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Critical metals in solid wastes from non-ferrous base metal production

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Abstract: Society advancement and security are impossible without use of some metals registered in the critical raw materials / minerals lists of different jurisdictions. Critical metals (CM) production from ores will not be able to meet the raising future demand. This review is aimed at highlighting the solid waste from primary non-ferrous metals production as a source of CM. Elsevier and Web of Science databases (as primary) and Google Scholar, USGS databases and official legislative documents (as additional) sources were searched - using suitable keywords and criteria for relevancy - covering recent 20 years. Slag from copper, lead, zinc and nickel production from sulphide ores is an essential source of Al, Sb, Bi, Co, Cu, Mg, Mn, Ni. Copper anode slime is rich in Sb and Bi, zinc leaching residues - in Al and Cu. Concentration ranges are presented for mentioned metals in the corresponding waste in various countries around the world. Pyro-, hydro- and bio-metallurgy are compared as technologies for CM recovery from the said waste. Process mineralogy is crucial for selecting the most effective metal recovery pathways. A conceptual technological approach is proposed for the metals' recovery from the solid waste from non-ferrous base metals primary production. Slurry electrolysis, use of supercritical fluids, and solvometallurgy (that employs ionic liquids and deep eutectic solvents) are presented as alternatives with promising laboratory results. Despite their advantages, these technologies require considerable further studies and development to reach commercialization. Necessity is highlighted of policies and standards for stimulating secondary raw materials usage.

Keywords: solid waste from nonferrous base metals extraction, critical metals, metals recovery

1. Introduction

Sustainable development of our society is impossible without the use of metals. We need metals for the development of advanced technologies, industrial progress, and our everyday life. The European Commission (2023) and the International Energy Agency (IEA, 2023) point out that sustainable economic growth and the low-carbon economy progress need a significant rise in the consumption of metals such as aluminium (Al), cobalt (Co), copper (Cu), lithium (Li), nickel (Ni), platinum group metals (PGM), rare earth elements (REEs), and many others.

Anticipated technological advancements are expected to drive the future demand for high-tech and strategic metals. For example, achieving global climate stabilization and decarbonization goals will increase demand for Li more than fortyfold by 2040, 20 to 25 times the demand for Ni and Co, and up to seven times the demand for REEs (IEA, 2022).

However, access to some metals is vulnerable to geological (depletion of ore deposits), economic (including technological and environmental), or geopolitical factors (Montana et al., 2025; Müller et al., 2025). Production of various metals required for high-tech advances is geographically concentrated– Table 1 (European Commission, 2023; USGS, 2026). The data for different producers reflect the situation in 2025 for mine production, except for data on Ga (for primary production) and on Al that reflect smelter production.

As shown in Table 1, China is the key producer of many high-tech metals (Al, Sb, Ga, REE), while Congo (Kinshasa) is the dominant producer of Co, and Indonesia is the dominant producer of Ni. South

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Table 1. EU dependence on some critical metals and their first three worldwide producers in 2025: Compiled by the authors based on data from USGS (2026) and the European Commission (2023)

Country Metal	EU Dependence (%)	1st Producer, Share (%)	2nd Producer, Share (%)	3rd Producer, Share (%)
Sb	100	China, 36	Russia, 29	Tajikistan, 20
Li	100	Australia, 32	China, 21	Chile, 19
PGM (Pt, Pd)	100	South Africa, 53	Russia, 29	Zimbabwe, 9
REE	100	China, 69	USA, 13	Australia, 8
Ga	98	China, 99	Russia, 0.666	Japan, 0.333
Al	89	China, 61	India, 6	Russia, 5
Co	81	Congo (Kinshasa), 74	Indonesia, 14	Russia, 3
Ni	75	Indonesia, 67	Philippines, 7	Russia, 5

Africa is the main producer of PGM and Australia – of Li. Table 1 highlights the strategic risks and dependencies characteristic of current supply chains. Table 1 presents the production of metals on which the European Union economy is highly dependent on imports ($\geq$ 75%). Some of the main EU sourcing countries/providers are politically unstable or are progressively decreasing their export quotas. This creates a strategic vulnerability that generally reinforces the adoption of the critical raw materials (CRM) lists.

The European Commission (2020, 2023), the United States (USGS, 2025), China (Ren, 2025), Australia (Parliament of Australia, 2025), and India (Ministry of Mines, 2023) have already identified many of the above-mentioned metals as critical and included them in the corresponding lists. In general, the basic premise of a Critical Raw Material (CRM) or Critical Mineral definition revolves around the essentiality of these minerals for modern industry and their possible supply chain risks. However, there are differences in the categorization introduced by the different jurisdictions – Table 2. Notwithstanding the methodological differences in CRM definitions, all mentioned lists share a common opinion regarding the strategic importance of metals that stimulate high-level technologies, green transition, and sustainable development. It is worth noting that Al, Sb, Co, Li, Ni, and REEs are included in all mentioned lists.

Recycling of end-of-life products may contribute to the supply of some metals. However, the recycling of many critical metals (Li, Ge, In, Bi, Ga) is very limited (European Commission, 2023). This highlights the need to use alternative sources. According to Lottermoser (2010) and Ndlovu et al. (2017), the solid waste from base non-ferrous metals production (mining and ore beneficiation waste, and metallurgical waste) can be a reliable source of critical metals. This technogenic waste from industrial production of primary nonferrous base metals can be regarded as a secondary resource for many metals.

A study calculated significant annual quantities of some metals in the EU extractive waste disposed in situ in tailings, as well as the availability of considerable amounts of Cu, Zn, lead (Pb), tungsten (W), and REEs in historical mining waste sites (Mathieux et al. 2017).

Our aim is to illustrate with data from the whole world that the solid waste from the production of nonferrous base metals from sulphide ores is a valuable source of critical metals, while available publications usually refer to a specific country or region. Further, we review the current technologies for metal recovery from this technogenic waste, highlighting their potential, pointing out limitations, and identifying future lines of study.

Attention is paid to hydrometallurgy as a more readily applicable technology for the commented solid waste treatment, with a special emphasis on new approaches such as the use of electrochemically aided leaching and solvometallurgy. Usually, authors pay attention either to the presence of metals in technogenic waste or to certain methods for their extraction. The number of publications that "close the circle" - from indicating technogenic waste as a source of critical metals, through pyrometallurgical, hydrometallurgical and bio-metallurgical technologies for CM extraction, to the necessary basic legislative changes that would support the production of metals from the specified technogenic raw materials is relatively low. We hope to fill this gap. Thus, readers can gain a complete picture of the potential to use waste from primary extraction of basic non-ferrous metals as a source of critical metals. By highlighting the valorisation of mining and metallurgical wastes though advanced technological solutions this paper contributes to mitigating the EU critical metals dependence, supports the industrial resilience of EU and reinforces the green energy transition.

