Chapter 11

Established technologies for metal recovery from industrial wastewater streams

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11.1 INTRODUCTION

Metals are essential to global economic and social development and play an essential role in the majority of the industry value chains of the 21st century. In order to keep up with the increasing demand for metals, the mining industry has shifted to the exploitation of low(er) grade ores, as higher-grade ores become scarcer. This shift not only reduces the economic viability but also comes with increased environmental cost. Population growth, expansion of industrial infrastructures, and technological advancement have also exponentially increased the demand for metals in recent decades, leading to supply-chain risks as well as economic and geopolitical challenges [1]. Low-carbon energy technologies (e.g., solar, wind, bioenergy, carbon capture and storage), catalytic processes, and electronic equipment require large amounts of metals with low natural abundance and unequal terrestrial distribution. These challenges are particularly relevant for metals classified as critical, including cobalt, selenium, tellurium, platinum group metals (PGMs) as well as rare earth elements (REEs) such as scandium and yttrium (see Table 11.1) [2]. About 90% of the supply of these critical metals comes from only nine countries, with China providing almost half of the total supply [3]. To illustrate the scarcity and uneven resource distribution of some of these metals (e.g., the use of platinum, palladium, and rhodium in catalytic converters in automobiles) to mitigate greenhouse gas emissions has been estimated to comprise about 39, 67, and 69% of the global production capacity, respectively [2]. The majority of the supply comes only comes from two countries only, namely, South Africa and Russia [3].

Table 11.1 Metal price and demand increase from 1993 to 2013 (metal prices from [4, 5]; metal demand adapted from [6]).

Metal			Price (US$/t)	Demand (%) Increase
EU Critical raw materials	Platinum-group metals	Iridium	47 580 000	Data not available
		Palladium	42 370 000	150
		Platinum	26 060 000	100
		Rhodium	95 025 000	Data not available
		Ruthenium	11 625 000	Data not available
	Rare earth elements	Praseodymium	99 000	275
		Neodymium	59 925	275
		Cerium	5475	275
		Terbium	581 250	275
		Dysprosium	248 250	275
		Yttrium (as oxide)	34	275
		Cobalt	42 000	500
		Tantalum	186 500	350
		Gallium	154	Data not available
		Germanium	1178	300
		Tungsten	42 750	Nr
		Indium	225 750	550
EU Raw materials with high relative economic importance		Iron ore	75	250
		Aluminium	1844	200
		Nickel	11 225	300
		Zinc	2476	150
		Molybdenum	26 000	250
		Lanthanum	5625	275

   To address the challenge of metal scarcity and gain long-term access to these materials at economic competitive costs and minimal environmental pollution, it is clear that a more circular management strategy for metals is needed. In this context, metal-containing wastewaters are considered an important and valuable secondary 'metal resource'. This chapter provides an introduction into the fundamentals of several established processes for metal recovery from industrial wastewater streams, with a focus on abiotic and biotic sulfur-based removal mechanisms. Specifically, guiding principles for the selection, design, and operation of sulfur-based metal recovery processes will be discussed, which are relevant to the recovery of copper, zinc, nickel, lead, iron, cobalt, cadmium, mercury, and less common metals such as thallium. Finally, an outlook for the future is provided by discussing some of the key challenges, opportunities, and research needs.

11.2 LEARNING OBJECTIVES

At the completion of this chapter you should be able to:

- Understand the importance of metals within the industry value chains of the 21st century in general and the global low carbon economy in particular.
- Describe some of the key metals that can be recovered from wastewater streams originating from various industrial activities including the oil and gas, mining, and metallurgical sectors.

- Describe and apply the fundamental principles and commonly applied technologies to recover metals from various wastewater streams and typical application area of each technology.
- Set a design basis for sulfide-based metal recovery, conduct preliminary reactor sizing, and calculate performance predictions.
- Calculate the size of reactors for sulfate reduction based on their influent characteristics.
- Calculate the pH at which one metal can be selectively precipitated as metal sulfide from a solution containing two metals, based on a difference in solubility product.
- Identify opportunities, challenges, and research needs for metal recovery from other streams in terms of environmental and economic benefits.

11.3 CONCEPTUAL OVERVIEW OF SULFIDE-BASED METHODS FOR METAL RECOVERY FROM WASTEWATER

Most metals are present in nature in the form of metal sulfides, which upon being (bio)leached are solubilized as metal ions in an acidic sulfate solution. Also, metals in solution can be precipitated as metal sulfides. As a result, technologies for metal recovery from aqueous streams have exploited this link between metals and sulfur, to recover metals in solution by means of sulfide precipitation. A key point here is the availability of hydrogen sulfide, which can be generated using sulfate already available in the wastewater or using externally supplied sulfur. This chapter will elaborate on both the principles of metal sulfide precipitation and biological sulfide production as key building blocks of current full-scale technologies for metal recovery. By treating effluents from the mining and metallurgical industry using these sulfur-based resource recovery technologies, the following valuable products can be recovered:

(1) *Metal sulfides*. The metal sulfides are produced at a dry matter content >90% and can be sold to smelters.
(2) *Water*. Sulfate can be reduced to concentrations below 250 mg·L^{-1}, pH can be raised to circumneutral pH values, and heavy metals are removed to concentrations at ppb levels. The recovered water can be used for agricultural purposes or as process water in industrial or mining applications.
(3) *Elemental sulfur*. Elemental sulfur is an insoluble essential nutrient that can be produced by means of oxidation of excess sulfide (not discussed here, but for reference you can consult Chapter 10). The recovered elemental sulfur can be re-used as a soil fertilizer or as a feedstock for sulfuric acid production.

The ultimate removal and recovery mechanism for metals in sulfur-driven processes is precipitation as metal sulfide. This precipitation can be achieved in a stand-alone abiotic process, or in a coupled abiotic–biotic process. Here we introduce the fundamental principles governing sulfur precipitation (Section 11.4), the application and design of these processes (Section 11.5), and the biological production of reduced sulfur to support precipitation (Section 11.6).

11.4 FUNDAMENTAL PRINCIPLES OF METAL SULFIDE PRECIPITATION

11.4.1 Precipitation reactions and solubility products

Most metals can be precipitated from wastewater with hydroxides or sulfides to very low concentrations, due to the low solubility products of most metal hydroxide and metal sulfides. As a result, chemical precipitation is the most commonly applied method for metal removal from industrial wastewater (it is estimated that ~90% of treatment plants use this method) [7]. The solubility product (K_{sp}) determines whether the metal will remain in solution or will precipitate. For a metal hydroxide:

$$M^{2+} + 2OH^- \rightarrow M(OH)_2 \tag{11.1}$$

where M^{2+} and OH^- represent the dissolved metal ions and the precipitant, respectively, while $M(OH)_2$ is the insoluble metal hydroxide.

$$K_{sp} = \left[M^{2+}\right]^x \left[OH^-\right]^y \tag{11.2}$$

Metals such as copper, zinc, nickel, lead, iron, cobalt, cadmium, and mercury, but also less common metals such as thallium, can be precipitated as metal sulfides. For a solid precipitate of metal sulfide $M_xS_y(s)$, the following general solubility expression can be written:

$$M_xS_{y(s)} \rightarrow xM^{2+} + yS^{2-} \tag{11.3}$$

where M_xS_x is the insoluble metal sulfide, M^{2+} represents the metal and S^{2-} represents the reactant sulfide in any of its forms (HS^-, S^{2-}, H_2S) depending on the pH of the solution. As such, the solubility product (K_{sp}) of the metal sulfide can be defined as:

$$K_{sp} = \left[M^{2+}\right]^x \left[S^{2-}\right]^y \tag{11.4}$$

where K_{sp} is in $mol^2 \cdot L^{-2}$ when $x = y = 1$, $[M^{2+}]$ is the equilibrium activity of metal ion M^{2+} ($mol \cdot L^{-1}$) and $[S^{2-}]$ is the equilibrium activity of S^{2-} ($mol \cdot L^{-1}$), varying strongly as function of pH.

The solubility products of several metals are presented in Figure 11.1 as a function of the pH at an initial metal concentration of 100 mM. The lines in Figure 11.1 represent the total metal in solution in equilibrium with the precipitate. The pH value at which a minimum metal solubility is achieved (i.e., highest removal efficiency) varies, depending on the metal species. The latter is important as this allows for the separation of metals by sequential precipitation at different pH values, thereby enabling selective recovery of the target metal(s). For example, copper sulfide still precipitates at pH 1.5 while iron sulfide precipitates only at pH values above 5.0. It is important to remember that the values of solubility will vary depending on the constituents in the wastewater, including complexing agents (e.g., cyanide, ethylenediaminetetra-acetic acid (EDTA), citrate) [8, 9]. Although purely abiotic processes can be operated across wide ranges of pH, processes which include biological sulfur reduction are generally operated at circumneutral pH.

