



# The Twelve Principles of Circular Hydrometallurgy

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## Abstract

In this academic position paper, we propose the 12 Principles of a novel and more sustainable approach to hydrometallurgy that we call “circular hydrometallurgy.” The paper intends to set a basis for identifying future areas of research in the field of hydrometallurgy, while providing a “sustainability” benchmark for assessing existing processes and technological developments. Circular hydrometallurgy refers to the designing of energy-efficient and resource-efficient flowsheets or unit processes that consume the minimum quantities of reagents and result in minimum waste. The application of a circular approach involves new ways of thinking about how hydrometallurgy is applied for both primary and secondary resources. In either case, the emphasis must be on the regeneration and reuse of every reagent in the process. This refers not only to the acids and bases employed for leaching or pH control, but also any reducing agents, oxidizing agents, and other auxiliary reagents. Likewise, the consumption of water and energy must be reduced to an absolute minimum. To consolidate the concept of circular hydrometallurgical flowsheets, we present the 12 Principles that will boost sustainability: (1) regenerate reagents, (2) close water loops, (3) prevent waste, (4) maximize mass, energy, space, and time efficiency, (5) integrate materials and energy flows, (6) safely dispose of potentially harmful elements, (7) decrease activation energy, (8) electrify processes wherever possible, (9) use benign chemicals, (10) reduce chemical diversity, (11) implement real-time analysis and digital process control, and (12) combine circular hydrometallurgy with zero-waste mining. Although we realize that the choice of these principles is somewhat arbitrary and that other principles could be imagined or some principles could be merged, we are nevertheless convinced that the present framework of *these* 12 Principles, as put forward in this position paper, provides a powerful tool to show the direction of future research and innovation in hydrometallurgy, both in industry and in academia.

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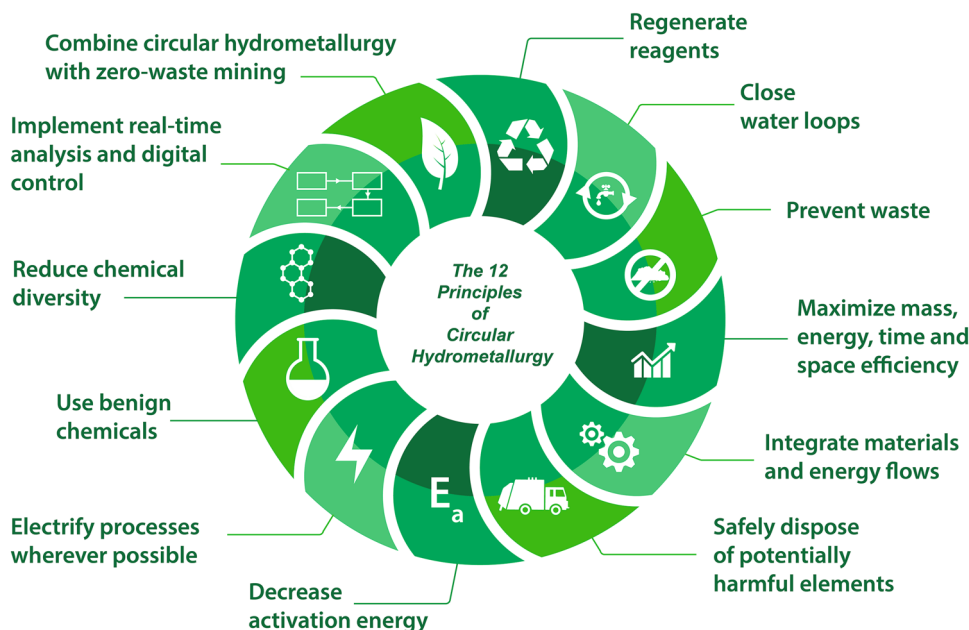
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## Graphical Abstract



**Keywords** Circular economy · Extractive metallurgy · Hydrometallurgy · Solution chemistry · Sustainability

## Introduction

Hydrometallurgy uses aqueous solutions to extract and refine metals [1, 2]. Although a typical metallurgical flowsheet tends to synergistically combine both pyrometallurgical and hydrometallurgical unit operations, the final steps in the purification and recovery of metals are nearly always hydrometallurgical. The transition to a climate-neutral society by 2050 relies heavily on the use of hydrometallurgy to extract critical raw materials, like cobalt, nickel, and lithium for batteries and rare-earth elements (REEs) for permanent magnets in electric motors and wind turbines. However, we must be careful to ensure that the processes applied to refine these metals needed for clean-energy production do not undermine our efforts by having an adverse environmental impact.

Large amounts of acids ( $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ), bases ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{NH}_3$ ,  $\text{NaOH}$ , or  $\text{Na}_2\text{CO}_3$ ), and sulfides for precipitation ( $\text{Na}_2\text{S}$ ,  $\text{NaHS}$ ,  $\text{H}_2\text{S}$ ) are consumed in processes such as leaching, the precipitation of iron and other impurities, the generation of intermediates (e.g., *mixed-hydroxide precipitate* (MHP) and *mixed-sulfide precipitate* (MSP)), and the solvent-extraction (SX) and ion-exchange (IX) processes required to separate and purify metals. By and large, conventional hydrometallurgical flowsheets can be described as predominantly “linear,” in the sense that the reagents consumed are not regenerated for subsequent reuse (although there are

examples where this is partially the case: cf., Section “Examples of (near) circular hydrometallurgical flowsheets” in the online Supplementary Information). This can be problematic because hydrometallurgical processes often give rise to substantial amounts of both solid waste (e.g., gypsum, goethite, or jarosite) and highly saline wastewater. Many hydrometallurgical processes leave a large carbon footprint because producing the reagents used in hydrometallurgy is often energy intensive. Two of the major culprits are  $\text{CaO}$  and  $\text{MgO}$ , which are obtained from carbonate raw materials ( $\text{CaCO}_3$  and  $\text{MgCO}_3$ ) that require a high-temperature calcination in kilns. It is estimated that between 978 and 1975 kg of  $\text{CO}_2$  are emitted per ton of  $\text{CaO}$  produced [3]. The numbers for  $\text{MgO}$  production are similar. The familiar Haber–Bosch and Solvay processes for ammonia production and sodium carbonate synthesis are both classed as energy intensive. Large amounts of energy can be consumed regenerating acids, a good example being the high-temperature pyrohydrolysis process to regenerate  $\text{HCl}$  from metal chloride salts [4, 5]. The electrorefining and electrowinning processes are also energy intensive [2], leading to large carbon footprints when the energy is generated from fossil fuels. We should also not underestimate the energy costs for transportation, e.g., chemicals from production facilities to mining sites or hydrometallurgical plants.

The past 10 years have been blessed with a much greater awareness of environmental issues in the extractive-metallurgy sector. This period has seen the launch of the *Journal of Sustainable Metallurgy* in 2015 [6] and an acknowledgment that the total environmental impact of a metallurgical process can only be properly evaluated via a *lifecycle assessment* (LCA) or, better still, via a *multicriteria assessment* (MCA). Unfortunately, such studies do not provide the metallurgist with practical guidelines as to *how* to improve the sustainability of a metallurgical flowsheet. In the area of environmentally friendly chemistry, the *Twelve Principles of Green Chemistry* have proven their worth in making chemical syntheses safer and greener (Table S1) [7, 8]. However, most of these principles are more closely associated with the synthesis of organic compounds and are not relevant to extractive metallurgy. The Twelve Principles of Green Chemistry were reformulated for engineering practice as the *Twelve Principles of Green Engineering* (Table S2) [9], and the *Nine Principles of Green Engineering* of the Sandestin Declaration (Table S3) [10]. Although some of these principles can be applied to extractive metallurgy, many others are less relevant because they were devised for manufacturing. At present, it is fair to say that such guidelines for extractive metallurgy are lacking. For this reason, we decided to formulate a set of design principles adapted to the field of hydrometallurgy that we hope will spur the development of more sustainable hydrometallurgical processes [11, 12]. These guidelines contribute to the targets of Goal 12 of the United Nations Sustainable Development Goals: Ensure sustainable consumption and production patterns [13].

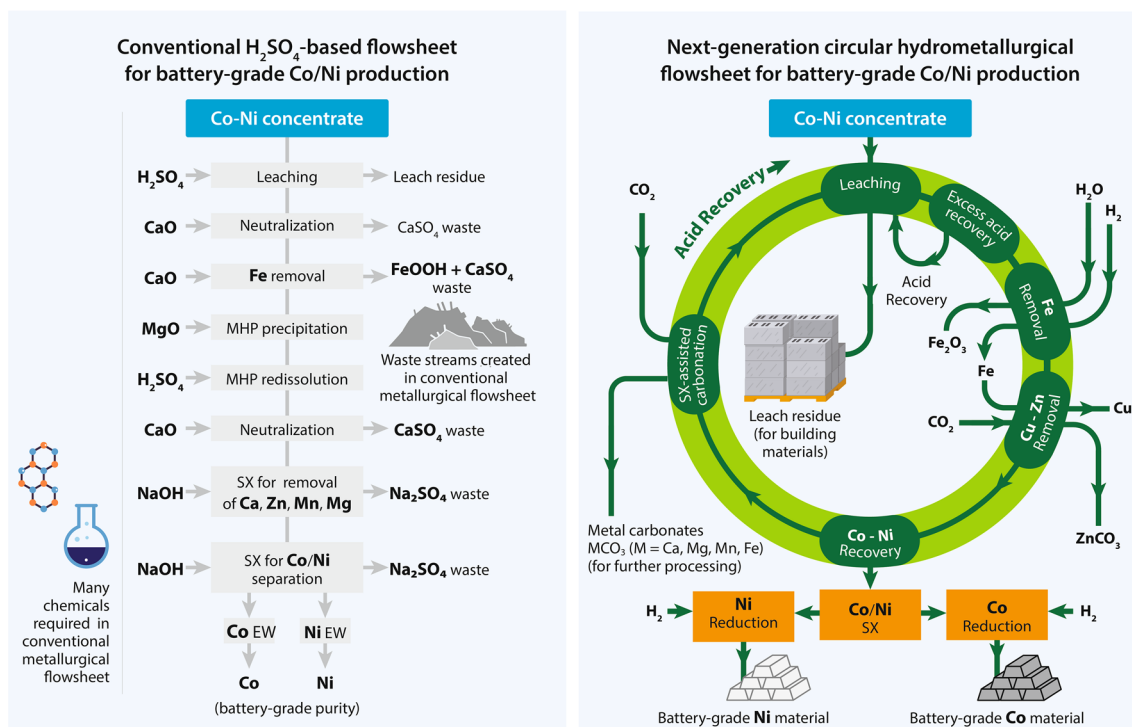
In this academic position paper, we are proposing a new approach to sustainable metallurgy and more particularly to sustainable hydrometallurgy. We refer to this new approach as “*circular hydrometallurgy*”. The paper intends to set a basis for identifying future areas of research in the field of hydrometallurgy, while providing a “sustainability” benchmark for assessing existing processes and technological developments. The Principles are applicable to flowsheets for both the processing of ores and concentrates from primary mining as well as to the recycling of end-of-life, metal-containing waste. They can also be applied to a wide variety of metal-containing aqueous streams, such as spent electrolytes from the electroplating industry. Finally, we will show how circular hydrometallurgy can be applied to all the metals that are processed via conventional hydrometallurgy routes. As the focus of our discussions is on the unit operations of hydrometallurgy (leaching, solution concentration and purification, and metal recovery from solution), the unit operations of minerals processing (comminution, sizing, physical separation methods, flotation, and drying) are not considered in detail.