Table 2. Comparison of different definitions of critical raw material/minerals

Region Country	Official term; Primary Definition Criteria	Focus	Number of currently included materials/minerals	Reference
European Union	Critical Raw Materials (CRM); Economic importance combined with supply risk	Green and digital transition, defense and space technologies	34 minerals, metals and specific groups (PGM, heavy REE and light REE), including strategic raw materials*	European Commission, 2023
United States	Critical Minerals; National/economic security and vulnerability to supply disruption	High technologies in energy, defense, society development, and the manufacturing of products, the absence of which would have significant consequences	60 minerals and metals needed; Critical REEs and PGM are named separately	USGS, 2025
China	Critical minerals; Strategic-ness predicted for national development, combined with "advantageous" market dominance	Not just on scarce imports, but also minerals where China holds the global supply monopoly (e.g., REEs) - with the aim to protect resources, control overproduction, manage environmental degradation, and dictate global prices	32 metals and minerals (REEs are grouped together)	Ren et al., 2025
Australia	Critical minerals list, Strategic materials list. Vital to global partner economies, combined with geological/ technological potential	Australia's role as a reliable global supplier and expanding domestic geological/technological potential	31 minerals, metals and specific groups (PGM and REEs)	Parliament of Australia, 2025
India	Critical Raw Materials (CRM); Economic development, national security, and high import reliance	Scaling up domestic manufacturing and clean energy infrastructure	30 raw materials (PGM and REEs are grouped)	Ministry of Mines, 2023

* a subset crucial specifically for green, digital, defense, and space technologies

2. Methods

Elsevier (ScienceDirect, Mendeley, Scopus) and Web of Science databases were used as the primary sources of publications because of their extensive coverage of high-impact journals, and Google Scholar was used as a supplementary source. In addition, the USGS databases were also searched. The initial search was carried out at the beginning of December 2025, and it was updated twice (June and August 2026). The survey covered the recent 20 years using the appropriate keywords, for example ‘’cobalt production’’, ‘’cobalt extraction hydrometallurgical’’, ‘’cobalt recovery hydrometallurgical technology'', ''cobalt hydrometallurgical recovery from copper production", ''cobalt hydrometallurgical recovery from lead production", ''cobalt hydrometallurgical recovery from nickel production'', and in the similar way - for all metals listed in the paper. Key words ''critical raw materials/metals", ''slag", "slime", "tailings", "leaching", ''zinc residue", precipitation", ''replacement'', "ion exchange", "solvent extraction", ''electrowinning'', etc. were also employed. A total of 38 records were removed due to duplication or other reasons. The initial search yielded relevant papers and book chapters (687) and reports (23), which were screened additionally (Fig. 1). Around 75 % of the works identified were from Elsevier, about 10 % from Web of Science, around 5 % from the USGS databases, and the left from the other mentioned sources.

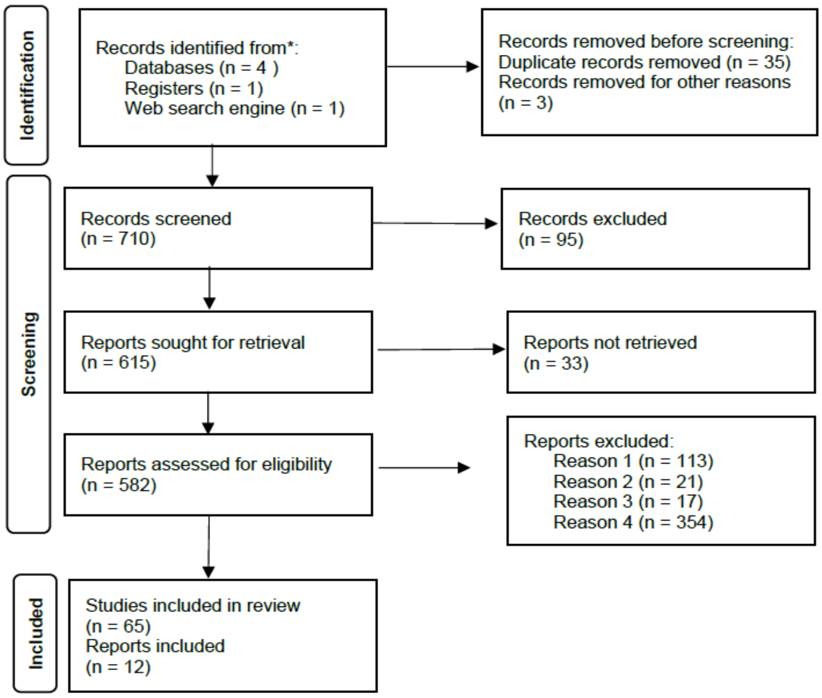

Fig. 1. Schematic representation of the process of searching and specifying the works included in this review– modified after https://www.prisma-statement.org/prisma-2020-flow-diagram

Out of the relevant publications (judged based on the abstracts), 95 were excluded due to the fact that they deal mainly with post-consumer and manufacturing industrial and waste; 33 were not retrieved as full papers. Further screening was based on full-text review. Papers/chapters/reports were chosen that were (i) focused on critical metals, including data on concentrations of those metals (reason 1 for publication exclusion from further consideration if not fulfilled); (ii) assessing the amounts of available metals, based on contemporary analytical and calculation methods (reason 2 for exclusion if not fulfilled). Reliable data on the recent statistics on production, future needs, and recycling have been collected (and cross-checked) for the metals tackled in this paper using unswerving (mainly official institutional documents) sources (reason 3 for exclusion if not confirmed by an official institution document). Corresponding documents of official political entities, such as the European Commission, the Australian Parliament, etc., were employed for data cross-checking. The recycling approaches have been assessed from the technological, environmental, and sustainability viewpoint (reason 4 for exclusion if not fulfilled), and the soundest ones are briefly presented here and compared. Finally, the obstacles to metal recovery from technogenic waste are briefly discussed.

