

# **Copper Removal from Sulphuric Leaching Solutions by Cementation**

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## **ABSTRACT**

The purpose of this work was to study the cementation of copper with zinc from a sulphate leaching solution produced from a zinc sulphide concentrate. Initially, cementation tests were carried out with synthetic solutions, to study the effect of pH, amount of sacrificial metal, copper concentration, temperature, stirring speed, the presence of  $Zn^{2+}$ ,  $Fe^{3+}$  and  $Fe^{2+}$ , zinc particles size and type of atmosphere. It was found that it is possible to reduce the content of copper to values close to 0 within few minutes of reaction, using zinc dust at pH=3 and a moderate agitation. In addition, iron (as Fe(II) or Fe(III)) present in the solution is also removed by cementation, although its kinetics is slower than copper's.

A final test was carried out with a real effluent, with the following composition: [Cu(II)]=67 mg/L, [Fe(II)]=582 mg/L, [Zn(II)]=10833 mg/L. It was possible to remove all the copper and to obtain a concentration of iron(II) of 0.02 mg/L. Therefore, the results obtained in this work allow to conclude that cementation may be used to purify the solution obtained in the sulphate leaching of a zinc sulphide concentrate after indium, iron and copper recovery by liquid-liquid extraction but before the zinc extraction step.

## **INTRODUCTION**

Cementation is described as the electrochemical precipitation of a metal by another more electropositive metal. This process has been used for centuries in hydrometallurgy for the purification of leaching solutions, and also for recovering toxic and precious metals from industrial waste streams (Sousa et al, 2007).

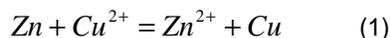
Cementation is a simple, easy to control technique, which allows the removal/recovery of toxic or valuable metals in their metallic and reusable form (Jackson, 1986). Its main disadvantage is the dissolution of the sacrificial metal into the solution, more critical at low pH values. Hence, an important aspect of this process is the use of non-toxic metal, or a metal which is already present in the solution, avoiding contamination with another ion. In this work, zinc was chosen as the precipitant metal. The use of several metals for copper cementation was already studied by several authors, who reported zinc to be more effective than iron and aluminium (Demirkiran et al., 2006). In fact, zinc has a higher oxidation potential than iron and therefore is a better precipitant than iron. Although aluminium has a higher oxidation potential than zinc, the protective oxidation layer formed on its surface during

cementation led to worse results. In this work, as the real leaching solution contains a significant amount of zinc in its composition, the use of a metal other than zinc in cementation would lead to a greater contamination of the solution and would surely make difficult the recovery of zinc in a later stage. Table 1 presents the electrochemical potential of several metal/ion systems.

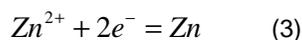
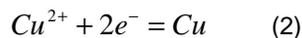
Table 1- Electrochemical reduction potentials of several metal/ion systems at 25°C (Jackson, 1986)

System	$E^0_{1/2 \text{ cell}}(\text{V})$
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1,66
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0,763
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0,44
$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$	-0,036
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	0,337
$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	0,77
$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	1,23

The basic cementation reaction for the copper(II)/zinc(II) system is:



Considering that copper is in the simple cationic form and that complex ions are not formed, the cementation reaction can be described in terms of its respective half cells:



The global reaction is an electrochemical reaction with an electrode potential, E, that may be calculated by the Nernst equation (equation 4). Therefore, considering that the activity of a pure solid in an aqueous solution equals 1, and knowing the activity coefficients,  $f_i$ , of the ionic species, the Nernst equation can be described in terms of concentrations:

$$E = E^0_{cel} - \frac{RT}{zF} \ln \frac{f_{N^{n+}} [N^{n+}]}{f_{M^{m+}} [M^{m+}]} \quad (4)$$

where  $E^0$  is the standard electrode potential, that can be calculated from the standard electrode potentials of the two half cells reactions (Table 1), M represents the noble metal and N the precipitant metal.

