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Critical raw material-containing residues

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1.1 Introduction

Mining, mineral processing, and metallurgical residues are the wastes generated along natural resources processing chain. These residues include the topsoil, overburden, waste rock, mining and process waters, tailings, slags, ashes, dusts, and other categories of waste, see Fig. 1–1 by Whitworth et al. (2022). Being generated at the different stages of the natural resource extraction and processing, these wastes are characterized with drastically different properties. These properties play an important role in the reprocessing flowsheet design, which is one of the key components allowing to reply to the crucial question “is it technologically and economically feasible to extract the metal of interest from this particular residue?” It is therefore necessary to discuss the properties of the major categories of the residues prior to addressing the technological solutions for their sampling and reprocessing.

Since the definition of criticality is not limited to the geological setting, the sources to recover critical raw materials (CRMs) are diverse. The metal wheel proposed by Verhoef et al. (2004), and presented in Fig. 1–2, shows the relationship between primary “carrier” metals (closest to the center of the circle) and the associated coproduct metals. The metals extracted as by-products occupy the white circle, and the metals that end up in the residue are located in the outermost part of the wheel. In this visualization, Al is considered sourced from bauxite ore. While many CRMs can be sourced as by-products of beneficiation of polymetallic ores (Bellenfant et al., 2013), in the beneficiation of oxide ores, CRMs often end up in the residues. Even though in some parts of the world the platinum group metals (PGMs) can be recovered as by-products of the refining of Ni

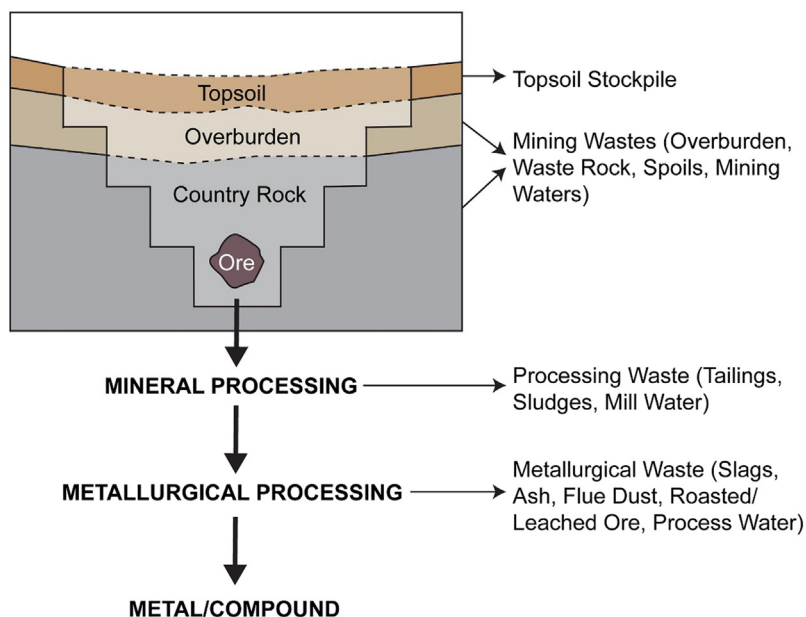


FIGURE 1–1 Illustration of residues origin. Reproduced from Whitworth, A. J., Vaughan, J., Southam, G., van der Ent, A., Nkrumah, P. N., Ma, X., & Parbhakar-Fox, A. (2022). Review on metal extraction technologies suitable for critical metal recovery from mining and processing wastes. *Minerals Engineering*, 182. Available from: <https://doi.org/10.1016/j.mineng.2022.107537>; <http://www.journals.elsevier.com/minerals-engineering/>, with permission from Elsevier.

laterites (Lauri et al., 2018; Valetton et al., 1987), in places like in Europe, the production is too small to consider them as a reliable source of CRMs. The same consideration applies to the metal recovery from titanium ores and by-products (Blengini et al., 2020). The beneficiation of iron ores leaves residues enriched in Mg, Ti, V, and rare earth elements (REEs, not included in the metal wheel). REEs are also recovered as by-products in phosphate beneficiation from apatite in Finland and Norway and bauxite in Italy, Greece, and Turkey (Goodenough et al., 2016). In addition, bauxite residues, the solid residue generated in the Bayer process for aluminum production, have attracted attention in the past years as a potential source of REEs (Balaram et al., 1995; Vind et al., 2018).

Another example of an element radar chart was included in the work of Piatak (2018) (see Fig. 1–3), created basing on the work of Nakajima et al. (2010); this chart represents the elemental distribution between the phases during the metallurgical processing of metal concentrates. In Fig. 1–3, circled elements belong to the CRMs' list of 2020.

This chapter addresses the general properties and characteristics of the following residue categories: mining wastes, mineral processing wastes or tailings, metallurgical wastes (slags, dusts, slimes, and muds), and wastewaters, including acid mine drainage (AMD), as well as their storage, disposal and a brief indication of associated environmental impacts.