3. Mining and metallurgical waste as secondary source of metals

Technogenic material (mining waste, beneficiation tailings, metallurgical slag and dust, anode slime) represents a secondary source of critical metals and can help in decreasing dependence on primary mining (Lottermoser, 2010; European Commission, 2020; IEA, 2023). Reuter et al. (2019) explained the reasons for the fact observed that the primary production of non-ferrous base metals, particularly from complex sulphide ores, can lead to losses of valuable elements in the technogenic waste, especially of so-called companion metals (many of them classified as critical) of the main base metals. The companion critical metals are linked in a complex manner in their carrier, which affects the metallurgical processing, including their refining and alloying. This causes inevitable losses to final residues. That is why metallurgical residues (slag, dust, slime) often contain economically relevant concentrations of critical metals. Two examples will be mentioned for illustration: (i) It is estimated that for the production of 1 Mg of nickel metal from sulphide ores, about 6-16 Mg of Ni slags are generated. Thus, the nickel industry generates globally about 150 Tg of slags per year (Bartzas et al., 2021); (ii) It is pointed out that mineral processing generates over 5 gigatons of technogenic waste per year (Reyes et al., 2026). More data on the amounts of waste generated, concentrations, and quantities of metals contained have been summarized recently (Panayotova et al., 2026). As a result, large amounts of technogenic waste from primary base-metal production are available worldwide.

In order to further illustrate and support that statement, data on availability and concentration ranges of different critical metals in various solid wastes from the primary production of Cu, Zn, Pb and Ni from sulphide ores worldwide are summarized in Table 3 (Guo et al., 2010; Piatak, 2015; Ashtari, 2015; Haghighi, 2015; Bartzas et al., 2021; Angelov, 2022; Šajn et al, 2022; Khakmardan, 2023; Mends et al., 2025; Mashingaidze, 2025; Panayotova et al., 2026; Reyes et al., 2026).

Table 3. Critical and strategic metals in some residues from non-ferrous base metals production

Waste Metal	Al wt.%	Sb wt.%	Bi wt.%	Co wt.%	Cu wt.%	Mg wt.%	Mn wt.%	Ni wt.%
Cu production								
tailings	0.7-4.59	0.001-0.01	0.004-0.008	0.001-0.004	0.10-0.40	NR	NR	0.001-0.009
slag	0.46-9.8	0.07-0.22	0.006-0.020	0.003-0.424	0.353-12.2	0.41-3.3	0.042-0.418	0.07-0.084
anode slimes	NR	0.5-5.0	0.2-2.0	NR	4.8-50	NR	NR	0.05-28.1
Pb production								
Tailings[1]	NR	0.0082	NR	0.0028	0.021	NR	NR	0.0007
hot filter cake	NR	NR	NR	0.5-3.0	0.07-0.08	NR	6-16	0.075-0.085
slag	1.37-5.02	0.001-0.11	0,0052 – 0,0110	0.001-0.018	0.005-0.25	0.62-3.26	0.12-1.89	0.003-0.21
Zn production								
tailings	NR	NR	NR	0.001-0.005	0.019-0.023	NR	NR	0.002-0.003
slag	2.67-7.58	NR	0.002-0.003	0.004-0.024	0.07-0.90	2.33-2.41	0.23-0.83	0.005-0.011
ZLR	0.21-1.15	NR	0.131[2]	NR	0.35-0.91	0.37[2]	1.41[2]	0.001
Ni production								
tailings	NR	NR	NR	0.025-0.050	0.08-0.29	9.15-18.72	0.120-0.122	0.22-1.32
slag	NR	NR	NR	0.024-0.18	0.014-0.391	NR	NR	0.60-0.65

ZLR – zinc leaching residue; NR - not reported in the cited literature; [1] averaged from 3 Pb-Zn deposits; [2] – reported in 1 paper

The concentration ranges summarize data for the aforementioned metals from numerous literature sources (as cited) and reflect various deposits in different countries around the world. For example, (i) The report of Reyes at al. (2026) is based on data from 653 Chilean copper tailing deposits; (ii) Šajn et al. (2022) present data from 40 potentially prospective for CM extraction mining and processing waste landfills from copper and Pb-Zn production – from West Balkan Region (Albania, Bosnia and Herzegovina, Kosovo, North Macedonia, Montenegro, and Serbia; (iii) Piatak (2015) presents data ranges for 10 slags from Pb production, 10 slags from Zn production and 25 slags from Cu production worldwide. The aim of the present work is to provide examples of the availability of critical metals in solid wastes from the production of base non-ferrous metals at concentrations high enough to be of interest for recovery, rather than to present precise geological and geographical location data. The cited works provide this information. The analytical methods primarily used by the quoted authors to determine CM concentrations are ICP–MS, ICP-AES, AAS, and XRF.

While not thorough, Table 3 provides an obvious picture of the type and concentrations of some critical metals in waste from the extraction of metals from sulphide ores. As can be seen in Table 3, the solid waste contains CM, sometimes at concentrations higher than in the ores (i.e., primary sources). In addition, the waste from Cu, Pb and Zn production in many cases bears Ba and Ti, and sometimes relatively high amounts of Au, Ag, Ge, Ga, PGM, V and even REE (Kaksonen et al., 2011; Reuter et al., 2019; Lobo, 2022; Huston and Bastrakov, 2024; Reyes et al., 2026).

Historically, the extraction and processing of metals remaining in mine wastes were considered economically and technologically unfeasible due to their low concentrations. However, elevated prices in recent years, declining ore grades, increasing supply pressure, and technological advancements have made reprocessing mine waste a more attractive option. Chile is an example of this. Over the last almost 20 years, Chile's average copper ore grade has declined from 0.9% to 0.6%. Today there are 100 tailings sites with ore grades that exceed primary production cut-off, totalling 2 million Mg of contained copper (IEA, 2024).

Residues generated by metals production from sulphide ores contain pyrite, which can dissolve upon contact with water and air, thereby generating acid mine drainage. Increased acidity facilitates leaching reactions, causing hazardous metals to migrate into groundwater and nearby soils. (Lottermoser 2010; Piatak et al., 2015; Minga et al., 2023). The recovery of CM from solid waste generated by base metals extraction from sulphide ores will not only contribute to the production of needed commodities but will also help to combat mobilization of hazardous metals and promote a cleaner and safer environment. Therefore, as illustrated above, solid wastes from the production of non-ferrous base metals from sulphide ores represent a viable source of critical metals, and efficient methods for their extraction and recovery must be developed.

4. Technologies for metals extraction from industrial and mining waste

4.1. Solid waste treatment

Pyrometallurgy and hydrometallurgy are the technologies typically employed for metal recycling, encompassing recovery from non-ferrous production wastes. To ensure good results, they are generally preceded by physical-mechanical pre-treatment: crushing and grinding, screening (sieving), gravity separation, and/or magnetic or electrostatic separation, and/or froth flotation (Lottermoser, 2010; Free, 2013).

