STUDIA UBB CHEMIA, LVII, 3, 2012 (p. 91 – 100)
(RECOMMENDED CITATION)

ECO-FRIENDLY LEACHING OF BASE METALS FROM WASTE PRINTED CIRCUIT BOARDS: EXPERIMENTAL STUDY AND MATHEMATICAL MODELING

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ABSTRACT. Our research aims the development of an eco-friendly leaching method for the separation of electronic components with high gold content, from other parts of waste printed circuit boards (WPCBs) without the use of any other separation technique. The base metals were removed in a specially designed leaching reactor using acidic $FeCl_3$ solution. The dependency of the dissolution rate of base metals on the amount of $FeCl_3$ and solid: liquid ratio was determined based on a kinetic model developed in MATLAB. The kinetic parameters identified by the experimental results indicate that the leaching rate of metals is more strongly dependent on the amount of $FeCl_3$ used than on the solid: liquid ratio. The optimal values of the operating parameters were established in order to maximize the amount of dissolved metals and minimize the oxidant consumption.

Keywords: *$FeCl_3$, waste printed circuit boards, metal dissolution, leaching rate.*

INTRODUCTION

The yearly accumulation of waste printed circuit boards (WPCBs) reaches 1.5- 2 million tons, which represents 3 wt. % of the total electronic waste [1-3]. Thanks to the high metal content (~ 40 wt. %), WPCBs are considered an attractive secondary source of metals which can help to preserve the natural resources. It is also important to note that many metals have significantly higher concentration in WPCBs than in mineral resources. For example the gold content in WPCBS can reach 25-250 g/ton compared to only 1-10 g/ton in gold ores. Despite the fact, that the amount of precious metals in WPCBs is less than 1 wt. %, thanks to their high price, they value ~13 €/kg WPCB, which represents more than 80% of the total intrinsic value of WPCBs [4-7]. The importance of metal recovery is also emphasized by the

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fact that the economically mineable reserves for Au, Ag, Cu and Ni will be depleted in the next fifty years [3-5]. As a result, precious metals are the main targets in WPCBs recycling, followed by Cu, Ni and other base metals [6, 7].

Nevertheless, it is important to consider that together with precious metals and other valuable materials, WPCBs contain various hazardous materials like chlorinated and brominated substances, toxic metals, photoactive and biologically active materials. Therefore many studies have been carried out with the aim of recovering the resources from WPCBs and at the same time preventing environmental contamination [8, 9]. The first industrial methods presented in the literature were based on pyrometallurgical processing; especially open burning, incineration and smelting [10]. These methods are simple but have major disadvantages like non-selectivity, hazardous operating conditions and emission of toxic gases and fumes metals [8-13]. For this reason recently the researches have been focused on hydrometallurgical methods which operate in less dangerous conditions and are more easily controlled [7, 15-17]. Through hydrometallurgical processing it is possible not only to separate the metals from the other main categories of materials but also to realize their selective extraction. This is very important because due to different chemical reactivity, concentration in the WPCBs and economical potential of the metals, diverse leaching agents and experimental conditions are required for their dissolution [18, 19]. For example, the use of a preliminary step in which the base metals are removed from the electronic waste is essential in the recovery of high purity precious metals. However in many situations the pre-concentration of noble metals is preceded or coupled with several separation techniques which can require large investments and increase the complexity of the process [10, 20]. Therefore it is necessary to simplify the recycling technologies by using selective hydrometallurgical methods which can extract the metals efficiently with minimal involvement of other pre-treatment techniques [20, 21].

The current study presents an alternative hydrometallurgical method for the separation of gold rich electronic components from the plastic and metallic parts of WPCBs without the use of any mechanical separation technique. The results show that acidic $FeCl_3$ solutions are efficient leaching agents in the removal of base metals from WPCBs leading to a solid residue containing the gold rich electronic components.

