



Depósito de Investigación
Universidad de Sevilla

Depósito de investigación de la Universidad de Sevilla

<https://idus.us.es/>

“This is an Accepted Manuscript of an article published by Elsevier in
Hydrometallurgy on January 2017, available
at: <https://doi.org/10.1016/j.hydromet.2016.10.023> .”

OXYGEN SOLUBILITY IN COPPER BIOLEACHING SOLUTIONS

Alfonso Mazuelos*, Carlos Jesús García-Tinajero, Rafael Romero, Nieves Iglesias,
Francisco Carranza

Department of Chemical Engineering of the University of Seville (Spain)

Address:

Department of Chemical Engineering of the University of Seville

c/ Profesor García González, Edf. Química

41012 Seville

Spain

* Corresponding author: A. Mazuelos

e-mail: mazuelos@us.es

fax: +34 954 55 64 41

Abstract

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 bio-leaching 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 is obtained the equation

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

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

Keywords: bio-leaching, bio-oxidation, Acidithiobacillus, aeration, oxygen solubility.

Highlights:

Methodology for measuring O_2 solubility under Cu bio-leaching operational conditions.

Equation for estimating O_2 solubility under typical Cu bio-leaching conditions.

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. (Smith et al 2007). 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 equation (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^o) and aqueous solution of the electrolyte (S_i) at the same partial pressure.

$$\text{Log}\left(\frac{S^o}{S_i}\right) = k_i \cdot C_i \quad (1)$$

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 $\text{Log}\left(\frac{S^{\circ}}{S_i}\right)$. Its simplest form is the equation (2), which is analogous to

Setchenov's equation (1):

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

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 (2). Tromans' model uses a very different equation (3a) to the former; for a single electrolyte:

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

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 the equation (3b).

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

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 $\text{H}_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3\text{-FeSO}_4\text{-H}_2\text{O}$ 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 $\text{Fe}(\text{SO}_4)_2^-$ and FeHSO_4^{2+} . Depending on the pH, these ions can interact with polymeric structures formed by partially hydrolysed ferric iron ($\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3^+$, $\text{Fe}(\text{OH})_4^-$) and colloidal ferric hydroxide (Dutrizac 1980, Fox 1987, Guikuan Yue, 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 1M. 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 minutes). 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 bottle before coming into contact with the liquid, which also helps avoid losses due to evaporation.
- Sterility. Working materials were sterilised in autoclave and solutions were sterilised by filtration with Millipore equipment using 0.45 micron filters. Avoiding biological contamination was fundamental since cellular respiration did not allow saturating conditions to be reached in any situation, and it altered medium composition.

- Temperature: 30°C. Dissolved oxygen measurement is very sensitive to temperature. Assays were performed at a constant temperature of $30 \pm 0.1^\circ\text{C}$, the optimal growth temperature for most ferro-oxidant microorganisms.

In order to satisfy these premises, the experimental setup shown in the diagram in figure 1 was used.

