filter

397 cakes again represent a key issue, requiring further incineration cycle in the MSWI plant for complete thermal  
398 destruction. The new FLUWA + FLUERE process allows up to 60–80% Zn, 80–95% Cd and 50–85% Pb and Cu  
399 removal (Quina et al., 2018). The FLUREC implemented in 2012 at MSWI plant Zuchwil, Switzerland, can  
400 recover up to 300 Mg/year Zn; however, purification of Zn-rich cake and filtrates is a prerequisite.

401 The use of MSWI-FA for the production of cement is sought because this can limit the enormous  
402 environmental impact of the cement industry tied to massive anthropogenic CO<sub>2</sub> (from calcination) and other  
403 gaseous emissions (NO<sub>x</sub>, organic compounds, and toxic volatile elements), the consumption of energy and  
404 natural resources (Lederer et al., 2017). The main options for MSWI-FA reutilization in the cement industry  
405 include the production of blended cement and the co-processing in the cement kiln to produce the clinker  
406 (e.g., Bertolini et al., 2004). Co-processing of MSWI-FA containing high amounts of Ca-bearing phases is viable  
407 to substitute a part of the raw material input (Chandler et al., 1997) up to about 40-50% (Saikia et al., 2015).  
408 Earlier studies suggested that the leaching rates of potentially toxic elements are very low in the short term.  
409 However, Lederer et al. (2017) surmised that volatile metals such as Cd and Pb are reincorporated into the  
410 cement during the regular production process. Considering that the chemical composition of MSWI-FA is not  
411 stable over time, particular care should be given to the final cement quality and the emissions at the  
412 smokestacks.

### 413 3. Biotechnology for MSWI ash management

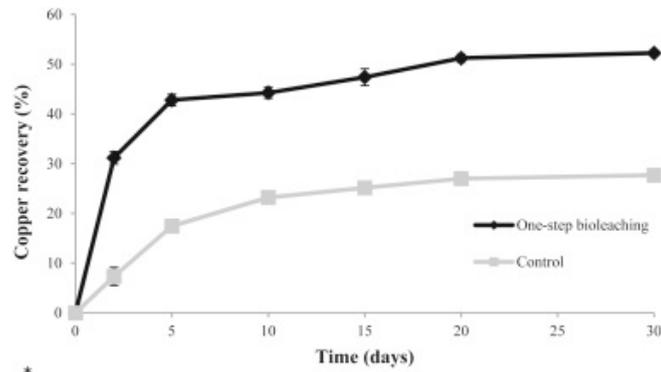
#### 414 3.1. Brief Overview of Biohydrometallurgy

415 Biohydrometallurgy is a branch of metallurgy devoted to hydrometallurgical extraction mediated by  
416 microorganisms. Its use in the recovery of metal from primary ores and in the treatment of mine tailings is  
417 factual while gaining more and more popularity in treating secondary resources.

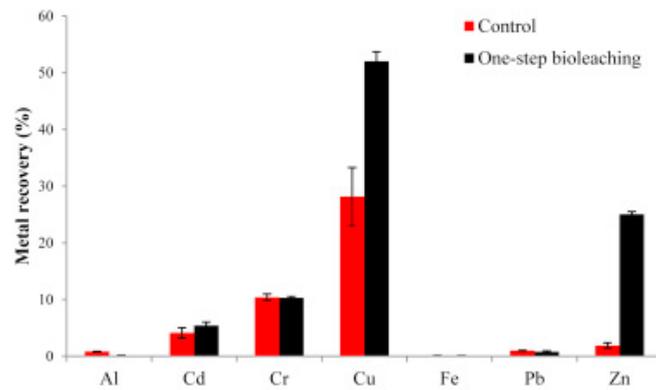
418 Extremophile microorganisms adapted to thrive under extreme environmental conditions (e.g.  
419 salinity, pH, temperature). In particular, acidophilic bacteria are able to grow, for example, in acid mine  
420 drainage (AMD) at low pH (< 2), high concentrations of sulfate and metals, particularly iron, giving it a deep  
421 red color. Microbiological studies conducted on Rio Tinto water streams demonstrated the occurrence of  
422 precise ecological niches of microbes. It is also not rare to identify new species of microorganisms. Their  
423 metabolism evolved towards the use of available nutrients (e.g., metals) contained in solid minerals (e.g.,  
424 pyrites) for their energy supply, enabling life in extreme environments. Minerals supposedly oxidize without  
425 bacteria or biological interactions, but microorganisms make the process much faster. It was demonstrated  
426 in the '70s that the oxidation of ferrous iron operated by *Acidithiobacillus ferrooxidans* was about a million  
427 times faster than abiotic chemical oxidation (Lacey and Lawson, 1970). Strains of extremely thermophilic  
428 archaea (*Acidianus sulfidivorans*) are found to withstand pH between 0.35 and 3.0, temperatures of 45-83°C  
429 in the presence of sulfur minerals such as pyrite, chalcopyrite and arsenopyrite (Brierley and Brierley, 2013).

430 Recently, improved kinetics of biomineralization and biodissolution has also been studied for carbon capture  
431 and storage e.g., by observing microbial carbonic anhydrase catalyses (Bhagat et al., 2018). Thermophilic  
432 microorganisms can survive at higher temperatures than mesophiles and guarantee faster kinetics and higher  
433 yields. However, the use of special catalysts can make the mesophiles exceptionally performing to bioleach  
434 complex minerals. For example, *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* strains  
435 supplemented with ferrous iron are valuable for treating chalcopyrite or molybdenite (Brierley and Brierley,  
436 2013). Empirical studies demonstrated that *Acidithiobacillus thiooxidans* and *Acidithiobacillus caldus* reduce  
437 sulfur accumulation and improve process efficiency, e.g., by enabling bioleaching for sphalerite and  
438 arsenopyrite (e.g., Suzuki, 2001; Vera et al., 2013). Bioleaching and biooxidation processes promoted  
439 sustainability in the recovery of base metals (Zn, Cu, Ni, Mo) and precious metals (Au, Ag) trapped inside  
440 sulfur minerals.

441 The knowledge of usable microorganisms has significantly increased over the past decades, with  
442 higher extraction rate of metals even from complex mineralogical assemblages like waste materials, as  
443 demonstrated by the use of extremophiles (e.g., Ramanathan and Ting, 2016) , which is illustrated in Figure  
444 3 for the kinetics and extent of recovery of metals via single-stage bioleaching. However, some criticalities  
445 were promptly highlighted, such as the need to monitor bacterial growth and the difficulty in guaranteeing  
446 the correct and stable functioning of the treatment plants over time. The development of corrosive  
447 conditions inside the reactors evoked investments in special building materials, reactors and propellers  
448 designs. It is necessary to continue contaminating knowledge in bioleaching by encouraging “among  
449 scientists and engineers to enhance development of this very important technology for an industrial sector  
450 whose successful future is increasingly dependent on technological advances”, as postulated by Brierley and  
451 Brierley (2013).



