Chapter 10

Biological recovery of rare earth elements from mine drainage using the sulfidogenic process

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10.1 INTRODUCTION

The rare earth elements (REE) include 15 elements of the lanthanide family, scandium (Sc) and yttrium (Y). They are generally classified as light-REE (La, Ce, Pr and Nd), middle-REE (Sm, Eu, Gd, Tb and Dy) and heavy-REE (Ho, Er, Tm, Yb, Lu and Y) (Cao *et al.*, 2019; Lefticariu *et al.*, 2020). Despite what the name suggests, rare earth elements are not rare or earth. They are found in the earth's crust in abundance. However, the term 'rare' is more related to the difficulty in exploiting the deposits, because of the low concentrations of the elements which often make the area economically non-viable for exploration (Edahbi *et al.*, 2018a). These elements have gained importance due to their excellent catalytic, optical, electronic and magnetic properties, in addition to having high economic value.

REE are mainly used in the electronic, catalyst, ceramic and glass, metallurgical, polishing and other industries. In hi-tech industries, these elements are applied for the production of hybrid and electric vehicles, automotive sensors, permanent magnets used in wind turbines, fuel cells, rechargeable batteries, cell phones, fluorescent lamps, computers, catalytic converters, driver discs, plates and screens (Lefticariu *et al.*, 2020; Salo *et al.*, 2020). They are also used in medicinal

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science, the pharmaceutical industry, clean energy devices (solar and wind), the zootechnical sector and agriculture (Migaszewski & Gałuszka, 2015).

From 2010, China began to control the REE market, creating a geopolitical problem in which the country holds about 90% of the world's production of REE ore (Mancheri *et al.*, 2019; Schlinkert & van den Boogaart, 2015; Skirrow *et al.*, 2013), followed by countries such as Australia, the United States and India. However, the world's four largest REE reserves are found in China, Brazil, Vietnam and Russia (US Geological Survey, 2020). The European Commission included REE in the list of critical raw materials due to the risk of shortages in the market and the lack of alternatives for their supply. The US Department of Energy also assessed the situation of yttrium and other REE as critical to supply in the medium term (until 2025) and stated the importance of this raw material for the development of clean energy (Amato *et al.*, 2019).

In addition, environmental problems associated with REE mining and its hydrometallurgical processing is of grave concern. For example, for each ton of REE oxides produced in China using the calcination technique at high temperatures with concentrated sulfuric acid, 9600 to 12000 m^3 of gaseous mineral waste including dust, sulfur dioxide, sulfuric acids and hydrofluoric acid, 75 m^3 of acidic water and approximately 1 ton of radioactive material are generated (Edahbi *et al.*, 2019; Hurst, 2010). In Baotou (China), where there are the largest lanthanide mining plants, it is estimated that 10 million tons of all types of wastewater are generated every year and are discharged without any effective treatment, contaminating the water supply, irrigation systems and the surrounding environment (Hurst, 2010). These problems are not only region specific, they are found throughout the world.

Therefore, alternative sources of REE, such as recovery from mining waste, waste/processing waters, electrical and electronic waste and industrial processing by-products, using sustainable technologies are necessary. Acid mine drainage (AMD) and phosphogypsum waste are some examples of secondary sources of REE in which recovery can be achieved by using biological treatments. Among them, sulfate-reducing bacteria (SRB), widely applied in metal recovery processes due to their versatility and metabolic diversity (Costa *et al.*, 2020; Cunha *et al.*, 2020; Hedrich & Johnson, 2014; Johnson & Sánchez-Andrea, 2019; Lens, 2020; Ňancucheo & Johnson, 2012), have also been used in the precipitation of REE and simultaneous sulfate removal from wastewaters (Mäkinen *et al.*, 2017; Nogueira *et al.*, 2019; Salo *et al.*, 2020, 2018). The biological processes encompassing wastewater treatment and REE recovery offer both environmental and economic benefits.

10.2 REACTIVITY OF REE-BEARING MINERALS

Rare earth minerals are integrated in the form of silicate, carbonate and phosphate crystal structures and can be replaced by other elements depending on the size of the ionic radius and charges of the ion. Cations Ca^{2+}, Na^{+}, Th^{2+} and U^{3+} can, for example, be replaced by rare earth cations (Edahbi *et al.*, 2019).

10.2.1 Reactivity of REE-bearing carbonates

The dissolution of carbonate complexes in natural systems occurs according to Reaction 10.1 and when there is the generation of sulfuric acid from the sulfide oxidation, it can promote the dissolution of the carbonate as presented in Reaction 10.2 (Edahbi *et al.*, 2019; Sherlock *et al.*, 1995). Where, M is Ba, Ca, U, Th, F, Sr or rare earth ions.

$$\text{(REE-M)CO}_3 + H_2O + CO_2 \rightarrow REE^{3+} + M + 2\,HCO_3^{-} \tag{10.1}$$

$$\text{(REE-M)CO}_3 + H_2SO_4 \rightarrow REE^{3+} + SO_4^{-} + M + 2\,HCO_3^{-} \tag{10.2}$$

The main factors that control the reactivity of carbonates are the following: pH, temperature, the presence of organic matter and the partial pressure of CO_2 in closed systems. The dissolution rate of carbonates is inversely proportional to pH, that is, the lower the pH, the greater the solubility of carbonates.

