STUDIA UBB CHEMIA, LVII, 3, 2012 (p. 41 - 49)
(RECOMMENDED CITATION)

# METALS LEACHING FROM WASTE PRINTED CIRCUIT BOARDS. PART II: INFLUENCE OF THIOUREA, THIOSULFATE AND THIOCYANATE CONCENTRATION ON THE LEACHING PROCESS

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**ABSTRACT.** This paper presents the possibility of achieving high selectivity and efficiency at low $FeCl_3$ and $CuCl_2$ concentrations by adding small quantities of thiourea, thiosulfate and thiocyanate into the solution. The overall metal dissolution in the presence of 0.1 M thiosulfate, thiocyanate and thiourea is significantly higher (60 % compared to 32 %), than in chloride medium, for both oxidants. However, the increase of ligand concentration decreases the global metal dissolution degree, but improves the selectivity of the leaching processes. The results show that different oxidant and ligand combination promote the dissolution of one metal or another, making possible the use of these leaching systems for selective metal dissolution.

***Keywords:*** *$FeCl_3$ and $CuCl_2$, leaching systems, thiosulfate, thiocyanate, thiourea*

## INTRODUCTION

Recently, due to the stringent environmental regulations the researches focused on the development of eco-friendly and energy-saving processes for the separation of metals and alloys from hazardous and non-metallic materials [1-8]. These can be very complicated considering the complex composition of the WPCBs and the variable chemical properties of the metals. However the improvements made to hydrometallurgical methods in the past few decades, allow an efficient extraction of metals from WPCBs. The use of caustic and acidic leaching mediums along with strong oxidizing agents and different lixiviants can dissolve efficiently the metals and with high selectivity [8-13]. This is very important especially in the case of noble metals which have high chemical stability and lower concentration in WPCBs than base metals [14].

Thus, based on the available literature data, thiourea, thiosulfate and thiocyanate were identified as the most appropriate ligands for the dissolution of noble metals [15-18]. According to previous studies [17-19] the leaching of gold can occur five times faster in the presence of these ligands than in aerated

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cyanide solution which has been banned in many countries. Moreover combining thiourea, thiosulfate and thiocyanate with more efficient oxidants like $Fe^{3+}$ and $Cu^{2+}$ researchers [19] obtained gold dissolution rates 25 times higher than in cyanide solution. It is also important to notice that these ligands can intensify the leaching process of base metals (Cu, Ni, Zn and Pb) too, by forming very stable complexes with some of them. However, there are possible several side reactions between these ligands and the oxidants (dissolved metals) which can hinder the leaching of metals. As a result the selectivity and efficiency of the dissolution processes will be very different from one metal to another when the oxidants ($CuCl_2$ and $FeCl_3$) are combined with thiourea, thiosulfate and thiocyanate [15-19].

The aim of this work was to study the beneficial effect of small additions of thiourea, thiosulfate and thiocyanate on the leaching of metals from WPCBs with $FeCl_3$ or $CuCl_2$. The results show the possibility of reducing the oxidant consumption and increasing the selective metal dissolution.

## RESULTS AND DISCUSSION

In order to demonstrate that the addition of small quantities of ligands can enhance considerably the dissolution of metals, leaching tests were performed at different ligand concentrations (0.1-0.5 M), while the concentration of $CuCl_2$ and $FeCl_3$ was maintained constant at 0.2 M. The choice of 0.2 M oxidant concentration instead of 0.1 M was necessary in order to ensure a little higher amount of oxidant than the stoichiometrically required for the total dissolution of metals. As it can be seen, from the global dissolution degrees in Table 1, at the same oxidant concentration the dissolution of metals is faster in the presence of thiosulfate and thiocyanate and lower in the presence of thiourea.