The Gibbs free energy change for an electrochemical reversible reaction at constant temperature and pressure may be calculated by:

$$\Delta G^0 = -z F E_{cel}^0 \quad (5)$$

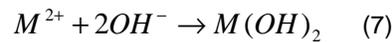
where F is the Faraday constant and z is the number of electrons transferred in the reaction (z=m).

When E>0 the reaction is spontaneous, whereas at the equilibrium E=0 and the equilibrium constant is given by:

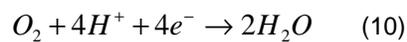
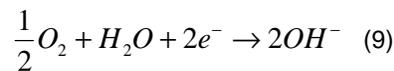
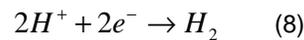
$$K_{eq} = \exp\left(\frac{zF}{RT} \times E_{cel}^0\right) \quad (6)$$

The Cu(II)/Zn(II) system exhibits large negative  $\Delta G^0$  values, which shows that the reaction is thermodynamically favourable (Jackson, 1986). Nevertheless, in practice, the complexity of the solutions may alter the half cell potential values of the reaction. Furthermore, competing reactions such as chemical precipitation and re-dissolution of the deposited metal, may lead to incomplete removal by cementation (Sousa et al, 2007).

Besides the reaction described by equation 1, during cementation other reactions can occur:



where M represents divalent metals present in the solution (in the case of this study Zn, Cu or Fe).



Equation 7 shows that an increase of the pH values may cause the passivation of zinc due to the precipitation of the metal hydroxides on its surface. In accordance to the metal hydroxide precipitant diagram (Jackson, 1986), Cu precipitates first (at pH values greater than 5), followed by Fe(II), which begins to precipitate at pH>8. On the contrary, at low pH values, the cementing metal may be spent in the reduction of H<sup>+</sup> ions (equation 8) and also in the reactions with the oxygen (9 and 10). Therefore, oxygen should be excluded away from the solution before the cementation reaction takes place.

In this work, the progress of the reaction described by equation 1 was followed by analysing the change of Cu<sup>2+</sup> and Zn<sup>2+</sup> contents in solution with time. It has been reported in the literature by several authors that cementation reactions mostly follow first order kinetics (Demirkiran et al., 2006). This was also assumed in this work. The model for the first order reaction for the Cu(II)/Zn(II) cementation system is:

$$\ln \frac{[Cu^{2+}]}{[Cu^{2+}]_0} = -k a_e \frac{w}{V} t \quad (11)$$

where  $V$  is the volume of the solution ( $m^3$ ),  $k$  the kinetic constant of the reaction ( $m/s$ ),  $a_e$  the specific area of the zinc particles ( $m^2/g$ ) and  $w$  the mass of zinc added ( $g$ ). The  $\ln([Cu^{2+}]/[Cu^{2+}]_0)$  versus time plots<sup>i</sup> will generate a straight line if:  $ka_e$  is independent of time, the reaction is first order concerning  $Cu^{2+}$ , and if copper's activity coefficient ( $f_{Cu^{2+}}$ ) doesn't significantly vary during the reaction. According to Blaser et al. (1983), one can consider that  $f_{Cu^{2+}}$  is practically constant during the time if the change of the ionic strength of the solution is minimal (Anacleto, 1994).

On the other hand, it is possible that the back-reaction occurs, resulting in the re-dissolution of the cemented metal. In terms of the difference of the standart half-cell potentials, one can consider that the reaction is irreversible if  $(E_M^0 - E_N^0) > 0.3V$  (Jackson, 1986). However, this condition is only valid at equilibrium. As a matter of fact, the experimental parameters, such as pH, time, initial concentration of the noble species and the presence of  $O_2$  can favour, or not, the re-oxidation of the deposit formed (Sousa et al., 2007).