## What Is Circular Hydrometallurgy?

*Circular hydrometallurgy* relates to the design of energy-efficient and resource-efficient flowsheets or unit processes that consume a minimum of reagents and produce as minimum waste as possible. “*Circularity*” refers to the regeneration and reuse of all the waste-generating reagents from the process. This not only includes the acids or bases used for leaching and pH control, but also any reducing agents, oxidizing agents, and other auxiliary reagents. In addition to minimizing the consumption of chemical reagents, the consumption of water must also be reduced. Ideally, there should be no net consumption of reagents and no net consumption of water, except for some evaporative losses. Obviously, “*zero waste*” is the ideal situation, but it will never be achievable in practice. If we attempted to valorize all the metals that are currently landfilled (often very diluted, at ppm levels), the energy consumption would be prohibitively high. Dilute streams are problematic because the energy needed to recover the metal from such streams does not increase linearly, but rather exponentially, with decreasing metal concentrations. Moreover, there are unwanted elements like arsenic, cadmium, and mercury that need to be safely disposed of. As a consequence, “*near-zero waste*” is a much more realistic term [14, 15].

In existing hydrometallurgical flowsheets, partial circularity is common (*cf.*, Section “Examples of (near) circular hydrometallurgical flowsheets” in the online Supplementary Information). For instance, in solvent-extraction processes the extractant is regenerated during the stripping of the metal from the loaded organic phase. However, circular hydrometallurgy goes one step further and dictates the regeneration of other reagents that are typically considered as consumables in conventional linear flowsheets. For instance, during the separation of cobalt and nickel by solvent extraction with acidic extractants, large amounts of bases and acids are consumed, respectively, for pH control and stripping [16]. As a result, significant volumes of salt solutions are produced (*e.g.*, Na<sub>2</sub>SO<sub>4</sub> solutions), which are typically discharged to surface waters. Although attention is being paid to the water balance in conventional flowsheets, the soluble salt balance, the energy balance, and the input of reagents and output of waste streams remain significant (Fig. 1). It must also be realized that the efficiency of chemical reagents is not 100%, due to the slow kinetics, impurities, side reactions, and surface activity, and that reagent losses occur at every stage, even though companies make great efforts to decrease their consumption to restrain costs.

It is always possible to design a circular flowsheet by regenerating the acids and bases that are consumed in the process. However, every regeneration process requires energy. In general, it is energetically more favorable to



**Fig. 1** Comparison of a simplified linear (left) and a circular (right) hydrometallurgical flowsheet for battery-grade cobalt and nickel production. For the circular process, a conceptual flowsheet is shown, with the re-introduction of protons to the system via hydrogen gas or

reduce the consumption of chemicals rather than regenerate them, just as it is better to prevent waste (as much as possible) rather than to treat it or clean it up after it has been created. To do this requires knowledge of the chemical reactions involved and careful control of the process.

The idea of circularity in hydrometallurgy is not new. About 100 years ago, Prof. M.H. Caron stressed the importance of cyclic processes in hydrometallurgy in his inaugural lecture at the Technische Hoogeschool Delft (now TU Delft) in the Netherlands: “*One of the most important requirements that, in general, will be imposed on the lixiviant in hydrometallurgy is that it can be used in cycles without losing its active properties or can be regenerated from its compounds without great losses or costs.*” (translated from Dutch) [17]. Unfortunately, the wide availability of cheap bulk chemicals such as H<sub>2</sub>SO<sub>4</sub> or CaO, and the *relatively* low costs associated with the landfilling of industrial process residues and wastes have slowed the development of genuinely circular metallurgical flowsheets. However, today’s mining and metallurgical engineers have the moral duty to minimize the impact of primary mining and of the downstream processing of the extracted metals on the environment. There is no alternative to transforming linear flowsheets into circular flowsheets. In Fig. 1, a comparison is made between these two approaches, as applied to the production of battery-grade Co/Ni starting from Co/Ni concentrates.

via SX-assisted carbonation with CO<sub>2</sub>. The acid is regenerated, and the base-metal impurities are removed as metal carbonates. The different parts of the circular flowsheet will become more evident from the discussions further in the text

## The 12 Principles of Circular Hydrometallurgy

As guidelines for the design of circular hydrometallurgical flowsheets, we are proposing an interrelated set of principles; *i.e.*, the *12 Principles of Circular Hydrometallurgy* (Table 1). These principles are to help metallurgical engineers achieve the goal of circularity in hydrometallurgy. As such, they are practical guidelines, presented in the form of

**Table 1** The 12 Principles of Circular Hydrometallurgy

1	Regenerate reagents
2	Close water loops
3	Prevent waste
4	Maximize mass, energy, space, and time efficiency
5	Integrate materials and energy flows
6	Safely dispose of potentially harmful elements
7	Decrease activation energy
8	Electrify processes wherever possible
9	Use benign chemicals
10	Reduce chemical diversity
11	Implement real-time analysis and digital process control
12	Combine circular hydrometallurgy with zero-waste mining

imperatives, with each principle elaborated in more detail below. The Principles of Circular Hydrometallurgy have been numbered from 1 to 12. Although one could argue that some principles are more important than others, their order does not reflect a strict hierarchy. Some principles are more general (e.g., Principle 1: Regenerate reagents), whereas others are more specific (e.g., Principle 8: Electrify processes wherever possible). The principles are not independent and can often be combined to even more powerful principles, as explained in a separate section.

## Principle 1: Regenerate Reagents

Regenerating all the waste-producing reagents is the main requirement when converting a linear flowsheet into a circular alternative. The regeneration must involve the minimum energy input and the smallest consumption of auxiliary reagents, with these reagents being regenerated whenever feasible. Furthermore, if we do not regenerate a reagent, we have to cover the costs of introducing fresh reagents (additional costs for logistics and warehousing) and waste treatment/management. The most common operations in hydrometallurgy that require the regeneration of reagents are leaching, solvent extraction (SX) and ion exchange (IX). Reagents to be generated are acids, bases, oxidizing and reducing agents, as well as other auxiliary products.

Acids are the most common lixiviants in leaching operations. A comparison of the most-often-used acids can be found in Table 2. In addition to sulfuric, hydrochloric, and nitric acid, also methanesulfonic acid (MSA) has been added to the list. Methanesulfonic acid is an emerging acid in hydrometallurgy [18, 19]. Protons are consumed either by reaction of the acid with the ore minerals during the leaching reaction or by reaction with a base. The latter neutralizes the excess acid after leaching and increases the pH for solution purification (e.g., removal of co-dissolved iron by precipitation as a hydroxide). If the anions of the acids are kept in the system, the acid can be regenerated by re-introducing the consumed protons to the system. This re-introduction of protons can be via (1) the direct reduction of dissolved metal ions by hydrogen gas [20], (2) the oxidation of water to oxygen gas at the anode during electrowinning (with release of protons) [21], (3) the hydrolysis of highly valent metal ions such as iron(III) [22], and (4) the formation of metal carbonates through the introduction of CO<sub>2</sub> to the solution [23]. Hence, protons originate either from hydrogen gas or from water. CO<sub>2</sub> only provides protons indirectly via its reaction with water.

*Sulfuric acid* (H<sub>2</sub>SO<sub>4</sub>) is the main acid used in hydrometallurgical flowsheets. However, it is not so easy to regenerate it from its sulfate salts by a low-temperature process. Na<sub>2</sub>SO<sub>4</sub> is a problematic by-product that is formed by neutralization

of excess H<sub>2</sub>SO<sub>4</sub> by NaOH. Na<sub>2</sub>SO<sub>4</sub> has a high solubility in water, so inhibiting its recovery from aqueous streams and its subsequent storage in a stable solid form. Impure Na<sub>2</sub>SO<sub>4</sub> also has a low commercial value, and the discharge of wastewater containing dissolved Na<sub>2</sub>SO<sub>4</sub> into the environment is not always allowed. The salt splitting of Na<sub>2</sub>SO<sub>4</sub> into H<sub>2</sub>SO<sub>4</sub> and NaOH is an attractive option because it solves the waste issue, while simultaneously regenerating the acid and base consumed in the process. Different electrochemical membrane processes have been developed to salt split Na<sub>2</sub>SO<sub>4</sub>. These are often based on electro dialysis, such as *Bipolar Membrane Electrodialysis* (BMED) [24, 25, 26]. The disadvantages of these methods are the slow kinetics and that the expensive membranes are easily clogged and fouled, requiring regular replacement.

*Hydrochloric acid* (HCl) is much easier to regenerate than H<sub>2</sub>SO<sub>4</sub>, which is driving the development of chloride hydrometallurgy. *Pyrohydrolysis* is applied in industry for the regeneration of HCl [4, 5]. This process is typically carried out in a spray roaster or a fluidized-bed reactor, where the metal chlorides react with steam at high temperatures to form the corresponding metal oxide and HCl gas. In theory, pyrohydrolysis can be used to hydrolyze the chloride of any multivalent metal ion to the corresponding oxide, but so far it has been restricted in industry to MgCl<sub>2</sub>, FeCl<sub>2</sub>, and NiCl<sub>2</sub>. Although pyrohydrolysis is an effective and well-proven technology, the process is capital and energy intensive. Nevertheless, there are major efforts to develop more energy-efficient versions of the classic pyrohydrolysis process. At the same time, low-temperature alternatives to pyrohydrolysis, which are more compatible with circular hydrometallurgy, are also being developed [4, 27]. Examples include sulfate crystallization and hydrolytic distillation. In electrowinning processes for the recovery of metals from chloride electrolytes, HCl is regenerated indirectly by collecting and burning chlorine gas evolved at the anode with hydrogen gas. However, collecting the Cl<sub>2</sub> gas at the anode during electrowinning is not straightforward, and the additional step of chlorine burning complicates the process. Therefore, the direct electrolytic regeneration of HCl without an intermediate step to form Cl<sub>2</sub> gas could be very beneficial to the development of circular hydrometallurgical flowsheets [28, 29]. If water is oxidized at the anode with release of oxygen gas, protons are formed simultaneously. These protons migrate to the cathode where they combine with chloride ions in solution to form hydrochloric acid. Recent advances in the direct electrolytic splitting of seawater, with O<sub>2</sub> gas being produced at the anode, could initiate research into the direct regeneration of HCl from hydrometallurgical solutions [30]. The *oxygen evolution reaction* (OER) could successfully compete with the *chlorine evolution reaction* (CER) at reasonably high current densities, if suitable anodes are used [31]. *Bipolar membrane electrodialysis* (BMED) has been

**Table 2** Comparison of the main acids used in hydrometallurgy, with the inclusion of methanesulfonic acid (MSA), an “emerging acid”