New expansions of known technologies (such as bio-metallurgy) and the development of new technologies (electrochemical, solvometallurgy) are being widely studied to permanently enter the field of metals recovery.

The chemical composition of the materials and the volumes to be processed are the main factors determining whether pyrometallurgy or hydrometallurgy will be applied. Pyrometallurgical methods, which are based on high temperatures to extract metals, play a central role in non-ferrous metal processing. These processes include smelting slags and other solid waste to recover elements such as Cu, Ni, V, and W; refining metals through oxidation and/or reduction; and applying integrated high-temperature techniques to recover precious metals from complex metallurgical wastes (Reuter et al., 2019).

Hydrometallurgy is a technology for recovering target metals from materials using suitable aqueous solutions (inorganic or organic). Compared to pyrometallurgy, hydrometallurgy is more easily controllable, suitable for changeable concentrations of the wanted metals and the changeable volumes of material to be treated. The different stages of hydrometallurgy are shown in Fig. 2.

The metals are dissolved and leached from the solid waste and then recovered from the pregnant leach solution (PLS). Metal recovery from the PLS involves purification and separation stages to isolate the target elements by applying different processes, such as precipitation/crystallization, ion adsorption or ion exchange, solvent extraction, electrochemical reduction, etc. (Panayotova and Panayotov, 2017) and membrane processes (Meschke et al., 2020). The pre-treatment stage generally includes grinding and particle-size separation but may also involve washing and magnetic separation.

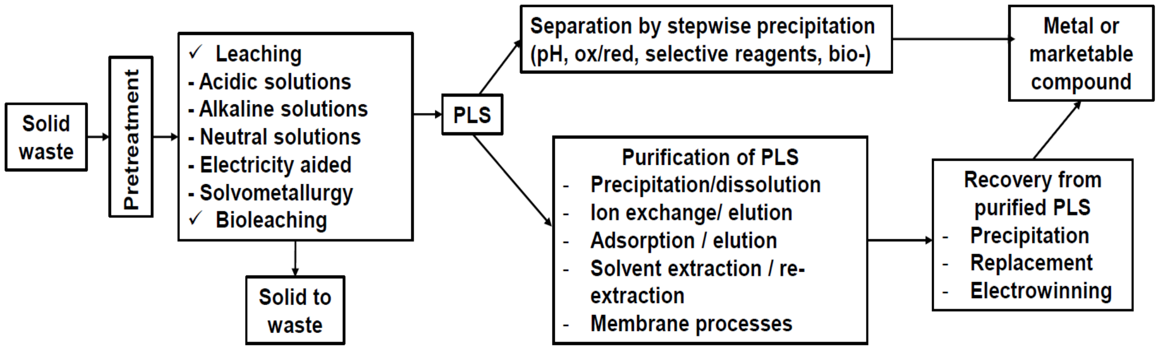

Fig. 2. Different stages of hydrometallurgical treatment of solid waste from base metals production

Solid-liquid separation is performed after the leaching stage, prior to PLS purification or direct metal/compound recovery. Depending on the nature of the processes and chemicals used in the stages of leaching or PLS purification, reagents or water solutions left after metal(s) or metal compound production are recycled to the leaching or PLS purification stages. To improve both the efficiency and purity of metal recovery, different processes (including precipitation, solvent extraction, ion exchange, membrane technologies, and electrowinning) can be integrated.

Electrochemically assisted hydrometallurgy and solvometallurgy, including supercritical fluid extraction, represent relatively new pathways currently being explored and implemented for metal recovery from industrial wastes. (Wu et al., 2022; Siwal et al., 2023; Mourdikoudis and Dominguez-Benetton, 2025). Electrochemical technology is encouraging due to minimal use of chemicals. Anodic current is (usually) used to facilitate the disintegration and leaching of solid materials. The leached metal ions can be electro-won in another electrolytic cell. Generally, this is an environmentally friendly technology; however, the generated sludge (often categorized as hazardous waste) requires additional treatment and disposal.

Slurry electrolysis (SE) is a relatively new hydrometallurgical technique that combines leaching, partial solution purification, and electrowinning in the same equipment (Zhanga et al., 2019). The technology utilizes the anodic (oxidation) half-reaction thus eliminating the need of oxidants addition to facilitate the metals dissolution and leaching from the sulphide bearing solid material. Simultaneously, metal ions produced in the slurry are reduced and electrodeposited on the cathode. The combination of anodic oxidation with cathodic reduction contributes to better use of energy. By controlling the process conditions and especially the oxidation-reduction potential, effective separation of the desired metals can be achieved. In addition, SE can oxidise the sulphide (S^{2-}) to elemental sulphur (S^0). This averts the generation of environmentally hazardous SO_2 during pyrometallurgical processing. Some of the problems faced by SE are relatively low current efficiency and high energy consumption, mainly ascribed to passivation and significant side reactions. That is why further studies (at lab scale) have combined electrolysis process with cyclone technology in a method denoted to as cyclone slurry electrolysis (Tian et al., 2025). This method reduces concentration polarization and mitigates harmful side reactions; it has been successfully used at laboratory scale to recover Sb with a purity of 98.6%. However, both slurry electrolysis and cyclone slurry electrolysis methods for CM recovery are currently developed at the level of laboratory demonstration. These promising methods need further studies and advances with the aim of (i) increasing current efficiency by suppressing possible parasitic or competing reactions (such as gas evolution or secondary precipitation) and increasing flow rates limited by high viscosity, (ii) raising the purity of metals obtained, (iii) overcoming problems with slurry instability and solid particle aggregation, as well as complications related to pumping abrasive solid-liquid mixtures (such as mechanical wear of flow channels, pumps, and separators).

Bio-metallurgical processing of solid waste utilizes microorganisms or biological materials to mobilize and extract metals. Bio-metallurgy includes bioleaching and biosorption. Bioleaching is a treatment in which specific microorganisms or their metabolites extract metals from a solid material into solution. The method is appropriate for solubilizing Cu, Mn, Zn, and Co from tailings, slag, and metallurgical dust (Sethurajan et. al., 2018; Kara et al., 2023). Simplicity, selectivity, flexibility, low cost, and environmental friendliness are the advantages of bioleaching. Biosorption is a process in which biomass is used to selectively separate already dissolved metals, such as Co, Cu, Ni, Mn, and Zn (Johnson, 2014).

Table 4 presents a short comparison of pyro-, hydro- and bio-metallurgy applicability (Habib et al., 2019; Kinnunen et al., 2020; Sonule et al., 2023; Wang et al., 2024, Georgiev et al., 2025; Phogat et al., 2025; Trucco et al., 2025; Nikolski et al., 2026). The recovery efficiencies and technology readiness levels (TRL) in Table 4 are indicative ranges derived from the literature, not universal process efficiencies and TRLs.