10.2.2 Reactivity of REE-bearing silicates

The dissolution of silicate minerals depends on the pH, temperature, mineralogical composition, mineral structure and external environmental factors. Silicates tend to solubilize generating secondary silicates as shown in Reaction 10.3 (Edahbi *et al.*, 2019; Sherlock *et al.*, 1995):

$$\text{(Ca, REE)}Al_{12}Si_2O_8 + 2\,H^{+} + H_2O \rightarrow Ca^{2+} + REE^{3+} + Al_2Si_2O_5(OH)_4 \tag{10.3}$$

10.2.3 Reactivity of REE-bearing phosphates

Phosphate minerals commonly rich in REE are as follows: apatite, monazite ((REE, Th) PO_4) and xenotime (YPO_4). The reaction of the dissolution of apatite in water and in response to the generation of acid is shown in Reactions 10.4 and 10.5, respectively (Edahbi *et al.*, 2019):

$$2\,\text{(Ca, REE)}_5(PO_4)_3F + 15\,H_2O \rightarrow 10\,Ca^{2+} + 10\,REE^{3+} + 6\,PO_4^{3-} + 2\,F^{-} + 30\,OH^{-} \tag{10.4}$$

$$\text{(Ca, REE)}_5(PO_4)_3F + 5\,H_2SO_4 \rightarrow 5\,\text{(Ca, REE)}SO_4 + H_3PO_4 + H^{+} + F^{-} \tag{10.5}$$

Once in solution, REE can precipitate as sulfates, phosphates and fluorides due to their low solubility (K_{sp}) under neutral pH conditions (Table 10.1) and also as secondary phosphates in the form of $REEPO_4$ or REE-F_3.

Table 10.1 Solubility product of rare earth compounds (from Edahbi *et al.*, 2019).

REE Compound	Formula	K_{sp} (25°C)
Carbonates	$RE_2(CO_3)_3$	$10^{-28.25}$ to $10^{-35.77}$
Yttrium fluoride	YF_3	8.62×10^{-21}
Yttrium hydroxide	$Y(OH)_3$	10^{-22}
Phosphates	$REEPO_4$	10^{-24}

10.3 CONVENTIONAL METHODS FOR RECOVERY OF REE

The efficiency of REE recovery depends on factors such as the type of technology used to recover the elements, the target elements that are desirable for recovery, types of gangue minerals, their origin, the amount of REE present (ranging from <mg to several g) and the conditions (pH and temperature) of the extraction process (Edahbi *et al.*, 2019; Jowitt *et al.*, 2018). The following are the most commonly used methods for REE extraction from ores or waste resources: chemical extraction with the hydrometallurgical process (Das & Das, 2013), reduction processes (Gupta & Krishnamurthy, 2004), total dissolution, selective dissolution and sequential leaching.

All REE have the same external electronic configuration [Xe]$6s^2$ $5d^1$ $4f^x$, where ‘x’ ranges from 0 to 14. The elements are trivalent cations (M^{3+}), except for Ce and Eu which have a charge of 2^+ and 4^+ (depending on the redox conditions), (Jaireth *et al.*, 2014). The main difference between each REE is in their ionic size which decreases from 1.2 to 0.7 Å as the atomic number increases from 57 to 71 (Edahbi *et al.*, 2019). The 4f orbitals are protected from the chemical environment by the 5s, 5p and 5d, 6s orbitals. Thus, when a compound is formed they do not directly participate in the bonding with other elements. This leads to the extremely similar physical and chemical properties of the elements, hindering the processes to separate them (Jaireth *et al.*, 2014), and thus making the REE recovery process more challenging.

These characteristics of REE allow their replacement by other metallic elements that have a similar ionic radius, such as Ca, Na and U (Edahbi *et al.*, 2019). When combined with anions, REE can be present in soluble (chlorides and nitrates) or insoluble (sulfides, fluorides, carbides, oxalates and phosphates) form. They can also form stable complexes with organic molecules (organic matter and fulvic acid) (Migaszewski & Gałuszka, 2015). Another difficulty faced in recycling is in the removal of impurities after extraction to yield pure single elements (Ali, 2014; Jowitt *et al.*, 2018), and they are not easy to precipitate and crystallize using a single method (Naidu *et al.*, 2019).

REE behavior in acid mine water depends on several parameters, such as the influence of iron oxides (Edahbi *et al.*, 2018b; Verplanck *et al.*, 2004), presence of aluminum, fluorine, sulfate, phosphate and temperature (Gimeno Serrano *et al.*, 2000), organic matter content (Edahbi *et al.*, 2019) and redox potential. The highly acidic pH of acid mine water also influences the solubility of REE and determines their fate after their release into surface and ground waters (Ayora *et al.*, 2016; Cravotta, 2008). Regarding the composition of rare earths, the reactivity of the compounds follows the order: carbonates > oxy/iron hydroxides > silicates (Linnen *et al.*, 2013).

The redox conditions play a significant role in the dynamics of REE (Linnen *et al.*, 2013): any change in redox potential could directly or indirectly change pH and the Fe (hydr)oxides, Mn (hydr)oxides, Al, S and dissolved organic carbon concentrations (Mihajlovic *et al.*, 2017), which can lead to changes in solubility, precipitation/co-precipitation and adsorption of REE (Edahbi *et al.*, 2019; Linnen *et al.*, 2013). Mihajlovic *et al.* (2017) reported a strong positive correlation between the release of REE and redox potential and a strong negative correlation between REE release and pH.

Table 10.2 summarizes the different recycling methods applied for recovery of targeted REE from various wastes (Jowitt *et al.*, 2018). Among secondary wastes for REE extraction and selective separation, the following technologies have been applied: adsorption, ion exchange, emulsion liquid membrane, supported liquid membrane and solvent extraction (liquid-liquid extraction) processes (Kumar *et al.*, 2020; Parhi *et al.*, 2018). The advantage and disadvantage of each of these extraction processes are shown in Table 10.3. Recycling of discarded electronic materials for REE recovery was reported by Binnemans *et al.* (2013) and Haque *et al.* (2014). Commercial recycling of these elements is still quite limited and it is estimated that less than 1% of all REE consumed is obtained through recycling of REE-containing wastes (Favot & Massarutto, 2019; Ganguli & Cook, 2018). The REE-bearing wastes that are mostly recycled for REE recovery are fluorescent lamps (Yang *et al.*, 2013), rechargeable batteries and permanent magnets (Binnemans *et al.*, 2013; Edahbi *et al.*, 2019; US Geological Survey, 2020).

The recycling processes still face a number of difficulties associated with the collection of material and its processing efficiency (Binnemans *et al.*, 2013). Another major challenge is regarding separation and purification of REE. The recovery of these metals from electronic equipment requires the use of advanced processes, for which many experimental studies are reported in the literature (Binnemans *et al.*, 2013; Favot & Massarutto, 2019), however, they are yet to reach industrial scale.

