

Bio-reduction of sulfide minerals to recover invisible gold

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Bio-reduction of sulfide minerals to recover invisible gold

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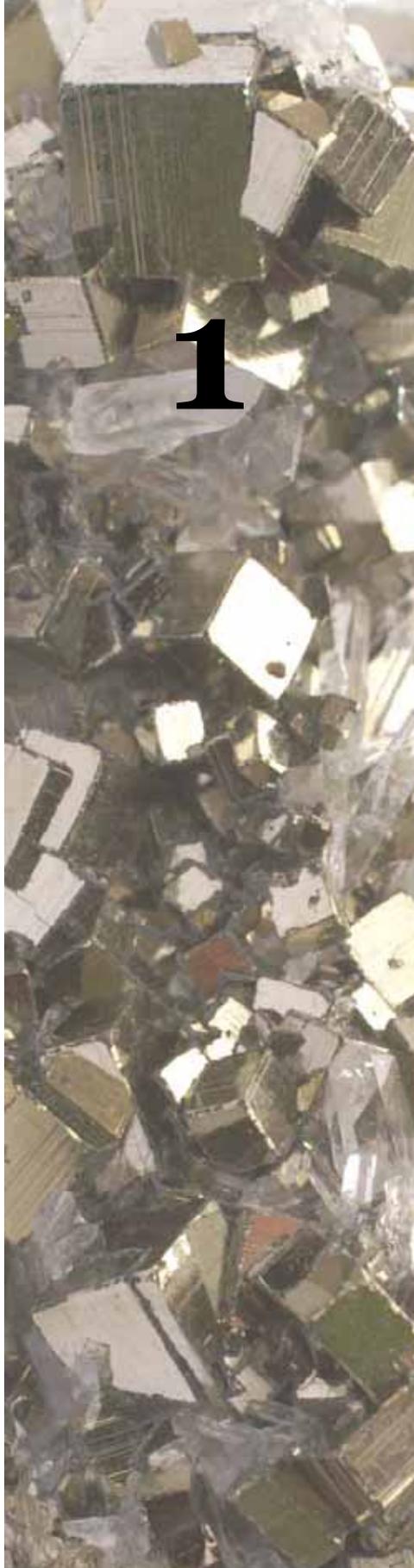
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General introduction

1



1 Bio-reduction of sulfide minerals

1.1 Invisible gold

Pyrite, FeS_2 , is an iron sulfide mineral with a metallic luster and a brassy yellow color. Due to these mineral characteristics pyrite is often confused with gold, from which its nickname “Fool’s gold” originates. However, small quantities of gold can indeed be present inside this mineral. This gold is often referred to as “invisible gold” as it cannot be seen under a scanning electron microscope (Dunn, 1995) as it is present as sub-micron particles (Au^0) and/or structurally bound gold (Au^{+1}) (Palenik, 2004; Reich, 2005). In its pure form pyrite can only contain a few ppm of gold whereas higher gold contents are associated with arsenic-rich compositions (Cook, 1990). Therefore, sulfide minerals like arsenian pyrite ($\text{FeAs}_x\text{S}_{2-x}$) and arsenopyrite (FeAsS) are common in sulfide gold bearing ores.

Due to the high gold price, large amounts of pyrite and arsenopyrite are nowadays mined to recover the invisible gold from these minerals. To harvest the invisible gold from pyrite and arsenopyrite it is necessary to remove the mineralogical barrier. Therefore these minerals are considered refractory. This means that free milling, reduction to a smaller particle size to increase the total surface area of the ore, is generally not sufficient to liberate the invisible gold in a way that the cyanide solution can access the gold. The degree of refractoriness depends on the way the gold is locked inside the sulfide lattice and the presence of reactive gangue mineralogy.

Refractory ores can be categorized as follows: mildly refractory (80-95% gold recovery), moderately refractory (50-80% gold recovery), or highly refractory (< 50% gold recovery) (Vaughan, 2004). Although, invisible gold in sulfide minerals is the most common cause of refractivity, ores containing high levels of Au-Ag tellurides (poor solubility in cyanide) or very fine grained inclusions of native gold in sulfides are often refractory as well (Vaughan, 2004). Ore types that also contain reactive gangue mineralogy can be further subdivided in preg-robbing carbonaceous ores that absorb leached gold from the solution, and ores in which the gold is associated with minerals that consume unacceptable quantities of leaching reagents. An ore is classified as double refractory when both sulfides and carbonaceous matter are present (Nanthakumar, 2007).

To increase the gold recovery from moderately and highly refractory ores to acceptable levels, mining companies have to install an additional (to the customary milling) treatment that will alter or destruct the sulfide mineral lattice in such a way that cyanide can access the gold. The choice of treatment depends on the tonnage and grade of the gold present in the ore. At time of writing, treatment options are available to recover gold from low-grade ores of less than 5 gram/ton (Kongolo, 1998; Butt, 2009), in green-field projects. In green-field locations where equipment has been installed, 2-3 gram gold/ton sulfide ore may even be economical to process with gold prices over US \$1000/troy ounce.

1.2 Invisible gold recovery from sulfide minerals

To liberate invisible gold from refractory ores, most commonly, chemical or biological oxidation techniques that alter or destruct the mineral lattice of the sulfides are used. Chemical oxidation is performed at elevated temperatures with either dry (roasters) or wet (autoclaves) ore. For bio-oxidation the ore is mixed with water and microorganisms in highly aerated continuous stirred tank reactors (CSTR's).

1.2.1 Chemical oxidation of sulfides

Dry oxidation involves the roasting of ores at high temperatures (600°C) in air or oxygen. Depending on the roasting conditions, the main reaction products for pyrite are hematite (Fe_2O_3), magnetite (Fe_3O_4), and gaseous sulfur dioxide (SO_2) (Tranquilla, 1998). Roasting of arsenopyrite generally results in Fe_2O_3 and gaseous arsenic trioxide (As_2O_3) and SO_2 (Mikhail, 1992). The gaseous products SO_2 and As_2O_3 have to be removed from the off gas prior to discharge into the atmosphere. This recovery, however, greatly increases the cost of the roasting route. Depending on location, the products of these two emissions, sulfuric acid and solid arsenic oxide, may have no commercial value. Arsenic requires regulatory scrutiny and regulations. On the positive side, roasting deals with both refractory sulfides and carbonaceous matter at the same time.

Wet (pressure) oxidation proceeds in autoclaves where a combination of high pressure, (acidified) ore, high temperature (above 170°C) and oxygen results in the formation of ferrous iron (Fe^{2+}), ferric iron (Fe^{3+}), sulfate (SO_4^{2-}) and elemental sulfur (S^0) for pyrite (Papangelakis, 1991). Wet oxidation of arsenopyrite initially results in Fe^{3+} , SO_4^{2-} and arsenate (H_3AsO_4), but

further reaction produces ferric arsenate, Fe_2O_3 , ferric sulfates and jarosite residues (Papangelakis, 1990; Weir, 1986). Prior to cyanide leaching the slurry pH is raised through the addition of $\text{CaCO}_3/\text{Ca}(\text{OH})_2$ and the resulting waste-product, impure gypsum, must be disposed of in an environmentally acceptable way.

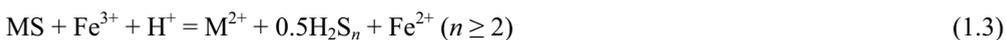
1.2.2 Biological oxidation of sulfides

Bio-oxidation is based on chemolithotrophic microorganisms using iron and/or sulfur as their energy source. In highly aerated CSTR's, operated at pH 1.6 and a temperature of 40°C (Rawlings, 2002), the finely ground mineral is mixed with inorganic nutrients to promote microbial growth. The primary role of the microorganisms in this process is the oxidation of aqueous Fe^{2+} into Fe^{3+} and the production of sulfuric acid. Microorganisms that play an essential role under mesophilic conditions are the acidophilic bacteria: *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, and *Leptospirillum ferrooxidans*. *T. ferrooxidans* is able to oxidize both ferrous iron and reduced sulfur compounds, whereas *T. thiooxidans* is able only to oxidize reduced sulfur compounds and *L. ferrooxidans* only ferrous iron (Schippers and Sand, 1999).

For the bio-oxidation of pyrite and arsenopyrite different ways of dissolution are proposed by Schippers and Sand (1999). Pyrite, being classified as acid insoluble, is oxidized via the thiosulfate mechanism, equation 1.1 and 1.2, where solubilization exclusively occurs through the attack of Fe^{3+} with thiosulfate ($\text{S}_2\text{O}_3^{2-}$) being the main intermediate and sulfate the main end product.



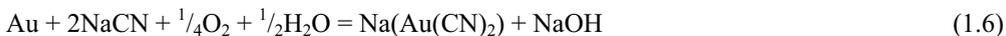
Arsenopyrite is classified as acid soluble (Rohwerder, 2003) and for this mineral solubilization occurs through the combined attack of acid (protons) and Fe^{3+} as described by the polysulfide mechanism, equation 1.3 and 1.4. The main intermediate of this mechanism is polysulfide and subsequently elemental sulfur, which can be further oxidized to sulfate by sulfur-oxidizing bacteria (equation 1.5).



Reaction products formed during the bio-oxidation of pyrite are metal sulfates and sulfuric acid. Bio-oxidation of arsenopyrite yields Fe^{3+} , H_3AsO_4 , and SO_4^{2-} , but jarosites and iron arsenates are also formed (Carlson et al., 1992; Tuovinen et al., 1994). To maintain the pH of the process, the sulfuric acid needs to be neutralized by the addition of $\text{CaCO}_3/\text{Ca}(\text{OH})_2$ and the resulting impure gypsum must be disposed of in an environmentally acceptable way. Energy consuming compressors and agitators are used in this process to supply the required amount of oxygen (air) needed to drive the reactions. As the process is exothermic, also a considerable amount of energy is required to cool and maintain the process at the desired temperature (Olson et al., 2003; Rawlings, 2004). Furthermore the prevention of bio-fouling of heat exchange surfaces is a challenge in this process.

1.2.3 Cyanide extraction and gold recovery

After the bio/chemical treatment the invisible gold can be leached from the ore residue by cyanidation as described by equation 1.6.



Lime or sodium hydroxide is added to this reaction until a pH of 10-11 is reached. This high pH value is required to prevent the formation of HCN gas. Oxygen is added to the extraction process to oxidize the gold to Au^{+1} , which is necessary to form the dissolved gold cyanide complex $\text{Au}(\text{CN})_2^-$. The cyanide leaching efficiency strongly depends on the presence of reactive gangue mineralogy, organic substances, and partially oxidized sulfides. Carbonaceous matter absorbs leached gold from the solution, organic substances consume dissolved oxygen, and partially oxidized sulfides (S^0) are known to be cyanide consumers (Kongolo and Mwema, 1998).

To recover the gold from the cyanide solution the standard method applied is the “Carbon-In-Pulp” (CIP) process. In this process granules of activated carbon are mixed with the pulp obtained after leaching. To separate the loaded carbon from the pulp, sieves are used. For ores

that contain carbonaceous matter, the CIL (Carbon-In-Leach) process is used where activated carbon is added to the leaching tanks.

Gold is recovered from the loaded carbon by treatment with an elution solution. After elution, the carbon is cleaned, reactivated and re-used in the process, while the gold is recovered from the eluate via electro winning.

1.2.4 Environmental effects of mining

Mining and metal extraction impacts the surrounding environment. In order to address the possible magnitude of the environmental burden, usually an environmental impact assessment (EIA) report is made describing in detail the situation previous to any exploration works (Peché and Rodriguez, 2009). The geographical and geological settings are key parameters in estimating the possible effects and hazards. Topography, geohydrology, proximity of surface waters, climate, types of soil, land use, biodiversity, and seismic activity all need to be considered in combination with the type of mining, the extraction process, and the mineralogical composition and setting of the rocks. The type of mining and extraction of gold can differ considerably depending on the type of ore deposit and the environmental impact can vary accordingly. Gold can be mined from placers, hydrothermally altered rocks, quartz veins, intrusions, contact deposits and disseminated ores (Walshe and Cleverley, 2009).

The waters from (abandoned) mine galleries, leached waste, surface runoff, and overflow from the spillway of tailings ponds gives often rise to acid mine drainage (AMD). The result is acidification of waters and soils and mobilization of heavy metals resulting in loss of biodiversity. Arsenopyrite in mine waste systems breaks down under oxidising conditions to release acids of As and S resulting in AMD with high concentrations of dissolved As (Corkhill and Vaughan, 2009). Leakage of cyanide from storage ponds at gold mines in Romania have led to an environmental and social disaster, as fish died in the Tisza river and the people depending on the river for fishery and agriculture were robbed of their income and living (Demuth, 2010). The resistance against new mining projects is therefore enormous and considered an ecological time-bomb (Vogel, 2003). Reducing waste streams during and after mining operations is therefore of high importance and research to limit or avoid these streams is desirable.

1.3 Aim of this thesis

The aim of this thesis is to describe the development of an innovative alternative biologically-based process that alters or destructs the sulfide lattice so that gold can be recovered via cyanidation. The process should have a lower environmental impact compared to the conventional methods, bio/chemical oxidative processes, which have a high energy consumption, use lots of chemicals, and produce environmentally challenging waste products. In this thesis, the opposite route to (bio) oxidation, namely bio-reduction, is investigated for its potential as an alternative gold liberation treatment.

1.4 Bio-reduction of sulfides

Bio-reduction is a biological, anaerobic (without oxygen), process that aims at the mineral-sulfur present in pyrite and arsenopyrite. In terms of oxidation states, pyrite can best be described as $\text{Fe}^{2+}(\text{S}_2)^{2-}$. In this structure iron is present in its most reduced ionic state, but the chemically bound sulfur is not. Reduction of pyrite-sulfur with hydrogen producing hydrogen sulfide may therefore result in an alternative method to alter or destruct this mineral. Also for arsenopyrite iron is expected to be present as Fe^{2+} , but X-ray absorption spectroscopic studies (XANES/EXAFS) indicated that arsenic could be either present as As^0 (Foster, 1998) or As^{-1} (Simon, 1999; Savage, 2000). In case the arsenic is present as As^0 , the arsenopyrite-sulfur is already present in its most reduced state (S^{2-}) and bio-reduction with hydrogen to hydrogen sulfide cannot proceed. However, X-ray photoelectron spectroscopy (XPS) done by Nesbitt (1995) indicated that 85% of the arsenic in arsenopyrite is present as As^{-1} with the remaining 15% present as elemental arsenic. Bio-reduction of arsenopyrite-sulfur could thus be a plausible alternative, since 85% of the sulfur is present as $(\text{As}^{-1})\text{S}^{-1}$.

Compared to the oxidation methods, the formation of hydrogen sulfide is advantageous, because H_2S can be re-used to produce high-purity elemental bio-sulfur (Janssen, 2001) and gold lixivants such as thiosulfate or bisulfide. Also, no oxygen (air) is required to complete the reactions, which will prevent the formation, and neutralization, of sulfuric acid. Furthermore less hydrogen, compared to oxygen, needs to be transferred to the reactors, which will save electrical energy. To keep the bio-reduction process at the desired temperature also less cooling will be required.

1.4.1 Selection of conditions

The selection of conditions for the bio-reduction process is based on three important factors: Microorganisms that are able to convert (dissolved) mineral-sulfur, the recovery of hydrogen sulfide from the reactor solution, and the stability of pyrite and arsenopyrite.

Microorganisms that are thought to be able to reduce pyrite and arsenopyrite are the sulfate (sulfur) reducing bacteria (SRB) as these obligately anaerobic microorganisms, belonging to many different families and genera, are able to use sulfate or other oxidized sulfur compounds as terminal electron acceptor (Lens and Kuenen, 2001). Electron donors used by sulfate reducing bacteria are usually organic compounds or hydrogen (Brüser et al., 2000). Genera belonging to the sulfate reducing bacteria are *Desulfovibrio*, *Desulfotomaculum*, and others whose name usually begins with “*Desulfo-*” (Brüser et al., 2000). Although the optimum pH for sulfate reducing bacteria is usually stated as circum neutral, sulfate reduction has been observed in the range pH 4 to 10. For application on industrial scale interesting reduction rates were only obtained between pH 5 and 8 (Bijmans, 2008). Regarding temperature, sulfate reduction has been reported for mesophilic (25-45°C) and thermophilic (>45°C) conditions (Bijmans, 2008).

The use of sulfate reducers limits the selection of conditions to a pH value between 5 and 8 and the choice between a mesophilic or thermophilic temperature. To obtain a thermophilic temperature more energy to heat the reactor solution is required and therefore a mesophilic temperature of 35°C, comparable to bio-oxidation, was selected. Furthermore, a lower temperature will allow more hydrogen to be transferred into the liquid phase. The selection of an appropriate pH was based on the dissociation of hydrogen sulfide in water (Figure 1.1) and the stability fields of pyrite and arsenopyrite (Figure 1.2).

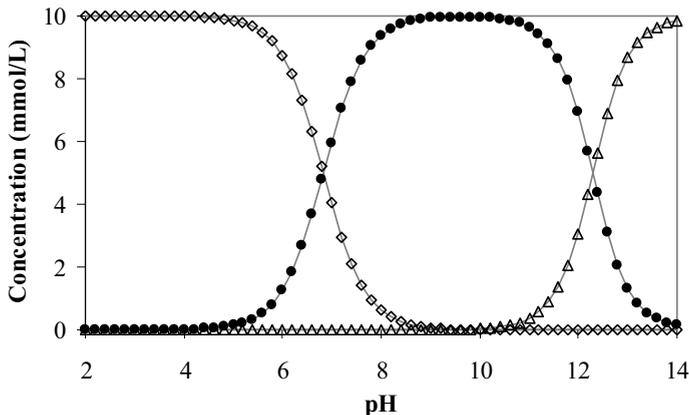


Figure 1.1: Speciation of hydrogen sulfide as function of pH at 35°C, 1 atm. Figure was constructed with OLI Studio 3.1 using 10 mmol/L H₂S as inflow. Species shown are: H₂S_(aq) (◇), HS⁻ (●) and S²⁻ (△).

To efficiently recover sulfide from the solution it should be present as H₂S_(aq) which can be removed as H₂S_(g). As shown by Figure 1.1, sulfide will be present in its undissociated form H₂S_(aq) at low pH values and therefore a pH value of 5, where sulfate reduction still can take place at industrial rates, is preferred. Furthermore, at pH 5 and under reducing conditions (between 0.0 and -0.5 V) arsenopyrite is expected to be less stable as its stability field is located more to the alkaline conditions (Figure 1.2). Pyrite is more stable under acidic conditions, but at pH 5 and a redox potential < -0.2 V also this mineral is expected to dissolve.

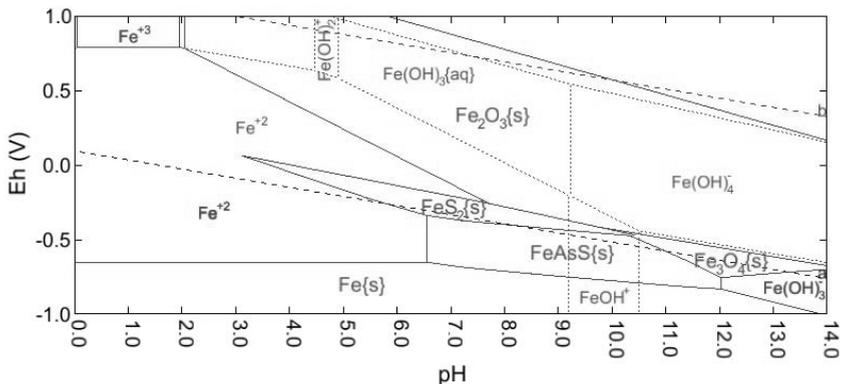


Figure 1.2: Eh-pH diagram for the Fe-As-S-H₂O system at 35°C, 1 atm. Figure was constructed with OLI Corrosion Analyzer 2.0 with iron as contact surface and an activity of 10⁻⁶ M for arsenic and sulfur.

1.4.2 Proposed reactions and thermodynamics

Bio-reduction of pyrite and arsenopyrite is a new concept and therefore no reactions are directly available from literature. However, at elevated temperatures (>400°C), chemical reduction with hydrogen is an already described process to generate pyrrhotite (FeS_(1+x)) from pyrite in coal (Lambert, 1980):



In this process hydrogen sulfide diffuses out of the pyrite lattice into a gaseous atmosphere and is subsequently stripped (Lambert, 1998). Bio-reduction will differ from this process as bacteria (instead of heat) are used as catalysts. Furthermore, the reaction will take place in aqueous solution, which makes the process pH dependent. The final product therefore doesn't necessarily have to be pyrrhotite and three different reactions are proposed for pyrite in Table 1.1.

Table 1.1: Bio-based reactions expected to occur under reducing conditions in the presence of pyrite and arsenopyrite. As a comparison also the bio-oxidation reactions for pyrite and arsenopyrite are shown. Standard reaction Gibbs free energy values were calculated at 35°C.

Eq.	Reaction	$\Delta G_r^0(T)$ (kJ/mol)*
<i>Bio-reduction of pyrite</i>		
1.8	$\text{FeS}_2 + 0.86\text{H}_{2(\text{aq})} = 1.14\text{Fe}_{0.877}\text{S} + 0.86\text{H}_2\text{S}_{(\text{aq})}$	-1.4
1.9	$\text{FeS}_2 + \text{H}_{2(\text{aq})} = \text{FeS} + \text{H}_2\text{S}_{(\text{aq})}$	12.1
1.10	$\text{FeS}_2 + 2\text{H}^+ + \text{H}_{2(\text{aq})} = \text{Fe}^{2+} + 2\text{H}_2\text{S}_{(\text{aq})}$	-4.7
<i>Bio-reduction of arsenopyrite</i>		
1.11	$\text{FeAsS} + \frac{1}{2}\text{H}_{2(\text{aq})} + \text{H}^+ = \frac{1}{2}\text{Fe}^{2+} + \frac{1}{2}\text{FeAs}_2 + \text{H}_2\text{S}_{(\text{aq})}$	-58.4
<i>Bio-reduction of sulfur</i>		
1.12	$\text{S}^0 + \text{H}_{2(\text{aq})} = \text{H}_2\text{S}_{(\text{aq})}$	-45.6
<i>Bio-reduction of sulfate</i>		
1.13	$\text{SO}_4^{2-} + 4\text{H}_{2(\text{aq})} + 2\text{H}^+ = \text{H}_2\text{S}_{(\text{aq})} + 4\text{H}_2\text{O}$	-303.7
<i>Bio-oxidation of pyrite and arsenopyrite</i>		
1.14	$\text{FeS}_2 + 3\frac{1}{2}\text{O}_{2(\text{aq})} + \text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{H}^+ + 2\text{SO}_4^{2-}$	-1234.3
1.15	$\text{FeAsS} + 3\frac{1}{4}\text{O}_{2(\text{aq})} + 1\frac{1}{2}\text{H}_2\text{O} = \text{Fe}^{2+} + \text{H}_3\text{AsO}_4 + \text{SO}_4^{2-}$	-1244.5

* from HSC Chemistry 6.12 (Outokumpu technology)

At pH 5 and 35°C, the formation of an iron sulfide precipitate ($\text{Fe}_{0.877}\text{S}$ or FeS) will only occur if sufficient sulfide is allowed in the system (see Figure 1.3). As sulfide will be stripped from the reactor solution, probably reaction 1.10 will take place for pyrite. Under the same conditions, reduction of arsenopyrite is also expected to result in the formation of ferrous iron and hydrogen sulfide, together with the formation of a sulfur depleted loellingite (FeAs_2) type of structure (equation 1.11).

