Oxygen solubility in copper bioleaching solutions

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A B S T R A C T

Oxygen is usually the limiting reagent in bio-leaching processes. For this reason, aeration is a key point to take into account when designing such processes, and the oxygen saturation concentration is an important variable to know. Currently, there is a lack of data or models to accurately predict the concentration at which oxygen saturates under the operational conditions during copper bio-leaching.

For this paper, oxygen solubility was measured in solutions containing the main electrolytes present in bioleaching solutions: sulphuric acid, ferrous sulphate, ferric sulphate, and copper sulphate; measurements were performed throughout the range of concentration that is characteristic to each electrolyte. These solutions were obtained by microbiological oxidation of ferrous sulphate, and were exposed to air, at atmospheric pressure, until oxygen saturation occurred. Measurements were taken using a dissolved-oxygen electrode. From the results, the equation is obtained:

$$S_i = S^° - 12.698 \cdot 10^{-pH} - 0.0555 \cdot \left[Fe^{2+} \right] - 0.0290 \cdot \left[Fe^{3+} \right] - 0.0265 \cdot \left[Cu^{2+} \right]$$

that predicts oxygen solubility in copper bio-leaching liquors from the simple measurement of pH and Fe^{2+}, Fe^{3+}, and Cu^{2+} concentrations.

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1. Introduction

Technical viability of hydro-metallurgical processes that are based on indirect bio-leaching is greatly dependant on the efficiency of the process that regenerates ferric iron, the leaching agent. Ferric iron is regenerated by microbiological catalysis in aerobic conditions, a process known as bio-oxidation (Watling, 2006). Aeration is a key element when designing indirect bio-leaching processes since oxygen usually limits the ferro-oxidant biological population's metabolic activity (Savic et al., 1998; Lizama, 2001; Mazuelos et al., 2002). Important theoretical and empirical efforts have been made, in order to determine oxygen transfer kinetics in bioleaching design (Petersen, 2010).

Efficient operation of aerobic biological reactors requires maximisation of oxygen transfer rate from the gas phase that initially contains it toward the cells (Bailey and Ollis, 1986). The rate of this mass transfer is a function of the flow characteristics, the magnitude of available surface for transfer between phases, and the concentration gradient between the gas-liquid interphase (source) and the cells (sink). The accepted models for quantifying solute mass transfer between phases postulate thermodynamic equilibrium at the interphase, implying that knowledge of the saturating concentration of such solutes —oxygen in this case— is a necessity.

Solubility of a gas in a liquid medium is dependent on the gas' partial pressure, temperature, and composition of the liquid medium. It decreases in the presence of ionic solutes, an effect known as salting-out.

Sechenov's equation is considered to be pioneering in modelling the salting-out effect on gas solubility in solutions with only one electrolyte (Clever, 1983). According to Eq. (1), the magnitude of the salting-out effect depends on the electrolyte and its concentration C_i, and is quantified by means of the ratio of solubilities of the gas in water ($S°$) and aqueous solution of the electrolyte (S_i) at the same partial pressure.

$$Log \left(\frac{S°}{S_i} \right) = k_i \cdot C_i \tag{1}$$

In this equation, k_i is an adjustment parameter known as Setchenov's saline effect parameter for electrolyte *i*.

After Sechenov's equation, modelling evolved in order to achieve equations that would allow for the estimation of gas solubility in liquids with multiple components (Shumpe, 1993), showing the following conceptual characteristics:

- Empirical nature. Mathematical formulations contain adjustment parameters with values that are specific to each solute and independent from solute concentration, temperature, and oxygen partial pressure.
- The magnitudes of each individual salting-out effect for all electrolytes are taken into account as a function of their concentration, considering

that they are not affected by the presence and concentration of other solutes.
- The overall decrease in solubility of a gas in a liquid with multiple components is calculated by arithmetic combination of the salting-out effects of each component of the mixture.

Shumpe's model (Shumpe et al., 1978) is commonly used as a model for the study of gas solubility in aqueous solutions containing several electrolytes. This model considers the salting-out effect of the different ions that form the aqueous mixture to be additive, and expressed as $Log\left(\frac{S^{\circ}}{S_i}\right)$. Its simplest form is Eq. (2), which is analogous to Setchenov's equation (Eq. (1)):

$$Log\left(\frac{S^{\circ}}{S_i}\right) = \sum_i h_i \cdot C_i \qquad (2)$$

h_i is an empirical parameter, specific to ion i, and independent from solute concentration, temperature, and partial pressure of the gas. Shumpe's model allows calculation of Setchenov's parameter k_i in liquids containing only one electrolyte (Lang and Zander, 1986).

Development of general solubility models for solutions with multiple components is a very complicated task (Clever, 1983; Groisman and Khomutov, 1990) since the salting-out effect usually shows noticeably different tendencies depending on the type, number, and concentration of electrolytes that are present in the solution (Tromans, 2000). Because of this, different models can result in divergent estimations even if they have similar mathematical formulation (Narita et al., 1983; Milero et al., 2003).

The need for precise estimations in certain engineering contexts has led to the development of models that are only valid under typical operational conditions. The models developed by Shumpe et al. (1978), Narita et al. (1983), and Tromans (1998) are particularly relevant to the context in which this work can be applied.

