Minerals Engineering 106 (2017) 64–70

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Influence of dissolved oxygen on the bioleaching efficiency under oxygen enriched atmosphere

Anne-Gwénaëlle Guezennec [a,*], C. Joulian [a], J. Jacob [a], A. Archane [b], D. Ibarra [c], R. de Buyer [c], F. Bodénan [a], P. d'Hugues [a]

[a] BRGM-Water, Environment & Ecotechnologies Division, 3, av. Claude Guillemin, BP 36009, 45060 Orléans Cedex 2, France
[b] Milton Roy Mixing, 10 rue du Bois Gasseau, 77210 Samoreau, France
[c] Air Liquide, CRCD, 1 chemin de la porte des Loges, BP 126, 78354 Jouy en Josas, France

ARTICLE INFO

Article history:
Received 5 August 2016
Revised 17 October 2016
Accepted 18 October 2016
Available online 25 October 2016

Keywords:
Bioleaching
Oxygen
Dissolved oxygen concentration
Sulfide
Bacteria monitoring
Stirred tank reactor

ABSTRACT

The use of oxygen enriched air is a common practice in high-temperature bioleaching tests (>70 °C) to overcome oxygen solubility limitation and reduced the energy costs of the process. Air is usually preferred in medium and low-temperature operations mainly for technical and economic constraints. Nevertheless, under high-sulfide loading conditions - high-grade metal sulfide concentrates and high solids concentration - the microbial and chemical demand for oxygen is significantly increased during the bioleaching process. If not satisfied, this high oxygen demand might limit the oxidation efficiency. Therefore it requires the injection of large amounts of air. Sparging with oxygen enriched gas instead of air may offer an interesting alternative process option to improve gas transfer in the bioleaching reactor and to provide an adequate oxygen supply in order to satisfy the oxygen demand. It might be useful to develop innovative alternative to the classical stirred tank reactor (STR) technology. However, the use of such conditions can lead to much higher dissolved oxygen (DO) concentrations than those encountered with air. Very few papers have been devoted to the study of the optimal range of DO concentrations for bioleaching processes. Most of them reported an inhibitory effect of DO concentrations above 5 ppm. The purpose of this study was to investigate the influence of DO on the bioleaching efficiency under oxygen-enriched atmosphere in 21 L stirred tank reactor at 42 °C. Bioleaching experiments were performed in continuous mode with sulfide-rich tailings wastes composed mainly of pyrite (51%) and quartz using the "BRGM-KCC" bacterial consortia. The solid load was close to 20% (w/w). Using various oxygen supply conditions (partial pressure, gas rate), the DO concentration in the reactor varied between 4 and 17 ppm. For a DO ranging from 4 to 13 ppm, a good bacterial oxidizing activity was observed and the sulfide dissolution efficiency increased with the DO concentration. It is assumed that this improvement of the bioleaching efficiency was linked to an increase of the oxygen transfer rate from the gas phase to the liquid phase rather than a direct effect of the DO level. When the DO concentration reached 17 ppm a significant decrease of the microbial activity and consequently of the oxygen consumption was noticed. These results show that there is a critical value above which the DO concentration is detrimental to the activity of the bioleach microorganisms present in the "BRGM-KCC" consortia but this value is much higher than the one usually mentioned in the literature.

1. Introduction

Biohydrometallurgy is well established for the treatment of certain sulfide minerals, where iron and sulfur-oxidizing bacteria are used for the leaching of low grade copper ores and the pretreatment of pyritic gold ores and concentrates. However part of the mining industry remains skeptical and reluctant to adopt biohydrometallurgical techniques as a reliable alternative option. Heap leaching is sometimes considered unsuitable due to space constraints, slow leaching kinetics and low recovery rate. The interest of using stirred tank reactor (STR) for the treatment of other minerals than refractory gold ores, such as the base metal sulfides, has already been demonstrated but some improvements are still needed to meet economic viability (d'Hugues et al., 2008; Spolaore et al., 2009; Kutschke et al. 2015). The main costs of bioleaching operations in STR are the costs associated with the leaching tanks and the gas mass transfer to the pulp. The main

---

* Corresponding author.
E-mail address: a.guezennec@brgm.fr (A.-G. Guezennec).

http://dx.doi.org/10.1016/j.mineng.2016.10.016

capital costs are the ones for the agitators and for the gas injection devices. The main operating costs are associated with the energy consumption required for slurry agitation and air compression, since air is usually used to provide oxygen in bioleaching operations (Rossi, 2001; Morin and d'Hugues, 2007; van Aswegen et al., 2007). The microorganisms involved in bioleaching processes get their energy through the oxidation of reduced sulfur compounds and iron (II). In these reactions oxygen is used as electron acceptor. In the case of pyrite bioleaching mechanisms involve the following oxidation reactions:

$$FeS_2 + 2Fe^{3+} \rightarrow 3Fe^{2+} + 2S^0 \quad (1)$$

$$2Fe^{2+} + 2H^+ + 1/2O_2 \rightarrow 2Fe^{3+} + H_2O \quad (2)$$

$$S^0 + 3/2O_2 + H_2O \rightarrow H_2SO_4 \quad (3)$$

The reactions (2) and (3) are biologically catalyzed by acidophilic Fe- and S-oxidizing bacteria, whereas the reaction (1) occurs through chemical oxidation. The combination of the three reactions leads to the overall bioleaching reaction (Eq. (4)) which shows that 3.5 mols of oxygen is required to oxidize 1 mol of pyrite.

$$2FeS_2 + 4H^+ + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4H_2SO_4 \quad (4)$$

Oxygen supply is thus a key issue, particularly in bioleaching processes with high-sulfide loading conditions where the microbial and chemical demand for oxygen is significantly increased. As a consequence, there is a need to inject large amounts of air which can be technically difficult and increases the costs of the process. Sparging with oxygen enriched gas instead of air may offer an interesting alternative process option to improve gas transfer and bioleaching efficiency by providing an adequate oxygen supply in order to satisfy high oxygen demand.