**Table 1.** Global dissolution degree of metals in 1 M HCl and 0.2 M oxidant concentration using different concentrations of thiocyanate, thiosulfate and thiourea.

| **Ligand conc., M** | **$FeCl_3$** | | | **$CuCl_2$** | | |
|---|---|---|---|---|---|---|
| | **$NH_4SCN$** | **$Na_2S_2O_3$** | **$CS(NH_2)_2$** | **$NH_4SCN$** | **$Na_2S_2O_3$** | **$CS(NH_2)_2$** |
| | **Global metal dissolution degree, %** | | | | | |
| 0 | | 32 | | | 37 | |
| 0.1 | 51 | 60 | 27 | 49 | 52 | 39 |
| 0.2 | 46 | 38 | 26 | 46 | 37 | 35 |
| 0.3 | 38 | 32 | 25 | 45 | 39 | 35 |
| 0.4 | 40 | 25 | 23 | 42 | 38 | 35 |
| 0.5 | 41 | 24 | 19 | 41 | 26 | 22 |

Also, by comparing with the results presented in Part I of this series of papers, it seems that the leaching process is more efficient if rather using a high oxidant concentration we use a lower one but along with small amount of ligands.

These differences are more accentuated in the case of $CuCl_2$ because the formation of very stable $Cu^+$ complexes increases the dissolution rate of cemented copper, which is a crucial step in the leaching of metals with $CuCl_2$. This is also reflected by the following equilibrium constant values calculated for the dissolution of cooper, using the thermodynamic data [21, 19] for copper complexes:

$$Cu + 4S_2O_3^{2-} + CuCl^+ \leftrightarrow 2[Cu(S_2O_3)_2]^{3-} + Cl^- \qquad K_1 = 1.06 \bullet 10^{19} \qquad (1)$$

$$Cu + 4CS(NH_2)_2 + CuCl^+ \leftrightarrow 2[Cu(CS(NH_2)_2)_2]^+ + Cl^- \qquad K_2 = 1.93 \bullet 10^{18} \qquad (2)$$

Differently from the previously two ligands, in the case of thiocyanate the process is more complicated, because besides $SCN^-$ ions the solution contains ammonium ions as well. Therefore the dissolution of copper or other metals will involve the formation of both copper-thiocyanate and copper-ammoniac complexes. Thus for copper the main reactions are the following:

$$Cu + 4SCN^- + CuCl^+ \leftrightarrow 2[Cu(SCN)_2]^- + Cl^- \qquad K_3 = 6.56 \bullet 10^{11} \qquad (3)$$

$$Cu + [Cu(NH_3)_4]^{2+} \leftrightarrow 2[Cu(NH_3)_2]^+ \qquad K_4 = 49.11 \qquad (4)$$

$$\begin{aligned} Cu + [Cu(NH_3)_4]^{2+} + 2SCN^- \leftrightarrow [Cu(NH_3)_2]^+ + \\ + [Cu(SCN)_2]^- + 2NH_{3(aq)} \end{aligned} \qquad K_5 = 8.42 \bullet 10^8 \qquad (5)$$

$$Cu + [Cu(NH_3)_4]^{2+} + 4SCN^- \leftrightarrow 2[Cu(SCN)_2]^- + 4NH_3 \qquad K_6 = 1.44 \bullet 10^{16} \qquad (6)$$

It seems like the equilibrium constant values for copper dissolution eq. (1-3, 6) are much higher in the presence of these ligands than in chloride medium. Furthermore, it can be observed, that the equilibrium constant value for the cementation of copper, discussed in Part I of this series of papers, is smaller than for its dissolution eq. (1-2, 6). In consequence the influence of copper cementation on the dissolution process of the metals is negligible in these experimental conditions. Similarly conclusions can be found by comparing the redox potentials of $Cu^{2+}/Cu^+$ redox couple in chloride medium with the ones calculated in the case of thiourea, thiosulfate and thiocyanate complexes:

$$CuCl^+ + 2S_2O_3^{2-} + e^- \leftrightarrow [Cu(S_2O_3)_2]^{3-} + Cl^- \qquad E^0 = 0.879\ V \qquad (7)$$

$$CuCl^+ + 2CS(NH_2)_2 + e^- \leftrightarrow [Cu(CS(NH_2)_2)_2]^+ + Cl^- \qquad E^0 = 0.857\ V \qquad (8)$$

$$CuCl^+ + 2SCN^- + e^- \leftrightarrow [Cu(SCN)_2]^- + Cl^- \qquad E^0 = 0.666\ V \qquad (9)$$

$$[Cu(NH_3)_4]^{2+} + e^- \leftrightarrow [Cu(NH_3)_2]^+ + 2NH_{3(aq)} \qquad E^0 = 0.01\ V \qquad (10)$$

$$[Cu(NH_3)_4]^{2+} + 2SCN^- + e^- \leftrightarrow [Cu(SCN)_2]^- + 4NH_3 \qquad E^0 = 0.416\ V \qquad (11)$$

