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Hydrometallurgical Treatment of a Zinc Concentrate by Atmospheric Direct Leach Process

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Abstract

A hydrometallurgical method is proposed to recover zinc and other valuable metals from a zinc sulphide concentrate. Atmospheric direct leaching in sulphate and chloride media was performed. The effect of the reaction time, solid-liquid ratio, temperature, oxidant (Fe^{3+}) concentration and pH on the leaching efficiency was investigated. The results showed that using a solid-liquid ratio of 5% it was possible to leach 95% of zinc after 2 hours, with a solution of 0.5 M H_2SO_4 and 0.5 M $Fe_2(SO_4)_3$ at 80ºC. Copper leaching was favoured by the use of chloride medium, where approximately 60% of extraction was observed after 2 hours of leaching at 80ºC, with a solid-liquid ratio of 10% and a solution of 0.5 M HCl, 1.0 M $FeCl_3$ and 1.0 M NaCl. Leaching tests with the addition of air, O_2 and H_2O_2 were also performed to increase the amount of Fe(III) versus Fe(II) in solution. An improvement of 20% on zinc extraction was observed when, under the same conditions, oxygen was added to the system.

Keywords: Zinc sulphide concentrate, Atmospheric leaching, Iron (II) oxidation

1. Introduction

Zinc is an important metal required for many applications from metal products to chemical, paint, and agriculture industries. It is mainly recovered from sphalerite (ZnS), which is commonly associated to other sulphide minerals, such as chalcopyrite ($CuFeS_2$), galena (PbS) and Pyrite (FeS_2).

Both pyrometallurgical and hydrometallurgical techniques are currently employed to recover zinc from zinc ores. The conventional method involves the roast-leach-electrowinning process. The roasting step produces sulphur dioxide and, as the policy on discharge of SO_2 becomes stricter, hydrometallurgical routes, that avoid SO_2 production, become more attractive. Modern zinc plants that employ the conventional method convert SO_2 produced in the roasting stage to sulphuric acid, nevertheless, the need to sell the sulphuric acid produced to an overloaded market may affect the economics of zinc production.

Direct atmospheric leaching or pressure leaching as an alternative to the conventional method have been proposed, and the success of such methods are evident by some large-scale applications (Filippou, 2004). Hydrometallurgy treatment processes are both economical and more environmental suitable. Furthermore, they allow to treat even low zinc containing materials and the sulphur may be converted into elemental sulphur, rather than sulphur dioxide, which remains in the residue. For this purpose, various leaching studies have been performed which include acidic ferric chloride leaching (Aydogan et al., 2005; Dutrizac, 1991), acidic ferric sulphate leaching (Filippou, 2004; Dutrizac, 2006), and ammonia leaching (Babu et al., 2002; Goosh et al., 2002).

Ferric ion, which is one of the most important oxidant used in leaching processes, in either sulphate or chloride media, can be used to leach zinc sulphide, according to the equation (Aydogan et al., 2005; Dutrizac et al., 2003):

$$\mathrm{ZnS} + 2\mathrm{Fe}^{3+} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{Fe}^{2+} + \mathrm{S}^{0} \qquad (1)$$

The reaction consumes the ferric ions, thus leading to the decrease of the redox potential and to the observed reduction of the leaching rate. Therefore, it is advisable to carry out the oxidation of the ferrous ion formed through reaction 1. Oxidant agents such as air, oxygen (O_2) and hydrogen peroxide (H_2O_2) may be used to promote the oxidation of ferrous ions in aqueous solution. In acidic solutions, the oxidation of ferrous ion with O_2 follows reaction 2 (Rönnholm, 1999):

$$\mathrm{Fe}^{2+} + \frac{1}{4}\mathrm{O}_2 + \mathrm{H}_3\mathrm{O}^{+} \rightarrow \mathrm{Fe}^{3+} + \frac{3}{2}\mathrm{H}_2\mathrm{O} \qquad (2)$$

Hydrogen peroxide is also used as an oxidant agent for iron. In fact, the reduction potential of the H_2O_2/H_2O pair (E_0 (H_2O_2/H_2O) = 1.77 V) is adequate to oxidize the ferrous ions in accordance with the following equation (Aydogan, 2006):

$$H_2O_2 + 2Fe^{2+} + 2H^+ \leftrightarrow 2H_2O + 2Fe^{3+} \qquad (3)$$

The objective of the present study was to investigate the dissolution of zinc and other valuable metals such as copper, indium and silver from a zinc sulphide concentrate. For this purpose, the effect of variables such as reaction time, solid-liquid ratio, temperature, oxidant concentration, addition of an oxidant agent and pH on the leaching efficiency were investigated.