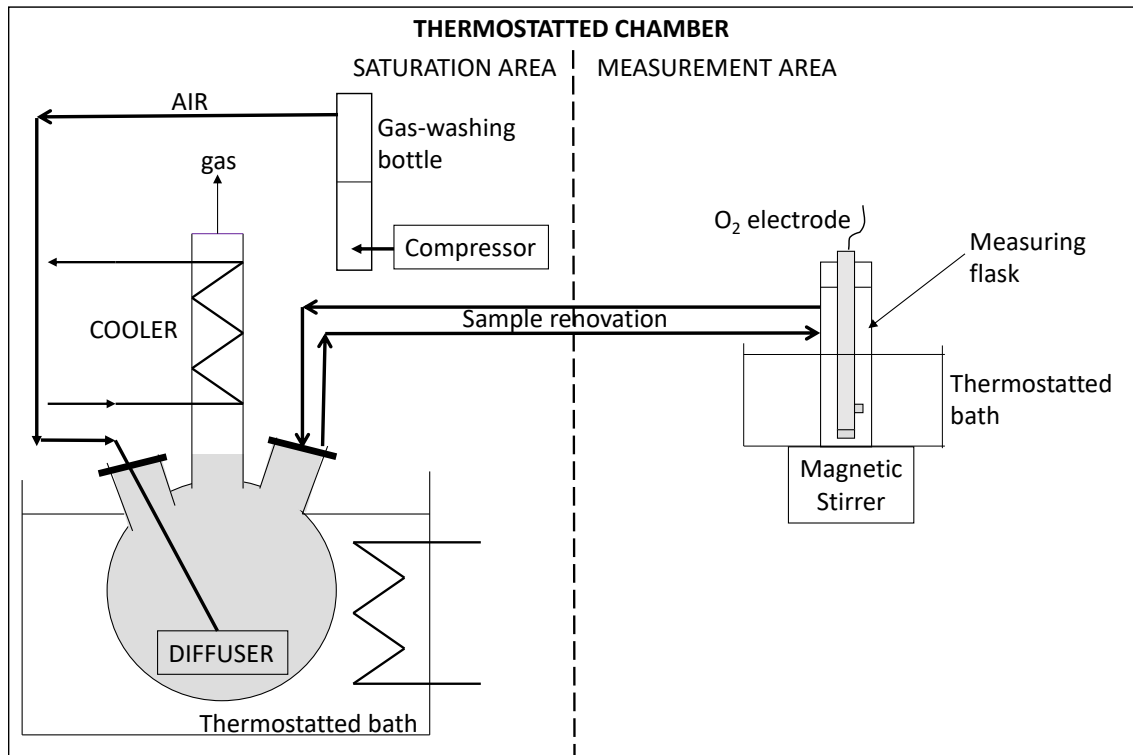


Figure 1: Diagram of the experimental setup used for measuring oxygen solubility in bio-leaching liquors.

The whole setup was placed inside a thermostatic chamber at 30 °C. The beaker for saturating the liquid with oxygen was partially submerged in a thermostatic bath at 30 °C to compensate heat loss due to evaporation.

The presence of bubbles and boundary layers in the vicinity of the membrane interfere with dissolved oxygen concentration measuring with a gas-semipermeable membrane electrode. In order to avoid these interferences, oxygen saturated liquid was sent, via a peristaltic pump (1L/h flow), to a 50 mL flask (measuring flask) where the electrode was located. Liquid in the measuring flask was mixed using a magnetic stirred. The measuring

flask was also kept in a thermostatic bath set at 30 °C. After circulating through the measuring flask, liquid was returned to the saturation flask. Like this, oxygen consumption inherent to measuring with a semipermeable membrane electrode was minimised. The volume of liquid in the circuit was 500 mL.

2.3. Solution preparation.

Copper sulphate and ferrous sulphate solutions were prepared by dissolving ferrous sulphate heptahydrate and copper sulphate pentahydrate in water, previously acidified to a pH value slightly above the target pH by adding sulphuric acid, until the desired concentration was reached. Finally, solutions were filtered through a 0.45 micron Millipore filter. Ferric sulphate solutions were prepared by biological oxidation of ferrous sulphate solutions. This was accomplished by inoculating a ferrous sulphate solution with a pellet of cells obtained by centrifuging an active mixed culture of *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* grown in 9K medium. The pellet was resuspended in water and centrifuged again to avoid contamination by 9K nutrient salts. After ferrous ion bio-oxidation was complete, the solution was filtered through a 0.45 micron Millipore filter to remove any biological material.

2.4. Analysis.

All pH measures were taken with a WTW-3310 pH-meter equipped with software for multi-buffer calibration. A Sentix 41 electrode by the same brand was used, which allows for measurement within a temperature range of 0 to 80 °C. Panreac buffer solutions at pH 1, 2, and 7 were used for calibration.

Fe (II) concentration was measured by redox titration with potassium dichromate. To this end, an automatic burette with potentiometric end-point control manufactured by Radiometer Copenhagen was used.

Total Cu and Fe concentration was measured by atomic absorption spectrophotometry (Perkin-Elmer, model 2380).

3. Results.

One thing bio-leaching liquors have in common is their acidic nature. Usual pH values are below 2, to avoid massive ferric precipitation, and above 1, to avoid deactivating the microbial population (Mazuelos et al 2010, 2012). Oxygen solubility was measured in saturated aqueous solutions of sulphuric acid at 30 °C; the results are shown in figure 2.

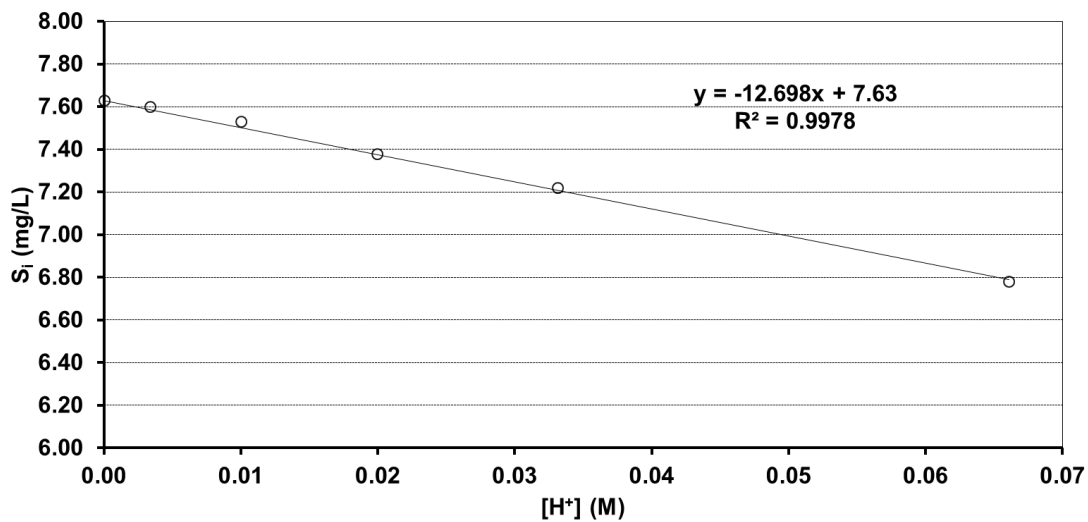


Figure 2: Oxygen solubility (S_i) in aqueous solutions of H_2SO_4 with different proton concentrations $[H^+]$ in contact with air at 30 °C and atmospheric pressure.