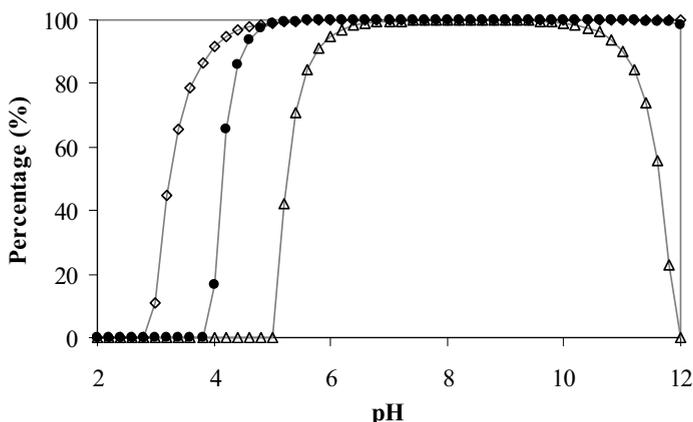


Figure 1.3: Percentage precipitated FeS at different H_2S concentrations as a function of pH at 35°C, 1 atm. Figure was constructed with OLI Studio 3.1 using 10 mmol/L Fe^{2+} and 10 (\diamond), 0.1 (\bullet) or 0.001 (\triangle) mmol/L H_2S .

For growth and maintenance bacteria need to obtain energy from the conversion reaction they facilitate. Literature sources estimate that the minimal amount of energy for bacterial activity is -20 kJ per mol reactant conversion (Schink, 1997). The reaction Gibbs free energy value should thus be more negative than -20 kJ/mol in order to allow a biologically mediated conversion of pyrite and arsenopyrite. As shown by Table 1.1 less energy can be obtained from the bio-reduction of pyrite and arsenopyrite compared to the bio-oxidation of these minerals. Nevertheless, for arsenopyrite a ΔG_r^0 even lower than sulfur reduction is obtained. For pyrite, bio-reduction will probably not proceed under standard conditions, but it cannot be completely excluded as the actual reaction Gibbs free energy value (equation 1.16) is mainly determined by the ratio between $\text{H}_2\text{S}_{(\text{aq})}(\text{product})/\text{H}_{2(\text{aq})}(\text{reactant})$.

$$\Delta G_r = \Delta G_r^0(T_1) + R \cdot T_1 \cdot \ln \left(\frac{[P_1]^{m_1} \cdot [P_2]^{m_2} \dots}{[r_1]^{n_1} \cdot [r_2]^{n_2} \dots} \right) \quad (1.16)$$

ΔG_r : Actual reaction Gibbs free energy

R : Universal gas constant, $8.314 \cdot 10^{-3}$ kJ/mol·K

p, r : Product, reactant

The removal of $H_2S_{(aq)}$ is thus essential to let the bio-reduction of pyrite proceed as it will drive the reaction to the product side. In this way, actual Gibbs free energy value < -20 kJ/mol can be obtained.

Sulfide removal is also important to preserve bacterial activity at pH 5, as it is toxic for many anaerobic bacteria at higher concentrations. The inhibitory effect of sulfide is caused by undissociated hydrogen sulfide, because only neutral molecules can permeate the cell membrane (Lens, 1999). Next to sulfide also arsenic can be toxic to bacteria. In solubilized form, arsenic primarily exists in two redox states: the reduced form, arsenite (As^{3+}), and the oxidized form, arsenate (As^{5+}) (Hallberg, 1996; Craw, 2003). Arsenate, with its structural similarity to phosphate, enters microbial cells readily through phosphate-uptake proteins. Its primary mode of toxicity is then to displace phosphate in the production of ATP. The resulting molecules hydrolyze spontaneously, causing the cell to deplete its energy stores rapidly. Arsenite is even more toxic, because once inside the cell it permanently disables enzymes (Ahmann, 2001). For bio-reduction of arsenopyrite the toxicity of arsenic is expected to be minimal as it will be present as solid $FeAs_2$ (equation 1.11) and not as arsenite.

1.4.3 Gold recovery from bio-reduced samples

The concentration as well as the heterogeneity of gold in sulfide minerals is different for each deposit and depends on the ore forming conditions. The presence of sub-micron particles (Au^0) in a sulfide mineral depends on the suitability of the host substrate for gold nucleation, initial gold solubility and solubility decrease with changing conditions leading to exsolution (Cook, 1990). The concentration of structurally bound gold in a sulfide mineral is determined by the gold content of the ore forming solution, the prevailing physicochemical parameters during ore

genesis or metamorphism, the simultaneous formation of gold minerals (native gold, electrum, gold tellurides), and the chemistry of the host (Cook, 1990).

An essential element for the incorporation of structurally bound gold in pyrite and arsenopyrite is arsenic. Gold is thought to be incorporated in As-rich pyrite and As-enriched arsenopyrite either via a coupled substitution, in which arsenic substitutes for sulfur and gold for iron (Abraitis, 2004; Arehart, 1993) or via chemisorption at As-rich, Fe-deficient, growth surfaces (Fleet, 1997). For both minerals the crystal structure and arsenic content is different. Pyrite crystallizes in cubic symmetry, whereas arsenopyrite adopts the orthorhombic marcasite (polymorph of pyrite) structure. Arsenic values of up to 10wt% are reported for arsenian pyrites (Abraitis, 2004), but calculations done by Reich (2006) showed that pyrite can host up to 6wt% arsenic in solid solution before unmixing into pyrite + arsenopyrite. For arsenopyrite the arsenic content is 46% based on its ideal composition FeAsS. In reality the As content of arsenopyrite is variable, ranging from FeAs_{0.9}S_{1.1} to FeAs_{1.1}S_{0.9} (Abraitis, 2004).

Bio-reduction of gold bearing arsenian pyrite and/or arsenopyrite will leave a solution containing Fe²⁺ and FeAs₂. If the gold does not stay behind in the sulfur depleted loellingite type of structure it should enter the solution. As gold is very stable in the majority of aqueous solutions, including strong acids (Marsden and House, 2006), it will probably enter the solution as colloidal gold (Au⁰) (Southam et al., 2009) unless a complexing ligand is present that reduces the stability of gold. Au⁺¹ forms its strongest complex with CN⁻ (Au(CN)₂⁻) (Williams-Jones et al., 2009), but other important complexes are Au(S₂O₃)₂³⁻ under oxidizing conditions and Au(HS)₂⁻ under reducing conditions (Vlassopoulos and Wood, 1990). In the bio-oxidation process gold is solubilized via the gold thiosulfate complex (Southam et al., 2009), but the formation of Au(HS)₂⁻ during bio-reduction of pyrite and arsenopyrite will probably not occur as sulfide will be removed from the system. The gold, if not reduced to colloidal gold, will therefore probably enter the solution as AuOH·(H₂O)⁰ (Vlassopoulos and Wood, 1990) or form a complex with an organic ligand (Vlassopoulos et al., 1990). Once in solution, colloidal gold and gold complexes can be adsorbed by organic matter, clays, iron and manganese minerals, as well as accumulated and mineralized by bacteria (Southam et al., 2009).

1.4.4 Waste disposal

Bio-reduction of pyrite and arsenopyrite is expected to result in the formation of hydrogen sulfide. The advantage of making hydrogen sulfide is that it can be further processed into high purity elemental bio-sulfur. In this process sulfide is scrubbed from the gas stream by contacting it with a slightly alkaline scrubbing solution (pH 8-8.5) (Janssen et al., 2001), see equation 1.17.



The scrubbing liquid is then brought into contact with aerobic bacteria of the genus *Thiobacillus* (Janssen et al., 2001) or *Thioalkalivibrio* (Van den Bosch, 2008), which are able to oxidize HS^- into elemental sulfur according to equation 1.18.



The removal of HS^- will regenerate alkalinity, so the effluent can be re-used as scrub solution. Compared to the hydrophobic character of chemical sulfur, biological produced sulfur has a hydrophilic character, which makes it possible to separate it by gravity sedimentation, and suitable to use as soil fertilizer (Janssen et al., 2001).

Next to sulfide, a waste stream containing Fe^{2+} and FeAs_2 will be generated. Depending on the refractory properties of loellingite this stream needs an additional oxidation treatment to liberate the gold or can be directly treated with cyanide. After cyanidation, iron(II) salts cannot be used for long term disposal (Welham et al., 2000). Best solution will therefore be to oxidize the iron to Fe^{3+} to form goethite (FeOOH) or ferric arsenate ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) were arsenic is also present in its most oxidized state (Welham et al., 2000).

1.5 Reactor choice

In the bio-oxidation process, CSTR's are used to mix the bacteria with the finely ground mineral and oxygen (air). However, to obtain an acceptable solid suspension and oxygen transfer, vigorous agitation and aeration is required (Acevedo et al., 1999; Ruitenbergh et al., 2001). This high agitation/aeration rate consumes lots of energy and can be reduced by the use of another reactor type. Bio-reduction of pyrite and arsenopyrite was therefore performed in a

gas lift loop reactor. In this type of reactor, mixing and suspension of solids is only induced via gas addition. The reactor contains two vertical columns, called the riser and downcomer (Figure 1.4). Gas is sparged at the bottom of the riser and causes an upflow of gas, liquid, solids and biomass. As the gas leaves at the top of the reactor, liquid, solids, and biomass (with or without a small amount of gas) will flow down via the downcomer. Due to the density difference a circulation flow is established.

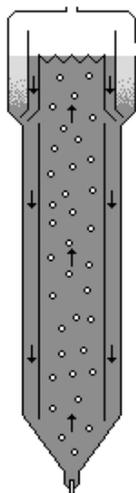


Figure 1.4: Schematic representation of the gas lift loop reactor with internal settler used for the bio-reduction of pyrite and arsenopyrite

The gas lift loop reactor was provided with an internal settler to establish a high solid retention and to prevent the wash out of sulfate reducers as these bacteria have poor attachment properties (Lens and Kuenen, 2001). Other important advantages of a gas lift loop reactor compared to a CSTR are the generation of a lower shear (no impeller) and lower investment (easy to scale up) and operational costs. Furthermore, gas transfer rates have been reported to be the same or better for gas lift loop reactors compared to CSTR's (Ruitenberget al., 2001), which is essential as hydrogen is less soluble in water than oxygen.

1.6 Outline of this thesis

The bio-reduction of pyrite and arsenopyrite is investigated in chapter 2 and 3, respectively. In chapter 3, also another treatment method for arsenopyrite called “anaerobic oxidation” is investigated. The idea behind this method is that sulfate (sulfur) reducers might be able to use the arsenic present as As^0/As^{-1} in arsenopyrite as electron donor for the reduction of sulfate

under anaerobic conditions. However, no conversion of pyrite and arsenopyrite was established via bio-reduction as well as anaerobic oxidation under the selected conditions. It appears that sulfate (sulfur) reducers are not able to recognize sulfur when enclosed by a crystal lattice. To make the mineral-sulfur bio-available for these bacteria in chapter 4 the partial bio-oxidation of a pyrite-arsenopyrite refractory ore is proposed and investigated. Via partial bio-oxidation the mineral-sulfur is oxidized to sulfur, which can be subsequently converted into hydrogen sulfide by sulfate (sulfur) reducing bacteria. This combined method gave positive results and therefore, in chapter 5, chemical partial oxidation, induced via milling, followed by bio-reduction of sulfur was investigated for an enargite-pyrite refractory ore. In chapter 6, the most important findings are discussed and an alternative process for (bio)oxidation, with short cost comparison, is proposed.

Bio-reduction of pyrite investigated in a gas lift loop reactor

2

This chapter is based on the published paper:
Hol, A., Van der Weijden, R.D., Van Weert, G.,
Kondos, P., Buisman, C.J.N., International Journal of
Mineral Processing, 2010, 94, 140-146.



Abstract

To liberate gold from refractory pyrite, oxidative destruction techniques that consume lots of energy and generate acidic waste streams are custom. As an alternative the “bio-reduction” of pyrite is proposed and investigated in this study. Bio-reduction is an anaerobic process based on sulfate/sulfur reducing bacteria which are thought to be able to use pyrite-sulfur as a possible electron acceptor. The conversion of pyrite-sulfur into hydrogen sulfide is advantageous because energy is saved and the generation of an acidic waste stream is prevented. In addition, the generated H₂S can be used to produce elemental sulfur, or even gold lixivants such as thiosulfate or bisulfide. Batch experiments under anaerobic conditions showed that two effects can inhibit bio-reduction; methane formation and sulfide accumulation. In a gas lift loop reactor operated at pH 5, temperature of 35°C, and with continuous sulfide removal no evidence of pyrite bio-reduction was found. Though the sulfate reducing bacteria survived, they did not utilize pyrite-sulfur as an electron acceptor under the chosen conditions.

1 Introduction

Sulfide minerals such as pyrite can contain significant concentrations of gold often present as sub-micron particles (Au^0) and/or structurally bound gold (e.g. Au^{+1}) (Fleet and Mumin, 1997; Simon et al., 1999; Palenik et al., 2004). Destruction or alteration of the pyrite lattice is required to liberate this “invisible gold”. At present, chemical (pyro and hydro) and biological oxidation techniques are the custom processes. Costs of chemical oxidation are increased by the high temperatures and/or pressures required, SO_2 removal from the off gas, and production of impure sulfuric acid that needs to be neutralized and disposed of. Similarly, the costs for bio-oxidation are increased by production of sulfuric acid, the use of compressors and agitators to provide sufficient oxygen (air), and cooling needed to maintain a temperature of 40°C (Olson et al., 2003; Rawlings, 2004).

A possible way to lower the energy demand and to prevent the formation of sulfuric acid is the reduction of sulfide minerals. Chemical reduction at elevated temperature with H_2 has been applied to generate pyrrhotite from pyrite in coal (Lambert et al., 1980). This proceeds according to the following reaction:



If it is possible to achieve this reduction reaction at low temperature using bacteria as catalysts to liberate gold from pyrite, the large amounts of oxygen, the need for cooling, and the neutralization of sulfuric acid can be avoided. Furthermore, the generated H_2S can be re-used to produce high-purity elemental sulfur (Janssen et al., 2001) and gold lixiviants such as thiosulfate or bisulfide.

This chapter investigates the feasibility of bio-reduction via thermodynamics, batch experiments, and a gas lift loop reactor experiment.

2 Theory

Although pyrite's cubic lattice is very stable, it is susceptible to biological oxidation reactions. The primary role of bacteria in the bio-oxidation process of pyrite is the conversion of aqueous Fe^{2+} into Fe^{3+} and the production of sulfuric acid from the pyritic S_2^{2-} group. The oxidative attack of Fe^{3+} results in the destruction of the sulfide mineral and the solubilization of its constituents (Rohwerder et al., 2003). For the biological reduction of pyrite the aim of attack is the S_2^{2-} group since iron is already present as Fe^{2+} . The idea is to make use of sulfate/sulfur reducing bacteria/archaea which are able to use hydrogen as electron donor and sulfur species as electron acceptor. In contrast to bio-oxidation, where an indirect mechanism results in the solubilization of pyrite, bio-reduction is assumed to proceed without intermediates (Figure 2.1).

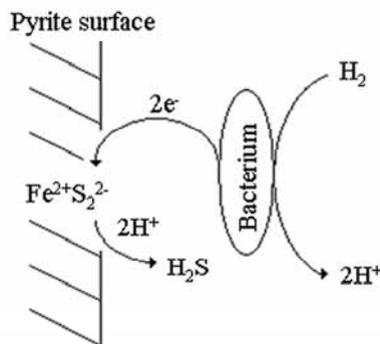


Figure 2.1: Proposed mechanism for bio-reduction of pyrite at neutral pH: Bacteria using hydrogen as electron donor transfer these electrons to the S_2^{2-} dipole of the pyrite mineral. This results in the net removal of sulfur from pyrite.

Under acidic conditions the bio-reduction of pyrite is expected to proceed as follows:



Depending on the pH conditions the products of bio-reduction (equation 2.2) will be free iron, hydrogen sulfide, or iron sulfide (e.g. pyrrhotite).

2.1 Thermodynamics: bio-reduction versus bio-oxidation

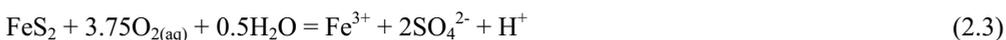
Bio-reduction, like bio-oxidation, is a bacterial dependent process, so the conditions selected should be favorable for sulfate/sulfur reducers. Temperature and pH values selected are: 35°C (mesophilic), 55°C (thermophilic), pH 5 (slightly acidic) and pH 7 (neutral). Bio-reduction at pH 5 is expected to proceed according to equation 2. At pH 7 the reaction can best be described by equation 2.1, since the iron sulfide solubility decreases with pH. For both equation 2.1 and 2.2 the standard reaction Gibbs free energy (ΔG_r^0) at 35°C and 55°C is shown in Table 2.1.

Table 2.1: Calculated standard reaction Gibbs free energy values for pyrite reduction

Reaction equation	Temp (°C)	$\Delta G_r^0(T)$ (kJ/mol)*
$\text{FeS}_2 + 0.86\text{H}_{2(\text{aq})} = 1.14\text{Fe}_{0.877}\text{S} + 0.86\text{H}_2\text{S}_{(\text{aq})}$	35	-1.4
	55	-2.9
$\text{FeS}_2 + 2\text{H}^+ + \text{H}_{2(\text{aq})} = \text{Fe}^{2+} + 2\text{H}_2\text{S}_{(\text{aq})}$	35	-4.7
	55	-5.6

* from HSC Chemistry 6.12 (Outokumpu technology)

Literature sources estimated that a minimum of -20 kJ per mol reactant conversion is necessary to obtain bacterial activity (Schink, 1997). As shown in Table 2.1, reduction of pyrite will not deliver enough energy for bacterial growth and maintenance under standard conditions since the minimum of -20 kJ/mol is not reached. This differs from bio-oxidation which gives a ΔG_r^0 of -1276.8 kJ/mol for the reaction described by Boon and Heijnen (1998) (equation 2.3) using the conditions 40°C (pH 1.6) reported by Rawlings (2002).



However, bio-reduction cannot be completely excluded since the actual reaction Gibbs free energy value (ΔG_r) is mainly determined by the ratio between $\text{H}_2\text{S}_{(\text{aq})}$ (product) and $\text{H}_{2(\text{aq})}$ (reactant). When $\text{H}_2\text{S}_{(\text{aq})}$ is taken as a variable and the maximum solubility concentration of hydrogen, $7.994 \cdot 10^{-4}$ mol/L at 35°C, is kept constant, the results shown in Figure 2.2 are obtained. It is thus possible to reach a ΔG_r < -20 kJ/mol, but it is essential to remove the sulfide. Removal of sulfide from the aqueous solution can be achieved, for example, by continuous $\text{H}_2\text{S}_{(\text{g})}$ stripping in a gas lift loop reactor. Next to sulfide, hydrogen also has an influence on the reaction Gibbs free energy. The $\text{H}_{2(\text{aq})}$ concentration in solution is probably

lower than its maximum solubility due to bacterial activity, which will shift the curves shown in Figure 2.2 to the more positive ΔG_r values. On the other hand if a $H_{2(g)}$ pressure (>1 atm) would be applied the curves will move to more negative ΔG_r values. Bio-reduction could thus be a process controllable via the gas composition. Another factor that increases the change in Gibbs energy are structural differences in pyrite caused by impurities (Abraitis et al., 2004).

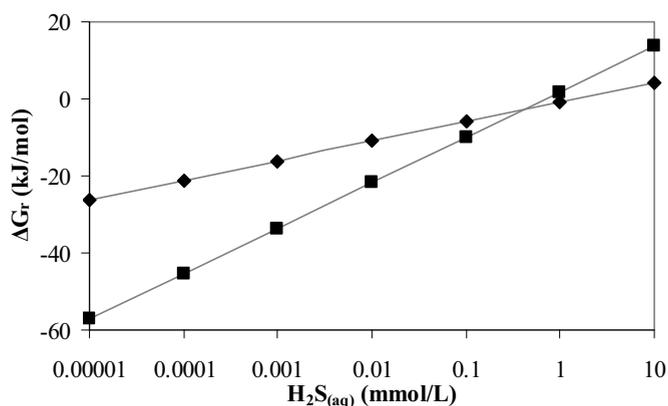


Figure 2.2: Effect of different $H_2S_{(aq)}$ concentrations on the actual reaction Gibbs free energy value for pyrite reduction at 35°C, pH 5 (■) and 7(◆). Concentrations used are the maximum solubility concentration for hydrogen in water at 35°C, 1 mol/L for pyrite and pyrrhotite, and $1 \cdot 10^{-6}$ mol/L for dissolved iron.

3 Materials and methods

3.1 Minerals

A hand specimen of pyrite from Huanzala, Peru, was ground to a particle size <1 mm using a Retsch SM2000 cutting mill. Particles <50 μm were hand sieved, and the sieve residue >50 μm , was successively milled by a Retsch jaw-crusher to a particle size <50 μm . Particle size distribution was analyzed by a Beckman Coulter laser LS 230 and found to be 25.7 μm on average. The mineral composition was analyzed via a combined microwave/ICP method. Microwave destruction of the mineral was performed with Aqua Regia ($\text{HCl}:\text{HNO}_3 = 3:1$). The resulting liquor was filtered, adjusted to a known volume, and analyzed by ICP. The mineral specimen was found to be a pure piece of pyrite containing some minor impurities of which the most important are (in wt%): Al, 0.05; As, 0.05; Ca, 0.11; Mg, 0.02 and Mn, 0.06.

Prior to addition to the experimental solutions the ground mineral was washed with 2 M HCl and thoroughly rinsed with demineralized water to remove surface oxides.

3.2 Growth media

A defined medium dissolved in demineralized water was used. All chemicals were of analytical grade and supplied by Merck. The medium of the batch tests contained (in g/L): KH_2PO_4 , 1.14; $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, 2.03; NH_4Cl , 0.30; NaCl , 0.30; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.10; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.10; Yeast Extract (Gibco BRL), 0.01; and 1 ml/L acid and alkaline trace elemental solution. Sodium acetate was added to the medium as (additional) carbon source with a concentration of 0.30 g/L. The pH of the prepared medium was approximately 7. For batch tests operated at pH 5 the 20 mM phosphate buffer composition was changed to 2.69 g/L KH_2PO_4 and 0.05 g/L $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (pH was set to 5 with 2 M HCl). The reactor medium contained (in g/L): KH_2PO_4 , 0.024; NH_4Cl , 0.19; KCl , 0.37; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.10; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.11; NaHCO_3 , 0.10; Yeast Extract, 0.01; and 1 ml/L acid and alkaline trace elemental solution.

Trace elemental solutions were based on Stams et al. (1993). Acid trace elemental solution contained in g/L: H_3BO_3 , 0.062; ZnCl_2 , 0.068; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.017; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.099; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.119; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.024; and 4.14 ml/L HCl. Alkaline trace elemental solution contained in g/L: $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$, 0.026; $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 0.024; $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 0.033; and NaOH, 0.400.

3.3 Bacterial sources

Sludges from different sources proven to contain bacteria that were able to reduce sulfate (sulfur) were used. One sample, sand-filter backwash water (BWW), was taken from the wastewater treatment plant of a Dutch oil refinery. Other sludges were obtained from a lab-scale sulfate reducing reactor operated at pH 5 (Bijmans et al., 2008), a vegetated marsh area near Skidaway (Oceanographic Institute in Georgia, USA) and from “Industrie water Eerbeek” (Eerbeek, The Netherlands). Eerbeek sludge is a mesophilic Upflow Anaerobic Sludge Blanket (UASB) granular sludge applied for the treatment of paper mill wastewater (Roest et al., 2005).