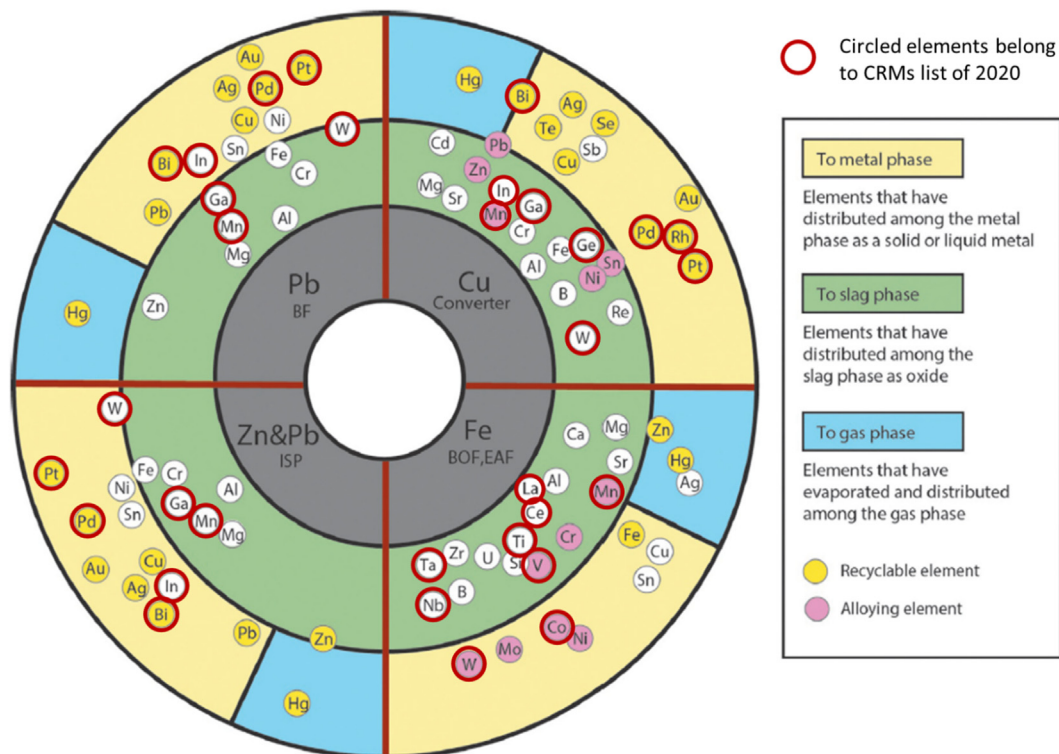


FIGURE 1-3 The element radar chart, featuring elemental distribution between the gas, slag, and metal phases during metallurgical processing. BF, Blast furnace; BOF, basic oxygen furnace; EAF, electric arc furnace; ICP, imperial smelting process. Reproduced from Piatak, N. M., 2018. *Environmental characteristics and utilization potential of metallurgical slag environmental geochemistry: Site characterization*. In *Data analysis and case histories (2nd ed., pp. 487–519)*. Elsevier. Available from: <http://www.sciencedirect.com/science/book/9780444637635.10.1016/B978-0-444-63763-5.00020-3>, with permission from Elsevier.

- The waste stockpiles are mostly low-grade material, on the basis of the target of processing plant feed. They have concentration below the cutoff grade.
- While high-grade stockpiles are mainly sent to the processing plant, low-grade stockpiles can be abandoned after mine closure.
- In the traditional mining business plan, waste stockpiles do not represent any economic return, while often they are a cost, due to the necessary land reclamation after mine closure.
- Blocks entering the waste stockpiles are sometimes mixed homogeneously and sometimes heterogeneously (mixture of low-grade and gangue or noneconomic rocks).
- Waste rocks are mostly dry at the time of piling, with various PSD from coarse, granular broken rock and boulders to the size range of sands.
- Abandoned low-grade stockpiles can have the same elements (and metals) of the mining area from which they were excavated. They are often associated with sulfide minerals

(such as pyrite), consisting of sulfur and metals, such as arsenic, copper, lead, and others. Most sulfide minerals, when dug up and exposed to the environment (oxygen, air temperature, and humidity levels), can oxidize and degrade to produce sulfuric acid and dissolved metals.

- The main consequence of degradation includes changes in material properties; therefore in these cases, long term and abandoned stockpiles do not contain the same minerals as identified by original characterization during the mine planning.
- Abandoned low-grade stockpiles can cause environmental hazards, whereas, on the other hand, they can become economically profitable for metals recovery due to cutoff grade variations with respect to the time of original mines exploration.

Since the main materials in mining wastes are noneconomic materials, various factors can affect the definition of mining wastes at the time of mine life, such as physical–chemical properties of the ore body, technical aspects of mining project, technological innovations at the time of mining extractions, and the economic context (Lèbre et al., 2017). Each of these parameters can importantly change the volume of produced mining wastes. As an example of physical–chemical properties of the ore body, if two copper ores have respective contents of 7.0% and 0.7%, for 1 t of produced copper, the first one will produce 11.5 t of waste while the second will produce 164.4 t of them (Charbonnier, 2001).

Mining wastes' properties vary both during the mining operation and then by remaining abandoned for decades. The PSD, the porosity, the hydraulic, and therefore the atmospheric conditions are the main parameters affecting the geochemical processes, physical transport mechanisms, hydrological, microbiological, and gas and heat transport aspects of waste rocks (Amos et al., 2015).

The first important attribute of mining waste chemical reactivity, which is responsible for the generation of AMD, specifically from metal mines, is the balance between reactive, acid-generating sulfide minerals (notably pyrite and pyrrhotite) and acid-neutralizing minerals (primarily calcite and other carbonate minerals, such as dolomite) (Jamieson, 2011). It is possible to evaluate this balance by static tests using acid–base accounting methods (Jambor et al., 2003).

As an example, sulfide minerals, when exposed to the atmosphere, tend to oxidize (often catalyzed by bacteria). In many mining wastes (specifically metal mines), pyrite and pyrrhotite are two common accessory minerals, and they generate the low-pH waters. Within this acid environment, and according to the ore deposit type, various elements dissolve and are released, such as Cu, Zn, Pb, Ni, Cd, Co, Hg, Al, Mn, and U, and metalloids, including As, Sb, and Se (Nordstrom, 2011).

The second important attribute is the association of various trace elements (precious, rare earth, or toxic elements) that are hosted in ore minerals or accompanying sulfides (Jamieson, 2011). To study the potential of these accompanying elements, various leaching tests (e.g., field test) can be performed to simulate the mine wastes weathering conditions (Price, 2009).

According to these attributes, and by the type of the ore deposit, it is possible to predict and analyze the consequences of the mining wastes environmental aspects. For example, in

volcanogenic massive sulfide base-metal deposits, the AMD is likely to be produced since the ratio of neutralizing carbonates to reactive sulfide minerals is low. Therefore the potentially toxic elements that could be released are Cu, Zn, Pb, and Cd. Another example is represented by gold deposits, which have less potential to produce AMD, because they have lower concentrations of sulfide minerals and often contain carbonate minerals (Jambor et al., 2003).