The re-dissolution of cemented metals has been observed by several authors, namely: Blander et al. (1975), Bockman et al. (2000) (for the cementation of cobalt with zinc) and also Sousa et al. (2007) (for the cementation of cadmium with zinc). One possible explanation for this phenomenon is the dissolution of the basic metal salts that may be formed near the zinc surface, by the formation of metal alloys or of solid solutions. In fact, the basic metal salts may be formed due to the high pH values close to the precipitant metal's surface, as a consequence of hydrogen evolution in this zone (equation 8). Their re-dissolution may occur when all the metallic zinc in the centre of the cement is spent, no longer existing a driving force to maintain a local high pH inside the porous particles and the basic salts previously formed may dissolve. The other possible explanation, given by the same authors, is the re-oxidation of the cemented metal by the reaction with oxygen (equations 9 and 10). Thus, the way to minimize the problem of the re-dissolution of the deposit is to maintain a high value of pH of the solution (decreasing  $H^+$  concentration) and to operate under an inert atmosphere, excluding the oxygen from the solution.

## EXPERIMENTAL

Most of the solutions used in this work were synthetic but at the end of the study, a real sulphuric leaching solution was used. All the solutions were prepared with demineralised water and using analytical grade reagents added as sulphates. As cementing metal, zinc was added, in the form of

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<sup>i</sup> In this work,  $\ln([M]/[M]_0)$  is referred to as  $\ln(1-X)$ , where  $X$  is the cemented fraction of metal ( $Cu^{2+}$ ,  $Fe^{2+}$  or  $Fe^{3+}$ ).

metallic granules (d: 0.3-1.5 mm) or dust (d<60 µm). Cementation tests were carried out in a 500 mL round glass reactor immersed in a temperature controlled water bath (Figure 1). For agitation, a single round Teflon paddle impeller was used (d=6.5 cm). pH values were adjusted by adding NaOH or H<sub>2</sub>SO<sub>4</sub> prior to cementation, and pH and redox potential values were measured in a Metrohm 827 pH Lab device. Samples were collected with a 5 mL pipette in the case of zinc granules, and with a syringe in the case of zinc dust addition<sup>ii</sup>. After dilution in a 665 Dosimat device, Cu, Zn and Fe were analysed by Atomic Absorption spectroscopy (AAAnalyst 200, Perkin & Elmer device). The content of ferrous iron was measured by titration with potassium dichromate (Correia, 1995).

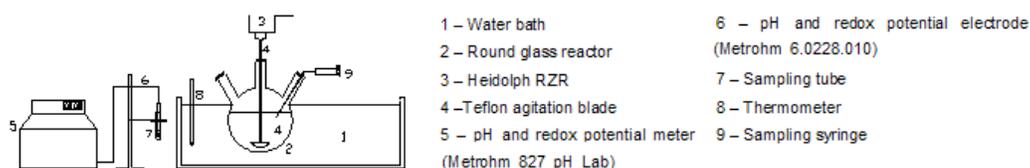


Figure 1 – Experimental set-up for the cementation tests

## RESULTS AND DISCUSSION

### Experiments with zinc granules

Tests were made in order to determine the effect of several variables on cementation: pH, Zn excess, initial Cu<sup>2+</sup> concentration, temperature, stirring speed and presence of Zn<sup>2+</sup> in the initial solution. The results show that a shift on the initial pH values from pH=3 to pH=4, doesn't affect significantly neither the cementation rate, measured by the  $k_{a_e}$  values, nor the cemented fraction of Cu<sup>iii</sup>. Thus, the value of 3 was chosen, since it is closer to real leaching solutions pH values. In the study of the influence of the initial molar ratio (MR) of Zn/Cu, for the solution with [Cu<sup>2+</sup>]=500mg/L, values of  $k_{a_e}$  were not affected by the variation of the MR from 1,5 to 2 and 3, but the lowest final copper concentration was attained with MR=3. For the 100mg/L copper solution, the use of a MR=10 allowed to obtain the highest values for copper removal (comparing to MR=1.5 and MR=15), whereas the highest  $k_{a_e}$  value was obtained for MR=15. For the further studies in this section, MR=1.5 was selected, to better understand eventual improvements on copper removal and/or cementation rate due to the change of the studied variables. The effect of stirring speed was investigated at 200, 400 and 500 rpm, and tests were conducted at T=50°C, [Cu<sup>2+</sup>]=500 mg/L, Zn/Cu MR=1.5. The results showed that the higher value of  $k_{a_e}$  was obtained at 400 rpm.