The redox potential values from eq. (7-8) confirm that the oxidizing power increases as the ratio between the stability constants of $Cu^+$ and $Cu^{2+}$ complexes is greater. Also it is remarkable that the redox potentials for $Cu^{2+}/Cu^+$ eq. (7-11) not only that are higher than in chloride medium, but in the case of thiosulfate and thiourea they also exceed the ones obtained for the $Fe^{3+}/Fe^{2+}$ redox couple as well. This can be attributed to the formation of more weakly complexes in the case of $Fe^{3+}/Fe^{2+}$, therefore the reduction of $Fe^{3+}$ to $Fe^{2+}$ occurs mainly by eq. (12) even in the presence of these ligands. Although, according to the literature [22], in parallel with eq. (5), there are also possible other reactions of which the most significant are the following:

$$[FeCl_2]^+ + e^- \leftrightarrow Fe^{2+} + 2Cl^- \qquad E^0 = 0.702\ \text{V} \qquad (12)$$

$$[Fe(CS(NH_2)_2)_2]^{3+} + e^- \leftrightarrow Fe^{2+} + 2CS(NH_2)_2 \qquad E^0 = 0.276\ \text{V} \qquad (13)$$

$$[Fe(SCN)_2]^+ + e^- \leftrightarrow Fe(SCN)^+ + 2SCN^- \qquad E^0 = 0.600\ \text{V} \qquad (14)$$

Despite the lower redox potentials in the case of $Fe^{3+}/Fe^{2+}$ (eq. 12-14), the results shown in Table 1, indicate the fact that for 0.1 M thiosulfate and thiocyanate concentration $FeCl_3$ is more efficient oxidant than $CuCl_2$, while at higher ligand concentrations $CuCl_2$ results in better performance. This can be attributed to the degradation of ligands, which becomes more pronounced with the increase of ligand concentration especially in $FeCl_3$ solutions due to the formation of more weakly $Fe^{3+}/Fe^{2+}$ complexes. In contrast, in the case of thiourea since both oxidants form stable complexes their diffusion is affected similarly. As a result the global dissolution degree is greater when $CuCl_2$ is used, due to the higher reduction potential of the $Cu^{2+}/Cu^+$ redox couple.

It is also important to note that the complexation of the oxidants and dissolved metals is strongly linked through the concentration of the ligands since they are competitive reactions. Given that initially the oxidants concentration is much higher, it is clear, that their complexation is faster and can lower the concentration of the ligands, more than the stability of the formed complexes is higher. Therefore, it is possible that the amount of free ligands, remained in the solution, is smaller than the required for the further complexation of the dissolving metals. In consequence the dissolution of the metals can be slower or in some cases quite impossible because their redox potential is more positive as the influence of metal complexation is weaker. However, for the most of the metals (ex. Zn, Ni) this competition between the two complexing processes has no influence on the dissolution degree, due to the fact, that their redox potential is sufficiently negative. On the other hand, there are particularly situations, like gold and silver, when this influence on the dissolution process cannot be ignored. As it is showed in Table 2 the dissolution degree of gold is very different in the case of $FeCl_3$ and $CuCl_2$ with one exception, when thiosulfate was used.

**Table 2.** Gold dissolution degree in 1 M HCl and 0.2 M oxidant concentration using different concentrations of ligands

| **Ligand conc., M** | **$FeCl_3$** | | | **$CuCl_2$** | | |
|---|---|---|---|---|---|---|
| | **$NH_4SCN$** | **$Na_2S_2O_3$** | **$CS(NH_2)_2$** | **$NH_4SCN$** | **$Na_2S_2O_3$** | **$CS(NH_2)_2$** |
| | **Global metal dissolution degree, %** | | | | | |
| 0.1 | 1.3 | 0.6 | 2 | 0.5 | 0.9 | 0.8 |
| 0.2 | 2.4 | 0.5 | 3.6 | 0.8 | 0.8 | 0.8 |
| 0.3 | 3.9 | 0.5 | 5.1 | 1.4 | 0.8 | 0.9 |
| 0.4 | 4.7 | 0.7 | 4.2 | 0.7 | 1 | 1.1 |
| 0.5 | 6.5 | 0.8 | 4.1 | 1.1 | 0.8 | 0.8 |