3.4 Experimental setup

Batch experiments with 5 gram ground pyrite were performed in 250 mL serum bottles. Sludge with a total volume of 2 mL, 1.6 mL BWW, 0.2 mL crushed (by a household blender) Eerbeek granules and 0.2 mL pH 5 sulfate reducing sludge, was added to 48 mL medium. Microwave destruction and ICP analysis showed that the most important impurities added via 2 mL sludge were Fe (0.23 mg) and S (2.12 mg). No sludge was added to mineral blanks, with a medium volume of 50 mL. Bottles were closed with a butyl rubber cap and fixed with an aluminum cap. The headspace was flushed 5 times with N₂ and 5 times with 100%H₂ (electron donor) or 80%H₂/20%CO₂ (electron donor + carbon source) and set on a small over pressure of 0.4 bar. Batch tests were incubated at 55°C and 35°C, and continuously mixed at 150 rpm.

A reactor experiment with 250 gram pyrite was performed in a gas lift loop reactor with 4.9 L medium. The sludge was a mix of 50 mL BWW, centrifuged at 4000 g for 10 minutes at 20°C and resuspended in medium before addition to the reactor, 10 mL pH 5 sulfate reducing sludge, and 10 mL Skidaway sludge. A schematic overview of the reactor setup is shown in Figure 2.3. The temperature of the reactor was maintained at 35°C by a Julabo 5 waterbath. The pH was measured using a custom made QIS electrode (KNO₃/3xCER) and controlled at pH 5 with 4 M HCl/NaOH (Bijmans et al., 2008) by an EH liquisys-M pH controller. The redox potential was measured using a standard QIS electrode and a PHM 210 Radiometer. The reactor was operated as a batch experiment. Influent, continuously sparged with N₂, was only added via a Stepdos 08RC liquid membrane pump if the liquid level needed to be refilled. Effluent from the reactor was collected in the external settler.

A gas composition of 95%H₂/5%CO₂ with a rate of 10 mL/min was added to the gas phase of the reactor by two Brooks 5850S thermal mass flow controllers connected to a Brooks 5878 control unit. The gas phase was recycled by a KNF-Verder N840.3FT.18 gas membrane pump. The gas recycle flow rate was measured on a Brooks R2-15-C (sapphire) SHO-rate and manually controlled between 6-8 L/min by a proportional valve. A condenser, connected to a Julabo F25 cooling bath, was set at a temperature of 20°C to cool down the gas stream. H₂S_(g) of the recycle stream was removed by a 10 L, 0.5 M, ZnCl₂ solution. Effluent gas was stripped 3 times with 1 M NaOH to remove H₂S_(g). NaOH is unusable as strip solution for the recycle stream, since it will remove the carbon source, CO₂, as well. The gas effluent rate was

measured by a Ritter MGC1 gas meter. A self-made rubber check valve was used as sparger. The reactor was made out of glass and packed in aluminium foil to exclude the effect of light. Tubing, connections, and valves, were all made of PTFE (Schott and Serto).

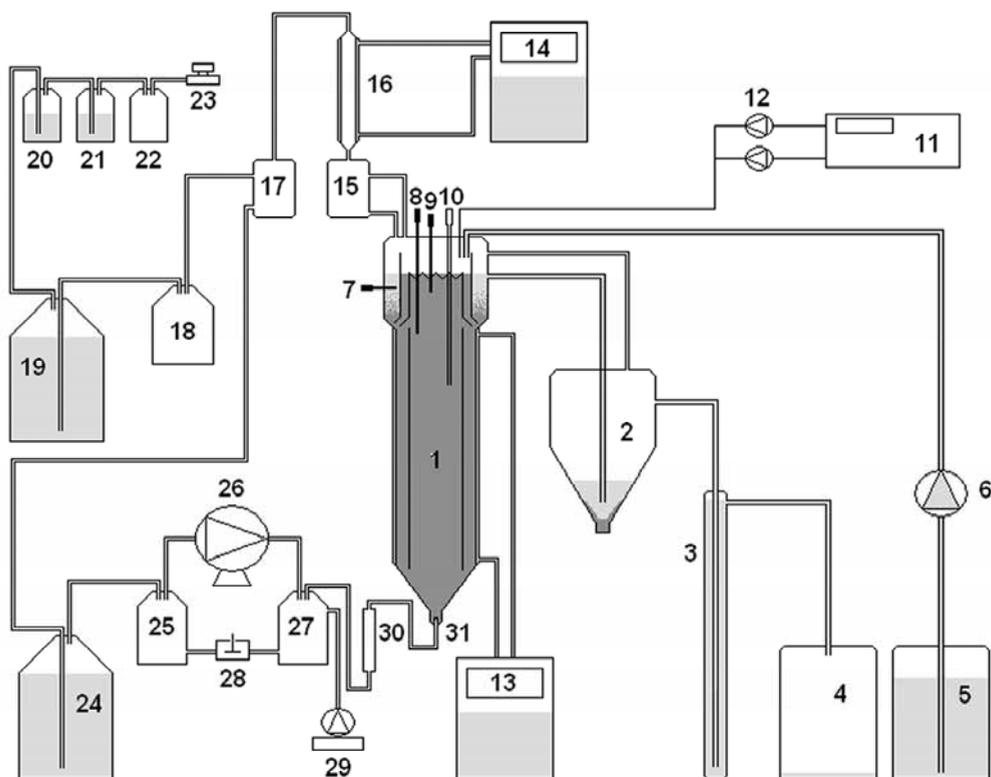


Figure 2.3: Schematic overview of the gas lift loop reactor with internal and external settler: 1. Gas lift loop reactor; 2. External settler (reactor effluent); 3. Water lock; 4. Water lock overflow; 5. Influent; 6. Influent pump; 7. Temperature sensor; 8. Redox electrode; 9. pH electrode; 10. Sample tube (Titanium); 11. pH controller; 12. Acid/base addition; 13. Water bath (heating); 14. Water bath (cooling); 15. Condense back flush; 16. Condenser; 17. Gas effluent split off; 18. Strip vessel back flush bottle; 19. Gas effluent stripper 1; 20. Gas effluent stripper 2; 21. Gas effluent stripper 3; 22. Ritter back flush; 23. Ritter (gas meter); 24. Gas recycle strip vessel; 25. Recycle bottle; 26. Recycle gas pump; 27. Pressure bottle; 28. Proportional valve; 29. H₂/CO₂ addition; 30. Sho-rate (flow rate); 31. Sparger.

3.5 Analysis techniques

Samples of solutions were filtered over a 0.2 μm filter and analyzed for their free metal composition by a Varian ICP-OES. Iron was also measured by Dr Lange kit LCK-320 (0.2-6.0 mg/L Fe^{2+/3+}) on a Hach Lange Xion 500 spectrophotometer. Sulfate was measured on a Dionex DX 600 Ion Chromatograph equipped with an Ionpac AS17 column (2mm x 250mm). Dr Lange sulfide kit, LCK-653 (0.1-2.0 mg/L S²⁻), and a Hach Lange Xion 500 spectrophotometer, were used to measure SulfideT(aq) (S²⁻+HS⁻+H₂S(aq)) in filtered (0.2 μm) solutions and to measure the amount of H₂S(g) in recycle and effluent strip vessels. Biogas was analyzed on a Hewlett Packard 5890 GC with a Varian molecular sieve 5A column (30m x 0.53mm) to measure H₂, O₂, N₂ and CH₄ or on a Interscience GC 8000 series with 2 parallel columns; a Varian Porabond-Q (50m x 0.53mm) and a Varian molecular sieve 5A (50m x 0.53mm) to measure O₂, N₂, CH₄ and CO₂. The pressure in the batch bottles was measured by a pressure sensor (0 – 3500 mbar, abs).

4 Results

4.1 Batch test description

Different conditions were applied for batch tests, in duplicate, with pyrite and sludge. Three parameters were varied per run: Gas composition, pH, and temperature. Batch codes are based on these conditions: The first number represents temperature ($^{\circ}\text{C}$), the second pH and the letter(s) H or HC refer to a gas phase of 100%H₂ or 80%H₂/20%CO₂ respectively. Batch tests performed are: 55-7-H, 55-7-HC, 55-5-H, 55-5-HC, 35-7-H and 35-5-H. Batch codes with an initial subscription Bl are blanks with only mineral and medium.

4.2 H₂/CO₂ consumption

The consumption of H₂/CO₂ by bacteria/archaea will result in a pressure decrease over time. Results of pressure measured in batch bottles operated at 55 $^{\circ}\text{C}$, pH 7 with a H₂ or H₂/CO₂ gas composition are shown in Figure 2.4.

A steady decrease in pressure, as a result of sampling and pressure measurement, was observed for pyrite exposed to a H₂ or H₂/CO₂ gas composition (blank). Addition of sludge makes no difference in pressure development when a hydrogen gas phase is applied. However, a rapid

pressure decrease is observed, between day 0 and 3, for gas composed of H_2/CO_2 . Experiments performed at $55^\circ C$, pH 5, show similar results, but the rapid pressure decrease with sludge and a H_2/CO_2 gas composition starts ~ 1 day later (data not shown).

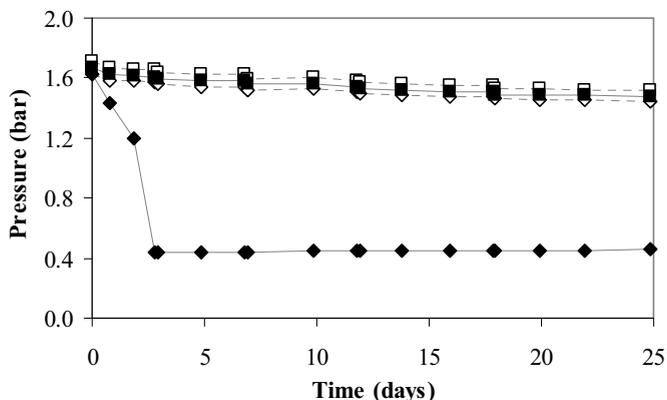


Figure 2.4: Pressure decrease measured in batch bottles BI-55-7-HC (◇), 55-7-HC (◆), BI-55-7-H (□) and 55-7-H (■). Experiments 55-7-HC and 55-7-H were performed in duplicate. Standard deviations are not shown because they were smaller than 5%. Blanks (BI) are singular experiments with only mineral.

The rapid pressure decrease observed in the batch tests 55-7-HC and 55-5-HC was found to be a result of methane formation: At the end of the experiment $\sim 74\%$ of the gas composition consisted of methane. Methane formation is also observed in batch tests with only sludge, where similar pressure trends were obtained for the H_2/CO_2 gas composition. When the gas phase was composed of hydrogen, small amounts of methane (0.3-2.1%) were detected for batches with only sludge and the combination mineral/sludge. Mineral in medium gives no detectable methane amounts for either H_2 or H_2/CO_2 . Temperature seems to have no effect on the pressure development since experiments at $35^\circ C$ with a H_2 gas composition show similar pressure trends to Figure 2.4.

4.3 SulfideT(aq) production

Together with the consumption of hydrogen, the formation of sulfide by bacteria/archaea could be an indication that pyrite is reduced, though pyrite reduction is not the only sulfide producing reaction. Under the selected conditions, sulfate (sulfur) can be reduced as well, which was

proven by blank sludge experiments (data not shown). Figure 2.5 gives an overview of sulfate concentrations measured in batch 55-7-H, 55-7-HC, 35-7-H and 35-5-H.

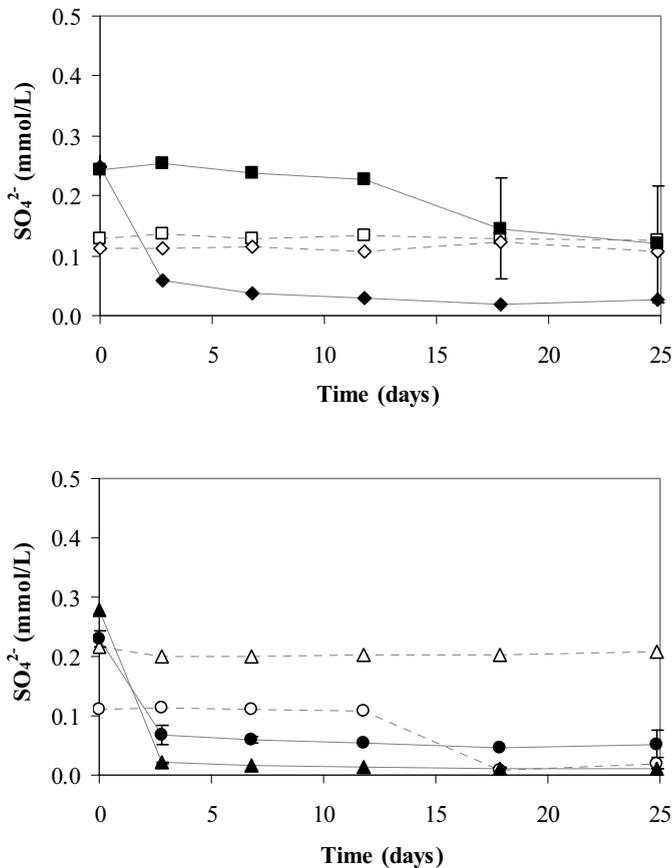


Figure 2.5: Sulfate concentrations measured with IC in filtered solutions of batch BI-55-7-HC (\diamond), 55-7-HC (\blacklozenge), BI-55-7-H (\square), 55-7-H (\blacksquare), BI-35-7-H (\circ), 35-7-H (\bullet), BI-35-5-H (\triangle) and 35-5-H (\blacktriangle). Experiments with sludge were performed in duplicate of which the average and standard deviations $>5\%$ are shown in the Figure. Blanks (BI) are singular experiments with only mineral.

A sulfate concentration of 0.1 to 0.2 mmol/L is measured in the batch tests due to addition of pyrite. Sludge addition increases the initial sulfate value with ~ 0.1 mmol/L. Blanks should give a stable sulfate line if no contamination with bacteria occurred. Except for BI 35-7-H this is indeed the case. Bacterial contamination of BI 35-7-H is possible since no biocides were added to mineral blanks. At pH 7 and 55°C sulfate reduction is observed for batch 55-7-HC and seems to be less favored at 55-7-H, since it takes 12 days before sulfate reduction starts in one

of the experiments. Slightly acidic conditions at 55°C are also not favored, because it takes a week before sulfate reduction starts in batch 55-5-HC and no sulfate reduction is observed in batch 55-5-H (data not shown). At 35°C rapid decreases in sulfate were observed for batch 35-7-H and 35-5-H and the effect of pH seems to be negligible.

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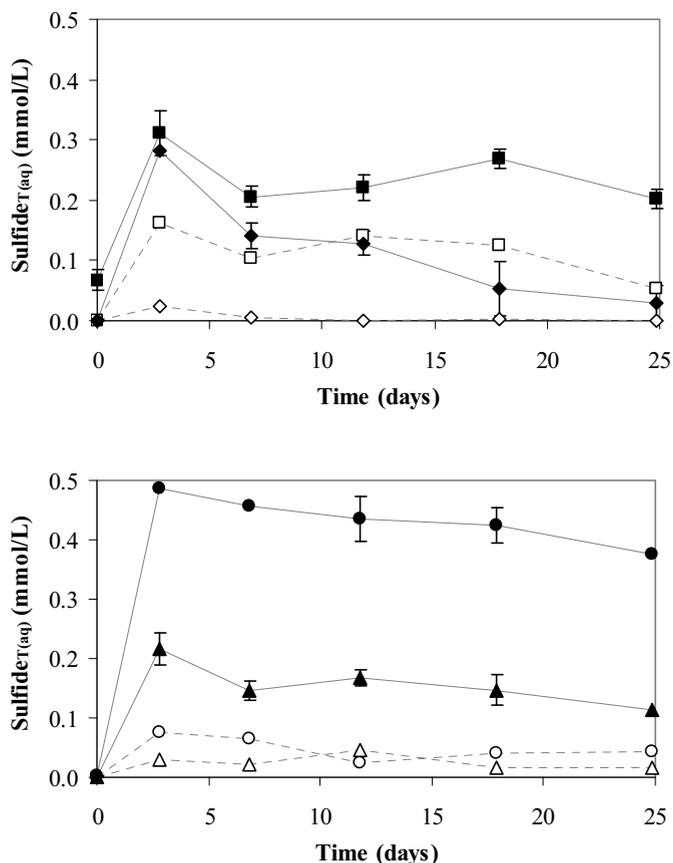


Figure 2.6: Sulfide_{T(aq)} concentrations measured with Dr Lange in filtered solutions of batch BI-55-7-HC (◇), 55-7-HC (◆), BI-55-7-H (□), 55-7-H (■), BI-35-7-H (○), 35-7-H (●), BI-35-5-H (△) and 35-5-H (▲). Experiments with sludge were performed in duplicate of which the average and standard deviations >5% are shown in the Figure. Blanks (BI) are singular experiments with only mineral.

Reduction of sulfate, either added via sludge and/or mineral, will contribute to the formation of sulfide_{T(aq)} according to the following reaction:



Sulfide_{T(aq)} measurements of filtered batch solutions are shown in Figure 2.6. Rapid formation of sulfide_{T(aq)}, as result of sulfate reduction (Figure 2.5) is observed for batch 55-7-HC, 35-7-H and 35-5-H. When sulfate becomes depleted, bacteria/archaea seek for another electron acceptor. Pyrite, being an electron acceptor, could thus be reduced after day 3, but a continued increase in sulfide_{T(aq)} was not observed. The decrease observed in sulfide_{T(aq)} after day 3 seems to be related to the pressure drop measured in the batch bottles. Pyrite in medium generates some sulfide_{T(aq)} as shown by the mineral blanks in Figure 2.6.

4.4 Selection of reactor conditions

Batch tests were useful to select conditions for the gas lift loop reactor experiment. Methane formation, an unwanted side reaction, should be prevented as much as possible by choosing a CO₂-poor gas composition. Batch tests at 55°C showed that a gas phase containing 20%CO₂ results in rapid methane formation. Without CO₂ the amount of methane is minimal, yet bacteria/archaea need a source of carbon. Therefore, a gas phase containing 5%CO₂ and 95%H₂ was selected for the reactor experiment.

The pH of the batch tests was buffered with phosphate. For pH 7 this worked, but batch tests performed at pH 5 started, through the addition of sludge, at an initial pH value of 5.7. The pH in the reactor was therefore kept constant by controlled acid/base addition instead.

To achieve bio-reduction of pyrite it is essential to keep the sulfide_{T(aq)} concentration of the reactor as low as possible (see Figure 2.2). Sulfide should thus be removed from the reactor and not accumulate. Removal of sulfide_{T(aq)} from the reactor liquor is favored at pH 5 compared to pH 7, since most of the sulfide_{T(aq)} will be present as H₂S. This can be easily removed from the gas phase by recycling through a ZnCl₂ solution. Thermodynamically, pH 5 is also favored over pH 7, since lower Gibbs free energy values are obtained when sulfide decreases (Figure 2.2).

At pH 5 sulfate reduction, and possible bio-reduction of mineral S, is favored at a temperature of 35°C as shown by batch test 35-5-H. Thermodynamically, a lower temperature is less favorable, but acceptable since the difference in energy change is small (Table 2.1).

4.5 Reactor results

Results of a gas lift loop reactor run with pyrite at pH 5, 35°C, 95% H_2 /5% CO_2 , are shown in Figure 2.7.

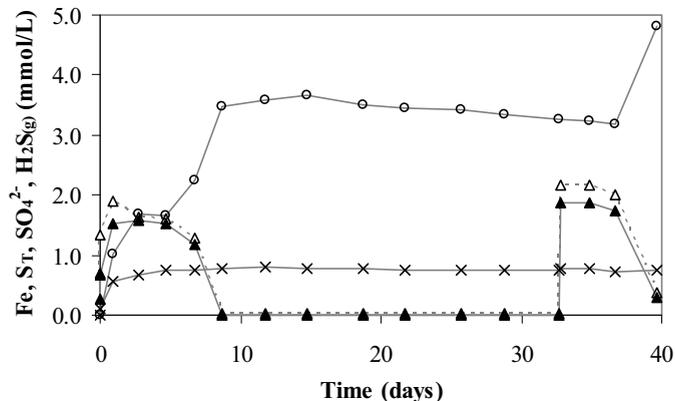


Figure 2.7: Bio-reduction of pyrite at pH 5, 35°C, 95% H_2 /5% CO_2 , in a gas lift loop reactor. Iron (×) and sulfur(T) (Δ) were both measured by ICP, sulfate (▲) by IC, and $H_2S_{(g)}$ stripped (○) is the calculated value of $H_2S_{(g)}$ removed per liter reactor volume via gas recycling through a 0.5 M $ZnCl_2$ solution. On day 33, 2 mmol/L Na_2SO_4 was added to the reactor.

Pyrite in medium gives an initial sulfate value of 0.3 mmol/L. Through the addition of sludge the sulfate concentration increases with another 0.4 mmol/L. In the first 3 days the sulfate concentration increases even further to 1.6 mmol/L. During that period, $H_2S_{(g)}$ is already removed from the reactor. After 3 days the first signs of sulfate reduction were observed: Sulfate reduction starts and an extra increase in $H_2S_{(g)}$ is measured. Sulfate as electron acceptor was depleted after 9 days and after that period bio-reduction of pyrite should start. That would mean that at pH 5, an increase in both iron and $H_2S_{(g)}$ is expected until day 33. Unfortunately, this increase is not observed: iron gives a stable line and $H_2S_{(g)}$ even slightly drops because a ZnS coating started to form on the glass wall of the recycle strip vessel. On day 33, 2 mmol/L Na_2SO_4 was added to the reactor to check for sulfate reducing activity. Sulfate reducers are still able to utilize sulfate at the end of the reactor run as proven by the decrease in sulfate and formation of $H_2S_{(g)}$ on day 40. No detectable $H_2S_{(g)}$ concentration was measured in the 1 M NaOH effluent strip vessel.

Other parameters measured during the reactor run are shown in Figure 2.8. In the first few days the redox potential drops to a stable value of -470 mV (Ag/AgCl). At this redox potential iron is present as Fe^{2+} , which was also confirmed by iron measurements with Dr Lange kit LCK-320 (data not shown). Together with the reduction of sulfate, CO_2 seems to be consumed as well during the first 9 days. The initial CO_2 concentration is <5%, which is probably caused by establishing equilibrium between gas and reactor liquor. After 9 days sulfate reduction stops and the CO_2 concentration starts to increase. Although bio-reduction was not observed between day 9 and 33 another reaction started to take place from day 22 on: methane formation.

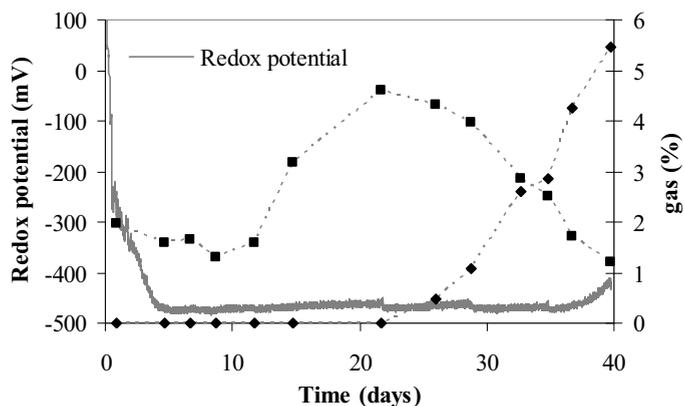


Figure 2.8: Redox potential (Ag/AgCl) and gas composition development during a gas lift loop reactor run with pyrite at pH 5, 35°C, 95% H_2 /5% CO_2 . Gas composition is only shown for CO_2 (■) and CH_4 (◆).