The third important attribute comprehends the physical characteristics affecting the mining wastes. The physical factor is generated by piling materials from different parts of extraction, with a mixed mineralogical content. This causes the heterogeneity of minerals within the mining wastes and influences the chemical weathering pattern and the transport processes. PSD is another physical property, which is linked with the geochemical and hydrogeological properties of waste rocks and can vary from fines to coarse materials. In addition, the permeability and the thermal conductivity are other important parameters controlling the chemical and the heat transport processes in waste-rock piles (Amos et al., 2015).

The study of mine wastes and their attributes is fundamental, not only from the environmental point of view, but also for the economic revalorization of low-grade sources, and potential exploitation of by-products (Dino et al., 2020; Helser et al., 2022; Kasmaee et al., 2010, 2018).

For example, Dino et al. (2020) presented a study on a historical case in north of Italy (Montorfano and Baveno granite quarrying area), to evaluate the economic and environmental impacts of the mining wastes facilities exploitation (for the ceramic industry and by-products for the building industry and infrastructures). This study is emphasized on the recovery of mining wastes that can significantly contribute to the environmental and land protection. Moreover, it is an added value to the safety of the quarries and the supply of CRMs.

In another example, Kasmaee et al. (2010, 2018) studied the possibility of grade-tonnage assessments of two mining wastes in an iron mine (low-grade and high-phosphate wastes) for the valorization of both cases as the feed in the new line of the processing plant.

In another case study, Helser et al. (2022) performed series of leaching tests and studied the mobilization of metals from several mining wastes and did a comparison between the construction materials (i.e., ceramics, alkali-activated materials and cement), the cleaned mine wastes (i.e., by performing bioleaching or flotation), and the uncleaned mining wastes. The mobility of metals from mine wastes is studied through various leaching tests to simulate the natural conditions at the mining sites. Results demonstrated that cleaning methods are not always efficient in removing metals and sulfur minerals from mine wastes.

Hence, nowadays mining wastes have gained high attention, not only for their managements considering the environmental hazards or releasing the toxic metals and elements but also for the high demand for raw materials and critical elements, highly connected to the development of green and digital technologies.

1.3 Mineral processing wastes (tailings)

Mineral processing wastes, commonly known as tailings, consist of the waste materials left after the target element (e.g., copper, zinc, iron, lead, aluminum) has been extracted from

the mineral ore (e.g., chalcopyrite, sphalerite, magnetite, hematite, galena, bauxite). The mineral processing is composed by many stages, varying according to the original rock and the target elements to be extracted. It consists in size reduction, classification, and mechanical separation operations (e.g., comminution, sieving, gravity concentration), as well as physicochemical separation methods (e.g., flotation).

In the first stage, commonly called ore dressing, the size of rock ore blocks is reduced by crushing, grinding and milling. Grinding usually involves the use of water. Afterwards, the different gravimetric, magnetic, electrical, or surface properties of mineral phases are used to separate the ore from the wastes. Some chemical additives are added to the flotation, varying according to the target element. After flotation, these additives end up in the wastes as well. A full recovery of target elements is impossible to reach and small amounts of valuable minerals end up in the wastes, too.

A large and heterogeneous quantity of wastes is derived from the processing phase. Due to the various operations, the residues consist of:

- rejected crushed rock;
- water;
- chemical additives; and
- trace quantities of metals.

Tailings consist of all of the above mentioned residues; tailings are typically present in the form of a particulate suspension that is a fine-grained sediment-water slurry, which is disposed on land in dedicated storage facilities. Chemical and physical properties of the tailings vary from one site to another. They include: mineralogy, geochemistry, specific gravity, permeability, density, settling behavior, consolidation behavior, rheology, viscosity, strength, soil plasticity, and leaching properties. The characterization of the tailings is generally studied at the exit of the processing plant.

Traditionally, tailings have been disposed, including plenty of process water, in decant ponds of tailing dams. This form of disposal has been representing a serious threat and a source of environmental hazard. With reference to the safety aspect, the mechanical collapse of the dams can provoke disasters to the areas located downflow. These disasters can cause environmental impacts on ecosystems, loss of life, and damage to property, air pollution through dust generation, release of radiation from tailings, and seepage from the tailings into ground and surface waters.

Cases of dam collapses have been frequent. Among others, it is worth to cite the following recent cases: the Jagersfontein diamond mine in South Africa (2022), the Marian and Brumadinho iron mines in Brasil (respectively, 2015 and 2019), the Hector iron mine in the United States (2018), the Loyuang aluminum refinery in China (2016), and the Ajka alumina plant in Hungary (2010). The updated full list of dam failures counts more than 70 notable cases, starting from the one occurred in 1928 at the Barahona copper mine in Chile ([Piciullo et al., 2022](#)).

By looking at the environmental aspect, the tailings disposed in decant ponds are basically a wet mixture of residues of the original mineral ore, together with the additives used

in milling and flotation. Therefore pollutant substances dissolved in water can infiltrate into the nearby soils due to leakage or drainage. Moreover, particle dusts can be transported by winds and deposited over fields and towns during the dry weather periods. Both the slurry leakage and drainage and the dust dispersion are potentially dangerous, since they can be pathogenic agents for the concentration level of the occurring toxic elements ([Pascucci et al., 2012](#); [Rowe & Fan, 2022](#)).

The tailings water can be decanted for reuse and pumped back to the plant. Recycling and reuse of process water and process chemicals makes economic sense and can reduce the load of contaminants contained in ponds and tailings dams. However, a proportion of the discharged process water remains in the tailing disposal facility. Various fractions of the chemical additives ultimately find their way into tailings, and tailings liquids often contain some levels of organic chemicals or surfactants, acids and bases, and other reagents used to achieve mineral recovery.

To prevent risks, the recent best practice requires to dispose the grain size materials (sands and silts) separately from wastewater. The reduction of water content has been possible by performing filtration and drying at the end of the process ([Healy, 2021](#)).