Characteristic	Sulfuric acid	Hydrochloric acid	Nitric acid	Methanesulfonic acid
Commercial use	Most commonly used acid in hydrometallurgy	Rather limited use in hydrometallurgy ( <i>e.g.</i> , PGMs, Au) but high potential	Limited use in hydrometallurgy; useful for processing of sulfidic ores and nickel laterites	Not used in hydrometallurgical industry yet, but very promising. Similarities with sulfuric acid but much better solubility of salts
Solubility of its salts	Sulfates are less soluble than salts of other acids; poorly soluble double salts	Chlorides are easily soluble in water, with the exception of $PbCl_2$ and $AgCl$ (dissolve via complex formation at high chloride concentrations)	Nitrates are highly soluble in water	Methanesulfonate salts are highly soluble in water
Volatility	Low volatility	High volatility	High volatility	Low volatility
Oxidizing/reducing character	Non-oxidizing in dilute solutions; oxidizing as concentrated acid	Reducing acid (formation of $Cl_2$ ); $HCl + Cl_2$ is strongly oxidizing	Oxidizing acid (formation of $NO_x$ )	Non-oxidizing in dilute and concentrated forms
Corrosiveness	Moderately corrosive for reactor materials	Highly corrosive (stainless-steel reactors cannot be used, but titanium reactors can)	Less corrosive than $HCl$ (stainless-steel reactors can be used)	Very low corrosivity
Compatibility with electrowinning	Electrowinning of numerous metals in $H_2SO_4$ solutions is used industrially and yields oxygen gas at anode	Electrowinning of metals in chloride solutions is uncommon because it is difficult to reduce chloro complexes and release $Cl_2$ gas at anode (unless special anodes are used)	Difficult to combine with electrowinning	Excellent acid for electrowinning and yields oxygen gas at anode. Used industrially ( <i>e.g.</i> , tin electroplating)
Ease of regeneration (Principle 1)	Difficult to regenerate	Easier to regenerate than $H_2SO_4$ , but often energy intensive; regeneration via metal sulfate precipitation possible	Easier to regenerate than $H_2SO_4$ ; regeneration via metal sulfate precipitation possible	Limited studies available on regeneration; regeneration via metal sulfate precipitation possible
Smell	Odorless	Pungent smell	Acrid odor	Odorless
Biocompatibility	Formed by oxidation of sulfide minerals by air or bacteria	Occurs in gastric acid (stomach acid)	Present in nature in very minute amounts	Part of the natural sulfur cycle
Cost (OPEX)	Cheap	Relatively cheap	Moderate cost	Moderate cost

successfully used to generate concentrated HCl and NaOH solutions from concentrated brines [32], and this method could be extended to concentrated chloride solutions, provided that membranes with sufficiently long lifetimes can be developed.

*Nitric acid* ( $\text{HNO}_3$ ) has been used for leaching much less than  $\text{H}_2\text{SO}_4$  or HCl, mainly because it is more expensive. In the past, nitric acid processes were often considered as environmentally unfriendly and unsafe. But this perception is changing:  $\text{HNO}_3$  leaching is gaining traction in hydrometallurgy, for instance in the processing of nickel laterites [33, 34, 35]. Metal nitrates are highly soluble in water. In fact, there are no poorly soluble metal nitrates, and even  $\text{Pb}(\text{NO}_3)_2$  is relatively soluble. This makes it possible to regenerate  $\text{HNO}_3$  via metal sulfate precipitation, for instance by precipitating gypsum with the addition of a  $\text{H}_2\text{SO}_4$  solution [36, 37, 38]. Iron can be recovered from  $\text{HNO}_3$  solutions by the hydrolysis of  $\text{Fe}(\text{NO}_3)_3$ , leading to the formation of hematite and the regeneration of  $\text{HNO}_3$  [39, 40].

When aqueous ammonia solution ( $\text{NH}_3(\text{aq})$  or  $\text{NH}_4\text{OH}$ ) is used for alkaline leaching (of Co, Ni, Cu, or Zn), the ammonia can be recovered from the leachate by boiling the solution. This will volatilize  $\text{NH}_3$  gas and the dissolved metals are precipitated as hydroxides. If leaching is done by a mixture of ammonia solution and ammonium carbonate (*Schnabel process*) [41], the excess of  $\text{NH}_3$  is driven out by steam heating and  $(\text{NH}_4)_2\text{CO}_3$  is thermally decomposed to  $\text{NH}_3$  and  $\text{CO}_2$ . The  $\text{NH}_3$  and  $\text{CO}_2$  gases are recovered and recombined to regenerate the lixiviant.

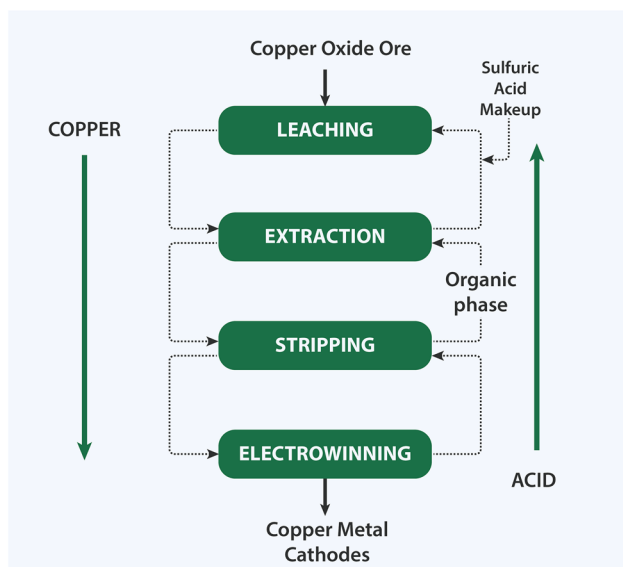
In addition to acids or bases, oxidizing agents are often used for leaching, especially in the processing of sulfidic ores and concentrates. If these oxidizing agents are transition-metal salts, such as  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{FeCl}_3$ , and  $\text{CuCl}_2$ , they can be regenerated after the leaching step. Different methods are available for the re-oxidation of Fe(II) to Fe(III), preferably by (1) electrolytic oxidation, (2) the addition of air or oxygen under pressure, (3) aeration at ambient temperature, or (4) the use of bacteria in the presence of oxygen gas [42].

Regeneration of reagents is common in *solvent extraction* (SX) and *ion exchange* (IX). For example, in SX, the solvent is regenerated during the stripping of metals of interest so that it can be reused for loading with metal in the next extraction cycle. In the case of solvating extractants (*e.g.*, TBP or Cyanex 923) and basic extractants (*e.g.*, Aliquat 336 or Alamine 336), stripping can be achieved with water and the metal is back extracted as a salt from the organic phase. Metals extracted by an acidic extractant (*e.g.*, D2EHPA or Cyanex 272) are stripped from a loaded organic phase, typically by using an aqueous solution of the acid. This acid exchanges its proton for a metal bound to the extractant, hence, regenerating the acidic extractant. Concerning the regeneration of reagents, ion exchange raises similar issues to solvent extraction. When cation exchangers are loaded

with metal ions, these metals can be removed from the loaded resin by treatment with an acidic aqueous solution, either in a batch reactor, in a continuous reactor or in a column, so that the metal ions are exchanged by protons and the resin is regenerated in its acidic form (*i.e.*, the  $\text{H}^+$  form). Strongly basic anion exchangers are transformed into their hydroxide form ( $\text{OH}^-$ ) by treating with an aqueous solution of a strong base, typically a NaOH solution.

A good example to illustrate how reagents are generated in hydrometallurgical flowsheets is the solvent extraction–electrowinning (SX-EW) process in copper metallurgy, sometimes referred to as the *leach–solvent extraction–electrowinning* (L-SW-EW) process (more details are shown in Section “Examples of (near) circular hydrometallurgical flowsheets” in the online Supplementary Information). This process represents the industrial benchmark for the extraction of copper from oxidic ores by leaching with dilute  $\text{H}_2\text{SO}_4$ , because of its simplicity, elegance, and small environmental footprint [43, 44, 45]. The process flowsheet is an almost completely closed cycle and, in theory, only copper oxide and electrical power are required to produce ultrapure copper metal. The flowsheet is composed of three interconnected closed circuits: the leaching (solubilization of Cu), solvent extraction (up-concentration and purification of Cu solution), and electrowinning (recovery of Cu metal) circuits. See Fig. 2 for a schematic representation. The protons that are consumed in the leaching step are regenerated in the electrowinning circuit by oxidizing the water at the cathode to oxygen gas, with the associated release of protons to the solutions. Via the SX circuit, the protons are transferred from the electrowinning circuit to the leaching circuit. The only waste produced by the process is the barren rocks that are left behind as tailings after the copper has been extracted from the ore by heap leaching. Although these tailings are visually not very appealing, they are physically and chemically stable and their storage does not pose environmental risks. Gypsum is formed as a secondary mineral if the copper deposit contains calcium-rich gangue minerals.

Although an SX-EW flowsheet for copper recovery and refining appears fully circular at first sight, we must realize that only the copper is recovered in the basic configuration of the flowsheet and none of the valuable trace elements that might be present in the copper ore (*e.g.*, Au, Ag, Te, Co) are valorized. The process is only of a closed-loop nature for copper; the  $\text{H}_2\text{SO}_4$  consumed in a reaction with impurities in the ore should be compensated by addition of a make-up acid.



**Fig. 2** Schematic flowsheet of the leach–solvent extraction–electrowinning (L–SX–EW) process for recovery of copper from oxidic ores. Adapted after ref. [43]

## Principle 2: Close Water Loops

Although water can be considered as a reagent (and can, thus, be addressed in Principle 1), the omnipresence of water in hydrometallurgical processes justifies a separate Principle devoted specifically to water recycling. Water has different functions in a hydrometallurgical plant [46]. Water is an efficient way to transport particles within and between processes as a pulp, and to mix particles. It can act as a solvent for acid, bases, and other auxiliaries used in hydrometallurgical processes. It dissolves metal salts, and it is important for washing of the solid residue after solid–liquid separation in the leaching process. Ideally, no more water is consumed than it is lost by evaporation or consumed by oxidation at the anode during electrowinning (releasing  $H^+$  and  $O_2$  gas). Closing water loops implies not only the recycling of process water, but also the purification of water to avoid the buildup of toxic elements or salts that might precipitate at undesired stages of the process. When closing water loops, the plant is technically isolated from any surrounding water systems [47]. In a hydrometallurgical plant, it is essential to monitor the *water balance*, which consists of the different input and output streams, as well as the internal recycle streams. Water balance analysis is essential for the design of the hydrometallurgical plant. The quality of the process water can have a direct impact on the different unit processes, as well as on the quality of the final products [48, 49].

This Principle is not limited to the recycling and reuse of process water; it also implies limiting the use of water [50]. One approach to achieve that objective is to increase the

solid-to-liquid ratio in the leaching process. This not only reduces the use of water and reagents, but also leads to more concentrated leachates so that further downstream processing is possible and metal recovery becomes more efficient. However, there are limits to the maximum concentrations of metals in solution, since exceeding the solubility product will lead to precipitation or crystallization. Concurrently, we can try to work with reagents that have concentrations which are as high as possible, without creating safety issues (*e.g.*,  $HCl$ ,  $H_2SO_4$ ,  $NaOH$ ,  $NH_3$ , and  $H_2O_2$ ).

Mining and beneficiation consume vast quantities of water, especially the flotation process. Flotation typically takes place at 25 to 35% solids by mass [51]. A flotation plant not reusing or recycling any water would, thus, require 1.9 to 3.0  $m^3$  of water per ton of ore processed.