All values for oxygen saturation concentration shown in figure 2 resulted from calculating the arithmetic average of 15 measurements, with a standard deviation below 0.03 mg/L in all cases.

Oxygen solubility decreases linearly as proton concentration in the medium rises, and it is possible to calculate oxygen solubility in mg/L in an aqueous solution of sulphuric acid that is exposed to air at 30 °C and atmospheric pressure with this equation:

$$S_i = S^o - 12.698 \cdot 10^{-pH} \quad (4)$$

in which $S^o = 7.63 \text{ mg/L}$, which is the average oxygen solubility in distilled water under the aforementioned conditions. Conceptually, it makes no sense to use this intercept in

bio-leaching processes since it is necessary for pH to be below 1.8 for Fe^{3+} to be soluble in concentrations as high as 20 g/L. Oxygen solubility in water at this pH is 7.43 mg/L.

The measured oxygen solubility values are shown in comparison to those obtained using Setchenov, Shumpe, Narita and Tromans' models in figure 3. By analogy with the most common graphic representations for these models, in which the salting-out effect is independent from the temperature and the partial pressure of oxygen in the gas, the common logarithm of the quotient of solubilities with and without sulphuric acid is shown against the molar concentration of H_2SO_4 . The Setchenov coefficient k_i used when applying Setchenov's equation (1) was 0.087 L/mol (Clever et al 2014).

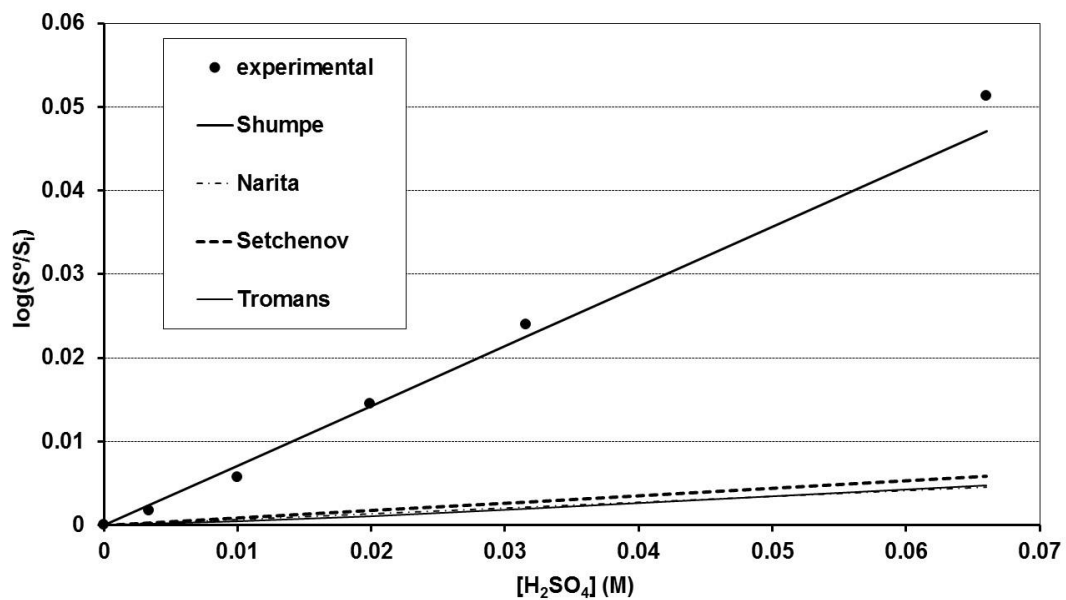


Figure 3: Salting-out effect for oxygen in aqueous solutions of H_2SO_4 as measured, and as estimated using Setchenov, Shumpe, Narita, and Tromans' models.

The oxygen solubility measurements obtained in these experiments were close only to the predicted values obtained using the model developed by Shumpe et al 1978; this model was conceived for application in fermentation, which is characterised by low concentrations of acid. The other models predict much lower values for $\log(S^\circ/S_i)$ and very little influence of sulphuric acid on oxygen solubility. It is worth pointing out, however, that the representations shown in figure 3 for Setchenov, Narita and Tromans' models are extrapolations; these models were obtained from experimental data

corresponding to oxygen solubility in sulphuric acid solutions with concentrations above 1M.

Oxygen solubility was examined in $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions within the ranges of pH and concentration that are characteristic to bio-leaching.