\* Copper recovery in one-step bioleaching(%) denotes the recovery obtained with the bacteria without subtracting the recovery obtained with the uninoculated media (control).



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453

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Figure 3. Kinetics of Cu bioleaching (top) and recovery of metals (bottom) from municipal solid waste incineration fly ash by *Alkalibacterium* sp. TRTP6 ( $n = 3$ ). Reproduced with permission from Elsevier (5493660184237) (Ramanathan and Ting, 2016).

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### 3.2. Bacterial leaching in sulfidic environments and their industrial applications

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The first attempt to understand the mechanism behind bacterial leaching was studying the metal sulfides bioleaching reactions. This effort was accomplished with a multi-disciplinary approach, including mineralogy, chemical bound theory, and biochemistry. In sulfidic environments it is possible to find many microorganisms sulfur and iron oxidizers such as, *Acidithiobacillus thiooxidans*, *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Acidianus/Sulfolobus* spp., *Metallogenium* spp., that can operate direct and indirect leaching *sensu* Sand et al. (1995). Although debated (Sand et al., 2001; Vera et al., 2013; Yin et al., 2019), some co-participated reactions can be drawn:

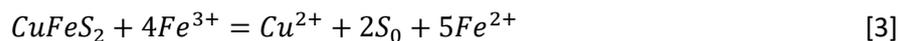
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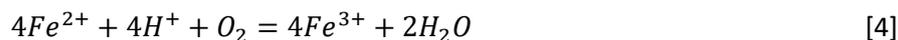
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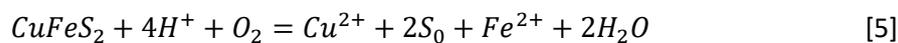
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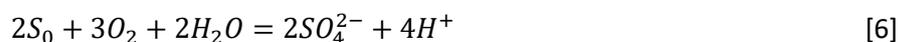
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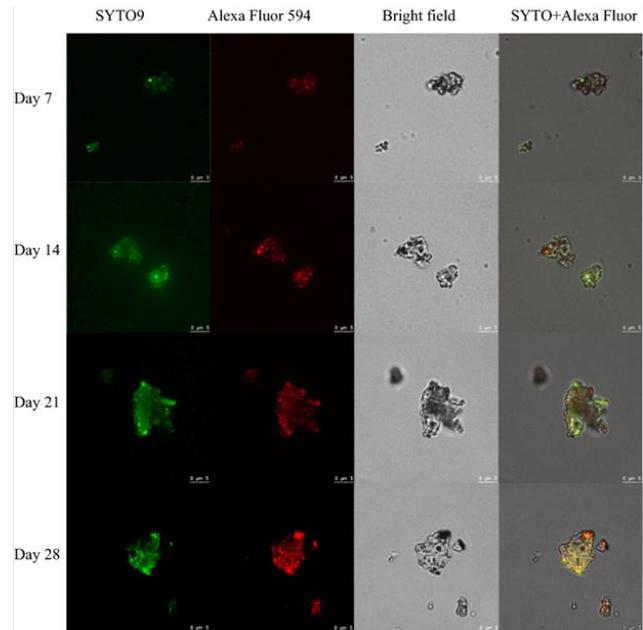
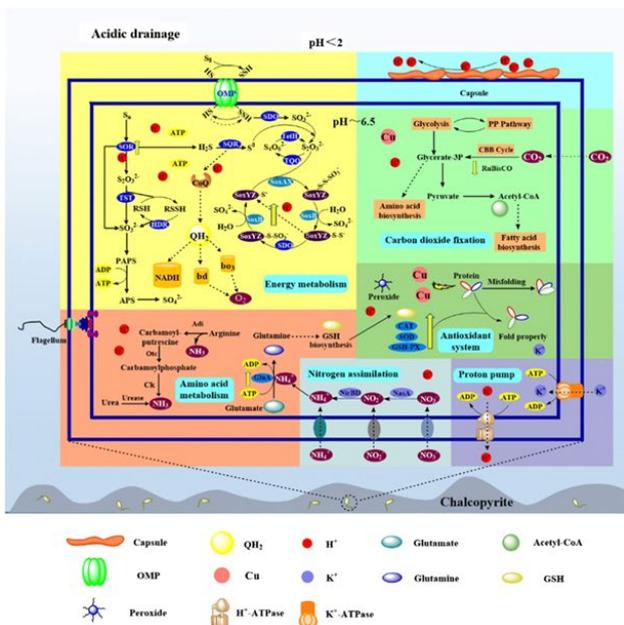


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469 Direct or contact bioleaching generally assumes a metal sulfide-attached cell oxidizes the mineral by  
470 an enzyme system with oxygen to sulfate and metal cations. To dissolve a metal sulfide [Eq. 1] the indirect  
471 or non-contact mechanisms grounds on the oxidizing capacity of  $\text{Fe}^{3+}$  ions. During this chemical reaction,  $\text{Fe}^{2+}$   
472 ions and elemental sulfur ( $\text{S}_0$ ) are poly-sourced [Eq. 3, 5], promoting a cyclic reaction where  $\text{Fe}^{3+}$  and sulfide  
473 moiety is reduced and oxidized progressively [Eq. 4, 6] thanks to an ancillary engine of S-oxidizers. It is worth  
474 mentioning Extracellular Polymeric Substances (EPS) allow contact and mineral decomposition that  
475 preferably start in crystal defects (Fletcher and Savage, 2013; Gehrke et al., 1998), where the  $\text{Fe}^{2+}$  ions are  
476 more accessible (Dziurla et al., 1998). The need for iron is as important as the S-cycle: when the  $\text{Fe}^{3+}$  interacts  
477 with the electronic structure and (leach) the surface of the mineral, and sulfur de-bonds from sulfide crystal  
478 lattice, the thiosulfate releases  $\text{Fe}^{2+}$  ion and protonation forms  $\text{H}_2\text{S}$ , which reacts with the oxidative  
479 compounds (e.g.,  $\text{Fe}^{3+}$ ,  $\text{O}_2$ ). This starts a radical chain reaction that produces  $\text{S}_0$  as an end-product, which is  
480 used by bacteria (e.g., *Acidithiobacillus thiooxidans*) to produce sulfuric acid.

