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

Valerio Funari[1, 2*], Simone Toller[1,3], Laura Vitale[2], Rafael M. Santos[4], Helena I. Gomes[5]

[1] Institute of Marine Sciences (ISMAR-CNR), Department of Earth System Sciences and Environmental Technologies, National Research Council of Italy (CNR), Bologna Research Area, 40129 Bologna, Italy

[2] Department of Marine Biotechnology, Stazione Zoologica Anton Dohrn (SZN), Via Ammiraglio F. Acton 55, 80133 Napoli, Italy

[3] University of Parma, Department of Chemical, Life and Environmental Sustainability Sciences (SCVSA), Parco Area delle Scienze, 17/A Parma, Italy

[4] School of Engineering, University of Guelph, Thornbrough Building, 50 Stone Rd E, Guelph, Ontario, N1G 2W1, Canada

[5] Food, Water, Waste Research Group, Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

*corresponding author: valerio.funari@bo.ismar.cnr.it

Abstract

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

Key Words: Circular economy; Waste-to-Energy (WtE) plants; Incineration wastes; Critical raw materials; Secondary raw materials; Resource recovery

1. Introduction

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

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

MSWI residues are a potential low-grade urban mine of ore metals thanks to the significant flows of substance bearing metals downstream of the municipal waste incineration process (Funari et al., 2015). For MSWI-BA, Funari and co-workers estimated a total flow of more than 350 t/a magnesium (Mg), 8.5 t/a Cr, 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, 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, Yb) is about 0.1 t/a. The Substance Flow Analysis (SFA) also shows considerable amounts of gallium (Ga) and 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 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), and also volatile elements such as Ag, Zn, and Sn have a considerable output retained in the solid FA. With further estimates coming from these figures, a total of 4500 tons Cu, 130 tons REEs, and 0.5 tons gold, are potentially recoverable from all MSWI-BA flowing on a national level. A the same time, the MSWI-FA output is a promising source of Zn, Sn, Sb, and Pb. Besides the relevance of metal recovery, successful urban mining strategies favour i) the reduction of the environmental impact, providing less dangerous leachates, ii) more control over nanoparticle pollution, and iii) high quality of post-treatment residues. In parallel, investigation of MSWI residues and related environmental media (e.g., topsoil nearby incinerators) would favour the development of finely tuned methods for urban mining with a close eye on sustainability. Looking ahead, the quality of MSWI feedstock materials and final solid residues, especially considering the 10-to-20-year life cycle of MSWI technology, needs continuous improvements from synergistic actions of both private and public stakeholders and the local communities.

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

2. Mineral resources and secondary raw materials from MSWI residues

2.1. Chemistry and Mineralogy of MSWI residues

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

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

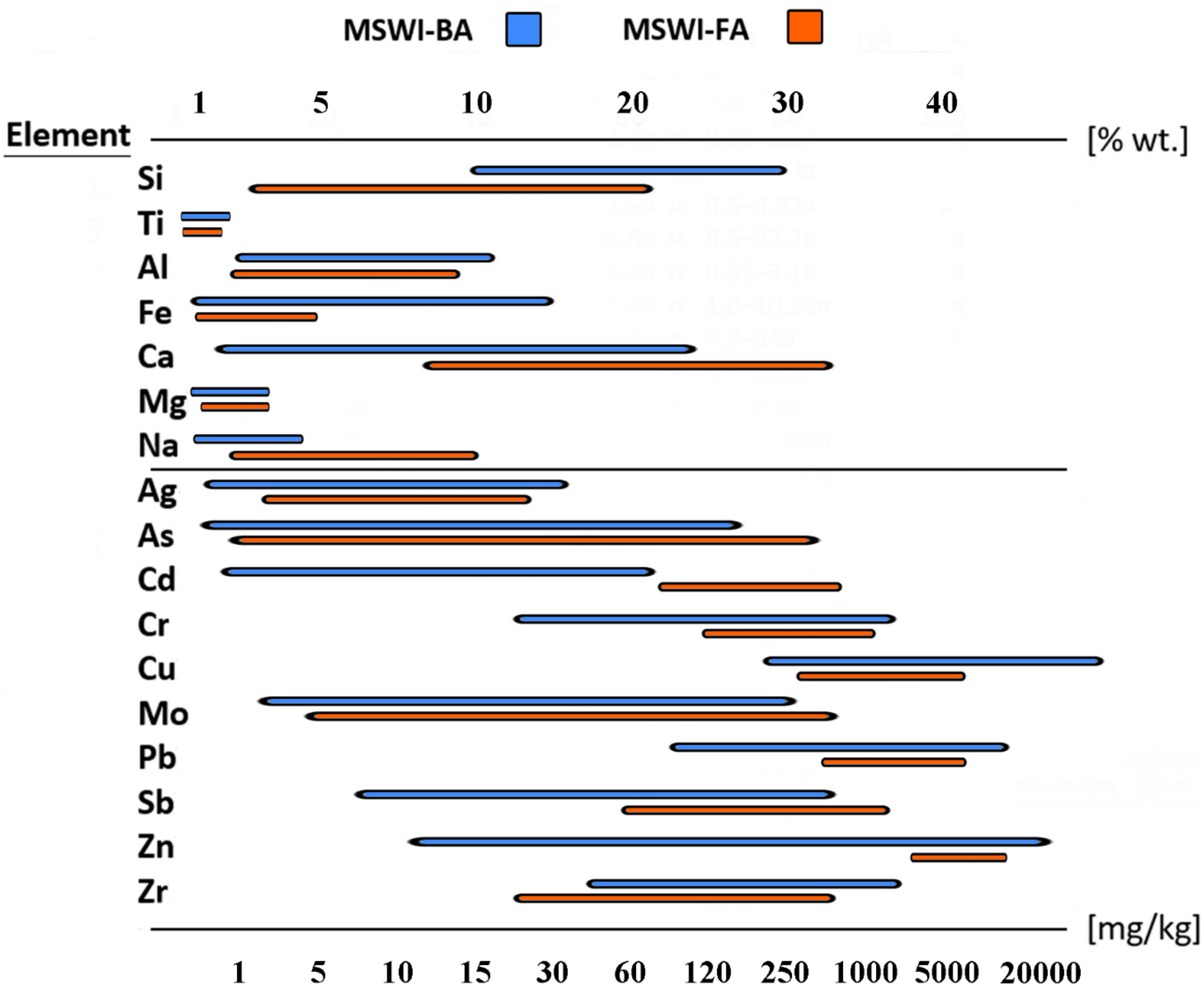

Figure 1. Chemical composition ranges of MSWI-BA and MSWI-FA for selected major, minor and trace elements (Izquierdo et al., 2002; Sabbas et al., 2003; Bayuseno et al., 2010; Funari et al., 2015; Astrup et al., 2016; Xiaomin et al., 2017; Huber et al., 2019; Wong et al., 2021; Maldonado-Alameda et al.,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