The results from experiments with $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions are shown in figure 4. Experiments were conducted at pH values 2, 1.5, and 1.18, and Cu^{2+} concentration ranged between 0 and 20 g/L. Markers match the experimentally obtained results.

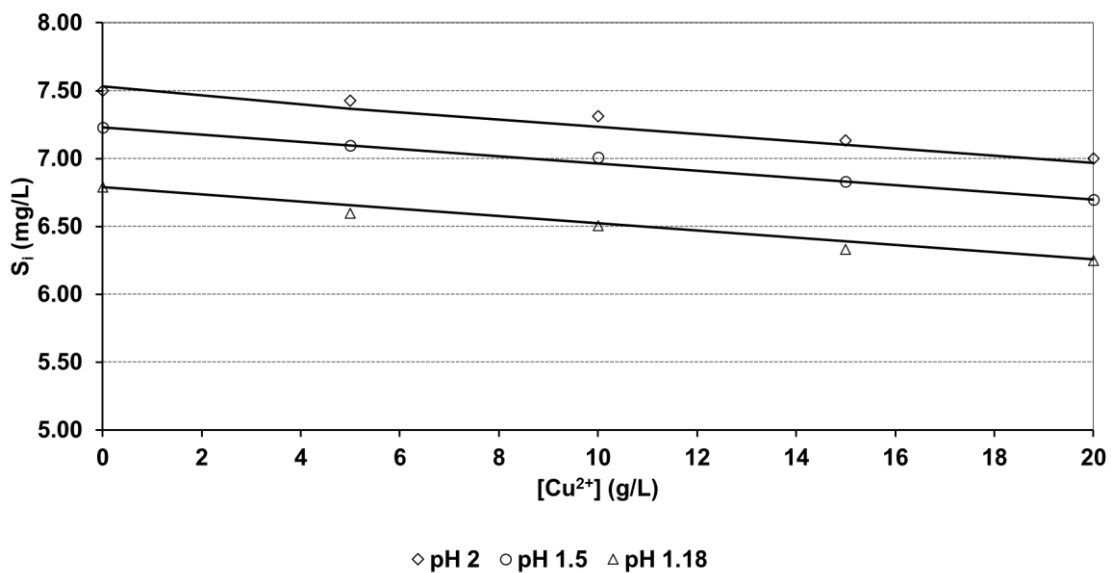


Figure 4: Oxygen solubility (S_i) in aqueous solutions of H_2SO_4 and CuSO_4 in contact with air at 30 °C and atmospheric pressure, at different copper concentrations $[\text{Cu}^{2+}]$ and pH values.

For every pH value that was studied, oxygen solubility decreases as CuSO_4 concentration rises, maintaining an inverse linear relationship with Cu^{2+} concentration; the graph slopes were similar in all cases. All Cu^{2+} concentration show a similar rise in oxygen solubility when pH varies, and an approximate value for this rise could be calculated using equation (4). This result appears to show that, under the conditions studied in this work, the salting-out effect associated with sulphuric acid is not affected by the presence of CuSO_4 . The authors postulate that the salting-out effects from these two electrolytes are additive and

propose the following equation as a way to estimate oxygen solubility in CuSO₄-H₂SO₄-H₂O solutions that have been exposed to air at 30 °C:

$$S_i = S^{\circ} - 12.698 \cdot 10^{-pH} - 0.0265 \cdot [Cu^{2+}] \quad (5)$$

[Cu²⁺] is the concentration of Cu²⁺ ions in g/L; the multiplier for [Cu²⁺] was determined by least squares adjustment. Hereinafter all concentration variables will be expressed in g/L. Equation (5) can be used to estimate oxygen solubility in CuSO₄-H₂SO₄-H₂O solutions that have been exposed to air at 30 °C with deviations no greater than 1% from the experimental data. Lines in figure 4 correspond to the representation of equation (5).

Following the same blueprint as with H₂SO₄-H₂O solutions, the results obtained from the CuSO₄-H₂SO₄-H₂O system are compared with those predicted by the aforementioned models. In this case, Narita's model cannot be applied since his work does not study Cu salts. Neither can Shumpe's model, as it was formulated in 1978, for the same reason. This same author modified his model in 1993 so as to extend its use to industrial applications other than fermentation (Shumpe 1993). These modifications do not affect the mathematical formula but do affect the adjustment parameter *h*. This parameter takes different values from those shown in 1978 for some ions. Furthermore, values for other ions that were not studied in 1978 are included, one of which is Cu²⁺. On the other hand, it must be borne in mind that application of Setchenov's model is limited to solutions with only one electrolyte, and that all models estimate the salting-out effect caused by sulphuric acid by default; for this reason this comparison is performed at the lowest studied sulphuric acid concentration, that is pH = 2. Figure 5 shows a graphic representation analogous to the one in figure 3; in this case, log S^o/S_i is plotted against the molar concentration of CuSO₄.