10.4 REE-RICH WASTEWATER ASSOCIATED WITH ACID MINE DRAINAGE

REE can be found in high concentrations in acidic waters resulting from mining activity, that is acid mine drainage (AMD), making AMD an important source of REE recovery (Ayora *et al.*, 2016). The formation of AMD can occur either inside the mine pit or in tailing deposition areas. AMD is formed when rocks and

Table 10.2 Potential sources of REE and their recycling processes (adapted from Jowitt *et al.* (2018) and Marra *et al.* (2018)).

Source for Recycling	Targeted REE	Primary Recycling Mechanism
Fluid catalytic cracking (FCC) catalysts	La and Ce	Hydrometallurgical processes (leaching, solvent extraction, selective precipitation); Microbial leaching (bioleaching)
Industrial processes and residues	Depending on the source material, the REE recycling process can target different REE	Pyrometallurgical processes (roasting, calcination); Hydrometallurgical processes (leaching, solvent extraction, selective precipitation); Physical separation & microbial leaching (bioleaching)
WEEE & 'End of Life' consumer goods; Fluorescent material (phosphor powder and fluorescent lamps)	La, Ce, Tb and Y	Pyrometallurgy (roasting, calcination); Hydrometallurgy (leaching, solvent extraction, selective precipitation); Gas phase extraction
Magnets	Nd, Dy and the other REE	Hydrometallurgical processes (leaching, solvent REE extraction, selective precipitation)
Batteries	La, Ce, Pr and Nd	Hydrometallurgical or pyrometallurgical recovery routes
Mobile phones	La, Ce, Pr and Dy	No information available
WEEE shredding dust	Ce, Eu, Nd, La and Y	Bio-hydrometallurgical processes (bioleaching)

WEEE: Waste electrical and electronic equipment.

other sulfide minerals are exposed to natural environmental factors such as water and air, resulting in the formation of sulfuric acid and the consequent solubilization of the metals present in rocks (Streten-Joyce *et al.*, 2013). The different processes involved in AMD generation are described in several previous works (Akcil & Koldas, 2006; Johnson & Hallberg, 2005; Rohwerder *et al.*, 2003; Streten-Joyce *et al.*, 2013).

The main factors that influence the AMD generation rate are: pH, temperature, weathering of rocks, chemical activity of Fe^{3+}, surface area of metal sulfides and microbial activity (Akcil & Koldas, 2006). Using pyrite (FeS_2) as an example, Reaction 10.6 expresses the general reaction that occurs in the oxidation process of pyrite (Kefeni *et al.*, 2017) forming $Fe(OH)_3$. When iron is the oxidizing agent (Reaction 10.7), complete oxidation of pyrite occurs more spontaneously

Table 10.3 Advantages and disadvantages of REE extraction from secondary wastes (Kumar *et al.*, 2020; Marra *et al.*, 2018).

Process	Advantage	Disadvantage
Adsorption and ion exchange	An economical process, easy in operation, applicable in a broad pH range and efficient for solutions containing a variety of metal ion concentrations.	Not effective for some metals.
Sorption	Effective and suitable adoption of low-cost materials such as clays, activated carbons, zeolites, agricultural waste, bio sorbents (bacteria, fungi and algae) and metal oxides.	Low selectivity, slow kinetics, complex extraction behavior for various functional groups on the sorbent and the surface – less potential for its application in commercial/field level operations.
Emulsion liquid membrane and supported liquid membrane	Good extractive ability over the solid support membrane phase for the recovery of the targeted metal ion.	High time consumption, low selectivity and low recyclability.
Solvent extraction	Several commercial and green solvents are adopted for clean REE separation from aqueous solutions.	Intermediated compounds could be formed and a secondary process required.
Bioleaching	An economical process, easy in operation and use of microorganisms.	Still limited to bench-scale applications.

compared to Reaction 10.8, in which oxygen is the oxidizing agent.

$$FeS_2 + 15\,O_2 + 7/2\,H_2O \rightarrow Fe(OH)_3 + 2\,SO_4{}^{2-} + 4H^+ \tag{10.6}$$

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+ \tag{10.7}$$

$$FeS_2 + 7/2\,O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4{}^{2-} + 2H^+ \tag{10.8}$$

The complete oxidation of pyrite also occurs when there is little contact between water and metal sulfide, expressed in Reaction 10.9 (Chen *et al.*, 2015).

$$FeS_2 + 15/4\,O_2 + 1/2\,H_2O \rightarrow Fe^{2+} + 2\,SO_4{}^{2-} + H^+ \tag{10.9}$$

Among the dissolved metals, Fe(II) is the one that is found in high abundance in acid mine drainage. A survey by Kefeni *et al.* (2017) shows variation in the concentration of Fe(II) from 400 to 2135 mg L^{-1}, and also Al (~194 mg L^{-1}), Zn (~460 mg L^{-1}) and sulfate (2853 to 3622 mg L^{-1}) are present in the various types of AMD. The presence of dissolved metals associated with AMD depends on the type of gangue mineral present in the oxidized rock (Akcil & Koldas, 2006).

Different mineral sources contain REE along with various commercially-important elements. For instance, the bastnäsite mineral deposit is estimated at 1.5 million metric tons, where the rare earth oxide content corresponds to 3.3% of the deposit volume (Gupta & Krishnamurthy, 2004). Due to this, in addition to the commonly found metals, REE is also present in AMD at various concentrations. Table 10.4 shows studies in which REE are part of the reported AMD composition.

Among the different sources, mineral coal mines (Xingyu *et al.*, 2013) and deactivated uranium mines (Miekeley *et al.*, 1992; Nogueira *et al.*, 2019) feature prominently. At the Ronneburg and Seelingstädt uranium mines (Germany), the sum of REE concentrations was up to 3 mg L^{-1} of mine drainage (Merten *et al.*, 2005). A large reservoir of AMD is present in the city of Caldas (Minas Gerais state, Brazil), originating from uranium mining, which started operations in 1982 and ceased its activities in 1995. The tailings dam located at the Osamu Utsumi mine, *Industrias Nucleares do Brasil* (Figure 10.1), with a volume of 1.97 million m^3, contains solid and liquid mine effluents, including high concentrations of uranium and thorium. In addition, there are several other lagoons with a high REE content present in the mine unit (Figure 10.2).