Numerous works elaborated the mineralogical composition of MSWI residues, e.g., by scanning electron microscope defining morphology, single-point chemical composition and the interaction between the different phases present inside the grains (Bayuseno and Schmahl, 2010; Bogush et al., 2015; Funari et al., 2018; De Boom and Degrez, 2012). The thin sections show structural variability and complexity under the microscope. Moreover, it is possible to verify the presence of glassy and crystalline material together with metallic and empty parts (e.g., Mantovani et al., 2021). The presence of wollastonite ($CaSiO_3$), with a dendritic crystallization in the glass matrix indicates a fast crystallization is frequent. There are also evident zoning and evidence of core recrystallization; sometimes, recrystallizations of fresh structures are observed within a metal matrix (Bogush et al., 2015). Iron, ubiquitous and present as a major element (> 0.1% by weight), undergoes a complex petrogenesis and can form a series of oxides and hydroxides, but also remain as nuggets of metallic Fe, or Fe-phosphides (e.g., schreibersite, associated with reducing conditions) and -sulfides (pyrite, pyrrhotite, greigite among many) (Funari et al., 2018; 2020), making hard to determine minor iron-bearing phases. Mineralogical analysis on magnetic separates showed the presence of small (<5 µm) spherules containing Fe in the form of agglomerates of particles or loose particles that could be attributable to technogenic spheres (*sensu* Magiera et al., 2011) readily dispersible during handling, being generally MSWI-FA dustier than MSWI-BA. Despite the great uncertainty on the stoichiometry and quantification of the crystalline phases, the X-ray diffractograms readily detect various carbonates such as calcite, soluble salts such as halite, silicates such as quartz, solid solutions gehlenite-akermanite, pyroxenes and feldspars, sulfates and phosphates and oxides of iron. However, the origin of certain mineralogical phases, i.e., if the minerals observed in MSWI-BA or MSWI-FA are derived from the incoming waste or freshly formed remains puzzling. This is due to different processing technologies, chemical composition of the incoming waste and combustion temperatures reached, which, in turn, can depend on local policies and have seasonality effects. The commonly identified minerals from MSWI-BA and MSWI-FA by XRD are in Table 1.

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

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

Mineral phase	**Chemical formula**	**MSWI-FA**	**MSWI-BA**
Silicates, aluminates, and alumosilicates			
Quartz	SiO_2	**X**	**XX**
Cristobalite	SiO_2	*n.d.*	**X**
Corundum	Al_2O_3	**X**	**XX**
Alkali Feldspars	$(K,Na)(Al,Si)_3O_8$	*n.d.*	**XX**
Plagioclase feldspars	$NaAlSi_3O_8$-$CaAl_2Si_2O_8$	**X**	**X**
	$(K, Ca, Na)(Al,Si)_4O_8$	**O**	**X**
Gehlenite	$Ca_2Al_2SiO_7$	**X**	**XX**
Anorthite	$CaAl_2Si_2O_8$		
Akermanite	$Ca_2MgSi_2O_7$	**X**	**XX**
	$Ca_2(Mg,Fe)Si_2O_7$	**O**	**X**
Calcium Pyroxene	$Ca(Mg,Fe)Si_2O_6$	*n.d.*	**X**
	$Ca(Mg, Al)(Si,Al)_2O_6$	**O**	**X**
	$(Na,Ca)(Fe,Mn)(Si,Al)_2O_6$	*n.d.*	**X**
Wollastonite	$CaSiO_3$	**X**	**X**
	Ca_2SiO_4	**X**	**X**
Portlandite	$Ca(OH)_2$	**X**	**X**
Gibbsite	$Al(OH)_3$	**O**	**XX**
Ettringite	$Ca_6Al_2(SO_4)_3 (OH)_{12} 26H_2O$	**X**	**X**
Carbonates			
Calcite	$CaCO_3$	**XX**	**X**
Other	$(Pb,Cd,Zn)CO_3$	**X**	**O**
Fe-bearing phases			
Magnetite	Fe_3O_4	**O**	**XX**
Hematite	Fe_2O_3	**X**	**O**
Wüstite	FeO	**X**	**X**
Goethite	$FeO(OH)$	*n.d.*	**X**
	$Fe(OH)_3$	**X**	**X**
	$FeCO_3$	**O**	**O**
	$Fe(Cr,Ti)_2O_4$	**O**	**X**
	$FeSO_4 7H_2O$	*n.d.*	**X**
S-based phases			
Anhydrite	$CaSO_4$	**XX**	**X**
Gypsum	$CaSO_4 2H_2O$	**X**	**XX**
	$Ca_6Al_2O_6(SO_3)_3 32H_2O$	*n.d.*	**X**
	$PbSO_4$	**X**	*n.d.*
Other oxides			
Lime	CaO	**XX**	**X**
	TiO_2	**X**	**X**
	PbO	**X**	**O**
	ZnO	**X**	**X**
	Na_2O	**XX**	**X**
	CuO	**X**	**XX**

	$CaMoO_4$	**O**	**X**
	$NaAsO_2$	**O**	**X**
Cl-based phases			
Friedel's salt	$Ca_2Al(OH)_6Cl\ 2H_2O$	*n.d.*	**X**
Hydrocalumite	$Ca_2Al(OH)6Cl_{1-x}(OH)_x\ 3H_2O$	*n.d.*	**X**
	$Ca_5(PO_4)_3Cl$	**O**	**X**
	$Ca_2SiO_3Cl_2$	**O**	**X**
	$CaCl_2$	**X**	*n.d.*
	$KCaCl_3$	**X**	*n.d.*
	$PbCl_2$	**X**	*n.d.*
	$ZnCl_2$	**X**	*n.d.*
	NaCl	**XX**	**X**
	KCl	**X**	*n.d.*
Other halides			
fluorides	CaF_2	**X**	*n.d.*
bromides	not specified	**O**	**O**
iodides	not specified	*n.d.*	*n.d.*
Other compounds			
organometallic compounds	organoarsenic compound	*n.d.*	**O**
Native elements			
zinc	Zn(0)	**X**	**X**
aluminium	Al(0)	**X**	**X**
copper	Cu(0)	**O**	**X**
gold	Au (0)	*n.d.*	**X**
other elements	Ti(0), Pb(0), Ag (0), Hg(0)	**X**	**O**

2.2. Hydrometallurgy for MSWI residues Urban Mining

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

Water, mineral acids (i.e., sulfuric acid, aqua regia), bases (i.e., sodium hydroxide, ammonia), organic acids (such as maleic acid), salt solutions, and combinations of these are common leaching reagents. The process optimization can be achieved by playing with pressure, temperature, reaction time, but also by adding oxidizing (e.g., H_2O_2, Cl_2, HClO, NaClO) or reducing (e.g., Fe^{2+}, SO_2) agents. The most used leaching methods include reactor leaching, heap leaching, vat leaching, dump leaching (heap without crushing), in-situ leaching (extractant pumped directly in the ore deposit) and autoclave leaching (high pressure and temperature). Galvanic, microwave, and ultrasound-assisted leaching are other methods investigated to enhance the efficiency of traditional leaching.