481 The regulatory strategies of *A. thiooxidans* during bioleaching of low-grade chalcopyrite were studied  
482 in-depth by Yin et al. (2019), illustrated in Figure 4, through physiological observations matched with  
483 transcriptomic approach. The authors observed that during the  $\text{CuFeS}_2$  bioleaching process the bacterium  
484 endeavor's three mechanisms to keep the pH homeostasis: i) externalizes  $\text{H}^+$  by ATPase activity; ii) the amino  
485 acid metabolism becomes more active lowering cytoplasmic acidification by proton consumption via the  
486 tricarboxylic acid (TCA) cycle (i.e., Krebs cycle); iii) prevents proton invasion increasing the amount of  
487 unsaturated fatty, particularly cyclopropane, and so far the density of the cell membrane. At the  
488 transcriptomic level the genes involved in sulfur metabolism were significantly up-regulated while those  
489 associated with the flagellar assembly and carbon metabolism were down-regulated, suggesting a strategy  
490 of alternative energy production from the first and reduction of energy consumption with the second.  
491 Noteworthy, confocal laser scanning microscopy (CLSM) analysis indicated that EPS and biofilm formation  
492 might also improve strain resistance to the stress condition (Figure 4). Niu et al. (2016) studied a real-scale  
493 bioleaching system of the Dexing Copper Mine (Jiangxi, China) to provide insights into the bacterial  
494 community structure and mechanisms involved at three different processing stages. According to  
495 phylogenetic analysis based on 16S rRNA metabarcoding, all three groups shared 259 OTUs (Operation  
496 Taxonomic Unit), but demonstrated a significant microbial shift in the process line. Gene arrays revealed a  
497 difference in functional gene structures of the microbial communities and metabolic pathways potentially  
498 related to bioleaching. Genes involved in carbon fixation, polyphosphate degradation, sulfur oxidation, and  
499 denitrification were abundant in a sample from the heap; while genes related to carbon degradation,  
500 polyphosphate synthesis, sulfite reductase, and nitrification in the spent medium leachate (Niu et al., 2016).



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Figure 4. Adaptation mechanism model of *A. thiooxidans* in bioleaching of low-grade chalcopyrite (left); visualization of EPS and cell attachment on chalcopyrite surface when bioleaching at 7, 14, 21, and 28 days by CLSM (right). Reproduced with permission from Springer Nature (5493660654399) (Yin et al., 2019).

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There is a long list of microorganisms used for sulfur-bearing ores bioleaching, but their adaptive mechanism to harsh environments remains disputed. Such acquired knowhow is of fundamental importance for creating strains with greater stress tolerance, crucial for commercial use in industrial bioleaching (Jerez, 2008). A review of bacterial strains possessing unique characteristics critical for commercial-scale bio-processing is reported elsewhere (Brierley and Brierley, 2013). The first significant biohydrometallurgical operation took place at the Rio Tinto copper-Cu mine in Spain from 1950 to 1980, where bioleaching was primarily done in heaps and dumps on-site. Several industrial plants for metal recovery (especially Cu and Au) have been started in America, South Africa, Uganda, and Australia. The percentages of minerals extracted were very high: up to 95% Au was extracted from crude high-graded ores and Cu yields were up to 65% from chalcopyrite and up to 98% from some sulfosalts (enargite). Around 85% Mo bioleaching is achievable from molybdenite ( $\text{MoS}_2$ ) using *A. ferrooxidans* and *L. ferrooxidans*, in a six-month timeframe (Bosecker 1997; Brombacher et al., 1998). After numerous developments, the BioCOP™ technology owned by BHP Billiton was commercialized at the Chuquicamata Mine in Chile, showing a production rate of 20000 Mg/year Cu using thermophilic microorganisms to leach sulfide mineral concentrates at temperatures up to 80 °C (Batty and Rorke, 2006). The BioCOP™ technology yields a high-value copper metal product after conventional solvent extraction and electrowinning.

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In commercial applications, biohydrometallurgical methods' advantages can offset net smelter royalties for metals production. For example, mineral beneficiation through bioleaching can decrease refineries and smelters penalty charge associated with high levels of impurity (Gericke et al., 2009). Moreover, secondary bioleaching or spent medium leaching can be used for on-site acid bioproduction to

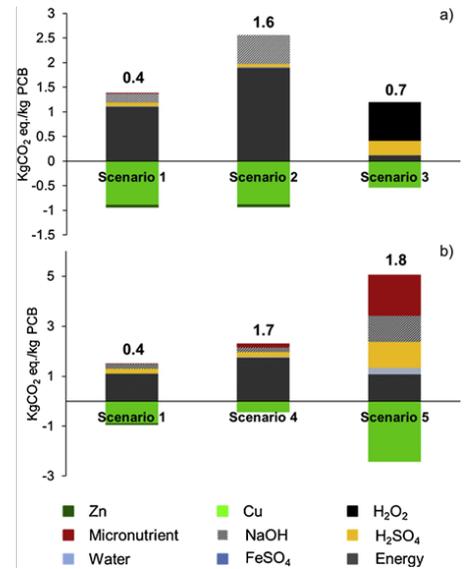
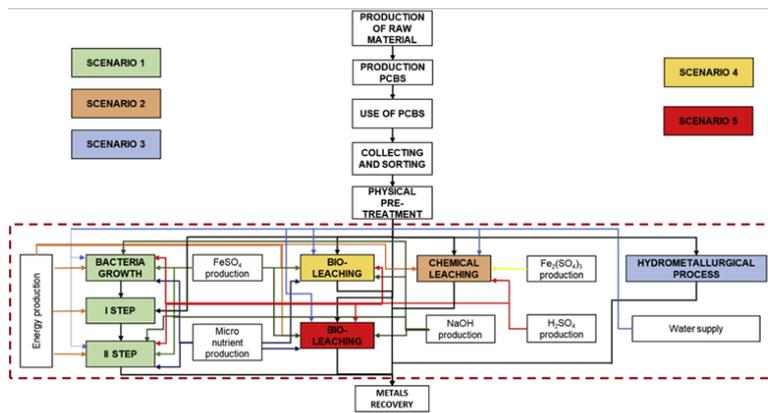
525 replace mineral acid purchases (e.g., Funari et al. 2017) although sulfuric acid costs can be volatile (Moore,  
526 2008). Biohydrometallurgical methods can fit existing infrastructure, such as wet technologies or  
527 electrorefining, avoiding new investments by the companies. Biomining processes are mostly carried out by  
528 stirred-tank and heap reactors, or both combined, especially when a spent medium leaching process is  
529 attempted. In general, they can be divided into irrigation-type and stirred tank-type, as the two main  
530 categories. Irrigation-type processing is primarily deployed *in situ* (e.g., heap, dump, and slope bioleaching  
531 techniques), being slope bioleaching more affordable compared to other techniques, while heap bioreactors  
532 represent the primary option because they are cheaper and easier to operate than stirred-tank reactors  
533 (Gahan et al., 2013; Rawlings, 2004). The latter, however, are less time-consuming and offer more control  
534 and predictable performances. A typical heap bioleaching system operates over a 400–600-day period,  
535 starting with the preconditioning phase of 1–6 weeks. In Chile, the Bala Ley plant for low-grade Cu minerals  
536 ore processing equips a dump bioleaching system, where cycles of preconditioning, irrigation, maturation,  
537 and washing can last years (Rawlings, 2002). Several (hybrid) irrigation-type methods were used to treat low-  
538 grade uranium ore at the Denison Mine in Ontario, Canada. The primary problems associated with impending  
539 leachate loss in the environment were addressed by these procedures (Bosecker, 1997; Rawlings, 2002; 2004;  
540 Rawlings et al., 2003). In South Africa and Australia, pilot-scale plants have demonstrated technical feasibility  
541 for Ni recovery, with Queensland Nickel as a relevant stakeholder (Gahan et al., 2013). Similarly, the  
542 Talvivaara mine in Finland tested heap bioleaching, with operations likely terminated in 2018. A famous  
543 example of biooxidation plant in stirred tank reactors is at the Fairview Mine in South Africa, which used the  
544 BIOX process for pretreatment of gold-bearing sulfide ores (Kaksonen et al., 2014). Bioleaching as a  
545 pretreatment in a multi-stage process increased recovery efficiency, especially for extraction of precious  
546 metals and Co. Gu et al. (2018) provide a new list of pretreatment methods based on bioleaching. BacTech  
547 Mining Company, Canada, can treat refractory Au concentrates with the further aim of recovering Co, Ni, and  
548 Ag, and remediating As-tailings (Rawlings et al., 2003; Gahan et al., 2013). Biooxidation plants equipped with  
549 stirred tank reactors to recover Co from enriched mining waste and tailings can be found at Sansu, Ghana,  
550 Liazhou, Shandong province, China, the Kasese Cobalt Kilembe Mine, Uganda, and Youanmi Gold Mine,  
551 Australia. The latter (Youanmi project) exploits some thermophilic bacteria possessing an optimum  
552 temperature between 45 °C and 55 °C (e.g., *Sulfobacillus thermosulfidooxidans*). Numerous pilot and  
553 demonstration-scale processes of stirred tank bioleaching prove the potential for recovering other metals  
554 from sulfides, including Ni, Co, Zn, and rare metals. Patented processes of Zn bioleaching involving solvent  
555 extraction and electrowinning are also available (Steemson et al., 1994).