Solvometallurgy uses non-aqueous solvents (molecular organic solvents, ionic liquids, deep eutectic solvents, or inorganic solvents – for example, concentrated sulfuric acid, liquefied ammonia, or supercritical carbon dioxide) with the aim of increasing the leachability and selectivity of the target metals (Binnemans and Jones, 2017; Matinde, 2018). The solvents employed can alter the solubility of materials that are poorly soluble in water (the medium used in classical hydrometallurgy), thereby enhancing selectivity and improving metal recovery rates. The technological steps are in general similar to those of classical hydrometallurgy – Fig. 2. However, they are all carried out in non-aqueous solution. This is particularly apparent when the PLS is purified by solvent extraction, as solvometallurgy employs a distribution between two immiscible organic phases. In many cases, these reagents can be recycled and reused in the leaching process.

For example, prop-2-enoic acid dissolved in 2:1 blend of water and the non-aqueous solvent methylbenzene is used to selectively extract Zn from blast furnace dust slurry (Steer and Griffiths, 2013).

Ionic liquids (ILs) are organic salts having melting points below 100 ◦C. They comprise organic heterocyclic cations and organic or inorganic anions. ILs are able to interact strongly with matter via ion pairing, hydrogen bonding, van der Waals forces, and electrostatic interactions (Khalid and Santos, 2025). Deep eutectic solvents (DESs) are formed by combining hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) (Binnemans and Jones, 2017). They are frequently considered a subclass of ILs. ILs (including DESs) are non-volatile, exhibit high solvating power, selectivity with respect to different metals, broad miscibility, and good regeneration ability. Generally, most DESs are inexpensive, readily available, biodegradable, and possess a wide electrochemical window. All these properties render ILs and DESs promising alternatives to conventional leaching reagents (acidic, basic, or chloride-based systems). ILs are successfully used to leach various critical metals from WEEE, PCBs, LCDs, etc. (Khalid and Santos, 2025). Li et al. (2023) effectively used commercial green ionic liquids based on 1-butyl-3-methylimidazolium hydrogen sulphate, [BMIM][HSO_4], [HOOCMIM]HSO_4, [BSO_3HMIM]HSO_4, and [BSO_3]Py.HSO_4) to leach Cu from sludge. Especially good results (100 % leached and fast leaching rate) were achieved with sulfonated versions.

A DES prepared by mixing 1 M choline chloride: 1.5 M urea: 0.5 M ethylene glycol is used to solubilize Zn from cupola furnace dust. The DES dissolved and extracted about 38% of the initial zinc present in the dust. Further, by applying a potential in the range (-1200 to -1500 mV vs. silver chloride electrode), metallic Zn with high purity was directly electrodeposited at high current efficiency (Bakkar and Neubert, 2019).

Qiao et al. (2023) developed a DES consisting of choline chloride and hydrated oxalic acid, which was applied to leach blast furnace dust in order to recover bismuth. A leaching efficiency of 94.9% was attained.

Hydrolysis and photoinduced reduction were used to remove zinc and iron impurities in the leach solution. The by-products produced ($ZnC_2O_4{\cdot}2H_2O$ and $FeC_2O_4{\cdot}2H_2O$) had purities of 86.6% and 96.8%, correspondingly. Further, in order to recover Bi from the leach solution, another hydrolysis was conducted, and BiOCl was obtained; the total Bi recovery efficiency was 89.1%.

Niu et al. (2023) also reported a high zinc recovery yield from zinc-bearing sludge using a DES formulated with choline chloride (hydrogen bond acceptor) and malonic acid (hydrogen bond donor), reaching a leaching rate of 91.61%. The leaching process conducted under ultrasound further increased the zinc leaching rate by 6.88%.

Table 4. A short comparison of pyro-, hydro-, and bio- metallurgy applicability to recover critical metals from solid waste from base non-ferrous metals production

Process/ Factors	**Pyrometallurgy**	**Hydrometallurgy**	**Bio-metallurgy (Biologically Mediated Metals Recovery)**
Short description	Set of processes using high temperatures to facilitate chemical reactions able to separate and purify metals from the gangue	Set of processes that use aqueous solutions to dissolve, purify and recover metals from solid materials (slag, tailings, slime, ZLR) under ambient to mildly elevated temperatures; it can be facilitated electrochemically or by applying pressure, oxidizing or reducing reagents	Set of processes that harness the power of microbes to extract valuable metals from mining waste by facilitating metal dissolution and metal separation under ambient temperature and natural environment
Applicability /Suitability	For big waste amounts, containing CM that are present in relatively high concentrations (i.e., Al, Cu, Ni, Zn, Ti, W)	For smaller and changeable waste amounts, containing a broad spectrum of metals, often in very low and changeable concentrations	For large amounts of solid waste bearing primarily specific metals, like copper and gold in low concentrations
Processing time and selectivity	Often faster than hydrometallurgy and bio metallurgy but generally is less selective	Generally slower than pyrometallurgy but usually provides better selectivity, especially at treating complex materials	Slower than traditional hydrometallurgy but can ensure higher selectivity for certain metals
Recovery efficiencies generally reported	90% - 98% for base metals available in the waste in relatively high concentrations, i.e., Cu, Zn, Al, etc.	85% to 95% for trace metals; can be increased by an additional impact, for example, preliminary roasting, ultrasonic	For the relatively well-known process of Cu leaching – in the range 50-91 % for waste from Cu production
Energy, water, and chemicals use	Energy intensive, reduced water use, minimal chemical usage	Lower energy consumption compared to pyrometallurgy, use of larger water volumes and chemicals	May need addition of amendments to improve conditions for some species; water usage can be optimized through recycling and reuse; low energy usage
Impact on the environment and human health	Gaseous emissions (SO_2, CO_2, etc.); Generally safe for workers if safety protocols and training are properly implemented; Need of flue gases and other smelter outputs proper management	Lower gaseous emissions than pyrometallurgy but generally secondary hazardous chemical waste may be generated; Safe for workers if proper training, adherence to safety protocols, and regular monitoring is ensured; Use of nontoxic / low-toxicity chemicals can enhance worker safety and minimize environmental risks	Lowest environmental impact – uses natural processes and minimizes the use of chemicals; Safe for workers if common safety measures are obeyed
Residue and waste management	Produced slag / other solid residues, which can contain hazardous materials requiring proper treatment and disposal	Generated waste streams demand further proper treatment/management to prevent environment contamination	Generally fewer solid and liquid wastes are generated compared to pyrometallurgy and some hydrometallurgical methods
Maturity, operational complexity	Mature technology, needs specific infrastructure and equipment; Relatively complex technology, requires specialized personnel;	Mature technology but with ability to faster implement innovative approaches and solutions compared to pyrometallurgy; Generally, readily available equipment and medium operational complexity; TRL – mainly from 4 up to 7-8	Promising technology for reprocessing mining waste; Widely available equipment; operational complexity ranges from low to medium, depending on the specific application TRL – mainly from 4 up to 7