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

Hydrometallurgical applications' primary purpose for managing MSWI residues is decontamination from harmful metals. In the earliest studies on pH-dependent leaching using HNO_3 (Eighmy et al., 1995), Ca, Cl, K, Na, and Zn dissolved easily, while other elements (Cr, Pb, Zn, Cu, and Al) exhibited amphoteric behavior with enhanced solubilization at low pH over a leaching period of 3h. Nagib and Inoue (2000) reported the recovery of different metals from MSWI-FA using acetic acid, sulfuric acid, sodium hydroxide, and hydrochloric acid, with a fixed L/S ratio of 7 ml/g. They found that most of Zn is dissolved quickly using sulfuric acid (10 wt. % H_2SO_4) leaching, while temperature was mainly affecting Fe and Mg solubility. Therefore, 30°C temperature and 5 min time were determined to be suitable for Zn acid leaching to suppress the solubility of Fe and Mg, which is significantly enhanced at 60°C (Nagib and Inoue, 2000). Hydrochloric acid (10 wt. % HCl) leaching dissolves 63% Zn and 40% Pb in 5 minutes, together with impurities such as Fe, Mg and Ca. Acetic acid (10 wt. % CH_3COOH) leaching was effective, and most Pb and Zn were dissolved in 60 minutes (Nagib and Inoue, 2000). Acid leaching is efficient because it can dissolve nearly all Pb and Zn, but further separation and purification steps may be required since other potential impurities (e.g., Fe Mg, Al, Ca) are acid soluble. Further implementation was applied to the recovery method of Al and Fe, combining physical and mechanical processes (e.g., Nayak and Panda, 2010). The use of thermal treatment combined with acidic leaching allows overcoming some limitations (with recovery efficiencies up to 86 % Al and 94 % Fe using sulfuric acid) and produced sintered pellets suitable as an inert and lightweight aggregate (Matjie et al., 2005; Li et al., 2007, 2009). However, the high costs for energy to reach the calcination temperatures (800-1200°C) and the time demand (up to 24h) make these processes uneconomic. The leaching behavior of antimony (Sb) is particularly chased because of its elevated concentrations in MSWI residues and environmental relevance tied to its speciation also during natural ageing. Cornelis et al. (2012) investigated the leaching of antimonate (Sb^{+5}) and antimonite (Sb^{3+}) in MSWI-BA as a function of degree of carbonation and pH. Results showed that acidification and carbonation increased Sb^{5+} leaching and decreased Sb^{3+} leaching, and pointed out that Sb solubility depends on pH and calcium cations availability (romeite minerals are found to play an important role in the antimonate leaching) (Cornelis et a., 2012). Alkaline leaching, on the other hand, is hampered by the limited solubility of valuable metals (e.g., Zn), but can have the advantage of leaving a lesser amount of impurities in the solid residue. Bipp et al. (1998) were among the first to suggest alkaline leaching for heavy metals extraction. They tested gluconic acid and molasses hydrolysate leaching with sugar acid addition (1.8%) in the typical pH range of MSWI residues, achieving good recovery performances for Zn, Pb, Cu, Cr, and Cd with the molasses hydrolysate under weak alkaline condition. In general, alkaline leaching carried out in pH conditions near the MSWI residue's starting pH showed limited performances (Lee and Pandey, 2012).

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

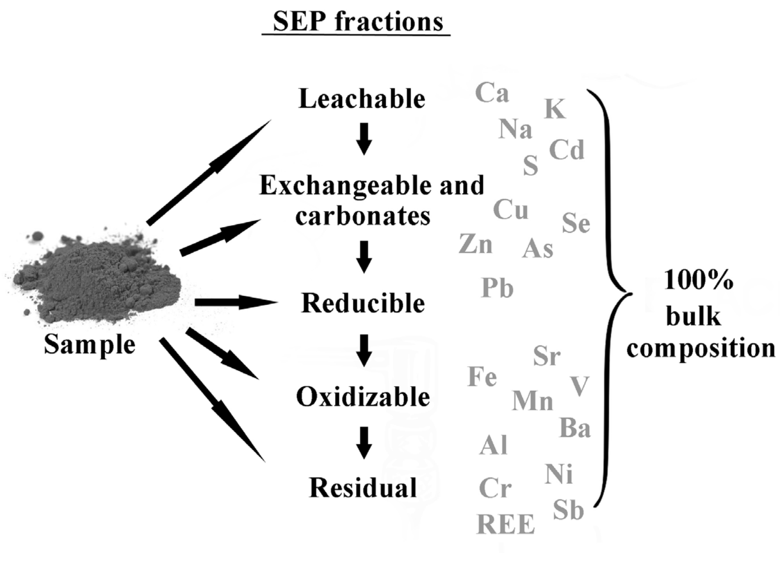

Figure 2. Generalization and summary of the fractions and analytes interested by Sequential Extraction Procedure (SEP) after Van Herck et al., 2000; Wan et al., 2006; Huang et al., 2007; Zhao et al., 2008; Chou et al., 2009; Chang et al., 2009.

Several authors investigated metal extraction using various aminopolycarboxylic acids such as DTPA, EDTA, NTA (Hong et al. 2000). Hong et al., 2000 underlined that the efficiency is not pH-dependent and solvent demanding (reagents concentration ranging between 0.5 wt. % and 1.0 wt. %); the extraction performed well for Pb (80 % recovery) in moderate alkaline condition with EDTA and DTPA, but the application of such chelating agents is uneconomic at the full scale for their high selling costs. Finally, experiments using batch extraction under similar conditions have shown that applying electric current can improve the solubility of some metals. Pedersen et al. (2005) evaluated different assisting agents for electrodialytic removals: the best aid in the removal of Cd was an NH_3 solution, perhaps because it helped build stable tetraamine complexes, while the best aid in the removal of Pb was Na-citrate. The optimum for removing a group of metals (up to 86% Cd, 81% Cu, 62% Zn, 44% Cr and 20% Pb) used 0.25 M ammonium citrate/1.25 % NH_3 solution (Pedersen et al., 2005).

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

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

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

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

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

2.3.1. Bottom ashes

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

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

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

Regarding commercially available treatment methods, MSWI-BA are usually sieved using bar seizers, trommel, vibrating screens, and flip flow screens (the latter only for wet treatments). In advanced plants, tens of fractions can be sorted for enhanced metal recovery. However, sieving can be expensive with a water content < 10 % because appropriate dust control during the handling of the material must be assured, and the crushing changes the size distribution likely precluding residual fraction utilization where well-sorted materials are required (Hyks and Hjelmar, 2018). Density separation is another effective method for the recovery of different components, such as copper, gold, and brass showing a significant density contrast compared to MSWI-BA matrix (2700 kg/m^3). Density separation does not apply for Al recovery because its density resembles that of bulk MSWI-BA, so it is preferably recovered using magnetic methods. Belt and drum are the two main devices commercially available. Multi-step magnetic separation is typically used for sieved fractions in advanced treatment plants before the Eddy current separation stage. Ballistic separation (patent WO 2009/123452 A1) is a cutting-edge technology used in advanced dry recovery processes that mechanically separates the fine particles (< 2 mm) associated with the moisture content. This device can couple with conventional dry separation processes, improving performance. Sensors-based separation technologies in MSWI residues processing are quite innovative and mainly used for separating glass and metal particles (Bunge, 2018). Among these, magnetic induction separation based on electromagnetic sensors is capable of identifying types of metals and alloys in the fraction coarser than 4 mm. Other types of sensors include X-ray fluorescence to detect different metals, optical sensors for distinguishing shapes, colored or transparent materials. Still, they are rarely applied to MSWI residues processing.