### 556 3.3. Biohydrometallurgical processes for the circular economy

557 In order to promote a circular economy, biotechnology for metal production should be eco-friendly  
558 and cost-effective and adapt to the waste management sector. The continuously increasing high demand for

559 critical raw materials and rare metals for technological development has led not only Europe, but also other  
560 industrialized countries, to look at diversified sources of supply such as mining waste, mine tailings, and  
561 alternate anthropogenic stocks and flows that frequently exhibit a hidden metal value (Baccini and Brunner,  
562 2012). Biomining is suitable for treating such materials because they are flexible for optimization and can  
563 prove beneficial to decontamination, coupling metal recovery with environmental remediation. This has led  
564 to recent advances in fine-tuned methods to treat anthropogenic wastes. Despite the modest and variable  
565 ore metal concentrations in anthropogenic flows like MSWI residues, bioleaching methods can allege lower  
566 capital costs than other robust technologies in waste management (Funari et al., 2017).

567         Bioleaching for metal extraction from anthropogenic materials such as electronic scraps, various  
568 types of slag and flying ashes, secondary solid wastes, and sludge is largely investigated as an economical and  
569 eco-friendly process (Gahan et al., 2013; Meawad et al., 2010; Lee and Pandey, 2012; Srichandan et al., 2019).  
570 Bioleaching of metals through the use of thermophilic and acidophilic bacteria has been primarily  
571 investigated to recover metals from electronic scrap, especially printed circuit boards (Ilyas et al., 2007).  
572 Among the strategies adopted to achieve higher speeds of metal leaching from electronic waste, it was found  
573 that a mixed consortium can show the maximum efficiency of leaching, and a pre-washing might be useful  
574 to remove easily soluble metals (e.g., Cl, Na) or light fractions (e.g., plastics) toxic for bacteria. Satisfactory  
575 leaching yields are achievable with *S. thermosulfidooxidans*, an example of moderate thermophilic bacteria,  
576 but the presence of Pb and Sn precipitation complicated separation and purification (Ilyas et al., 2007).  
577 Recently, Becci et al. (2020) confirmed that pre-crushing to obtain a granulometry > 0.5 mm is a good strategy  
578 to enhance bioleaching of printed circuit boards using iron oxidizers. However, the formation of passivation  
579 layers (e.g., jarosite) remains a limiting factor that reduces kinetics dramatically. In their experiments,  
580 bioleaching processes using monoclonal cultures of *A. ferrooxidans* and *L. ferrooxidans* were compared,  
581 emphasising oxidation of iron species. The latter microorganisms are very sensitive to metals toxicity and  
582 perform a slow conversion of Fe<sup>2+</sup> in Fe<sup>3+</sup>, resulting in relatively low recovery of around 40% Cu and 20% Zn,  
583 while bioleaching with *A. ferrooxidans* yielded around 95% Cu and 70% Zn and showed high conversion of  
584 Fe<sup>3+</sup>. Further comparing different scenarios in terms of carbon footprint (Figure 5), they found the optimum  
585 condition with further bioreactor size reduction can achieve four times reduction of the CO<sub>2</sub>-eq per kilogram  
586 of treated material compared to the best bioleaching processes reported in the literature (Becci et al., 2020).



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Figure 5. System boundaries considered for the carbon footprint assessment (left); carbon footprint of the five considered approaches (right). (Function unit: 1 kg of shredded PCBs). Reproduced with permission from Elsevier (5493661285952) (Becci et al., 2020).

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The ability of microorganisms to interact with Rare Earth Elements (REE) is suitable for metallurgical separation and environmental technology. The microbial capacity to interact with REE and the REE adsorption sites were investigated in depth using synchrotron-based techniques on genetically engineered strains clarifying the REE adsorption mechanisms. Recognized patterns can be generalized: surface adsorption, adsorption on extracellular biopolymers, cellular absorption, and adsorption on extracellular biominerals (Moriwaki and Yamamoto, 2013). The binding sites of the bacterial cell wall suggested to interact the most with REEs and determine the strain selectivity are phosphate and carboxyl groups. In the recovery of metals such as Ni, Co, and Mo from spent catalysts low yield were reported for acidophilic bacteria, however, it could be improved using *Escherichia coli* due to its capacity to produce reducing conditions even in acidic environments (Vyas and Ting, 2020). Vyas and Ting (2020) reported that higher Mo extraction (from 72 to 96 %) was observed in the spent medium leaching when *E. coli* biomass was kept in contact with the pregnant solutions in a two-step bioleaching procedure. The result suggests a possible biosorption or bioaccumulation mechanism operated by *E. coli* using spent medium indicating a significant involvement of active metabolites such as amino acids. Also, recent studies demonstrate that autochthonous bacteria can be present in wastes and that they could be isolated and tailored for bioprocessing (Ramanathan and Ting, 2016) and bioremediation (Piervandi et al., 2020).