The concern with respect to mining activity goes beyond the environmental problems, and includes the loss of significant quantities of material with commercial value that also have mining potential. Consequently, research efforts have been made to recover metals and REE from AMD, converting it into an attractive alternative source for REE. Currently, physico-chemical methods are still the main AMD treatment processes, but they are plagued by problems such as high costs and generation of wastes that are difficult to dispose of AMD

Table 10.4 REE composition present in AMD from different mining sites.

Location	pH	Y (μg L^{-1})	Ce (μg L^{-1})	Nd (μg L^{-1})	La (μg L^{-1})	Sm (μg L^{-1})	Reference
Pennsylvania Coal Mine	2.7–7.3	0.11–530	0.01–370	0.006–260	0.005–140	<0.005–79	Xingyu *et al.* (2013)
Osamu Utsumi (GW47)	3.57	—	6270	6490	13500	764	Miekeley *et al.* (1992)
Waterman, (CMD-L)	4.1	9.47	4.34	3.83	1.13	1.30	Stewart *et al.* (2017)
Strattanville, (CMD-P)	4.4	575	255	86.2	32.9	28.9	Stewart *et al.* (2017)
Osamu Utsumi (BNF)	3.4	4100	24900	9550	40100	—	Nogueira *et al.* (2019)

Figure 10.1 Pit at the Osamu Utsumi Mine, located in Caldas (Minas Gerais, Brazil). On the left side is the location of the pond where the sludge from the treatment plant is deposited. (From the author).

Figure 10.2 Four lagoons with a high REE and uranium content at the Osamu Utsumi Mine unit (Brazil). (From the author).

treatment of this tailing dam consists of active treatment (physico-chemical), which involves addition of alkaline chemicals aiming to raise the pH to the dischargeable limits and also precipitate many of the metallic pollutants. The treated volume can exceed 300 $m^3 h^{-1}$, depending on the volume of rainfall. The material precipitated during the physico-chemical treatment is removed from the treatment unit and deposited inside the pit at the Osamu Utsumi mine (Figure 10.1).

In 2018, the company spent R$ 1.8 million, buying calcium hydroxide with low magnesium content (Nogueira *et al.*, 2019). In addition to the high operational cost, another problem associated with the physico-chemical treatment is the high amount of sludge generated (Sahinkaya *et al.*, 2018), which is still an environmental issue.

Due to these problems, researchers are endeavoring to develop alternatives for efficient and economically viable treatments for the AMD treatment and recovery of metals present in mine tailings. In this regard, anaerobic biological treatment can provide an alternative solution for simultaneous REE recovery and AMD treatment. The sulfate reduction process allows sulfate removal and the generation of alkalinity, important for raising the pH and maintaining it at levels adequate for safe release. Sulfate present in AMD is reduced mainly due to the metabolism of sulfate-reducing bacteria (SRB), which use it as a final electron acceptor, and the sulfide produced is utilized for metal precipitation. The work developed by Nogueira *et al.* (2019) for the biological treatment of the Osamu Utsumi AMD is presented in the following section along with the main challenges (see Section 10.5).

10.5 RECOVERY OF REE THROUGH BIOLOGICAL TREATMENT

10.5.1 SRB treatment of REE-containing mining waste

A limited number of studies have reported on the possibility of recovering REE from waste or wastewater using the sulfidogenic process. Previous studies reported on recovering REE from phosphogypsum (PG) waste leachate (Mäkinen *et al.*, 2017; Salo *et al.*, 2018, 2020) and actual AMD (Nogueira *et al.*, 2019) using sulfate-reducing bacteria.

The application of sulfate-reducing bacteria in the treatment of AMD allows the removal of sulfate, concomitantly with the generation of alkalinity as shown in Reaction 10.10. The product of sulfate reduction, hydrogen sulfide (H_2S), reacts with metals in solution and precipitates them as metal sulfides (Reaction 10.11) (Sahinkaya *et al.*, 2009):

$$SO_4^{2-} + e^- + 2\,H^+ \rightarrow H_2S + 2\,HCO_3^- \tag{10.10}$$

$$\text{Metal} + H_2S \rightarrow MeS + 2\,H^+ \tag{10.11}$$

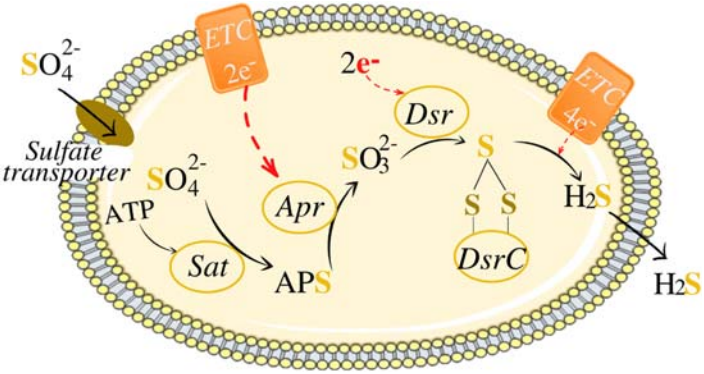

Figure 10.3 Metabolic pathway of dissimilatory sulfate reduction. Adapted from Jørgensen *et al.* (2019). ETC: electron transfer complex; DsrC: dissimilatory (bi) sulfite reductase complex; Dsr: dissimilatory (bi)sulfite reductase; APS: adenosine-5′-phosphosulfate; Apr: adenylyl-sulfate reductase; Sat: ATP sulfurylase.