2. Experimental

2.1. Materials

All the chemicals were of Analytical Grade and all solutions were prepared with deionised water. Measurements of the pH and of the redox potential were obtained with a pH/E meter from Metrohm. The solutions were analysed for metals concentration by atomic absorption spectroscopy (Perkin Elmer, AAnalyst 200) and ferrous ion was determined by volumetric analysis with potassium dichromate (Vogel, 1972).

The zinc concentrate was gently supplied by Somincor and was produced from the Neves-Corvo Portuguese ore. Table 1 shows the chemical composition of the zinc concentrate, which was determined by chemical attack using a microwave digestor (CEM 2000). The X-Ray diffraction analysis showed that the concentrate contained mainly ZnS, FeS_2, and $CuFeS_2$.

Table 1: Chemical analysis of zinc concentrate (wt. %).

Element	(%)[1]
Zn	42 ± 1
Fe	11.5 ± 0.6
Cu	3.9 ± 0.1
In	0.018 ± 0.002
Ag	0.008 ± 0.001

2.2. Experimental procedure

Leaching tests were carried out in a five-necked round bottom reactor (1 L, 13 cm diameter) heated by a thermostatic oil bath. For stirring, a single round paddle (6.5 cm diameter) was used. The leaching solution ($Fe_2(SO_4)_3$ + H_2SO_4 or $FeCl_3$ + HCl + NaCl) was added to the reactor and when the temperature was reached, the solid was added and the stirring started. The redox potential of the solution was monitored throughout the experiments with a silver/silver chloride reference electrode.

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[1] For 95% confidence interval

At pre-set time intervals, samples were then withdrawn from the reactor and analysed by AAS against appropriate standards. The solid residues obtained in the leaching tests were washed, dried and stored in plastic bags under vacuum. If necessary, small volumes of H_2O_2 or a known flow of air/O_2 were also added to the reactor. The experimental set-up for the tests with air/O_2 is illustrated in Figure 1.

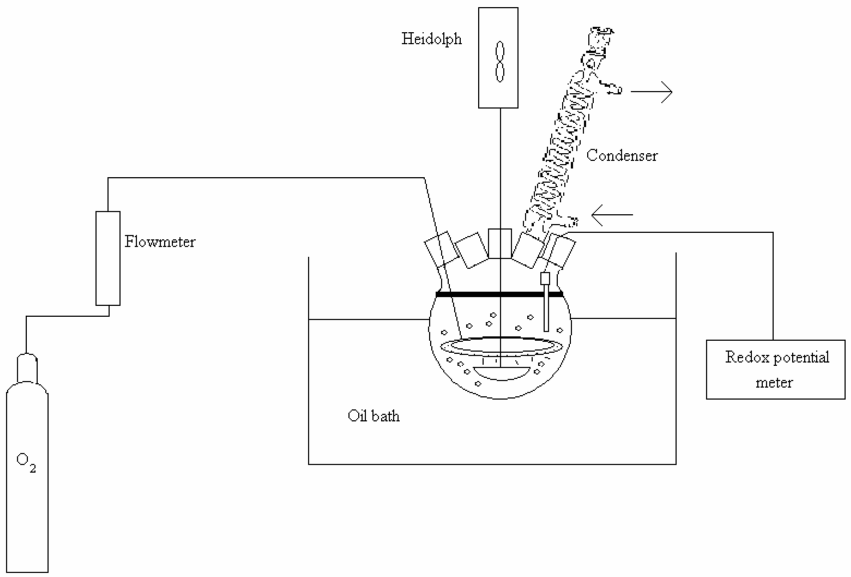

Figure 1: Experimental set-up for the leaching tests with iron oxidation.

3. Results and Discussion

3.1. Effect of the reaction time

The effect of the reaction time on metals leaching is shown in Figure 2 and, as expected, the extraction of metals increased with time.

Figure 2 shows that the leaching kinetics may be divided in two stages. In the first stage, which occurs up to the first 30-60 minutes of reaction, the kinetics of metals dissolution is fast, whereas the second stage presents a much lower leaching rate. In fact, about 90% of the final extraction of metals was obtained in the first stage. The results also allowed to conclude that, in sulphate medium, zinc and indium presented the same behaviour, because indium is probably associated with spharelite, whereas copper is more difficult to leach.