<sup>ii</sup> When syringes were used, the density of the solution, as well as the mass of the samples collected, were determined, in order to calculate the volume withdrawn.

<sup>iii</sup> In pH effect tests, the value of pH was not controlled. For this reason, the final pH of the solution was similar in both cases (around 5)

To determine the effect of the initial  $\text{Cu}^{2+}$  concentration, 5 experiments were carried out (25, 100, 250, 500 and 1000 mg/L of  $\text{Cu}^{2+}$ ). It was possible to conclude that, generally, higher initial concentrations of Cu in solution led to lower contents of Cu at the end of the experiment (Figure 2). An exception occurred with  $[\text{Cu}]_i=250$  and 500 mg/L, where the final contents of Cu were the same in both cases.

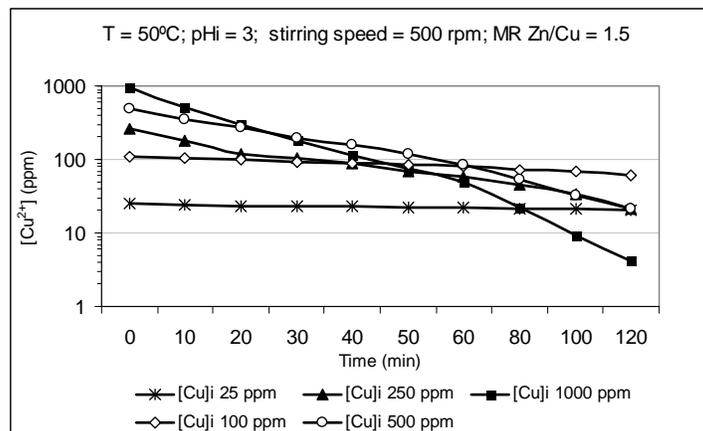


Figure 2 – Variation of Cu concentration with time at different initial Cu concentrations (zinc granules)

Tests carried out with different temperatures (22, 30, 40 and 50°C) allowed reaching two conclusions. First, the raise of the temperature favours cementation kinetics (as it is shown on Figure 3), and also augments the amount of Cu removed. Secondly, and assuming Arrhenius type relation,  $\ln k_{ae}$  versus  $1/T$  should result in a straight line (Figure 4), from which it is possible to estimate the apparent activation energy,  $E_a$ , of the process. In this case,  $E_a=16$  kJ/mol, which is a typical value of diffusion controlled processes, that exhibit activation energies between 8 and 25 kJ/mol (Miller, 1973).

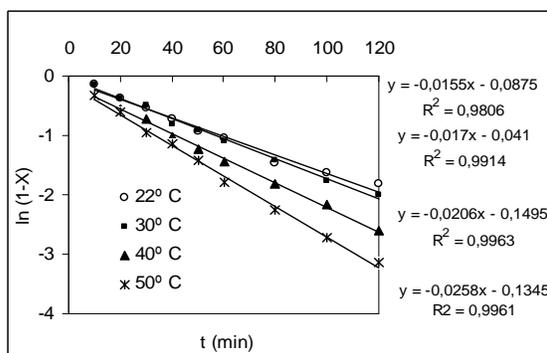


Figure 3 – Plot of  $\ln(1-X)$  vs. time for various temperatures

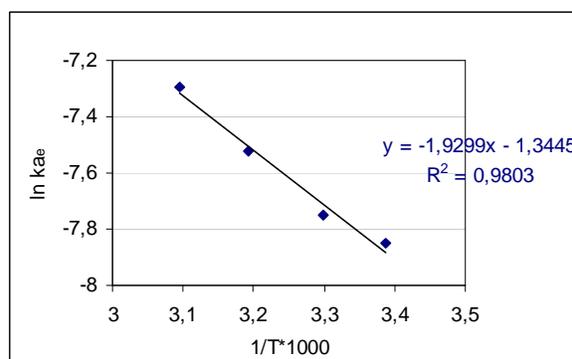


Figure 4 – Arrhenius plot for copper cementation with zinc granules

The effect of the presence of  $\text{Zn}^{2+}$  on the initial solution was studied with the solution containing 100 mg/L of  $\text{Cu}^{2+}$ , 20 g/L of  $\text{Zn}^{2+}$ , 500 rpm,  $T=40^\circ\text{C}$ ,  $\text{pH}=3$  and  $\text{MR}=10$ . It was observed that, in these conditions, the presence of the  $\text{Zn}^{2+}$  ions increases the cementation rate and cemented fraction of Cu.