RESULTS AND DISCUSSIONS

Influence of solid: liquid ratio on the leaching process

The influence of solid: liquid (S:L) ratio on the dissolution of metals (Me) was studied in the range of 1:8 – 1:64 (g:mL) using an acidic 0.21 M $FeCl_3$ solution. Figure 1 shows that the amount of dissolved Me (representing the sum of the total amount of dissolved Cu, Sn, Zn and Pb) increases significantly with the decrease of S:L ratio, reaching a maximum at the value of 1:40. As it can be seen the further decrease of the S:L ratio to 1:64 does not improve the performances of the dissolution process. This can be easily explained considering that the leaching of metals occurs through a diffusion controlled process due to the unstirred solution. Therefore it will be a well defined volume of leaching solution which contains the maximum quantity of $FeCl_3$ which can be transported through diffusion from the bulk to the reaction surface during the experiments. The results shown in Figure 1 indicate that in our experimental conditions this volume is 200 mL which corresponds to a S:L ratio of 1:40. Higher volumes of solutions even if contain more $FeCl_3$ cannot give better performances because only a part of the leaching agent is able to diffuse to the reaction surface during the experiment.

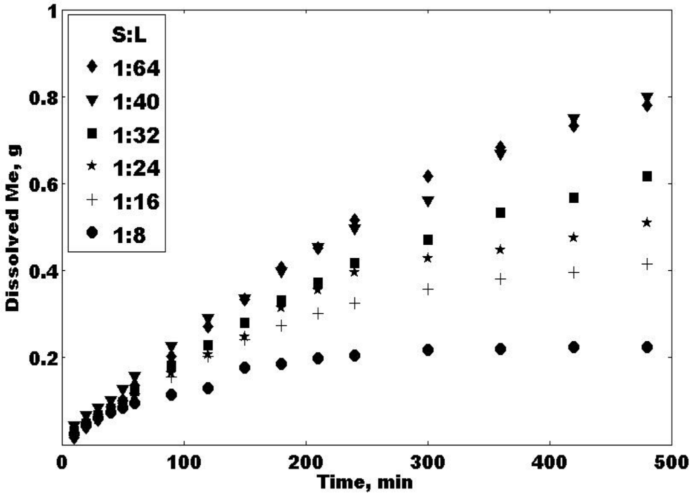

Figure 1. Amount of dissolved Me vs. time at different S:L ratios using 0.21 M $FeCl_3$ in 0.3 M HCl solution

Moreover the use of low S:L ratios is not desired since it can cause difficulties in the further processing of the leaching solutions. Therefore several experiments were carried out in order to determine if it is possible to obtain the same or better performances by using higher S:L ratios than 1:40 and higher oxidant concentrations than 0.21 M. The leaching solutions with different S:L ratios and $FeCl_3$ concentrations were obtained by dissolving the $FeCl_3$ quantities, used in the previous experiments (used to maintain the concentration at 0.21 M), in each volume of solution (Table 2).

Table 2. Oxidant concentrations for different combinations of S:L ratios and $FeCl_3$ quantities

Volume, mL	**40**	**80**	**120**	**160**	**200**	**320**
$FeCl_3$, g	**Concentration, M**					
1.38	0.21					
2.76	0.42	0.21				
4.15	0.64	0.32	0.21			
5.53	0.85	0.42	0.28	0.21		
6.92	1.06	0.53	0.35	0.26	0.21	
11.07	1.70	0.85	0.56	0.42	0.34	0.21

At constant volume of leaching solutions the use of higher $FeCl_3$ concentrations can improve significantly the dissolution rate of Me. As Figure 2 shows the leaching rate, at the S:L ratio of 1:8, increases almost 10 times by increasing the oxidant concentration 8 times.