Gas mass transfer in bacterial leaching systems has been widely studied and is well documented (Bailey and Hansford, 1993a; Bailey and Hansford, 1994; Boon and Heijnen, 1998; Savic et al., 1998; Veglio et al., 1998). Transfer to liquid theory (illustrated schematically in Fig. 4) indicates that the O_2 mass transfer rate, called R_{O2} (quantity of oxygen transferred in liquid phase per unit of time) is given by:

$$R_{O2} = K_La \times (C^* - C_L) \quad (5)$$

where: R_{O2} is O_2 transfer rate (mol m^{-3} s^{-1})
K_La is the volumetric oxygen mass transfer coefficient (s^{-1})
$C*$ is the oxygen solubility in reactor conditions (mol m^{-3})
C_L is the oxygen concentration in the liquid phase (mol m^{-3})

Several authors (Lui et al., 1987; Bailey and Hansford, 1994; Jordan et al., 1995; Myerson, 1981; Bailey and Hansford, 1993b) have pointed out that the lack of adequate gas mass transfer is a rate limiting step in many bacterial leaching processes. The gas-liquid mass transfer rate depends on a number factors (Van Weert et al., 1995; d'Hugues et al., 1997; Boon and Heijnen, 1998) such as the reactor type, geometry and size, the gas-flow rate, sparger design and depth, the stirring speed, particle shape and size, pulp density and viscosity. However oxygen can become a limiting factor in bacterial leaching because of its low solubility: only 0.26 mM O_2 (8.32 ppm) can dissolve per liter of water at 25 °C in an air/water mixture. As mentioned by Witne and Phillips (2001), one way of increasing the solubility of oxygen in water or media solution is by increasing the driving force, i.e. raising the oxygen partial pressure in the gas stream supplied to the leach pulp. This mechanism is described by Henry's gas law which gives the solubility of oxygen in solution in relation to the oxygen partial pressure in the gas phase:

$$C^* = (P^\circ/H) \quad (6)$$

where: $C*$ is the oxygen concentration of the nutrient solution;
P° is the partial pressure of the gas in the gas phase;
H is Henry's constant, which is specific for the gas and the liquid phase.

Henry's gas law shows that the solubility of O_2 in the leach pulp increases with increasing oxygen partial pressure in the gas stream. Higher O_2 partial pressures could be attained when the bioreactor air or gas stream is enriched with added pure oxygen. This approach was used for the development of processes using high thermophiles culture by teams working on the development of STR processes for the bioleaching of chalcopyrite concentrates (Dew et al., 1999; d'Hugues et al., 2002). In these studies, oxygen was used instead of air because of the low solubility of O_2 at high temperature. When working with mesophilic or moderately thermophilic microorganisms, they might be various interests of using O_2 enriched air such as (i) to decrease the flow of gas stream injected in the pulp, reducing energy consumption linked to agitation and compression of air (ii) to improve gas transfer to satisfy higher oxygen demand associated with higher sulfide concentration. Using O_2 enriched air is a promising alternative that might be useful to develop innovation to improve the classical STR technology. Air Liquide, Milton Roy Mixing and BRGM are currently testing an innovative bioleaching process using floating agitators to mix and to suspend solids in the solution as well as to inject gases in the pulp. This new concept enables to decrease the costs of bioleaching processes by operating in lagoons or ponds instead of using costly tanks, and at higher solid loading (>20%) than in conventional stirred tank bioreactors. In these conditions of high solid load, the microbial and chemical demand for oxygen is significantly increased and air could be replaced by oxygen enriched gas to provide an adequate oxygen supply in order to satisfy the oxygen demand.

However the use of such conditions can lead to much higher dissolved oxygen (DO) concentrations than those encountered with air sparging. Very few papers have been devoted to the study of the optimal range of DO concentrations for bioleaching processes. However most of them reported an inhibitory effect of DO concentrations above 5 ppm (de Kock et al., 2004; Wang et al., 2015).

The purpose of this study was to investigate the influence of DO on the bioleaching efficiency of a mesophile to moderate thermophile consortium. The bioleaching tests were carried out under oxygen-enriched atmosphere in a 21 L stirred tank reactor at 42 °C in continuous mode with sulfide-rich tailings wastes composed mainly of pyrite (51%) and quartz. The solid load was closed to 20% (w/w). The DO concentration in the reactor was varied between 4 and 18 ppm by increasing the gas flow rate. The influence of the DO level on the bioleaching efficiency was investigated through the monitoring of the sulfide leaching kinetics, the sulfide dissolution yield and the structure and the abundance of the microbial community.

2. Materials and methods

2.1. Characterization of the sulfidic materials

The experiments were performed using flotation tailings coming from a European copper mine. The mineral of economic interest in the ore body is chalcopyrite ($CuFeS_2$). At site, the ore is ground and valuable chalcopyrite is then separated from pyrite by flotation. Copper contained in the chalcopyrite is recovered by smelting whereas pyrite is discharged in tailings, from which the material used in this study was sampled. The tailings are mainly composed of pyrite (51%) containing cobalt (0.06%), copper