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CO_2 mass transfer in bioleaching reactors: CO_2 enrichment applied to a complex copper concentrate

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ABSTRACT

In bioleaching processes using autotrophic bacteria, carbon dioxide (CO_2) is the carbon source for the growth of the microorganisms and its availability is dependent on gas mass transfer. The objective of this study was to investigate the demand in CO_2 in complex sulfidic copper (Cu) concentrate bioleaching operations and to optimise CO_2 supply. Batch tests in 2 L-stirred reactors at $10\%_{w/v}$ solid concentration were performed to study the need for CO_2-enrichment and to determine the adequate CO_2 partial pressure in the gas inlet. The results show that ferrous iron (Fe(II)) oxidation, and thus microbial activity, is delayed when air is injected without CO_2-enrichment; the carbonates present in the solid are not sufficient to provide the CO_2 required for the activity of Fe oxidising bacteria. CO_2-enrichment improves leaching kinetics since the copper dissolution rate increases from 84 $\text{mg L}^{-1}\text{h}^{-1}$ with air solely to 120 $\text{mg L}^{-1}\text{h}^{-1}$ when CO_2 is added to air. A CO_2 enrichment influences both the composition of the bacterial community and the abundance of the bioleaching species. This study proposes also a methodology to determine gas/liquid transfer components and to assess CO_2 limitations in the system. It shows that the microorganisms are not only sensitive to the transfer rate of CO_2 from the gas to the liquid phase, but also to the availability of CO_2 in solution.

1. Introduction

In bioleaching processes using autotrophic microorganisms, carbon dioxide (CO_2) and oxygen (O_2) are two key gaseous substrates. CO_2 is the carbon source for cell growth. O_2 is used as the terminal electron acceptor in the oxidation process of iron and sulfur. During bioleaching operations both gases must be provided continuously to secure that their transfer rate may equal, at least, the O_2 and CO_2 demand. When the gas transfer is too slow, cell growth and microbial activity decrease, which affects significantly the kinetics of sulfide leaching.

The gas to liquid (G/L) mass transfer rate is given by the following relation:

$$R_{G/L} = k_L a \times (C^* - C_L) \quad (1)$$

Where: $R_{G/L}$ is the transfer rate from the gas to the liquid phase ($\text{g m}^{-3}\text{s}^{-1}$), k_La is the volumetric mass transfer coefficient (s^{-1}), C^* is the liquid phase gas concentration which is in equilibrium with the bulk gas phase (g m^{-3}), C_L is the concentration of gas in the liquid phase (g m^{-3}).

The volumetric mass transfer coefficient for a given gas depends on a number of factors, the main ones being the geometry of the reactor, the gas-flow rate and the stirring speed. The difference $(C^* - C_L)$ is the driving force of the gas to liquid mass transfer phenomenon. The driving force is greatly influenced by the partial pressure of the gas in the injection stream according to Henry's law which gives the gas saturation concentration:

$$C^* = H \times P^0 \quad (2)$$

Where 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, the composition thereof, and the temperature.

When the changes of CO_2 concentration in the liquid phase over time are slow (which is usually the case in acidic conditions), the CO_2 transfer rate is also equal to the CO_2 consumption rate (also called CO_2 uptake rate, CUR). The carbon dioxide uptake rate is usually determined by analyzing the gas phase at the inlet and outlet of the bioreactor and making a mass balance between both streams. The concentration of CO_2 in the liquid phase is the only parameter that

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Table 1
Summary of studies investigating CO2 enrichment in bioleaching operations.

Authors	Acevedo et al., 1998	Witne and Phillips, 2001	Nagpal et al., 1993	Cautivo and Gentina, 2009	Astudillo and Acevedo, 2009	de Kock et al., 2003	D'Hugues et al., 2008	Petersen et al., 2010
Substrate	Enargite/pyrite Au concentrate	Chalcopyrite/ pyrite concentrate	Arsenopyrite/pyrite concentrate	Chalcopyrite concentrate	Pyrite, enargite, chalcopyrite concentrate	9 k Medium with potassium tetrathionate	Pyrite concentrate	Cu ore (chalcopyrite and secondary Cu sulfides)
Microorganisms	Acidithiobacillus (At.) ferrooxidans	At. ferrooxidans, Sulfobacillus accidophilus, Sulfolobus	At. ferrooxidans	Sulfolobus metallicus	Sulfolobus metallicus	Sulfolobus sp.	Leptospirillum, Acidithiobacillus, Sulfobacillus	Not characterized
Temperature	35 °C	30, 50, 70 °C	35 °C	70 °C	70 °C	78 °C	40 °C	40 °C
Reactor	1.3 L, Batch	1 L, Batch	14 L, Continuous	3.3 L, Continuous	3 L, Batch	1.5 L, Batch	100 L, Continuous	COLUMN, 6*1*0.32 m
Solid concentration	4%w/v	3%	6 and 16%	150 g L^{-1}	15% w/v	–	20% w/w	–
Gas	Air	Air, or air + O_2	Air	Air	Air	O_2 + N_2 mixture	Air	Air
CO_2 enrichment	1 to 6%$_{v/v}$	5 to 15% (total ratio in the gas stream)	0.5 to 2.38%$_{v/v}$	5%$_{v/v}$	0.5 to 25%$_{v/v}$	Up to 25%$_{v/v}$, (total ratio in the gas stream)	1%$_{v/v}$	1000 and 2000 ppm
Results	Optimal CO_2 enrichment: 4%	Optimal CO_2 enrichment: 10%	Optimal dissolved CO_2 concentration ~ 5 mg L^{-1}. Inhibitory above 10 mg L^{-1}	Cu extraction increases from 55% up to 74% when air was supplemented with CO_2	Optimal CO_2 enrichment: 5%	Optimal inlet CO_2 concentration: between 7% and 17%	Pyrite dissolution increases from 65% up to 90% when air was supplemented with CO_2	Stimulation of microbial growth and CO_2 consumption when air was supplemented with CO_2