	TRL – generally 7-9, although studies continue on application for trace metals - at TRL 4-6		
Challenges	High energy consumption, emission control required; solid waste stabilization	Chemicals handling and wastewater treatment	Slow reaction rates, limited scalability, metal specificity
Cost[1]	High cost of implementing and maintaining the necessary equipment and infrastructure ($100 -$200 per Mg of material processed)	Generally cheaper than pyrometallurgy ($50-$100 per Mg of material processed)	The lowest cost ($20-$50 per Mg of material processed)

TRL - Technology Readiness Levels; [1] - Figures are from Sonule et al. (2023)

Sudová et al. (2024) experimentally proved (at small laboratory scale) the feasibility to use deep eutectic solvents, especially the mixture of choline chloride and ethylene glycol to which iodine is added as oxidizing agent, as leaching reagent for Sb extraction from Čučma mining tailings.

The application of supercritical fluids (SCFs) for metal extraction from solid technogenic waste is considered a promising new method for processing these secondary resources (Lin et al., 2014). By using SCFs, the mass transfer limitations that slow dissolution and leaching reactions are surmounted.

Carbon dioxide (critical point of 31.1°C and 73.8 bar) is the most widely utilized supercritical fluid owing to its non-toxicity, non-flammability, plenitude, and environmental compatibility. The process is facilitated by addition of different acids, organic solvents, complexes-forming or chelating reagents, etc. – in dependence of the metal(s) to be extracted (Wu et al., 2022). Use of SCFs technology may enable selective extraction and recovery of specific metals from complex waste streams by using different pressures and temperatures. The commercial deployment of supercritical CO_2 technology is primarily limited to extracting spices, pigments, and animal fats. Its utility in metal extraction is proved predominantly only at the laboratory level. However, in order to be implemented at commercial scale, it needs an advanced infrastructure and suitable regulatory framework. The main technical challenge is the high capital investment required for equipment capable of withstanding supercritical conditions. Another important obstacle is the high energy consumption during pressurization and temperature maintenance. While modern systems feature advanced heat recovery capable of reclaiming up to 85–90% of thermal energy, energy efficiency is still a key determinant of the commercial viability and environmental sustainability of SCF processes. An additional challenge is the need for process optimization for different feedstock types, since the efficiency of SCF extraction varies substantially depending on the waste composition. Therefore, further research must focus on the interaction mechanisms of metals within ligand–supercritical CO_2 systems, specifically addressing matrix effects, ligand selection, phase interface behaviour, and complex solubility.

Environmental regulations pose another significant challenge. At the international level, the Stockholm Convention on Persistent Organic Pollutants and the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal are the primary frameworks to comply with, while at the EU level, compliance is governed by the Waste Framework Directive and the Industrial Emissions Directive. In addition, following supercritical extraction, the recovered metals must undergo downstream processing to separate the individual elements from the multi-metal mixture.

4.2. Limitations, challenges and future directions

Examples shown in Table 3 reveal that mining, mineral processing, and metallurgical solid wastes have to be regarded as resources of CM. However, metal recovery is linked with different obstacles. Frequently, metal concentrations are low, often representing an analytical challenge, and requiring the processing of large amounts of material, which leads to high energy and financial costs. Standard mineral beneficiation and hydrometallurgical methods are not always applicable due to the chemical complexity and mineralogical heterogeneity of the wastes. Furthermore, a report indicates (European

Commission, 2020) that the reprocessing of old tailings can create environmental risks, such as site erosion, groundwater contamination, and the generation of acid drainage. The aforementioned highlights the need to address various technological, environmental, and regulatory challenges in the future.

Insufficient information on the presence, concentrations, spatial distribution, and forms of existence of critical metals in solid technogenic waste sites is one of the issues awaiting a solution.

The low metal concentrations, combined with complex mineralogy, including the isomorphic incorporation of some critical metals into the crystal lattice of the main sulphides, point to the need for a wider application of contemporary process mineralogy tools (especially Quantitative Evaluation of Minerals by SCANning - QEMSCAN, Mineral Liberation Analysis - MLA, and Electron Probe Microanalysis - EPMA). The mentioned tools map the mineral phases, distribution of elements, and grain size of solid mining waste (Heather et al., 2015; Warlo et al., 2019). The data obtained help in deciding on the most economical processing route by revealing, for example, whether valuable metals are exposed as free sulphides (allowing flotation), locked inside stable silicates (needing roasting or pressure leaching) or finely disseminated in iron sulphides (requiring direct bioleaching). QEMSCAN and MLA data provide information on the size of valuable mineral particles as well as whether the metals of interest are in liberated minerals or locked inside gangue minerals. The associated mapping identifies which minerals in the waste material host valuable metals. EPMA provides high-resolution information on concentrations of different elements inside tiny mineral grains. It detects so-called "refractory, invisible" metals (such as Au, Cu) that are chemically bound inside a crystal lattice, like pyrite or arsenopyrite (Morishita et al., 2008; Llovet et al., 2021).

The high degree of liberation (typically >50% exposed surface area) and coarse grain sizes of the target minerals, combined with EPMA data confirming that target elements reside within distinct mineral phases rather than as trace impurities in the gangue, demonstrate the feasibility of beneficiation (such as flotation or magnetic separation) for pre-concentrating the valuable minerals (Pascoe et al., 2007; Escalante et al., 2026). Low liberation, extreme fine-graining, or substantial surface coating of valuable minerals (e.g., iron oxide rims on sulphide minerals, anglesite on galena) necessitate the implementation of hydrometallurgical routes to dissolve the entire solid matrix. When EPMA reveals that target minerals are structurally complex or locked as solid solutions within silicate or carbonate matrices, a hydrometallurgical approach—utilizing acids, bases, specific lixiviants (e.g., ammonium hydroxide for Cu-bearing tailings), or pressure digestion—represents the optimal treatment route. In such cases, when QEMSCAN identifies a high concentration of acid consumers (e.g., calcite and dolomite) in the material to be treated, this rules out simple acid leaching and steers the project toward alkaline leaching or pressure oxidation. Bioleaching is usually the preferred option for non-carbonaceous solid waste where target metals are trapped inside sulphide minerals (e.g., pyrite, pyrrhotite, arsenopyrite, and chalcopyrite) that can be oxidized and dissolved by acidophilic bacteria, thereby allowing the valuable metals to enter the leachate cost-effectively.