Although relatively small volumes of water are used in hydrometallurgical flowsheets, and the environmental impact of this water use is less severe than water use in the mining industry, using less water should still be a major objective in the development of circular flowsheets in hydrometallurgy. Major efforts have been made to reduce the consumption of water in the mining industry, and several of these techniques are applicable to the hydrometallurgical industry as well [47, 52].

After leaching, a solid–liquid separation step, such as countercurrent decantation or filtration with cake washing, is applied to the leach slurry to separate the solid residue from the pregnant leach solution [53]. In general, most of the water entering the system originates from washing of the leach residues or other filter cakes. An optimum must be found between the metal recovery and the cost to eliminate and reuse the excess water. Filtration equipment needs to be designed not only for efficient solid–liquid separation, but also for efficient washing with the minimum consumption of water. In some cases, a belt filter with countercurrent washing is the best option; in other cases, a membrane filter press is a better choice. Efficient dewatering of the solid residue is essential for closing the water loop [54, 55]. This dewatering can include a drying step, but this is normally an energy-intensive process. Emerging technologies for dewatering and drying include (1) enhanced dewatering with flocculants, surfactants, and super-absorbents [56, 57]; (2) electric-field-assisted dewatering, also called electro-dewatering [58]; and (3) microwave drying [59].

It is essential to avoid the buildup of impurities in the water streams. Multivalent metal ions can be removed from aqueous solutions by ion exchange if the metal concentrations are low, with solvent extraction being more suitable for higher concentrations ( $> 500$  ppm) [60]. A more modern approach to the treatment of hydrometallurgical effluents is the use of membrane techniques [26]. However, the technological feasibility of membrane processes, which are considered delicate, remains an issue in hydrometallurgy.



Impurities in end-of-pipe streams need to be reduced to very low concentrations (often to ppb level) to avoid membrane fouling. Impurities include not only multivalent metal ions, but also fluoride and carbon compounds. Also, the generation of solutions with high acid concentrations by salt splitting is complicated due to the limited resistance of many membrane types to highly acidic solutions. A method that is particularly common for the removal of low concentrations of metals from aqueous solutions, especially for potentially harmful elements, is the use of *adsorbents* [61]. Another method is the electrolytical removal of metals by means of a *fluidized-bed electrode* (FBE) [62, 63]. This method can be used to reduce the metal concentrations to below  $1 \text{ mg L}^{-1}$ , but it can only be applied to metal ions that can be electrodeposited from aqueous solutions. These include copper, cobalt, nickel, zinc, cadmium, lead, and precious metals. For more information on fluidized-bed electrodes, see Principle 8. To avoid the buildup of impurities in the aqueous stream, the whole volume of the liquid stream can be treated or it can be opted for one or more bleed streams that are treated to eliminate difficult to remove impurities.

Low concentrations of metal-containing sulfate solutions can be treated by the bacterial reduction of transition-metal sulfates to their sulfides (*e.g.*, ZnS and CuS) with sulfate-reducing bacteria and the subsequent use of the biogenic sulfide precipitate as a raw material. This is a waste-free process to clean water from metal sulfates [64].

### Principle 3: Prevent Waste

Waste generated by hydrometallurgical processes can be divided into two main categories: (1) parts of the raw materials that do not find a use (*e.g.*, tailings, leach residues, soluble salts); (2) remains of reagents that are not recycled (*e.g.*, sulfates precipitated as (impure) gypsum, chlorides in wastewater). The first category also includes elements that are fundamentally unusable and often hazardous or toxic that need safe disposal (see Principle 5). This category also includes potentially usable elements, but of insufficient quality and/or quantity for economic valorization, such as residues rich in iron, calcium, or silicon.

All new hydrometallurgical processes need to be designed to prevent waste as much as possible, while existing processes must be adapted to produce less waste. An additional issue is that with decreasing grades of metal ores, the feed materials are becoming more complex and contain more impurities. In particular, the increasing iron content in a feed raises concerns. Consequently, it takes more reagents and energy to process these low-grade raw materials into usable products and metals.

The treatment of ores or concentrates by conventional hydrometallurgy produces solid residues and liquid waste

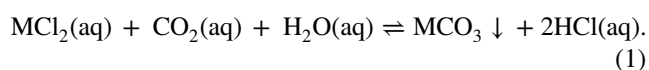
solutions [65]. While slags produced by pyrometallurgy are relatively stable when being stored outside, the residues left after leaching are generally much less stable and usually contain soluble components. The disposal of these residues in tailing ponds might be hazardous because of the danger of contaminating the surface and ground waters. Tailings-dam failures can lead to environmental disasters and even to the loss of human life, as illustrated by the 2010 Ajka alumina refining plant accident in Hungary [66]. Furthermore, tailing ponds often occupy large areas of land, which is especially problematic in densely populated regions [67].

Leaching residues could find applications as raw materials to produce construction materials such as bricks, but extensive testing is required to establish the immobilization and non-leachability of traces of heavy metals. These leaching studies must conform to regulations, but these regulations are very country specific. Leachable heavy metals are a showstopper for the valorization of industrial process residues, including metallurgical leaching residues. Even if the material conforms to the regulations, there will be concerns over the potential release of immobilized heavy metals if these materials are to be recycled in the future (*cf.* second life) [14].

Depending on the way the ore is treated, an element might end up in a waste stream or it could be transformed into a valuable resource. Take for instance sulfur, which is of key relevance given the huge importance of sulfidic ores in primary mining and the related acid mine drainage problems created by sulfur-rich tailings. The complete oxidization of sulfide ions to sulfate might be followed by the removal of the sulfate ions as gypsum, which could be used as raw material in the construction industry. However, the gypsum for this application must be of high purity, free of toxic trace elements, and radioactive impurities. Unfortunately, the gypsum precipitated from pregnant leach solutions is seldom of an acceptable purity, so that the impure gypsum creates a waste problem. However, sulfur from sulfidic ores can also be removed in the form of elemental sulfur [68], which is a useful raw material for the chemical and construction industries [69, 70]. At present, most sulfur is produced by the desulfurization of crude oil. Given the transition away from fossil fuels, it is likely that in the near future, the elemental sulfur produced in oil refineries will not be sufficient to meet the demands of the chemical industry. A strong acid can be used to release  $\text{H}_2\text{S}$  gas from sulfidic ores or concentrates. Although  $\text{H}_2\text{S}$  is a toxic gas, it can be accommodated by the chemical industry, and intensive research activities are directed towards more sustainable  $\text{H}_2\text{S}$  control. In the chemical industry, the *Claus process* is widely used to remove  $\text{H}_2\text{S}$  from gas streams [71, 72] by catalytically converting the  $\text{H}_2\text{S}$  to elemental sulfur. The  $\text{H}_2\text{S}$  released by the acid leaching of sulfides can be collected and used in another part of the flowsheet for sulfide precipitation, for instance in the

formation of *mixed-sulfide precipitates* (MSPs). It is also possible to convert the sulfidic ores and concentrates directly to elemental sulfur by selecting suitable oxidation conditions. Careful control of the reaction conditions is required to avoid partial oxidation of the sulfide to oxidation states higher than the zero-valent state of elemental sulfur. The quality of the sulfur might be challenging due to the metal impurities.

Also waste generation by gaseous emissions must be considered in hydrometallurgical processes. Emission can be due to formation of gaseous reaction products during the leaching (*e.g.*, H<sub>2</sub>S or CO<sub>2</sub>), or to volatile lixivants (*e.g.*, NH<sub>3</sub> or HCl). Gaseous emission control is only possible if the leaching operation is carried out in a closed reactor such as an autoclave or if the gases can be collected via air extraction points above an open vessel. It is very difficult to have gaseous emission control in large-scale open leaching operations, such as in the case of heap leaching. In the previous paragraph, it was described how H<sub>2</sub>S formed by non-oxidative acid leaching of sulfides can be treated and transformed into elemental sulfur. Large volumes of CO<sub>2</sub> are generated during the leaching of carbonates with acids. Formation of CO<sub>2</sub> during leaching can be avoided by switching to leaching with aqueous ammonia solution or by mixtures of ammonia solution and ammonium salts. In principle, it is possible to develop hydrometallurgical processes with negative CO<sub>2</sub> emissions, *i.e.*, processes that consume rather than emit CO<sub>2</sub>, providing that the CO<sub>2</sub> emitted during acid leaching is captured and the divalent metal impurities in the process streams are precipitated in the form of metal carbonates: MCO<sub>3</sub> (M = Ca, Mg, Mn, Fe). These carbonates are environmentally friendly and are similar to natural carbonate minerals. The carbonates can be precipitated by the addition of Na<sub>2</sub>CO<sub>3</sub>, but this consumes valuable chemicals, and it does not reintroduce protons to the system to close the proton loop (so no acids are regenerated). Therefore, we could use CO<sub>2</sub> as a precipitating agent (M = Ca, Mg, Mn, Fe) [73]:



This reaction will not go to completion when the generated HCl remains in the liquid phase because the equilibrium in Eq. (1) is shifted to the left. The solution to this problem is removal of the HCl from the aqueous solution by solvent extraction to drive the equilibrium to the right (= *SX-assisted carbonation*, see also Fig. 1) [74, 75].

#### Principle 4: Maximize Mass, Energy, Space, and Time Efficiency

Hydrometallurgical processes should be designed to maximize mass, energy, space, and time efficiency. This is also one of the principles of green engineering [9]. This Principle is not only important for the design of sustainable processes; it also matters to the economics of a hydrometallurgical plant, since it maximizes the recovery of valuable elements or products at minimum cost.

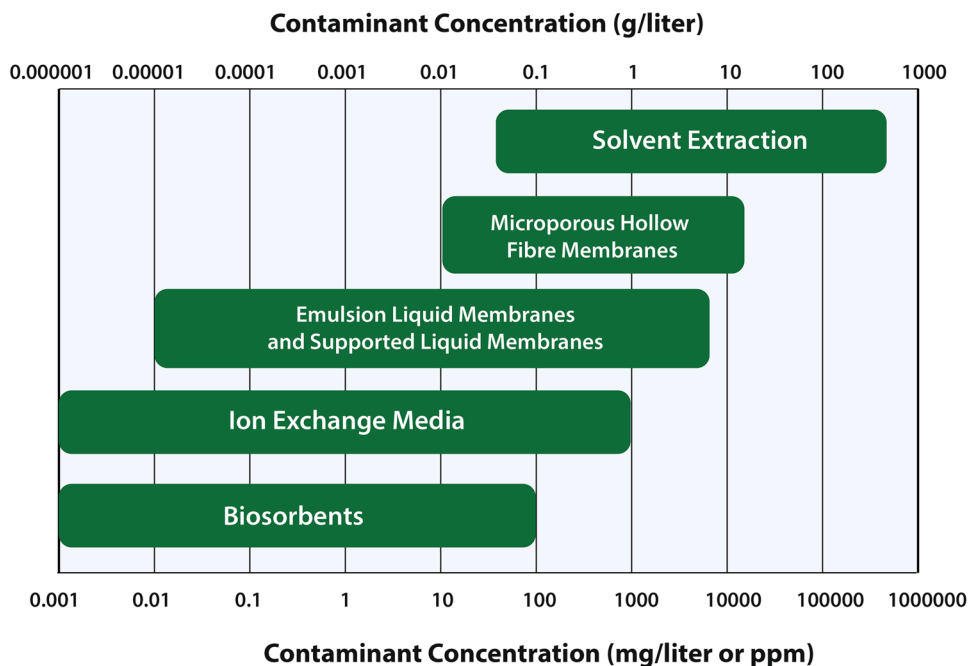
*Maximizing mass efficiency* implies minimizing the consumption of reagents. For instance, leach with an excess of acid should not be done, which subsequently needs to be neutralized by the addition of base. Maximizing mass efficiency is closely related to Principle 3 (Prevent waste) and is equivalent to the concept of “atom economy” in green chemistry.