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### 3.3.1. Bioleaching of MSWI residues

Bioleaching of MSWI residues mainly involves ferrous iron and sulfur-oxidizing bacteria (e.g., *A. ferrooxidans*, *A. thiooxidans*), and several species of fungi (e.g., *Aspergillus niger*), which can grow on and around the waste material. Despite numerous bench-scale experiments, no commercial processes for MSWI residues bioleaching are available so far. Biohydrometallurgical processing of MSWI residues suffers

612 considerable limitations when a high pulp density is required to justify short to medium term investments.  
613 The high content of toxic metals, organic materials, and a highly alkaline starting pH can impede microbial  
614 growth and process efficiency. Various leaching organisms show a high tolerance to toxic metals (i.e., 50 g/l  
615 Ni, 55 g/l Cu, 112 g/l Zn), but also the mineralogical composition is of primary importance: a high calcium  
616 carbonate content, such as for several types of MSWI-FA, would be unfavorable because high alkalinity and  
617 the precipitation of gypsum can occur, affecting the overall costs.

618 Bioleaching can extract valuable metals, especially Cu, Zn, Pb, As, Sb, Ni, Mo, Au, Ag and Co, from  
619 MSWI residues with less energy and environmental impact than pyro- or hydro-metallurgical methods.  
620 Ishigaki et al. (2005) studied the bioleaching of Cr, Cu, Zn, Cd, and As from MSWI-FA by sulfur-oxidizing and  
621 iron-oxidizing bacteria, as pure cultures and a mixture of both. The mixed culture showed the best  
622 performance (67% Cu, 78% Zn and 100% for Cr and Cd at 1 % w/v pulp density). Characterization of metal  
623 bioleaching revealed that the acidic and oxidizing conditions remained stable throughout the experiment.  
624 The redox mechanisms coupled with the sulfate leaching brought an increase of ferrous iron enhancing the  
625 Cr, Cu, and As leaching. However, they found that at a higher pulp density (3 % w/v) chromium remained  
626 virtually undissolved (4 % Cr yield). The presence of degradable and non-degradable organic compounds in  
627 MSWI residues exerted no significant changes in the leachability of metals other than Zn (Ishigaki et al., 2005).  
628 An earlier study on microbial leaching (Mercier et al., 1999) elucidated that the following elements can be  
629 removed in decreasing order of extraction rate: Cd, Zn, Pb, Cu, using a pure culture of *A. ferrooxidans*. In the  
630 same work, four different leaching tests were conducted for environmental compliance of the final residues,  
631 and the authors concluded that the leachate from Toxicity Characteristic Leaching Procedure (TCLP) was  
632 within the acceptance criteria only if the final residue's pH was increased to five after the biological  
633 treatment. Still, Cd releases could be an issue concerning regulatory limits. The investigation by Krebs (2001)  
634 reported an example of co-treatments of MSWI-FA using a mixture of strains (*Thiobacillus* genus) in a  
635 suspension of water and nutrients (1 % w/v  $S_0$  powder) and 4 % w/v sewage sludge. The cultivation was  
636 compared to pure *A. thiooxidans* or sewage sludge alone, over 1-3 months. The inoculation with the  
637 combination of sewage sludge and bacteria showed a fast decrease in pH and increased microbial growth. In  
638 the final pH of 1, the efficiency of metal leaching was very similar, with pulp density ranging from 0.5 % to 1  
639 %. More than 80 % Cd, Cu, and Zn, around 60 % Al, up to 30 % Ni and Fe, less than 10% Cr and Pb were  
640 mobilized (Krebs, 2001). Autochthonous bacteria can be used for bioleaching as reported in a study on MSWI-  
641 FA produced in Singapore incineration plant (Ramanathan and Ting, 2016). Thirty-eight different microbes  
642 were isolated and characterized to find the most suitable autochthonous microbe with inherent fly ash  
643 tolerance and ability to thrive in alkaline pH (thus avoiding any pre-acidification of the ash). Besides  
644 *Firmicutes* (90 % relative abundance), three other phyla were identified: *Bacterioidetes*, *Actinobacteria*, and  
645  *$\alpha$ -Proteobacteria*. Among six isolates displaying Cu recovery of about 20% or more, *Alkalibacterium* sp. was

646 tolerant to pH and fly ash, making it a suitable candidate for MSWI-FA bioleaching. Indeed, a one-step  
647 bioleaching with *Alkalibacterium sp.* on MSWI-FA showed 52% Cu and 25% Zn recovery. The high tolerance  
648 of *Alkalibacterium sp.* to metals and substantial bioleaching ability can prompt scaled-up bioleaching with  
649 alkaline bacteria that, at present, do not reach acidophile bioleaching in terms of Cu and Zn removal rates. A  
650 clear advantage of alkaline bioleaching is the higher pulp density (more than 20% w/v), signifying less water-  
651 demand. Hong et al. (2000) tested saponin, a biosurfactant produced by microorganisms and plants, for  
652 metal removal from MSWI-FA. They compared the efficiency of saponins with that of other solvent extraction  
653 (HCl and EDTA) in the pH range 4-9. The saponins leaching was more effective than control acid treatments  
654 for Cr, Cu, and Pb with yields up to 45 %, 60 % and 100 %, respectively, whereas the Fe, Si, Al, and Zn  
655 extraction was not significant. Gonzalez et al. (2017) used cementing bacteria to stabilise MSWI-FA. After  
656 bacteria cementation assays and the assessment of the ad/absorption of metals in the cemented fly ash, they  
657 concluded that *Sporosarcina pasteurii* and *Myxococcus xanthus* are suitable for multiple metal stabilization  
658 (As, Cd, Cr, Cu, Ni, Pb, Sn, and Zn) with some differences concerning trace elements mobility, depending on  
659 the starting concentrations in the samples (Gonzalez et al., 2017).