This differences appear due to the fact that $Cu^{2+}/Cu^{+}$ decreases more the concentration of the ligands, since forms more stable complexes than $Fe^{3+}/Fe^{2+}$. In the case of thiosulfate it seems like both oxidants have the same efficiency in the dissolution of gold. This can be explained by the passivation of gold surface (similarly for other metals) due to the generation of different sulfur species in the reaction among the oxidants and thiosulfate [15-19]. The influences of similarly side reactions have also been reported for thiourea and thiocyanate [23-25]. However the degradation of these ligands is less pronounced thanks to their higher chemical stability. Moreover the presence of ammonium ions, in the experiments with thiocyanate, has a benefit effect on both ligand stabilization and metal dissolution. Therefore, in contrast with the other two ligands the global dissolution degree decreases the less with the increase of $NH_4SCN$ concentration. Similarly, it seems like, the increase of thiocyanate concentration gives the best performances in the dissolution of gold as well.

The experimental results also highlight that the individual dissolution degree of metals differs more when the oxidants are used with these ligands instead of chloride ions. Furthermore, it seems like, these divergences become even more significant as the concentration of the ligands increases. Fig. 1-3 shows the experimental data for the dissolution of metals at the highest ligand concentration (0.5 M).

It can be observed that different oxidant and ligand combinations promote the dissolution of one or another of the metals. For example $FeCl_3$ with thiosulfate dissolves efficiently the majority of metals with the exception of Au, Ag, and Cu. Moreover the same oxidant in the presence of thiocyanate allows the separation of base metals from gold and copper. An even higher selectivity can be noticed in the case of $CS(NH_2)_2$ since $FeCl_3$ favors the dissolution of Ag while $CuCl_2$ dissolves more efficiently Zn. Therefore it can be concluded that by using the leaching systems in the most appropriate sequence, it is possible to selectively extract the metals from the WPCBs.