cannot be measured easily. Indeed, chemical sensors cannot be used in acidic media such as in bioleaching systems, and the optical sensors are only adapted to a CO_2 concentration higher than 20 mg L^{-1}. However, it can be deduced from Eq. (1) when the CUR is known.

Several authors (Lui et al., 1987; Bailey and Hansford, 1994; Jordan et al., 1995; Myerson, 1981; Bailey and Hansford, 1993; Guezennec et al., 2017) have pointed out that the lack of adequate gas mass transfer is a rate-limiting step in many bacterial leaching processes. In bioleaching operations, air is usually used to provide O_2 and CO_2. The latter can become a limiting factor because of its low concentration in water: the concentration of CO_2 in air is 0.03%$_{v/v}$, which corresponds to a saturation concentration of 0.44 mg L^{-1} at 25 °C. Supplemental CO_2 may be included in the aeration regime with the intention of improving microbial (and thus operational) performance. The papers dedicated to this topic are very few and the reported data were obtained in a wide spectrum of operating conditions as can be seen in Table 1.

Most of them report an improvement of the bioleaching efficiency with CO_2-enrichment compared to injection of air solely. One of them have also shown that bioleaching might be affected when CO_2 partial pressure in the inlet gas becomes too high. However, most of these studies do not provide information related to gas mass transfer in their experimental setup. Moreover, none of them makes the link between CO_2-enrichment and CO_2 availability and consumption. These results are thus difficult to apply for scale-up purposes. At that time the level of CO_2-enrichment needed and the associated potential benefit remain unclear.

The objective of this study was to study the influence of CO_2 enrichment on the bioleaching of a complex copper concentrate. Batch tests in 2 L-stirred reactors at 10%$_{w/v}$ solid concentration were performed. The copper concentrate used in this study is produced by flotation of a black shale organic rich sulfidic ore; it contains appreciable amounts of carbonates which can dissolve in acidic conditions and produce CO_2. Increasing CO_2 enrichment and air flow rate were tested and CO_2 supply due to carbonate dissolution was also examined. Operating conditions were selected to maintain the k_La constant throughout the series of experiments. Only CO_2 partial pressure in the gaseous inlet was increased to improve CO_2 transfer rate, and thereby to increase CO_2 availability. CUR was also determined to characterize completely the G/L transfer in the system. The influence of these parameters on bioleaching efficiency was investigated through the monitoring of the iron (Fe) oxidation kinetics, the copper leaching rates, the sulfide dissolution yield and the structure and the abundance of the microbial community.

2. Materials and methods

2.1. Sulfide materials

The experiments were performed using a copper concentrate retrieved from a black shale type ore (Kupferschiefer, Lubin mine, Poland). The concentrate is produced from a mixture of sandstone (79%,) shale (11.8%), and dolomite (9.2%). According to EDX (Energy Dispersive X-ray)-based particle analysis, the concentrate consists of gangue minerals (57%), mainly represented by dolomite and silicate minerals (illite, feldspar, and quartz), and sulfides (43%). The latter are dominated by chalcopyrite, pyrite, and galena, but contain also moderate amounts of bornite, chalcocite, and idaite as determined at the University of Halle as previously described by Kamradt et al. (2018). Mineral distribution also revealed that besides base metal sulfides, the copper concentrate contains a noticeable portion of sulfates (at least 3.2%, mainly under the form of jarosite, gypsum and anglesite). The chemical composition of the copper concentrate is given in Table 2. Major and trace metal contents were determined by ICP-AES after oxidising digestion according to protocols dedicated to ore analysis (degradation of all sulfides). Total carbon and total sulfur were determined using a Leco analyser: i.e. non-dispersive infrared analysis of