5 Discussion

A thermodynamic evaluation of pyrite bio-reduction showed that in theory it is possible for bacteria/archaea to gain enough energy from this reaction for their growth and maintenance. However, to achieve this, sufficient hydrogen should be available and the concentration of $\text{H}_2\text{S}_{(\text{aq})}$ should be as low as possible. Batch tests performed under various conditions, pH, temperature, and gas composition, showed that two processes, methane formation and sulfate reduction, affected the conditions needed for bio-reduction.

Methanogenic bacteria/archaea are able to convert hydrogen and carbon dioxide to methane according to the following reaction:



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This reaction, with a standard reaction Gibbs free energy of -228.1 kJ/mol at 55°C is strongly favored compared to bio-reduction. The formation of 1 mol methane, out of 4 mol hydrogen and 1 mol CO₂, will result in a significant pressure drop. This drop is indeed observed in batch tests operated with a gas composition of 80%H₂/20%CO₂. The consumption of hydrogen through this unwanted side reaction has a retarding, or even inhibiting effect on bio-reduction, where a high concentration of hydrogen is essential to reach a reaction Gibbs free energy value <-20 kJ/mol. Furthermore, side consumption of hydrogen gas will increase the cost of the process. Therefore, it is necessary to reduce the methanogenic activity as much as possible. There are various ways to suppress methanogenic activity, but the most obvious solution is to reduce the amount of CO₂. Prove of this approach was found in batch tests operated with hydrogen, where only minimal amounts of methane were detected.

Another side reaction is sulfate reduction. Sulfate reduction, as described in equation 2.4, results in the following standard reaction Gibbs free energy values: -303.7 kJ/mol at 35°C and -306.9 kJ/mol at 55°C. This reaction is favorable compared to bio-reduction of pyrite at both temperatures. As shown in Figure 2.2, it is essential to keep the sulfide concentration in the solution as low as possible. However, through the reduction of sulfate (Figure 2.5), sulfide starts to accumulate (Figure 2.6) in the batch experiments and reaction Gibbs free energy values > -20 kJ/mol are easily reached. Sulfide accumulation should thus be prevented. Total removal of sulfate from the pyrite surface is, especially by acid washing on a large scale, an infeasible task. A better approach would be the removal of sulfide via hydrogen gas stripping. The continuous addition of hydrogen allows H₂S_(g) to escape from the solution, which results in a low H₂S_(aq) value. The sulfate concentration, however, should be kept as low as possible since sulfate reduction consumes 4 times more hydrogen compared to bio-reduction of pyrite. Thus, costs will increase if more sulfate is present.

To avoid methane formation and the accumulation of sulfide a controlled experiment was performed in a gas lift loop reactor at pH 5 and a temperature of 35°C. A gas composition of 95% H_2 /5% CO_2 was used to suppress methanogenic activity. Sulfide was removed continuously from the reactor liquor by recycling the gas phase through a $ZnCl_2$ solution. This way of removing $H_2S_{(g)}$ was found to be efficient since no sulfide (>0.1 mg/L) was detected in the reactor liquor. At pH 5 a concentration of 0.003 mmol/L (0.1 mg/L) sulfide is already low enough to obtain a reaction Gibbs free energy value <-20 kJ/mol (see Figure 2.2). Since the sulfide concentration in the reactor was even lower, enough energy for the bacteria could be gained from the reduction of pyrite. However, bio-reduction of pyrite was not observed in the reactor experiment. Though sulfate reducing bacteria were present during the whole run, they were not able to use pyrite as an alternative electron acceptor. Possibly it has something to do with transport of electrons to a solid phase instead of an ion. Bio-oxidation of pyrite is also not a process whereby bacteria accept 15 electrons directly from the mineral. Bio-oxidation proceeds because bacteria are able to oxidize aqueous Fe^{2+} into Fe^{3+} and S^{2-} into sulfuric acid. The oxidative attack of Fe^{3+} results in the destruction of pyrite and the solubilization of its constituents (Rohwerder et al., 2003).

If bio-reduction of pyrite is not feasible via direct donation of electrons, but depends on the dissolution of the mineral, the reaction is expected to proceed very slowly at pH 5, 35°C since no increase in iron was observed after 7 days during the reactor run. In that case, the selection of more acidic conditions to stimulate the dissolution of pyrite could be worth investigating. Alkaline conditions are not favored since the accumulation of HS^- will inhibit the reaction. The reactor was operated over a period of 40 days. The time needed to develop a bacterial strain able to reduce pyrite could have been too short. Since the Gibbs free energy value for methane formation is more favorable than bio-reducing pyrite, these bacteria will finally take over the system.

One source of hope for bio-reduction as a process is that this study only investigated cubic and rather pure pyrite. Thermodynamics for this type of pyrite are less favorable than for gold bearing pyrite ores, which always have high amounts of arsenic (Reich et al., 2005). The incorporation of metal impurities affects the stability of the structure of pyrite. These minerals are not only easier to reduce, but also tend to contain the higher gold concentrations and are thus economically more interesting.

6 Conclusion

The use of batch tests was found to be efficient to screen different conditions for the bio-reduction process. In theory, bio-reduction is possible when hydrogen sulfide concentrations are kept sufficiently low. In batch tests two side reactions occurred: methane formation and sulfide accumulation as a result of sulfate reduction. To suppress methane formation and accumulation of sulfide a gas lift loop reactor run was performed at pH 5, 35°C, 95% H_2 /5% CO_2 . Although these conditions were met, a bio-reduction reaction of pyrite did not occur. More research is necessary to investigate if bio-reduction can be achieved at other conditions, such as operation under pressure or using a different set of microbes, and whether the rates under such conditions will support industrial reduction to practice.

The effect of anaerobic processes on the leachability of an arsenopyrite refractory ore

3

This chapter is based on the published paper:
Hol, A., Van der Weijden, R.D., Van Weert, G., Kondos,
P., Buisman, C.J.N., Minerals Engineering, 2011, 24,
535-540.



Abstract

Gold is commonly liberated from sulfide minerals via oxidative destruction techniques. To circumvent the formation of sulfuric acid and to reduce the amount of energy required for these processes two alternative anaerobic processes based on sulfate reducing bacteria are investigated for arsenopyrite in this study. The first alternative, “bio-reduction” is expected to alter the structure of arsenopyrite via reduction of the mineral-sulfur to hydrogen sulfide, yielding a sulfur depleted residue that probably contains the gold. The second alternative “anaerobic oxidation” focuses on the mineral-arsenic which under anaerobic conditions can be oxidized to arsenite and subsequently precipitates as orpiment, which may contain the gold.

Both alternatives were investigated with gas lift loop reactor experiments performed at pH 5 and 35°C. These experiments showed that sulfate reducers were able to reduce sulfate from the reactor fluid, but that they were not able to use arsenopyrite as an electron acceptor (bio-reduction) or donor (anaerobic oxidation) under the selected conditions. As a result the gold leachability of the ore concentrate was not improved. To make the mineral more accessible for the leach solution the solubilization of lattice constituents from arsenopyrite that can be biologically reduced/anaerobically oxidized, should be stimulated. In addition, the concentration of arsenite needs to be limited to preserve the activity of sulfate reducing bacteria.

1 Introduction

Gold is a precious metal commonly associated with sulfide minerals like arsenian pyrite ($\text{FeAs}_x\text{S}_{2-x}$), and arsenopyrite (FeAsS). Since the gold is encapsulated in the crystal lattice of these minerals, destruction or alteration of the ore to liberate the submicron and/or structurally bound gold is necessary. Fine grinding is generally not sufficient for these refractory ores and additional chemical techniques are necessary. Most commonly, oxidation techniques like roasting, pressure oxidation and bacterial oxidation are used to liberate the gold.

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Costs of roasting arsenopyrite (AsPy) are increased by the $\text{As}_2\text{O}_{3(g)}$ and $\text{SO}_{2(g)}$ removal from the roaster gas effluent, since there is no market for the products (Mikhail and Turcotte, 1992). Pressure oxidation in autoclaves results, initially, in Fe^{3+} , SO_4^{2-} and H_3AsO_4 , but further reaction produces ferric arsenate (scorodite), hematite, ferric sulfates and jarosite residues (Weir and Berezowsky, 1986; Papangelakis and Demopoulos, 1990). Addition of $\text{CaCO}_3/\text{Ca}(\text{OH})_2$ to this slurry increases the pH needed for cyanide extraction, but yields impure gypsum that must be disposed of in an environmentally acceptable way. Bio-oxidation of AsPy yields Fe^{3+} , H_3AsO_4 , and SO_4^{2-} , but jarosites and iron arsenates are also formed (Carlson et al., 1992; Tuovinen et al., 1994). Similar to pressure oxidation, costs of bio-oxidation are increased by the neutralization of sulfuric acid prior to cyanidation. Costs of bio-oxidation are also increased by the use of compressors and agitators to provide sufficient oxygen (air) and cooling needed to maintain a temperature of 40°C (Olson et al., 2003; Rawlings, 2004).

In this chapter two alternative processes, bio-reduction of mineral-sulfur and anaerobic oxidation of mineral-arsenic are theoretically and experimentally investigated for the treatment of refractory ores containing AsPy. These alternatives may have a lower energy and chemicals demand and produce lower volumes of valueless waste products than with the oxidative processes.

2 Theory

Both bio-reduction and anaerobic oxidation are processes based on sulfate (sulfur) reducing bacteria. Process conditions selected, pH 5 and 35°C, are therefore those where these bacteria seem to thrive well as demonstrated in chapter 2. In theory bio-reduction of pyrite is feasible, but under the selected conditions no reduction reaction was established (chapter 2). Compared to pyrite, AsPy can be expected to be more susceptible to bio-reduction, because of the different crystal structure due to incorporation of arsenic (Abraitis et al., 2004). In addition, gold tends to concentrate in sulfide minerals that contain arsenic (Dunn et al., 1995), which for AsPy can increase up to thousands of ppm (Abraitis et al., 2004; Reich et al., 2005).

Bio-reduction is expected to alter the mineral via reduction of the AsPy-sulfur, which may act as an electron acceptor when not present in its most reduced (S^{2-}) state. Iron in AsPy is most likely present as Fe^{2+} , but arsenic could either be present as As^0 (Foster et al., 1998) or As^{-1} (Simon et al., 1999; Savage et al., 2000) as indicated by X-ray absorption spectroscopic studies (XANES/EXAFS). X-ray photoelectron spectroscopy (XPS) performed by Nesbitt et al. (1995) indicated that 85% of the arsenic in AsPy is present as As^{-1} with the remaining 15% present as elemental arsenic. Bio-reduction of AsPy is therefore plausible since 85% of the sulfur is present as $(As^{-1})S^{-1}$. As shown by Eq. (3.1), the bio-reduction of AsPy is expected to result in Fe^{2+} , H_2S , and a sulfur depleted Loellingite ($FeAs_2$) type of structure that probably contains the gold.

In contrast to bio-reduction, anaerobic oxidation will result in complete dissolution of the mineral via oxidation of the arsenic. The proposed theory is that sulfate reducing bacteria might be able to use arsenic, next to hydrogen, as electron donor since arsenic is present as As^0/As^{-1} , which can be oxidized to As^{3+} . For anaerobic oxidation with sulfate as electron acceptor, the reaction in Eq. (3.2) is proposed. Initially, Fe^{2+} , H_3AsO_3 and H_2S are formed but at pH 5, 35°C, H_3AsO_3 is expected to precipitate with H_2S as yellow As_2S_3 (orpiment) see Figure 3.1 and Eq. (3.3). Next to being the phase where the gold will probably end up (Renders and Seward, 1989; Cardile et al., 1993), the formation of orpiment is essential in the anaerobic oxidation process because the toxic compound H_3AsO_3 (Jackson et al., 2003) is removed in that way, and bacterial activity is maintained.

Table 3.1: Stoichiometry and calculated standard reaction Gibbs free energy values at 35°C for conversions proposed to take place under anaerobic conditions in the presence of AsPy.

Eq.	Reaction	$\Delta G_r^0(T)$ (kJ/mol)*
<i>Bio-reduction</i>		
3.1	$\text{FeAsS} + \frac{1}{2}\text{H}_2 + \text{H}^+ = \frac{1}{2}\text{Fe}^{2+} + \frac{1}{2}\text{FeAs}_2 + \text{H}_2\text{S}$	-58.4
<i>Anaerobic oxidation</i>		
3.2	$\text{FeAsS} + \frac{1}{2}\text{SO}_4^{2-} + \frac{1}{2}\text{H}_2 + 3\text{H}^+ = \text{Fe}^{2+} + \frac{1}{2}\text{As}_2\text{S}_3 + 2\text{H}_2\text{O}$	-198.0
<i>Orpiment formation</i>		
3.3	$\text{H}_3\text{AsO}_3 + 1\frac{1}{2}\text{H}_2\text{S} = \frac{1}{2}\text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$	-75.2
<i>Sulfate reduction</i>		
3.4	$\frac{1}{2}\text{SO}_4^{2-} + 2\text{H}_2 + \text{H}^+ = \frac{1}{2}\text{H}_2\text{S} + 2\text{H}_2\text{O}$	-151.8

* from HSC Chemistry 6.12 (Outokumpu technology)

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The standard reaction Gibbs free energy (ΔG_r^0) at 35°C (Table 3.1) shows that both bio-reduction and anaerobic oxidation yield enough energy to allow a biologically mediated conversion of AsPy, since values lower than -20 kJ/mol per mol reactant conversion are obtained (Schink, 1997). Anaerobic oxidation of AsPy gives an even lower ΔG_r^0 than sulfate reduction, Eq. (3.4).

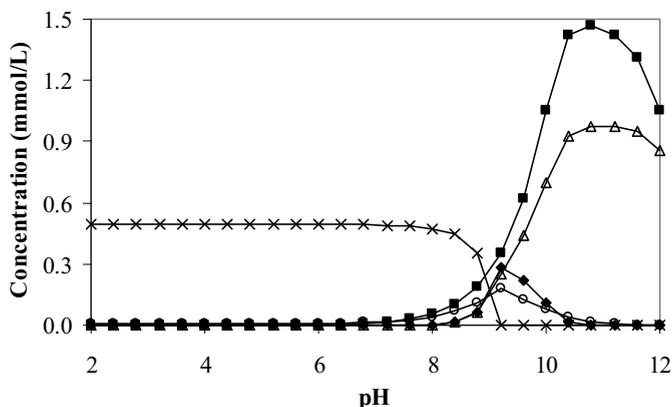


Figure 3.1: Solubility of orpiment at 35°C, 1 atm, as function of pH. Figure was constructed with OLI Stream Analyzer 2.0 using 1 mmol/L H_3AsO_3 and 1.5 mmol/L H_2S as inflow. Species shown are: As_2S_3 (x), HS^- (■), AsO_2^- (△), $\text{As}_2\text{S}_4^{2-}$ (◆) and HAsO_2 (○).

The environmental impact of the anaerobic processes is reduced, since no acidic waste streams are produced. Energy is also saved in the anaerobic processes by the lower gas demands needed to complete the reactions compared to bio-oxidation. Furthermore, the generated H_2S in the bio-reduction process can be further processed into high-purity bio-sulfur (Janssen et al., 2001) that can be used as soil fertilizer or for the production of gold lixiviants such as thiosulfate or bisulfide. Removal of H_2S from the system will also, either via gas stripping (bio-reduction) or precipitation (anaerobic oxidation), stimulate the reaction to proceed to the product side. The production of orpiment for anaerobic oxidation, although good to maintain the process, is environmentally less favorable, since it is known to be an unstable waste product (Robins et al., 2001).

In order to investigate the amount of gold that can be liberated from AsPy via bio-reduction or anaerobic oxidation, gas lift loop reactor experiments were performed.

3 Materials and methods

3.1 Minerals

A refractory concentrate was obtained from Red Lake District, NW. Ontario (Goldcorp). Ore from this location is cyanide leached in the mill and then floated into a totally refractory (to cyanide leaching) concentrate. The dried concentrate was additionally homogenized using a Retsch SM2000 cutting mill. Particle size distribution was analyzed, in triple, by a Beckman Coulter laser LS 230 and found to have a P80 of 34 μm on average. The concentrate composition was analyzed via a combined microwave/ICP method. Microwave digestion of the concentrate was performed with Aqua Regia ($\text{HCl}:\text{HNO}_3 = 3:1$). The resulting liquor was filtered, adjusted to a known volume, and analyzed by ICP. Most important elements measured in the concentrate are (in wt%): Al, 2.3; As, 8.6; Ca, 3.9; Fe, 20.4; Mg, 1.7; and S, 12.6. Based on the arsenic percentage, the concentrate contains 18.7 wt% AsPy. Next to AsPy (FeAsS), XRD analysis detected other minerals in the concentrate of which the most important are; quartz (SiO_2), dolomite ($\text{CaMg}(\text{CO}_3)_2$), pyrite (FeS_2) and pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$). Refractory gold (~ 100 g/ton) is mainly present in the AsPy grains as indicated by microprobe analysis. Prior to addition to the reactor, the ground concentrate was washed with 2 M HCl and thoroughly rinsed with demineralized water, to remove surface oxides and the majority of carbonates.

3.2 Growth media

For the bio-reduction experiment (Eq. 3.1) a defined medium as described by chapter 2 was used. For the anaerobic oxidation experiment (Eq. 3.2) a comparable medium was used with 0.41 g/L KH_2PO_4 , 0.30 g/L NH_4Cl , alkaline trace elemental solution without $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, and 2.13 g/L Na_2SO_4 as sulfate source. All chemicals were of analytical grade and supplied by Merck.

3.3 Bacterial sources

Sludges from different sources proven to contain bacteria that were able to reduce sulfate (sulfur) were used. One sample, sand-filter backwash water (BWW), was taken from the wastewater treatment plant of a Dutch oil refinery. Other sludges were obtained from a lab-scale sulfate reducing reactor operated at pH 5 (Bijmans et al., 2008) and from a vegetated marsh area near Skidaway (Oceanographic Institute in Georgia, USA) (King et al., 2000).

3.4 Experimental setup

Gas lift loop reactor experiments were performed in the same reactor setup as described by chapter 2. An overview of the experimental details is given in Table 3.2.

Table 3.2: Gas lift loop reactor experiments performed to investigate the bio-reduction and anaerobic oxidation of an AsPy concentrate.

Experimental details	Bio-reduction	Anaerobic oxidation
Start amount of concentrate (gram)	500	500
Reactor volume (L)	4.70	4.65
Operation mode	Batch	Continuous
Hydraulic Retention Time (days)	-	7
Gas recycle flow rate (L/min)	6-8	6-10
Gas addition (10 mL/min)	95% H_2 /5% CO_2	95% H_2 /5% CO_2
ZnCl_2 (0.5 M) gas recycle stripping	yes	no
NaOH (1 M) gas effluent stripping	yes	yes

Both bio-reduction and anaerobic oxidation were operated at pH 5 and a temperature of 35°C. The sludge mixture added to the experiments composed of 50 mL BWW, centrifuged at 4000 g for 10 minutes and resuspended in medium before addition to the reactor, 10 mL pH 5 sulfate reducing sludge, and 10 mL Skidaway sludge. As the anaerobic oxidation experiment was operated continuously, influent (medium) sparged with N_2 was added to the reactor at a rate of 0.46 mL/min.

The effluent left the reactor via the internal settler, external settler, water lock, and was collected in the effluent vessel (water lock overflow). The gas recycle strip vessel was disconnected for the anaerobic oxidation experiment, so H_2S , formed in excess, was able to build up in the system. The sparger used in the anaerobic oxidation experiment consisted of three holes, one operating sparger and two back-ups. For the bio-reduction experiment the reactor was packed in aluminum foil to exclude the effect of light.

3.5 Analysis techniques

Samples of solutions were filtered over a $0.2\ \mu\text{m}$ filter and analyzed for their free metal composition by a Varian ICP-OES. Iron was also measured by Dr Lange kit LCK-320 ($0.2\text{--}6.0\ \text{mg/L Fe}^{2+/3+}$) on a Hach Lange Xion 500 spectrophotometer. Sulfate was measured on a Dionex DX 600 Ion Chromatograph equipped with an Ionpac AS17 column ($2\text{mm} \times 250\text{mm}$). Dr Lange sulfide kit, LCK-653 ($0.1\text{--}2.0\ \text{mg/L S}^{2-}$), and a Hach Lange Xion 500 spectrophotometer, were used to measure Sulfide_{T(aq)} ($\text{S}^{2-} + \text{HS}^- + \text{H}_2\text{S}_{(\text{aq})}$) in filtered ($0.2\ \mu\text{m}$) solutions and to measure the amount of $\text{H}_2\text{S}_{(\text{g})}$ captured in recycle and effluent strip vessels. Additionally, this method was used to measure $\text{H}_2\text{S}_{(\text{g})}$ in the gas recycle stream. Gas samples were injected into a vial containing a $0.1\ \text{M NaOH}$ solution to capture the $\text{H}_2\text{S}_{(\text{g})}$ as $\text{HS}^-/\text{S}^{2-}$. Via this additional step $\text{H}_2\text{S}_{(\text{g})}$ becomes available for sulfide determination with Dr Lange. Biogas was analyzed on an Interscience GC 8000 series with 2 parallel columns; a Varian Porabond-Q ($50\text{m} \times 0.53\text{mm}$) and a Varian molecular sieve 5A ($50\text{m} \times 0.53\text{mm}$) to measure O_2 , N_2 , CH_4 and CO_2 .

4 Results

4.1 Bio-reduction of arsenopyrite

To make bio-reduction of AsPy proceed to the product side, the $\text{H}_2\text{S}_{(\text{aq})}$ concentration was kept as low as possible by recycling the gas phase through a $0.5\ \text{M ZnCl}_2$ solution. This way of removing H_2S was found to be efficient since no sulfide ($>0.003\ \text{mmol/L}$) was detected in the reactor solution during the experiment (data not shown). Since N_2 -sparged medium was only added manually to maintain a constant reactor volume, the experiment can be considered as a batch with the results as shown in Figure 3.2.

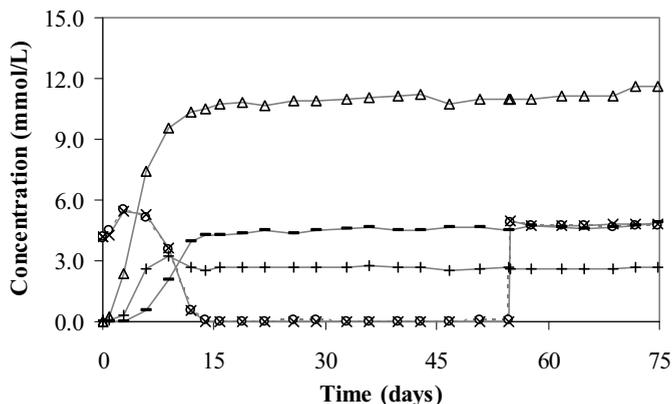


Figure 3.2: Bio-reduction of Red Lake concentrate at pH 5, 35°C, 95% H_2 /5% CO_2 , in a gas lift loop reactor. Sulfur(T) (○), iron (Δ) and arsenic (+) were measured by ICP, sulfate (×) by IC, and $H_2S_{(g)}$ stripped (-) is the calculated value of $H_2S_{(g)}$ removed per liter reactor volume via gas recycling through a 0.5 M $ZnCl_2$ solution. On day 55, 5 mmol/L Na_2SO_4 was added to the reactor to check for remaining sulfate reducing activity.

In spite of the fact that prior to addition to the reactor, the concentrate was washed with acid and thoroughly rinsed with demineralized water, sulfate was present and increased from 4.2 to 5.4 mmol/L in the first few days. After 3 days, sulfate reduction commences, as indicated by the decrease in sulfate and production of $H_2S_{(g)}$. Sulfate as electron acceptor was depleted after 2 weeks and after that period bio-reduction of AsPy (Eq. 3.1) should start. Based on Eq. (3.1) an extra increase in sulfide (in the strip vessel) and iron could thus be expected, but was not observed.