However, the dissolution of the zinc metal during cementation is higher, when compared to the  $Zn^{2+}$  ions free solution.

### Experiments with zinc dust

In the experiments where zinc dust was used as reducing agent, the following variables were studied: initial  $Cu^{2+}$  concentration, molar ratio (Zn/Cu), presence of  $Zn^{2+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  in the solution and the type of atmosphere. It was possible to observe that varying the initial Cu concentration from 25 to 500 mg/L (25, 100, 250 and 500 mg/L), doesn't affect Cu removal. In fact, as seen in Figure 5, even for the solution containing 25 mg/L of copper, it was possible to attain a final concentration of  $[Cu^{2+}] \approx 0$  mg/L.

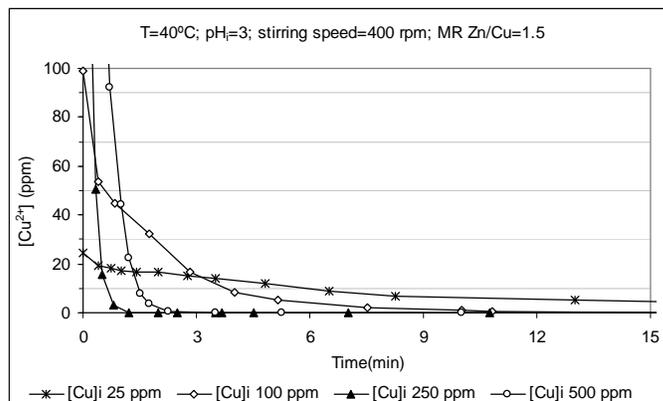


Figure 5 - Variation of Cu concentration with time at different initial Cu concentrations (zinc dust)

Table 2 - Apparent kinetic constant,  $ka_e$ , for different initial Cu concentrations (zinc dust)

$[Cu]_i$ (mg/L)	Slope $\times 10^3$ ( $s^{-1}$ )	$ka_e \times 10^2$ ( $m^3/Kg.s$ )
25	$2.0 \pm 0.7$	$5.2 \pm 1.7$
100	$9.5 \pm 2.1$	$6.1 \pm 1.3$
250	$102.8 \pm 15.5$	$26.6 \pm 4.0$
500	$46.0 \pm 5.9$	$5.9 \pm 0.8$

Table 2 shows that the higher values of  $ka_e$  were obtained for the solution containing 250 mg/L of copper. Furthermore, it is important to emphasize that the  $ka_e$  values obtained were 10 to 100 times higher with zinc dust than with zinc granules.

The study of the effect of the Zn/Cu molar ratio was carried out with the solutions containing 25 and 100 mg/L of Cu at:  $T=40^\circ C$ , 400 rpm,  $pH=3$ . The results allowed to conclude that the removal of copper was equivalent for the values of Zn/Cu MR tested, 1.5 and 3. Nevertheless, with  $MR=3$  the cementation rates attained were higher, and its use may be advantageous if it is important to reduce reaction time. Finally, the use of a  $N_2$  atmosphere enhances the kinetics of copper cementation because, as mentioned in the introduction, the reactions of the precipitant metal with  $O_2$  (equations 9 and 10) are avoided and more zinc is available for cementation.

The leaching solution obtained after the removal of iron and copper by solvent extraction should contain zinc and residual amounts of iron and copper. Therefore, the effect of the presence of  $Zn^{2+}$ ,  $Fe^{3+}$  e  $Fe^{2+}$  ions on copper cementation was investigated using the conditions presented in Table 3.

The composition of these target solutions was established having in consideration the preliminary results of the solvent extraction tests with the real leaching solution.