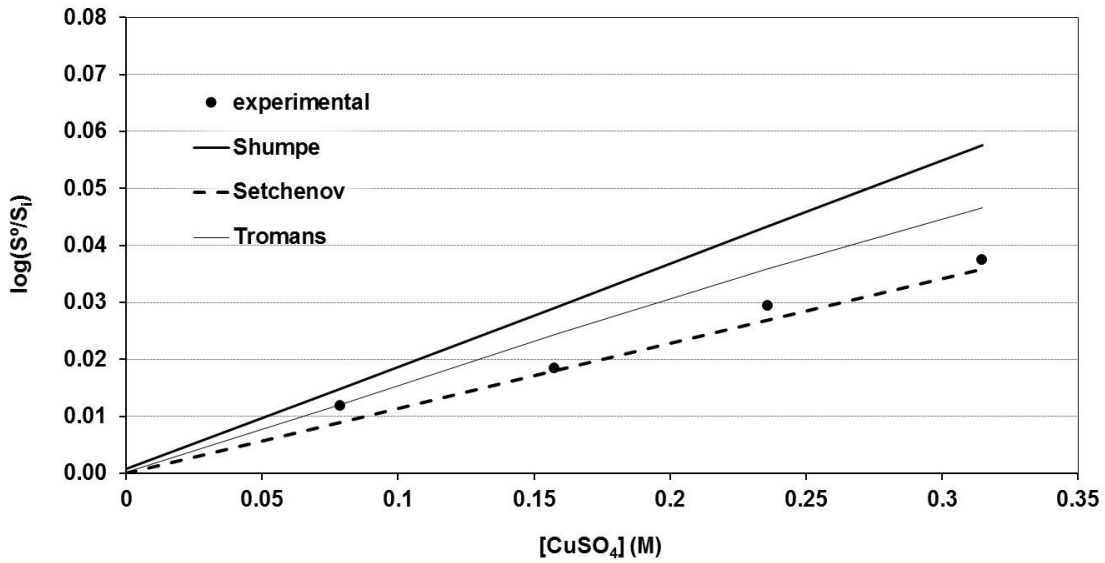


Figure 5: Salting-out effect in aqueous solutions of H₂SO₄ and CuSO₄ as measured, and estimated with Setchenov, Shumpe, Narita, and Tromans' models.

As with the H₂SO₄-H₂O system, estimations calculated with the different models are extrapolations; the lowest CuSO₄ concentration studied when developing these models was 0.5M. This may be the main reason why measured values differ from those estimated by most models. Similar values are only obtained when using Setchenov's model.

Figures 6 and 7 show the results that were obtained from the experimental study of oxygen solubility in FeSO₄-H₂SO₄-H₂O and Fe₂(SO₄)₃-H₂SO₄-H₂O solutions respectively. Tests were carried out at pH values 2, 1.75, 1.5, 1.3, and 1.18. Fe²⁺ and Fe³⁺ concentrations ranged between 0 and 20 g/L. Markers show the experimentally obtained values.

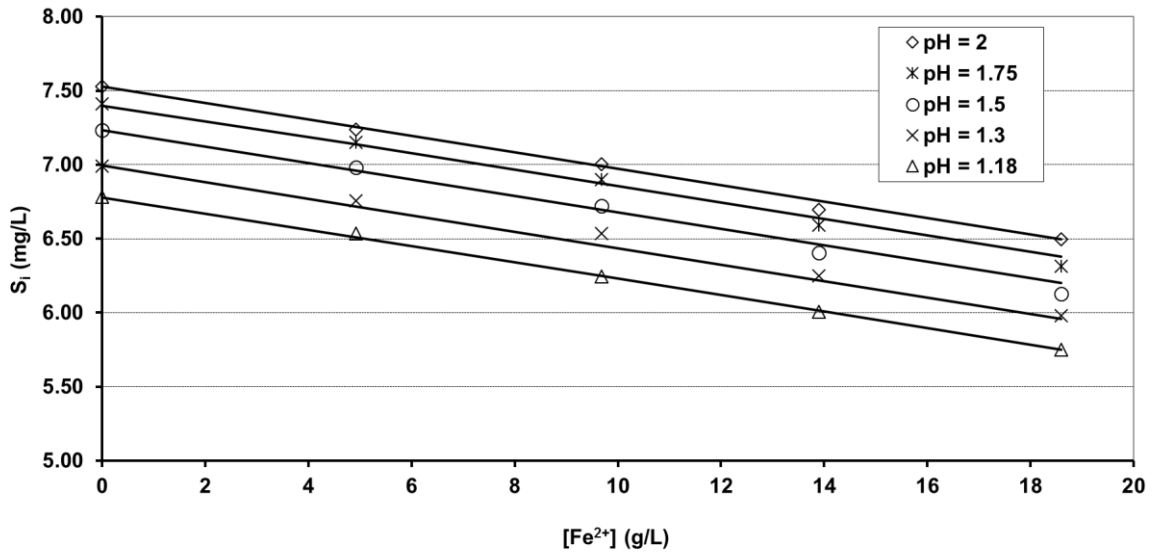


Figure 6: Oxygen solubility (S_i) in aqueous solutions of H_2SO_4 and $FeSO_4$, in contact with air at 30 °C and atmospheric pressure, at different pH values and ferrous iron concentrations $[Fe^{2+}]$.