On the other hand, a constant monitoring of wastes composition, and the subsequent adoption of multimetal recovery processing strategies, can allow reducing the quantity of toxic elements disposed in tailings ([Kasmaeeyazdi et al., 2021](#)).

In general, the more efficient the mineral processing is and the more environmental safety measures are applied, the more the tailings are dry and inert.

However, after mineral processing, still, a part of precious and strategical materials remains within the tailings, because of different reasons:

- technical (no specific processing is present for metals other than the target);
- economic (no economic value of separating metals others than the target); and
- technical probabilistic (not all target metals are separated in the processing plant).

Some examples are presented:

1. Tin mine tailings can include significant amounts of tantalum and niobium. An example of recovery is represented by the Sn tailings in Penouta, Spain. During the mine operation, milling was not present and only material smaller than 2 mm was treated, thus resulting in sand tailings with a high concentration of Sn, Ta, and Nb. The Spanish company Strategic Minerals Spain S.L. in 2018 began to extract those metals from the old tailing ponds ([Blengini et al., 2019](#));
2. Copper mine tailings can include significant amounts of cobalt. A biohydrometallurgical process was used to recover Co from Cu pyrite concentrate in Kasese, Uganda ([D'Hugues et al., 1997](#));
3. Gold mine tailings, with monazite in their composition, can include significant amounts of REEs. A preliminary evaluation has been conducted over the Bagre–Nechí mining tailings in Colombia, showing significant potential for Ce, La, and Nd recovery ([Echeverry-Vargas & Ocampo-Carmona, 2022](#));

4. Similarly to the monazite, several other types of phosphate rock tailings can include high amounts of REEs. An example is the phosphogypsum mine tailings of Sfax, in Tunisia, where, according to the investigations, Ce, La, Nd, and Y can be profitably recovered ([Hammas-Nasri et al., 2016](#));
5. PGMs can be found in chrome tailings. Processes are being operational in South Africa, especially inside the Bushveld Complex, while other applications can be found in Russia, Zimbabwe, the United States, and Canada ([Glaister & Mudd, 2010](#); [Nel, 2011](#)). Chrome tailings have proven to contain significant quantities of nickel and iron, as well. Some preliminary studies have been carried out in the Sukinda ferrochrome deposits, in India ([Kumar et al., 2021](#));
6. Flotation tailings of lead and zinc mines can contain sphalerite which was not recovered. Therefore important amounts of cadmium and indium can be present. Some preliminary tests have been conducted in the Freiberg mining field in the lower Erzgebirge mountains ([Martin et al., 2015](#)).

By definition, many properties of tailings are affected directly by the processing techniques. In addition to the content of the tailings, their pH is influenced by the applied processing technique. For example, in the flotation process, sulfuric acid can be added. Sulfide oxidation and AMD may take place. The generation of AMD is slower in fine-grained sediments with relatively low permeability than coarser, and more permeable waste rocks from the same deposit. In some cases, acid or alkaline tailings are generated by processing techniques with high concentration of dissolved and soluble salts, metals ([Lottermoser, 2010a](#)).

Therefore in summary, mining tailings have the following characteristics:

- Tailings are composed by the residuals after treatment in the processing plant.
- Characterization of tailings is generally made at the exit of the processing plant.
- Metals' concentration of tailings differs from the original concentration of the mine, since the target metals were separated in the processing plant.
- Tailings may be disposed as a composite slurry or have sands and fines disposed separately; thickening or filtration is performed at the end of the process to reduce the water content.
- Tailings can be a source of environmental hazard; hence, they have to be treated to prevent environmental damage.

1.4 Metallurgical wastes

1.4.1 Slags

Slag is a residue or a by-product generally produced from reduction of gangue minerals and added chemical agents (fluxes) during pyrometallurgical processing of metal concentrates. The properties and characteristics of slag depend on the following inputs: composition of the concentrate (chemical and mineralogical), target metal for extraction and efficiency of

its extraction, conditions of operation of smelting furnace, and the cooling conditions, types, and amounts of fluxes added (Piatak & Ettler, 2021; Piatak, 2018). Major categories of slag include ferrous slags (generated during recovery of Fe), ferroalloy slags, and nonferrous slags, such as base metal slags (generated during recovery of Cu, Ni, Pb, Zn); some examples can be seen in Fig. 1–3. In the function of their chemistry and mineralogy, slags can be considered waste, building material, or secondary resource for metal recovery (Piatak & Ettler, 2021). In addition, Piatak and Ettler (2021) have pointed out that studies dedicated to different kinds of slag have different focuses: studies addressing physical and mechanical properties are more frequent for the ferrous slags due to their use in the construction sector, whereas base metal slags are strongly associated with environmental studies largely due to their tendency to release metals to the environment during weathering.

Historical lead smelter slag of Santo Amaro, Brazil, was studied by De Andrade Lima and Bernardez (2011) due to the raised concerns about its negative environmental and human health impacts. The authors identified major slag constituents as follows: 28.10% of Fe_2O_3 , 23.11% of CaO , 21.39% of SiO_2 , 9.47% of ZnO , 5.44% of MgO , 4.06% of PbO , 3.56% of Al_2O_3 , 2.26% of C , 1.44% of MnO , 0.27% of Na_2O , 0.37% of S , 0.26% of K_2O , and 0.25% of TiO_2 , with major phases being wüstite, olivine, kirschsteinite, franklinite, and metallic lead. In addition, among trace elements, even though mostly in little quantities, some CRMs were identified, including Sr, Sb, Co, some REEs, In, Bi, and others. After performing the leachability study, the authors concluded that the slag is relatively stable in weak acidic environment, at $\text{pH} > 2.8$.

Another study dedicated to the weathering of the historical zinc smelting slag in Upper Silesia, Poland, was conducted by Tyszkiewicz et al. (2014). Chemically, the major components of the slag samples (65% all together) were FeO , SiO_2 , and CaO ; 5%–8% of Al_2O_3 , 5%–9% of MgO , and up to 5.4% and 2.7% of Zn and Pb, respectively, were found. Up to 638 mg/kg of Sr was detected in the samples. The slag was characterized with the presence of the following primary phases: franklinite, pyrrhotite, rutile, titanite, zircon, galena, brownmillerite, ilmenite, Pb silicate, sphalerite, and quartz. Secondary phases were gypsum, calcite, hematite, hemimorphite, cerussite, zincite, weathered melilite and pyroxene, and clay minerals.