As shown in Table 3, for the solutions 2, 3 and 4 it was decided to use a molar ratio of zinc/noble metals, MR, of 3.75, since it corresponds to 50% excess of metallic zinc, the same excess used with the simple solutions.

Table 3 – Compound solutions tested, and parameters

Composition of the solution	pH	rpm	MR (Zn/noble metals)	T(°C)	Atmosphere
1 - 24 mg/L Cu <sup>2+</sup> , 40 g/L Zn <sup>2+</sup>	3	400	3.14	40	Air
2 - 28 mg/L Cu <sup>2+</sup> , 210 mg/L Fe(III)	natural (2.40)	400	3.55	40	Air
3 - 24 mg/L Cu <sup>2+</sup> , 40 g/L Zn <sup>2+</sup> , 217 mg/L Fe(III)	natural (2.98)	400	3.50	40	Air
4 - 22 mg/L Cu <sup>2+</sup> , 40 g/L Zn <sup>2+</sup> , 200 mg/L Fe(II)	3	400	3.80	40	Air

The results obtained showed that, for the experiment carried out with solution 1, the re-dissolution of the cemented Cu occurred after 11 minutes of reaction. Moreover, the addition of Zn<sup>2+</sup> ions caused a decrease in the reaction kinetics and in the amount of copper removed (before re-dissolution). It is important to emphasize that the re-dissolution of the cement was also observed in the experiment where zinc granules were used to cement the copper from a solution containing the same amount of copper and zinc. Therefore, it is possible to anticipate that the presence of zinc in the solution favoured the re-dissolution of the cement. However, as it is shown on Figure 6, the re-dissolution problem is more critical when dust is used, but Table 4 shows that the  $k_{a_e}$  values are about 100 times higher when metallic dust is used.

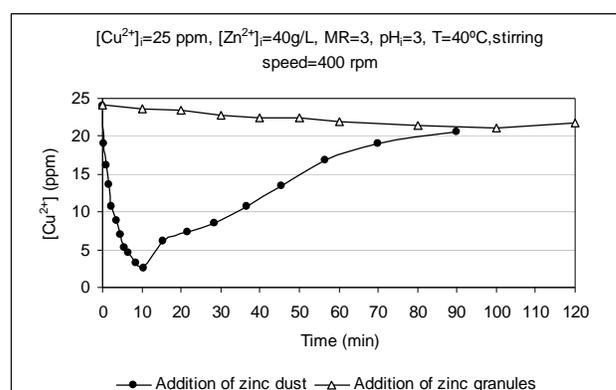


Figure 6 – Effect of the zinc particles size on copper cementation.

Table 4 - Apparent kinetic constant,  $k_{a_e}$ , for the types of zinc particles tested

Zn particles type	Slope x 10 <sup>3</sup> (s <sup>-1</sup> )	$k_{a_e}$ x 10 <sup>-2</sup> (m <sup>3</sup> /Kg.s)
Granules	0.03 ± 0.009	0.04 ± 0.01
Dust	3.8 ± 0.4	4.9 ± 0.5

The addition of 200 mg/L of Fe<sup>3+</sup> to solution 1 (solution 3 containing Cu<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup>, Figure 7) favoured the removal of copper and avoided the occurrence of the re-dissolution of the cement. However, the value of the kinetic constant,  $k_{a_e}$ , for the experiment carried out with solution 2 (Cu<sup>2+</sup> and Fe<sup>3+</sup> present), indicates that the kinetics of copper removal by cementation is slower, when compared to the Fe<sup>3+</sup> free solutions. Furthermore, zinc consumption was also higher with solution 2 for almost

the entire reaction time (Figure 8). This is because zinc is also consumed in the reduction reactions of ferric ions (Fe(III) to Fe(II) and Fe). For the tests with solutions 2 and 3, with Fe(III), a titration with potassium dichromate was conducted, after collecting the samples. It was concluded that Fe(III) is reduced to Fe(II) after few minutes of reaction.