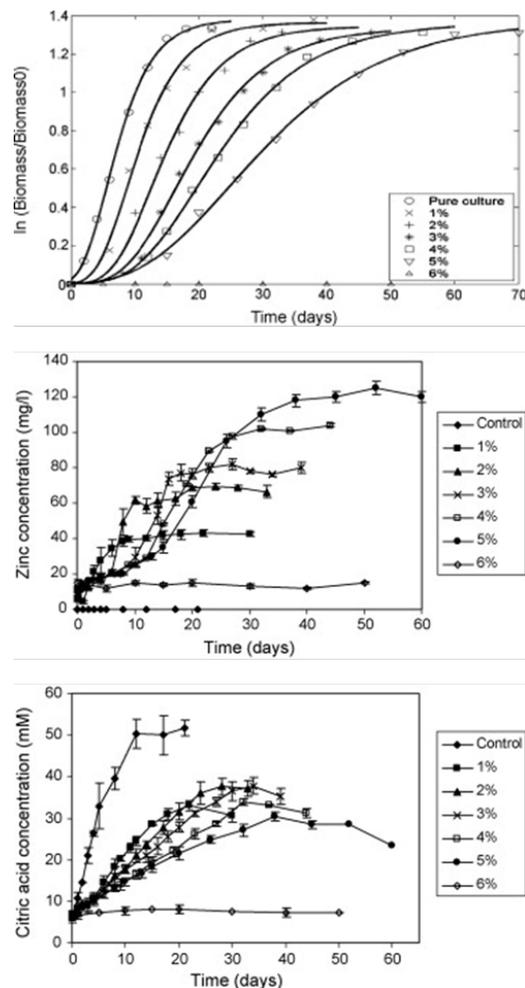
660 MSWI-BA bioleaching has received less attention in the scientific literature because of its less  
661 hazardous nature than MSWI-FA, which allows for direct reuse in the construction sector with minimum  
662 pretreatment. Aouad et al. (2008) studied *Pseudomonas aeruginosa* and MSWI-BA interactions foreseeing  
663 real exposition of MSWI residues to halotolerant bacteria at landfill site. Bioleaching experiments using a  
664 pure culture of *P. aeruginosa* was carried out for 133 days at 25 °C using a modified Soxhlet's device and a  
665 culture medium in a closed, unstirred system and resulted in an increase in pH, a greater immobilization of  
666 Pb, Ni and Zn, and weaker alteration rate of treated MSWI-BA compared to the abiotic control. The authors  
667 explained that the biofilms acted as a protective barrier, thus preventing dissolution by promoting  
668 biomineralization (Aouad et al., 2008). Many halotolerant bacteria can be found at MSWI disposal site since  
669 tolerating the salinity of MSWI residues, but little information is available about the interaction between  
670 bacteria and landfill waste (Sun et al., 2016). *Firmicutes*, *Proteobacteria*, and *Bacteroidetes* as the dominant  
671 phyla, with dominant genera as *Halanaerobium*, *Lactococcus*, *Methylohalobius*, *Ignatzschineria*,  
672 *Syntrophomonas*, *Fastidiosipila*, and *Spirochaeta* are characteristic in municipal waste landfills (Wang et al.,  
673 2017)

674 The acid bioleaching behavior of both MSWI FA and MSWI-BA was investigated at the bench scale  
675 and compared to abiotic leaching (H<sub>2</sub>SO<sub>4</sub>, 10% pulp density, 30 °C, 150 rpm) looking at a wide range of metals  
676 (Funari et al., 2017). A mixed acidophilic culture composed of iron and sulfur-oxidizing bacteria tested on a  
677 one-step bioleaching process yielded >85% Cu, Al, Mn, Mg, and Zn and significant removals of Co, Cr, Pb, Sb,  
678 and REE. Unvalued elements like Ca, Si, and Ti showed low mobility with the tendency to remain in the solid  
679 phase, while the solubility of other trace elements might be selectively enhanced by the cyclic supply of Fe<sup>+3</sup>

680 produced by iron-oxidizing bacteria. Moving ahead, Mäkinen et al. (2019) tested the possibility of heap  
681 bioleaching for the recovery of Zn and Cu from MSWI-BA at the bench scale via column experiments. Leaching  
682 yields varied 18–53% Zn and 6–44% Cu, and they noted that appropriate aeration is the main critical factor  
683 needing further adjustments in future testing. Potentially high Fe and Al, easily dissolved in sulfuric acid  
684 solutions, and different heap behavior due to the heterogeneity of the material can also impede bioleaching  
685 utilization in MSWI residues treatment. However, a balance between bacterial adaptive mechanisms and  
686 nutrient supply can generate savings compared to processes relying on abiotic procedures. Electrochemical  
687 technologies are also promising in the optimization of acidophile bioleaching for MSWI residues (Gomes et  
688 al., 2020), possibly to offset the CO<sub>2</sub> generation of full-scale applications.