The most used processing options are dry technologies tailored for wet discharged MSWI-BA (e.g., Holm and Simon, 2017), even though dry discharge is experiencing a renaissance tied to its ability to avoid or minimise the negative effects of the formation of reaction by-products after quenching, mainly credited by $Ca(OH)_2$, $CaCO_3$, Friedel's salt and hydrocalumite (Inkaew et al., 2016). The KEZO MSWI plant in Switzerland is one example of dry treatment of dry discharged MSWI-BA that yields around 10 % FeF, 4.5 % n-FeF, and 1.1 % glass, generating a total revenue of 95 CHF/t of dry MSWI-BA with a total consumption of about 16 kWh/t of treated waste (Böni and Morf, 2018). However, efficient recovery of the heavy n-FeF can increase the revenues due to its precious metals content. Notably, the fraction with particles < 0.3 mm is sold without treatment at a likely depreciated value despite a potentially significant content of marketable metals.

On the other hand, fervor is on the development of wet technologies for the treatment of MSWI-BA that, however, implies a massive use of water as a primary limiting factor. Ageing is typically not included in the treatment to avoid a detrimental effect from the formation of mineral coatings. The first wet technology pilot plant for metal recovery came in 2005 in Amsterdam, The Netherlands. The treatment plant allows to recover inert granulates for building materials and marketable metal fractions of different levels of purity, equipped with several wet processing stages such as wet gravity separator, the wet eddy current separator, and the wet magnetic separator (Muchova et al., 2009). Although a recovery efficiency up to 83 % FeF and 73 % n-FeF, the plant never went to full scale, mainly due to the high water-demand and costs for water treatment. Another example is the Brantner&Co. plant in operation since 2013, located on an Austrian landfill site (Stockinger, 2018). With a treatment capacity of about 40,000 Mg/year of MSWI-BA, it counts on two-step magnetic separation, including overbelt magnets, separating iron scraps, and fine (>50mm) and large (<50 mm) fractions. A wet jig further separates material streams by density: a fraction of carbon-based materials and floating plastics, the heavy (density < 4,000 kg/m^3) n-FeF containing copper, brass, stainless steel, and precious metals, and the light n-FeF mainly composed of Al-bearing materials. One wet technology, installed in 2016 in Alkmaar, The Netherlands, and first developed by the Boskalis Company in response to the Netherlands' Green Deal, has a treatment capacity of about 240,000 Mg/year of MSWI-BA. This technology separates different fractions using dry sieving instead of a wet drum sieve, and then each fraction is washed to remove soluble salts and metals. A bar sizer separates fine (>40mm) and large (<40mm) particles, followed by magnetic separation for large particles, which, in turn, removes iron scrap and stainless steel as a first value-added material. The fine particles fraction undergoes a wet drum sieve and a vibrating screen. However, the main drawback is the production of large amounts of sludge with a high concentration of heavy metals according to the mass balance of the Alkmaar plant (Born, 2018).

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

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

2.3.2. Fly ashes

Disposal of MSWI-FA through backfilling also after packaging in "big bags" made of a resistant material is viable underground in natural cavities such as salt mines. The most used option is landfilling after an appropriate treatment such as stabilization or solidification using other types of wastes (e.g., co-landfilling with red mud) or binders (Quina et al., 2018; 2008). The stabilization processes suffer, however, some limitations such as increased mass and volumes that may result in unsustainable space demand. Landfilling after thermal stabilization (vitrification, sintering, thermal treatment with mixed wastes) is widely used as it can reduce leaching of inorganic pollutants and destroy toxic organic components. However, LCA analysis demonstrated that thermal treatments of MSWI-FA are uneconomic due to the high energy demand to achieve suitable treatment temperatures (Fruergaard et al., 2010). The poor magnetic susceptibility of MSWI-FA compared to MSWI-BA, due to lower concentration of Fe and magnetic minerals (Funari et al., 2020), prevents the use and scalability of magnetic separation methods for material upgrading and FeF and n-FeF recovery that is rarely attempted.

Decontamination/detoxification is the first pathway towards recovery and recycling of MSWI-FA as secondary raw material for other applications avoiding landfilling (e.g., reuse for preparation of geopolymers; Sun et al., 2013). Different methods can be performed, such as carbonation (Costa et al., 2007; Wang et al., 2010), washing, leaching or bioleaching (Benassi et al., 2016; Funari et al., 2017), electrodialysis (Parés Viader et al., 2017), and mechanical methods, e.g., ball milling (Chen et al., 2016). MSWI-FA for the production of secondary raw materials is well suited for ceramic materials, epoxy composites, glass-ceramics, zeolite-like materials, low-cost stabilizers and buffering agents, lightweight aggregates and secondary building materials for geotechnical applications, adsorbents including high capacity materials for energy storage (Quina *et al.*, 2018 and reference therein). Other practical applications include biogas production, CO_2 sequestration (Baciocchi et al., 2010), filler for embankment and landfill top cover (Brännvall and Kumpiene, 2016). The primary aim of MSWI-FA washing is the removal of easily soluble salts to improve decontamination/detoxification treatments. The Solvay Process developed during the 1860s is extensively used to recycle sodium chloride from MSWI-FA produced by wet or semi-dry APC system (Chandler et al., 1997), especially from FA collected at the sodic bag filters. Recently, Stena Recycling A/S developed the HALOSEP® process to remove and recover chlorine salts (mostly $CaCl_2$) and a concentrate metal cake from MSWI-FA. The key application for these salt products is road de-icing in compliance with the criteria CEN TC 337 WG1. The metal filter cake shows an average concentration of around 38-40 wt. % Zn, so it is particularly suited for Zn recovery at the smelter.

Several efforts have been made in recent years for metal recovery from MSWI-FA with commercial potential, such as Zn (Fellner et al., 2015), P (Kalmykova et al., 2013), Cu, and other precious and rare metals (Morf et al., 2013; Allegrini et al., 2014; Funari et al., 2016). The removal or stabilization of hazardous substances using traditional robust means such as water washing or co-landfilling is preferred over methods aiming at metal recovery so that, for example, bioleaching and electrocoagulation or eventual landfill mining strategies are still far from industrial rollout. However, some successful examples exist at the demonstration scale such as co-mixing with rice husks (Benassi et al. 2016) to recover an environmentally compatible secondary raw material. The FLUWA process dedicated to recovering Cu and volatile toxic metals such as Zn, Pb, Cd, and organic substances started in 1997 in Switzerland (Bühler and Schlumberger, 2010). It further allows metal separation and recovery through multistep acidic and neutral scrubbing and oxidation, providing a residual MSW-FA less prone to environmental leaching. Organic substances remaining in the filter cakes again represent a key issue, requiring further incineration cycle in the MSWI plant for complete thermal destruction. The new FLUWA + FLUEREC process allows up to 60–80% Zn, 80–95% Cd and 50–85% Pb and Cu removal (Quina et al., 2018). The FLUREC implemented in 2012 at MSWI plant Zuchwil, Switzerland, can recover up to 300 Mg/year Zn; however, purification of Zn-rich cake and filtrates is a prerequisite.

The use of MSWI-FA for the production of cement is sought because this can limit the enormous environmental impact of the cement industry tied to massive anthropogenic CO_2 (from calcination) and other gaseous emissions (NOx, organic compounds, and toxic volatile elements), the consumption of energy and natural resources (Lederer et al., 2017). The main options for MSWI-FA reutilization in the cement industry include the production of blended cement and the co-processing in the cement kiln to produce the clinker (e.g., Bertolini et al., 2004). Co-processing of MSWI-FA containing high amounts of Ca-bearing phases is viable to substitute a part of the raw material input (Chandler et al., 1997) up to about 40-50% (Saikia et al., 2015). Earlier studies suggested that the leaching rates of potentially toxic elements are very low in the short term. However, Lederer et al. (2017) surmised that volatile metals such as Cd and Pb are reincorporated into the cement during the regular production process. Considering that the chemical composition of MSWI-FA is not stable over time, particular care should be given to the final cement quality and the emissions at the smokestacks.