Finally, since iron may also be present as Fe(II) in the leaching solution, solution 4 (containing  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$ ) allowed to study the effect on Cu cementation of the replacement of  $\text{Fe}^{3+}$  ions by  $\text{Fe}^{2+}$ . The results allowed to conclude that the reaction kinetics is favoured by the presence of Fe(II) (Figure 9) and zinc consumption also decreased (Figure 10). In fact, in this case, the cementing metal is not spent in the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and is therefore available for copper cementation. Figure 9 indicates that for the solutions containing iron as Fe(II or III) the presence of Zn(II) and Fe(II) is kinetically favourable.

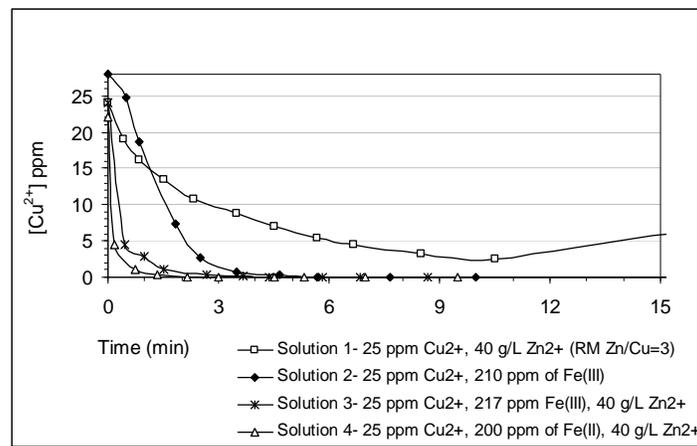


Figure 7 – Cu cementation with compound solutions

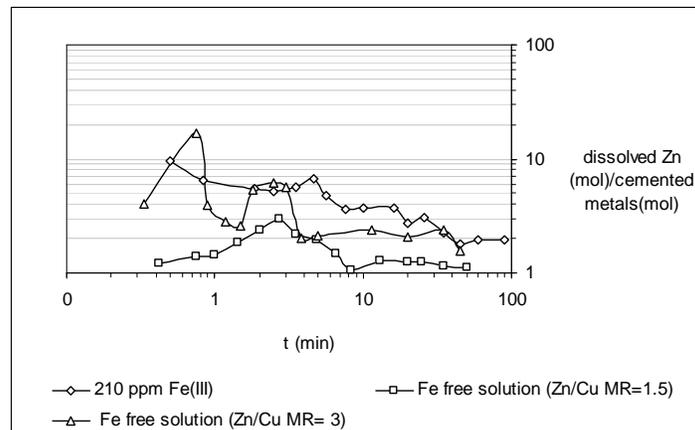


Figure 8 – Effect of the presence of Fe(III) on zinc consumption

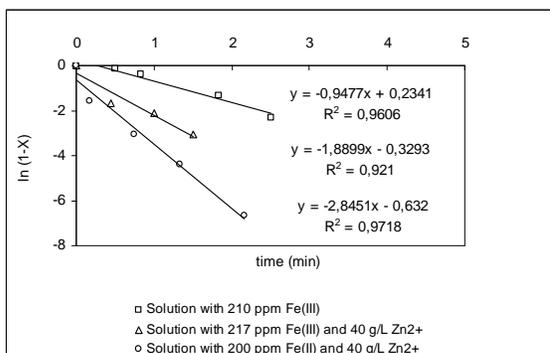


Figure 9 - Plot of  $\ln(1-X)$  vs. time for the experiments with solutions containing iron

