Chapter 15
Reductive Mineral Bioprocessing

Ana Laura Santos and Axel Schippers

Abstract While biomining is currently restricted to reduced (sulfide) ores, many commercially valuable metals can be found in significant concentrations in oxidised ores. These comprise laterites, polymetallic marine nodules, and ores from oxidation of sulfide deposits. Currently, these oxide ores are processed using pyro- or hydrometallurgical techniques, but these can have several drawbacks which have restricted their exploitation. This chapter summarises reductive bioprocessing options for metal oxide ores and focuses chiefly on laterites for recovery of nickel and cobalt. Over the past 40 years, several laboratory studies have demonstrated the possibility of bioleaching saprolitic and limonitic laterite ores, as well as tailings, using organic acids generated by heterotrophic bacteria or fungi. However, pilot-scale tests have not been reported and the viability of this approach is questionable. The anaerobic reductive dissolution of iron and manganese oxy-hydroxide minerals coupled to the oxidation of elemental sulfur is catalyzed by acidophilic, chemolithotrophic bacteria such as *Acidithiobacillus ferrooxidans* and has shown to be a more promising approach, especially for bioprocessing of limonitic laterite ores, as an integral part of the *Ferredox* process. Aerobic reductive dissolution of laterites with *Acidithiobacillus* species has also been demonstrated at low pH (<1). These promising bioprocessing options for limonitic laterites are currently awaiting full process development.

Keywords Reductive bioleaching · Laterites · Cobalt · Nickel · *Ferredox* process · *Acidithiobacillus*

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D. B. Johnson et al. (eds.), *Biomining Technologies*,
https://doi.org/10.1007/978-3-031-05382-5_15

15.1 Introduction

Biomining is a well-established global biotechnology which uses aerobic, acidophilic microorganisms to catalyze the oxidative dissolution of sulfide minerals present in ores, concentrates, and mining wastes. Mineral bioprocessing at commercial scale is currently restricted to sulfide ores where the target metal is either surrounded by sulfide minerals obstructing its extraction (e.g., refractory gold ores) or present within the structure of host minerals (most base metals). In both cases, mineral dissolution occurs via oxidative processes in extremely acidic conditions and in the presence of acidophilic prokaryotes, whose main role is to generate ferric iron and sulfuric acid. Many commercially valuable metals are also, or sometimes exclusively, found in (iron and manganese-rich) oxide ore bodies, and in some cases their mineral reserves are more extensive (and accessible) than their sulfide counterparts (e.g., nickel in laterites).

While oxidative bioleaching of sulfide ores has been studied extensively and applied commercially for over 50 years, bioprocessing of silicate and oxide ores falls behind in theory and application. Oxide ores comprise laterite ores, polymetallic marine nodules, and oxidised ores from sulfide deposits. Currently, such oxide ores are processed, if at all, using pyro- or hydrometallurgical techniques (Stanković et al. 2020). Apart from environmental issues, these have been associated with high capital and operational costs due to high demand for energy (e.g., smelters and high-pressure acid leaching—HPAL) or slow leaching rates (e.g., heap leaching). The mining industry is therefore seeking alternative processes to cope with both continuous depletion of high-grade sulfide ore reserves and tightening environmental regulations.

The use of microbially mediated reductive processes to extract economically valuable metals from oxide (and oxy-hydroxide-containing) ores is a novel biotechnology that is currently receiving considerable attention. This chapter provides an overview of the mechanisms and recent applications of bioreductive dissolution of metal oxide ores with a focus on laterite ores for recovery of nickel and cobalt.