The cellular mechanism associated with sulfate reduction in SRB is illustrated in Figure 10.3. Sulfate (SO_4^{2-}) gets inside the cell via sulfate transporters and is activated with adenosine triphosphate (ATP) in the cytoplasm by the enzyme ATP sulfurylase (Sat) to form adenosine-5′-phosphosulfate (APS). The enzyme adenylyl-sulfate reductase (Apr) assists in the reduction of APS to sulfite, receiving electrons from a membrane-bound electron transfer complex (ETC). Then, sulfite is reduced to H_2S by the dissimilatory sulfite reductase (Dsr) complex via a DsrC-bound trisulfide and diffuses out of the SRB cell membrane (Jørgensen *et al.*, 2019).

10.5.2 Treatment of phosphogypsum waste leachate

10.5.2.1 Bioreactor performance

Regarding phosphogypsum (PG) waste leachate, it is generated during the wet chemical phosphoric acid treatment process, or ‘wet process’ from apatite ores using sulfuric acid leaching to produce phosphoric acid and fertilizers (Kovler, 2012). Phosphate fertilizers are mainly obtained from phosphorus ore deposits, where they occur as apatite minerals (Cooper *et al.*, 2011).

It is estimated that approximately 5 tons of PG by-product is generated from each ton of phosphoric acid produced (Mäkinen *et al.*, 2017). This waste is characterized by acidity and elevated metal concentrations, containing radioactive impurities as well as REE. Thus, it requires treatment and is a potential source of valuable elements, such as REE (Salo *et al.*, 2018).

In the study presented by Mäkinen *et al.* (2017), batch experiments and a continuous column bioreactor were used for simultaneous sulfate removal and

Table 10.5 REE-concentrations of prepared PG-saturated water used as the influent (*Source*: Mäkinen *et al.*, 2017).

REE	La	Ce	Y	Nd	Dy	Eu	Gd	Pr	Sm
Concentration (μg L^{-1})	2.87	5.13	0.67	3.32	0.27	0.13	0.33	1.16	0.49

recovery of REE from synthetic PG leachate. The main characteristics of the wastewater solution containing REE used in both experiments are presented in Table 10.5. For the batch experiment, *Desulfovibrio desulfuricans* was used as inoculum and lactate and yeast extract as the carbon and nutrient source. The continuous bioreactor was inoculated with 500 mL anaerobic granular sludge collected from an industrial wastewater treatment plant and filled up with PG-saturated water. Ethanol was used as an electron donor during the column study and a sulfate concentration of 1340–1414 mg L^{-1} SO_4^{2-} was maintained to treat the PG-saturated water. The pH of the influent solution to the reactor was maintained between 5.9 and 6.6.

The sulfate reduction efficiency varied from 40–80%, and at its best performance (80% removal efficiency), a sulfate removal rate of 1080 g SO_4 m^{-3} d^{-1} was achieved and only 280 mg SO_4 L^{-1} in the effluent remained. In both batch and continuous flow bioreactors, the authors confirmed REE precipitation and accumulation in the sludge (Mäkinen *et al.*, 2017) and concluded dissolved REE can be precipitated in biological sulfate reduction systems (Table 10.6).

Initial anaerobic sludge represents the sludge used as inoculum for the continuous experiment; Final anaerobic sludge represents the sludge after the continuous experiment, enriched with REE.

Salo *et al.* (2018) evaluated the treatment potential of PG leachate using biological sulfate reduction and the possibility of REE recovery. In this study, two identical upflow anaerobic sludge blanket (UASB) bioreactors (BR1 and BR2) were operated in a continuous flow mode for 333 days at 20–22°C. The concentration of different REE in the PG leachate is shown in Table 10.7. The leachate also contained an average sulfate concentration of 1608 mg L^{-1}. Sodium

Table 10.6 Measured REE concentrations in precipitates of batch experiment and sludge of a continuous experiment (Mäkinen *et al.*, 2017).

REE (mg kg^{-1})	La	Ce	Y	Nd	Dy	Eu	Gd	Pr	Sm
Batch experiment	30, 400	66, 200	8800	n.a.	2400	1730	6750	10, 000	6310
Initial anaerobic sludge	7.3	13	3.6	7.2	0.8	0.2	1.02	1.69	1.4
Final anaerobic sludge	202	477	48.8	295	12.8	10.7	31.3	67.3	43.2

Table 10.7 REE concentration range (µg L^{-1}) of the PG leachate where the pH solution was 5.5–6.2 (*Source*: Salo *et al*., 2018).

	Ce	**Dy**	**Er**	**Eu**	**Gd**	**Ho**	**La**	**Lu**
Concentration (µg L^{-1})	BD–11.8	BD−0.15	BD−0.08	BD−0.14	BD−0.46	BD−0.05	BD−2.30	BD−0.03
	Nd	**Pr**	**Sm**	**Tb**	**Tm**	**Y**	**Yb**	
Concentration (µg L^{-1})	0.31–2.42	BD- 0.62	0.02–0.38	BD–0.06	BD–0.03	0.24–0.58	BD–0.06	

BD: below detection level.

lactate was used as the carbon source and electron donor in the study. In both bioreactors, a ~ 100% sulfate reduction efficiency was achieved at the beginning. However, from day 200 until 308, the sulfate reduction efficiency reduced (60–70% sulfate removal) and the sulfate removal rate was ~5000 mg L^{-1} d^{-1}. Alkalinity generated from sulfate reduction increased the effluent pH from 5.5–6.2 to 6.5–7.5, the redox potential was between −270 and −350 mV and the sulfide concentration in the effluent was 120–400 mg L^{-1} (Salo *et al.*, 2018).

This study was the first research to describe how REE precipitate under biological treatment using sulfate reducing conditions. Regarding REE precipitation, the REE content in BR1 precipitates was higher than in BR2 (Salo *et al.*, 2018). The main minerals in the final precipitates were apatite, ardealita, gypsum, gypsum-apatite mix, REE-apatite and gypsum-silicate mix. BR1 produced more apatite and gypsum, while BR2 produced more REE-apatite, sulfur, gypsum-silicate mix and carbonate. The great difference in the REE content between BR1 and BR2 was attributed to the additional inoculum added to BR1 and the slight difference in the effluent pH of the two bioreactors, 6.9–7.3 (BR1) and 6.5–7.1 (BR2), since changes in pH affect the structure of the precipitate (Salo *et al.*, 2018).