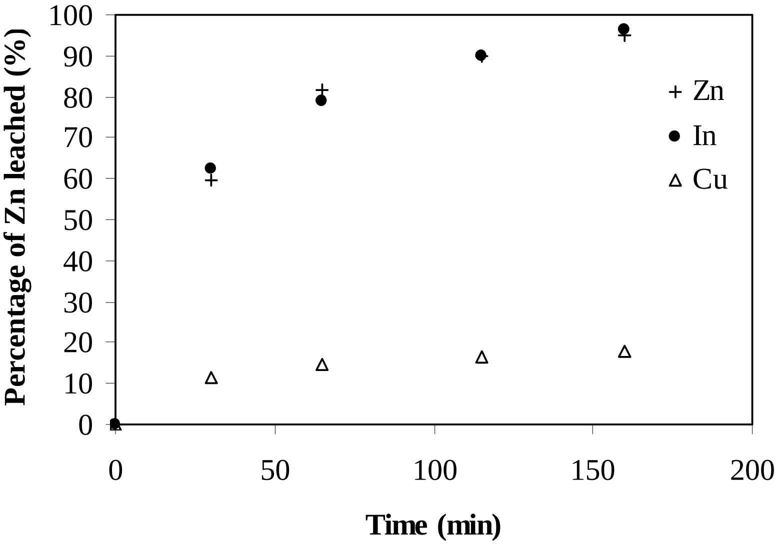

Figure 2: Effect of time on metals leaching. Experimental conditions: s/l=5% (w/v), leaching solution with 0.5 M H_2SO_4 + 0.5 M $Fe_2(SO_4)_3$, T=80 ± 3 ºC, v=320 rpm.

3.2. Effect of the solid-liquid ratio

The influence of the pulp density on the leaching results was investigated in order to optimize the consumption of the leaching reagents for an effective recovery of the metals.

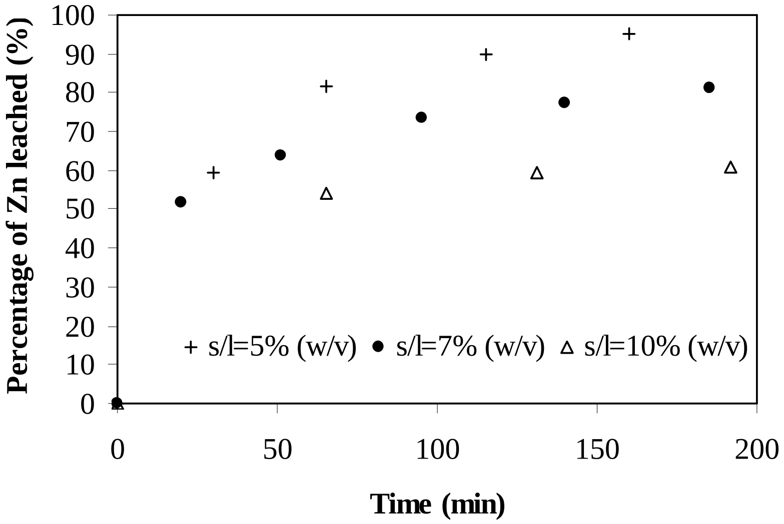

Figure 3: Effect of solid-liquid ratio on zinc leaching. Experimental conditions: leaching solution with 0.5 M H_2SO_4 + 0.5 M $Fe_2(SO_4)_3$, T=80 ± 3 ºC, v=320 rpm.

As illustrated in the previous Figure, it is necessary to use a solid-liquid ratio of 5% to leach all the zinc contained in the concentrate in one leaching stage. In fact, the augment of the solid-liquid ratio to 7 and 10% decreased the extraction of zinc to values of about 80 and 60% after 3 hours of leaching, respectively. The leaching behaviour of the other metals also followed a similar pattern.

3.3. Effect of the temperature

The extraction of metals is very sensitive to temperature. In fact, when temperature decreased from 80 to 40ºC, zinc and copper extraction decreased 40% and 10%, respectively.

3.4. Effect of the concentration of sulphuric acid and ferric sulphate

The composition of the leaching solution was varied in order to identify the cross effects of the sulphuric acid and ferric sulphate concentrations on the leaching of the metals, Figures 4 and 5 present the results.