15.2 (Bio)Hydrometallurgical Processing of Oxide Ores

15.2.1 Laterite Ores

Laterites are supergene ore bodies (i.e., they occur relatively near the surface) originating from chemical and mechanical weathering processes of ultramafic rocks in tropical and subtropical areas. Chemical weathering processes mobilise the most soluble elements (Mg, Ca, and Si) and concentrate the least soluble elements (most transition metals as well as aluminium). These iron-rich ore deposits contain several types of iron oxides, hydroxides, and oxy-hydroxides in which atoms of iron (mostly ferric iron) are linked to oxygen and/or hydroxyl groups. Laterite ore

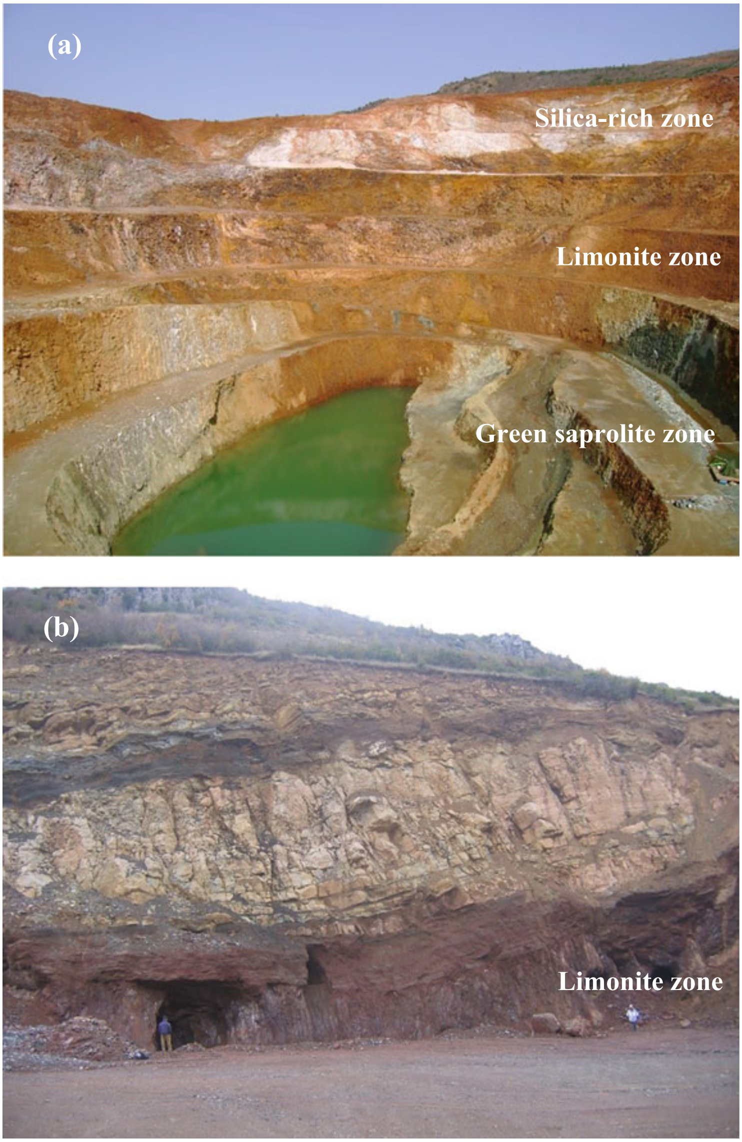

Fig. 15.1 Laterite ore deposits. (**a**) Zoned profile of the Çaldag mine (Turkey). A green saprolite zone at the base is covered with a thick brown limonite layer (goethite-rich zone) and a white silica-rich cap; (**b**) ancient weathering profile at the Treni mine (Albania). At the base of the pit is a thin saprolite zone, which is overlain by goethite-rich, partly reworked limonite zone. The weathered profile is covered by later sedimentary deposits (sandstones and limestones)

deposits follow a similar weathering profile (Fig. 15.1) which is generically divided into three main layers. At the bottom, there are clay silicates with dominant nickel-smectites, above which there is a silicate-rich saprolitic layer, often rich in magnesium-nickel hydrous silicates. On top, there is an oxide zone of limonitic laterite, consisting of iron oxides dominated by goethite (α-FeO·OH) or limonite (FeOOH·nH_2O), and manganese oxides such as asbolane ($(Ni,Co)_xMn(O,OH)_{4n}H_2O$) and lithiophorite $(Al,Li)MnO_2(OH)_2$; Butt and Cluzel 2013).