To check if sulfate reducing bacteria were still active, 5 mmol/L Na_2SO_4 was added to the reactor on day 55. In the next 20 days no decrease in sulfate or increase in sulfide was observed. The activity check was continued in batch tests, in duplicate, to be certain that no sulfate reducers were present anymore. Closed serum bottles with a gas phase of 80% H_2 /20% CO_2 , were inoculated with 50 mL unfiltered or 0.2 μm filtered (blank) reactor solutions and incubated at 35°C. In these tests sulfate reduction also did not occur since no decrease in sulfate was observed in blanks and unfiltered reactor solutions over an additional period of 50 days (data not shown).

As the redox potential of the solution was around -180 mV (Figure 3.3), iron dissolves as Fe^{2+} , which was confirmed by iron measurements with Dr Lange kit LCK-320 (data not shown), and aqueous arsenic is most likely present as H_3AsO_3 . Analysis of the gas composition showed that methanogens were also not active after 15 days as no methane was detected (Figure 3.3). The drop in CO_2 observed around day 45 could thus not be ascribed to methanogenic activity.

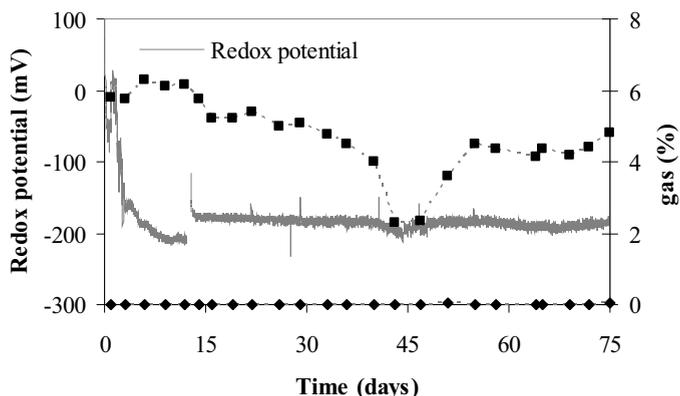


Figure 3.3: Redox potential (Ag/AgCl) and gas composition development during the bio-reduction of Red Lake concentrate at pH 5, 35°C, 95% H_2 /5% CO_2 . Gas composition is only shown for CO_2 (■) and CH_4 (◆). The change in redox potential on day 12 is due to a power failure of 14 hours, during which the desired pH remained unchanged, but the temperature dropped from 35°C to 24°C (not shown in Figure).

At the experimental pH and the amount of sulfide produced over time, one could expect all aqueous arsenic to be removed as orpiment (Figure 3.1). The formation of orpiment was indeed observed as a yellow precipitate started to coat stationary reactor parts (internal settler). Based on the slight drop in arsenic, observed after day 9 (Figure 3.2), it can be calculated that 15% of the produced sulfide precipitated as orpiment and 85% was removed by the ZnCl_2 solution. Precipitation of arsenic only seems to occur when sulfate reduction reaches its highest conversion rate as indicated by the steep decrease between day 9 and 12 (Figure 3.2).

4.2 Anaerobic oxidation of arsenopyrite

In order to let anaerobic oxidation of AsPy proceed, the gas phase was maintained at 95% H_2 /5% CO_2 and sulfate was added to the reactor. An overview of the results is given in Figure 3.4.

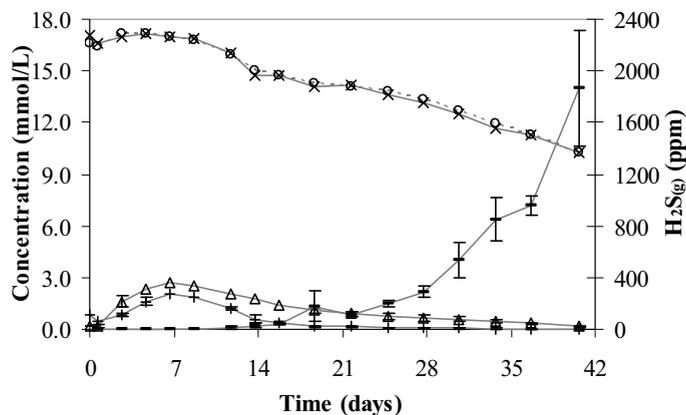


Figure 3.4: Anaerobic oxidation of Red Lake concentrate at pH 5, 35°C, 95% H_2 /5% CO_2 , in a continuous (liquid) gas lift loop reactor. Sulfate was added at a concentration of 15mmol/L. Sulfur(T) (○), iron (Δ) and arsenic (+) were measured by ICP, sulfate (×) by IC. $H_2S_{(g)}$ (-) represents the amount of sulfide able to build up in gas phase of the reactor. The reactor experiment was performed in duplicate of which the average and standard deviations (>5%) are shown with a vertical bar.

The concentration of sulfate in the reactor liquid and influent is 15 mmol/L. In Figure 3.4, an initial concentration of 16 mmol/L sulfate is measured, which indicates that similar to bio-reduction sulfate is released from the concentrate after washing. After a week, sulfate reduction is obvious, since the concentration of sulfate drops below 15 mmol/L. The availability of sulfide causes arsenic to precipitate, as indicated by its fast decrease in Figure 3.4. After 2 weeks, sulfide starts to build up in the gas phase and the arsenic became depleted. Aqueous sulfide (not shown) increased from 0 up to 0.065 mmol/L comparable to the trend obtained for $H_2S_{(g)}$ (Figure 3.4). The curve for aqueous iron seems to be dominated by the wash-out of the solution.

In the first week, a drop in the redox potential to -200 mV is observed for both reactors, see Figure 3.5. For a few days this redox potential was stable, but started to drop further to -380 mV. This drop was not observed in the bio-reduction experiment (Figure 3.3) and is therefore probably related to the accumulation of sulfide. Finally, a redox potential of approximately -270 mV is obtained for both reactors.

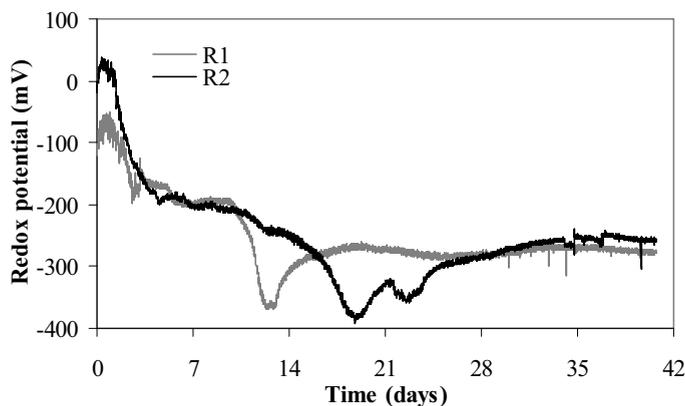


Figure 3.5: Redox potential (Ag/AgCl) development for the anaerobic oxidation of Red Lake concentrate at pH 5, 35°C, 95% H_2 /5% CO_2 , in a continuous (liquid) gas lift loop reactor without H_2S removal. The experiment was performed in duplicate and the measured redox potential for both reactors (R1 and R2) is shown separately.

At pH 5 and a redox potential of -270 mV, iron and arsenic are expected to be in solution as Fe^{2+} and H_3AsO_3 . Iron was indeed present as Fe^{2+} (Dr Lange kit LCK-320, data not shown). The evidence for dissolution of As via H_3AsO_3 was visually observed by precipitation of yellow orpiment on stationary reactor parts (internal and external settlers) within the first two weeks. A black precipitate started to form as well, which became the predominant color with time. This occurrence was different from that in the bio-reduction experiment.

SEM-EDX analysis of the final coating showed that the yellow precipitate, with a nodule like shape, consisted of amorphous orpiment. The black precipitate was found to be a mixture of two different iron containing minerals: crystalline baricite ($(Mg,Fe,Mn)_3(PO_4)_2 \cdot 8H_2O$) and amorphous FeS .

4.3 Cyanide leach of the treated residues

Results of CIL (Carbon In Leach) gold extraction tests are summarized in Table 3.3. Gold is more concentrated in the residues obtained after treatment. This small difference can probably be related to the acid wash, which was used to clean the concentrate prior addition to the experiments. ICP analysis showed that during the acid wash 13.5 gram Ca and 4.4 gram Mg were removed from 500 gram concentrate. If it is assumed that both Ca and Mg were present as carbonates, 48.9 gram was removed from the concentrate. Since untreated concentrate was not cleaned with acid the calculated amount of gold for an acid cleaned concentrate is therefore 104.3 g/t.

Table 3.3: Gold leachability of untreated concentrate from Red lake and of its residues after bio-reduction and anaerobic oxidation.

Analysis	Untreated concentrate	Bio-Reduction	Anaerobic oxidation	
			R1	R2
Total gold content (g/t)	94.1	101.9	103.8	112.8
Distribution solution (%)	0.4	0.2	0.1	0.1
Distribution activated carbon (%)	5.8	5.3	4.7	6.0
Distribution residue (%)	93.8	94.5	95.2	93.9

Though the gold is more concentrated in the residues, its gold recovery is not improved, since ~ 95% of the gold is still not leachable. Red Lake concentrate retains its refractory character despite a bio-reduction or anaerobic oxidation treatment.

A calculation for the anaerobic oxidation experiment was done to investigate if the initiated reactions were a result of incomplete removal by the 2M HCl acid wash of oxidized fractions in the concentrate. To determine the oxidized fraction of the concentrate, an acid wash at pH 2 (N₂ flushed) was performed in the gas lift loop reactor. Effluents were collected and measured for their metal composition by ICP (Table 3.4).

Table 3.4 shows that an acid wash at pH 2 removes more iron, arsenic, and sulfur from the concentrate than when cleaned with 2M HCl. The 2M HCl wash is thus by far not efficient enough to remove the complete oxidized fraction of this concentrate, which became available in the reactor (Table 3.4f). If it is assumed that sulfate, after conversion to sulfide, reacted with arsenic and iron able to dissolve into the reactor solution, 11.1 mmol As₂S₃ and 68.1 mmol FeS could have been precipitated. If the assumption is correct, the excess of sulfide, 16.4 mmol,

should thus be recovered in the 1M NaOH vessel used to strip the effluent gas. With a recovered sulfide concentration of 17.8 mmol this balance fits. The excess amount of sulfide captured in the strip vessel can possibly be ascribed to the formation of baricite, which precipitated part of the iron. Gold recovery is not improved, because only the oxidized fraction reacted.

Table 3.4: Balance for iron, arsenic, and Sulfur (T) based on ICP measurements of the 2 different acid washes and reactor solutions of the anaerobic oxidation experiment.

Balance	Fe (mmol)	As (mmol)	S _T (mmol)
a. Removed via acid wash at pH 2 (2 days)	182.4	36.3	68.1
b. Removed via wash with 2M HCl (¹ / ₂ hour)	95.9	2.6	59.7
c. Able to dissolve in the reactor (c=a-b)	86.5	33.7	8.4
d. Added via medium	0.0	0.0	511.2
e. Recovered from effluents	18.4	11.5	401.8
f. Reacted/precipitated (f=(c+d)-e)	68.1	22.2	117.8

A similar balance as in Table 3.4 was made for the bio-reduction of AsPy and the reactions/products observed during this experiment can also be ascribed to the incomplete removal of the oxidized fraction from the concentrate (calculation not shown).

5 Discussion

Thermodynamic calculations showed (Table 3.1) that the requirement of a ΔG_r^0 (35°C) value <-20 kJ/mol for bacterial growth is reached for both the bio-reduction and anaerobic oxidation of AsPy. However, experiments under the chosen conditions did not result in bio-reduction or anaerobic oxidation. AsPy is thus not used by the sulfate (sulfur) reducers as a possible electron acceptor/donor, which probably can be ascribed to one, or a combination, of the following factors:

- The lack of liberation of AsPy
- The sulfur and arsenic in AsPy are not readily bio-available
- The lack of removal of toxic dissolved arsenic as orpiment

Liberation refers to the surfaces of AsPy grains that are available to take part in a bio-reduction or anaerobic oxidation reaction. As shown by microprobe analysis, performed on polished slide sections of Red Lake concentrate, most of the AsPy occurs as free grains but a part is also enclosed by other minerals. Only the surfaces of the free AsPy grains are in principle accessible for bacteria. In case the AsPy is enclosed by quartz or pyrite this part will not

become accessible during bio-reduction or anaerobic oxidation of this concentrate. Quartz is inert and bio-reduction of pyrite does not occur under the chosen conditions as shown in chapter 2. In case the AsPy is enclosed by feldspar or carbonates, the associated mineral will dissolve under the selected conditions. At pH 5, liberation of AsPy is thus not expected to be an inhibiting factor, since the majority of the AsPy surfaces in this Red Lake concentrate were available for the bacteria.

Another factor that may influence the process is the phase in which the energy source is provided to the bacteria. Ideally, to be bio-available an element should be within the physical proximity of the bacteria and be dissolved in the aqueous phase. Elements fixed in the crystal matrix of a mineral are thus generally considered to be unavailable. Since sulfur and arsenic are both fixed in the crystal lattice of AsPy, a reaction that induces dissolution of these elements should occur. In the reactor experiments, dissolution of arsenic and sulfur from the concentrate is observed, but calculations can ascribe this to the inefficient removal of oxidized species during the acid wash. In the bio-oxidation of AsPy, dissolution is indirectly induced by the combined attack of Fe^{3+} and sulfuric acid. Under anaerobic conditions the role of Fe^{3+} is negligible, but protons could induce a dissolution reaction. Though at pH 5, 35°C, the effect of acid dissolution seem to be rather small as no continuous increase in iron is observed in Figure 3.2. Since AsPy is a semiconducting mineral, next to the effect of protons, dissolution can also be triggered electrochemically. In the gas lift loop reactor experiments redox potentials of -180 mV (bio-reduction) and -270 mV (anaerobic oxidation) are reached. Eh-pH diagrams reported by Beattie and Poling (1987) and Vink (1996) show that at pH 5, -180 mV, Fe^{2+} and H_3AsO_3 are the dominant species, which shifts to Fe^{2+} and As_2S_3 at -270 mV. Cyclic voltammograms obtained by Almeida and Giannetti (2003) at pH 4.5, 25°C, showed that there are three reduction potentials for AsPy: Following the voltammogram to more reducing conditions, first Fe^{3+} is reduced to Fe^{2+} , then orpiment-like compounds are reduced, and finally S reduction takes place. Since the species observed during the bio-reduction and anaerobic oxidation experiment are in agreement with the Eh-pH diagrams for the chosen conditions, the obtained redox potentials were not low enough to electrochemically decompose AsPy. Dissolution of arsenic and sulfur is thus negligible under the chosen conditions and therefore sulfate reduction with hydrogen (Eq. 3.4) is preferred.

As shown by the bio-reduction of AsPy, sulfate reducers were not able to maintain themselves during the period sulfate was absent. As the rate of gas recycling through a $ZnCl_2$ solution removed sulfide too fast from the reactor solution to allow orpiment formation, it is believed that the toxicity of arsenic is the main cause for the loss of sulfate reducers. The un-complete removal of arsenic from the solution might therefore be a reason to not completely exclude the possibility of bio-reduction.

Different from the bio-reduction of pyrite (chapter 2), is that methane was not produced when sulfide production ceased. So, like sulfate reducers, methanogens do not seem to be able to survive an arsenic concentration of 2.7 mmol/L either. According to Sierra-Alvarez et al. (2004) an arsenic concentration of 79.2 μM is already enough to decrease the activity of hydrogen-utilizing methanogens by 80% (IC_{80}). At an arsenic concentration 34x higher than IC_{80} , it is thus logical to observe no methanogenic activity at all. In order to maintain biological activity, it is thus necessary to control the arsenic concentration.

Under the chosen conditions, bio-reduction and anaerobic oxidation were found to be limited by the bio-availability of arsenic and sulfur. Bio-reduction was also inhibited by the presence of dissolved arsenic. Selection of conditions that promote dissolution of AsPy and that could maintain a low dissolved arsenic concentration are therefore still worth investigating. Changing the pH to more alkaline conditions could be interesting, since the redox potential of a solution decreases with pH. However, at higher pH values the solubility of orpiment increases (Figure 3.1) and iron sulfides, that possibly coat the mineral, start to precipitate. In addition, the liberation of AsPy decreases at higher pH values, because feldspar/carbonates will not dissolve. Lower pH values are thus preferred. Under acidic conditions, orpiment formation occurs if sufficient sulfide is available. To prevent the increase in arsenic, as observed in the bio-reduction experiment, the stripping efficiency should thus be lowered or controlled to allow sulfide in the system. Precipitation of orpiment is not expected to have an influence on the liberation of AsPy, since it only seems to precipitate in reactor parts free of motion. The liberation of AsPy can be increased by further milling, but this will make the process more expensive and not lead to a significant improvement for this concentrate. At pH 5, the solubility of AsPy was found to be negligible, but as shown by Mc Kibben et al. (2008), non-oxidative dissolution of AsPy at pH 2 is also not significant compared to oxidation by Fe^{3+} and dissolved O_2 . Changing the pH to promote dissolution by acid is thus not recommendable. A lower pH and/or a higher temperature will induce a shift to a different set of microbes, which

may be able to use AsPy as electron acceptor/donor. To obtain bio-reduction and anaerobic oxidation at pH 5, 35°C, the best option is to stimulate electrochemical dissolution, which may be achieved either by the addition of a redox mediator or via external addition of electrons.

6 Conclusion

The anaerobic processes, bio-reduction and anaerobic oxidation, investigated at pH 5 and 35°C, were found to be unsuccessful in improving the leachability of an AsPy containing refractory concentrate. Although sulfate reducers were able to reduce sulfate under these conditions and deal with high iron concentrations, they were not able to use AsPy as an alternative electron acceptor/donor. To increase the bio-availability of arsenic and sulfur the dissolution of AsPy should be stimulated and to maintain sulfate reducing activity arsenic should be removed from the solution.

**Processing of
arsenopyritic gold
concentrates by
partial bio-oxidation
followed by bio-
reduction**

4

This chapter is based on the submitted paper:
Hol, A., Van der Weijden, R.D., Van Weert, G., Kondos,
P., Buisman, C.J.N., 2011.



Abstract

Gold is commonly liberated from sulfide minerals by chemical and biological oxidation. Although these technologies are successful, they are costly and produce acidic waste streams. Removal of mineral-sulfur to overcome the mineralogical barrier could also be done by bio-reduction, producing H_2S . To make the sulfur in these minerals available for bio-reduction, the use of partial bio-oxidation as a pre-treatment to oxidize the sulfides to elemental sulfur was investigated in gas lift loop reactor experiments. Experiments at $35^\circ C$ using a refractory concentrate showed that at pH 2 arsenopyrite is preferentially partially oxidized over pyrite and that elemental sulfur can be subsequently converted into hydrogen sulfide at pH 5 via bio-reduction using H_2 gas. A single partial bio-oxidation/bio-reduction cycle increased the gold recovery of the concentrate from 6% to 39%. As elemental sulfur seems to inhibit further oxidation by covering the mineral surface, several cycles may be required to reach a satisfactory gold recovery. Depending on the number of cycles this method could be an interesting alternative to bio-oxidation.

1 Introduction

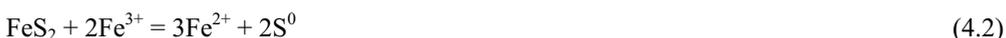
Gold is a precious metal commonly associated with refractory sulfide minerals. Fine grinding is often not sufficient to liberate the gold and therefore additional oxidation techniques like roasting, pressure oxidation and bacterial oxidation are required. Although these techniques have proven to be successful to reach satisfactory gold recoveries there are some drawbacks. Operating costs of roasting are high due to $As_2O_{3(g)}$ and $SO_{2(g)}$ removal from the off gas. Pressure (chemical) oxidation requires expensive equipment and pure oxygen gas for oxidation. Bio-oxidation yields impure sulfuric acid and consumes lots of energy to provide sufficient oxygen (air) and cooling to the reactors (Olson et al, 2003; Rawlings, 2004).

To reduce the costs and environmental impact of existing oxidation methods the bio-reduction of pyrite and arsenopyrite at pH 5 and 35°C was previously proposed and investigated (chapter 2 and 3). The resulting hydrogen sulfide, could be further processed into high purity elemental bio-sulfur, which, for example, can be used as a soil fertilizer (Janssen et al, 2001). However, it appeared that sulfur, when bound in the crystal lattice of a sulfide mineral, cannot be directly utilized by sulfate/sulfur reducing bacteria under those conditions. To make the mineral-sulfur bio-available for these anaerobic bacteria a combination between partial bio-oxidation and bio-reduction is therefore proposed in this chapter.

As with bio-oxidation, partial bio-oxidation is performed under acidic conditions with the main role of the bacteria to regenerate Fe^{3+} (Rohwerder et al, 2003), see equation 4.1.



The difference with bio-oxidation is that for partial bio-oxidation the oxygen concentration is kept at a level, high enough to bio-regenerate Fe^{3+} , but too low to allow the formation of sulfuric acid. In that case the oxidative attack on pyrite and arsenopyrite is expected to result in the formation of elemental sulfur as described by equation 4.2 and 4.3:



As no sulfuric acid is formed during partial bio-oxidation, 62-86% oxygen (and therefore aeration electrical energy) is saved compared to the conventional oxidation methods. Furthermore, less heat is generated and therefore less cooling is required.

Elemental sulfur can serve as a substrate for the sulfur/sulfate reducing bacteria. The removal of elemental sulfur by these bacteria, as described by equation 4.4, is essential as the presence of elemental sulfur will increase the cyanide consumption of the gold extraction process (Van Staden et al, 2008).



Another aspect is that elemental sulfur, when not metabolized by sulfur oxidizing bacteria, can accumulate and form a layer on the mineral surface preventing further oxidation by Fe^{3+} (Dopson and Lindström, 1999; Rohwerder et al, 2003). Depending on the concentrate properties, in particular its size distribution, a number of partial bio-oxidation/bio-reduction (ox/red) cycles may thus be required to obtain a satisfactory gold recovery (>90%). This chapter investigates the effect of one ox/red cycle on the leachability of an arsenopyrite refractory concentrate from Red Lake District (chapter 3).

2 Materials and methods

2.1 Pre-cultivation of iron oxidizers

To obtain an iron oxidizing culture a pre-cultivation with 3 different sludges/sediments and one pure culture was performed in a CSTR. The sludges/sediments known to contain iron oxidizers were collected from the Rio Tinto River (Spain), Chessy les Mines (France), and Black Hawk (CO, USA). The pure culture consisted of *Ferroplasma acidarmanus*, an iron oxidizing archaeon isolated from Iron Mountain, CA, USA (Dopson et al, 2004). To cultivate these bacteria the medium as described by Dopson and Lindström (1999) was enriched with Yeast extract (0.2 g/L), $FeSO_4 \cdot 7H_2O$ (20 g/L), 1 mL/L acid and alkaline trace elemental solution (chapter 2), and H_2SO_4 to set the desired pH. In the CSTR, the medium (1 L) was sparged with air, mixed at 400 rpm (magnetic stirrer), controlled at 35°C, and maintained at the desired pH with 4 M HCl/NaOH.

Initially, the 4 different oxidizing bacterial sources were mixed and cultivated at pH 3, the optimum pH to grow *Thiobacillus ferrooxidans* (Evangelou, 1998). After complete Fe^{2+} consumption, 50 mL of the pH 3 culture was transferred into fresh medium (end volume 1L) and cultivated at pH 2. This reactor solution was harvested, stored at 4°C, and used as inoculum for the partial bio-oxidation periods of the reactor experiments.