When the solid waste is metallurgical slag, it contains amorphous glass phases alongside complex, synthetic crystal structures, all of which form due to rapid cooling (Schulz et al., 2020). Valuable metals are frequently trapped evenly inside an amorphous silicate glass matrix rather than forming distinct mineral grains; The resulting crystalline phases are typically highly complex and closely intergrown at the sub-micron scale. The slag frequently contains metallic prills (droplets of copper, lead, iron, or matte) or distinct oxide phases (like magnetite, spinels).

When the QEMSCAN/MLA shows liberated metallic prills (e.g., of Cu, Pb) or distinct phases that are highly liberated at a size above 20–30 microns, beneficiation is a suitable (pre-)treatment process (Chen and Zhang, 2025). If QEMSCAN shows "emulsion-like" textures, where micro-droplets (< 5 μm) are completely encapsulated by glass, the hydrometallurgical route is suitable. However, silica gel formation due to the silicates' dissolution in strong acids has to be taken into account since it hinders the filtration process. High-arsenic speiss phases (in Pb metallurgy slag) generally require oxidative pressure leaching.

If the slag matrix is highly crystalline and contains residual iron sulfides, iron-oxidizing bacteria can attack it to expose the metal, for example, copper. When the slag contains significant sulphur/matte phases hosting lead and zinc, bioleaching using mixed cultures of iron- and sulphur-oxidizing bacteria may be considered. However, if EPMA data reveal high concentrations of arsenic or other heavy metals dissolved in these phases, these elements can poison the bacteria, ruling out bioleaching as a suitable processing route.

In summary, results from the characterization of the material to be treated, employing contemporary process mineralogy and chemical analysis tools, are the solid basis for deciding about the subsequent treatment stages.

Pre-concentration and beneficiation may serve as important and useful first-stage strategies for upgrading low-grade technogenic waste. These methods are based on utilisation of the mechanical or physical properties of materials without altering their chemical composition. Key methods include (Lottermoser, 2010; Reuter et al., 2019): (i) Crushing and grinding – reducing the size of the material to fractions appropriate for further processing; (ii) Screening (sieving) – separating materials by size or shape; (iii) Gravity separation – utilizing differences in mineral density using jigs, sluices, or spiral concentrators; (iv) Magnetic or electrostatic separation – sorting out magnetic or conductive minerals from low or non-magnetic and nonconducting ore components; (v) Froth flotation – a physico-chemical method that concentrates minerals grounded on differences in their surface properties. Pre-concentration/beneficiation rejects barren gangue early, reduces the mass of the materials to be processed in the subsequent treatment, and concentrates valuable metals before hydro- or pyrometallurgical extraction. This lowers the overall energy consumption, as well as reagent and water requirements. In addition, pre-concentration and beneficiation maximize metal recovery across the entire processing line while minimizing the volume of final hazardous residues that require specialized disposal. In summary, involving a pre-concentration and beneficiation stage (where technologically feasible) generally lowers the costs of valuable metal recovery from solid mining and metallurgical waste.

Processing substantial quantities of solid waste with low CM concentrations generally renders hydrometallurgy a more viable primary option than pyrometallurgy. Nevertheless, the environmental and technological challenges associated with deploying strong mineral acids or highly alkaline sulphide leaching reagents must be carefully addressed.

The development of electrochemically aided leaching, especially slurry electrolysis (SE) (Siwal et al., 2023), and solvometallurgy represent promising directions for overcoming these problems. However, the relatively low current efficiency and the high energy consumption associated with SE must be overcome (Tian et al., 2025).

Compared to classical aqueous hydrometallurgy, solvometallurgy possesses significant advantages (Binnemans and Jones, 2017). First, it utilizes a highly limited amount of water, thereby avoiding the generation of wastewater. Second, leaching and PLS purification by solvent extraction can be integrated into a single step, ensuring a more simplified process flowsheet. Finally, solvent leaching is generally more selective compared to aqueous leaching, which reduces the number of required purification steps. Solvometallurgy is able to leach solid material, including mining and metallurgical solid waste, rich in soluble silica because no silica gel is formed. In addition, energy consumption by solvometallurgy is much lower than that of high-temperature processes. Although solvometallurgy is far from commercial adoption, it provides advantages such as high selectivity, the ability to recover the valuable metals in their pure states, and the capability to detoxify and produce environmentally benign residues.

However, although they represent promising alternatives to traditional hydrometallurgical solvents, ILs and DESs exhibit several disadvantages (Binnemans and Jones, 2023). Their viscosity is typically 2–3 times greater than that of molecular organic solvents or water which presents challenges from technological point of view in industrial context (pumping, mixing, solid-liquid separation, handling of wetted solid surfaces due to the low volatility of ILs / DES, difficulties in solvents regeneration). The high viscosity hinders mass transport, thereby retarding the chemical reactions that take place during leaching, solvent extraction, or electrodeposition. As summarised by Binnemans and Jones (2023) some studies have concluded that IL organic phases are too viscous to operate within the most often used systems (mixer-settler) at room temperature. High-viscosity liquids tend to adhere to the surface of the residue particles, thereby causing solvent losses. Filtering, washing, and drying operations, usually employed in hydrometallurgy, generally cannot be straightforwardly applied when ILs (including DESs) are used as solvents. Washing the solid residue must be conducted using either water or a molecular organic solvent, which subsequently requires separate process steps to recover the washing agents. When real solid material with a complex matrix is dissolved using ILs, impurity metals are co-dissolved. Subsequent steps of target metal recovery leave impurities in the ILs, thereby hindering IL recycling.

Ionic liquids demonstrate restricted chemical stability under typical metallurgical conditions, like leaching and electrowinning. Within hydrometallurgical systems, the presence of transition metals can catalyse oxidation reactions that degrade the ILs. The resulting decomposition products often exhibit chemical properties different from those of the original ionic liquids. The fact that organic solvents and extractants, especially ILs, are more expensive than water and mineral acids represents another obstacle to their rapid adoption in the industry. The complete recycling of these reagents remains a crucial yet unsolved task. A better comprehension of the interactions between metal ions and solvent molecules will contribute to resolving these problems.