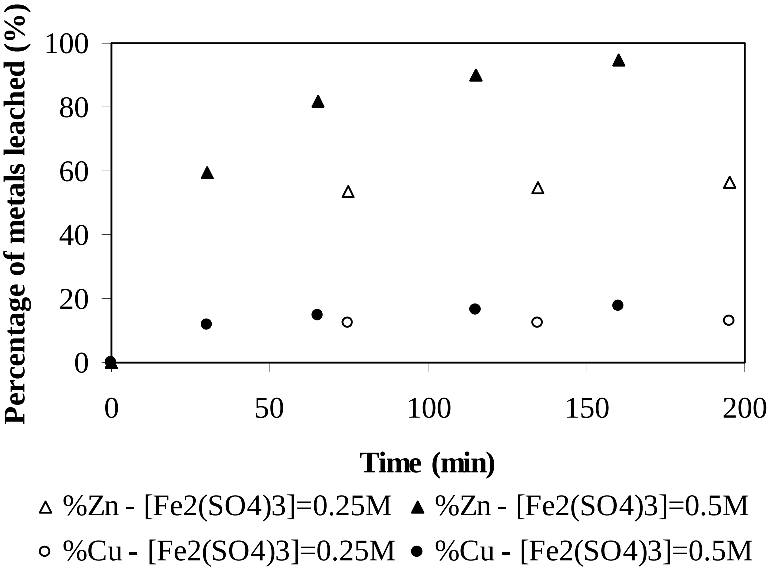

Figure 4: Effect of the concentration of ferric sulphate on the leaching of metals. Experimental conditions: s/l=5% (w/v), leaching solution with 0.5 M H_2SO_4 + 0.25 or 0.5 M $Fe_2(SO_4)_3$, T=80 ± 3 ºC, v=320 rpm.

Figure 4 shows that the extraction of Zn is strongly affected by the decrease of the concentration of ferric sulphate from 0.5 to 0.25 M. In fact, ferric ions are directly involved in the leaching reaction and so it is expected that the ferric sulphate concentration should be an important parameter. On the other hand, zinc sulphide is easily attacked by the ferric ion and Figure 4 shows that the increase of the ferric concentration from 0.25 to 0.5 M was not enough to favour the leaching of copper.

The results also show that the reduction of the sulphuric acid concentration from 2 to 0.25 M was less important (Figure 5).

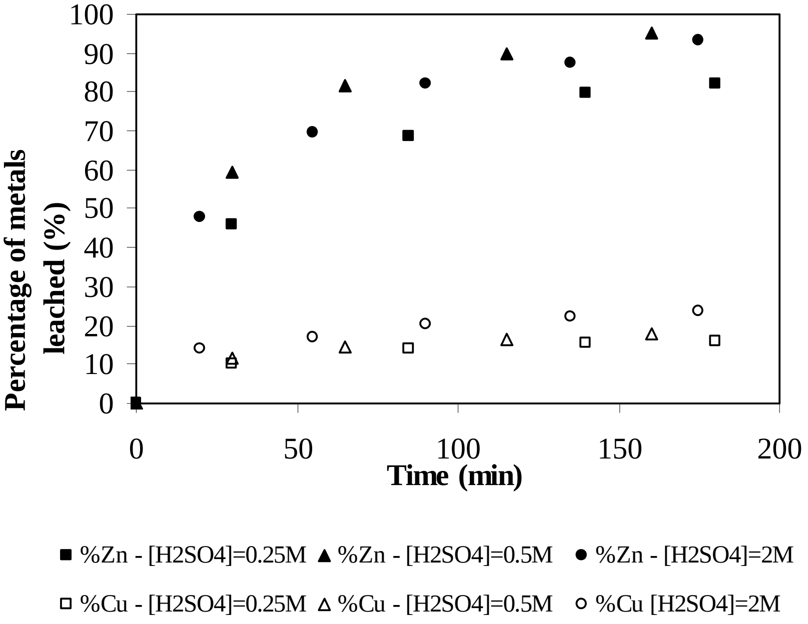

Figure 5: Effect of the concentration of acid on the leaching of metals. Experimental conditions: s/l=5% (w/v), leaching solution with 0.5 M $Fe_2(SO_4)_3$ + 0.25 or 0.5 or 2 M H_2SO_4, T=80 ± 3 ºC, v=320 rpm.