2.2 Experimental setup

An overview of the gas lift loop reactor experiments performed on refractory concentrate from Red Lake District (chapter 3), is given in Table 4.1. For the experiments, named after the concentrate (RL), the same reactor setup as described by chapter 2 was used. For experiment RL-1(ox/red) the pre-cultivation medium was adjusted and contained (in g/L): NH_4Cl , 0.19; KH_2PO_4 , 0.024; KCl , 0.10; NaCl , 0.116; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.10; $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.014; Yeast Extract, 0.01; and 1 mL/L acid and alkaline trace elemental solution. The medium for experiment RL-2(ox) was slightly different with a NH_4Cl and KH_2PO_4 concentration of 0.38 and 0.048 g/L, respectively. Both gas lift loop reactor media were set at pH 2 with H_2SO_4 . For RL-2(ox) this was done with 2.5 mL/L 4M H_2SO_4 . For the bio-reduction period of RL-2 the medium as described by chapter 2 was used.

Table 4.1: Gas lift loop reactor experiments performed to investigate the combination between partial bio-oxidation and bio-reduction on Red Lake (RL) concentrate.

Experiment	RL-1	RL-2.1	RL-2.2 ⁽¹⁾
Weighed concentrate (g)	500	1000	-
Acid wash	yes	yes	-
Concentrate used ⁽²⁾ (g)	440	889	141
Reactor volume (L)	4.61	4.34	4.79
Partial bio-oxidation	batch	continuous	continuous
Bio-reduction	batch	batch	batch
Demi wash ⁽³⁾	no	yes	yes
Gas composition ox. period	5%O ₂ 95%N ₂	5%O ₂ 5%CO ₂ 90%N ₂	5%O ₂ 5%CO ₂ 90%N ₂
Gas composition red. period	5%CO ₂ 95%H ₂	5%CO ₂ 95%H ₂	5%CO ₂ 95%H ₂
Sludge for oxidation ⁽⁴⁾	100 mL CSTR	100 mL CSTR 25 mL RL-1(ox)	100 mL CSTR 50 mL RL-2.1(ox)

(1) Solids left after RL-2.1 were used

(2) Calculated amount based on elements recovered from acid wash (ICP)

(3) A 2 day reactor wash with demi water (HRT ~ 12 hours)

(4) For bio-reduction the sludge composition is the same as described by chapter 2

The temperature of the reactors was maintained at 35°C and the pH was controlled at 2 (partial bio-oxidation) and 5 (bio-reduction) with 4 M HCl/NaOH. Influent (HRT ~ 7 days), continuously sparged with N₂, was only added if the reactor was operated continuously. Effluent, collected in the external settler, was manually drained in an effluent vessel to keep the water-lock clean. Gas, with the composition as described in Table 4.1, was added to the reactor at a rate of 10 mL/min. The gas recycle flow rate was manually controlled at 3 ± 1 L/min for the partial bio-oxidation period and 9 ± 2 L/min for the bio-reduction period. The condenser was set at a temperature of 20°C to cool down the gas stream. When operated under reducing conditions the recycle stripper was filled with 0.5 M ZnCl₂ solution and the effluent stripper with 1 M NaOH to capture H₂S_(g). A WUR designed rubber check valve was used as a sparger. The gas lift loop reactors were packed in aluminum foil to exclude the possible effect of light.

2.3 Analysis techniques

Aqueous samples were filtered over a 0.2 µm filter and analyzed for their free metal composition by a Varian ICP-OES. Iron was also measured by Dr Lange kit LCK-320 (0.2-6.0 mg/L Fe^{2+/3+}) on a Hach Lange Xion 500 spectrophotometer to distinguish between Fe²⁺ and Fe³⁺. Sulfate was measured either on a Dionex DX 600 Ion Chromatograph equipped with an Ionpac AS17 column (2mm x 250mm) or on a HPLC with a Vydac 302IC4.6 column, potassium biphthalate as a mobile phase (flow 1.20 mL/min), and a conductivity detector. Dr Lange sulfide kit, LCK-653 (0.1-2.0 mg/L S²⁻), and a Hach Lange Xion 500 spectrophotometer were used to measure Sulfide_{T(aq)} (S²⁻+HS⁻+H₂S_(aq)) in filtered (0.2 µm) solutions and to measure the amount of H₂S_(g) captured in recycle and effluent (H₂S) strip vessels. Samples for elemental sulfur analysis were dried overnight with nitrogen. The residues obtained were re-suspended in acetone (using glass pearls and ultrasound) and extracted for 3 days on a shaker (150 rpm). After 3 days the extracts were centrifuged (5 min, 10000 rpm) and analyzed with HPLC on a C₁₈ column (2 x 10 cm), 96:4 methanol/water as a mobile phase (flow 1.00 mL/min), and a UV detector at 254 nm. Standard solutions of elemental sulfur in acetone were used for calibration. Biogas was analyzed on an Interscience GC 8000 series with 2 parallel columns; a Varian Porabond-Q (50m x 0.53mm) and a Varian molecular sieve 5A (50m x 0.53mm), or on an Interscience GC 8000 series with a 1/2 mL loop and a Haysep Q (2m) and Molsieve 5A (2m) column to measure O₂, N₂, CH₄ and CO₂.

3 Results

3.1 Batch experiment RL-1

Partial bio-oxidation of Red Lake concentrate at pH 2 is expected to result in the formation of elemental sulfur (equation 4.2 and 4.3), which via bio-reduction at pH 5 (equation 4.4) can be subsequently converted into hydrogen sulfide. Aqueous iron and arsenic will increase as long as no complete elemental sulfur coating is formed on the sulfide particles. Therefore, the concentration of iron was selected as a key parameter to control the process.

RL-1 was operated in batch mode and therefore iron and arsenic were able to build up in the reactor solution during the period of partial bio-oxidation, day 0-41, see Figure 4.1a. On day 41, the iron concentration started to reach a maximum value and the settings were changed to reducing conditions. This change involved several steps performed under continuous flushing of nitrogen: The recycle vessel with $ZnCl_2$ was connected, the pH was adjusted from 2 to 5 by the addition of NaOH, sulfur (sulfate) reducing sludge was added to the reactor, and finally the nitrogen stream was changed to 10 mL/min 95% H_2 /5% CO_2 .

The change in settings from partial bio-oxidation to bio-reduction resulted in a drop of the iron and arsenic concentration (Figure 4.1a). Part of this drop can be ascribed to sampling and the wash out initiated to set the pH, but for the most part it is the result of a precipitation reaction. As indicated by Dr Lange analysis (data not shown) iron was present as Fe^{2+} and therefore probably precipitated, together with arsenic, as $Fe(OH)_2$ to which arsenic adsorbs (O'Day et al, 2004), or as ferrous arsenite, $Fe_3(AsO_3)_2 \cdot xH_2O$. During the bio-reduction period, day 41-77, iron and arsenic seem to follow the same trend.

From Figure 4.1b it becomes clear that partial bio-oxidation indeed results in the formation of elemental sulfur, which was also confirmed by XRD analysis (data not shown). Although the maximum value of elemental sulfur was already reached on day 23, iron increased further (Figure 4.1a) as the formation of aqueous sulfur species continued. Since only part of the $S_{Total(aq)}$ consists of sulfate, other sulfur species, probably thiosulfate, were formed as well.

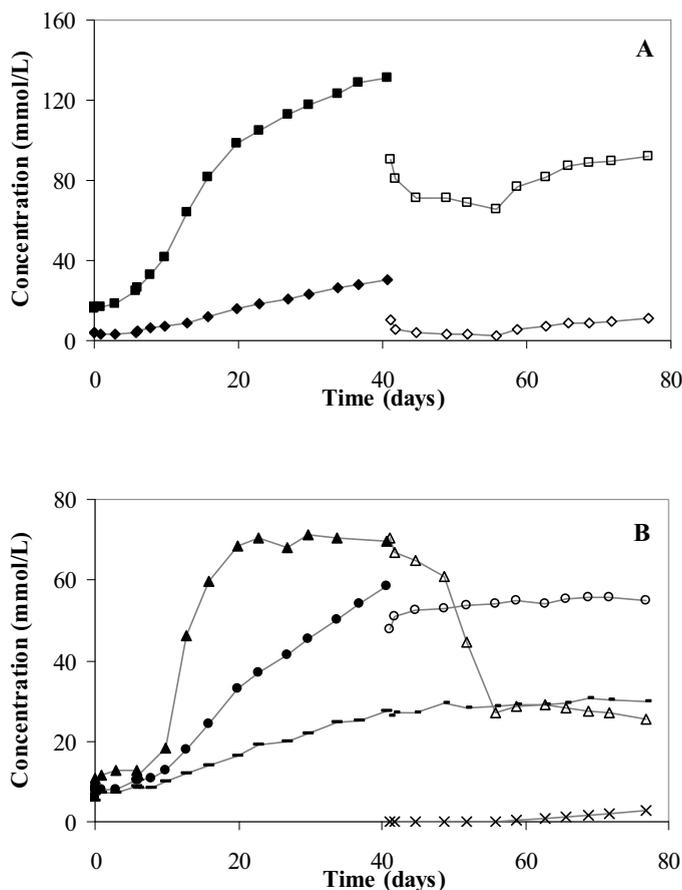


Figure 4.1: (a) Fe (■) and As (◆) concentrations measured by ICP for experiment RL-1. (b) Sulfur species measured for experiment RL-1, with $S_{(s)}$ (▲) measured by HPLC, $S_{Total(aq)}$ (●) by ICP, sulfate (-) by IC, and $H_2S_{(g)}$ (x) is the calculated value of $H_2S_{(g)}$ removed per liter reactor volume via gas recycling through a 0.5 M $ZnCl_2$ solution. On day 41 partial bio-oxidation (solid symbols) was stopped and bio-reduction (open symbols) started.

The elemental sulfur formed during partial bio-oxidation can be bio-reduced as shown by the decrease for elemental sulfur after day 41. As only a small part of the produced sulfide (6%) was captured in the $ZnCl_2$ solution, most likely a precipitation of sulfide with iron and arsenic occurred inside the reactor solution. However, between day 49 and 56 no clear decrease is observed for these two elements in Figure 4.1a. It is therefore suggested that the produced sulfide either reacted with or resulted in the concurrent dissolution of iron hydroxides/arsenites formed during the pH adjustment.

Partial bio-oxidation gives a redox potential (Ag/AgCl) around 350 mV and for bio-reduction values from -120 to -190 mV were obtained (Figure 4.2). The gas composition used during partial bio-oxidation of RL-1 consisted of a mixture of air/nitrogen and a low CO₂ concentration is therefore measured during this period. Oxygen, kept at 5% was apparently added in excess, which could explain the increase observed for S_{Total(aq)} (sulfate) in Figure 4.1b.

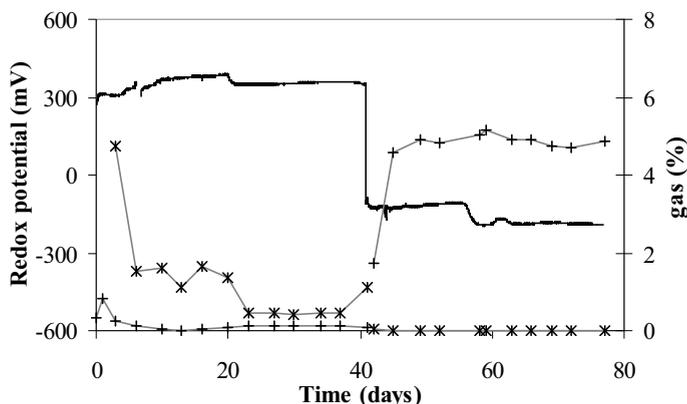


Figure 4.2: Redox potential versus Ag/AgCl (black line) and gas composition during experiment RL-1. Gas composition is only shown for CO₂ (+) and O₂ (*).

3.2 Experiment RL-2

A second experiment was performed to increase the production of recoverable sulfide and decrease the amount of sulfate formed by doubling the amount of concentrate and keeping the oxygen concentration at 5%. Furthermore, medium was added continuously during the partial bio-oxidation period and a 2 day demi wash under N₂ prior to bio-reduction was added to reduce the amount of aqueous metals. After 2 days, the recycle (ZnCl₂) and effluent (NaOH) vessels were connected, salts to obtain the reduction medium were added to the reactor, and the pH controller was set to pH 5. Finally, the sulfur reducing sludge was added to the reactor and the nitrogen flush was switched to H₂/CO₂. The solids remaining after the first ox/red cycle were submitted to partial oxidation for a second time in RL2.2.

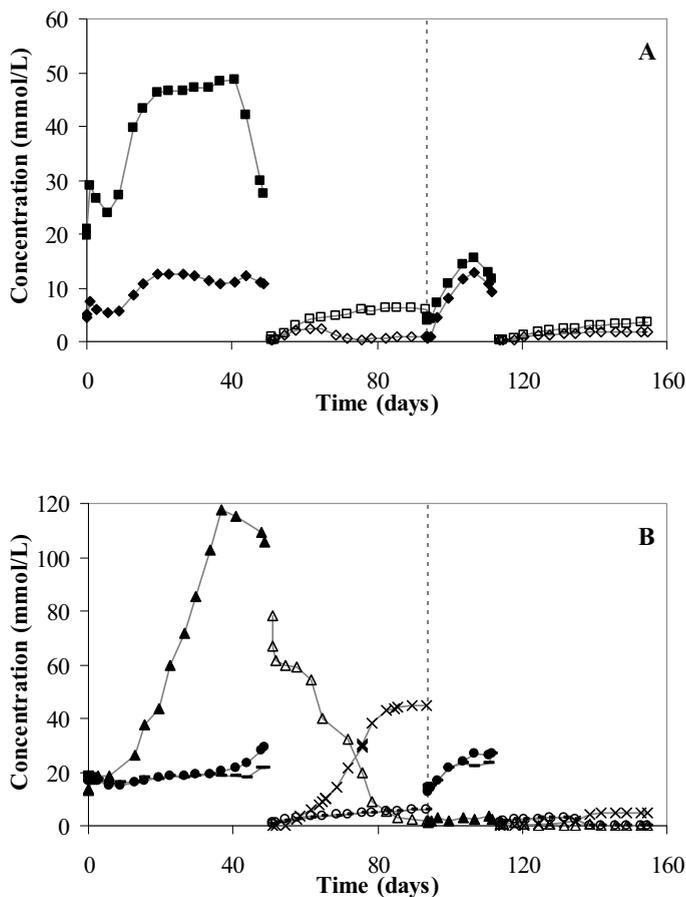


Figure 4.3: (a) Fe (■) and As (◆) concentrations measured by ICP for experiment RL-2. (b) Sulfur species measured for experiment RL-2, with $S_{(s)}$ (▲) measured by HPLC, $S_{Total(aq)}$ (●) by ICP, sulfate (-) by HPLC, and $H_2S_{(g)}$ (x) is the calculated value of $H_2S_{(g)}$ removed per liter reactor volume via gas recycling through a 0.5 M $ZnCl_2$ solution. The first partial bio-oxidation/bio-reduction cycle was performed from day 0-94 and the second cycle from day 94-155. Partial bio-oxidation (solid symbols) was operated continuously and bio-reduction (open symbols) in batch. Prior to bio-reduction the reactor was washed with demineralized water for 2 days.

Comparable to RL-1, partial bio-oxidation of RL-2, day 0-49 and 94-112, resulted in an increase in iron and arsenic (Figure 4.3a). As the reactor was operated continuously for this part of the experiment, conditions were changed as soon as the iron started to wash out. During the bio-reduction periods, performed in batch, day 51-94 and 114-155, only small amounts of iron and arsenic were released into the solution.

During the first ox/red cycle, respectively, a clear increase and decrease for elemental sulfur is observed in Figure 4.3b. The difference with RL-1 is that for this experiment a clear increase in captured sulfide in the strip vessel during reduction (69% versus 6%) is measured. The formation of elemental sulfur during the first partial bio-oxidation period of RL-2 was also confirmed by XRD analysis (data not shown). For the second ox/red cycle no significant increase in elemental sulfur (and thus sulfide production) was seen. As only 16% of the concentrate solids remained present at the start of the second ox/red cycle, which can be ascribed to the combination of dissolution, sampling, and wash-out during the first ox/red cycle, enough oxygen was available to allow complete bio-oxidation of the solids. A fast increase in $S_{\text{Total(aq)}}$ (sulfate) between day 94-112 is indeed observed. The sulfide produced during the bio-reduction period of the second cycle could be due to sulfate reduction.

4

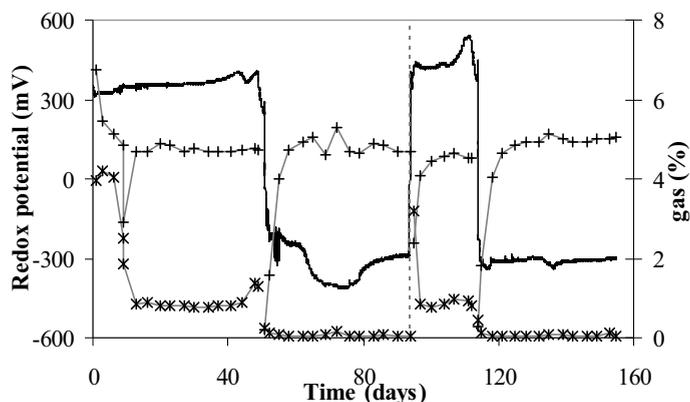


Figure 4.4: Redox potential versus Ag/AgCl (black line) and gas composition during experiment RL-2. Gas composition is only shown for CO₂ (+) and O₂ (*).

The redox potentials observed during the partial bio-oxidation periods of RL-2 (see Figure 4.4) are comparable to RL-1. However, for the bio-reduction periods lower redox potentials, around -300 mV, are measured. For the first bio-reduction period in RL-2 the redox potential even drops below -300mV, which is likely caused by the reduction of elemental sulfur (Figure 4.3b).

The amount of oxygen consumed during the first and second partial bio-oxidation period is similar, see Figure 4.4. Since the L/S ratio was higher in the second cycle, there was relatively more oxygen to oxidize the mineral, which resulted in the formation of sulfate instead of sulfur.

3.3 Fe-As-S solubilization efficiencies

An overview of the Fe-As-S solubilization efficiencies, which is given as the percentage to which an element dissolved from the concentrate into solution during an ox/red cycle, is given in Table 4.2.

Table 4.2: Fe-As-S solubilization efficiencies and gold leachability obtained for experiment RL-1 and RL-2.

Exp.	Conditions	Fe _(aq) (%)	As _(aq) (%)	S _{Total(aq)} (%)	S _(s) (%)	Leachable Gold (%)
RL-1	Ox.	32.1	22.5	12.7	14.7	34.7
	Red.	-9.0	-19.1	1.3	-14.5	
RL-2.1	Ox.	37.3	29.6	10.0	26.5	39.4 ⁽¹⁾
	Red.	2.5	0.9	2.3	-22.3	
RL-2.2	Ox.	31.2	80.7	34.7	2.8	63.8 ⁽¹⁾
	Red.	6.2	9.5	-1.2	-1.1	

(1) Average from residual reactor solids and solids collected from effluents and demi wash.

Negative values for reduction in Table 4.2 indicate that the element was either precipitated or stripped from the reactor solution. The change in settings for RL-2.1 to obtain lower values for S_{T(aq)} compared to RL-1 worked, but the amount of oxygen added was still enough to form a considerable amount of S_{Total(aq)}. Oxygen was also added in excess during RL-2.2, where complete bio-oxidation of the concentrate resulted in the production of sulfate instead of sulfur and an arsenic release of 81% into solution. According to the Fe-As-S solubilization efficiencies of RL-1 and RL-2.1 one partial bio-oxidation treatment results in an ore conversion of ~30%. For RL-2.1 this resulted in a gold leachability improvement from 6% (chapter 3) to 39%.

To investigate if the in-complete ore conversion could be ascribed to the formation of an elemental sulfur layer around the particles, ESEM analysis on samples from RL-2.1 were performed, see Figure 4.5.

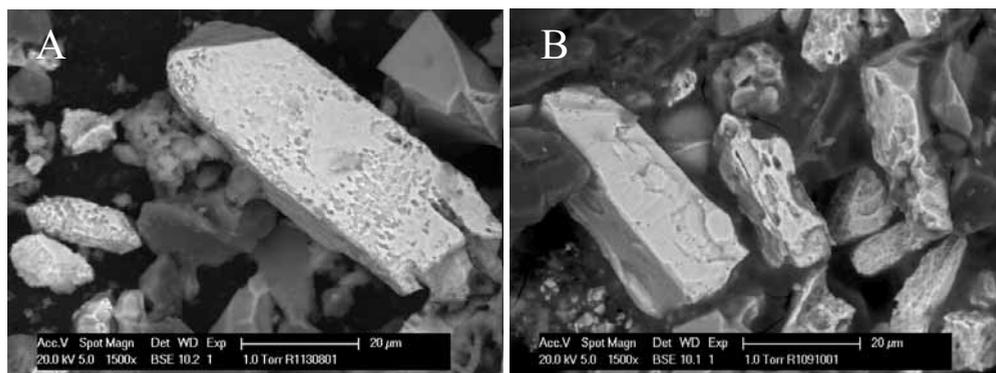


Figure 4.5: ESEM photographs of Red Lake concentrate after partial bio-oxidation (a) and bio-reduction (b) obtained during the first cycle of experiment RL-2. The bright particles were classified as arsenopyrite.

4

Figure 4.5a does not directly show that partial bio-oxidation results in a clear layer of elemental sulfur around the arsenopyrite particles. However, after bio-reduction (Figure 4.5b) most of the arsenopyrite particles seem to be more severely damaged, which indicates that a precipitate, most likely elemental sulfur, is removed from the arsenopyrite surface during this treatment. Pyrite seems not to be affected by partial bio-oxidation and bio-reduction as no clear pit corrosion was observed for this mineral (photographs not shown). The preferential leaching of arsenopyrite was also confirmed by XRD analysis, where no arsenopyrite, but only pyrite, was found for experiment RL-2.2 (data not shown).

4 Discussion

This chapter showed that it is possible to partially oxidize Red Lake concentrate to elemental sulfur, which can be subsequently converted into hydrogen sulfide via bio-reduction. The process conditions selected, pH 2 (ox), pH 5 (red), and a temperature of 35°C, were found to be appropriate to establish the reactions.

To obtain high sulfide recoveries, it appears to be essential to clean the reactor solution from iron and arsenic prior to bio-reduction. Without appropriate cleaning (RL-1), part of the sulfide will not be recovered as it precipitates with iron and arsenic. Cleaning is furthermore required to prevent the formation of precipitates like $\text{Fe}(\text{OH})_2$ and/or $\text{Fe}_3(\text{AsO}_3)_2 \cdot x\text{H}_2\text{O}$ during the pH adjustment, which will lead to an unnecessary consumption of OH^- .

Experiment RL-2 showed that lower iron and arsenic concentrations can be obtained by the continuous addition of medium followed by a 2 day demi wash.

Partial bio-oxidation seems to preferentially oxidize arsenopyrite over pyrite and offers the economic advantage that not all the iron has to be oxidized. As shown by Table 4.2 the average solubilization efficiency obtained after one ox/red cycle is about 30%, which increased the gold leachability of the concentrate from 6% (chapter 3) to 39%.

As shown by the photographs in Figure 4.5 the ore solubilization efficiency is probably limited by the formation of a precipitate that accumulates on the arsenopyrite particles. Although there is no consensus in literature that accumulation of elemental sulfur will prevent further oxidation of the arsenopyrite surface (Corkhill and Vaughan, 2009), the possibility that another precipitate coated the arsenopyrite particles during partial bio-oxidation is expected to be rather small. At pH 2, only ferric iron can cause precipitation reactions, but only ferrous iron was detected during experiment RL-1 and RL-2.1. Ferric iron (data not shown) was detected for experiment RL-2.2, where complete oxidation took place, but also for this experiment no precipitation reaction with iron occurred (Figure 4.3a).