Furthermore, not all ILs and DESs are environmentally benign. Their environmental performance is highly dependent on chemical composition, synthesis route, toxicity, and recyclability. For health, safety, and environmental reasons, not all solvents with high capability to dissolve metals are to be used - benzene, nitrobenzene, carbon tetrachloride, carbon disulphide are some examples of solvents that are phased out or banned by different environment and human health protection authorities in many political entities.

According to Binnemans and Jones (2023), this developing branch of extractive metallurgy remains at the 'experimental proof-of-concept' or 'technology validated in lab' stage, corresponding to TRL 3–4. The reported studies and results are of too limited scale to serve as a basis for establishing the real potential of these technologies in the industry. Therefore, before stating that solvometallurgy can be applied at an industrial level, substantial further research, development, and innovation are required, at least on a pilot scale, to study the behaviour of these solvent systems over the long term. Specifically, data on the rheology, chemical stability, phase disengagement, impurity build-up, solvent losses, recyclability, and entrainment in solvent extraction of these systems, as well as mass and energy balances, and CAPEX and OPEX calculations, are critically required.

Bioleaching can be a potential method for reprocessing mine tailings; it provides economic and environmental benefits, but its low recovery rate, long operation time, and applicability only to specific metals require further research.

Future research, aimed at enhancing metal recovery from solid metal extraction waste and overall efficiency, should focus on the development of flexible, multi-stage, integrated approaches that combine physical, hydro- and/or pyrometallurgical, and biotechnological methods. Integrated and hybrid solutions combining different technologies to recover valuable metals from mining, mineral processing and metallurgical waste are regarded as a potential game-changer for ensuring enough metals for the society sustainable development (Gomez et al., 2025; Vo et al., 2026). Technology integration has to be based on the physical, chemical, and mineralogical properties of the materials to be processed and waste amounts.

Based on the discussion above, we propose the following conceptual technological approach for the treatment of solid waste from the primary production of non-ferrous base metals:

Initial characterization of solid waste → chemical and mineralogical characterization → (liberation / association) → selection of treatment technology → (pre-concentration) → conduction pyro-/hydro-/bio-/solvometallurgical treatment to recover metal(s) → residue treatment and recycling to the process or disposal → environmental and economic assessment.

Depending on the material characteristics, the stages in brackets may be omitted.

In addition, overlooking non-technical factors represents a critical oversight. Economic parameters are of paramount importance: (i) generally, implementing new technologies requires substantial capital expenditure; and (ii) the primary production of a specific metal can sometimes be more cost-effective than its recycling from waste sources (Matinde et al., 2018). With regard to capital and operational costs, the proposed technological flowsheet should be tailored to small and medium-sized enterprises.

Additional crucial directions for future studies to foster the sustainable utilization of mining and metallurgical wastes as CM sources include: (i) the application of these wastes in the synthesis of nanomaterials (Wong-Pinto et al., 2020; Shirmehenji et al., 2021), and (ii) the integration of artificial intelligence into processing operations (Tatiya et al., 2025).

The following primary non-technological barriers to recovering CMs from solid technogenic waste have been identified: (i) high initial capital investment required for specialized reprocessing plants; (ii) fluctuating primary metal prices that make recycling projects financially unpredictable; (iii) unclear legal ownership of historical waste sites that hinders commercial investment; and (iv) a lack of standardized methodologies for assessing anthropogenic sources.

The European Commission (2023) emphasizes insufficient incentives and regulatory frameworks to support investment in secondary resource recovery, calling for collaborative efforts among industry, governments, and research organizations. To address these challenges, the European Commission (2024) adopted the Critical Raw Materials Act, which focuses on recovering critical raw materials from extractive waste facilities in historical mining regions. From this perspective, solid mining wastes, beneficiation tailings, and metallurgical residues from the primary production of metals can serve as significant secondary sources of critical metals.

5. Conclusions

Mining and metallurgical solid wastes represent the largest available secondary resources for CRMs. Copper slag constitutes a viable source for the recovery of Al, Sb, Bi, Co, Cu, and Ni, whereas copper anode slime is highly enriched in Sb, Bi, Cu, and Ni. Lead slag serves as a potential source of Bi, ZLR provides opportunities for Bi and Cu recovery, and nickel slag can be utilized for the extraction of Co, Cu, and Ni.

Currently, pyrometallurgical and hydrometallurgical routes represent mature, commercially established technologies. Pyrometallurgy is inherently suited for treating large volumes of waste characterized by relatively high concentrations of specific critical metals (e.g., Al, Cu, Ni, Zn, Ti, and W). Hydrometallurgy is highly appropriate for managing smaller, fluctuating waste volumes containing a broad spectrum of metals, often present in very low and variable concentrations. Biometallurgy is well-developed for the large-scale treatment of solid wastes bearing predominantly specific target metals, such as low-grade copper and gold.

Advanced methods—including slurry electrolysis, supercritical fluid extraction, and solvometallurgy employing ionic liquids (ILs) and deep eutectic solvents (DES)—remain confined to laboratory and pilot scales. Although these emerging technologies exhibit highly promising results, extensive research and development are still required to bridge the gap toward industrial scale-up and market readiness.

Several key strategies can drive future progress in the sustainable recovery of critical metals from the aforementioned secondary resources:

- Establishing integrated process flowsheets that synergistically combine different approaches, including mineral beneficiation, hydrometallurgy, pyrometallurgy, and biotechnology. Within this framework, solvometallurgy can be incorporated as a complementary component. Adopting the conceptual technological approach proposed in this study may serve as a valuable foundation for such integration.
- Fostering research and innovation from laboratory to industrial scales, with a dual focus on: (i) developing novel, highly efficient, and environmentally benign lixiviants, alongside effective pathways for recovering high-purity metals or metal compounds from the resulting pregnant leach solutions; and (ii) shifting emphasis toward the direct synthesis of advanced functional materials utilizing critical metals retrieved from technogenic solid wastes.
- Standardizing methodologies for resource assessment and quality control, which is paramount for the seamless integration of waste-derived critical metals into industrial supply chains.
- Moving forward with policies that stimulate secondary raw materials usage by creating and implementing suitable legislative measures and financial incentives for recycling and application of technogenic waste-derived metals. Advancing regulatory policies that stimulate the utilization of

secondary raw materials through the creation and implementation of tailored legislative frameworks and financial incentives, thereby promoting the recycling and industrial application of metals reclaimed from technogenic waste.

Bridging the gap between interdisciplinary research and the industrial deployment of advanced technologies—supported by robust policy frameworks and strategic investments—will guarantee a secure, resilient, and sustainable supply of these critical resources for decades to come.

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