*Maximizing energy efficiency* can be achieved by processing at room temperature or at slightly elevated temperatures, and under atmospheric pressure. The heat generated in one process is used to supply the heat to another process (see also Principle 5). The pumping of solutions is limited as much as possible, because these processes are very energy intensive. Tailored agitators are used for efficient stirring of solutions. This is essential for good process control and mass transfer. Reactions are employed, which generate product streams that are as pure as possible, so that the number of separation steps and recycling streams can be minimized. If possible, use *selective reagents*, or better still, *specific reagents*. Unfortunately, most of the reagents used in hydrometallurgy are neither selective nor specific. But selectivity can be increased by determining the optimum process conditions.

*Maximizing space efficiency* means processes should be designed in such a way that they occupy the smallest possible space. This will inevitably lead to a reduced environmental footprint because smaller reactor volumes require less heating or cooling, lower volumes of wastewater are generated, etc. An additional benefit of space efficiency is that smaller reactor vessels, and, more generally, smaller plants are required, which has a positive effect on the CAPEX of the process. One obvious approach to maximizing space efficiency is to work with concentrated rather than dilute solutions. Also, the choice of the technology is important, for instance mixer-settlers *versus* columns in solvent extraction.

*Maximizing time efficiency* means striving for faster reaction kinetics (see also Principle 7). The longer a reaction takes to proceed, the more time is required for the throughput of the ore or concentrate through the flowsheet. This leads to the inefficient use of infrastructure and impedes a high space efficiency.

**Fig. 3** Solute concentration ranges for separation technologies. Adapted from ref. [60]



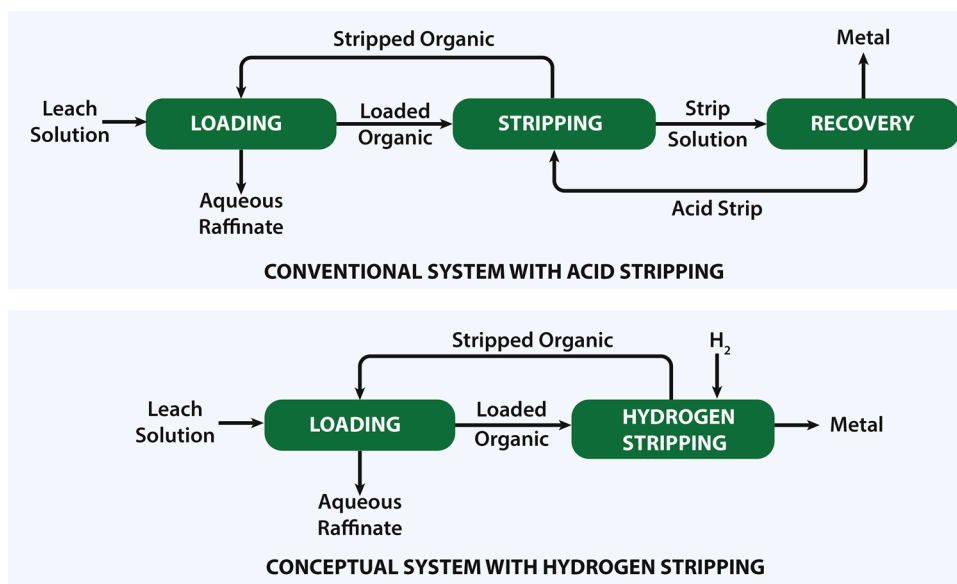
To maximize efficiency, the hydrometallurgical industry can look to the good practices of the chemical industry. Continuous processes are to be preferred over batch processes. Reactions in closed systems allow a better control of emissions and effluents. Recent findings have emphasized the benefits of process intensification, making it possible to reduce the physical size of chemical plants [76]. Although solvent-extraction processes are typically run in a continuous mode, and ion exchange can be continuous, we are convinced that there remain opportunities in hydrometallurgy for flow technology. It is important to realize that the different techniques that are used for solution purification or for separation have an optimum concentration range (Fig. 3) [60]. For instance, solvent extraction is the method of choice for concentrated solutions, whereas ion exchange is preferred for dilute solutions (although there is some overlap). Of course, a separation technique can be used outside its optimum concentration range, but it will be less efficient.

In many cases, it is preferable to purify process solutions by solvent extraction or ion exchange, rather than by precipitation. When compounds are precipitated from solutions containing high concentrations of impurities, there is a major risk of co-precipitating impurities, either by the incorporation of impurity ions in the crystal structure of the precipitated solids, by the occlusion of small droplets of the mother liquor in the solid, or by adsorption of metal ions on the surface of the precipitate. At first sight, this might appear advantageous because potentially harmful elements can be removed together with the main impurities, for example, during the combined removal of arsenic and iron from leachates. However, as discussed later (Principle

6), this approach leads to contaminated solids that are difficult to valorize. The purification of solutions by multiple precipitations and re-dissolutions implies a large number of solid–liquid separations, and these are less attractive from an engineering point of view than liquid–liquid separations. If possible, the pregnant leach solution should be purified by unit process operations that do not require precipitation steps (*e.g.*, solvent extraction or ion exchange) and the formation of solids should be restricted to the recovery step, where the final product is recovered from a purified process solution by precipitation or crystallization.

An example of how the efficiency of hydrometallurgical processes can be enhanced is by pressure hydrogen stripping of the metal from the loaded organic phase after solvent extraction (Fig. 4) [77]. In a conventional flowsheet that involves solvent extraction with an acidic extractant, the metal is stripped from the loaded organic phase by an acid and the metal is recovered from the aqueous stripping solution by, for instance, electrowinning. The replacement of the conventional aqueous strip solution by pressure hydrogen stripping could provide a way to combine stripping and metal recovery (as a metal powder) into a single-process step. The technique could be applied to copper, cobalt, nickel, and precious metals. Hence, the flowsheet could be simplified by hydrogen stripping.

**Fig. 4** Conventional solvent-extraction flowsheet with stripping followed by metal recovery from the aqueous phase compared with a conceptual flowsheet with pressure hydrogen stripping from the loaded organic phase. Adapted from ref. [77]



## Principle 5: Integrate Materials and Energy Flows

The design of hydrometallurgical processes must include integration and interconnectivity with available energy and materials flows. On a lab scale, there is a tendency to focus on a single unit process, rather than the flowsheet, making it inefficient in terms of energy and materials use. As an example, the optimization of one unit process might result in the suboptimal performance of other unit operations in the same flowsheet [50]. A metallurgical flowsheet must be developed with a holistic, integrated approach. Moreover, several metallurgical flowsheets include both pyrometallurgical and hydrometallurgical unit processes. The heat generated in pyrometallurgical processes or exothermic hydrometallurgical process steps can be recovered and used during other stages in the flowsheet to increase the reaction rate or drive an endothermic process. Thus, energy integration can be described as the use of hot streams to heat cold streams, and *vice versa*, before other energy sources are used to do the heating or cooling. This results in cost savings, increased throughput and a reduction in emissions and environmental impact. An example can be found in zinc metallurgy, where the hot water from the absorbers in the sulfuric acid plant is used to preheat the spent acid from the electrowinning operation that is going to the leaching step. The heat generated in the roasting step can be used to generate the process steam. The combined use of hydrometallurgical and pyrometallurgical processes is often a smart approach to optimizing energy efficiency.

The *Verbund* system of the German chemical company BASF is an example of efficient value chains that extend

from basic chemicals to high-value-added fine chemicals and materials [78]. In addition, the by-products of one plant are often used as the starting materials of another. In this system, chemical processes consume less energy, produce higher product yields, and conserve resources. In this way, BASF saves on raw materials and energy, minimizes emissions, cuts logistics costs and fosters synergies. Such a *Verbund* approach can be extended to the metallurgical industry. An example is Umicore's integrated smelter-refinery facility for recycling metals at Hoboken, close to Antwerp in Belgium [79, 80]. This facility contains different hydrometallurgical flowsheets that are coupled, such as a copper-leach and electrowinning facility, a lead refinery, a precious metals' refinery and a special metals' refinery.

## Principle 6: Safely Dispose of Potentially Harmful Elements

The primary mining of ores not only provides access to targeted metals, but also to unwanted elements for which there are very few or no applications, or others that are *potentially harmful elements* (PHEs). These are also known as "*elements of concern*" [15], and the best known of these elements are arsenic, mercury, cadmium, thallium, thorium, and uranium. The presence of these PHEs in metal ores is the main reason why the ideal of zero-waste metallurgy is impossible to achieve and that near-zero-waste metallurgy is a more practical target [81].

Most of the PHEs are included as minor elements in the ore minerals (up to a few thousand ppm), but they can also be present as major components, such as arsenic in nickeline

(NiAs), enargite ( $\text{Cu}_3\text{AsS}_4$ ), or tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ). Similarly, most rare-earth ores contain radioactive thorium, up to 15 wt%  $\text{ThO}_2$  [82]. PHEs can also be an issue in urban mining; for instance, the mercury present in end-of-life fluorescent lamps [83].

As we cannot avoid co-extracting these PHEs during mining and subsequent downstream processes, we must find sustainable solutions. The economic dimension of the safe disposal of PHEs should not be underestimated as they are “*penalty elements*” and additional charges are demanded for their disposal. It is important not to dilute PHEs in large-volume waste streams such as jarosite, goethite, or gypsum. By doing this, we simply create enormous volumes of contaminated streams that cannot find applications and that might have a negative environmental impact. The PHEs are better concentrated in solid compounds so that much smaller volumes of these PHEs need to be managed, which is much easier. The most obvious approach to mitigating the PHE problem is to incorporate these elements into highly insoluble compounds that have a long-term stability [84]. Moreover, these insoluble compounds must be straightforward to form, *i.e.*, avoid cumbersome syntheses and strive for economic feasibility. Because a compound with zero solubility does not exist, a realistic compromise must be identified to confine the PHEs so that they can be stored safely and will not contaminate ground-water reservoirs. A good knowledge of the mineralogy of PHEs helps identify promising mineral phases for immobilization. Furthermore, synthetic inorganic compounds could be used as well in host matrices. A recent development for the immobilization of PHEs is *encapsulation technology* [85, 86], a method in which a PHE in the form of either small particles or larger chunks is isolated within an inert compound with a high structural integrity. This minimizes the surface area of the hazardous waste exposed to water in the environment, so that the dissolution of the hazardous element is minimized as well. The immobilized PHEs could be landfilled in monitored industrial landfills or stored underground, for instance, in abandoned mine galleries. Different adsorbents have been developed for the adsorption of PHEs from wastewater, often based on activated carbon [87].