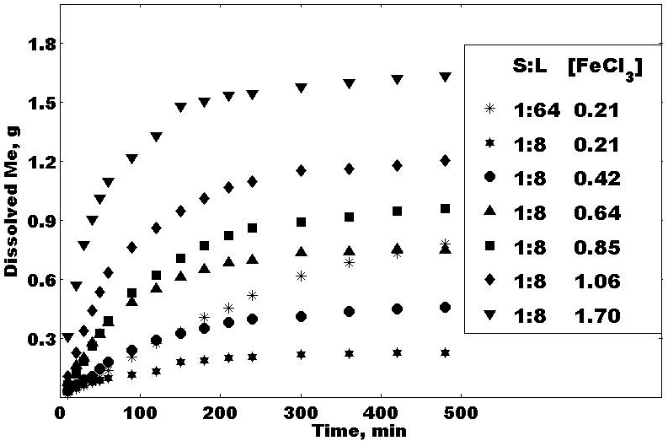

Figure 2. Amount of dissolved Me vs. time at different $FeCl_3$ concentrations and S:L ratios in 0.3 M HCl solution

Furthermore, it can be observed that from the 0.64 M $FeCl_3$ concentration upwards the S:L of 1:8 becomes more efficient than the other ones at 0.21 M $FeCl_3$ concentration. It is also important to note that the higher dissolution rate at the S:L of 1:8 and 0.64 M $FeCl_3$ was achieved using an amount of $FeCl_3$ three times smaller than the one used in the experiment with the S:L of 1:64 and 0.21 M oxidant concentration. It can be concluded that higher S:L ratios can use more efficiently the same amount of oxidant than lower ones. This is also confirmed by comparing the S:L ratios at different concentrations, obtained at a constant amount of $FeCl_3$ (Figure 3).

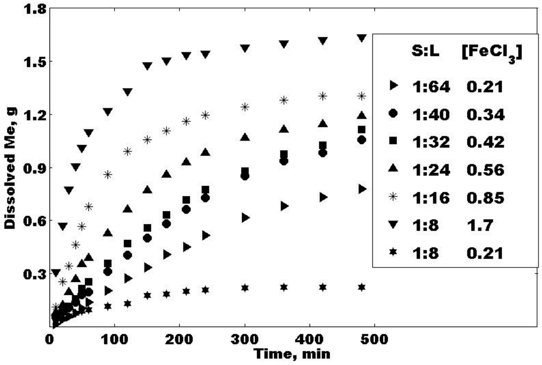

Figure 3. Amount of dissolved Me vs. time at 11.07 g $FeCl_3$ dissolved in different volumes of 0.3 M HCl solution

The results shown in Figure 3 indicate that the highest dissolution rate was achieved by using the highest S:L ratio (1:8) at the highest oxidant concentration (1.7 M).

Mathematical modelling of the leaching process

Since there are many possible combinations of $FeCl_3$ quantities and S:L ratios (Table 2) a mathematical model was developed and implemented in MATLAB in order to determine the dependency of the Me dissolution rate on the operating parameters. The material balance equations for the leaching process were written considering that the dissolution of Me occurs in a batch reactor by the following reaction:

$$2Fe^{3+} + Me \rightarrow Me^{2+} + 2Fe^{2+} \tag{1}$$

Based on the mass balance equations the dependency of the dissolution rate of Me (r) on the concentration of $FeCl_3$ ($C_{Fe^{3+}}$) can be defined by the following rate equation:

$$r = \frac{1}{\nu_{Me}} \cdot \frac{dC_{Fe^{3+}}}{dt} = \frac{1}{2} \cdot k \cdot C_{Fe^{3+}}^{a} \tag{2}$$

Since the volume of the leaching solution can be considered constant during the experiments the rate is expressed in g min^{-1} instead of g min^{-1} L^{-1}:

$$r = \frac{1}{2} \cdot k \cdot m_{Fe^{3+}}^{a} \cdot \frac{M_{Me}}{M_{Fe^{3+}}} \tag{3}$$

Also another term V was introduced in eq. (3) in order to link the dissolution rate of the Me to the S:L ratio:

$$r = \frac{1}{2} \cdot k \cdot \frac{M_{Me}}{M_{Fe^{3+}}} \cdot m_{Fe^{3+}}^{a} \cdot V^{b} \qquad (4)$$