Although complex in structure, laterite deposits may contain exploitable reserves of nickel in one or more of these layers, and therefore they have been commercially defined as “Ni-laterite ores”. In addition to nickel, laterite deposits may also include appreciable amounts of cobalt, copper, and scandium and, in some cases, rare earth elements. Nickel in limonitic ores is typically associated with ferric iron minerals (e.g., goethite) whereas cobalt is associated with Mn(IV) minerals, such as asbolane. Rare earth elements are generally associated with phosphate minerals present in lateritic deposits (Ñancucheo et al. 2019). Laterite ores usually contain between 0.8–3% nickel and 0.05–0.2% cobalt, though geochemical and mineralogical characteristics may differ significantly even amongst neighbouring deposits (Table 15.1).

Production of nickel from laterite deposits in New Caledonia began in 1875. However, with the discovery of sulfide deposits containing nickel and copper in Canada in the late 1800s, the focus diverted towards processing of sulfide ores, and by the 1950s, approximately 90% of the nickel was produced from the latter. Nickel laterites account for 72% of the world’s nickel reserves and are mostly found in equatorial regions (e.g., Southeast Asia, Northern Brazil, Northern Australia, and Cuba), though some of these deposits occur in nontropical areas, such as Greece in Europe, the Urals in Russia, Turkey and Kazakhstan in Asia, and USA (Oregon, California and North Carolina; US Geological Survey 2020).

Complex and heterogeneous mineralogy, costly energy requirements, and remoteness from processing and distribution facilities are amongst the reasons why laterite processing was overlooked in the past (Marrero et al. 2020). However, due to a greater demand for nickel (and cobalt) in the last few decades, the development of new processing technologies as well as the rapid depletion of sulfide ore deposits, nickel production from laterite ores increased to 46% by 2008, exceeded 50% of global production in 2010 and it is expected to reach 72% by 2022 (Oxley et al. 2016).

Nickel laterites currently contribute 20–30% of total global supply of cobalt. This metal is mostly obtained as a co-product of copper and nickel sulfide ore processing, with the Democratic Republic of Congo currently being the world’s leading source. The global demand for cobalt has increased exponentially over the past 30 years, reflecting its increased use in high-tech materials (e.g., rechargeable batteries) as society moves towards a more sustainable economy. In 2011, the European Commission added cobalt and other materials to the list of “*critical raw materials (CRMs) for the European Union economy*”, which are fundamental to industry, essential for enabling technological development, and in need of reliable and sustainable supply.

Currently, nickel extraction from laterite ores is mainly performed using pyrometallurgical techniques for the production of ferro-nickel and matte smelting, though this is only suitable for saprolite zones of lateritic ores, and limonite layers are often not utilised. Hydrometallurgical processing for nickel and cobalt recovery

Table 15.1 Geochemical composition of different limonitic laterite deposits

	Çaldag, Turkey	Piaui, Brazil	Nkamouna, Cameroon	Acoje, Philippines	Shevchenko, Kazakhstan	Kastoria mine, Greece	Evia mine, Greece	Ag Ioannis mine, Greece	Penamax, New Caledonia	Tiebaghi, New Caledonia
SiO_2[a]	35.4	48.8	12.4	14.2	42.7	30.6	36.2	26.9	2.15	1.36
Fe_2O_3[a]	39.3	27.5	40.8	45.3	25.3	22.9	30.7	49.4	69.6	47.8
Cr_2O_3[a]	1.5	0.86	1.01	2.27	0.96	0.99	1.52	2.69	2.95	1.85
Al_2O_3[a]	4.6	2.37	20.9	7.99	4.33	0.99	3.92	5.49	5.5	18.6
MnO[a]	0.4	0.41	6.98	0.61	1.72	0.30	0.28	0.29	1.19	7.34
MgO[a]	1.71	7.63	0.36	4.31	8.37	17.4	6.99	3.46	0.47	0.71
Ni[a]	1.16	1.78	0.87	0.99	1.47	1.02	0.56	0.82	1.35	0.75
Co[b]	710	902	10850	626	2700	334	274	516	1640	12450
Cu[b]	60	1710	553	108	35	17	23	38	56	85
Sc[b]	40	13	43	58	24	19	24	47	59	42
As[b]	163	<5	6	8	8	<5	17	7	<5	<5
V[b]	117	45	15	271	128	66	122	197	157	128