11.4.2 Nucleation and crystallization

Precipitation occurs when a solution is supersaturated, meaning the solute concentration is higher than the solid–liquid equilibrium value [7, 11]. The kinetic phenomena associated with precipitation are nucleation and crystallization. Figure 11.2 shows the schematic representation of the saturation zones driven by solute concentration, where nucleation and crystallization occur. Crystallization only occurs if the system is supersaturated [12]. In general, high supersaturation levels favor nucleation, thus to produce crystals the supersaturation should be minimized. At high levels of supersaturation, both phenomena compete for the available solute [13]. Depending on the conditions, either nucleation or crystal growth may be predominant over the other, and as a result, crystals with different sizes and shapes can be obtained [14]. When one wishes to produce large crystals of high crystallinity and purity, precipitation should be conducted under low supersaturation conditions. Nevertheless, the combined processes of nucleation, crystallization, and agglomeration of the metal precipitates determine the particle size distribution (PSD), which in turn affects the feasibility of recovery of the metal precipitates through settling or flotation.

It should be noted that biological reactors are usually operated at circumneutral pH, which is optimal for sulfidogenic microorganisms. In addition, in such bioreactors an excess of $\sim$5–10 mM total sulfide (the sum of [H_2S], [HS^-], and [S^{2-}]) is maintained to keep the ORP (oxidation reduction potential) low, which is also a requirement for optimal microbial growth. The circumneutral pH, the presence of a few mM of total sulfide, and the extremely low solubility of relevant metal sulfides
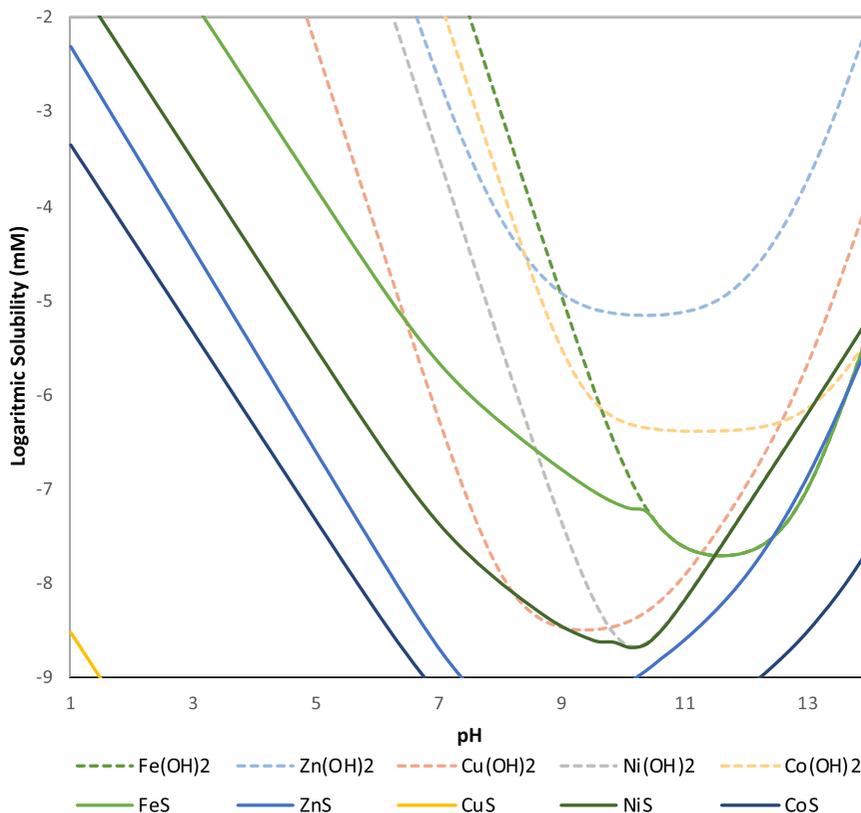
Figure 11.1 Solubility of metals at different pH values. Diagram elaborated with the MEDUSA software [10]. Equilibrium values were taken from the HYDRA database at pKa 25°C, based on initial metal concentrations of 100 mM.

(especially CuS, ZnS, NiS) implies that bioreactor solutions are highly oversaturated, with little control over the supersaturation. Therefore, for current applications of biological metal sulfide precipitation, particle size distributions cannot be controlled according to the crystallization theory explained above.

11.4.3 The impact of pH on sulfide precipitation

As already hinted in Figure 11.1, the calculation of the solubility of a metal sulfide is rather complex, due to the effect of pH, occurrence of metal sulfide complexes, and the wide range of (and sometimes conflicting) solubility products reported in the available literature. It would reach beyond the purpose of this textbook to elucidate all these complexities. Among all factors, pH has the most prominent effect on sulfide precipitation, as it strongly governs the availability of S^{2-}. Figure 11.3 depicts the speciation of the different sulfide fractions as a function of the pH.

Sulfide is in equilibrium with bisulfide (HS^-) and hydrogen sulfide (H_2S). The thermodynamic equilibrium of hydrogen sulfide can be expressed as follows [11]:

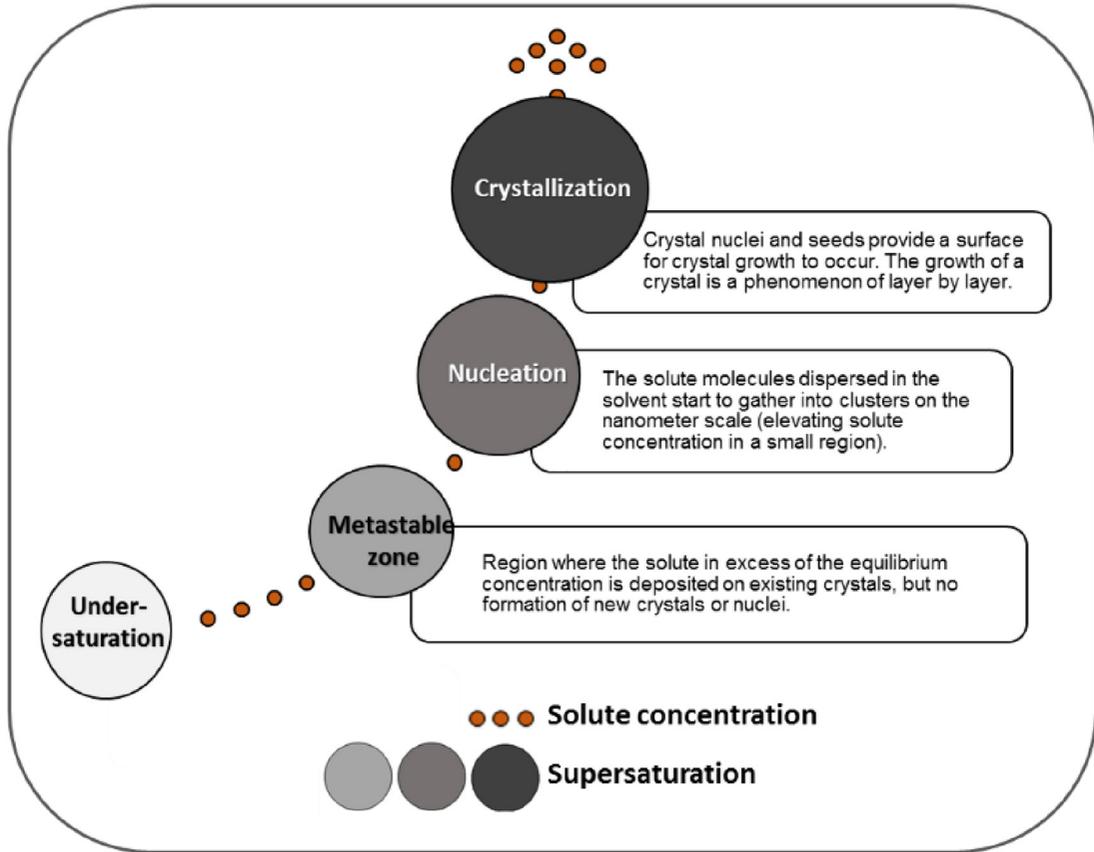$$H_2S \xleftrightarrow{\quad Ksp1 \quad} HS^- + H^+ \tag{11.5}$$

Figure 11.2 Schematic representation of the saturation zones driven by the solute concentration, where nucleation and crystallization occur (adapted from [15]).

$$\frac{[H^+]\cdot[HS^-]}{[H_2S]} = 10^{-7.0} = K_{a1}\,(pK_{a1} = 6.99) \tag{11.6}$$

$$HS^- \xleftarrow{\;Ksp2\;} S^{2-} + H^+ \tag{11.7}$$

$$\frac{[H^+]\cdot[S^{2-}]}{[HS^-]} = 10^{-17.4} = K_{a2}\,(pK_{a2} = 17.4) \tag{11.8}$$

in which S^{2-} represents the sulfide concentration. The pK_{sp} is defined as $-^{10}\log K_{sp}$, analogous to the definition of pH as measure for the proton concentration. The total dissolved sulfide (S_{tot}) concentration is given as:

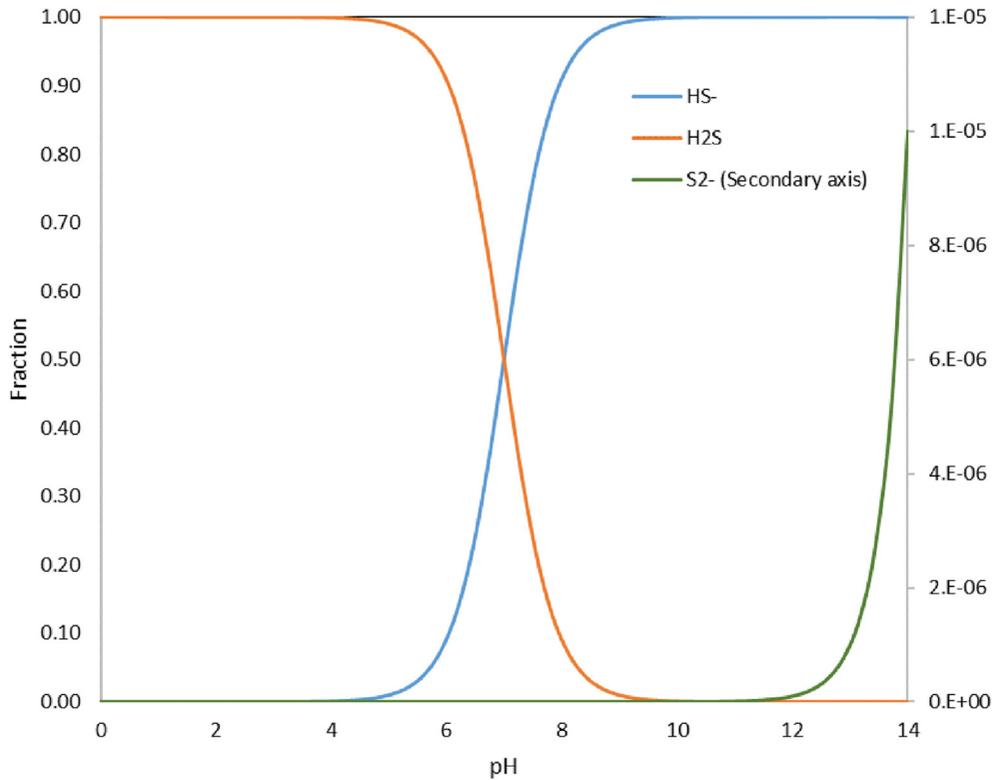$$S_{tot} = [H_2S] + [HS^-] + [S^{2-}] \tag{11.9}$$

Figure 11.3 Sulfide solubility chart showing the relative fraction of each sulfide species at different pH values; H_2S, HS^-, S^{2-}. Diagram generated with the MEDUSA software [10].

The total dissolved sulfide concentration can be measured with chemical analysis. Therefore, it is useful to express $[S^{2-}]$ as a function of the total sulfide concentration and the proton concentration (given by the pH, Equation (11.10)), derived from the above equations:

$$[S^{2-}] = \frac{[S_{tot}]}{1 + ([H^+]/K_{a2}) + ([H^+]^2/K_{a1} * K_{a2})} \tag{11.10}$$

A simplified model of metal sulfide precipitation is presented below, with zinc as example. For simplicity, it is assumed that the activity coefficients are equal to 1. The precipitation of zinc sulfide can be represented as:

$$Zn^{2+} + S^{2-} \leftrightarrow ZnS \tag{11.11}$$

At equilibrium:

$$[Zn^{2+}] \cdot [S^{2-}] = 10^{-24.7} = K_{sp}(pK_{sp} = 24.7) \tag{11.12}$$

Thus, at a pH of 7.0, and a total sulfide concentration of 6 mM, the sulfide concentration $[S^{2-}]$ is then 8.0×10^{-14} M. The $[Zn^{2+}]$ at equilibrium is 2.5×10^{-12} M.

11.5 APPLICATION AND DESIGN OF SULFIDE-BASED METAL PRECIPITATION

In abiotic precipitation processes, a critical design parameter relates to achieving sufficient mixing as a means to minimize supersaturation conditions by dispersing the reactants to promote crystallization over nucleation [16]. Various designs have been proposed and can be implemented, albeit the most commonly used reactor configurations for sulfide-based metal precipitation are: (i) completely stirred tank reactor (CSTR); (ii) pipe reactor; and (iii) fluidized bed reactor (FBR) [7]. Figure 11.4 provides a simplified schematic representation of each of these types of reactor designs.

Among these three configurations, the most common reactor used by industry is the CSTR, with sulfide being added at a single point and mixed into the reactor bulk solution using a central impeller. This method leads to poor crystallization, since mixing may not be adequately fast to avoid conditions that support nucleation. Pipe reactors have a pipe junction design where dosing of the precipitant agent (most commonly sulfide) is controlled, so crystallization can be favored. The advantages of pipe reactors include their simplicity and ease of operation. A disadvantage is that the local supersaturation induced by introducing the sulfide in this manner decreases the size of the precipitates in the contact zone. FBR systems have been identified as an effective reactor configuration for processes in which the product is a sparingly soluble species that is difficult to separate. Fluidized bed reactors provide ideal conditions for controlled precipitation because: (1) fluidization allows for good mixing on both the macro and meso-scale; (2) supersaturation can be controlled through multiple reagent inlet ports; (3) the precipitates can be separated from the treated water using gravitational separation; and (4) fines generated during precipitation can be recycled and allowed to agglomerate, thus forming large particles which can be recovered and thereby increase solid–liquid separation efficiency. In a fluidized bed reactor, the vessel is charged with a batch of pre-characterized seeds, which are subsequently fluidized by the aqueous metal stream entering the reactor from the bottom. The reagent is fed through inlet ports situated on the side of the reactor. As precipitate is deposited on the seeding material, the particle size distribution along the height of the column changes. Larger, denser particles migrate to the bottom of the reactor where they are removed as a product, while the lighter particles remain suspended higher up in the bed. In continuous processes, new seeding material is introduced at the top of the reactor, while large particles are removed at the bottom to maintain a constant bed height.
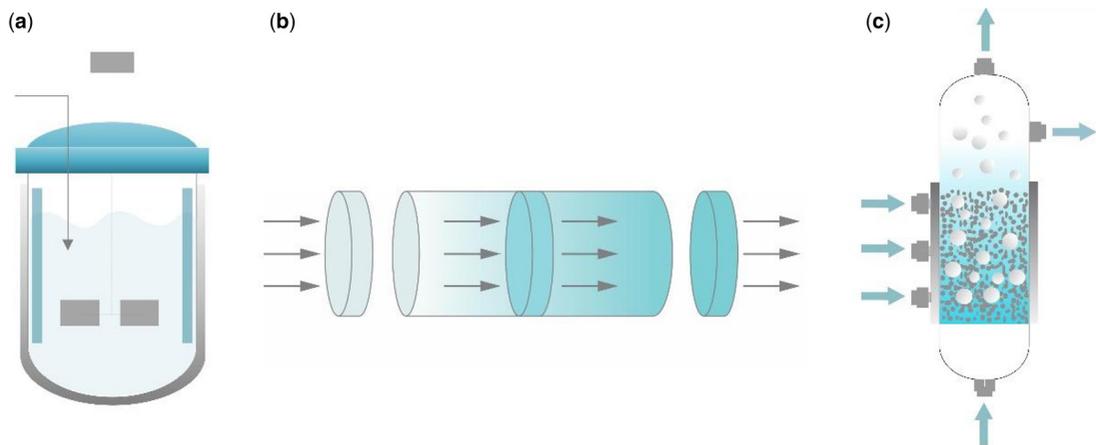

Figure 11.4 Simplified schematic representations of commonly used reactor configurations for metal precipitation using: (a) a completely stirred tank reactor (CSTR), (b) a pipe reactor, and (c) a fluidized bed reactor (adapted from [7]).

Another important design parameter is the pH value. As depicted in Figure 11.1, the solubility product of specific metal sulfide is strongly affected by the pH. This allows for selective recovery of certain metals by adjusting the pH of the solution. In practice, multiple precipitation reactors can be operated in series – each at a different pH level – as a means to sequentially recover different metals to very low concentrations to well below concentrations of 0.01–1 ppm [17].

It is important to emphasize that the use of hydrogen sulfide requires specific safety measures, as it is a toxic gas, with air concentrations of 1000 ppm leading to acute death [18]. Also, corrosion-resistant construction materials like polypropylene and high-density polyethylene are needed, as hydrogen sulfide induced corrosion may occur with concrete or steel materials [19, 20].

As discussed in Section 11.4.1. and shown in Figure 11.1, metals can also be precipitated as metal hydroxides through the addition of lime ($Ca(OH)_2$), caustic soda (NaOH), and ammonium hydroxide (NH_4OH) [8]. Of these chemicals, lime addition is the most commonly applied as it is an inexpensive, non-toxic, and non-corrosive chemical that does not require special occupational health and safety (OH&S) precautions and special storage materials. Lime is dosed in two forms, namely, in solid form as CaO (s) or as a slurry $Ca(OH)_2$. Consequently, lime addition is still commonly applied by the industry. Nevertheless, lime addition comes with disadvantages, especially in the context of metal recovery. First, lime addition results in the production of large volumes of sludge – containing a mixture of gypsum ($CaSO_4$) and metal hydroxides – which is difficult to dewater. Dewatering difficulty complicates selective metal recovery and incurs additional operational costs with respect to sludge handling and disposal. Furthermore, lime is often overdosed to ensure efficient metal removal in the presence of wastewater constituents such as complexing agents that negatively interferes with the precipitation process [8]. An important advantage of sulfide precipitation over hydroxide precipitation within a recovery context is that the sulfide precipitates that gypsum is not formed, and moreover, typically has lower levels of impurities [9]. In addition, metal sulfide precipitates can be formed in more diluted aqueous solutions due to the very low solubility product of the metal sulfides (see Figure 11.1). Equally important, the generated metal-sulfide sludge has much better dewaterability characteristics, generating a more concentrated metal sulfide product reducing the cost for transportation and further processing of the produced metal concentrates. Finally, beyond these operational benefits in terms of metal removal and lower sludge volumes, sulfide precipitates can be directly recycled within the process, as most metal refineries treat metal sulfide ores [21].