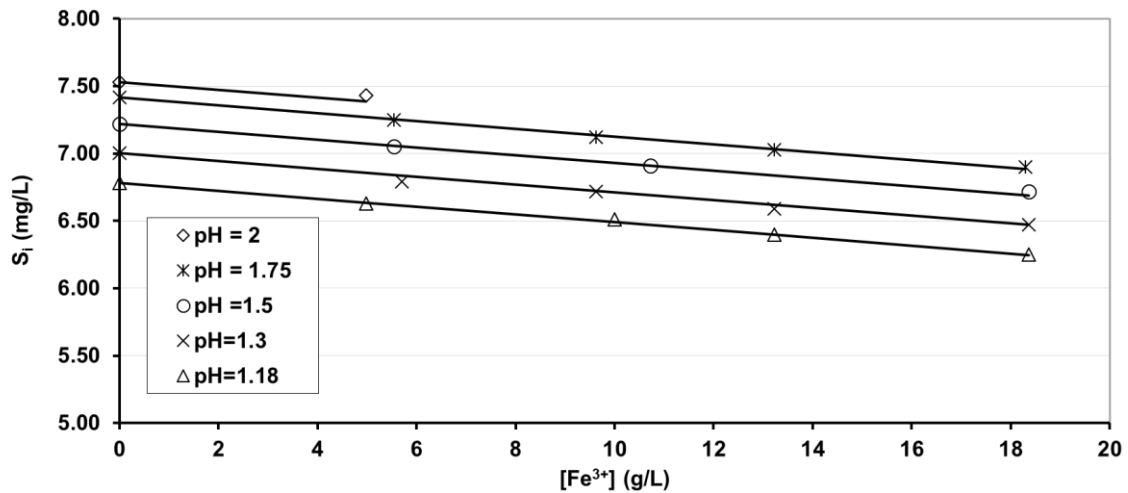


Figure 7: Oxygen solubility (S_i) in aqueous solutions of H_2SO_4 and $Fe_2(SO_4)_3$, in contact with air at 30 °C and atmospheric pressure, at different pH values and ferric iron concentrations $[Fe^{3+}]$.

In figure 7, the solubility curve for pH 2 does not span the full Fe^{3+} concentration range since it is not possible to obtain higher concentrations of dissolved Fe^{3+} at this pH due to precipitation.

Both graphic representations (figures 6 and 7) show that:

- For every pH value studied, oxygen solubility decreased linearly as concentrations of ferrous or ferric sulphate rose.
- For both Fe salts, the obtained curves for the different pH values were almost parallel.
- For a given Fe^{2+} or Fe^{3+} concentration, the mean solubility increments for different pH values are the same and equal to those obtained in $H_2SO_4-H_2O$ solutions, and they could be calculated with equation (4).

That is to say, the results obtained with $FeSO_4-H_2SO_4-H_2O$ and $Fe_2(SO_4)_3-H_2SO_4-H_2O$ are conceptually similar to those obtained with $CuSO_4-H_2SO_4-H_2O$ solutions. This suggests that it is possible to broaden the previously formulated hypothesis, about the salting-out effects of different present electrolytes being additive, and perform a mathematical treatment similar to the one used to develop equation (5). The resulting mathematical functions for $FeSO_4-H_2SO_4-H_2O$ and $Fe_2(SO_4)_3-H_2SO_4-H_2O$ solutions respectively are the following:

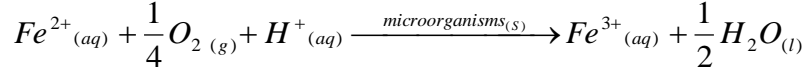
$$S_i = S^o - 12.698 \cdot 10^{-pH} - 0.0555 \cdot [Fe^{2+}] \quad (6)$$

$$S_i = S^o - 12.698 \cdot 10^{-pH} - 0.0290 \cdot [Fe^{3+}] \quad (7)$$

Both equations (6) and (7) make it possible to estimate oxygen solubility in $FeSO_4-H_2SO_4-H_2O$ and $Fe_2(SO_4)_3-H_2SO_4-H_2O$ solutions, which have been exposed to air at 30°C and atmospheric pressure, respectively, and these estimates differ from experimentally obtained results by no more than 1%. Equations (6) and (7) are shown in figures 6 and 7 as continuous lines.

Oxygen solubility was studied in liquid media that are representative of Cu bio-leaching, that is in $CuSO_4-FeSO_4-Fe_2(SO_4)_3-H_2SO_4-H_2O$ solutions. Ferrous ion bio-oxidation is an essential step in indirect bio-leaching, so this study can be useful beyond the field of hydrometallurgy, in other applications of ferrous ion bio-oxidation like gas desulphurisation and acid mine drainage remediation.