Shumpe's model was initially developed to be used in the field of microbial fermentation. Narita's and Tromans' models were developed for quantification of oxygen solubility in hydro-metallurgical leaching processes involving oxygen. Narita's model is represented mathematically by an equation identical to that of Shumpe's model (Eq. (2)). Tromans' model uses a very different equation (Eq. (3a)) to the former; for a single electrolyte:

$$\frac{S_i}{S^{\circ}} = \phi; \quad \phi = \left\{\frac{1}{1 + \kappa(C_i)^{\gamma}}\right\}^{\eta} \qquad (3a)$$

κ, γ y η are adjustment parameters with specific values for each electrolyte. C_i is the molal concentration of the electrolyte.

This model, when extended for solutions with multiple components, is expressed by Eq. (3b).

$$\frac{S_i}{S^{\circ}} = \phi_{eff}; \quad \phi_{eff} = \phi_1 \left(\prod_2^z \phi_i\right)^q \qquad (3b)$$

Subindex 1 refers to the main electrolyte, subindex i refers to the rest of the z electrolytes that are present in the mixture, and q is an adjustable index; commonly $q = 0.8$.

Copper bio-leaching liquors are acid solutions in sulphate medium that contain Fe and Cu amongst their main components, at concentrations below 20 g/L. Usually, pH ranges between 1 and 2.5; the lower limit is determined by biological activity and upper one by the precipitation equilibrium of Fe hydroxides and oxyhydroxides (Mazuelos et al., 2010, 2012). Within this pH range, bisulphate ion is partially dissociated. Iron with $+2$ charge is mainly found as independent Fe^{2+} ions. Iron with a charge of $+3$ found as free Fe^{3+} is a minority (concentration below 5%) (Fox, 1987; Yue et al., 2014). This is because iron with a

charge of $+3$ is involved in hydrolysis reactions and in coordination complex formation with SO_4^{2-}, HSO_4^-, and OH^- ions. Speciation in H_2SO_4-$Fe_2(SO_4)_3$-$FeSO_4$-H_2O solutions is very complex, and strongly dependant on pH and iron concentration in its ferrous and ferric forms. It has been postulated that, while the main species of Fe with a $+3$ charge is $FeSO_4^+$, there is also a significant presence of $Fe(SO_4)_2^-$ and $FeHSO_4^{2+}$. Depending on the pH, these ions can interact with polymeric structures formed by partially hydrolysed ferric iron ($Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_4^-$) and colloidal ferric hydroxide (Dutrizac, 1980, Fox, 1987, Yue et al., 2014). The diverse speciation of bio-leaching liquors results in an unfavourable setting for use of the formerly described solubility models due to calculus difficulty and the amount of information they require (Popovic et al., 1979; Groisman and Khomutov, 1990).

There is a wealth of literature showing oxygen solubility data in ionic media. The most recent and extensive of these publications is the data compilation by Clever et al. (2014). Unfortunately there is no data on oxygen solubility in aqueous media containing ferrous ions, and information about media with ferric ions is limited, showing only data from solutions with concentrations above 1 M. Information about oxygen solubility in sulphuric acid, and copper sulphate solutions is more abundant. In most cases, solubility data was obtained by using pure oxygen. It is worth mentioning that atmospheric N_2 and CO_2 are also found dissolved in bio-leaching liquors that are exposed to air. Groisman and Khomutov (1990) examines this matter and explains that the presence of other gases than oxygen in a liquid can alter its chemical characteristics, and thus oxygen solubility in it.

The lack of information regarding oxygen solubility in bio-leaching processes has led the authors of this paper to define the following goals:

- Obtain experimental data regarding oxygen solubility in conditions that are representative of bio-leaching processes; this means liquors that contain sulphuric acid, copper sulphate, ferrous and ferric sulphate resulting from microbiological oxidation of ferrous ions, and are saturated with oxygen due to contact with air at atmospheric pressure.
- Build an empirical correlation for estimating oxygen solubility in bio-leaching liquors using variables that can be measured quickly and easily.

2. Materials and methods

2.1. Oximetry

Oxygen concentration was measured with an Orion oximeter (3 Star model) equipped with an internal barometer for pressure compensation, and with a 081010MD Termo Scientific dissolved-oxygen electrode. This device allows for continuous measuring of the dissolved oxygen concentration with a resolution of 0.01 mg/L and a relative accuracy of 1.25%.

2.2. Oxygen solubility measurement

Assays were performed using the oximeter described above in order to determine oxygen solubility. Experiments were conducted under the following conditions:

- Oxygen saturation. To saturate the liquid with oxygen, air was pumped through it until the oxygen concentration remained constant (approximate transition time was 25 min). A 500 mL round flask equipped with a porous ceramic diffuser was used as saturation flask.
- Minimal evaporation. Injection of air into the liquid favours solvent evaporation. In order to minimise its effect on solvent composition, fumes from the saturation beaker were cooled and returned.
- Humidity saturation. Because the air that is introduced must be compressed, it is partially desiccated. Air was humidified in a gas-washing