3. Biotechnology for MSWI ash management

3.1. Brief Overview of Biohydrometallurgy

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

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

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

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

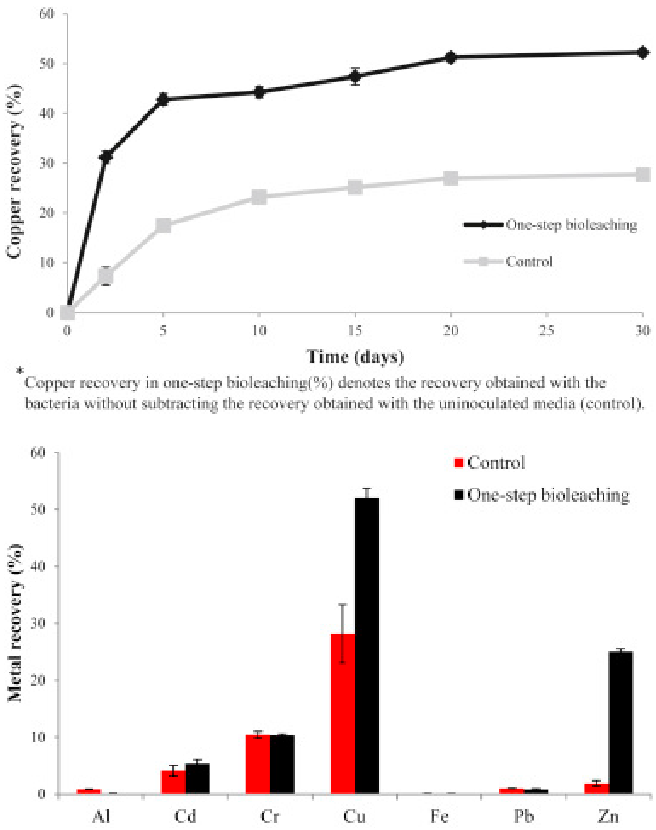

Figure 3. Kinetics of Cu bioleaching (top) and recovery of metals (bottom) from municipal solid waste incineration fly ash by *Alkalibacterium* sp. TRTYP6 (*n* = 3). Reproduced with permission from Elsevier (5493660184237) (Ramanathan and Ting, 2016).

3.2. Bacterial leaching in sulfidic environments and their industrial applications

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:

$$S_xO_n^y + O_2 + H_2O \rightarrow SO_4^{2-} + H^+ \quad [1]$$

$$3Fe^{3+} + 2SO_4^{2-} + 6H_2O + K^+ = KFe_3(SO_4)_2(OH)_6 + 6H^+ \quad [2]$$

$$CuFeS_2 + 4Fe^{3+} = Cu^{2+} + 2S_0 + 5Fe^{2+} \quad [3]$$

$$4Fe^{2+} + 4H^+ + O_2 = 4Fe^{3+} + 2H_2O \quad [4]$$

$$CuFeS_2 + 4H^+ + O_2 = Cu^{2+} + 2S_0 + Fe^{2+} + 2H_2O \quad [5]$$

$$2S_0 + 3O_2 + 2H_2O = 2SO_4^{2-} + 4H^+ \quad [6]$$

Direct or contact bioleaching generally assumes a metal sulfide-attached cell oxidizes the mineral by an enzyme system with oxygen to sulfate and metal cations. To dissolve a metal sulfide [Eq. 1] the indirect or non-contact mechanisms grounds on the oxidizing capacity of Fe^{3+} ions. During this chemical reaction, Fe^{2+} ions and elemental sulfur (S_0) are poly-sourced [Eq. 3, 5], promoting a cyclic reaction where Fe^{3+} and sulfide moiety is reduced and oxidized progressively [Eq. 4, 6] thanks to an ancillary engine of S-oxidizers. It is worth mentioning Extracellular Polymeric Substances (EPS) allow contact and mineral decomposition that preferably start in crystal defects (Fletcher and Savage, 2013; Gehrke et al., 1998), where the Fe^{2+} ions are more accessible (Dziurla et al., 1998). The need for iron is as important as the S-cycle: when the Fe^{3+} interacts with the electronic structure and (leach) the surface of the mineral, and sulfur de-bonds from sulfide crystal lattice, the thiosulfate releases Fe^{2+} ion and protonation forms H_2S, which reacts with the oxidative compounds (e.g., Fe^{3+}, O_2). This starts a radical chain reaction that produces S_0 as an end-product, which is used by bacteria (e.g., *Acidithiobacillus thiooxidans*) to produce sulfuric acid.

The regulatory strategies of *A. thiooxidans* during bioleaching of low-grade chalcopyrite were studied in-depth by Yin et al. (2019), illustrated in Figure 4, through physiological observations matched with transcriptomic approach. The authors observed that during the $CuFeS_2$ bioleaching process the bacterium endeavor's three mechanisms to keep the pH homeostasis: i) externalizes H^+ by ATPase activity; ii) the amino acid metabolism becomes more active lowering cytoplasmic acidification by proton consumption via the tricarboxylic acid (TCA) cycle (i.e., Krebs cycle); iii) prevents proton invasion increasing the amount of unsaturated fatty, particularly cyclopropane, and so far the density of the cell membrane. At the transcriptomic level the genes involved in sulfur metabolism were significantly up-regulated while those associated with the flagellar assembly and carbon metabolism were down-regulated, suggesting a strategy of alternative energy production from the first and reduction of energy consumption with the second. Noteworthy, confocal laser scanning microscopy (CLSM) analysis indicated that EPS and biofilm formation might also improve strain resistance to the stress condition (Figure 4). Niu et al. (2016) studied a real-scale bioleaching system of the Dexing Copper Mine (Jiangxi, China) to provide insights into the bacterial community structure and mechanisms involved at three different processing stages. According to phylogenetic analysis based on 16S rRNA metabarcoding, all three groups shared 259 OTUs (Operation Taxonomic Unit), but demonstrated a significant microbial shift in the process line. Gene arrays revealed a difference in functional gene structures of the microbial communities and metabolic pathways potentially related to bioleaching. Genes involved in carbon fixation, polyphosphate degradation, sulfur oxidation, and denitrification were abundant in a sample from the heap; while genes related to carbon degradation, polyphosphate synthesis, sulfite reductase, and nitrification in the spent medium leachate (Niu et al., 2016).