3.5. Chloride medium as an alternative to copper leaching

The comparison between the extraction of zinc, copper and silver on sulphate and chloride media is presented in Table 2. The results show that the extraction of metals is higher in chloride medium, this effect being much more important for copper. As expected, in sulphate medium silver was not dissolved, whereas in chloride medium it was possible to leach more than 50% of this metal. The influence of the addition of sodium chloride is also shown in Table 2 this influence being negligible for zinc. In contrast, copper and silver leaching is favoured by the addition of sodium chloride up to a concentration of 1 M, which is a direct consequence of the formation of chloride complexes that increase the solubility of the metals in the leaching solution.

Table 2: Effect of sulphuric and chloride media on metals extraction. Experimental conditions: s/l=10% (w/v), T=80ºC, v=350 rpm.

	Time (min)	[H_2SO_4] (M)	[$Fe_2(SO_4)_3$] (M)	[HCl] (M)	[$FeCl_3$] (M)	[NaCl] (M)	Zn (%)	Cu (%)	Ag (%)
Sulphate medium	192	0.5	0.5	-	-	-	61	10	-
Chloride medium	180	-	-	0.5	1	0	70	44	53
	180	-	-	0.5	1	1	69	56	60
	180	-	-	0.5	1	2	71	56	60

3.6. Effect of the use of oxygen and hydrogen peroxide

There are several advantages of performing the oxidation of Fe(II) to Fe(III) during the leaching. In fact, this procedure would allow maintaining the concentration of the oxidant during the leaching thus minimizing the consumption of fresh reagent. Furthermore, to achieve an effective separation of iron from zinc by solvent extraction, the Fe(II) must be oxidized to Fe(III).

To determine the most favourable conditions to carry out the oxidation of iron, some tests were firstly performed using synthetic solutions containing only ferrous sulphate and sulphuric acid but without the addition of the zinc concentrate. Therefore, a 7 L cylindrical reactor (diameter=14.5 cm) heated with an oil bath was used. The reactor was equipped with 4 baffles (height=38 cm, width=2 cm), two radial turbine separated by 5 cm, with 4 blades each (external diameter=8 cm, 1.5 cm blade height and 1.5 cm blade width) and an air entrance 5.5 cm below the centre of the impeller.

Air and H_2O_2 were used as oxidant agents for Fe(II) and the results are presented in Figure 6. As seen in this Figure, hydrogen peroxide is more effective and the time required to obtain the oxidation of 60% of the ferrous ion decreased by about 15 hours with the addition of H_2O_2.

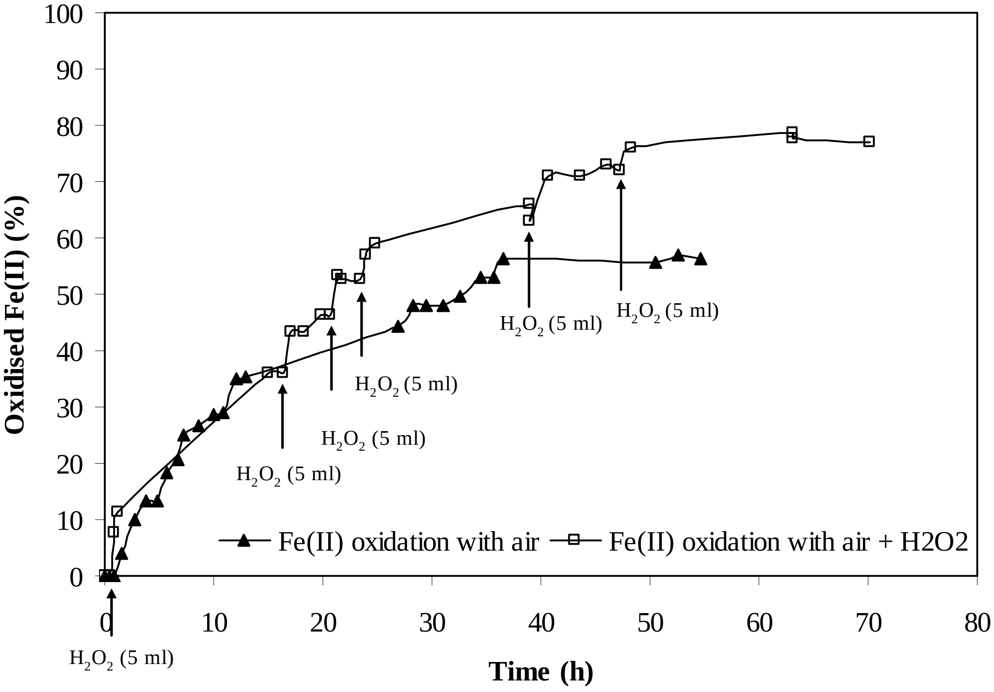

Figure 6: Effect of the addition of air and hydrogen peroxide on Fe(II) oxidation. Experimental conditions: solution with $[Fe(II)]_{initial}$=15 g/L, $V_{solution}$=4.5 L, pH_i=1.0, T=80 ± 3 ºC, v=520 rpm, air=64 L/h, V_{H2O2} =30 ml (solid symbols-air; open symbols-air + addition of H_2O_2 (30% by volume)).