For process simplicity and cost control a high gold recovery (>90%) should be obtained within one or two ox/red cycles. To accomplish this aim the state of art is thus to produce as much elemental sulfur as possible within one step. One option to increase the elemental sulfur production is milling the ore to finer particle sizes to increase its total surface area, but this will increase the costs of the process (Corrans and Angove, 1991).

Another option would be to increase the solubilization efficiency of the ore by the formation of an elemental sulfur product that does not (or only partly) inhibit the transfer of Fe^{3+} . Selection of other conditions (pH, temperature) could possibly lead to the formation of a sulfur layer that does not passivate the mineral surface as found by McGuire et al. (2001). Next to the formation of a layer, elemental sulfur can also appear as S-globules in the liquid medium and in the periplasms of the bacteria (Dopson and Lindström, 1999). Therefore, if it is possible to increase the production of S-globules that appear in the liquid medium and not as a sulfur layer on the mineral the solubilization efficiency will be increased.

Partial bio-oxidation followed by bio-reduction

As the sulfur layer is expected to be of a different structure than the bulk mineral it probably can also be removed physically. One method that is compatible with gold milling is to circulate the partially bio-oxidized concentrate through a regrind mill. The use of ultrasound energy could also be considered, if compatible with biomass activity.

To operate partial bio-oxidation correctly, no sulfuric acid should be produced. In experiment RL-2.1 still sulfuric acid is produced and thus the concentration of oxygen added, for this particular concentrate, should be < 5% for a solid percentage of 20 w/v %. Another alternative is to control the redox state of the solution (Janssen et al., 1998).

If a 1-2 cycle process can be established the sulfide formed during bio-reduction can be further processed into high purity elemental sulfur or even gold lixivants such as thiosulfate or bisulfide. Next to sulfide there is also a stream that contains a high concentration of ferrous iron and arsenite, which via oxidation can be removed as scorodite (Welham et al, 2000) or biogenic scorodite formation (Gonzalez-Contreras et al, 2010).

**Bio-reduction of
elemental sulfur to
increase the gold
recovery from
enargite**

5

This chapter is based on the submitted paper:
Hol, A., Van der Weijden, R.D., Van Weert, G., Kondos,
P., Buisman, C.J.N., 2011.

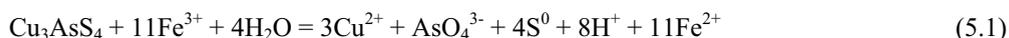


Abstract

The mineral enargite can be of interest to the mining industry as a copper and precious metal source. The mineral has a refractory character towards oxidation, which is ascribed to the formation of elemental sulfur that seals off the mineral surface. In this study it was investigated whether elemental sulfur resulting from oxidation during industrial milling can be converted into hydrogen sulfide via bio-reduction. The removal of this elemental sulfur will clean the mineral surfaces for subsequent oxidation and prevents interference with the cyanide extraction process. HPLC analysis confirmed that indeed elemental sulfur was formed during industrial milling of an enargite-pyrite gold concentrate. Removal of elemental sulfur via bio-reduction was found to be feasible and improved the gold leachability from 48.9% to 69.6%. The combination between milling and bio-reduction was therefore concluded to be a possible route to liberate metals. Further research is necessary to investigate if the enargite to sulfur conversion can be improved to obtain economically satisfactory (>90%) gold recoveries.

1 Introduction

Enargite, Cu_3AsS_4 , is a copper arsenic sulfide mineral often mined for its copper content. In addition to copper, this mineral can also carry economic quantities of precious metals like gold. To liberate the copper (and gold) from this refractory mineral destruction or alteration of the enargite lattice is required. As this mineral cannot be easily digested in aqueous media (Filippou et al., 2007) conventional treatment includes roasting. Costs of this treatment are high due to the need for As_2O_3 and SO_2 removal from the roaster gas effluent as there is no market for the generated products. Pressure oxidation of enargite is also possible (Padilla et al., 2008), but needs expensive equipment and results in the formation of sulfuric acid, which needs to be neutralized and disposed off as impure gypsum. As a cost-effective alternative with a lower environmental impact bio-leaching has been considered for enargite, but so far only considerable success has been obtained with extreme thermophilic bacteria/archaea (Escobar et al., 2000; Muñoz et al., 2006). It appears that at ambient temperature enargite responds to bio-oxidation much less than pyrite and probably as poorly as chalcopyrite (Filippou et al., 2007). This refractory character of enargite can possibly be ascribed to the formation of elemental sulfur that rapidly seals off the underlying mineral for further oxidation. As described by Dutrizac and MacDonald (1972) ferric leaching results in elemental sulfur according to the following reaction:



Bacteria facilitate this reaction by regenerating ferric iron and the removal of elemental sulfur from the mineral surface (Muñoz et al., 2006). To prevent the toxicity of arsenic on the bacterial activity, ferric arsenate precipitation is preferred (Escobar et al., 2000).

Another alternative that has been tried for enargite is ultra fine grinding (UFG) as this mineral is reactive when reduced to a smaller particle size (Baláž et al., 1999; Welham, 2001a). At ambient temperatures enargite is thought to oxidize in grinding mills according to the following equation (Welham, 2001a):



UFG is thus also expected to result in the formation of elemental sulfur, but offers the advantage that no iron addition is required. Furthermore, CuSO_4 and As_2O_3 can be removed via a wash step leaving a solution with un-reacted enargite and elemental sulfur. Removal of elemental sulfur can be accomplished via bio-reduction where it is biologically converted into hydrogen sulfide. Removal of elemental sulfur could let both reactions (equation 5.1 and 5.2) proceed further to the product side. The produced hydrogen sulfide can be further processed into high purity elemental sulfur (Janssen et al., 2001).

As enargite is essentially an orthorhombic cuprous thioarsenate: $\text{Cu}_3^{\text{I}}\text{As}^{\text{V}}\text{S}^{\text{II}}_4$ (Filippou et al., 2007) there is a possibility that under reducing conditions the arsenate is reduced to arsenite, which will precipitate as orpiment, see equation 5.3.



However, the chance that equation 5.3 takes place is expected to be rather small as direct solid phase bio-reduction was not observed for pyrite (chapter 2) and arsenopyrite (chapter 3).

This chapter investigates the presence of elemental sulfur for an industrially milled enargite-pyrite gold concentrate and whether its removal via bio-reduction will improve gold leachability.

2 Materials and methods

2.1 Mineral

An industrial milled enargite-pyrite gold concentrate from Pascua Lama was provided by Barrick. Its particle size distribution was analyzed by a Beckman Coulter laser LS 230 and found to have a P80 of 32 μm on average. Next to enargite (Cu_3AsS_4) and pyrite (FeS_2), XRD analysis also detected quartz (SiO_2), Alunite ($\text{K}(\text{Al}_3(\text{SO}_4)_2(\text{OH})_6)$) and elemental sulfur (S). Gold is present at a concentration of 32 g/ton. The concentrate composition was also analyzed via a combined microwave/ICP method. Microwave digestion of the concentrate was performed with Aqua Regia ($\text{HCl}:\text{HNO}_3 = 3:1$). The resulting liquor was filtered, adjusted to a known volume, and analyzed by ICP. Prior to addition to the reactor, the ore was washed with 2 M HCl and thoroughly rinsed with demineralized water.

2.2 Experimental setup

A gas lift loop reactor experiment was performed in the same reactor setup as described previously (chapter 2). The reactor was filled with 250 gram concentrate, 4.85 L defined medium, and a sludge mixture containing sulfur/sulfate reducing bacteria (chapter 2). The temperature of the reactor was maintained at 35°C and the pH was controlled at 5 with 4 M HCl/NaOH. The reactor was operated batch-wise and the effluent (due to pH control) was collected in the external settler. Gas, consisting of 95% H_2 /5% CO_2 , was added to the reactor at a rate of 10 mL/min. The gas recycle flow rate was manually controlled at 8 ± 2 L/min. The condenser was set at a temperature of 20°C to cool down the gas stream. To capture $H_2S_{(g)}$ the recycle stripper was filled with 0.5 M $ZnCl_2$ solution and the effluent stripper with 1 M NaOH. A WUR-made rubber check valve was used as a sparger. The gas lift loop reactor was packed in aluminum foil to exclude the possible effect of light.

2.3 Analysis techniques

Aqueous samples were filtered over a 0.2 μm filter and analyzed for their free metal composition by a Varian ICP-OES. Sulfate was measured on a Dionex DX 600 Ion Chromatograph equipped with an Ionpac AS17 column (2mm x 250mm). Dr Lange sulfide kit, LCK-653 (0.1-2.0 mg/L S^{2-}), and a Hach Lange Xion 500 spectrophotometer were used to measure Sulfide $_{T(aq)}$ ($S^{2-}+HS^-+H_2S_{(aq)}$) in filtered (0.2 μm) solutions and to measure the amount of $H_2S_{(g)}$ captured in recycle and effluent (H_2S) strip vessels. Samples for elemental sulfur analysis were dried overnight with nitrogen. The residues obtained were re-suspended in acetone (using glass pearls and ultrasounds) and extracted for 3 days on a shaker (150 rpm). After 3 days the extracts were centrifuged (5 min, 10000 rpm) and analyzed on a HPLC with a C_{18} column (2 x 10 cm), 96:4 methanol/water as a mobile phase (flow 1.00 mL/min), and a UV detector at 254 nm. Standard solutions of elemental sulfur in acetone were used for calibration. Biogas was analyzed on an Interscience GC 8000 series with a $1/2$ mL loop and a Haysep Q (2m) and Molsieve 5A (2m) column to measure O_2 , N_2 , and CO_2 on a HWD and CH_4 on a FID.

3 Results

3.1 Concentrate composition

To analyze the composition of the enargite-pyrite gold concentrate microwave digestion was performed. The amount of elemental sulfur was measured via HPLC after acetone extraction. Results of both methods are shown in Table 5.1.

Table 5.1: Composition of enargite-pyrite concentrate (250 g) as provided by Barrick and obtained after the acid wash. Values are all in mmol.

Concentrate	Cu	As	Fe	S _{Mineral} ¹	S _{elemental}
As-received	228	80	837	1625	254
After acid wash	222	78	715	1483	254 ²

1. Calculated value from total sulfur (digestion) minus the amount of elemental sulfur (HPLC).

2. Elemental sulfur was assumed not to be removed via the acid wash

Elemental sulfur is present in the concentrate at a concentration of 3.3 wt%. Based on the copper (and arsenic) percentage after the acid wash, the concentrate contains 11.7 wt% enargite. Pyrite, based on sulfur, is present for 28.5 wt%. The presence of excess iron suggests that the enargite fraction was enriched in iron or depleted in sulfur.

3.2 Reduction of elemental sulfur

Due to the presence of elemental sulfur, bio-reduction of the enargite-pyrite gold concentrate is expected to result in the formation of hydrogen sulfide. Process conditions selected, pH 5 and 35°C, are therefore those where sulfur reducing bacteria seem to thrive well as demonstrated in chapter 4. Without effect of the acid wash, a starting concentration of elemental sulfur close to 52.4 mmol/L should be found in the reactor solution. As shown by Figure 5.1 this is indeed the case.

From the first day, bio-reduction of elemental sulfur is prominent as indicated by its decrease in concentration and the production of hydrogen sulfide. Although elemental sulfur reduction seems to be preferred, sulfate probably added via the mineral is reduced as well. At the end of the experiment 90.5% of the expected sulfide was recovered in the recycle strip vessels.

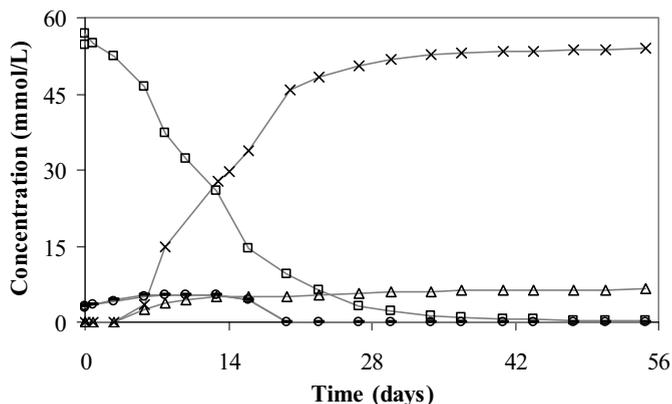


Figure 5.1: Bio-reduction of an enargite-pyrite gold concentrate at pH 5, 35°C, 95% H_2 /5% CO_2 in a gas lift loop reactor. Iron (Δ) and sulfur_{T(aq)} (\circ) were both measured by ICP, sulfate (-) by IC, elemental sulfur (\square) by HPLC, and $H_2S_{(g)}$ (\times) is the calculated value of $H_2S_{(g)}$ removed per liter reactor volume via gas recycling through a 0.5 M $ZnCl_2$ solution.

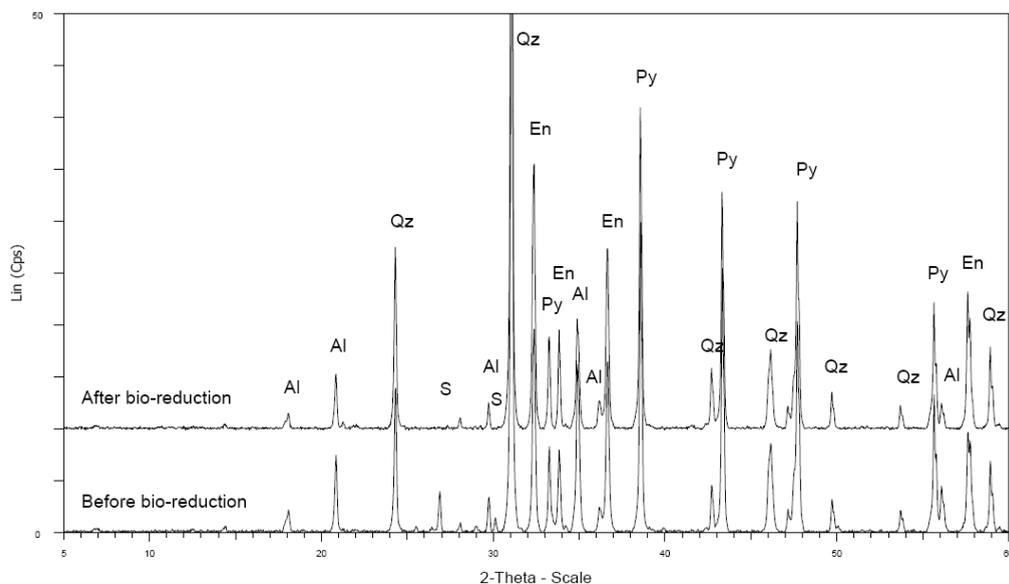


Figure 5.2: XRD analysis of an enargite-pyrite gold concentrate before and after bio-reduction: En (Enargite), Py (Pyrite), S(Sulfur), Qz (Quartz), Al (Alunite).

The rest of the sulfide probably precipitated inside the reactor solution or was lost as ZnS coating the glass wall of the recycle strip vessel. Neither copper nor arsenic (data not shown) was released from the concentrate in any detectable amount. The increase in iron from 0.0 to 6.5 mmol/L seems not to originate from FeSO_4 and could be an indication that bio-reduction of iron-enriched enargite took place. However, no confirmation (Cu_2S and As_2S_3) for this reaction was obtained from XRD analysis, see Figure 5.2.

Under the selected conditions, the only reaction that can be confirmed by XRD analysis (Figure 5.2) is the reduction of elemental sulfur. Other parameters measured during the bio-reduction of the enargite-pyrite concentrate are shown in Figure 5.3.

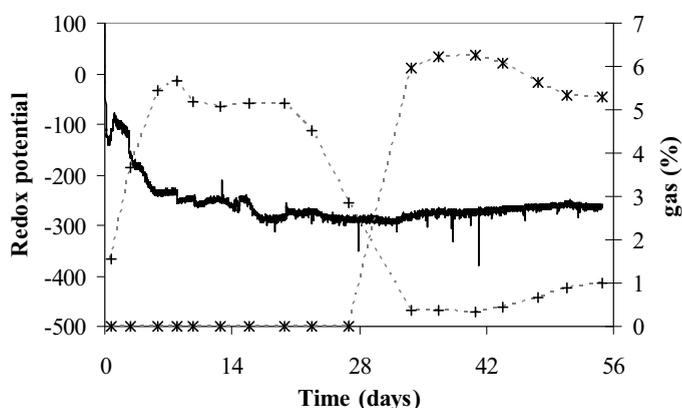


Figure 5.3: Redox potential versus Ag/AgCl (black line) and gas composition development during the bio-reduction of an enargite-pyrite gold concentrate at pH 5, 35°C, 95% H_2 /5% CO_2 in a gas lift loop reactor. Gas composition is only shown for CO_2 (+) and CH_4 (*).

Together with the decrease in elemental sulfur, the redox potential dropped as well and stabilized around -290 mV (Ag/AgCl). After 20 days, the H_2S production stops and the CO_2 concentration suddenly started to drop to < 1%, which can be ascribed to the formation of methane.

3.3 Gold leachability

Results of CIL (Carbon In Leach) gold extraction tests of the pyrite-enargite gold concentrate are summarized in Table 5.2.

Table 5.2: Gold leachability of the enargite-pyrite gold concentrate as provided by Barrick and of its residue after bio-reduction.

Analysis	Provided concentrate	Bio-reduction
Total gold content (g/t)	32	42.6
Distribution solution (%)	3.5	1.3
Distribution activated carbon (%)	48.9	69.6
Distribution residue (%)	47.5	29.2

The enargite-pyrite gold concentrate gives a gold leachability of 48.9% for the untreated sample. The removal of elemental sulfur, via bio-reduction, improved this leachability to 69.6%.

4 Discussion

The industrial milled enargite-pyrite gold concentrate provided by Barrick was found to contain 3.3 wt% elemental sulfur. As elemental sulfur is not commonly associated with enargite (Filippou et al., 2007; Lattanzi et al., 2008) and pyrite is essentially inert to grinding (Welham, 2001b), the elemental sulfur is thought to be the result of the partial oxidation of enargite as a result of grinding (Welham, 2001a). Bio-reduction of the elemental sulfur on the milled enargite improved the gold leachability from 48.9% to 69.6%. A combination of further oxidation and regrinding of the enargite fraction to elemental sulfur could thus be the solution to obtain a satisfactory gold recovery (>90%) for this particular concentrate.

Enargite conversion to elemental sulfur can be obtained via bio-leaching (equation 5.1) or ultra fine grinding (equation 5.2). For an enargite-pyrite gold concentrate oxidative bio-leaching is not preferred as the biological attack will mainly focus on pyrite (Canales et al., 2002). As the gold is not expected to be present in pyrite, such bio-leaching would thus only lead to an unnecessary oxygen consumption. The advantage of milling is that it seems to selectively oxidize enargite over pyrite, which saves oxygen and the neutralization of sulfuric acid.

Furthermore, in case of dry milling, no oxygen has to be transferred into a liquid phase, which saves costs. More oxygen can be saved if the formation of CuSO_4 during milling (equation 5.2) can be limited.

Bio-reduction of the mineral enargite was not found to occur as no evidence was found from XRD analysis (Figure 5.2). Most likely the arsenic is not available for the bacteria as enargite is not expected to dissolve at pH 5 and a redox of -290 mV (Ag/AgCl) (Kantar, 2002). Chemical reduction of enargite is feasible via carbothermic reduction (Igiehon et al., 1994), but only proceeds at elevated temperatures. Milling under reducing conditions has so far not been investigated and could be interesting to liberate gold due to the reactive character of enargite during size reduction.

Under the selected conditions, pH 5 and 35°C, sulfur reduction seems to be preferred. Sulfate reduction starts as soon as most of the elemental sulfur has been consumed from the reactor solution. After consumption of both sulfur sources, methanogens will take over the system (Figure 5.3). To prevent methane formation, unwanted CO_2 and H_2 consumption, the H_2 supply should be adjusted to the sulfur to sulfide conversion.

The reduction of elemental sulfur from the enargite-pyrite gold concentrate was found to be very effective as 90.5% of the expected sulfide was recovered from the reactor solution. Of the total concentrate sulfur amount 16% sulfur was removed, which increased the gold recovery with 21%. The removal of elemental sulfur is thus essential as it interferes with the cyanide extraction process.

5 Conclusion

Industrial milling of an enargite-pyrite gold concentrate resulted in the formation of elemental sulfur due to size reduction and partial oxidation of enargite. Milling to a particle size with a p_{80} of 32 μm resulted in the formation of 3.3wt% elemental sulfur and gave a gold recovery to activated carbon in a CIL test of 48.9%. Bio-reduction of the elemental sulfur improved this recovery to 69.6%. Milling enargite in combination with bio-reduction is therefore an interesting alternative and further research is necessary to investigate whether a higher leachability can be obtained by various milling-bio-reduction cycles as well as its feasibility on a large scale.

General discussion

6



1 General discussion

Sulfide minerals, such as pyrite and arsenopyrite, are of economical interest due to the presence of invisible gold locked inside these minerals. To liberate the invisible gold from these refractory minerals fine grinding is often not sufficient and lattice destruction techniques are required to access the gold via cyanidation. Techniques applied nowadays to liberate the gold are based on chemical and biological oxidation processes. Although these processes have proven to be successful to reach satisfactory gold recoveries, operation costs are high and challenging waste streams are produced. In the search for a more environmentally friendly alternative to oxidation, the bio-reduction of pyrite and arsenopyrite was proposed and investigated in this thesis.

1.1 Bio-reduction of sulfide minerals

Bio-reduction, the opposite of bio-oxidation, is a biologically anaerobic process, which aims at mineral-sulfur present in pyrite and arsenopyrite. Reduction of mineral-sulfur with hydrogen, producing hydrogen sulfide, has as major advantage that the hydrogen sulfide can be recovered from the solution and further processed into high purity elemental bio-sulfur leaving a waste stream without diluted sulfuric acid. Furthermore, electrical energy will be saved as less hydrogen, compared to oxygen, needs to be transferred to the reactors and less cooling will be required to keep the bio-reduction process at the desired temperature.

Microorganisms selected to catalyze the bio-reduction reaction of pyrite and arsenopyrite are the sulfate (sulfur) reducing bacteria (SRB) as these obligately anaerobic microorganisms, belonging to many different families and genera, are able to use sulfate or other oxidized sulfur compounds as terminal electron acceptor (Lens and Kuenen, 2001) and organic compounds or hydrogen as electron donor (Brüser et al., 2000). Conditions selected for the bio-reduction process were therefore determined by the use of these bacteria.

Chapter 1 describes the selection of conditions and concludes that industrially interesting reduction rates for pyrite and arsenopyrite could possibly be obtained at a temperature of 35°C and pH 5. Chapter 2 and 3 both show that the selected conditions were appropriate to establish a bio-reduction reaction for aqueous sulfate, but unfortunately this was the only sulfur-related

reaction observed. For pyrite, chapter 2, and arsenopyrite, chapter 3, no confirmation of an anaerobic bio-(induced)conversion reaction was found.

Although thermodynamic calculations indicated that bio-reduction should be feasible under the selected conditions, SRB appeared not to be able to use sulfur when fixed in the crystal lattice of pyrite or arsenopyrite as an electron acceptor. In order to make the mineral-sulfur bio-available for these bacteria the sulfur should enter the solution, which may be achieved via selection of other conditions (pH, redox, and temperature) or via a different process approach like anaerobic oxidation or partial oxidation.