The link between bio-leaching and ferrous ion bio-oxidation restricts Fe^{2+} , Fe^{3+} , and pH values. If copper bio-leaching conditions are to be reproduced, it makes sense to study them by means of bio-oxidation stoichiometry:



Taking this into account, oxygen solubility was measured in $CuSO_4$ - $FeSO_4$ - $Fe_2(SO_4)_3$ - H_2SO_4 - H_2O media in which ferro-oxidant microorganisms had grown. Ferrous sulphate solutions were prepared with a target concentration of 20 g/L and these were then inoculated with pellets from centrifugation of an active mixed culture of *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* that had grown in 9K medium. Discrete 500 mL samples were taken at different moments of growth and were filtered through 0.45 micron Millipore filters and oxygen solubility was measured with no cells present. Copper sulphate was added to these solutions until the target concentrations of 5, 10, and 15 g/L Cu^{2+} were reached; oxygen solubility was then measured in each solution. Results are shown in table 1.

pH	[Fe^{2+}] g/L	[Fe^{3+}] g/L	[Cu^{2+}] g/L	S_i mg/L	$S_{i(EQ.8)}$ mg/L
1.36	17.3	5.3	0	5.78	5.76
1.36	17.3	5.3	4.93	5.56	5.63
1.35	17.3	5.3	11.2	5.37	5.45
1.35	17.3	5.3	17.3	5.22	5.29
1.50	11.3	11.0	0	6.11	6.08
1.51	11.3	11.0	5.08	5.92	5.95
1.50	11.3	11.0	10.56	5.74	5.81
1.51	11.3	11.0	16.4	5.59	5.66
1.69	7.5	14.9	0	6.46	6.32
1.68	7.5	14.9	4.99	6.22	6.18
1.68	7.5	14.9	9.15	6.10	6.07
1.69	7.5	14.9	15.8	6.08	5.90

Table 1: Oxygen solubility (S_i) in aqueous $CuSO_4$ - $FeSO_4$ - $Fe_2(SO_4)_3$ - H_2SO_4 - H_2O solutions obtained by microbiological oxidation in contact with air at 30 °C and

atmospheric pressure. Solubility values as predicted by equation (8) ($S_{iEQ.8}$) under the same conditions.

Based on the previously formulated hypothesis, which considers the salting-out effects from different electrolytes to be additive, one can reach equation (8), which results from combining equations (4), (5), (6) and (7):

$$S_i = S^\circ - 12.698 \cdot 10^{-pH} - 0.0555 \cdot [Fe^{2+}] - 0.0290 \cdot [Fe^{3+}] - 0.0265 \cdot [Cu^{2+}] \quad (8)$$

Table 1 shows the oxygen solubility values estimated with equation (8) ($S_{iEQ.8}$) together with measured oxygen solubility values (S_i). It can be seen that equation (8) can be used to estimate oxygen solubility in $CuSO_4$ - $FeSO_4$ - $Fe_2(SO_4)_3$ - H_2SO_4 - H_2O solutions that have been exposed to air at 30 °C with deviations from experimental data that do not exceed 3%.

In this work, all experiments were conducted at 30 °C, and the equations that were developed are valid for this temperature. To estimate oxygen solubility at other temperatures T , other authors (Narita et al 1983, Tromans, 2000) use correction factors that are applied to S° . Tromans' correction is expressed as equation (9) when the reference temperature is 30 °C:

$$S^\circ_T = S^\circ \cdot e^{\left(\frac{1336}{273.15+T} - \frac{1336}{303.15} \right)} \quad (9)$$

T is the temperature in degrees Kelvin, and S°_T is the reference solubility measured at a temperature T other than 30 °C.

Conclusions

A method for precisely measuring oxygen solubility in Cu bio-leaching liquors using dissolved-oxygen electrode has been put into practice in this work. Experimental data on oxygen solubility in H_2SO_4 - H_2O , $CuSO_4$ - H_2SO_4 - H_2O , $FeSO_4$ - H_2SO_4 - H_2O , $Fe_2(SO_4)_3$ - H_2SO_4 - H_2O , $FeSO_4$ - $Fe_2(SO_4)_3$ - H_2SO_4 - H_2O , and $CuSO_4$ - $FeSO_4$ - $Fe_2(SO_4)_3$ - H_2SO_4 - H_2O solutions was gathered using this methodology. Results seem to indicate that the salting-out effects exerted by different electrolytes in them are additive. Based on this premise

and the experimentally obtained data, simple empirical equations using easy to measure variables were built for estimating oxygen solubility. Finally, a model for oxygen solubility in Cu bio-leaching liquors exposed to air at 30 °C was developed (equation (8)). This model allows to estimate oxygen solubility by simple measurement of pH and $[\text{Fe}^{2+}]$, $[\text{Fe}^{3+}]$ and $[\text{Cu}^{2+}]$.