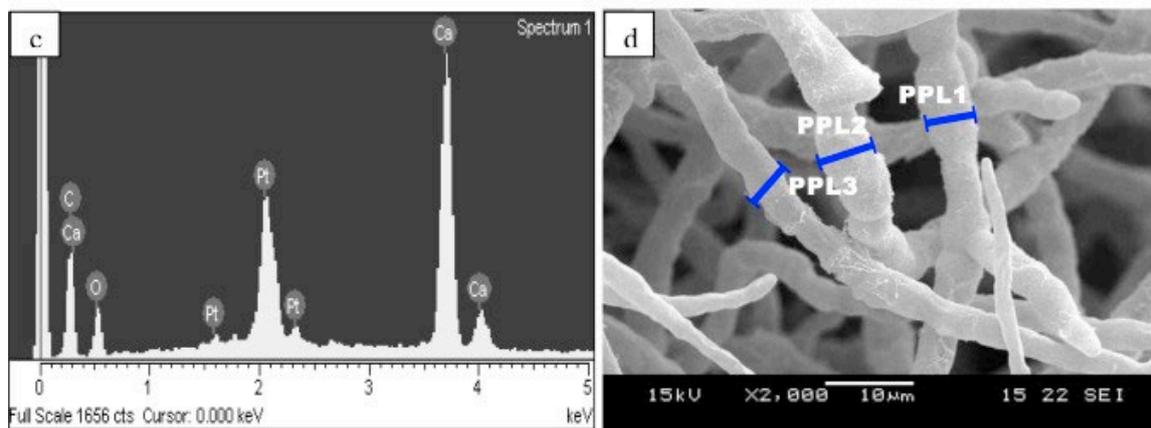
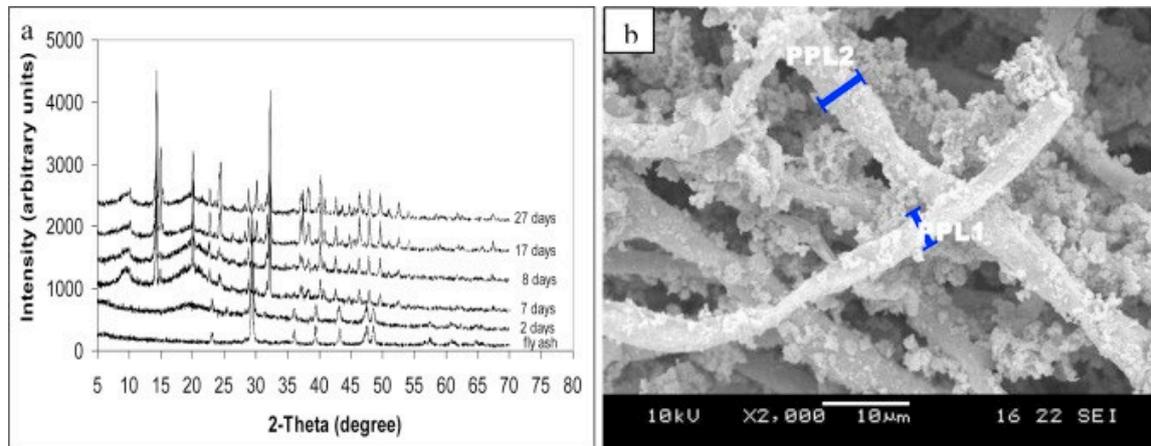
689 Fungi have considerable industrial importance in biomining. Several studies demonstrate the  
690 applicability of a bioleaching process to MSWI residues using fungal metabolic substances and reactions.  
691 However, data on a limited spectrum of genera are available (i.e., *Aspergillus* and *Penicillium*). The  
692 bioleaching ability of *Aspergillus* has been primarily ascribed to metal dissolution by organic acid excretion  
693 (e.g., citric acid). Bosshard et al. (1996) compared biological leaching of MSWI-FA by *Aspergillus niger* in batch  
694 cultures 5% pulp density to chemical leaching, and they found that bioleaching was only slightly lower than  
695 chemical leaching with commercial citric acid. They also noted that, in the presence of MSWI-FA, *A. niger*  
696 produced gluconate, whereas, in its absence, citrate. Xu and Ting (2009) investigated the bioleaching kinetics  
697 of *A. niger* with MSWI-FA at various pulp densities (1-6%) in a batch system; Figure 6 illustrates the key  
698 results. A modified Gompertz model was used to evaluate growth and acid production by the fungus, while  
699 a Monod inhibition model served to assess growth kinetics in the presence of toxic and inhibitory  
700 components of the MSWI-FA. The metals present in the MSWI-FA at high concentrations acted as inhibitors,  
701 decreasing the *A. niger* bioleaching yield. A gradual decrease of the fungal growth rate was observed with  
702 the increase of the pulp density, likely in relation to the primary inhibitory mechanisms that include inhibition  
703 of critical functional groups of enzymes, conformational changes of cell's polymers, and alteration of the  
704 integrity of the cell membrane. Nonetheless, the acid excretion by the fungus played a direct role in metal  
705 solubility (Al, Fe, and Zn) since the concentration of organic acid increases with biomass and time during  
706 fungal leaching of MSWI-FA (Xu and Ting, 2009). The optimal MSWI-FA concentration for fungal leaching is  
707 up to 10 % (w/v) in the medium (Bosshard et al., 1996). Yang et al. (2009a) reported bioleaching experiments  
708 of MSWI-FA by using single-metal adapted, multi-metal adapted, un-adapted *A. niger*. The effect of pH and  
709 concentration of the extracted metals on the fungus growth was evaluated by comparing the diameter of the  
710 fungal colonies. The authors found that multi-metal adapted AS3.879 can tolerate the greatest pulp densities  
711 and the Al-adapted strain AS3.879 is the best candidate for MSWI-FA decontamination according to the TCLP  
712 test on final residues (Yang et al., 2009a). The biosorption of metals in their ionic form operated by *A. niger*  
713 was further elucidated contacting MSWI-FA leachate made from gluconic acid leaching and the fungus for

714 120 minutes at 6.5 pH: Al, Fe and Zn fitted a pseudo-first-order kinetic and Pb a pseudo-second kinetic;  
 715 regarding the isotherm models, Pb, Zn and Fe fitted the Langmuir model, while Al Freundlich's (Yang et al.,  
 716 2009). Moreover, microscope observations revealed that fungal morphology was significantly affected during  
 717 both one-step and two-step bioleaching, with precipitation of calcium oxalate hydrate crystals at the surface  
 718 of hyphae (Xu et al., 2014), as illustrated in Figure 7, leading to noteworthy implications for after-use. Metal  
 719 richness in solution or contact surface can be toxic to microorganisms, but finely tuned pre-treatment and  
 720 adaptation strategies would overcome this limitation in industrial bioprocessing. For example, water washing  
 721 pre-treatment of MSWI-FA was simultaneously evaluated in both one-step and two-step bioleaching  
 722 procedures using *A. niger* (Wang et al., 2009). The results (under optimum pulp density of 1% w/v) showed  
 723 that the fungi lag phase (i.e., the timeframe of steady pH level and after which the pH starts to drop quickly)  
 724 in the absence of pre-treatment lasts about 260 hours, while less than 150 hours if water washing is deployed  
 725 (yielding 96% Cd, 91% Mn, 73% Pb, 68% Zn, 35% Cr, 30% Fe at the end of the experiment; Wang et al., 2009).  
 726 Water washing pre-treatment improves the production of organic acids thanks to partial removal of other  
 727 components, leading to a reduction of the experiment duration and overall costs.



728

729 Figure 6. Growth of *A. niger* in the presence of fly ash: solid lines are Modified Gompertz model, and no growth was seen at 6%  
 730 pulp density (top). Effect of fly ash pulp density (1–6%, w/v) on: the bioleaching of zinc (middle); the production of citric acid  
 731 (bottom). Reproduced with permission from Elsevier (5493670696531) (Xu and Ting, 2009).



732 Figure 7. (a) Undefined XRD analyses of the fungal pellet in two-step bioleaching confirming the formation of calcium oxalate  
 733 crystals and dissolution of fly ash particles from Day 7; (b) micrograph of the fungal pellet in two-step bioleaching on Day 7 showing  
 734 small particles on the hyphae and increased diameter of hyphae (PPL1 = 4.45 mm and PPL2 = 5.97mm); (c) EDX analyses of the  
 735 fungal pellet in two-step bioleaching at Day 7 confirming the presence of calcium oxalate crystals on the fungal surface; (d) surface  
 736 of the fungal pellet in two-step bioleaching at Day 8 showing abnormally short, swollen and high-branched hyphae (PPL1 = 5.59  
 737 mm, PPL2 = 6.32 mm and PPL3 = 5.32 mm). Reproduced with permission from Elsevier (5493670100485) (Xu et al., 2014).  
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## 739 4. Perspectives and Future Developments

### 740 5. 4.1 Challenges and Opportunities

741 Bioleaching applied to metal recovery and other biomining operations (e.g., biooxidation for mineral  
 742 beneficiation, bioremediation of mining waste) can be considered more environmentally friendly than  
 743 traditional methods. The application of bioleaching, which often refers to mimicking natural processes, is one  
 744 of the most prominent methods capable of balancing environmental and economic costs in the waste  
 745 management sector.