PSD of the slag varies greatly. For example, in the work of Tyszkiewicz et al. (2014), the authors report observing 2-m slag boulders on the surface of the slag heap, as well as 5-cm particles within the heap. In addition, the sieving of their slag samples has shown the presence of particles below 50 μm —particles that can cause dust pollution.

The environmental threats related to slags, however, are mostly related to the leaching of slag components during their prolonged storage in the landfill. The chemical stability of the slag is a function of the characteristics of the ore concentrate and the metallurgical process applied, as well as the slag PSD and the environment of the disposal site (De Andrade Lima & Bernardez, 2011; Tyszkiewicz et al., 2014).

Schlesinger et al. (2011a) list several possible uses of copper slags, including use in cement and concrete, ceramic tiles, as abrasive grit for blasting operations, and as sand replacement in land reclamation.

1.4.2 Dusts

Metallurgical dust is a solid residue generated during the pyrometallurgical processing of the metal concentrates. The dusts generally have two main origins: (1) solidified particulate mechanically entrained with the flow of gases and precipitated in the dust capturing system and (2) chemically formed dust—particles created through matter vaporization and its subsequent condensation from the gas in the cleaning system (Nair et al., 2022; Okanigbe et al., 2017).

In steel-making industry, dusts originate from such processes as sintering, blast furnace, converter, and electric arc furnace processing. In function of the characteristics of the pyrometallurgical plant feed (metal concentrate) and the fuel used, the captured dusts can contain various valuable elements, such as In, Bi, Cd, Rb, Cs, Tl, Sb, and Sr, frequently, in elevated concentrations in comparison to the plant feed (Li et al., 2022). Dusts generated in steel industry are typically rich in iron (up to 50–60 wt.% in the sintering and blast furnace dusts), with relatively high carbon content (up to 40% in some blast furnace dusts), with other components being Zn, Pb, Na, K, Cd, SiO₂, CaO, MgO, and Al₂O₃ present to a different extent (Li et al., 2022). The same authors report the chemical composition of the secondary dust (Zn-rich dust) originating from the rotary hearth furnace and rotary kiln, where the quantities of Zn, Bi, In, and Cd can reach 49, 0.34, 0.04, and 0.1 wt.%, respectively. Dusts are characterized with fine PSD, frequently, below 30 μm, and large specific surface area. The mineral phases that can be found in dusts from steel industry include wüstite, hematite, magnetite, franklinite-jacobsite, quartz, zincite, laurionite, sylvine, halite, calcite, portlandite, and others, as well as iron metal (Jabłońska et al., 2021).

The elemental composition of the dusts originating from the nonferrous metal processing will differ from that given above for the dusts generated in the steel making industry. For example, Okanigbe et al. (2017) studied a copper smelter dust collected from the electrostatic precipitator attached to the reverberatory furnace in Limpopo copper plant, South Africa. Their analysis suggests that the dust sample contained 18.02% of CuO, 13.36% of Fe₂O₃, 3.44% of S, 0.27% of Zn, 0.12% of PbO, 0.02% of Bi₂O₃, 3.52% of CaO, 2.86% of MgO, 1.11% of TiO₂, 33.06% of SiO₂, and 22.19% of Al₂O₃; the major phases identified in the dust were cuprospinel, chalcopyrite, mullite, gypsum, quartz, and magnetite. The sieving conducted on the dust sample resulted in more than 80 wt.% of the dust passing through the sieve with a 53-μm aperture (the smallest aperture size used). Schlesinger et al. (2011a) give an example of copper smelter dust from electrostatic precipitator of Rönnskär Smelter of Boliden, containing 20.2% of Cu, 25.6% of Fe, 12.3% of Zn, 3.0% of Pb, 0.05% of Sb, 1.88% of As, 7.5% of S, and 0.02% of Sn. The dust collected in the baghouse in the converter stage at Rönnskär Smelter of Boliden contains 1.56% of Fe, 20.2% of Pb, and 4.51% of As. Reader's attention is brought to the relatively high iron, lead, and arsenic contents in these dusts.

Jabłońska et al. (2021) analyzed elemental and mineralogical composition of dusts generated in the zinc rectification process and lead refinery in Poland. The dusts obtained in zinc rectification were characterized with 4.60% of Cd, 1% of Pb, 4.3% of Zn, 215 mg/kg of Cu, 14 mg/kg of Mn, and 2.5 mg/kg of V; no iron was found in the sample. Mineral phases

identified in this sample included zincite, otavite, and monteponite. The dusts of the lead refinery, on the other hand, were characterized with 0.15% of Cd, 0.2% of Fe, 3.3% of Pb, 3.2% of Zn, 2484 mg/kg of Cu, and 2.5 mg/kg of V; with mineral phases identified as zincite, palmierite, anglesite, lanarkite, and sylvine. [Jabłońska et al. \(2021\)](#) suggested that typical particle size for nonferrous metallurgical dusts is below 10 μm .

The landfilling of dusts or dust-bearing products is associated with high pollution risk, occupies large land area, and is subject to element release through weathering and leaching. To reduce the element leaching and dust transportation with the wind, the stabilization or solidification process, which involves mixing the dust with binder or cementitious material prior to disposal, can be applied ([Nair et al., 2022](#)).