When working with arsenic-containing solutions in hydrometallurgy, we must be aware of the risk of generating highly toxic *arsine* ( $\text{AsH}_3$ ) gas under reducing conditions [88]. In general,  $\text{AsH}_3$  is formed whenever hydrogen is produced in the presence of arsenic-containing solutions. This can happen during the cementation of cadmium by zinc powder, or in electrometallurgical processes; in both cases, hydrogen gas can be formed in a side reaction. All arsenic compounds are toxic, but  $\text{AsH}_3$  poses massive challenges. Several fatal accidents have occurred, which means that  $\text{AsH}_3$  levels must be monitored and control measures must be taken if there is a risk of  $\text{AsH}_3$  formation [89]. For

instance, during cementation with zinc powder, the conditions should be maintained above pH 3. Cadmium is typically only cemented from solutions that are largely free of arsenic. Fortunately,  $\text{AsH}_3$  formation is often kinetically suppressed.

## Principle 7: Decrease Activation Energy

Because hydrometallurgical processes are carried out at ambient (or slightly elevated) temperatures compared to the much higher temperatures used in pyrometallurgy, their reaction rates are in general much slower [90]. Slow kinetics are a major issue for the leaching of solid materials because heterogeneous reactions are involved that can only take place at the liquid/solid interface. The reaction rates can then be slowed down even further if the surface of the solid material is passivated by the formation of an insoluble surface layer. Slow reaction rates can cause bottlenecks in hydrometallurgical processes, especially if we want to maximize time efficiency (Principle 4).

To increase the reaction rate of a thermodynamically favorable reaction with slow kinetics at moderate temperatures, we can try to decrease the activation energy using a catalyst. Although catalytic reactions are omnipresent in the chemical industry, they are not as common in hydrometallurgy. The best-known examples are the silver-catalyzed leaching reactions of chalcopyrite [91, 92, 93]. Likewise, catalysis is used in zinc metallurgy: in the Goethite Process, we need about  $1 \text{ g L}^{-1}$  of Cu(II) ions as a homogeneous catalyst to efficiently oxidize the Fe(II) to Fe(III) ions with oxygen in the hydrolysis step [94].

The use of catalysts is even less common in solvent extraction. This is because solvent extraction using acidic, basic, and solvating extractants is rapid, and chemical equilibrium is attained within a few minutes. However, the reactions of chelating extractants are often slow, and in these cases, catalysts are added [95]. Catalysts in solvent extraction are often called “*accelerators*.”

The authors are convinced that there is still a lot of untapped potential in the field of application of catalysts to chemical reactions relevant to hydrometallurgy, especially in the case of oxidation and reduction reactions. A glance at the older literature on redox titrations in analytical chemistry shows that many inorganic redox reactions can be catalyzed by different inorganic ions. For instance, the iodide ion has often been used as catalyst in cerimetry (redox titrations with  $\text{Ce}^{4+}$  ions) and also silver ions are known to catalyze cerium(IV)-mediated oxidation reactions [96].

A further example of this Principle is found in the electro-winning of metals. The most common anode reaction is oxygen formation by oxidation of water (*oxygen evolution reaction*, OER). The high overpotential for the OER leads to

a much higher energy consumption for electrowinning than predicted by thermodynamic calculations. This overpotential is responsible for about 20 to 25% of the energy costs of zinc electrowinning, so that a decrease of the overpotential can lead to a significant reduction in energy consumption. Such a decrease in overpotential can be achieved by the development of new anode materials [21].

Besides adding a catalyst, the activation energy for leaching can also be lowered by the activation of the solids prior to the leaching. A lot of academic research has been devoted to the mechanical activation of minerals prior to leaching by means of a planetary ball mill [97, 98]. Although this can yield very good leaching efficiencies, planetary ball mills cannot be scaled up easily to an industrial scale. Therefore, an IsaMill is recommended [99], although the energies involved are much smaller. Milling will result in smaller particle sizes and, hence, in a larger specific surface area, while the freshly exposed surfaces facilitate leaching. High-energy milling can also induce defects in the crystal lattice or even amorphization, rendering the solids more susceptible to attack by the lixiviant. However, milling remains an energy-intensive process [100, 101].

Ultrasound-assisted leaching is becoming increasingly popular in hydrometallurgy. The technique is known to enhance reactions at the solid–liquid interface. It has also been found to help reduce the consumption of reaction metal during cementation, *e.g.*, the amount of zinc powder needed to purify the  $\text{ZnSO}_4$  electrolyte in zinc metallurgy [102]. Ultrasound removes the metals deposited on the zinc surface, exposing clean metal surfaces to the solution. Robust industrial ultrasonicators for use in hydrometallurgy are commercially available, so that ultrasound-assisted leaching or cementation is feasible on an industrial scale and not only on lab scale.

## Principle 8: Electrify Processes Wherever Possible

The most sustainable way to conduct oxidation and reduction reactions in hydrometallurgy is via electrochemistry, as this approach does not introduce ionic impurities into the solution. Alternatively, the reducing and oxidizing reagents can be regenerated electrochemically in a separate step. Far-reaching electrification of hydrometallurgical processes can facilitate circular hydrometallurgical flowsheets and render hydrometallurgy more sustainable. The necessary condition is, however, the availability of ample quantities of green electricity.

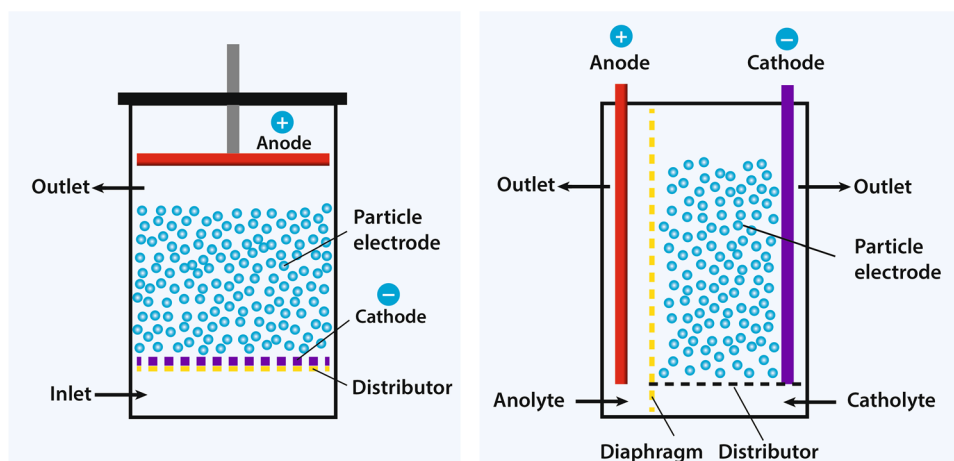
The use of electricity has a long tradition in hydrometallurgy. The electrowinning and electrorefining of metals that can be electrodeposited from aqueous solutions (such as copper, zinc, nickel, cobalt, and precious metals) have been

applied in the industry for more than a century. Large R&D efforts are attempting to make electrorefining and electrowinning more sustainable, and more energy efficient. Since electrorefining and electrowinning consume substantial amounts of energy, small improvements in energy efficiency result in significant energy savings. A detailed discussion of these developments is beyond the scope of this paper. However, one important research domain that should be mentioned here is the design of new anodes that promote the *oxygen evolution reaction* (OER) over the *chlorine evolution reaction* (CER). The ability to suppress the evolution of chlorine gas is important for the electrowinning of metals from chloride electrolytes and is a missing link in chloride hydrometallurgy [28].

The conventional approach to electrowinning with parallel-plate electrodes immersed in an electrolyte tank, works well to recover metals from concentrated electrolytes, which feature rapid mass transfer and where high current densities can be achieved. Conversely, this approach is much less efficient for the recovery of metals from dilute aqueous solutions. Performance issues for dilute solutions can be mitigated by switching from two-dimensional (2D) to three-dimensional (3D) electrodes [103, 104]. Different types of 3D electrodes have been developed, each with their own pros and cons. Examples include porous electrodes, screen, and grid electrodes, packed-bed electrodes, circulating-bed electrodes, and fluidized-bed electrodes. Among these 3D electrodes, the *fluidized-bed electrode* (FBE) has particular promise to efficiently recover metals from (1) dilute aqueous solutions, such as dilute leach solutions or process solutions from hydrometallurgical processes, (2) metal-contaminated waste waters, and (3) natural metal-bearing aqueous solutions such as *acid mine drainage* (AMD). A FBE consists of a bed of electrically conductive particles fluidized by an upward flow of electrolyte (Fig. 5). The entire bed behaves as an electrode with a high surface area. The surface area of a FBE is several orders of magnitude larger than that of conventional electrodes, which means excellent efficiency and high space–time yields. FBEs are not a recent development; they were first devised in the 1960s [105, 106] and were used in several pilot studies of hydrometallurgical processes in the 1970s [107]. That being said, interest in FBEs faded after 1990, although there seems to be a revival of research activities in this field at the moment [62, 108].

The oxidative leaching of ores can be replaced by the more sustainable process of *electrochemical leaching* (electrochemical dissolution), where the material of interest is dissolved at the anode. This process is similar to anode dissolution in an electrorefining process, with the difference being that the metal of interest is present as a compound rather than in its elemental state. The anodic dissolution reaction can be coupled with cathodic deposition of the dissolved metal, but other reduction reactions might take place

**Fig. 5** Schematic diagram of two common types of fluidized-bed electrode (FBE) reactors: the “plane-parallel design” reactor (left) and the “side-by-side design” reactor. Adapted from ref. [62]



as well. An obvious condition for the application of anodic dissolution is that the material to be leached has sufficient electrical conductivity. This is the case for sulfidic minerals that show semiconducting properties. In general, the sulfide ions are transformed into elemental sulfur, but they can be further oxidized to sulfate ions by a more positive potential. The advantage of electrochemical leaching is the simultaneous recovery of elemental metal and sulfur in a single leaching step [109].

Oxidizing and reducing agents used in leaching processes can also be synthesized electrochemically. The most obvious compound that can be produced electrochemically is chlorine gas, which is formed at the anode during the electrowinning of metals from chloride electrolytes. Chlorine gas for leaching can also be electro-generated intentionally [110], whereas  $\text{H}_2\text{O}_2$  can be produced electrochemically from water and oxygen [111].

## Principle 9: Use Benign Chemicals

Although it is evident that no dangerous, harmful, or highly toxic chemicals should be used in hydrometallurgical processes, this is less straightforward than it might seem. First, the toxicity is highly concentration dependent. Second, the metals need to be solubilized before they can be further purified in an aqueous solution. However, several ore minerals are very resistant to attack by chemicals and high concentrations of strong acids or bases are needed to decompose the ore minerals and bring their metal content into the solution.

We must distinguish between processes that involve direct contact with the environment, such as *in situ* leaching (ISL), heap leaching, or dump leaching, and processes that are carried out in chemical reactors, such as vat leaching or autoclave leaching. It is much easier to control the release of potentially harmful chemicals to the environment from reactor-based operations, although attention needs to be

paid to wastewater treatment, and accidental spills cannot be excluded. Hence, the requirements for chemicals to be used in open reaction systems are much stricter.