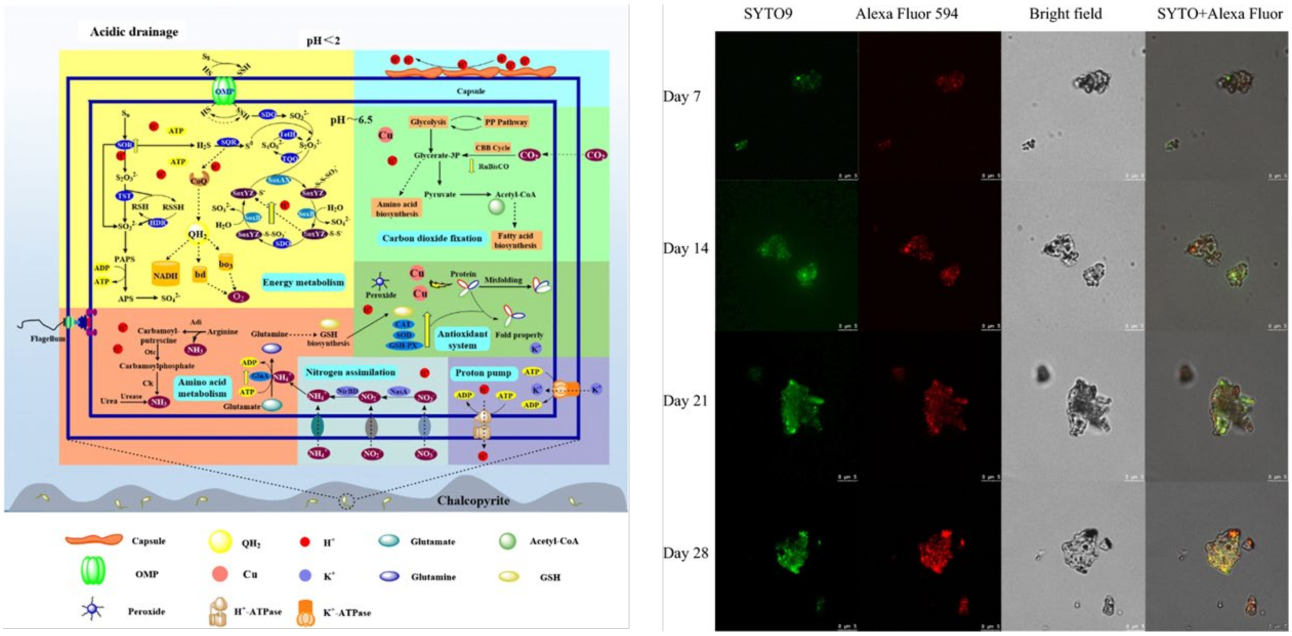

Figure 4. Adaptation mechanism model of *A. thiooxidans* in bioleaching of low-grade chalcopyrite (left); visualization of EPS and cell attachment on chalcopyrite surface when bioleaching at 7, 14, 21, and 28 days by CLSM (right). Reproduced with permission from Springer Nature (5493660654399) (Yin et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

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 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 (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.

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

3.3. Biohydrometallurgical processes for the circular economy

In order to promote a circular economy, biotechnology for metal production should be eco-friendly and cost-effective and adapt to the waste management sector. The continuously increasing high demand for critical raw materials and rare metals for technological development has led not only Europe, but also other industrialized countries, to look at diversified sources of supply such as mining waste, mine tailings, and alternate anthropogenic stocks and flows that frequently exhibit a hidden metal value (Baccini and Brunner, 2012). Biomining is suitable for treating such materials because they are flexible for optimization and can prove beneficial to decontamination, coupling metal recovery with environmental remediation. This has led to recent advances in fine-tuned methods to treat anthropogenic wastes. Despite the modest and variable ore metal concentrations in anthropogenic flows like MSWI residues, bioleaching methods can allege lower capital costs than other robust technologies in waste management (Funari et al., 2017).

Bioleaching for metal extraction from anthropogenic materials such as electronic scraps, various types of slag and flying ashes, secondary solid wastes, and sludge is largely investigated as an economical and eco-friendly process (Gahan et al., 2013; Meawad et al., 2010; Lee and Pandey, 2012; Srichandan et al., 2019). Bioleaching of metals through the use of thermophilic and acidophilic bacteria has been primarily investigated to recover metals from electronic scrap, especially printed circuit boards (Ilyas et al., 2007). Among the strategies adopted to achieve higher speeds of metal leaching from electronic waste, it was found that a mixed consortium can show the maximum efficiency of leaching, and a pre-washing might be useful to remove easily soluble metals (e.g., Cl, Na) or light fractions (e.g., plastics) toxic for bacteria. Satisfactory leaching yields are achievable with *S. thermosulfidooxidans*, an example of moderate thermophilic bacteria, but the presence of Pb and Sn precipitation complicated separation and purification (Ilyas et al., 2007). Recently, Becci et al. (2020) confirmed that pre-crushing to obtain a granulometry > 0.5 mm is a good strategy to enhance bioleaching of printed circuit boards using iron oxidizers. However, the formation of passivation layers (e.g., jarosite) remains a limiting factor that reduces kinetics dramatically. In their experiments, bioleaching processes using monoclonal cultures of *A. ferrooxidans* and *L. ferrooxidans* were compared, emphasising oxidation of iron species. The latter microorganisms are very sensitive to metals toxicity and perform a slow conversion of Fe^{2+} in Fe^{3+}, resulting in relatively low recovery of around 40% Cu and 20% Zn, while bioleaching with *A. ferrooxidans* yielded around 95% Cu and 70% Zn and showed high conversion of Fe^{3+}. Further comparing different scenarios in terms of carbon footprint (Figure 5), they found the optimum condition with further bioreactor size reduction can achieve four times reduction of the CO_2-eq per kilogram of treated material compared to the best bioleaching processes reported in the literature (Becci et al., 2020).

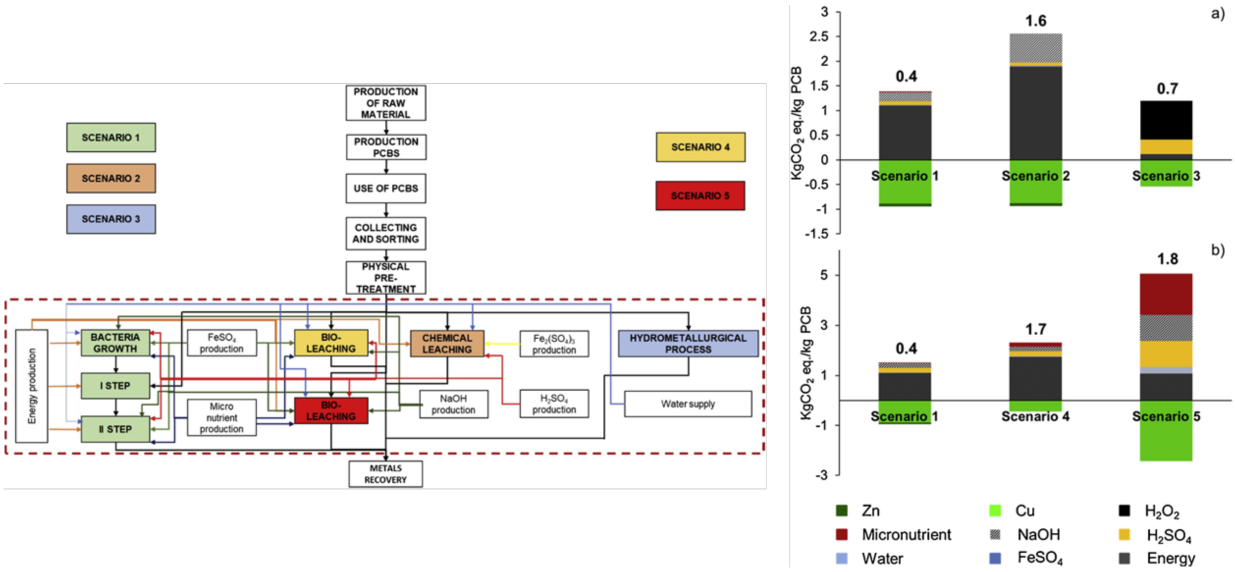

Figure 5. System boundaries considered for the carbon footprint assessment (left); carbon footprint of the five considered approaches (right). (Function unit: 1 kg of shredded PCBs). Reproduced with permission from Elsevier (5493661285952) (Becci et al., 2020).