1.2 Anaerobic oxidation of arsenopyrite

The presence of arsenic also creates another possibility to convert arsenopyrite anaerobically. The proposed theory is that SRB might be able to use arsenic, next to hydrogen, as electron donor since arsenic is present as $\text{As}^0/\text{As}^{-1}$ in arsenopyrite, which can be oxidized to As^{3+} . To prevent the toxicity of dissolved arsenic, some sulfide (from the reduction of sulfate) should be allowed in the reactor to precipitate arsenic as orpiment (As_2S_3). Comparable to the bio-reduction of arsenopyrite reduction of sulfate was observed in the anaerobic oxidation experiment (chapter 3), but no proof was found for an anaerobic reaction that converts the mineral. Arsenic, when enclosed by the crystal lattice of arsenopyrite was therefore also found not to be bio-available for SRB at pH 5, 35°C.

1.3 Partial bio-oxidation of sulfide minerals

To make the mineral-sulfur bio-available for SRB a combination between partial bio-oxidation and bio-reduction was investigated for an arsenopyrite refractory concentrate in chapter 4. Partial bio-oxidation is based on the already existing bio-oxidation process where sufficient oxygen (air) is provided to the reactors operating at pH 2 to allow complete bio-oxidation of pyrite and arsenopyrite via bacteria with iron and sulfur oxidizing capacities. However, if the oxygen concentration is kept at a level high enough to bio-regenerate Fe^{3+} , but too low to allow the formation of sulfuric acid, the oxidative attack on pyrite and arsenopyrite is expected to result in the formation of elemental sulfur. One matter of concern may be that accumulation of sulfur on particles inhibits the partial bio-oxidation process. Furthermore, elemental sulfur is known to interfere during the cyanide extraction process increasing the cyanide consumption. Because SRB are able to reduce elemental sulfur to hydrogen sulfide, a combination of partial

bio-oxidation with bio-reduction can solve this. The combination of these processes prevents the generation of sulfuric acid and reduces the oxygen consumption while liberating precious elements.

In chapter 4 it is illustrated that it is indeed possible to partially oxidize an arsenopyrite concentrate to elemental sulfur, which can be subsequently converted into hydrogen sulfide via bio-reduction. Via the process conditions selected, pH 2 (partial oxidation), pH 5 (bio-reduction), and a temperature of 35°C, a solubilization efficiency (percentage of concentrate dissolved into solution) of 30% was reached after one ox/red cycle. At the same time this increased the gold leachability of the concentrate from 6% to 39%. Furthermore, it was found that arsenopyrite is preferentially oxidized over pyrite.

For application on industrial scale satisfactory gold recoveries (>90%) preferably should be reached within 1 or 2 ox/red cycles. Via the set-up as applied in chapter 4, probably more cycles are necessary and therefore a different process set-up is required. Furthermore, the amount of shifts in pH from 2 (partial bio-oxidation) to 5 (bio-reduction) should be minimized as this will result, unless free metals are removed, in unwanted precipitation reactions. Also a stable waste product (e.g. ferric arsenate) should be formed from the effluent to safely store the arsenic and iron released during the partial bio-oxidation process.

1.4 The alternative process proposed

The aim of this thesis was to develop a more environmental friendly biological alternative compared to the oxidative routes, which preferably also reduces the amount of costs. Bio-reduction appeared not to be a suitable alternative, but in combination with partial bio-oxidation it offered opportunities. In order to be interesting on industrial scale this combination should:

- Produce enough elemental sulfur within one ox/red cycle to yield a satisfactory gold recovery.
- Form stable end-products that can be safely stored.
- Prevent multiple pH switches.
- Limit the toxicity of free arsenic on the bacteria during reduction.

General discussion

To meet these guidelines multiple process steps are necessary. Figure 6.1 gives an illustration of the alternative three step “Paroxsul” (partial oxidation to sulfur) process proposed, which combines bio-oxidation, ferric leaching, and bio-reduction to partially oxidize the ore to produce elemental bio-sulfur as a final end-product.

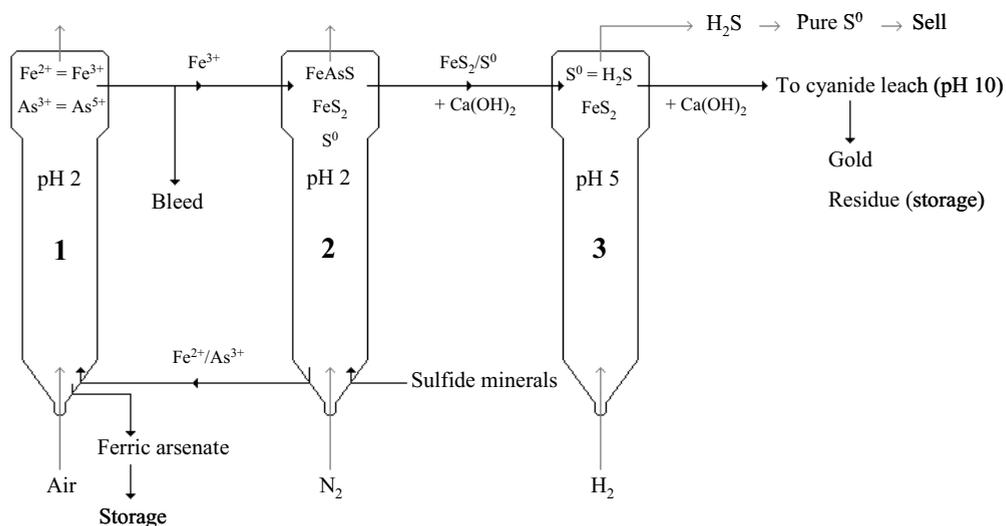
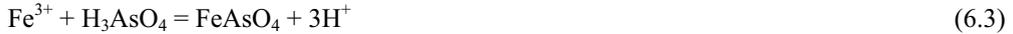


Figure 6.1: Proposed Paroxsul process for the alteration/destruction of sulfide minerals to liberate gold at a lower environmental impact. Step 1: Bio-oxidation of iron and arsenic to regenerate Fe^{3+} and to remove arsenic as ferric arsenate. Step 2: Ferric leaching to produce elemental sulfur. Step 3: Bio-reduction of elemental sulfur towards hydrogen sulfide, which can be subsequently converted into pure elemental bio-sulfur.

Bio-oxidation, the first step in this process, is used to regenerate Fe^{3+} with bacteria like *T. ferrooxidans* or *L. ferrooxidans* (Schippers and Sand, 1999) and to oxidize the arsenic to arsenate. In this biological step, performed at pH 2, sufficient oxygen is supplied to the reactor to allow complete oxidation of iron and arsenic according to equation 6.1 and 6.2.



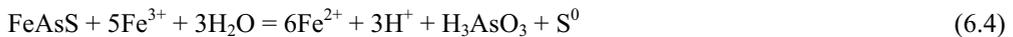
The formation of ferric iron and arsenate in this step also results in the simultaneous precipitation of ferric arsenate (equation 6.3), which can be recovered and stored as a stable waste product.



To transfer only ferric iron into the second step of the process the reactor of choice for example could exist of a gas lift loop reactor in combination with an external settler or a membrane bio-reactor.

In the second step the crushed and ground sulfide minerals are added to the process and chemically oxidized to elemental sulfur by ferric iron. To reach satisfactory gold recoveries this step should result in a high mineral-sulfide to sulfur conversion efficiency. As no bacteria are involved in this step it is possible to regrind the minerals or to apply ultrasound in the reactor (or re-grinder) if the formation of elemental sulfur that may seal off the underlying mineral cannot be prevented by the selection of appropriate conditions.

As ferric leaching will mainly attack arsenopyrite, because it is preferentially oxidized over pyrite by ferric iron (Chapter 4), the reaction of step 2 will be dominated by equation 6.4.



Depending on the amount of iron resulting from the partial oxidation of pyrite a bleed may be required to prevent the accumulation of ferric iron between step 1 and 2.

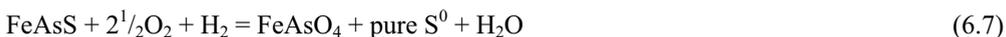
After the ferric leach, the residue containing sulfur and un-reacted pyrite is transferred to the third and last reactor. In this step the generated elemental sulfur is reduced by SRB towards hydrogen sulfide in a gas lift loop reactor. To establish this biological reaction the pH needs to be increased by lime to a pH of 5. The produced hydrogen sulfide, equation 6.5, needs to be recovered from the reactor gas effluent.



This recovery can be achieved via gas effluent stripping through an alkaline solution from which the sulfide can be recovered as elemental bio-sulfur (Janssen, 2001), see equation 6.6.



Combination of equation 6.1 to 6.6 gives 6.7, which is the overall reaction obtained for partial oxidation via the Paroxsul process.



Next to ferric arsenate also another waste stream containing pyrite and other un-leached minerals, like quartz, will be formed that need to be stored.

Additional research is necessary to prove that the Paroxsul process indeed will result in a satisfactory gold recovery within one ox/red cycle. In case multiple ox/red cycles still need to be applied multiple pH switches should be prevented. A possible way to prevent pH switches is to biologically reduce the elemental sulfur at pH 2, the same pH used for the partial oxidation step. As described by Ohmura et al (2002) *T. ferrooxidans* is able to reduce sulfur with hydrogen to hydrogen sulfide at pH 2. First experimental data, which are not included in this thesis, confirm that the bacterial populations, used to perform the partial oxidation steps in chapter 4, are indeed able to switch to reducing conditions and produce hydrogen sulfide out of elemental sulfur.

1.5 Cost comparison

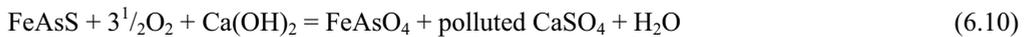
To get an impression of the operating costs involved in the Paroxsul process a comparison with the bio-oxidation process of arsenopyrite is made. If sufficient oxygen is added to completely oxidize arsenopyrite and ferric arsenate is considered as the main end-product the following reaction is obtained for the bio-oxidation of arsenopyrite:



Next to ferric arsenate the bio-oxidation of arsenopyrite also results in the formation of diluted sulfuric acid, which needs to be neutralized by lime ($\text{Ca}(\text{OH})_2$), see equation 6.9. The resulting CaSO_4 is polluted by heavy metals, has no commercial value, and needs to be stored safely.



Combination of equation 6.8 and 6.9 gives 6.10, which is the overall reaction used for the bio-oxidation of arsenopyrite in the cost comparison.



When equation 6.7 and 6.10 are compared, the Paroxsul process offers the advantages that no neutralization is required and that the final product, pure elemental bio-sulfur, can be sold as fertilizer, etc. Furthermore, less heat (Table 1) is generated in the Paroxsul process, so less energy is needed to cool and maintain the reactors at the desired temperature. As the amount of gas that needs to be transferred and dispersed into the liquid media is the same for both reactions ($3\frac{1}{2}$ mol) this part contributing to the power consumption is assumed to stay the same. Costs involved in both processes are also shown in table 6.1.

Table 6.1: Values used to make a cost and energy comparison between the Paroxsul and bio-oxidation process of arsenopyrite.

Parameter	Value	Unit	Reference
ΔH (35°C) Paroxsul process	-1085	kJ/mol	HSC Chemistry 6.12
ΔH (35°C) bio-oxidation	-1531	kJ/mol	HSC Chemistry 6.12
Price $\text{Ca}(\text{OH})_2$	66	\$/ton H_2SO_4	(National Lime Association, 2000)
Price H_2	0.21	\$/m ³	(Bijmans, 2008)
Price elemental sulfur	150	\$/ton	Assumption (highly variable)

The values reported by Tranquilla and Gordon (1998) for a 2000 ton per day (tpd) mill operation and bio-oxidation of 200 tpd arsenopyrite concentrate were used to set up the operational cost comparison, see Table 6.2.

General discussion

Table 6.2: Operational cost comparison between the Paroxsul and bio-oxidation process in US\$/ton ore containing 10% arsenopyrite.

Description	Bio-oxidation ^[1]	Paroxsul process
Concentrate preparation	4.74	4.74
Labour	0.54	0.54
Reagents ^[2]	2.95	2.95
Maintenance supplies	0.04	0.04
Operating supplies	0.08	0.08
Power consumption ^[3]	4.37	4.05
Miscellaneous	0.38	0.38
CIP Leaching	1.30	1.30
Effluent neutralization	3.98	0.00
Hydrogen	0.00	3.16
Value of by-products	0.00	-2.95
G&A total	1.29	1.29
Total	19.67	15.58

[1] Values from Tranquilla and Gordon (1998) with exception of the effluent neutralization costs

[2] Used for pH control, nutrients for bacterial growth, and water treatment (Rawlings and Johnson, 2007)

[3] Assumed to consist of 75% aeration energy and 25% cooling energy

According to table 6.2, 21% of the operational costs can be saved via the Paroxsul process. Most important saving is the prevention of effluent neutralization, calculated from the amount of $\text{Ca}(\text{OH})_2$ needed to neutralize the generated H_2SO_4 . The power consumption is also slightly reduced as 29% less cooling, calculated from the difference in standard reaction enthalpy, is required to maintain the process temperature. Hydrogen used for the reduction of elemental sulfur increases the costs of the Paroxsul process, but the production of pure elemental sulfur that can be sold almost offsets these costs.

Although the costs for the Paroxsul process are a rough estimation they can possibly even be further reduced by the selection of reactor types like gas lift loop reactors. In the bio-oxidation process the power input is mainly determined by the generation and dispersion of air required to complete the reactions in CSTR's (Rawlings and Johnson, 2007). No impellers are required in gas lift loop reactors, which will reduce the operational and capital costs.

1.6 Application to other minerals

Next to pyrite and arsenopyrite, partial oxidation can also be applied to other minerals. In chapter 5, partial oxidation was therefore investigated on another sulfide mineral: Enargite. Enargite, Cu_3AsS_4 , is a copper arsenic sulfide mineral often mined for its copper content, but it may also contain interesting quantities of precious metals like gold. To liberate the copper (and gold) from this refractory mineral destruction or alteration of the enargite lattice is required. In contrast to pyrite and arsenopyrite, enargite behaves very reactive when exposed to grinding. During grinding enargite is already expected to partially oxidize to yield elemental sulfur, which excludes the use of bacteria. Costs of the Paroxsul process can therefore even be further reduced as no air needs to be transferred into a liquid phase. Only an elemental sulfur reducing bio-reactor is required.

As shown by chapter 5 industrial milling of an enargite-pyrite concentrate indeed results in the formation of elemental sulfur, which can be efficiently converted into hydrogen sulfide by SRB. The removal of sulfur improved the gold extraction from 48.9% to 69.6%. Further oxidation of the enargite fraction to elemental sulfur could thus be the solution to obtain a satisfactory gold recovery (>90%) for this particular concentrate.

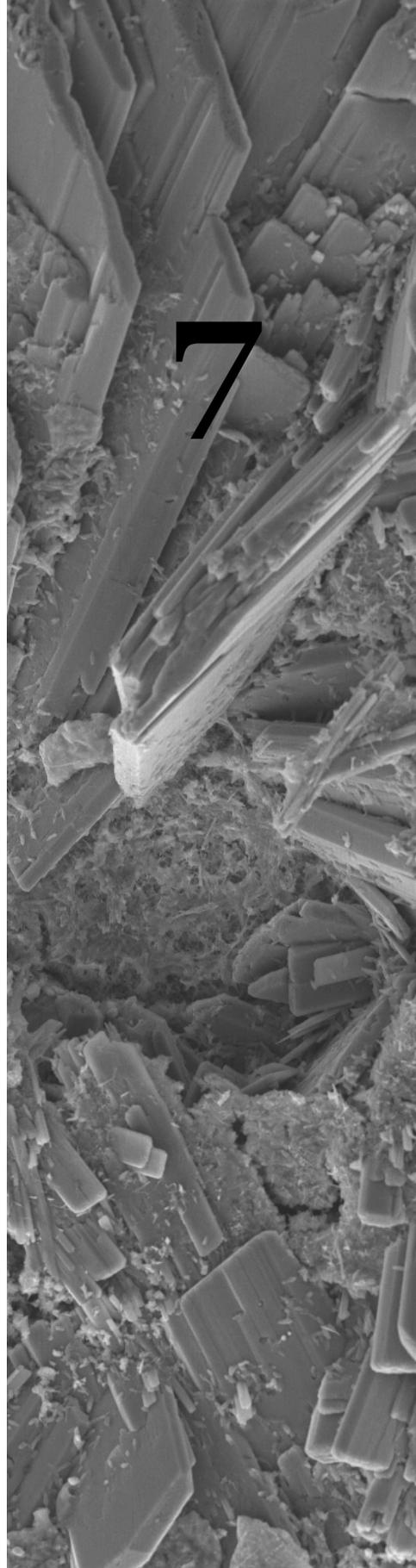
Another mineral that may well be treated via the Paroxsul process is sphalerite (ZnS) as ferric leaching also results for this mineral in the formation of elemental sulfur (Fowler and Crundwell, 1999).

1.7 Concluding remarks

Bio-reduction of pyrite and arsenopyrite at 35°C and pH 5 was found not to be an interesting alternative to replace the already existing oxidation methods, as mesophylic SRB were found not able to reduce elemental sulfur when fixed in the crystal lattice of a sulfide mineral. The conversion of mineral-sulfide to elemental sulfur was found to be the solution to overcome this problem. The final proposed Paroxsul process is therefore based on this finding. More research is necessary to investigate if the combination between bio-oxidation, ferric leaching, and bio-reduction, will result in satisfactory gold recoveries on an industrial scale. If so, a new method with a lower environmental impact, less costs, and application to multiple minerals, is ready to be introduced to the precious metal industry.

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Summary

Sulfide minerals, like pyrite and arsenopyrite, are of economical interest due to the presence of invisible gold locked inside these minerals. As fine grinding is often not sufficient to liberate the gold from these minerals, additional destruction techniques, based on chemical and biological oxidation processes, are required to access the gold via cyanidation. Although these techniques have proven to be successful to reach satisfactory gold recoveries, operation costs are high and challenging waste streams are produced. In the search for a more environmentally friendly alternative to oxidation, the aim of this thesis was to find an innovative alternative biologically based process with a lower environmental impact.

Initially, the bio-reduction of pyrite and arsenopyrite with hydrogen was proposed. Compared to the oxidation methods, reduction of mineral-sulfur with hydrogen, producing hydrogen sulfide, has as major advantage that the hydrogen sulfide can be recovered from the solution (to produce bio-sulfur) leaving a waste stream without diluted sulfuric acid. Furthermore, electrical energy will be saved as less hydrogen, compared to oxygen, needs to be transferred to the reactors and less cooling will be required to keep the bio-reduction process at the desired temperature. Theoretically, this process was found to be possible, but at pH 5 and a temperature of 35°C sulfur/sulfate reducing bacteria apparently were not able to use sulfur when fixed in the crystal lattice of pyrite and arsenopyrite. In order to make the mineral-sulfur bio-available for these bacteria the sulfur should enter the solution, which may be achieved via selection of other conditions (pH, redox, and temperature) or via a different process route.

As a different process route the combination between partial bio-oxidation and bio-reduction was investigated. Partial bio-oxidation results in the formation of elemental sulfur, which can serve as a substrate for the sulfur/sulfate reducing bacteria. This combined method was found to be successful at 35°C at pH values of 2 (partial bio-oxidation) and 5 (bio-reduction) as the gold leachability of the used concentrate was increased from 6% to 39%. Furthermore, it was found that arsenopyrite is preferentially oxidized over pyrite. Optimization of this process is required as satisfactory gold recoveries (>90%) preferably should be reached within 1 or 2 ox/red cycles to be applied on large scale. To meet this guideline the three step Paroxsul (partial oxidation to sulfur) process is recommended. If a satisfactory gold recovery can be reached via this process, a new method with a lower environmental impact, less costs, and application to a large number of minerals, is ready to be introduced to the precious metal industry.

Samenvatting

Sulfide mineralen, zoals pyriet en arsenopyriet, zijn economisch interessant door de aanwezigheid van onzichtbaar goud dat in deze mineralen zit opgesloten. Omdat het pulveriseren van deze mineralen vaak niet voldoende is om het goud vrij te maken, worden additionele destructietechnieken, gebaseerd op chemische en biologische oxidatieprocessen, toegepast om het goud via cyanide te kunnen winnen. Deze technieken hebben bewezen dat ze succesvol zijn in het vrijmaken van goud, al zijn de operationele kosten hoog en worden er discutabele afvalstromen gevormd. Het doel van dit proefschrift is, om een alternatief voor oxidatie te zoeken in een innovatief biologisch proces met een geringere invloed op het milieu.

In eerste instantie is gekeken naar de bioreductie van pyriet en arsenopyriet met waterstof. Vergeleken met de oxidatiemethoden heeft de reductie van mineraalzwavel met waterstof tot waterstofsulfide het grote voordeel, dat waterstofsulfide kan worden teruggewonnen vanuit de oplossing (als biozwavel). Hierdoor wordt een afvalstroom vrij van verdund zwavelzuur verkregen. Daarnaast levert het een besparing op in het energieverbruik, omdat er minder waterstof vergeleken met zuurstof hoeft te worden getransporteerd naar de reactoren en er minder koeling nodig is om het bioreductieproces op de gewenste temperatuur te behouden. Theoretisch bleek dit proces mogelijk, maar bij pH 5 en een temperatuur van 35°C bleken zwavel/sulfaat reducerende bacteriën niet in staat om zwavel te gebruiken als het zit opgesloten in de kristalstructuur van pyriet en arsenopyriet. Om het mineraalzwavel biologisch bereikbaar te maken voor deze bacteriën is het van belang dat het zwavel eerst in oplossing komt. Dit kan mogelijk worden behaald door selectie van andere condities (pH, redox, en temperatuur) of via een alternatief proces.

Als alternatief proces is de combinatie tussen partiële bio-oxidatie en bioreductie onderzocht. Partiële bio-oxidatie resulteert in elementair zwavel, welke als substraat kan dienen voor de zwavel/sulfaat reducerende bacteriën. Deze combinatie van methoden bleek succesvol bij 35°C en een pH van 2 (partiële oxidatie) en 5 (bioreductie), omdat de winning van goud toenam van 6% naar 39% voor het gebruikte concentraat. Daarnaast bleek arsenopyriet gemakkelijker te oxideren dan pyriet. Optimalisatie van dit proces is nog vereist, omdat op grote schaal bij voorkeur voldoende goud (>90%) moet kunnen worden gewonnen binnen 1 a 2 ox/red cycli. Om aan deze vraag te voldoen, wordt het drie stappen Paroxsul (partieel oxideren naar zwavel) proces aanbevolen. Als men in staat blijkt voldoende goud te kunnen winnen via dit proces is er een nieuwe methode, met een lagere impact op het milieu, minder kosten en toepasbaar op meerdere mineralen klaar om te worden geïntroduceerd in de waardevolle metalen industrie.

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Alex

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Alex Hol was born on the 4th of February 1983 in Bernisse, the Netherlands. He grew up in Zuidland and obtained his Bachelor in biotechnology at Hogeschool Rotterdam. In 2004 he continued his study at Wageningen University where he received his Master in Process Biotechnology in 2006. In that same year he started as a PhD student at Wageningen University, department Environmental Technology. His project, “The bio-reduction of sulfide minerals to recover invisible gold”, with the results described in this thesis was finished halfway 2010. Since the 1st of November 2010 he started at Sustec BV, a company that develops new innovative technologies to serve today and the near future for a sustainable world.





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- o Hydrometallurgy, August 17 – 20, 2008, Phoenix, USA

Oral Presentations

- o Bio-reduction of sulfide minerals, Novel cost effective technologies for wastewater treatment and bio-energy production, September 5, 2008, Wageningen, The Netherlands
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