10.5.2.2 Mineralogy of the REE precipitates

It should be noted that before this study of Salo *et al.* (2018), the precipitation mechanisms of REE under sulfidogenesis conditions were still unknown and the idea of REE precipitation as metal sulfide was one of the possibilities proposed by Mäkinen *et al.* (2017). However, no REE sulfide was detected and precipitation mechanisms for REE remained unclear and the authors suggested that REE tend to precipitate in the SRB system as phosphates instead of sulfides (Salo *et al.*, 2018).

In 2020, a new study was carried out by the same group, this time focusing on acid leaching of REE from phosphogypsum and subsequent treatment using biological sulfate reduction for REE recovery (Salo *et al.*, 2020). H_2SO_4 was used to leach the REE into solution with two different H_2SO_4 concentrations (0.01 and 0.02 M). The concentrations of REE in the solution were much higher than in the previous research reported by Salo *et al.* (2018), with REE dissolution reaching up to 62%. The REE content in the leachate of 0.02 M H_2SO_4 was higher than in the leachate obtained with the 0.01 M H_2SO_4 solution. The leachate obtained was directly fed to the sulfidogenic reactor. The reactor was operated using sodium lactate as the electron donor and the sulfate concentration varied from 1600 to 3800 mg L^{-1}.

The sulfate removal efficiency was stable at around 80% when 0.01 M H_2SO_4 leachate was used as the feed. Moreover, the performance improved (~95%) when the feed was changed to 0.02 M H_2SO_4 as the influent with only a slight decline in the effluent pH from 7.5 to 6.8, indicating a good stability of the bioreactor. However, with the increase in the feed load, the bioreactor performance in terms of sulfate reduction deteriorated. The authors attributed the decline in performance to the low influent pH and high concentration of sulfate. The sulfide concentration was as high as 600 mg L^{-1} when fed with PG leaching water and 0.01 M H_2SO_4 leachate (Salo *et al.*, 2020).

The average REE removal efficiency was 99%, with an influent concentration of maximum 20 μg L^{-1} and effluent below 1 μg L^{-1} even when the sulfate removal efficiency was as low as 40%, suggesting an efficient system for REE removal and recovery (Salo *et al.*, 2020). Final precipitate analyses showed a very high amount (12.4 g total REE) of REE recovered. Inductively coupled plasma (ICP) analyses showed that the REE concentrations approximately doubled after treatment compared to the initial PG material (Salo *et al.*, 2020). The La and Gd elements were the most enriched REE compared to the initial concentration, showing that this treatment can enrich REE from an acidic PG leachate.

The mineralogy of the original PG sample, before the treatment, consisted mostly of a gypsum phase (Wt. 97.53%). After 208 operational days of biological treatment, the final precipitate diagnosed by energy dispersive (ED) spectrometry showed 14 stand-alone phases in total. The main mineral phases found were apatite-francolite (33.53%), pure Ca (22.20%) and Ca-Fe-Al phosphate-sulfate, with traces of F^- or/and OH^- (18.75%). Eleven other phases together corresponded to 25.52% which are pure Ca with trace sulfur (5.50%), Ca with trace sulfur and silicon (0.57%), Ca with trace sulfur, aluminum and phosphorus (0.57%), pure sulfur (1.88%), pure sulfur with trace calcium (1.07%), Ca-Fe-Al phosphate-sulfate (8.27%), Zn-Fe-Na-Al apatite with trace sulfur (2.5%), gypsum relic (1.61%) and apatite-francolite with trace S (0.66%). REE-containing phases corresponded to 2.54% of the sample: Na-Al-REE apatite with trace sulfur (1.66%) and high Ca phosphate-sulfate of REE with trace aluminum (0.88%) (Salo *et al.*, 2020).

Figure 10.4 shows images from bioreactor precipitates analyzed by a mineral liberation analyzer (MLA) (Salo *et al.*, 2020). Electron probe micro analysis (EPMA) showed that REE are distributed not only in separate phases, but also mixed in apatite-resembling phases containing Ca and P (Table 10.8). The mineralogical analyses indicated possible recoverable REE phases.

According to Edahbi *et al.* (2019), REE could precipitate as carbonates, sulfates, phosphates, hydroxides and fluorides due to the low solubility product (K_{sp}) under neutral pH conditions (Table 10.1). However, there was no evidence of REE-sulfide as MLA analyses were not able to detect any REE in the sulfide phase, suggesting REE are probably precipitated as a result of the pH increase rather than interactions with sulfide (Salo *et al.*, 2020). REE-hydroxide precipitation at a pH higher than 8 was described by Miskufova *et al.* (2018) and as carbonate by Rodriguez-Blanco *et al.* (2014).

The positive results presented by Mäkinen *et al.* (2017) and Salo *et al.* (2018, 2020) were very important in clarifying REE precipitated mineral phases mediated by biological sulfate reduction systems. These studies showed that the