A rule of thumb is that a chemical that comes into contact with the environment should have no more than a transient effect on it. This means that natural or biodegradable chemicals should be used as lixivants. Examples include  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , methanesulfonic acid (MSA),  $\text{NaOH}$ , ammonia, and natural organic acids like citric acid or lactic acid. MSA is an unusual member of this list (see also Table 2). It is an example of a strong organic acid that can be considered as a green chemical [18]. This acid has a low toxicity, is readily biodegradable, and is part of the natural sulfur cycle, but its salts are far more soluble in water than sulfates and it is commercially available at low cost. The high solubility of methanesulfonate salts can assist in reducing water consumption and maximizing space efficiency.

Poorly biodegradable or persistent chemicals should be avoided. An example is ethylenediaminetetraacetic acid (EDTA). Although EDTA is often used for the remediation of soils contaminated by lead and other heavy metals, it is poorly biodegradable [112]. Likewise, fluorinated chemicals such as perfluorooctane sulfonates (PFOS) must be avoided because they are highly persistent in nature and can survive in ecological systems for decades, if not centuries. There is no place in circular hydrometallurgy for these “*forever chemicals*” [113, 114]. Furthermore, we must realize that many ionic liquids that are considered as green solvents for ionometallurgy often contain fluorinated anions such as bis(trifluoromethylsulfonyl)imide (*vide infra*). A good example is betainium bis(trifluoromethylsulfonyl)imide, [HBet][Tf<sub>2</sub>N], which is a powerful lixiviant for oxide minerals, but which combines persistency with a relatively high solubility in water [115, 116].

Different solvent-selection guides have been developed by industry to classify organic solvents according to how sustainable (“green”) they are and how safe they are to work

with [117]. It is important to realize that these solvent-selection guides were drawn up for the chemical and pharmaceutical industries and not for activities in extractive metallurgy. Nevertheless, some conclusions have general validity. Avoidable solvents are those that (1) have a very low flash point, (2) easily form explosive peroxides, (3) are ozone-depleting substances, (4) have other environmental issues, or (5) are toxic or carcinogenic. For a detailed discussion about the use of (green solvents) in extractive metallurgy, the reader is referred to our review paper on solvometallurgy [118].

The preferred oxidizing agents are air and oxygen gas because these are cheap and yield clean oxidation reactions, since they do not introduce impurities into the solution. A disadvantage is that pressures above atmospheric are needed for rapid reactions so that the use of autoclaves is required. In the case of the oxidative leaching of sulfidic concentrates, there is a danger of the over-oxidation of sulfides to sulfates. Another example of a benign oxidizing agent is hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), since it forms water as a reaction product [119, 120]. A disadvantage of  $\text{H}_2\text{O}_2$  is its tendency to disproportionate into oxygen gas and water, especially in the presence of redox-active metals. The handling and transport of  $\text{H}_2\text{O}_2$ , as well as its availability, might be an issue [121]. Likewise,  $\text{H}_2\text{O}_2$  is more expensive than some other oxidants.

When strongly oxidizing conditions are required and pressurized oxygen gas does not suffice, the use of ozone ( $\text{O}_3$ ) is an option [122]. Ozone has been used to leach different types of refractory sulfide minerals, such as chalcopyrite [123] and even pyrite [124, 125]. The ozone treatment of refractory gold ores is a sustainable alternative to a roasting pre-treatment step [126, 127].

Special attention must be paid to hydrogen gas ( $\text{H}_2$ ), which is a key chemical for closing hydrometallurgical flowsheets because the reduction of metal ions by hydrogen gas re-introduces protons to the system [128, 20]. Hydrogen gas is a clean reducing agent and is not toxic, although there are fire and explosion risks when mixed with air. We should also remember that hydrogen is only a sustainable chemical when its synthesis is sustainable as well.

For an assessment of how benign a chemical is, its non-corrosivity should be included as a criterion. Non-corrosive chemicals are not only safer to use, and they also impose fewer requirements on the construction materials for reactors, pipes, and other pieces of equipment that come into contact with the chemical reagents.

Finally, the sustainability of a reagent in hydrometallurgy should not only be assessed during its use and recycling phase. The sustainability of its production must also be fully considered (*vide supra*).

## Principle 10: Reduce Chemical Diversity

The fact that an infinite number of molecules can be designed and synthesized by chemists might give the wrong impression that the use of new, more sustainable chemicals is the key to the development of circular hydrometallurgical flowsheets. However, the history of development of extractants for solvent extraction clearly shows that the discovery of new reagents is not necessarily the way forward. A wide range of new extractants, designed with selectivity for one particular metal or for a group of metals, have been developed over the years. Many of these extractants that were once considered as silver-bullet solutions, have been discontinued, due to stability issues and/or too small markets. Examples include Cyanex 301 and 302 [129, 130].

What is more, there are strict legislations for the introduction of new chemicals on the market. In Europe, the need to register new chemicals under the so-called REACH (Registration, Evaluation, Authorization and restrictions of Chemicals) regulations makes the commercialization of new chemicals cumbersome [131, 132]. The very expensive and time-consuming environmental and toxicological studies that are required by REACH or their equivalents elsewhere, undoubtedly impose a formidable obstacle to the adoption of new chemicals in the hydrometallurgical industry. REACH is also an impediment to the use of a known chemical to be applied in a new process, as even in that case a company needs to go through the registration procedure. As corroborated by industrial experts, the use of widely available and well-known reagents is highly recommended, since this greatly facilitates the development and implementation of a new flowsheet. Design engineers prefer well-known chemicals over novel compounds because of the easily available data and the mitigation of safety risks and process-performance risks. The same holds for health, safety, and environment (HSE) advisors and the authorities who deliver the required safety and environmental permits to authorize the building and startup of a new plant.

Therefore, rather than spending excessive time and effort on developing new, exotic reagents and solvents, it makes more sense to fully exploit the possibilities of existing chemicals. We can even take this a step further and ask which of the chemicals that are presently used in hydrometallurgy could be made obsolete in the future. Apart from reducing the amount of chemicals consumed in hydrometallurgical flowsheets, we should also aim to reduce the number of chemicals used. In other words, reducing the diversity in chemicals rather than promoting it. We already know that existing chemicals can be combined in new ways to obtain synergistic effects, for example, extractants [133]. However, the smarter use of existing chemicals is possible only if their chemical and thermodynamic properties, as well as



the chemical reactions involved, are well understood. This emphasizes the importance of *metallurgical chemistry* in the development of circular hydrometallurgical flowsheets.

### Principle 11: Implement Real-Time Analysis and Digital Process Control

Real-time analysis and digital process control are required for resilient flowsheets that can cope with fluctuations in feed composition and maximize efficiency. Reliable and quickly available analytical data on various aspects of the process streams, such as metal concentrations, pH, density, etc. are essential inputs for flowsheet modeling and for process control. Analytical measurements should not only monitor the major and minor elements, but the impurities and trace elements as well.

In practice, on-line and in-line process analyses are compatible with the requirements of digital process control. Periodic sampling in combination with off-line sample analysis is too slow. The dead time between sampling, analysis, and the adjustment of the process parameters might result in inefficient conditions in the process circuits. The effective use of real-time, on-line/in-line analysis eliminates the excess lag time between sampling and adjustments to the process parameters in the circuit. Process parameters such as temperature, pressure, pH, oxidation–reduction potential (ORP), mass density, and viscosity are routinely measured on-line/in-line with robust, dedicated probes, and sensors. Although the real-time analysis of hydrometallurgical streams has long been hampered by the lack of instrumental methods and sensor development for on-line/in-line analysis of metals, this has been changing rapidly in recent years. Nevertheless, real-time on-line/in-line monitoring of concentrations of metal ions in complex process solutions still presents a formidable challenge. This is true for the major components, and even more so for the trace elements. One-size-fits-all solutions do not exist for process analysis; different analytical techniques have to be used depending on the concentration ranges of the metals and the salt content of the aqueous and organic process solutions.

The most useful and powerful method for real-time measurements of metal content is without doubt X-ray fluorescence (XRF), especially in the form of energy-dispersive X-ray fluorescence (EDXRF) [134]. XRF has been widely used in the mining and mineral-processing industries for real-time on-line measurements [135, 136, 137]. The technique is also routinely used by the metallurgical industry to measure metal concentrations in solutions, but these are typically not real-time on-line measurements, but rather off-line analyses. On-line XRF would be a very interesting technique for monitoring hydrometallurgical processes, but on-line XRF analyzers for solutions are not routinely available

yet. In hydrometallurgy, inductively coupled plasma optical emission spectrometry and mass spectrometry (ICP-OES and ICP-MS) are often the analytical methods of choice for the off-line analysis of complex liquid process streams, but it is not straightforward to adapt these techniques to on-line applications.

If the metal ion absorbs electromagnetic radiation in the UV–VIS–NIR region of the electromagnetic spectrum, optical absorption spectroscopy can be used for the on-line monitoring of solvent extraction [138]. However, optical absorption spectroscopy is less suitable for the concentrated, complex process streams found in hydrometallurgy, because of the too strong light absorption and many overlapping absorption bands. If the solvent-extraction process involves anions with characteristic vibration bands, FTIR, or Raman spectroscopy can be used for the on-line monitoring of the process [138].

In these days of rapidly developing *artificial intelligence* (AI), it is not surprising that the different branches of AI, such as expert systems, fuzzy logic, neural networks, and machine learning, could find applications in efficient process control for hydrometallurgy. However, the implementation of AI methods in hydrometallurgy is slower than in related industrial domains, such as minerals processing [139]. Still, AI methods have been applied to leaching processes [140], solvent extraction [141, 142], and electrowinning [143, 144]. Decision and optimization methods can be used to decide between alternative hydrometallurgical unit processes [145, 146], while the digitalization of a hydrometallurgical process can be seen as part of a broader narrative, *i.e.*, the digitalization of the circular economy [147, 148].

### Principle 12: Combine Circular Hydrometallurgy with Zero-Waste Mining

Metallurgy has always been closely connected with mining and mineral processing (beneficiation), and these ties will become even closer in the future with the ongoing paradigm shift in the mining industry towards “*zero-waste, multi-metal/mineral mining*” or “*responsible mining*” [149, 150]. The multi-metal/mineral aspect implies that not only the primary metal of interest is recovered (*e.g.*, lithium in hard-rock pegmatite ore) but also the accessory metals (*e.g.*, niobium, tantalum and tin) and the industrial minerals (*e.g.*, quartz, feldspar) that are present in the same ore body (*cf.* Horizon Europe EXCEED project).

Of all the different approaches to zero-waste mining, the most relevant to hydrometallurgy is “*Invisible Zero-Waste Mining*,” *i.e.*, the concept of a mining with no impact on the surface [151]. This can be achieved with the technique of *in situ leaching* (ISL), also known as *in situ recovery* (ISR), or *solution mining*. This technique is well established

in the uranium mining industry [152, 153]. The technology has proven its usefulness for the extraction of soluble salts (*e.g.*, potassium salts) and copper. It is likely that its importance will increase in the future and that ISL will be extended to other metals [154]. It is very useful for deep ore deposits, although ISL cannot be used if the hydrogeology or the permeation of the rocks is unfavorable. For example, there is always the environmental concern of contamination of ground water by lixiviants. Bacterial ISL is a promising alternative for leaching with chemical lixiviants, while experience gained in heap leaching by bacteria (bioleaching) could be very helpful in the further development of bacterial ISL. Given the fact that ISL results in dilute aqueous streams from which the metals must be recovered, the close link between ISL and hydrometallurgy is obvious, ion exchange (IX) is the recommended technique to recover the dissolved metals, with the ion-exchange resins either packed in a column, or added directly to the solution (resin-in-solution, RIS). Alternatively, adsorbents such as activated carbon can be used.