[a] wt. %

[b] mg kg^{-1}

Table 15.2 Summary of hydrometallurgical techniques used for extraction of nickel from laterites

Process	HPAL	Caron Process	Heap Leaching	Acid leaching	Direct Nickel	Neomet process
Ore type	Limonite	Limonite	Saprolite	Limonite and Saprolite	Limonite and Saprolite	Limonite and Saprolite
Lixiviant	H_2SO_4	NH_3-$(NH_4)_2CO_3$	H_2SO_4	H_2SO_4	HNO_3	HCl
Leaching time	90 min	n.a.	120–150 days	12 h	2–4 h	n.a.
Temp (°C)	245–250	850	Ambient	95	105	100–110
Ni and Co extraction (%)	90–95	80–85	70–80	85–95	> 90	> 95

Modified from Stanković et al. (2020)

can, however, be applied for both, saprolitic and limonitic layers of laterite ores. Table 15.2 summarises existing metallurgical technologies developed for extraction of nickel from laterites. All these methods require high energy and/or reagent consumption, expensive capital equipment costs, and incur several technical and environmental challenges. In addition, hydrometallurgical processing of limonitic ores results in the co-dissolution of gangue minerals, increasing the complexity and cost of recovering valuable metals as well as treatment and disposal of wastes. For this reason, in most existing mines, limonitic laterite ores are currently being stockpiled as mining waste.

Although it is widely acknowledged that processing limonite can be a major solution to meet the future demand of Ni and contribute to the supply of Co, Cu, Sc, and V, there is still a lack of novel and sustainable robust processing routes allowing reduced energy and reagent inputs and producing non-polluting residues. Biohydrometallurgy has a potentially major role in this context.

15.2.2 Biological Processing of Ni–Co Laterites

Although still mostly studied at laboratory scale, the biological processing of lateritic ores has recently received more attention due to the increasing demands for nickel and cobalt. Over the past 40 years, several studies have demonstrated the use of acid bioleaching of both saprolitic and limonitic laterite ores, as well as laterite tailings by organic acids generated by heterotrophic bacteria or fungi (e.g., Bosecker 1977; Nasab et al. 2020). Metal dissolution by heterotrophic microorganisms generally involves an indirect process with microbial production of organic acids, such as citric, oxalic and gluconic, as metabolic by-products (Bosecker 1986). Solubilisation of metals occurs by direct displacement of metal ions from the ore matrix by protons and by the formation of soluble metal complexes and chelates. Bioprocessing of laterites using filamentous fungi of the genera *Aspergillus* and *Penicillium* with the production of organic acids and other metabolites had been demonstrated to be effective in previous studies (Bosecker 1986; Coto et al. 2008). *Bacillus* spp. have been shown to solubilise nickel from a low-grade nickel saprolite ore at circumneutral pH values (Giese et al. 2019). However, heterotrophic (fungal and bacterial) approaches have a number of issues which may impact bioleaching operations and downstream processing, such as large biomass production, cost of growth substrates, prevention of growth of undesired microorganisms, stability of metal–organic acids complexes, adsorption of metals by fungal biomass and relative low dissolution rates.