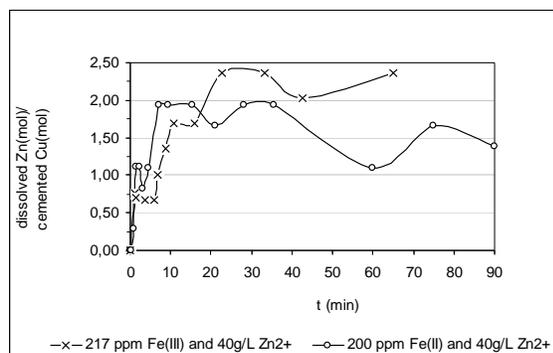


Figure 10 – Effect of the oxidation state of iron on zinc consumption

### Cementation of copper from a real leaching solution

At the final stage of this work, a test was carried out with the real solution obtained in the leaching of a zinc concentrate. The leaching process was carried out with a solution 0.5M of  $\text{Fe}_2(\text{SO}_4)_3$  and 0.25M of  $\text{H}_2\text{SO}_4$ , and the average composition of the leachate is:  $[\text{Zn}] = 35 \text{ g/L}$ ,  $[\text{Cu}] = 1,5 \text{ g/L}$  and  $[\text{Fe}] = 41 \text{ g/L}$  (as Fe(III) and Fe(II)). After indium and copper extraction, the iron present in the leachate is oxidized to iron(III), being extracted with a selective extractant. The composition of the leachate used in the cementation test is presented on Table 5:

Table 5- Partial Composition of the real leaching solution

Metal	Cu	Zn	Fe(II)
Concentration (mg/L)	67	10833	582

After the determination of the composition of the real leaching solution, a cementation test was performed with a synthetic solution containing:  $[\text{Cu}^{2+}] = 70 \text{ mg/L}$ ,  $[\text{Fe}^{2+}] = 600 \text{ mg/L}$  and  $[\text{Zn}^{2+}] = 11 \text{ g/L}$ , using the conditions previously defined as the more favourable for cementation (MR (Zn/noble metals) = 3.75;  $T = 40^\circ\text{C}$ ;  $\text{pH}_i = 3$ ; 400 rpm). The results showed that after 2 minutes, copper content was reduced to 0.008 mg/L and 99% of the iron was removed after 90 minutes of reaction ( $[\text{Fe}^{2+}]_{\text{final}} = 4 \text{ mg/L}$ ). Therefore, the experiment with the real leaching solution was carried out in the same conditions and the results for copper cementation are presented in Table 6.

Table 6 – Cementation of Cu from the real leaching solution (Conditions: MR=3.75,  $T=40^\circ\text{C}$ ,  $\text{pH}_i=3$ , 400 rpm)

Time (min)	$[\text{Cu}^{2+}]$ (mg/L)
0	67.0
0.33	2.4
0.58	0.8
1.00	0.2
3.00	≈0
6.50	≈0

Note:  $[\text{Fe}] = 0.02 \text{ mg/L}$  in 90 min

The  $k_{a_e}$  value obtained in this case  $(2.1 \pm 1.0) \times 10^{-2} \text{ m}^3/\text{Kg.s}$  is smaller than the value obtained with the above mentioned synthetic solution ( $k_{a_e} = 1.0 \pm 0.9 \text{ m}^3/\text{Kg.s}$ ). This is probably due to the fact that the real leach contains other metals that interfere in the cementation but were not added to the synthetic solution.

## CONCLUSIONS

The results obtained in this work allow to conclude that cementation with zinc may be used to remove copper from solutions containing zinc and iron. The use of zinc is chemical and environmentally favourable, because zinc is the main component of the real leaching solution. The best results concerning the kinetics of copper cementation were attained using a solution containing 250 mg/L of copper for the experiments carried out with zinc dust or granules at 400 rpm and  $T = 50^\circ\text{C}$ . The calculated activation energy ( $E_a = 16 \text{ kJ/mol}$ ) allowed to conclude that cementation of copper with zinc is a diffusion controlled process.

The presence of zinc and iron (as ferric or ferrous ion) enhances the kinetics of the reaction. On the other hand, the addition of zinc to the initial solution favours the re-dissolution of the cement, which is more important when the zinc dust is used as a precipitant. However, this phenomenon is delayed/avoided by the presence of iron ions. This metal is also removed from the solution, but the kinetics of this reaction is much slower than copper's cementation kinetics.

The application of cementation with zinc to a leaching solution obtained in the hydrometallurgical treatment of a zinc concentrate shows that this technique is effective. In fact, it is possible to reduce the copper contents from 67 mg/L to values close to 0 in 3 minutes. Iron is also removed by cementation, and it is possible to attain a concentration of 0.02 mg/L of iron in 90 minutes of reaction.

## REFERENCES

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