11.6 BIOLOGICAL H$_2$S PRODUCTION FOR METAL RECOVERY

In the section above, we have discussed the principles of sulfide-based metal precipitation. Hydrogen sulfide is commonly added in aqueous form as Na_2S, NaHS, and $(NH_4)_2S$. Alternatively, it can also be dosed in gaseous form in the form of H_2S (g). An interesting alternative that has found widespread implementation at full-scale is the onsite production of sulfide through microbial (i.e., biologically mediated) reduction of the sulfate present in the wastewater by sulfate reducing bacteria (SRB), or alternatively by reduction of added elemental sulfur by sulfur reducing bacteria. These approaches are discussed in more detail in the sub-sections below.

11.6.1 Fundamental principles of microbial sulfate and sulfur reduction

Sulfate and elemental sulfur can be reduced to hydrogen sulfide under anaerobic conditions by a diverse group of anaerobic microorganisms usually named as sulfate reducing bacteria (SRB). These microbes use oxidized sulfur compounds as electron acceptor in their metabolic pathways. These sulfide-generating bacteria are able to conserve energy by the reduction of sulfur oxyanions like sulfate, sulfite, and thiosulfate [22]. SRB are considered as a group because of their common ability to use sulfate as terminal electron acceptor for energy-generating degradation of hydrogen and/or

organic substrates such as ethanol, methanol, or volatile fatty acids (VFAs). To illustrate this, for example, the reduction of sulfate with hydrogen and ethanol as electron donor proceeds as:

$$SO_4^{2-} + 4H_2 \rightarrow H_2S + 2H_2O + 2OH^- \tag{11.13}$$

$$3SO_4^{2-} + 2C_2H_5OH \rightarrow 3H_2S + 4HCO_3^- + 2OH^- \tag{11.14}$$

Besides SRB, other microorganisms carry out dissimilatory reduction of elemental sulfur, such as mycobacteria, and a variety of prokaryotes: for example, bacteria in hypersaline sediments, thermophilic archaea, and so on. The utilization of elemental sulfur as the source of sulfide needs four times less electron donor compared to sulfate, since only 2 moles electron-equivalents to 1 mol H_2 are needed for the reduction of sulfur to sulfide instead of the eight electrons equivalent to 4 moles H_2 needed for the reduction of sulfate to sulfide:

$$S^0 + H_2 \rightarrow H_2S \tag{11.15}$$

Like SRB, sulfur reducing microorganisms are highly diverse. Especially interesting is sulfur reduction at low pH, as this additionally enables selective precipitation of metals [23].

11.6.2 Applications and design of biological sulfate and/or sulfur reduction

Hydrogen sulfide is produced in biological reactors and contacted with the metals of interest for precipitation. This can be done in different configurations depending on whether or not the wastewater with metals contains (sufficient) sulfur/sulfate for the production of adequate amounts of hydrogen sulfide for subsequent metal precipitation. In general we can identify four different types of configurations, namely (Figure 11.5): (a) sulfate is present in the same stream as metals and sulfur reduction and metal sulfide precipitation occur in the same step; (b1) sulfate is present in the same stream as metals, but sulfur reduction occurs in a secondary stage, with the H_2S-rich wastewater being recirculated to the first stage for precipitation; (b2) sulfate is present in the same stream as metals, but sulfur reduction occurs in a secondary stage, with H_2S being supplied to the first stage for precipitation as a gas; and (c) the wastewater does not contain sulfur, and a source of sulfur needs to be provided in the second step, which functions analogously to (b1) and (b2). In cases where the water may be inhibitory to the microorganisms (due to pH, temperature, salinity, or other factors), it is also possible to generate H_2S in a side-stream process and recirculate it back to the metal sulfide precipitation reactor, such that the microorganisms do not come in contact with the contaminated water (configuration not shown).

Beyond the presence of sulfate or sulfur, another important aspect for biological sulfate reduction is the presence of an organic or inorganic (hydrogen) electron donor. In general, metal-rich wastewaters, especially those generated in the mining and metallurgical industries, normally do not contain sufficient electron donor to reduce the desired amount of sulfate to sulfide. Electron donors must then be supplied to the sulfate reduction process from an external source. For instance, organic waste materials such as molasses support sulfate reduction as the electron donor. However, such organic waste materials are often only available in relatively small quantities, generally limiting its applicability to streams with a low sulfate load. Furthermore, the composition of these organic waste materials is complex, which could result in less efficient availability for sulfate reduction. For instance, growth of methane producing microbial populations is more likely on such substrates. The use of organic materials may also lead to additional biochemical oxygen demand in the effluent of the process. The use of organic matter/waste is especially suitable for low-engineered systems such as permeable reactive barriers [24]. Here we will focus on the use of relatively pure bulk chemicals as electron donors for high-rate engineered processes. Hydrogen and ethanol are often used as these support high volumetric sulfate reduction rates (Table 11.2).
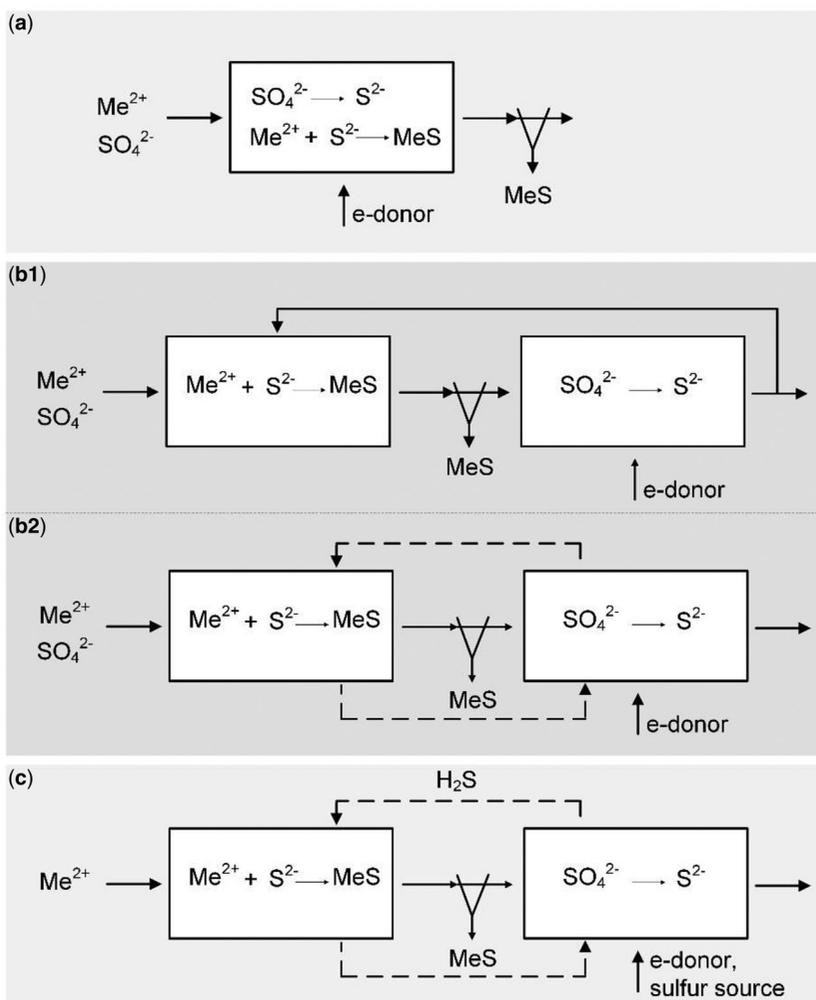
Figure 11.5 Configurations for the sulfur-associated precipitation of metals. When sulfate and metals are both in the influent stream, sulfur reduction and metal sulfide precipitation can: (a) occur in the same step; or (b) separate stages. When in separate stages, reduced sulfur can be recirculated to the first stage (where metals are present) with (b1) H_2S-rich wastewater or (b2) H_2S-containing gas; (c) When wastewater does not contain sulfur, a source of sulfur needs to be provided in the second step.

For small sulfate loads ($<$2–3 tons $S \cdot day^{-1}$), the use of ethanol is preferred because at such loads it is more economical than the use of hydrogen. Hydrogen gas must be produced (if not available on-site) by catalytic conversion of methanol or methane. From both methane and methanol, a mixture of H_2 and CO_2 is produced. Although the chemical costs for ethanol are somewhat higher than for hydrogen, the investment is lower since no catalytic conversion step is needed with ethanol. Ethanol can directly serve as electron donor for sulfate reducing bacteria, whereas methane and methanol support only low rates of sulfate reduction. There is an exception, however, as methanol is an effective direct electron donor under thermophilic (65°C) conditions [31]. Another cost-reducing factor for

Table 11.2 Sulfate and sulfite conversion rates as demonstrated in laboratory bioreactors with various electron donors.