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).

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

Bioleaching can extract valuable metals, especially Cu, Zn, Pb, As, Sb, Ni, Mo, Au, Ag and Co, from MSWI residues with less energy and environmental impact than pyro- or hydro-metallurgical methods. Ishigaki et al. (2005) studied the bioleaching of Cr, Cu, Zn, Cd, and As from MSWI-FA by sulfur-oxidizing and iron-oxidizing bacteria, as pure cultures and a mixture of both. The mixed culture showed the best performance (67% Cu, 78% Zn and 100% for Cr and Cd at 1 % w/v pulp density). Characterization of metal bioleaching revealed that the acidic and oxidizing conditions remained stable throughout the experiment. The redox mechanisms coupled with the sulfate leaching brought an increase of ferrous iron enhancing the Cr, Cu, and As leaching. However, they found that at a higher pulp density (3 % w/v) chromium remained virtually undissolved (4 % Cr yield). The presence of degradable and non-degradable organic compounds in MSWI residues exerted no significant changes in the leachability of metals other than Zn (Ishigaki et al., 2005). An earlier study on microbial leaching (Mercier et al., 1999) elucidated that the following elements can be removed in decreasing order of extraction rate: Cd, Zn, Pb, Cu, using a pure culture of *A. ferrooxidans*. In the same work, four different leaching tests were conducted for environmental compliance of the final residues, and the authors concluded that the leachate from Toxicity Characteristic Leaching Procedure (TCLP) was within the acceptance criteria only if the final residue's pH was increased to five after the biological treatment. Still, Cd releases could be an issue concerning regulatory limits. The investigation by Krebs (2001) reported an example of co-treatments of MSWI-FA using a mixture of strains (*Thiobacillus* genus) in a suspension of water and nutrients (1 % w/v S_0 powder) and 4 % w/v sewage sludge. The cultivation was compared to pure *A. thiooxidans* or sewage sludge alone, over 1-3 months. The inoculation with the combination of sewage sludge and bacteria showed a fast decrease in pH and increased microbial growth. In the final pH of 1, the efficiency of metal leaching was very similar, with pulp density ranging from 0.5 % to 1 %. More than 80 % Cd, Cu, and Zn, around 60 % Al, up to 30 % Ni and Fe, less than 10% Cr and Pb were mobilized (Krebs, 2001). Autochthonous bacteria can be used for bioleaching as reported in a study on MSWI-FA produced in Singapore incineration plant (Ramanathan and Ting, 2016). Thirty-eight different microbes were isolated and characterized to find the most suitable autochthonous microbe with inherent fly ash tolerance and ability to thrive in alkaline pH (thus avoiding any pre-acidification of the ash). Besides *Firmicutes* (90 % relative abundance), three other phyla were identified: *Bacteriodetes*, *Actinobacteria*, and *a-Proteobacteria*. Among six isolates displaying Cu recovery of about 20% or more, *Alkalibacterium* sp. was tolerant to pH and fly ash, making it a suitable candidate for MSWI-FA bioleaching. Indeed, a one-step bioleaching with *Alkalibacterium sp*. on MSWI-FA showed 52% Cu and 25% Zn recovery. The high tolerance of *Alkalibacterium* sp. to metals and substantial bioleaching ability can prompt scaled-up bioleaching with alkaline bacteria that, at present, do not reach acidophile bioleaching in terms of Cu and Zn removal rates. A clear advantage of alkaline bioleaching is the higher pulp density (more than 20% w/v), signifying less water-demand. Hong et al. (2000) tested saponin, a biosurfactant produced by microorganisms and plants, for metal removal from MSWI-FA. They compared the efficiency of saponins with that of other solvent extraction (HCl and EDTA) in the pH range 4-9. The saponins leaching was more effective than control acid treatments for Cr, Cu, and Pb with yields up to 45 %, 60 % and 100 %, respectively, whereas the Fe, Si, Al, and Zn extraction was not significant. Gonzalez et al. (2017) used cementing bacteria to stabilise MSWI-FA. After bacteria cementation assays and the assessment of the ad/absorption of metals in the cemented fly ash, they concluded that *Sporosarcina pasteurii* and *Myxococcus xanthus* are suitable for multiple metal stabilization (As, Cd, Cr, Cu, Ni, Pb, Sn, and Zn) with some differences concerning trace elements mobility, depending on the starting concentrations in the samples (Gonzalez et al., 2017).

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

The acid bioleaching behavior of both MSWI FA and MSWI-BA was investigated at the bench scale and compared to abiotic leaching (H_2SO_4, 10% pulp density, 30 °C, 150 rpm) looking at a wide range of metals (Funari et al., 2017). A mixed acidophilic culture composed of iron and sulfur-oxidizing bacteria tested on a one-step bioleaching process yielded >85% Cu, Al, Mn, Mg, and Zn and significant removals of Co, Cr, Pb, Sb, and REE. Unvalued elements like Ca, Si, and Ti showed low mobility with the tendency to remain in the solid phase, while the solubility of other trace elements might be selectively enhanced by the cyclic supply of Fe^{+3}

produced by iron-oxidizing bacteria. Moving ahead, Mäkinen et al. (2019) tested the possibility of heap bioleaching for the recovery of Zn and Cu from MSWI-BA at the bench scale via column experiments. Leaching yields varied 18–53% Zn and 6–44% Cu, and they noted that appropriate aeration is the main critical factor needing further adjustments in future testing. Potentially high Fe and Al, easily dissolved in sulfuric acid solutions, and different heap behavior due to the heterogeneity of the material can also impede bioleaching utilization in MSWI residues treatment. However, a balance between bacterial adaptive mechanisms and nutrient supply can generate savings compared to processes relying on abiotic procedures. Electrochemical technologies are also promising in the optimization of acidophile bioleaching for MSWI residues (Gomes et al., 2020), possibly to offset the CO_2 generation of full-scale applications.