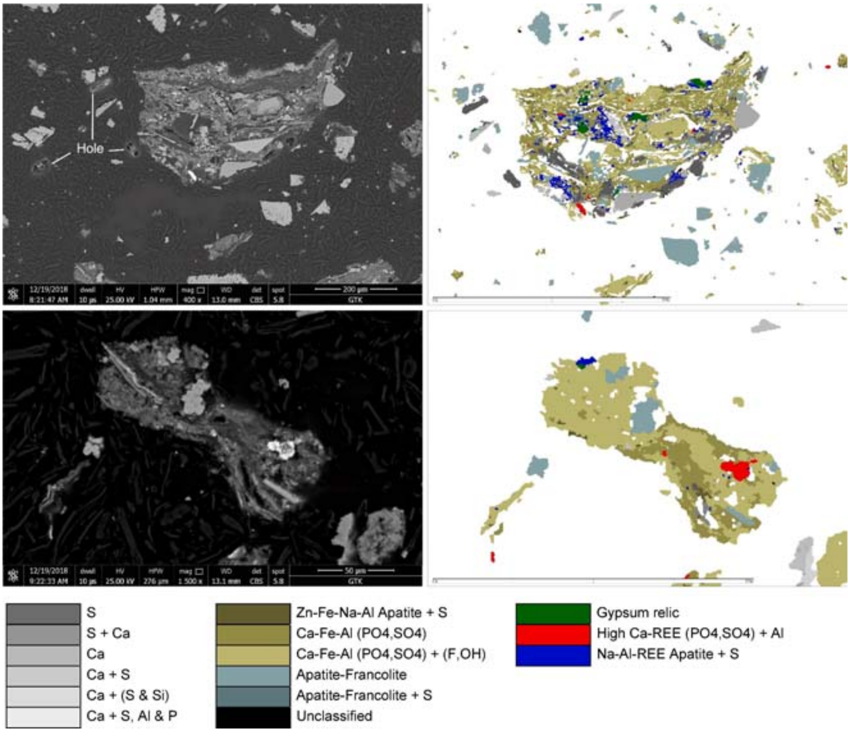

Figure 10.4 Amount of released REE from PG leachate analyzed with a mineral liberation analyzer (MLA) (*Source*: Salo *et al.*, 2020, with permission).

bioreactor treatment accumulated REE, and mineralogical analyses indicated the possibility of REE recovery.

10.5.3 Sulfidic treatment of AMD

10.5.3.1 Bioreactor performance

Another study on REE removal using biological sulfate reduction was reported by Nogueira *et al.* (2019). In contrast to the other studies presented previously, this study treated actual AMD with high concentrations of REE in solution which did not require any leaching process. The AMD used in this study, collected from an acidic lake at the Osamu Utsumi Uranium Mine, has the highest concentration of REE ever described in the literature. Table 10.9 shows the concentration of the main REE in the actual AMD used.

In the Osamu Utsumi mine water, the concentration of dissolved organic carbon is 1–4 mg L^{-1} (Miekeley *et al.*, 1992). Since AMD completely lacks or has a very low concentration of organic matter and other nutrients (Cravotta, 2008; Deng &

Table 10.8 Bioreactor precipitate (BR) REE analysis by ICP spectrometer and EPMA for REE (*Source*: Salo *et al.*, 2020).

	Total (mg kg^{-1})	REE content (mg kg^{-1})			
REE	**BR**	**All main phases**	**High Ca-REE (PO_4^{3-}, SO_4^{2-}) + Al**	**Na-Al-REE Apatite + S**	**Total**
Ce	1815	61.91	1702.6	3.0	1767.5
Dy	32.52	22.91	16.9	7.3	47.2
Er	7.48	94.73	2.1	5.9	102.7
Eu	33.75	—	74.8	1.7	76.5
Gd	917.8	49.21	43.7	3.7	96.7
Ho	4.22	59.6	0.5	5.1	65.3
La	886.91	31.34	686.5	1.5	719.4
Lu	<1	47.66	0.5	2.6	50.7
Nd	879.1	109.4	664.1	8.0	781.5
Pr	229.54	50.45	183.4	8.2	242.0
Sm	133.42	84.88	91.7	4.3	180.8
Tb	8.70	84.92	1.5	9.4	95.8
Tm	0.52	—	7.6	1.6	9.2
Y	68.17	26.16	58.4	1.9	86.5
Yb	1.99	56.3	0.2	3.1	59.6

Table 10.9 Sulfate and REE concentrations of the actual AMD used for biological treatment (*Source*: Nogueira *et al.*, 2019).

REE	**La**	**Ce**	**Pr**	**Nd**	**U**	**Y**	**SO_4^{2-}**
Concentration (mg L^{-1})	40.1	24.9	3.6	9.55	4.15	4.10	890 (±80)

Lin, 2013; Miekeley *et al.*, 1992), the external addition of electron donor and nutrients is necessary to enable SRB to perform. In this case, sugarcane vinasse was used as the electron donor and source of nutrients (Nogueira *et al.*, 2019).

The main operational parameters of the bioreactor are described by Nogueira *et al.* (2019). It is noteworthy that La and Ce concentrations are in excess of 20 mg L^{-1}, up to 6 times higher than the Ce concentration and up to 19 times higher than the La concentration reported by Salo *et al.* (2020).

Sulfate reduction was very instable during the treatment and average reduction varied from 10 to 90%. As the volume of treated AMD increased, less sulfate reduction performance was achieved, mostly due to the low influent pH values

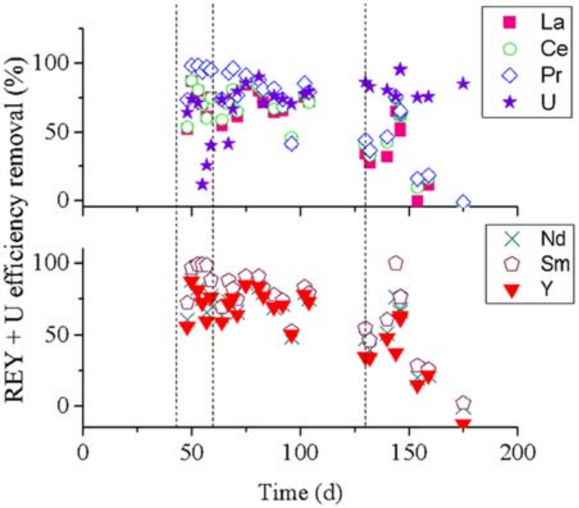

Figure 10.5 Rare earth elements and yttrium (REY) and U removal from the dissolved fraction of a down-flow fixed-structured bed reactor treating actual AMD of the Osamu Utsumi mine (Brazil) (Nogueira *et al*., 2019).

and AMD characteristics. However, the alkalinity produced due to sulfate reduction increased the average pH of the system from influent pH values of 5.0–7.0 to effluent pH values of 6.4–7.5 (Nogueira *et al*., 2019).

The REE removal efficiency using the sulfidogenic bioreactor is presented in Figure 10.5. The removal efficiencies for La, Ce, Nd and Y were more than 70%, while Pr and Sm showed more than 80% removal. The results are related to the increase in the pH of the liquid medium, precipitating the REE and other elements in the bioreactor. In addition, the authors suggested that the obtained removal of REE could be due to co-precipitation with aluminum or ferric iron, as a metal sulfide or directly as $REE(OH)_3$ (Nogueira *et al*., 2019).