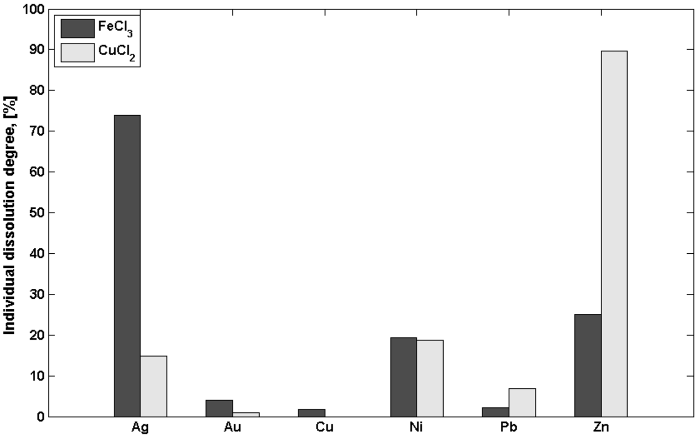

**Figure 1.** Individual metal disolution degree in 0.5 M $CS(NH_2)_2$ using 1 M HCl and 0.2 M oxidant concentration.

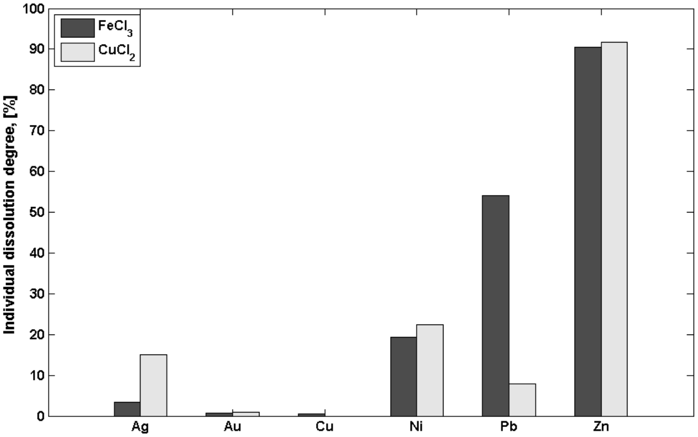

**Figure 2.** Individual metal dissolution degree in 0.5 M $Na_2S_2O_3$ using 1 M HCl and 0.2 M oxidant concentration.

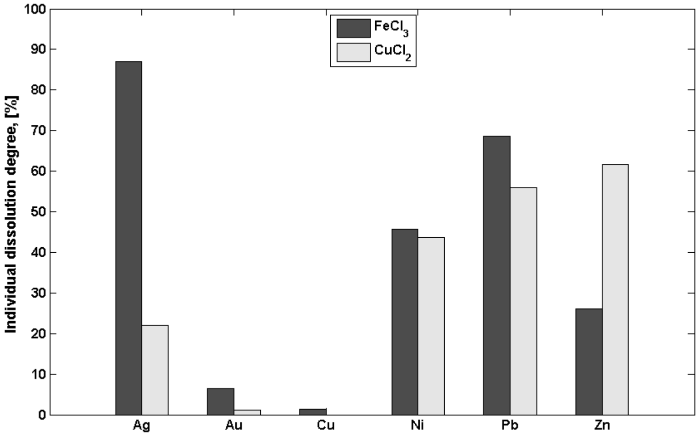

**Figure 3.** Individual metal dissolution degree in 0.5 M $NH_4SCN$ using 1 M HCl and 0.2 M oxidant concentration.

## CONCLUSIONS

The study presents the possibility of reducing the oxidant consumption and improving the selectivity of the process by adding small quantities of thiourea, thiosulfate and thiocyanate into the leach solution. At the same oxidant concentration the global dissolution degree is higher in the presence of these ligands than in their absence. It is also important to note that the increase of ligand concentration leads to several side reactions which decrease the global metal dissolution degree. The influence of ligand degradation is more pronounced for thiourea and thiosulfate and less for thiocyanate. The higher stability of thiocyanate is due to the presence of ammonium ions which have a catalytic effect on the process. This is the reason why the global metal dissolution degree decreases less with the increase of $NH_4SCN$ concentration. On the other hand, it seems like high ligand concentrations are favorable for the selective leaching of metals. The experimental results show that $FeCl_3$ with thiosulfate dissolves efficiently the majority of metals with the exception of Au, Ag and Cu, while the presence of thiocyanate allows the separation of gold and copper from the rest of the metals. Similarly, in the case of thiourea, $FeCl_3$ favors the dissolution of Ag while $CuCl_2$ dissolves more efficiently Zn. From these results it can be concluded that by using the leaching systems in the most appropriate sequence, it is possible to selectively extract the metals from the WPCBs.

## EXPERIMENTAL

Leaching tests were performed using the same WPCB samples characterized by XRD, EDAX spectra and metallic composition analysis in the first part of our study. Similarly to the previous studies the WPCBs were crushed to smaller pieces (3.1-3.8 $cm^2$) in a preliminary mechanical step followed by the selective leaching of Al in 50 mL solution of unstirred 2.5 M NaOH for 24 h. After that, the aluminium free samples were used to determine the extent of dissolution of overall and individual metals in different leaching solutions. The oxidants used were hydrochloric acid and ferric (III)-chloride (Fluka) or copper (II)-chloride (Merck) while the ligands were: thiourea (Merck), sodium thiosulfate pentahydrate and ammonium thiocyanate (Fluka). All leaching experiments were conducted in 100 ml unstirred solution, at room temperature, over a period of 72 h. The pH was kept in strong acid medium by using 1 M HCl acid (Merck). The solid liquid ratio in the leaching experiments was 1:5. The concentration of metals in the leaching solutions and in the residue at the end of the experiments was determined by atomic adsorption spectroscopy.

## ACKNOWLEDGEMENTS

The authors acknowledge the following project for financial support: *Investing in people!* Ph.D. scholarship, Project co-financed by the SECTORAL OPERATIONAL PROGRAM FOR HUMAN RESOURCES DEVELOPMENT 2007 – 2013. Priority Axis 1. "Education and training in support for growth and development of a knowledge based society". Key area of intervention 1.5: Doctoral and post-doctoral programs in support of research. Contract nr.: POSDRU/ 88/1.5/S/60185 – “INNOVATIVE DOCTORAL STUDIES IN A KNOWLEDGE BASED SOCIETY”, Babeş-Bolyai University, Cluj-Napoca, Romania.

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