Electron Donor	T (°C)	SO_4^{2-} Conversion Rate $kg \cdot m^3_{reactor}^{-3} \cdot day^{-1}$	SO_3^{2-} Conversion Rate $kg \cdot m^3_{reactor}^{-3} \cdot day^{-1}$	Reference
Molasses	31	2.4	n.a.	[26]
Synthesis gas	30	10	n.a.	[27]
H_2/CO_2	30	30	n.a.	[28]
Ethanol	30–35	29	n.a.	[29]
Acetate	33	9.4	n.a.	[30]
Methanol	65	14	18	[31]
H_2/CO_2	55	7.5	9.3	[32]

n.a. = no sulfite added, Note that the data represents a selection of the most common electron donors used for full-scale applications. A broader overview can be found elsewhere [25].

ethanol is that it requires fewer occupational health and safety measures compared to hydrogen. With ethanol, the upflow anaerobic sludge blanket (UASB) reactor is the standard reactor design. This reactor type was originally developed for anaerobic digestion of organic waste [33], and typically has a height of 4–5 meters. UASB reactors are characterized by a high biomass concentration of up to 50 kg VSS $\cdot$ m^{-3}, present as granular or floccular suspended biomass. As already indicated in Table 11.2, sulfate conversion rates of 29 kg $\cdot$ m$_{reactor}^{-3} \cdot$ day^{-1} are possible with ethanol (see references in Table 11.2 for more details of reactor design and performance).

For larger sulfate loads at moderate temperatures (25–40°C), hydrogen gas, catalytically produced from natural gas, becomes an economic alternative to ethanol, as the increased investment for the catalytic natural gas reformer may balance the reduced cost for the electron donor. The resulting gas also contains carbon dioxide, which is used as a carbon source by the sulfate reducing bacteria. For optimal hydrogen mass transfer from gas to liquid, gas-lift loop bioreactors are used. With this design, sulfate conversion rates of 30 kg $\cdot$ m$_{reactor}^{-3} \cdot$ day^{-1} can be achieved. Under thermophilic conditions (65°C), the use of hydrogen is less efficient due to the formation of the by-product methane from H_2 and CO_2 [32]. A relatively small part of the electron donor, typically 5–10% of the total consumed electron donor, is used for anabolic pathways to produce sulfate reducing microbial biomass.

The total sulfide concentration (i.e., the sum of hydrogen sulfide [H_2S], bisulfide [HS^-] and sulfide [S^{2-}]) in sulfate reducing reactors is kept below about 600 mg $\cdot$ L^{-1} at pH 7, in order to prevent inhibition of the sulfate reducing bacteria by the end product hydrogen sulfide. The sulfide concentration can be kept lower when metal sulfides are precipitated simultaneously. With respect to process economics (minimal electron donor consumption), it would be optimal to only produce the stoichiometric amount of sulfide needed for metals precipitation. However, in order to avoid the presence of free metals, which would severely inhibit the microbial population, sulfide is typically kept in excess of about 200 mg $\cdot$ L^{-1}. In this way, temporary decreases in sulfide production (e.g., as a result of temperature variations) or unintentional increases of the metal load can be dealt with, without compromising process stability. It does, however, imply that a post-treatment step is needed in which the excess sulfide is removed. The latter can be done by means of aeration in order to produce elemental sulfur (see Chapter 10 for more detail).

11.6.3 Case studies of implementation
11.6.3.1 Sulfate reduction for metal removal at the Nyrstar Budel zinc production facility
Nyrstar operates a zinc (Zn) smelter in the Netherlands, which produced 268 000 tons of zinc in 2018. Historically, zinc slags and polluted gypsum were stored in ponds at the site, which led to groundwater contamination. Groundwater contamination was also caused by the old pyrolytic

zinc production process, which was stopped in 1973 and replaced by a roast-leach-electrolysis (RLE) process. The conventional RLE zinc production process used at the Nyrstar site produced various wastewater streams containing sulfate, chloride, fluoride, and metals (mainly zinc). Until the year 2000, the chloride and fluoride bleed streams were treated with the conventional process by neutralization with lime to produce a mixture of gypsum, metal hydroxides, and calcium fluoride. After new governmental regulations prohibited this approach, a wastewater treatment process was designed based on biological sulfate reduction, without generation of solid waste. More specifically, two streams generated at the site needed treatment, first, the scrubber discharge from the roaster gas cleaning plant, the so-called Wash Tower Acid (WTA). This wastewater stream has a typical flow of $25 \, \text{m}^3 \cdot \text{h}^{-1}$ containing $15 \, \text{g} \cdot \text{L}^{-1} \, H_2SO_4$, $3 \, \text{g} \cdot \text{L}^{-1}$ HF, $4 \, \text{g} \cdot \text{L}^{-1}$ HCl, and $1.5 \, \text{g} \cdot \text{L}^{-1} \, Zn^{2+}$. The second wastewater stream requiring treatment is the Magnesium bleed. This bleed is necessary to prevent build-up of magnesium in the leaching and electrolysis circuit (which would cause operational issues due to the formation of inorganic scaling). Typically, $0.5 \, \text{m}^3 \cdot \text{h}^{-1}$ of purified solution and/or spent acid is bled from the circuit. A fraction of this Mg bleed is used to make maximum use of the capacity of the sulfate reducing bioreactor. Figure 11.6 provides a simplified process flow sheet consisting of seven biological, chemical and physical stages: (i) Neutralization of Wash Tower Acid with calcine and sodium hydroxide; (ii) Fluoride removal as CaF_2 together with oxidation of As and Fe; (iii) Mixing with
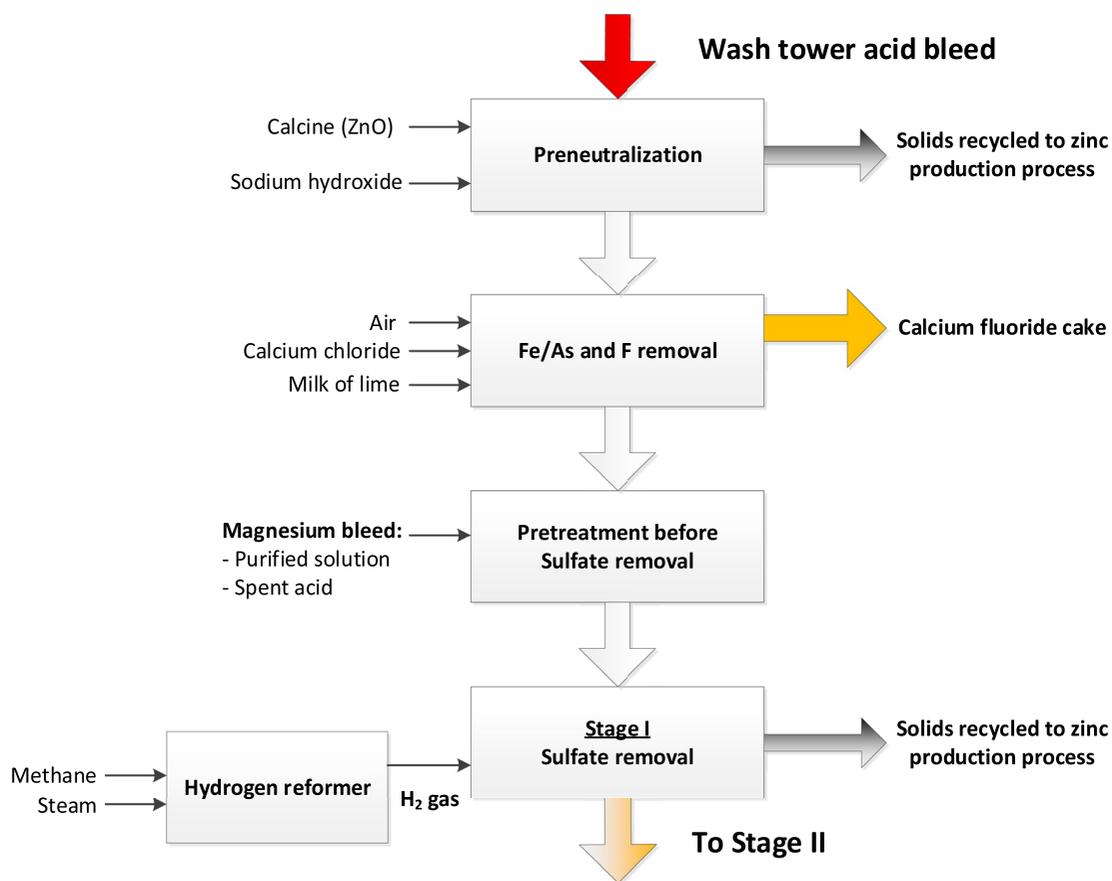

Figure 11.6 Process design for the full-scale installation for integrated sulfate reduction and zinc precipitation.

magnesium bleed (Zinc electrolyte), nutrient addition, pH, and temperature control; (iv) biological conversion of $ZnSO_4$ to ZnS, with H_2 as an electron donor; (v) separation of the formed ZnS; (vi) de-watering of the formed ZnS; and (vii) effluent of the bioreactor is further treated in the ethanol-fed bioreactor where metal traces are removed and excess sulfide is converted into elemental sulfur.