1.4.3 Slimes

Anode slimes are the residue generated at the electrorefining stage of metal production. This residue/by-product is often associated with valuable metals, such as gold and silver, PGMs, as well as other elements, including Bi, Co, Sb, Se, Te, Pb, Cu, Ni, and others ([Schlesinger et al., 2011b](#)). Thanks to this fact, once removed from the bottom of the refining cell, the slimes are often sent for valuable component recovery. [Schlesinger et al. \(2011a\)](#) composed a summary of elemental composition of 23 copper anode slimes from different plants, two of these will be given here as examples—anode slimes from Potrerillos, Chile, and Saganoseki, Japan. Copper anode slime from Potrerillos in Chile contains 7.8% of Cu, 15.42% of Ag, 0.47% of Au, 8.65% of Se, 0.66% of Te, 9.22% of As, 10.45% of Sb, 0.41% of Bi, 1.16% of Pb, 0.19% of Fe, and 0.02% of Ni. Copper anode slime from Saganoseki, Japan, contains 25.2% of Cu, 19% of Ag, 2.1% of Au, 12.1% of Se, 3.9% of Te, 3.3% of As, 1.8% of Sb, 0.7% of Bi, 4.0% of Pb, 0.21% of Fe, 0.4% of Ni, and 3.2% of S. Copper anode slime mineralogy is usually represented by various copper phases, oxides of Sb, As, and Bi, lead sulfate, and gold and silver selenides and tellurides ([Schlesinger et al., 2011a](#)). To extract valuable components from the slimes, they can be subjected to leaching, roasting, and smelting; the residue (in the form of slag) resulting from this process is discarded.

1.4.4 Muds

Metallurgical wastes in the form of mud are produced by the processing of bauxite ore to recover aluminum using the Bayer process. The aluminum-bearing minerals in bauxite are gibbsite, boehmite, and diaspore, which are found in association with quartz, clay minerals (mainly kaolinite), and iron oxides and hydroxides, such as goethite, hematite, and maghemite ([Binnemans et al., 2015](#)).

In Bayer process, the bauxite ore undergoes the processes of predesilication, digestion, settling, washing, and thickening or filtration. The result is a solution rich in Al_2O_3 and a mixture of no-soluble compounds known as bauxite residue or red mud. The high alkalinity (pH 9.7–12.9) and sodicity of red muds—which are the result of the complex solid-state and solution phase interactions and the use of caustic soda during the process—are a matter of environmental concern ([Power et al., 2011](#)). The composition of the bauxite residue is

complex and depends upon the type of bauxite and the specific parameters used during the Bayer process (Tables 3.1 and 3.2) (Binnemans et al., 2015; Gräfe et al., 2011).

The methods for disposing of red mud depend upon the content of solids and the availability of land for disposal. In turn, the content of solids depends on the amount of impurities in the bauxite ore and the intensity of the last stages in the Bayer process (i.e., thickening and filtration). Red mud with a low percentage of solids is discarded using marine disposal or lagooning. Despite the low costs, these methods have been strongly discouraged as they have more potential to create adverse environmental impacts and accidents. Dry stacking and dry cake disposal minimize the potential hazards and facilitate the recovery of solids for alternative uses (Power et al., 2011). Some applications for bauxite residue include cement and ceramic production and recovery of major (Al, Fe, Ti) and minor metals (Klauber et al., 2011). More recently bauxite residues have been getting attention as alternative resources of CRMs, in particular, REEs and scandium (Binnemans et al., 2015; Ujaczki et al., 2018). Scandium, iron, titanium, and vanadium are present in interesting concentrations in alumina refinery tailings. The prototype for sustainable and economic extraction of Sc from bauxite tailings has been in development in recent years in Greece, while the use of bauxite residues for road cements, due to the advanced strength, is already a relatively standard practice (when economically profitable) (Davris et al., 2022).

1.5 Wastewaters and acid mine drainage

1.5.1 Generation of wastewater

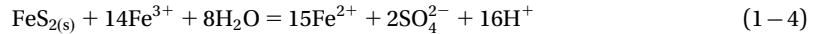
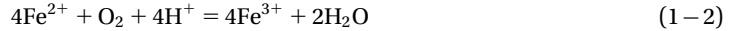
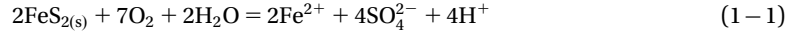
At mining operations, thousands of liters of water are used for mineral processing, hydro-metallurgical extraction, and dust suppression, among others. During the dewatering of minerals, water also comes as a by-product of the operations. In modern operations, unwanted water is deemed waste and must be discharged in settling ponds and tailings dams. However, in historical sites, water was discarded directly into the environment. The water used in mining operations usually contains dissolved and particulate matter. If the wastewater comes into the environment, it can cause turbidity and sedimentation in water bodies and alter their chemistry, having deleterious effects on the vegetation and animal life of the surrounding area (Lottermoser, 2010b).

1.5.2 Generation of acid rock drainage

Acid rock drainage (ARD) or AMD is generated when the minerals in stockpiles, tailing dams, waste rocks, and heap leach piles are exposed to oxidation in the presence of water. Unlike wastewater, water responsible for ARD comes from natural sources (e.g., meteoric or groundwater) that becomes acidic through the interaction with, mainly, sulfide minerals (Lottermoser, 2010b). The best-known mechanism of ARD generation is the oxidation of pyrite. However, other sulfides, such as arsenopyrite, chalcopyrite, galena, pyrrhotite, and

sphalerite, have also been identified as generators of acid drainage (Chopard et al., 2017; Geoffrey & Sehliselo, 2014).

Although pyrite is relatively stable under acidic and alkaline conditions, in the presence of oxidants, such as O_2 and Fe^{3+} , it reacts as follows:



In the presence of water and oxygen, pyrite is oxidized and releases ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and hydrogen (H^+) ions (Eq. 1–1). The dissolved iron and sulfate ions cause an increase in the total dissolved solids in the water, and the release of hydrogen ions results in an acidic solution. In oxidizing conditions, Fe^{2+} is further oxidized to Fe^{3+} (Eq. 1–2), which can precipitate as a hydroxide $Fe(OH)_3$ (Eq. 1–3). Alternatively, depending on the pH of the system, the available Fe^{3+} can continue to dissolve pyrite (Eq. 1–4). The reactions in Eq. 1–4 are, in principle, limited to conditions where the pH is lower than 4. In natural environments, the microbial activity enhances pyrite oxidation in Eq. (1–1), producing ARD with a $pH < 3$ and creating favorable conditions for further pyrite oxidation by Fe^{3+} (Eq. 1–4) (Park et al., 2019). However, the dissolution of carbonate minerals, Fe and Al oxyhydroxide minerals, and aluminosilicate minerals can buffer the pH, maintaining it in circumneutral conditions and slowing down the oxidation of pyrite (Amos et al., 2015).