Acknowledgements: The authors wish to thank the FEDER INTERCONECTA program (project TC-20111083) for the financial support given for this study. The research group would like to thank Mr. Charles Nisbet for his work translating this document from Spanish and revising it prior to publication.

References:

- Bailey, J.E., Ollis, D.F., 1986, in: *Biochemical Engineering Fundamentals*, 2nd ed. McGraw-Hill, 457-512.
- Clever, H.L., 1983, Sechenov salt-effect parameter, *Journal of Chemical and Engineering Data*, 28, 340-343.
- Clever, H.L., Battino, R., Miyamoto, H., Yampolski, Y., Young, C.L., 2014, IUPAC-NIST Solubility Data Series. 103. Oxygen and Ozone in Water, Aqueous Solutions, and Organic Liquids (Supplement to Solubility Data Series Volume 7), *Journal of Physical and Chemical Reference Data* 43, 3.
- Dutrizac, J.E., 1980, The physical chemistry of ion precipitation in the zinc industry, In Cigan J.M., Mackey, T.S., O'Keefe, T.J., (Eds.) *Lead-Zn-Tin'80*. AIME. New York, 532-564.
- Fox, L.E., 1987, The solubility of colloidal ferric hydroxide and its relevance to iron concentrations in river water, *Geochimica et Cosmochimica Acta*, 52, 771-777.
- Groisman, A.S., Khomutov, N.E., 1990, Solubility of oxygen in electrolyte solutions, *Russian Chemical Reviews*, 59, 1217-1250.
- Lang, W., Zander, R., 1986, Salting-out of oxygen from aqueous electrolyte solutions: prediction and measurement, *Industrial Engineering Chemistry Fundamentals*, 25, 775-782.

Lizama, H.M., 2001, Copper bioleaching behaviour in an aerated heap, *International Journal of Mineral Processing*, 62, 257-269.

Mazuelos, A, Moreno, JM, Carranza, F., Palomino, C., Torres, A., Villalobo, E., 2012, Biotic factor does not limit operational pH in packed-bed bioreactor for ferrous iron biooxidation. *Journal of Industrial microbiology and biotechnology*, 39, 1851-1858.

Mazuelos, A., Carranza, F., Romero, R., Iglesias, N., Villalobo, E., 2010, Operational pH in packed-bed reactors for ferrous ion bio-oxidation, *Hydrometallurgy*, 104, 186–192.

Mazuelos, A., Romero, R., Palencia, I., Carranza, F., Borjas, F.J., 2002, Oxygen transfer in ferric iron biological production in a packed-bed reactor, *Hydrometallurgy* 65, 15-22.

Milero, F.J., Huang, F., Graham, T.B., 2003, Solubility of oxygen in some 1-1, 2-1, and 2-2 electrolyte as a function of concentration at 25°C, *Journal of Solution Chemistry*, 32, 473-487.

Narita, E., Lawson, F., Han, K.N., 1983, Solubility of oxygen in aqueous electrolyte solutions, *Hydrometallurgy*, 10, 21-37.

Petersen, J., 2010, Determination of oxygen gas-liquid mass transfer rates in heap bioleach reactors, *Minerals Engineering*, 23, 504-510.

Popovic, M., Niebelschütz, H., Reuss, M., 1979, Oxygen solubilities in fermentation fluids, *European Journal of Applied Microbiology and Biotechnology*, 8, 1-15.

Savic, D.S., Veljkovic, V.B., Lazic, M.L., Vrvic, M.M, Vucetic, J.I., 1998, Effect of oxygen transfer rate on the ferrous iron oxidation by *Thiobacillus ferrooxidans*. *Enzyme and microbial technology*, 23, 427-431.

Schumpe, A., 1993, The estimation of gas solubilities in salt solutions, *Chemical Engineering Science*, 48, 153-158.

Shumpe, A, Adler, I., Deckwer, W.D., 1978, Solubility of oxygen in electrolyte solutions; *biotechnology and Bioengineering*, 20, 145-150.

Smith, J.M., Van Ness, J.C., Abbott, M.M., 2005, in: *Introduction to Chemical Engineering Thermodynamics*, 7th Edition, McGraw Hill, 378-456.

Tromans, D. 2000, Modeling Oxygen Solubility in water and electrolyte solutions. *Industrial Engineering Chemistry Research*, 39, 805-812.

Tromans, D., 1998, “Oxygen Solubility Modeling in Inorganic Solutions: Concentration, Temperature and Pressure Effects”, *Hydrometallurgy*, 50, 279-296.

Watling, H.R., 2006, The bioleaching of sulphide minerals with emphasis on copper sulphides — A review, *Hydrometallurgy* 84 (2006) 81–108.

Yue, G., Zhao, L., Olvera, O.G., Asselin, E., 2014, Speciation of the $\text{H}_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3\text{-FeSO}_4\text{-H}_2\text{O}$, system and development of an expression to predict the redox potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple up to 150 °C. *Hydrometallurgy*, 147-148, 196-209.