In the bioreactor, sulfate reducing bacteria convert the $ZnSO_{4(aq)}$ into $ZnS_{(s)}$ using hydrogen as electron donor:

$$ZnSO_{4(aq)} + 4\,H_2 \rightarrow ZnS_{(s)} + 4\,H_2O \tag{11.16}$$
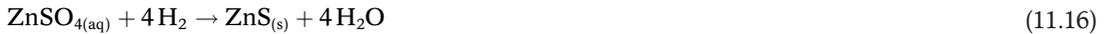
Hydrogen gas is produced on-site from natural gas in a reformer. In the reformer unit, natural gas is converted with steam into a mixture of mainly H_2 (80%) and CO_2 which is fed to the bioreactor. CO_2 is used as a carbon source for the bacteria. In order to achieve good mixing without introducing high shear forces, a gas-lift loop type reactor is used (Figure 11.7). A small amount of the gas recirculation flow is discharged in order to bleed inert components (mainly nitrogen and methane, the latter either coming from the product gas or from methanogenic activity). This bleed gas is recycled to the reformer burner. About 15 kg of dry biomass is produced per ton of sulfate converted. The precipitated ZnS is separated in a thickener, combined with solids from the groundwater treatment and sulfide precipitation and subsequently sent to a decanter centrifuge for dewatering. Flocculant is added to obtain a clear decantate and a manageable cake. ZnS cake is recycled to the zinc production process.

The 500 m³ bioreactor (Figure 11.7) was started up with 20 m³ of sludge containing sulfate-reducing bacteria. Within 2 weeks, the biological activity was sufficient to treat the entire WTA flow. In 2018, the average flow to the reactor was 25 m³ · h⁻¹ with 3.8 g · L⁻¹ Zn in the influent. The removal efficiency for zinc was 99.8%, while for Cd (32 mg · L⁻¹ in the influent) removal efficiency was 99.9%. More data on long-term performance of the bioreactor can be found elsewhere [34]. The precipitated ZnS,
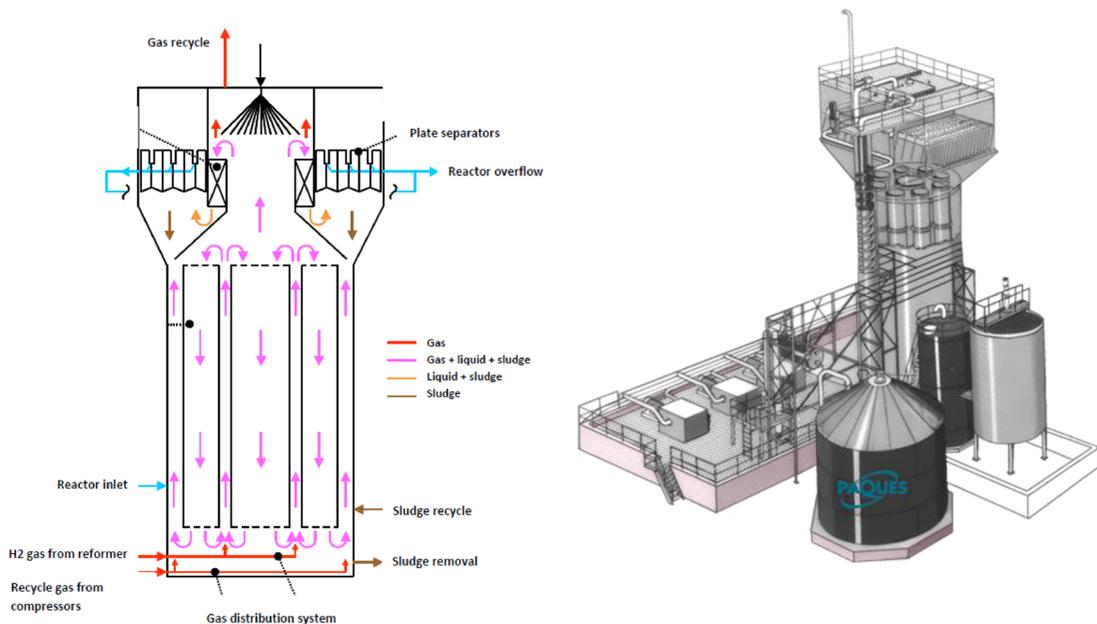

Figure 11.7 (Left) Simplified representation of a hydrogen fed SRB Gas-Lift Loop Type Reactor and (right) Full-scale sulfate reducing bioreactor for zinc and sulfate removal at Nyrstar, the Netherlands.

5 tons $\cdot$ day^{-1}, is returned to the zinc smelter as feedstock, such that this process produces no solid waste. For comparison, removing the zinc and sulfate with the conventional chemical lime process would result in 9 tons $\cdot$ day^{-1} of metal contaminated gypsum waste which is unsuitable for reuse or recycling, creating a long-term legacy as it has to be stored.

In addition to the bioreactor for integrated sulfate reduction and zinc precipitation, a second bioreactor has been in operation at the Nyrstar site in the Netherlands since 1992 for treatment of 300 m$^3 \cdot$ h^{-1} metal-contaminated groundwater at maximum capacity. In this bioreactor, SO$_4^{2-}$ is reduced to H$_2$S with ethanol as an electron donor, followed by precipitation of metal sulfides, thereby removing sulfate, zinc, and other metals to concentrations below discharge consent values. From the year 2000 onwards, process wastewater has also been treated in the installation, and the hydrogen bioreactor installation described above also feeds into the bioreactor. Expansion of the groundwater treatment to a maximum of 400 m$^3 \cdot$ h^{-1} was also executed. Until 2009, sulfate reduction and metal sulfide precipitation were carried out simultaneously in the same reactor. In 2011, a separate metal sulfide precipitation was installed to optimize bioreactor performance. Excess sulfide in the metal-depleted effluent is biologically oxidized to elemental sulfur with the Thiopaq™ technology (see Chapter 10 for more details). The product of this process, a metal sulfide sludge (mainly consisting of ZnS), is recycled to the main zinc production process. The current process flow scheme is shown in Figure 11.8. The system has consistently met the required discharge limits with concentrations for sulfate, zinc, and cadmium of 450, <0.05, and <0.001 mg $\cdot$ L^{-1}, respectively.
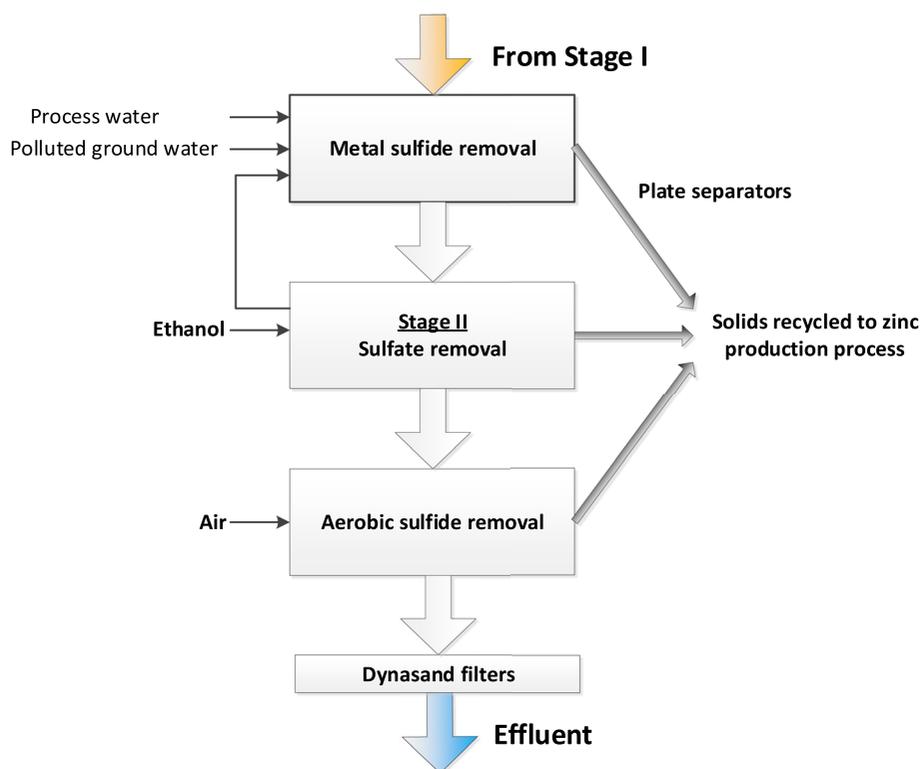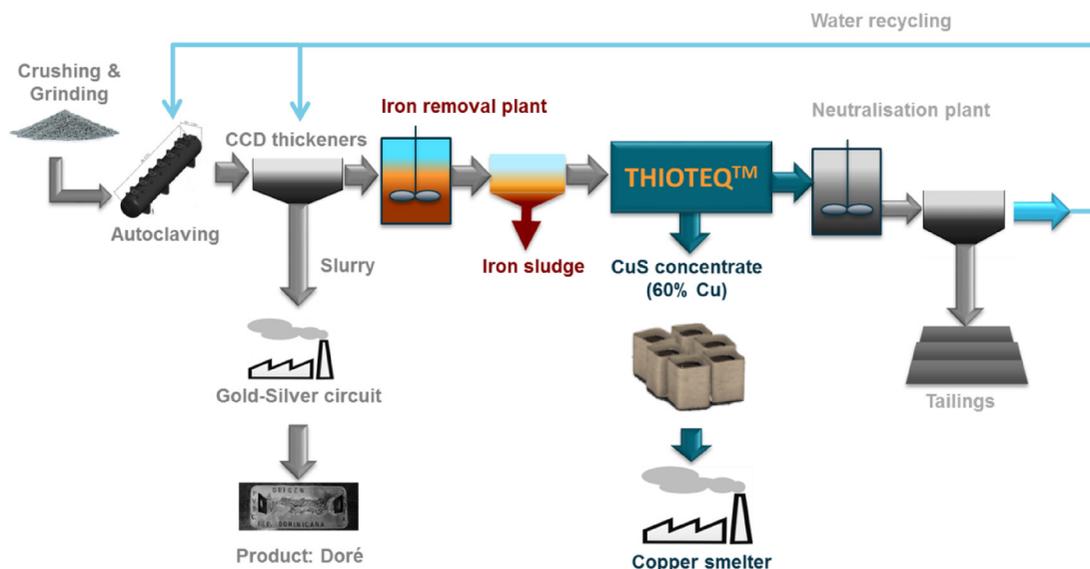

Figure 11.8 Process flow scheme of the sulfate reducing bioreactor for treatment of metal-contaminated groundwater at Nyrstar, the Netherlands.