The rate of pyrite oxidation, and subsequent ARD generation, is influenced by the particle size, porosity, and surface area of pyrite particles, which are determined by the mining, crushing, and milling of pyrite-bearing rocks. In addition, pyrite's crystallinity and trace element substitution make it more or less susceptible to chemical attack. Furthermore, the oxidation of pyrite is an exothermic reaction that increases the temperature of the waste, which is advantageous for the growth of thermophilic bacteria. These conditions enhance microbial activity, catalyzing further pyrite oxidation (Lottermoser, 2010c).

1.5.3 Classification

Wastewater and mine or rock drainage are commonly classified based on their acidity. However, they can also be radioactive, corrosive, and highly toxic depending on the content of dissolved metals and metalloids (Nordstrom, 2011). There are different classification schemes based on the following parameters (Lottermoser, 2010b):

- Abundance of cations (e.g., Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (Cl^- , SO_4^{2-} , CO_3^{6-} , HCO_3^{3-});
- pH: defined classes are extremely acidic (<1), acidic (pH 1–5), circumneutral (pH 6–8), or strongly basic (pH 8–12) (Nordstrom, 2011); the mine water can also be classified as

saline if the pH is highly variable, influencing the concentrations of aqueous ions (Morin & Hutt, 2001);

- pH, and Fe^{2+} and Fe^{3+} concentration;
- pH versus total dissolved metals (Zn, Cu, Cd, Pb, Co, Ni); the categories vary from ultra-acid–ultra-metal (pH < 1, sum of dissolved metals > 10,000,000 µg/L) to near-neutral–low metal (pH > 5.5, sum of dissolved metals < 1,000 µg/L) (Plumlee & Logsdon, 1999);
- Alkalinity versus acidity: these parameters, determined by titration, allow the classification of mine waters based on their treatability using passive methods; and
- Alkalinity versus acidity and sulfate concentration.

Other parameters that need to be taken into account when characterizing mine waters but that are not considered in the previous classifications are: (1) elevated concentrations of arsenic, antimony, mercury, cyanide, and other process chemicals and (2) concentrations of iron, manganese, and aluminum, which are common in ARD waters (Lottermoser, 2010b).

1.5.4 Impacts of wastewater and acid drainage

Mine waters—waste and acid drainage—may have acidic pH and contain contaminants in solution (heavy metals, metalloids, salts) and particulate material (iron precipitates). If these waters are released into the environment without any treatment, they can cause severe negative impacts on surface and groundwater, soils, and living species (Geoffrey & Sehliselo, 2014; Lottermoser, 2010b).

1.5.4.1 Acidity

Mine waters with pH < 4.5 discharged into the environment acidify water bodies and soils. The low pH and mobilization of metal ions diminish the drinking water quality and hinder its availability for human consumption. In addition, acidified lakes and ponds might be lethal for aquatic life. Soils with low pH retain nitrogen, phosphorus, and potassium, limiting their availability to plants. These soils are also depleted in calcium and magnesium but enriched in aluminum, iron, and manganese, thus becoming low in nutrients and high in toxins for plants.

1.5.4.2 Iron precipitates

Precipitation of iron oxides and hydroxides turns the water orange, reducing the light in the water column, which affects photosynthetic biota. Iron precipitates also increase turbidity and contaminate the substrate, affecting the food source of benthic organisms and impacting the entire food chain. These precipitates also smother benthic organisms and clog up fish gills.

1.5.4.3 Dissolved heavy metals and metalloids

Heavy metals (copper, lead, zinc, cadmium, cobalt, nickel, mercury, arsenic, and antimony) persist in natural ecosystems for an extended period. High concentrations of metals in plants result in cellular damage and affect plant growth. Acute (i.e., short term, high concentration)

exposure of aquatic life to heavy metals results in the death of organisms, whereas chronic exposure (i.e., long term, low concentration) can result in stunted growth, reduced reproduction, deformities, or lesions. In addition, dissolved metals and metalloids reduce drinking water quality, as contaminated water disrupts the function of important human organs.

1.5.4.4 *Total dissolved salts*

Dissolving calcium, magnesium, potassium, sodium, iron, aluminum, silicon, manganese, and sulfate in concentrations greater than 100 mg/L reduces drinking and stock water quality. At those high concentrations, salts precipitate and contaminate the soils and sediments and get encrusted in human-made structures, causing damage.

1.5.5 Acid rock drainage prediction

To prevent the negative impacts of ARD on ecosystems, it has become a common practice in the industry to perform a series of static and kinetic tests that assess the acid-producing nature of materials. The information retrieved from such tests supports waste management strategies. However, despite their popularity and usability, static and kinetic tests also have limitations in that they do not fully represent the spatial and temporal scales of the processes leading to ARD formation (Dold, 2017; Parbhakar-Fox & Lottermoser, 2015).

1.5.5.1 *Static tests*

Static tests are deployed as short-term (hours or days) experiments and use relatively low-cost tools. The tests are applied to processed samples after a series of field tests have been completed and are designed to quantify the acid-forming or neutralizing potential (Neutralization Potential Ratio or NPR) of a sample. The most popular tests are acid-based accounting (ABA) and net acid generation (NAG). The results of these tests are commonly used to classify waste materials as potentially acid-forming, nonacid-forming (NAF), or uncertain (Parbhakar-Fox & Lottermoser, 2015).

1.5.5.1.1 **Carbon**

The acid-neutralizing capacity (ANC) of a waste material is assessed by measuring the total and inorganic carbon using induction furnace methods. Inorganic carbon reflects the presence of carbonate minerals and therefore its neutralizing capacity.