The recovery of metals from dilute aqueous mining streams will become more important in the future, and not only in combination with ISL. Several aqueous streams exist that could be treated with hydrometallurgical methods, for the removal of toxic elements, but also for the recovery of valuable elements. Typical examples are *acid mine drainage* (AMD) and other effluents from abandoned mines [155, 156], effluents of mine tailings and landfills, process waters from the metallurgical industry, and effluents from the electroplating industry. Here, water purification could be combined with the recovery of metals [64]. Small, modular, mobile hydrometallurgical plants can be designed to recover metals from aqueous streams at remote locations [157, 158]. In this way, metal recovery could be combined with the decontamination of soils contaminated by heavy metals.

## Combining Different Principles

Although there is no strict hierarchy among the principles and their numbering is somewhat arbitrary, Principle 1 (Regenerate reagents) is by far the most important principle because no circular hydrometallurgical flowsheets can be designed without regeneration of reagents. The 12 Principles are not independent, and they can be combined to even more powerful overarching principles. Hence, there can be synergies between the principles. Principle 4 (Maximize mass, energy, space, and time efficiency) is related to several other principles. Integration of materials and energy flows (Principle 5) leads to higher efficiencies (Principle 4). More efficient processes with a lower reagent consumption (Principle 4) result in less need for regeneration of reagents (Principle 1). Real-time analysis and digital process control (Principle

11) induce more efficient processes (Principle 4), while combination of circular hydrometallurgy with zero-waste mining (Principle 12) is a form of process intensification (Principle 4) as it allows to largely omit mineral-processing operations, linking mining directly to hydrometallurgy. Less minerals processing also translates into a substantial energy saving since size reduction by milling and grinding is highly energy intensive (energy efficiency is addressed in Principle 4). By decreasing the activation energy of hydrometallurgical processes (Principle 7), mass, energy, space, and time efficiency can be maximized (Principle 4). Concentration of potentially hazardous elements and their encapsulation in an inorganic host matrix (Principle 6) represent a form of waste prevention (Principle 3). Reduction of the chemical diversity (Principle 10) facilitates the regeneration of reagents (Principle 1). Many methods for regeneration of reagents (Principle 1) constitute electrochemical methods, thereby boosting Principle 6 (Electrify processes wherever possible).

What is more, there are also key interactions between the different principles. Optimization of a process towards a certain principle may lead to a worse performance in terms of another principle. For instance, for the regeneration of reagents (Principle 1), the consumption of acids should be minimized. This can be achieved by carefully controlling the pH using a pH-stat and adding acid at the same rate as it is consumed by the leaching reactions [159], so that only a small excess of acid is consumed with respect to the stoichiometric demands of the target mineral. This is feasible only for compounds that easily dissolve in dilute acids, such as copper and zinc oxides and carbonates. However, lower acid concentrations have a negative effect on the kinetics of the leaching reactions. Slower kinetics are bad for space and time efficiency (Principle 4). To maximize the driving force of leaching, but with a minimum of acid consumption, multistage countercurrent leaching could be used, although this leaching technique cannot be applied to all types of feed. For instance, clay-rich feeds are problematic because they generate suspensions with solid-liquid separations that are too slow. One could also opt for leaching with an excess of acid, followed by recycling of the residual acid (*i.e.*, the excess acid remaining after leaching). For this acid recycling, solvent extraction is the preferred technique because it is possible to select solvents in such a way that the extracted acid can be stripped thermally with hot water instead of stripping with the use of a base [160, 161]. These examples, therefore, corroborate that there are no easy solutions or shortcuts to circular hydrometallurgy: a comprehensive, system-level approach towards the 12 Principles is key.

## Implementation of Circular Hydrometallurgical Flowsheets

The metallurgical sector is rather conservative, as large capital investments are required to build new factories. Thus, it would be naïve to assume that metallurgical companies would suddenly embrace new disruptive technologies without proven long-term viability. Moreover, every project is unique; each project must be studied individually, and many factors must be considered, *e.g.*, location, logistics, availability of suitable labor force, local environmental legislation, and governmental incentives.

A major advantage of metallurgical processes is that they have a modular structure, making it possible to plug in various unit operations as part of existing flowsheets. Circular hydrometallurgy can be introduced by adapting or optimizing existing flowsheets, rather than by developing new flowsheets from scratch. We could compare the transition from linear to circular hydrometallurgy to the renovation and energy optimization of an existing building. In most cases, an older building is not razed to the ground and rebuilt according to the latest insight into energy efficiency (although this is an ideal situation to strive for). However, it is a good starting point to perform a thorough analysis of the existing building and to first address those issues where the greatest gains can be achieved. In a similar way, existing hydrometallurgical flowsheets should be scrutinized using state-of-the-art lifecycle assessment (LCA) and multicriteria assessment (MCA) methodologies [162, 163]. These can reveal the problematic hotspots of the flowsheet in terms of energy, water, and chemical consumption. Those parts of the flowsheets with the largest environmental (and economic) impacts can be addressed first, by plugging in new unit operations or replacing older unit operations.

When evaluating or comparing the sustainability of different processes or flowsheets (see 4 case-studies of (near) circular hydrometallurgical flowsheets in the online Supplementary Information: Table S4, Figs. S1–S4), it is necessary to include the type of final product. A process that leads to a product that does not need much refining is preferred to a process that generates an intermediate product that still needs several refining stages. Producing an intermediate product in a circular flowsheet, which ultimately ends up in a non-circular process for further treatment, is not that circular.

Researchers working in academia are inclined to underestimate the importance of the economics of hydrometallurgical processes. We should not only assess the technological feasibility and the sustainability metrics for a new unit operation of a flowsheet but also perform an economic assessment. For LCA and MCA studies, a detailed flowsheet with mass balances and energy balances is required. A simplified

conceptual flowsheet is not sufficient. The challenge is that if we want to close all the loops, the CAPEX and OPEX will skyrocket in a way that the process would only be profitable after many years of operation. The question arises as to whether there will be enough feedstock for the kind of raw materials the process was designed for. Often, however, there are not enough materials close to the industrial site. In principle, raw materials can be transported to the site from another location, but transportation is expensive and has a large CO<sub>2</sub> footprint.

*Flowsheet modeling* is important for the design and operation of hydrometallurgical plants. As such, flowsheet modeling is an essential tool in circular hydrometallurgy. While initial bench-scale and pilot-scale studies can provide valuable information about the chemistry of the system, the required long-term testing in a pilot plant is notoriously expensive. Therefore, the use of flowsheet modeling to assist in project evaluation is becoming more widespread. Simulation software can be used for process development to study alternatives, assess feasibility and preliminary economics, and interpret pilot-plant data. Hardware and flowsheets can be optimized to estimate equipment and operating costs and to investigate feedstock flexibility. During plant operation, modeling helps reduce chemical reagent and energy use, to increase yield, to control pollution, and to analyze troubled operations. Commercial modeling packages (*e.g.*, METSIM, Aspen Plus, OLI Systems Stream Analyzer, HSC Chemistry) are continuously being updated, as new computational techniques are being developed and our knowledge of unit operations is improved.

The design of an efficient hydrometallurgical process requires expert knowledge of the mineralogy of the ores or ore concentrates, and not just knowledge of the chemical composition [90]. As hydrometallurgy is often applied to low-grade or complex ores, the feed materials are more complex in terms of mineralogy and chemical composition than the feed materials for pyrometallurgical processes. In pyrometallurgy, the spatial complexity of the feed materials is of little importance. While knowledge of the chemical composition provides an indication of (1) the minimum amount of reagent that is required to solubilize the targeted metals and (2) which impurity elements can be expected in the leach solution, the mineralogy is of vital importance for the selection of the reagents and the most suitable process conditions. For instance, knowledge of the mineralogy of the metal ores and of the gangue minerals might make it possible to select leaching conditions with a minimum co-dissolution of the gangue. Of course, efficient hydrometallurgical flowsheets also require the mineralogical and chemical compositions of the feed to remain relatively constant over time. Careful process control is required to compensate for fluctuations in the feed composition, while simultaneously keeping the process stable.

An enormous saving in terms of consuming chemicals and energy can be achieved by avoiding what is termed “*over-purification*” of the final product in a hydrometallurgical flowsheet. In theory, it is possible to purify metals to any desired purity, but higher purity means a higher price. Hence, before designing a flowsheet for the purification of a metal, we should ask what level of purity is required to deliver the properties we need.

## Conclusions

In this academic position paper, we have outlined our vision of how hydrometallurgical flowsheets could be redesigned to lower reagent consumption, reduce waste, and increase energy efficiency. By and large, traditional flowsheets can still be considered as (predominantly) linear flowsheets, whereas the next-generation flowsheets should be (near) circular. Circular flowsheets are at the heart of circular hydrometallurgy (see also Section “Examples of (near) circular hydrometallurgical flowsheets” in the online Supplementary Information). At the limit, no reagents are consumed, with the exception of some unavoidable losses due to the Second Law of Thermodynamics. Added to this, the energy must come from renewable resources.

To provide a compass that can guide the metallurgical engineer in developing circular flowsheets in hydrometallurgy, a set of design rules has been provided, *i.e.*, the 12 Principles of Circular Hydrometallurgy. Although we realize that the choice of these principles is somewhat arbitrary and that other principles could be imagined, we are nevertheless convinced that these principles make powerful tools to show the direction of future research and innovation in hydrometallurgy, also in academia. This is especially the case if these qualitative rules are combined with quantitative assessments of the materials and energy balances for newly developed hydrometallurgical flowsheets. Because only by applying sustainability metrics (*e.g.*, LCA and MCA) it is possible to objectively compare different options for new processes, for both primary mining and recycling flowsheets. A circular use of chemicals in a primary-mining-based process might beat a non-circular use in a concurrent recycling flowsheet. The question is what we should do if we develop a very elegant circular flowsheet that is not economical to build. Which of the principles can be sacrificed first? Is there a hierarchy to these principles? There is no easy answer. Only a system-level approach will work. What is key is that, instead of introducing more complexity, we should aim for minimalism and simplicity, so that the hydrometallurgy of the future evolves to a form of low-energy-input, circular hydrometallurgy.

Research in hydrometallurgy should not focus too much on the development of new reagents and solvents, but rather

on the smarter use of existing reagents, or even the elimination of as many chemicals as possible. The unnecessary use of chemicals must also be avoided. We are convinced that genuine breakthroughs in hydrometallurgy will come from a deeper understanding of hydrometallurgical processes at a molecular level. Knowledge of the interactions at a molecular level, the chemical speciation, and the redox chemistry of process solutions is essential. The development of analytical techniques for the in-line and on-line detection of ionic and molecular species is important. Experiments should be complemented with computational chemistry methods and with thermodynamic models for multiphase, multicomponent systems.

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## Declarations

**Conflict of interest** No conflicts of interest to declare.

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