Many species of acidophilic bacteria are well known for their ability to catalyze the oxidative dissolution of metal sulfide minerals. Some of them, including species of both heterotrophic and autotrophic acidophiles, are facultative anaerobes and have been shown to be able to catalyze the dissimilatory reduction of soluble ferric iron to ferrous iron [reviewed in Marrero et al. (2020)] and, in some cases, to mediate the reductive dissolution of ferric iron minerals (Bridge and Johnson 1998). Brock and Gustafson (1976) first reported that the chemolithotrophic prokaryotes *At. ferrooxidans*, *At. thiooxidans*, and *Sulfolobus acidocaldarius* were able to reduce soluble ferric iron when growing on elemental sulfur as an energy source, but it was not confirmed that these acidophiles could actually respire on ferric iron. Pronk et al. (1992) later demonstrated that *At. ferrooxidans* was able to grow by using ferric iron as an alternative electron acceptor to oxygen, and Bridge and Johnson (1998, 2000) reported that moderately thermophilic iron-oxidising bacteria and *Acidiphilium* SJH (an obligately heterotrophic and mesophilic acidophile) were able to solubilise a range of ferric iron-containing minerals (e.g., goethite and magnetite) under anaerobic conditions. Subsequent to this, Hallberg et al. (2011) screened four pure cultures of acidophilic bacteria for their ability to accelerate the reductive dissolution of a low-grade Ni-laterite ore using relatively low temperatures (< 30–$45\ ^\circ$C) and acidic conditions (pH < 2). The acidophilic heterotroph *Acidicaldus organivorus* (using glycerol as electron donor) and the chemolithotroph *At. ferrooxidans* (using elemental sulfur) were able to solubilise nickel present in the ore under anaerobic conditions.

Reductive mineral dissolution requires the provision of an extraneous electron donor since the mineral itself does not contain the energy supply to promote growth of the microorganisms. Both organic and inorganic substrates can be provided depending on the energy requirements of the microorganisms driving iron reduction. For heterotrophic iron-reducing prokaryotes, small molecular weight organic compounds (such as glucose and glycerol) are often the substrate of choice, though complex organic carbon compounds, such as those from agricultural or food industries (e.g., sugar beet molasses) might also be considered. These substrates can, however, significantly increase operational costs, and contamination by undesirable bacteria and fungi is also highly likely.

In the case of chemolithotrophic microorganisms, such as the facultative anaerobe *At. ferrooxidans*, the oxidation of inorganic compounds (e.g., H_2 and elemental sulfur) can be coupled to the reduction of ferric iron in the absence of oxygen. In extremely acidic conditions (pH <2), chemolithotrophic iron-reducing acidithiobacilli use ferric iron as electron acceptor when oxygen is absent, since (1) ferric iron tends to be more bioavailable due to its greater solubility, and (2) the high redox potential of the Fe(II)/Fe(III) couple (~700 mV at pH 2, in sulfate-rich liquors) makes ferric iron a thermodynamically attractive alternative electron acceptor to molecular oxygen.

Reductive dissolution of ferric iron oxy-hydroxides, such as goethite, is highly consumptive of protons, though when sulfur is used as electron donor less acid is required per mol of goethite (Eq. 15.1) than when reductive dissolution is coupled to, for example, glucose oxidation (Eq. 15.2). In addition, the direct acid dissolution of goethite (Eq. 15.3) consumes almost twice as many protons than sulfur-enhanced reductive bioleaching.

$$6\ \mathrm{FeO} \cdot \mathrm{OH} + \mathrm{S}^0 + 11\ \mathrm{H}^+ \rightarrow 6\ \mathrm{Fe}^{2+} + \mathrm{HSO_4}^- + 8\ \mathrm{H_2O} \tag{15.1}$$

$$6\ \mathrm{FeO} \cdot \mathrm{OH} + 0.25\ \mathrm{C_6H_{12}O_6} + 12\ \mathrm{H}^+ \rightarrow 6\ \mathrm{Fe}^{2+} + 1.5\ \mathrm{CO_2} + 10.5\ \mathrm{H_2O} \tag{15.2}$$

$$6\ \mathrm{FeO} \cdot \mathrm{OH} + 18\ \mathrm{H}^+ \rightarrow 6\ \mathrm{Fe}^{3+} + 12\ \mathrm{H_2O} \tag{15.3}$$