10.5.3.2 Mineralogy of REE precipitates

ICP results from four samples of precipitated bioreactor sludge showed significant amounts of several elements had accumulated in the sludges (Table 10.10). The highest concentration of precipitated REE was La which reached around 700 mg L^{-1} in the collected sludge. The concentration of REE precipitated was proportional to the value considered in the wastewater that was fed to the bioreactor (Nogueira *et al*., 2019), except for U, where the behavior differs from the other elements and a small concentration of U was detected in only one bioreactor precipitate sample.

Table 10.10 Concentration of precipitated REE in the bioreactor (*Source*: Nogueira *et al.*, 2019).

Day	La	Ce	Pr	U	Nd	Sm	Y	Mn	Al	Fe	Si
57	86	67	4	n.d	23	3	9	34	243	236	41
90	245	176	20	n.d	52	6	24	80	702	135	75
137	194	136	17	5	45	5	22	87	620	87	71
110*	696	484	55	n.d	155	15	79	735	2587	406	76

*Sample collected from the conical bottom of the water level equalizer. Values are in mg L^{-1}.

10.5.3.3 *Toxicity of REE to bioreactor sludge*

This AMD treatment system was efficient for REE recovery, however, when actual AMD fed to the reactor reached 75% of the total volume, the sulfate removal efficiency started to decline and the effluent pH decreased until the bioreactor performance collapsed. Nogueira *et al.* (2019) attributed the failure of the bioreactor system to the low influent pH and the high concentration of toxic metals. The precipitation of the elements in the support material containing biomass can also be a cause of the bioreactor failure, as the precipitated metals could exert inhibitory effects on the SRB and can increase the mass transfer limitation (Nogueira *et al.*, 2019).

Under normal conditions, metals play essential biochemical roles in the cell. However, when metals accumulate above threshold concentrations, they become toxic. In situations where the metal ions are in excess in the microbial cells, they can block the functional groups of enzymes, inhibit transport systems and displace essential metals from their native binding sites, thus disrupting cellular membrane integrity (Dopson *et al.*, 2003). In order to avoid this inhibition, autochthonous microorganisms present in AMD and acidic environments that are adapted (due their heavy metal resistance) could be enriched and used as bioreactor inoculum.

10.6 ECONOMIC FEASIBILITY OF REE RECOVERY FROM SECONDARY SOURCES

The recovery of REE and metals from secondary resources such as AMD and coal mine drainage (CMD) was investigated by Ayora *et al.* (2016), Lefticariu *et al.* (2020) and Nogueira *et al.* (2019) using different processes. Ayora *et al.* (2016) reported that using passive remediation systems, the average ΣREE concentrations treated in the Monte Romero AMD and in the Almagrera AMD were 7.9 and 3.5 mg L^{-1}, respectively. The authors estimated that around 70 to 100 t of REY_2O_3 could be recovered annually from 150 AMD points of the

Iberian Pyrite Belt (IPB, southwest Spain), as the natural processes of AMD generation are expected to continue for centuries or thousands of years (Younger, 1997).

Lefticariu *et al.* (2020) evaluated the potential alternative source of REY and metals from CMD in the Illinois Basin. The average concentration of REE detected in the CMD was 1059 µg L^{-1} for La, Ce, Gd, Sm, Pr, Ho, Er, Tm, Yb and Lu, while the average concentration of critical REE, *viz.* Nd, Eu, Tb, Dy and Y was 611 µg L^{-1}. Lefticariu *et al.* (2020) concluded that valuable metals could be co-extracted with REE and recovered to enhance the economic values of CMD. Phosphogypsum waste is another source of REE recovery and was reported by Mäkinen *et al.* (2017) and Salo *et al.* (2018, 2020) using biological treatment as discussed in Section 10.5.

Waste electrical and electronic equipment (WEEE) also represents an important secondary REE source (Sahan *et al.*, 2019). Sahan *et al.* (2019) characterized the metal and REE concentration of waste in mobile phones analyzing Blackberry and Nokia devices. Lanthanum, cerium, praseodymium and dysprosium were the REE found in displays. They reported that 0.2 g kg^{-1} La and 0.13 g kg^{-1} Ce were detected in Blackberry display samples, while 0.48 g kg^{-1} La, 0.004 g kg^{-1} Ce, 0.03 g kg^{-1} Pr and 0.02 g kg^{-1} Dy were detected in Nokia display samples. Balaram (2019) reported that 100,000 iPhones have the potential to yield 11 kg of REE. According to Balaram (2019), Apple is committed to using only recycled materials in its supply chain, including REE and metals such as Al, Co, Cu, Au, Ag and W.

Favot and Massarutto (2019) studied the economic viability of recycling and recovering the element yttrium from used lamps, based on the HydroWEEE project by the Italian recycling company, Relight Ltd. The authors investigated the lowest selling price of Y in the market that would make it profitable to recycle the element instead of exploiting the virgin source, which also accounted for the environmental costs of mining.

10.7 FINAL CONSIDERATION

Although there are several studies on metal recovery from wastewater in laboratory-scale systems, recovery of REE is still scarce, and there is a lack of understanding of REE behavior and precipitation in biogenic sulfate-reducing systems. Biological treatment of wastewater containing REE has been shown to be an effective and low-cost treatment system for REE-recovering reactors. However, more research should be conducted in order to improve and optimize the bioreactor system. To achieve proper operation of the REE-recovery reactor, suitability of the organic substrate used, characteristics of the SRB metabolism, their interaction with REE, and optimum REE concentration which can be treated without causing inhibition need to be examined. REE recovery from wastewater could be used to offset the treatment costs, in addition to the environmental benefits.

Recovery and recycling of REE from secondary and waste based sources is thus not only providing an alternative source for these economically-important, critical elements, but also easing the demand for some of the REE and minimizing exploitation of new deposits. However, more efforts need to be put towards improving REE recovery efficiency in actual AMD, besides integrating studies on industrial-scale systems for future commercial applications.

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