The next step was to investigate the effect of promoting the oxidation of iron during the leaching tests. For this purpose, leaching tests of the zinc concentrate were carried out using a solution containing ferric sulphate and the simultaneous addition of air, oxygen or hydrogen peroxide. Figure 7 reports the results.

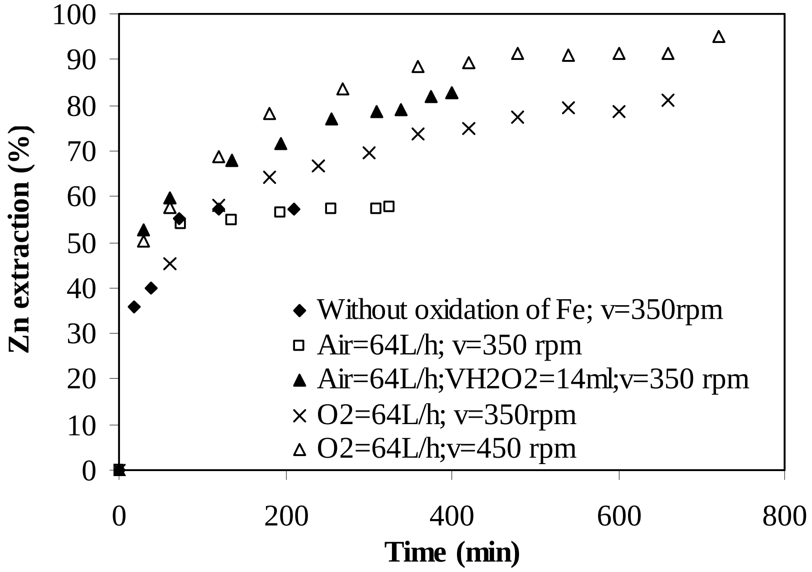

Figure 7: Effect on zinc leaching of performing the oxidation of Fe(II) during the leaching. Experimental conditions: s/l=5% (w/v), solution with 0.5 M H_2SO_4 + 0.25 M $Fe_2(SO_4)_3$, T=80± 3 ºC.

The experiments without the oxidation of Fe(II) and with the addition of air to the solution presented similar results and after 60 minutes of reaction almost all the iron (≈ 90%) was in the ferrous form. However, when O_2 was added to the solution, after 10h of reaction about 45% of the iron was oxidized to Fe(III). The benefits of iron oxidation are visible on the extraction rates of the metals. In fact, after 3 hours of reaction, the percentage of the zinc leached increased from 60% to 80% with the addition of O_2. The addition of H_2O_2 together with air to the leaching solution was also very effective. Finally, as seen in Figure 7, in these experiments the stirring speed was also an important parameter. In fact, increasing the stirring speed from 350 to 450 rpm allowed increasing about 10% the zinc extraction.

Conclusions

The results obtained in this work show that it is possible to leach all the zinc contained in the Neves-Corvo concentrate. The solid-liquid ratio, temperature and the concentration of Fe(III) have a great effect on zinc extraction, whereas the leaching results are nearly independent on the sulphuric acid concentration.

Without the addition of external oxidants, it was possible to leach almost all the zinc from the concentrate in one single stage using 0.5 M H_2SO_4, 0.5 M $Fe_2(SO_4)_3$, and a solid-liquid ratio of 5% during 3 hours at 80ºC.

Copper and silver leaching was favoured by chloride medium. In one stage, 60% of the copper and silver were leached using 0.5 M HCl, 1 M $FeCl_3$, 1 M NaCl and a solid-liquid ratio of 10% at 80ºC.

The regeneration of the ferric ions in situ would allow a significant decrease of the consumption of fresh ferric oxidant, without decreasing the leaching efficiency. In fact, zinc extraction was considerably enhanced when the oxidation of the ferrous iron to the ferric state ions was performed during the leaching reaction. It was demonstrated that hydrogen peroxide, as well as oxygen, may be used to perform the oxidation of the ferrous iron.

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