In addition, using elemental sulfur as an electron donor for iron reduction has other advantages: (1) it is a more cost-effective alternative to organic electron donors, (2) elemental sulfur is produced in vast quantities as a secondary product, for example, in removing hydrogen sulfide from natural gas reserves, (3) elemental sulfur oxidation (coupled to oxygen (Eq. 15.4) or soluble ferric iron reduction) generates sulfuric acid which helps to maintain the pH at suitable levels for acidophilic bacteria and retaining metals in solution, and (4) since most acidophiles that oxidise elemental sulfur are autotrophic, using sulfur for enhancing bioleaching consumes rather than produces $\mathrm{CO_2}$.

$$\mathrm{S}^0 + 1.5\ \mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{HSO_4}^- + \mathrm{H}^+ \tag{15.4}$$

Coto et al. (2008) compared the use of organic and inorganic bio-acids on the recovery of cobalt and nickel from laterite tailings. Sulfuric acid was biologically generated by the oxidation of elemental sulfur by *At. thiooxidans* in aerobic conditions. Results showed that production of sulfuric acid by sulfur oxidation was more effective in extracting nickel than organic acids produced by fungi. In this study, 80% Co and over 99% Mn and Ni present in the tailings were solubilised in a period of 15 days. The advantage of biologically produced sulfuric acid as leaching agent in comparison to hydrometallurgical sulfuric acid leaching is that the cost of sulfur is less than that of sulfuric acid, and generating sulfuric acid biologically at a remote mine site can reduce hazards and costs involved in its transportation, though an additional bioreactor would be required.

While acid leaching seems to be the only (indirect) bioprocessing route for saprolitic laterites, du Plessis et al. (2011) developed an innovative biohydrometallurgical approach to extract valuable metals from limonitic laterites

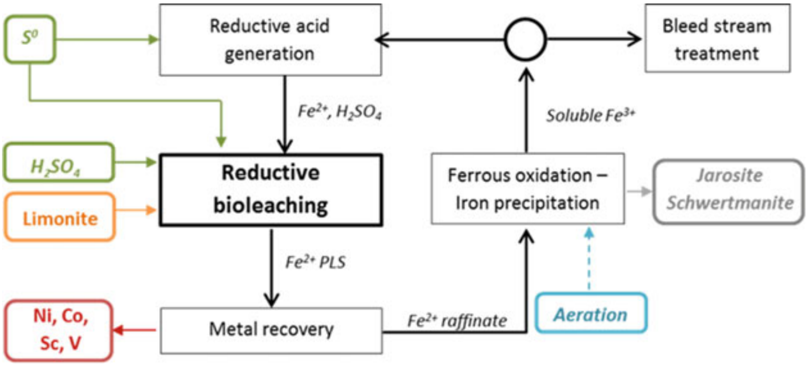

Fig. 15.2 Bioprocessing of laterite ores based on *Ferredox* concept (du Plessis et al. 2011, modified)

using mild pH and temperature. The *Ferredox* process was firstly designed to treat limonitic ores for nickel and cobalt recovery by means of anaerobic reductive dissolution of iron and manganese oxy-hydroxide minerals. Overall the proposed process consists of four components: (1) acid-consuming reductive leaching of limonitic laterite ores, (2) recovery of valuable metals (nickel, cobalt, and copper) by direct sulfide precipitation or solvent extraction or ion exchange, (3) aerobic oxidation and precipitation of ferric iron as jarosites or schwertmannite, and (4) a reductive generation of sulfuric acid which can then be used to assist the leaching step (Fig. 15.2; du Plessis et al. 2011).

The anaerobic reductive bioleaching stage of the *Ferredox* process was described previously by Hallberg et al. (2011). This consisted of two stages: an aerobic phase in which oxidation of sulfur generated acidity and promoted bacterial growth, and an anaerobic mineral leaching stage. The abiotic dissolution of ferric iron minerals proceeds via proton attack which releases ferric iron (Eq. 15.3). The abiotic rate of ferric iron solubilisation by acid is relatively slow, and is related to the crystallinity of the mineral. In the presence of iron-reducing acidophiles, soluble ferric iron is reduced relatively rapidly which causes a disequilibrium between ferric iron in the mineral phase and that in solution thereby supporting the chemical dissolution of the ferric mineral.