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

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

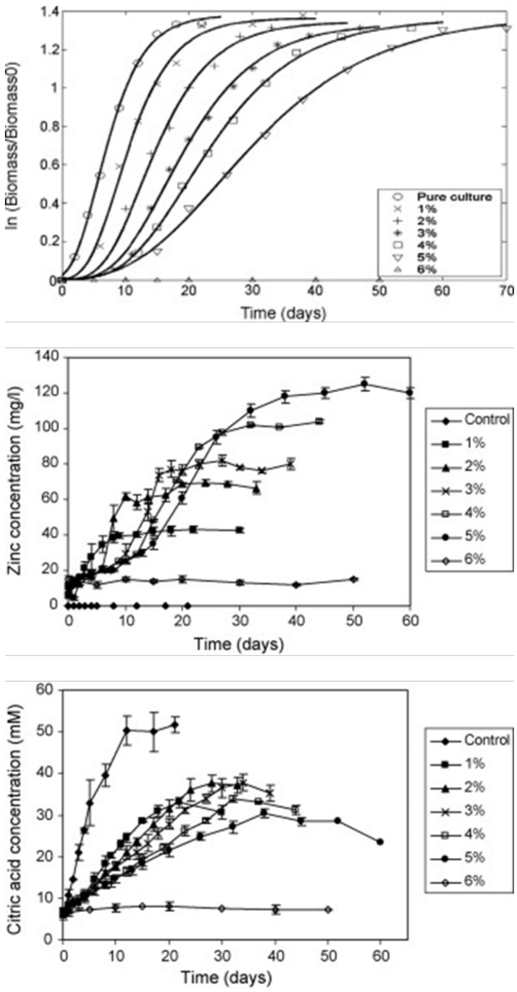

Figure 6. Growth of *A. niger* in the presence of fly ash: solid lines are Modified Gompertz model, and no growth was seen at 6% pulp density (top). Effect of fly ash pulp density (1–6%, w/v) on: the bioleaching of zinc (middle); the production of citric acid (bottom). Reproduced with permission from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

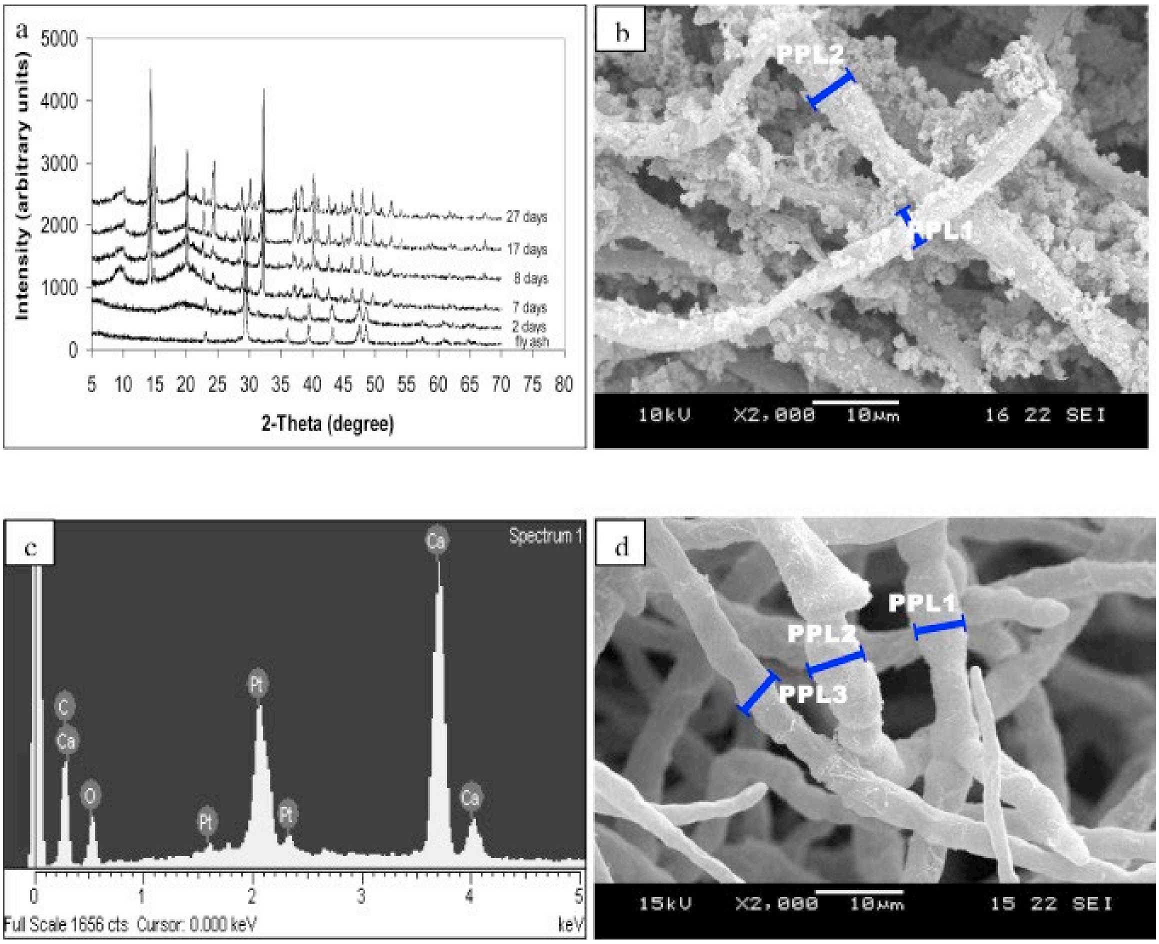

Figure 7. (a) Undefined XRD analyses of the fungal pellet in two-step bioleaching confirming the formation of calcium oxalate crystals and dissolution of fly ash particles from Day 7; (b) micrograph of the fungal pellet in two-step bioleaching on Day 7 showing small particles on the hyphae and increased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

4. Perspectives and Future Developments

5. 4.1 Challenges and Opportunities

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

MSWI residues are mineral assemblages resulting from an elaborated petrogenesis and, thus, after appropriate metallurgical treatments, can fit many potential after-uses. MSWI urban ores show metal concentrations equivalent to low-grade primary ores (Funari et al., 2015). Therefore, urban mining can be affordable. Critical raw materials and strategic elements for green and high-tech applications can be recovered from anthropogenic resources like MSWI residues which are an ever-present flow of loose material and not natural ores to be drilled/crushed to the detriment of the environment. Many countries with limited mineral reserves could find urban mines a compelling resource supply and income option.

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

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

Reducing carbon footprint could receive attention and leverage the development of bioleaching to mitigate climate change. For example, carbon sequestration and accelerated carbonation of alkaline wastes mediated by microorganisms are promising (Mayes et al., 2018; Gomes et al., 2020). Further opportunities are represented by i) fine-tuned bioleaching (enhanced selectivity for specifically chased metals as Li, Co, Cu, REE); ii) microbial recovery cell (consisting in a combination of galvanic leaching and bioleaching). In relation to the last case, an electrodialytic in-situ bioleaching can be tested expecting great results. Several authors 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 electrodialytic 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 of bioleaching bacteria and their nutrients. Certainly, a profound knowledge of the leaching mechanism and behavior of microorganisms is vital for identifying new promising species or consortia. Pulp density is another issue that makes the process uneconomic unless clear water recirculation solutions are developed. Evaluation of the process economics may be properly examined in the long run after identifying the best metal to recover based on the commercial bioleaching applications in primary ore mining. Although bioleaching yields are a step below compared to abiotic leaching, engineered inocula can be tailored to the target materials and express their functionalities to sustain or prevent metal leaching from the treated waste.

Statements

-Ethical Approval

Not applicable

-Consent to Participate

Not applicable

-Consent to Publish

Not applicable

-Authors Contributions

Conceptualization: Valerio Funari; Methodology: Valerio Funari, Helena I. Gomes, Rafael Santos; Writing - original draft preparation: Valerio Funari; Writing - review and editing: Valerio Funari, Helena I. Gomes, Simone Toller, Laura Vitale; Supervision: Valerio Funari, Helena I. Gomes, Rafael Santos.

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-Competing Interests

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

-Availability of data and materials

The data that support the findings of this study are available from the corresponding author, V.F., upon reasonable request.

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