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

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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 ($FeAs_xS_{2-x}$), 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.

Costs of roasting arsenopyrite (AsPy) are increased by the $As_2O_{3(g)}$ and $SO_{2(g)}$ 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 $CaCO_3/Ca(OH)_2$ 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 paper 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.

1.1. 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 a previous paper on the bio-reduction of

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pyrite (Hol et al., 2010). In theory bio-reduction of pyrite is feasible, but under the selected conditions no reduction reaction was established (Hol et al., 2010). 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. (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. (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 Fig. 1 and Eq. (3). Next to being the phase were 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.

The standard reaction Gibbs free energy (ΔG_r^0) at 35 °C (Table 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. (4).

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).

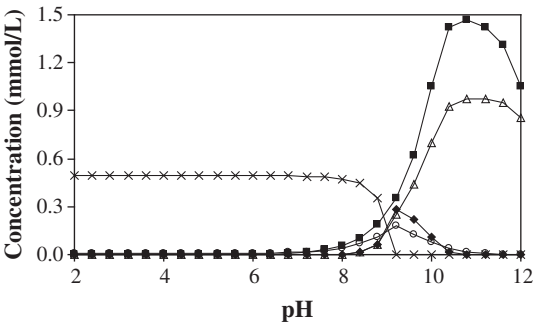

Fig. 1. Solubility of orpiment at 35 °C, 1 atm, as function of pH. Figure was constructed with OLI stream analyzer 2.0 using 1 mmol/L H_3AsO_3 and 1.5 mmol/L H_2S as inflow. Species shown are: As_2S_3 (x), HS^{-1} (■), AsO_2^{-1} (△), $As_2S_4^{-2}$ (♦) and $HAsO_2$ (○).

Table 1
Stochiometry 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	ΔG_r^0 (kJ/mol)*
	Bio-reduction	
1	$FeAsS + {}^1/_2H_2 + H^+ = {}^1/_2Fe^{2+} + {}^1/_2FeAs_2 + H_2S$	−58.4
	Anaerobic oxidation	
2	$FeAsS + {}^1/_2SO_4^{2-} + {}^1/_2H_2 + 3H^+ = Fe^{2+} + {}^1/_2As_2S_3 + 2H_2O$	−198.0
	Orpiment formation	
3	$H_3AsO_3 + 1\,{}^1/_2H_2S = {}^1/_2As_2S_3 + 3H_2O$	−75.2
	Sulfate reduction	
4	$^1/_2SO_4^{2-} + 2H_2 + H^+ = {}^1/_2H_2S + 2H_2O$	−151.8

* From HSC chemistry 6.12 (Outokumpu technology).

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.

2. Materials and methods

2.1. 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 ($HCl:HNO_3$ = 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 ($CaMg(CO_3)_2$), pyrite (FeS_2) and pyrrhotite ($Fe_{(1-x)}S$). 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.

2.2. Growth media

For the bio-reduction experiment (Eq. (1)) a defined medium as described by Hol et al. (2010) was used. For the anaerobic oxidation experiment (Eq. (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 $Na_2WO_4{\cdot}2H_2O$, and 2.13 g/L Na_2SO_4 as sulfate source. All chemicals were of analytical grade and supplied by Merck.