Another important reaction in the anaerobic reductive dissolution of laterite ores is the dissolution of manganese oxy-hydroxide minerals. As mentioned previously, cobalt (and some nickel) is chiefly concentrated in manganese oxy-hydroxides such as asbolane and lithiophorite. The sulfur-enhanced reductive dissolution of a generic manganese oxy-hydroxide mineral can occur either directly via biological dissimilatory reduction of Mn(IV) to Mn(II) (Eq. 15.5) or indirectly via manganese reduction by ferrous iron (Eq. 15.6) derived from goethite dissolution (Eq. 15.1). The resulting soluble ferric iron may then be biologically reduced (du Plessis et al. 2011).

$$Mn_3O_3(OH)_6 + S^0 + 5\ H^+ \rightarrow 3\ Mn^{2+} + 5\ H_2O + HSO_4^- \quad (15.5)$$

$$Mn_3O_3(OH)_6 + 6\ Fe^{2+} + 12\ H^+ \rightarrow 3\ Mn^{2+} + 6\ Fe^{3+} + 9\ H_2O \quad (15.6)$$

Anaerobic sulfur-enhanced reductive bioprocessing of limonitic laterite, laterite overburden, and processing residues using pure cultures or consortia of acidophilic bacteria has been investigated at laboratory scale for extracting different primary target metals, including nickel, cobalt (Johnson et al. 2013; Marrero et al. 2020), and copper (Ñancucheo et al. 2014). Table 15.3 shows examples of studies on metal extraction from laterite ores and processing residues using acidophilic, sulfur-oxidising bacteria.

As an alternative approach to anaerobic processing, aerobic reductive dissolution of laterites with *Acidithiobacillus* species has been demonstrated at low pH (<1), including the use of pure cultures of *At. thiooxidans* (Marrero et al. 2015, 2017). Since dissimilatory reduction of ferric iron has not been described for *At. thiooxidans* the question of the mechanism of how this occurs arises. It is possible that intermediary sulfur compounds, such as thiosulfate, formed during enzymatic oxidation of elemental sulfur to sulfuric acid, serve as a chemical reductant for iron and manganese oxides, as suggested for enhanced dissolution of seafloor manganese nodules in aerobic bioleaching experiments with *At. thiooxidans* (Kumari and Natarajan 2001), though this has not been proven. Aerobic reductive bioleaching has some potential advantages over anaerobic reductive dissolution of laterites, including a lower requirement for acid and the lack of a requirement to ensure oxygen-free conditions. Aerobic reductive bioleaching using *At. thiooxidans* was reported to be more efficient in extracting total iron, ferrous iron, manganese, and cobalt than the anaerobic process using *At. ferrooxidans* (Marrero et al. 2015, 2017, 2020). The downsides include the relatively slow abiotic reduction of ferric iron in cultures of sulfur-oxidising acidophiles such as *Acidithiobacillus caldus* and the fact that in a commercial operation it would hardly be feasible to exclude iron-oxidising bacteria that are also active at pH ~1, such as *Leptospirillum* spp., that would probably regenerate ferric iron and thereby counteract the reductive bioleaching process.

15.2.3 Biological Reductive Dissolution of Other Oxide Minerals

Besides iron and manganese oxides in limonitic laterites, reductive bioleaching could be applied for dissolution of other oxide minerals or as a pre-treatment step for refractory ores such as gold, platinum group element (PGE) oxide ores (Hedrich et al. 2020) or rare earth elements (Ñancucheo et al. 2019).