746 MSWI residues are mineral assemblages resulting from an elaborated petrogenesis and, thus, after  
 747 appropriate metallurgical treatments, can fit many potential after-uses. MSWI urban ores show metal

748 concentrations equivalent to low-grade primary ores (Funari et al., 2015). Therefore, urban mining can be  
749 affordable. Critical raw materials and strategic elements for green and high-tech applications can be  
750 recovered from anthropogenic resources like MSWI residues which are an ever-present flow of loose material  
751 and not natural ores to be drilled/crushed to the detriment of the environment. Many countries with limited  
752 mineral reserves could find urban mines a compelling resource supply and income option.

753 Biotechnologies, with their relatively low running costs and capital, have a central role in the supply  
754 of raw materials and eco-friendly alternatives. It is ideal for remediation and metal recovery from legacy sites  
755 and other mining wastes, even and especially in developing countries (Acevedo, 2002). Some strength points  
756 of MSWI residues bioleaching have been elucidated after about twenty years of laboratory testing at different  
757 scales (Rawlings, 2002; Hennebel et al., 2015; Srichandan et al., 2019; Gomes et al., 2020), such as, less energy  
758 and solvent consumption, high boosting potential, easiness to suite existing infrastructures, etc. However,  
759 bioleaching of MSWI BA and FA results slower than chemical leaching, and the state-of-the-art highlights the  
760 need for improvements concerning dissolution kinetics. For industrial rollout, this limiting factor makes the  
761 sole bioprocessing unaffordable and less appealing for MSWI plants than aggressive acid extractions or  
762 energy-demanding physical methods.

763 Safety measures must be continually adapted to the desired technology, and fundamental  
764 information from basic research is required for process development. Using strains from lab collections and  
765 indigenous uncultured strains or mixtures from the natural environments may overcome some limitations,  
766 such as the long reaction times to obtain satisfactory yields. As a fact, it became clearer that mixed cultures  
767 instead of monoclonal strain showed synergistic effects, favoring biomass growth against heavy metals  
768 inhibition and maintaining a reasonable trade-off between microbial community succession and their energy  
769 type metabolisms. The use of nutrients, e.g., iron and sulfur for acidophilic bacteria or organic sources for  
770 fungi and cyanobacteria, and the mineral acids/bases to maintain a predetermined pH setpoint can increase  
771 overall processing costs (Srichandan et al., 2019). Moreover, each microorganism must be adapted to the  
772 waste material to be treated as its resistance might strongly depend on the heterogeneity the matrix and  
773 standard pH. As in the case of alkaline wastes, such as MSWI ashes, where acidophile cultures can be  
774 unaffordable in bioleaching, additional data on alkaline bioleaching or fungal bioleaching is required.

775 Reducing carbon footprint could receive attention and leverage the development of bioleaching to  
776 mitigate climate change. For example, carbon sequestration and accelerated carbonation of alkaline wastes  
777 mediated by microorganisms are promising (Mayes et al., 2018; Gomes et al., 2020). Further opportunities  
778 are represented by i) fine-tuned bioleaching (enhanced selectivity for specifically chased metals as Li, Co, Cu,  
779 REE); ii) microbial recovery cell (consisting in a combination of galvanic leaching and bioleaching). In relation  
780 to the last case, an electrodialytic in-situ bioleaching can be tested expecting great results. Several authors  
781 argued that some magnetic separates from MSWI residues via electrodynamic fragmentation (Bluhm et al.,

2000; Seifert et al., 2013), can suite as ideal substrate material (e.g., Panda, 2020) which, at some point, could effortlessly combine to electro-dialytic bioleaching. In Europe, metal recovery exploiting ferrous fraction separation has been valued at 60-100 € per ton (of MSWI-BA), while the economic value of the non-ferrous fraction is significantly higher (Šyc et al., 2020). Interestingly, the ferrous metal fraction >3/4 mm is still virtually unemployed, although it could contain a significant amount of precious metals (Muchova et al., 2009; Holm and Simon, 2017). Since they contain many impurities, these separated by-products are generally sold to a third party at low cost. Again, fine-tuned bioprocessing can enter the treatment chains if sufficient trials are available to achieve better market values. New contractors for MSWI residues bioprocessing indeed produces new job and business models which, in turn, aside from economic feasibility, depends on:

- i. geographic location
- ii. desired final quality of recovery
- iii. throughput (i.e., large vs small MSWI plants)
- iv. type of MSWI residue (e.g., MSWI-BA vs MSWI-FA, quenched MSWI-BA vs dry MSWI-BA)
- v. type of treatment plant (e.g., on-site, at the landfill, mobile processing plant)
- vi. space requirements
- vii. proposed technology (e.g., one step vs multistep bioleaching)
- viii. management options for end-products (landfilling vs inert re-use)

## 4.2 Future research

The reproducibility of MSWI ashes bioprocessing is uncertain due to the lack of pilot-scale treatment results and considering the significant diversity and obsolescence (lifespan of 20-30 years) of the technologies used in MSWI management and municipal waste feed heterogeneity. During prototyping phase the assessment of biological hazards via standardized tests must be completely developed and adapted to the proposed technologies. BA and FA contain hazardous substances, such as mobile harmful elements Pb, As, Mo, Cd, Zn, and Sb, and also organic contaminants such as halides, hormones, prion, ionic liquids and rare volatile metals like osmium, and other ultrafine particles (Funari et al., 2016; 2020; Turner and Filella, 2017; Richardson and Kimura, 2017). Target and non-target chemical analyses, toxicological studies, and endpoint metrics (such as antibiotic resistance, genotoxicity, superparamagnetism, etc.) are necessary to protect the environment and the human health.

Despite the general skepticism in the application of biological processes, feasibility studies ascertain the urgent need to establish process efficiency in appropriate scale reactors or heaps to optimize the process, reactor design, and cost-benefit analysis towards cleaner waste management and minimization of loss of resources in the production chains. Optimizing the dissolution kinetics to speed up the reaction can be improved by optimizing pH, pulp density, temperature, pre-treatments, reaction time, and the careful choice

816 of bioleaching bacteria and their nutrients. Certainly, a profound knowledge of the leaching mechanism and  
817 behavior of microorganisms is vital for identifying new promising species or consortia. Pulp density is another  
818 issue that makes the process uneconomic unless clear water recirculation solutions are developed.  
819 Evaluation of the process economics may be properly examined in the long run after identifying the best  
820 metal to recover based on the commercial bioleaching applications in primary ore mining. Although  
821 bioleaching yields are a step below compared to abiotic leaching, engineered inocula can be tailored to the  
822 target materials and express their functionalities to sustain or prevent metal leaching from the treated waste.

## 823 Statements

824 -Ethical Approval

825

826 Not applicable

827

828 -Consent to Participate

829

830 Not applicable

831

832 -Consent to Publish

833

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836 -Authors Contributions

837

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839 *original draft preparation: Valerio Funari; Writing - review and editing: Valerio Funari, Helena I. Gomes,*  
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846

847 -Competing Interests

848

849 *The authors have no relevant financial or non-financial interests to disclose.*

850

851 -Availability of data and materials

852

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861

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