11.6.3.2 Copper recovery at the Pueblo Viejo gold mine, Dominican Republic

Soluble copper can be found in hydrometallurgical streams resulting from gold/copper mineral processing sites. Pueblo Viejo Dominicana Corporation (PVDC) mines ores in the Dominican Republic that contain gold, silver, and copper. These ores are processed by conventional crushing, grinding, and pressure oxidation in autoclaves, cyanidation, and refining. After autoclaving, the remaining solids are washed using counter current decantation (CCD). The CCD thickeners separate the slurry (which continues to the gold/silver circuit) from the clarified liquid, which contains soluble copper at concentrations between 100 and 400 mg · L^{-1} and high concentrations of iron and zinc. In the past, this stream was neutralized before being recirculated to the CCD thickeners (without recovery of copper). The soluble copper was precipitated during the neutralization stage and was disposed in the tailings with the precipitated gypsum. In 2014, a THIOTEQ™ plant was started to recover the copper upstream of the neutralization plant by using biological sulfur reduction technology to produce H_2S (Figure 11.9). The use of gaseous H_2S instead of chemical NaHS avoids sodium addition to the closed loop water system, which would hamper the plant's neutralization performance. The plant was designed and commissioned by Outotec Oyj (Finland) and Paques B.V. (the Netherlands) and consists of three copper sulfide precipitation reactors and a 2000 m³ sulfidogenic bioreactor connected by a gas recirculation system operated at 8–10% H_2S concentration in the gas. With this technology, this copper recovery plant recovers valuable copper that would be lost in the tailings while decreasing the metal content in the tailings. The process does not affect the neutralization plant performance, enabling water to be recycled back to the CCD thickeners.

Between the CCD thickeners and the copper recovery plant, an iron removal unit removes dissolved ferric iron, which is present in high concentrations. Leaving the ferric in solution would consume H_2S and lower the copper grade in the final product, because ferric iron is chemically reduced by H_2S, with ferrous iron and elemental sulfur as products of the reaction. Ferric is precipitated at high

Figure 11.9 Barrick Pueblo Viejo simplified process flowsheet with copper precipitation using biogenic sulfide [35].

temperatures (>70°C) by the addition of limestone at a pH below 3, while copper and zinc remain in solution. In the copper precipitation step, the pH is not controlled and drops slightly due to the reaction with sulfide. At this low pH, zinc remains in solution, effectively making the precipitation step highly selective for copper. Although the zinc concentration in the feed is typically ten times higher than the copper concentration, the zinc content in the final product remains low at a level of around 0.2%.

The required sulfide in the form of H_2S gas is generated on-site and on-demand, at ambient temperature and pressure, in a bioreactor fed with elemental sulfur and ethanol (Figure 11.10). The reactor was seeded with naturally occurring bacteria. The bioreactor is operated 'offline' (i.e., the bacteria are not in direct contact with the metal-containing stream). The copper plant at PVDC was designed for the recovery of 12 000 tons per year of copper requiring around 20 tons of H_2S to be produced per day, making this system the largest biological H_2S generator in operation. Ground elemental sulfur is kept in excess together with a small supply of nutrients. The amount of ethanol is added based on the H_2S requirement. On average, copper removal efficiencies around 85% are achieved and are expected to increase to 95% with further optimization.

The precipitated copper settles in a 50 m diameter thickener and reaches 40% sludge density at the bottom. After dewatering in a filter press, the product is bagged and shipped to copper smelters. The produced copper concentrate contains more than 90% CuS and less than 10% gypsum, resulting in a copper grade of around 60%.
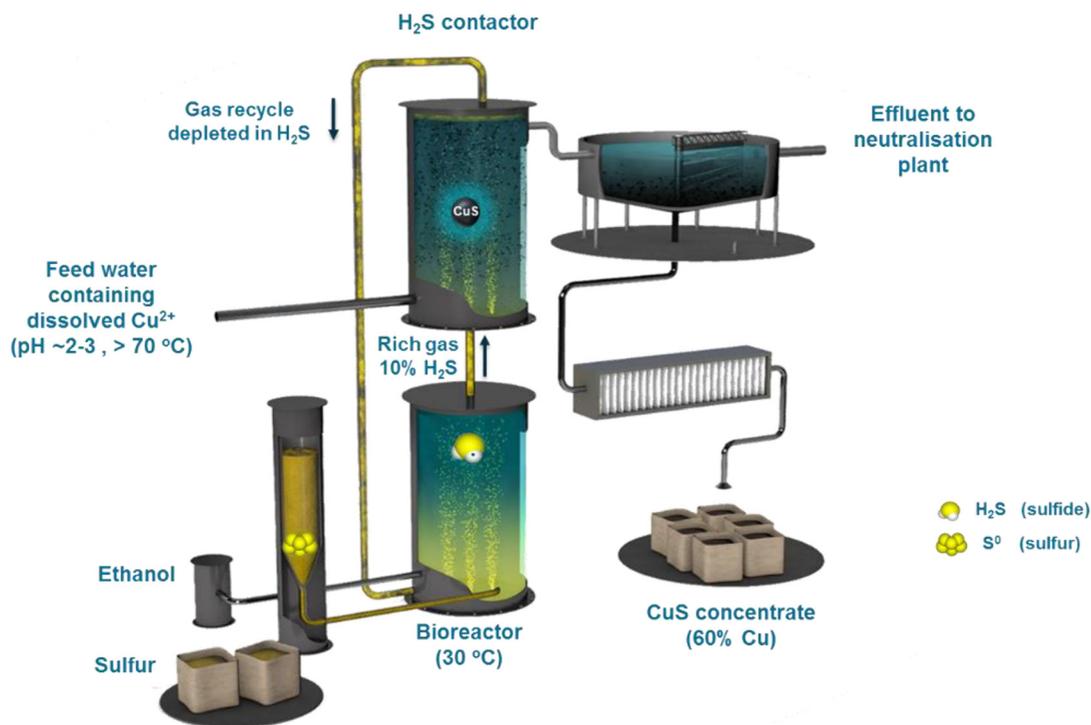
Figure 11.10 The THIOTEQ™ bioreactor produces cost-effective on-site and on-demand H_2S.

11.7 CHALLENGES, OPPORTUNITIES AND RESEARCH NEEDS

Technologies that recover metals through biological sulfur and sulfate reduction are currently applied in niche-markets. For more widespread application, the challenge is to reduce the costs of the electron donor and to widen the operational window, especially for the process parameters temperature and pH. In this respect, further development of elemental sulfur reduction technologies seems most promising. Elemental sulfur is widely available and mostly produced as a byproduct when removing sulfur-containing contaminants from natural gas and petroleum (see Chapter 10 for further details). As previously discussed, sulfide produced from elemental sulfur reduction requires four times less electron donors than from sulfate reduction. Secondly, sulfur reducers appear to span a wider range of pH (especially in the acidic range) and temperature at which they can thrive. With operation at lower pH values, sulfur reduction technologies will further generate added value for industry, as selective metal removal becomes a feasible possibility. This technology must first be investigated in more detail to obtain optimal process flowsheets.

11.8 CHAPTER SUMMARY

In this chapter, several microbial conversions of the sulfur cycle were presented, representing the basis of scalable bioreactor technologies for sulfide, sulfate, and heavy metal removal from industrial aqueous process and waste streams. These bioreactors are open, meaning that the composition of the microbial population is not controlled. However, the processes are designed to give competitive advantage to microorganisms that carry out desired conversions. For sulfate reduction, the choice of electron donor and temperature is relevant in this respect. Hydrogen and ethanol electron donors support high rates of sulfate reduction under mesophilic conditions. Sulfate reduction technologies remove sulfate and are also used for metal removal and recovery.

Although still less widespread, sulfate reduction technologies are applied in the chemical and metallurgical industries. As these sectors are not generally familiar with the use of biotechnologies, there still remains some reluctance to make full use of their potential. However, it may be expected that the technologies will increasingly penetrate the market, as they fit well with the aims of a circular economy. The recovery of reusable/recyclable products from waste streams (i.e., elemental sulfur and metal sulfides) with no or minimal solid waste production aligns especially well with this new paradigm.