There is considerable potential for applying reductive bioleaching to extract metals from mining and industrial wastes. For example, a combination of oxidative and reductive bioleaching was shown to be highly effective in extracting Cu from tailings (Falagán et al. 2017). Extraction of Al and rare earth elements from red mud

Table 15.3 Examples of laboratory-scale studies on bioleaching of laterite ores and processing residues using acidophilic, sulfur-oxidising bacteria

	Coto et al. (2008)	Hallberg et al. (2011)	Marrero et al. (2015)	Marrero et al. (2017)	Smith et al. (2017)	Santos et al. (2020)
Sample type	Laterite tailings	Limonite	Laterite tailings	Laterite overburden	Limonite	Limonite, filter dust, and slag
Aerobic/anaerobic	Aerobic	Anaerobic	Aerobic/Anaerobic	Aerobic	Anaerobic/aerobic	Anaerobic
Organism	*At. thiooxidans*	*At. ferrooxidans*	*At. thiooxidans*, *At. ferrooxidans*	*At. thiooxidans*	Acidophilic consortium	Acidophilic consortium
Pulp density (% w/v)	10	5	10	5	5	5
Leaching time (days)	12–15	20–30	7	7	22	25–30
Temp (°C)	30	30	30	30	35	35
pH	1.5	1.8	1.8	0.8	1.8	1.5
% Co extracted	~70	~50	55–60	85	99/70	39–49
% Ni extracted	80	70	53–57	16	70/20	37–68

has been demonstrated by a two-stage aerobic and anaerobic bioleaching process. In the anaerobic stage *Acidianus manzaensis* dissolved jarosites via ferric iron reduction coupled with sulfur oxidation (Zhang et al. 2020). Reductive dissolution of jarosite, schwertmannite, and other ferric iron-containing minerals by heterotrophic acidophiles such as *Acidiphilium* species have also been demonstrated (Bridge and Johnson 2000).

Deep-sea polymetallic deposits such as manganese nodules and crusts also represent an important resource of metals, including Co, Cu, Ni, V, and Mo. They consist mainly of manganese and iron oxides with valuable metals incorporated within the structure of the host minerals. Conventional pyro- and hydrometallurgical techniques as well as bioleaching can be applied to process marine nodules (Kumari and Natarajan 2001). Since the minerals in the nodules are present in their oxide form, acidophilic bacteria are able to reduce iron and manganese oxides via sulfuric acid production both aerobically and anaerobically. Heller and Schippers (2015) reported preliminary results of aerobic reductive bioleaching of manganese nodules using a mixed culture of acidophilic chemolithotrophic iron- and sulfur-oxidising bacteria (*At. thiooxidans*, *At. ferrooxidans*, *L. ferrooxidans*, *L. ferriphilum*) and *A. cryptum*. Data showed that 40% Ni, 25% Cu, 1.2% Mn, 0.3% Co, 1% Fe, 70% Zn, and 70% Zr were leached from the Mn-nodules after 56 days. Chemical anaerobic reductive dissolution was also tested in this study by incremental addition of soluble ferrous iron. Ferrous iron was capable of reducing Mn (IV) to Mn (II) with up to 82% Ni, 98% Co, 68% Cu, and 97% Mn leached in these experiments.

15.3 Summary

This chapter has reviewed the fundamentals of mineral reductive bioprocessing and highlighted its challenges and potential advantages over existing pyro- and other hydrometallurgical techniques. The bioprocesses described have the potential to increase metal recovery in existing mines and to transform the categorisation of some unexploited ores, limonite stockpiles, and tailings from laterite ore processing, as well as deep-sea nodules, into valuable resources. Most studies are, however, still at the laboratory stage and additional pilot-scale operations are required to explore the technical (e.g., bioleaching in heaps, ponds, or large tank reactors) and economic potential of this new development in biomining technology.

Acknowledgements Ana Laura Santos is grateful for the financial support from the European Union Framework Programme for Research and Innovation Horizon 2020 (CROCODILE project; grant reference 776473) and the Natural Environment Research Council (UK) under its Security of Minerals Supply programme (grant reference NE/M010899/1). Axel Schippers thanks for financial support from the German BMBF (CLIENT II project BioProLat, FKZ 033R271A). Also, we would like to thank Prof. Richard Herrington (Natural History Museum, London, UK) for providing the photographs and Dr. Paul Schofield and Dr. Agnieszka Dybowska (Natural History Museum, London, UK) for sharing the data on geochemical composition of laterites.

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