1.5.5.1.2 **Sulfur**

The maximum potential acidity (MPA) of a waste material is determined by the total sulfur (S_{Total}) content. Total sulfur is used to reflect the presence of sulfide minerals as indicators of the acid-forming capacity of the material. Nevertheless, NAF S-bearing species (i.e., sulfates) are also included in the analyses.

1.5.5.1.3 **Acid–base accounting**

It calculates the net acid-producing potential (NAPP) or NPR of a waste material using the MPA and ANC parameters: $\text{NAPP} = \text{MPA} - \text{ANC}$; $\text{NPR} = \text{ANC}/\text{MPA}$. The determination

of the ABA is a common practice in the industry, making the results easy to communicate among practitioners.

1.5.5.1.4 Net acid generation

It determines the acid-forming potential capacity by adding H_2O_2 to a waste material. Like the ABA tests, NAG tests are a common practice in the industry. NAG versus NAPP plots are widely used for waste classification.

1.5.5.1.5 Acid buffering characteristic curve

It measures the effective ANC of a waste material by HCl titration.

1.5.5.1.6 Leachable metals

It determines the metal mobility in waste materials using a synthetic precipitation leach procedure and assesses the risk of water contamination caused by the leaching of mine wastes.

1.5.5.2 Kinetic tests

Kinetic tests are deployed in laboratory-based leaching columns, humidity cells, and field-based test pads to enable longer test times (months to years) and volumes of material than static tests. They aim to serve as drainage quality predictors by simulating weathering conditions using wet/dry cycles and different flushing rates for waste materials.

1.5.5.2.1 Humidity cell tests

Humidity cell tests mimic the weathering of waste rocks and assess the leachate chemistry. The accelerated weathering experiments intend to model the rates of oxidation and chemical release in the field ([Lapakko & Antonson, 2006](#)).

1.5.5.2.2 Column leach tests

Column leach tests monitor the leachate quality over time. Data include sulfide reactivity, oxidation kinetics, metal solubility, and leaching behavior of waste materials measured over weekly or monthly cycles.

1.5.5.2.3 Field test methods

Field test methods deployed in small- to large-scale trials using tubs, barrels, or test piles. The mine waste material is exposed to natural climatic and microbiological conditions relevant to the test site. They are mainly used to assess potential capping and remediation methods after closure.

1.5.6 Valorization

The recovery of by-products from mine wastewaters and ARD creates value while helping to tackle the adverse environmental impacts associated with the disposal of mine waters. There are numerous technologies for wastewater treatment that lead to resource recovery and water reuse. For example, valorization activities are carried out to recover clean water, valuable minerals and metals and sulfuric acid. In addition, it is possible to generate electricity and support the treatment of municipal and industrial wastewater.

1.5.6.1 Water reclamation

The recovery of clean water that is deemed safe for human consumption can be achieved by removing the particulate material in mine waters using membrane separation technologies, such as electrodialysis, membrane distillation, and permeation reaction (Yuan et al., 2022). The removal of metals in solution and neutralization of pH is done by reverse osmosis, electrodialysis, microfiltration, ultrafiltration, and nanofiltration techniques (Masindi et al., 2022).

1.5.6.2 Recovery and synthesis of valuable minerals and metals

Dissolved metal ions, such as iron, copper, zinc, lead, aluminum, and manganese, can be recovered using precipitation. The precipitation of metals is achieved by pH neutralization using alkaline materials or by oxidative precipitation using oxidant agents. The dissolved metals are converted into hydroxides that precipitate and can be recovered (Masindi et al., 2022). Other methods for metal recovery include membrane distillation, nanofiltration, chemical oxidation, electrochemical and selective separation and solvent extraction. There are also emerging technologies that create synthetic minerals from recovered metals (e.g., hematite, goethite, magnetite, gypsum) and produce water of drinking quality (Yuan et al., 2022). Nevertheless, many of these technologies have not achieved commercial maturity yet and need to be further developed to generate an actual cost–benefit.

1.5.6.3 Recovery of sulfuric acid

Removing the acid fraction helps to prevent the adverse impacts of acidic wastewater and ARD. Sulfuric acid can be recovered using methods, such as thermal decomposition, electrolytic precipitation and decomposition, ion exchange, distillation, solvent extraction, crystallization, acid retardation, and electrodialysis (Geoffrey & Sehliselo, 2014; Yuan et al., 2022). The recovered sulfuric acid can be safely disposed of or used to produce phosphate fertilizers for agriculture and enhance flotation performance in mineral processing.

1.5.6.4 Production of electricity

Microbial fuel cells are a technology to convert organic waste—including wastewater—into electricity by leveraging the metabolic activity of microorganisms. It produces electricity and clean water and can help offset the operational costs of wastewater treatment plants (Geoffrey & Sehliselo, 2014).

1.5.6.5 Treatment of municipal and industrial wastewater

The neutralization of mine wastewater and ARD involves using alkaline reagents, resulting in the precipitation of metals in a hydroxide sludge. Treatment plants for municipal and wastewater normally use coagulants, such as alum, ferric chloride, and lime. Sludges from the treatment of mine waters can be used as an alternative for iron and aluminum coagulants (Geoffrey & Sehliselo, 2014).

1.6 Conclusions

Understanding of the residue characteristics is indispensable for selection of an appropriate reprocessing strategy. It has to be kept in mind that the prolonged storage of these residues is often associated with continuously worsening environmental conditions, land occupation, and increased risk of dam failure. Therefore if recovery of critical metals is not achievable in the current circumstance, other options have to be considered, such as use in the building materials or water treatment with purification technologies.

The effort should be made to localize and correctly identify the residues, such as old tailings, abandoned mines and stockpiles, sources of AMD, abandoned metallurgical wastes, and others. A summary/database compiling maps, available historical records, issued permits can be a useful tool for the identification of sites eligible for material reprocessing and CRM extraction or for further remediation.

Different residue categories necessitate different sampling and characterization strategies. In the following chapter, the reader will be introduced to the techniques available for residue sampling and characterization.

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