11.9 EXERCISES

Exercise 11.1: A wastewater containing zinc and iron, both at a concentration 0.10 M, are aimed to be recovered through chemical sulfide precipitation. Estimate the required pH to precipitate the amount of zinc but not of iron if the initial H_2S concentration is 0.1 M. Use the equation for the metal dissolution in an acidic solution below and rearrange so the single unknown is H_3O^+. For this, calculate the solubility-product constant in acid ($K_{sp}a$). The K_{sp} values are provided in the table below and in Equation (11.5) for sulfide dissociation in acid conditions.

$$K_{spa} = \frac{k_{sp}}{k_w k_{sp1}}$$

$$MS(s) + 2\,H_3O^+(aq) \rightleftarrows M^{2+}(aq) + H_2S(aq) + 2\,H_2O(l)$$
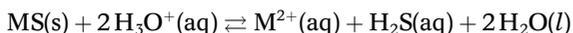
Data for this question:

Compound	Formula	K_{sp}
Iron(II) sulfide	FeS	8×10^{-19}
Zinc sulfide (alpha)	ZnS	2×10^{-25}

Exercise 11.2: Estimate the amount of lime ($Ca(OH)_2$) required per year to remove the sulfate and metals from acid mine drainage (AMD) in the table below at a flow rate of $40 \, m^3 \cdot h^{-1}$. Sulfate concentration in this AMD is $3360 \, mg \cdot L^{-1}$ [36].

| Wastewater Source	Acid Mine Drainage (mg/L) [24]	Wastewater Source	Acid Mine Drainage (mg/L) [24]
Magnesium	342	Nickel	3.78
Aluminum	54.3	Copper	44.9
Chromium	0.12	Zinc	5.9
Manganese	6.05	Cadmium	0.01
Iron	391	Lead	6.9
Cobalt	8.99		

(a) Estimate the amount of sludge generated per year as $CaSO_4$ and $Me(OH)_2$ and the associated costs of disposal if the cost of sludge disposal is €100/ton and the lime cost is €150/ton. Assume a solids content in the sludge of 40%.

(b) Compare this cost with the costs of using biological sulfate reduction instead with ethanol as electron donor. Consider EtOH purity 30%, density $0.95 \, kg \cdot L^{-1}$, and price $100 \, € \cdot m^{-3}$.

(c) Based on your calculations above, what is more attractive from an economic point of view, lime dosing or biological sulfate removal.

(d) Provide three non-economic benefits of biological sulfate removal compared with lime dosing.

Exercise 11.3: Given the operational parameters of the Thiopaq® process (Section 11.6.3) at a flowrate of $30 \, m^3 \cdot h^{-1}$ and initial and final sulfate concentrations at 15 and $3 \, g \cdot L^{-1}$, respectively. Calculate the consumption of H_2 in $m^3 \cdot h^{-1}$ in the biological sulfate reduction stage (Equation (11.16)).

Exercise 11.4: Given that the Thiopaq® process reported a recovery of $8.5 \, ton \cdot d^{-1}$ of ZnS:

(a) How much air is used to oxidize all sulfides remaining from the calculation of exercise 11.3 in the sulfide oxidizing stage? Assume sulfides are oxidized according to:

$$H_2S + 0.5\,O_2 \rightarrow S^0 + H_2O$$
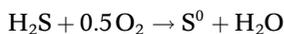
(b) Given air pump efficiency of 50%, energy consumption of $110 \, Wh \cdot Nm^{-3}$, and electricity cost of $0.05 \, € \cdot kWh^{-1}$. What is the cost of the aeration?

Exercise 11.5: In 2014, the plant from the company Paques, THIOTEQ™ Metal technology, started operation at a goldmine located in the Dominican Republic to recover copper sulfide from an acidic process water stream. The process consists of two stages: a chemical (precipitation) stage and a biological process where sulfide is produced from elemental sulfur (instead of sulfate) and ethanol. A simplified representation of the governing reactions for metal precipitation and for hydrogen sulfide production can be described as follows:

$$H_2S + M^{2+} \rightarrow MS_s + 2\,H^+$$

$$C_2H_5OH + 6\,S + 3\,H_2O \rightarrow 6\,H_2S + 2\,CO_2$$

The technology is able to recover 20 000 ton of Cu per year at the goldmine. Based on this amount, estimate the following:

(a) The amount of S that is being added.

(b) The amount of ethanol that is being added (ethanol: 30%, density: $0.95 \text{ kg} \cdot \text{L}^{-1}$) in order to reduce sufficient sulfur to sulfide for Cu precipitation. Assume a 100% ethanol conversion efficiency.

(c) What is the advantage of using S instead of sulfate as in the Thiopaq® technology? Hint: how much ethanol would have to be added if SO_4^{2-} was the electron acceptor?

(d) Despite the advantage highlight in c), discuss a disadvantage from a process point of view.

Exercise 11.6: Give the redox equation for sulfate reduction with methanol, assuming that methanol is oxidized to HCO_3^-. Write sulfide as HS^-.

Exercise 11.7: A wastewater contains sulfate ($2.5 \text{ g} \cdot \text{L}^{-1}$) and zinc ($1 \text{ g} \cdot \text{L}^{-1}$ Zn^{2+}) and will be treated biologically. Methanol (CH_3OH) is selected as electron donor for sulfate reduction. Calculate how much methanol ($g \cdot \text{L}^{-1}$) needs to be added considering that:

- all zinc precipitates as zinc sulfide;
- an excess of $200 \text{ mg} \cdot \text{L}^{-1}$ total sulfide is targeted;
- 5% of the consumed methanol is used as carbon source;
- no hydrogen sulfide is stripped.
- How much sulfate is left in the effluent?

Exercise 11.8: Zinc needs to be removed to a level of $0.1 \text{ mg} \cdot \text{L}^{-1}$. What is the theoretically required *total sulfide* level (in $\mu g \, L^{-1}$) to achieve this, assuming equilibrium for ZnS precipitation is reached. The pH is 7, the pK_{sp} for ZnS is 24.7.

Exercise 11.9: It turns out that besides zinc, there is also copper ($1 \text{ g} \cdot \text{L}^{-1}$ Cu^{2+}) present in the waste stream. CuS has a pK_{sp} of 36.2:

(a) Will CuS precipitate at the pH and total sulfide concentration at which the zinc precipitates under Exercise 11.8?

(b) What consequence will the presence of $1 \text{ g} \cdot \text{L}^{-1}$ Cu^{2+} have on zinc precipitation?

(c) How would you solve the problem that emerged in the answer of part b?

Exercise 11.10: Zinc and copper sulfide precipitate simultaneously in the process. At which pH is selective precipitation possible?

11.10 DISCUSSION QUESTIONS

Question 11.1 (governance, market stability, self-sufficiency, political drivers). The increase in metal demand and associated supply risks have increased along with the volatility of metal prices (see Table 11.1). A good example is the significant increase in demand and price of cobalt with an increase in price of ∼500 times between 1993 and 2013. The latter is related to the use of cobalt in emerging technologies, such as smartphones, electric vehicles, and the lithium-ion battery sector. Within this context, Africa has historically been the largest source of cobalt minerals. Due to a rising demand for cobalt, discuss why there is a general interest as well as political support for incentives to promote approaches that enable recovery of cobalt from wastewater. Discuss what positive impact this can have on the R&D roadmap and market implementation of technologies that enable cobalt recovery.

Question 11.2 (process control, OH&S considerations). The pH is an important driver of the biological sulfate reduction process. Discuss the implications of decreasing or increasing the pH for a one stage process, where metal precipitation and sulfate reduction occur in 1-stage, as compared to a multi-stage process (see Figure 11.5 for schematic representation of 1-stage and multi-stage configuration).

Question 11.3 (economic considerations, market demand vs. recovery potential, process limitations). In Chapter 2 of this book, a table is provided showing an overview of metals concentrations in different wastewater streams. Select two wastewaters from this table and discuss their economic potential and practical feasibility for metal recovery. In your discussion, pay particular attention to: (i) estimated volumes discharged in industry; (ii) metal concentration; (iii) market demand and price; (iv) possible process interferences/difficulties; and (v) product quality.

Question 11.4 (geopolitical considerations, non-renewable resource, political incentives). The opportunity and necessity of technologies for metal recovery is said to be evident due to the future scenarios of metal scarcity as well as potential geopolitical challenges as sources/deposits of various important metals are restricted to a limited amount of geographical locations. Based on the EU metals listed as critical metals with, moreover, relatively high economic importance, analyze which metals could be 'high on the political agenda' in the context of financial and governmental support to academia/industry to develop new technologies enabling their recovery.

Question 11.5 (ease of operation, OH&S considerations, reluctance to change, wastewater composition). As discussed in this chapter, chemical precipitation is the most common method for removal of dissolved metals from wastewater. Despite the need to change to a circular use of resources and recover metals from wastewater as well as the potential benefits of sulfide-based precipitation (both of which have been clearly identified in this chapter), at present the use of lime as a precipitation aid remains widespread. Formulate various reasons behind the latter in relation to: (i) ease of operation and OH&S considerations of the use of lime over sulfide; (ii) wastewater composition in terms of sulfate concentrations and metal concentrations and their respective discharge limits; and (iii) reluctance to change if you were in charge of the treatment facility and you have over 20 years of experience with lime dosing.

ACKNOWLEDGEMENTS

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