By including the constants from eq. (4) into the apparent rate constant (k_{app}):

$$k_{app} = \frac{1}{2} \cdot k \cdot \frac{M_{Me}}{M_{Fe^{3+}}} \qquad (5)$$

The following rate equation is obtained:

$$r = k_{app} \cdot m_{Fe^{3+}}^{a} \cdot V^{b} \qquad (6)$$

The optimal values for the reaction orders (a, b) and k_{app} were identified by using the least square method and the optimization toolbox provided by MATLAB. The regression method defines the estimate of these parameters as the values which minimize the sum of the squares (hence the name least squares) between the measurements and the model (i.e., the predicted values) [22]. Inserting the best fitting values of the parameters into the objective function the following expression was obtained for the dissolution rate of the Me:

$$r = 1.97 \cdot 10^{-4} \cdot m_{Fe^{3+}}^{3.33} \cdot V^{-0.98} \qquad (7)$$

The amount of dissolved Me calculated on the basis of the above equation gives a good fit to the experimental data (Figure 4).

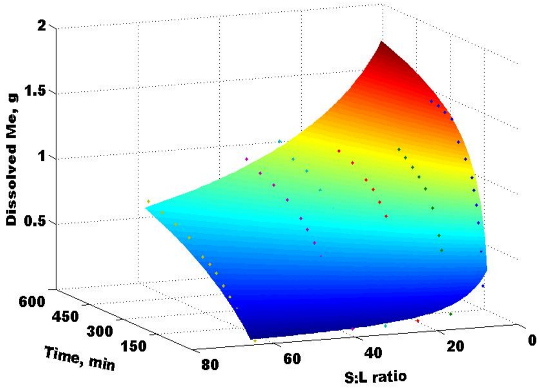

Figure 4. Fitting of the model result to the experimental data

The value of the relative error determined was approximately 8 %. This can be explained by the fact that this model does not include the influence of the reaction surface area modification with time, because it was not possible to measure it, due to the complex structure of the WPCB samples. However it can be considered that the initial surface area of the Me is identical from one sample to another, because their composition volume and weight is the same in each experiment.

Nevertheless, it is obvious from Figure 4 that the predicted values by the model fit very well with the experimental results. Moreover the values found for a = 3.33 and b = -0.98 sustain the conclusion that the dissolution rate of the Me is more strongly dependent on the amount of $FeCl_3$ used than on the applied S:L ratio. Therefore the amount of dissolved Me will increase with the increase of the amount of $FeCl_3$ and with the increase of the S:L ratio. Moreover the tendency of the dissolution rate suggests that the process can be improved even more by using higher S:L ratio and higher amounts of oxidants than those from the studied range. However, the use of higher S:L ratio is not possible since the uncrushed WPCB samples cannot be covered entirely by smaller volumes of leaching solutions than the one corresponding to the S:L ratio of 1:8.

The efficiency of higher oxidant concentrations than 1.7 M was evaluated by comparing the conclusions drawn from the values of the dissolution rate and a new parameter $f_{met/ox}$. The equation for the efficiency factor ($f_{met/ox}$) was defined as the ratio between the amount of the dissolved Me and total amount of $FeCl_3$ used in the experiment:

$$f_{met/ox} = \frac{\text{Total dissolved metals}}{\text{Amount of FeCl}_3\text{ used}} \quad \frac{[\text{g Me}]}{[\text{g FeCl}_3]} \tag{8}$$

The values of $f_{met/ox}$, obtained for several experimental conditions (Table 2), show how many grams of Me can be dissolved by using one gram of $FeCl_3$. This parameter reveals which $FeCl_3$ concentration and S:L ratio allows to use more efficiently the existing amount of oxidant. Considering its physical meaning, it is obvious that the efficiency factor is a more important criterion in the identification of the best operating conditions than the dissolution rate. However, in the case of the S:L ratio both parameters give the value of 1:8 as the most suitable for the dissolution of Me. In contrast, for the $FeCl_3$ concentration the two parameters lead to differing conclusions. While the dissolution rate increases with the oxidant concentration, reaching a maximum at 1.7 M $FeCl_3$, the efficiency factor reaches a minimum at the same concentration. The value of $f_{met/ox}$ shows that the dissolution rate is not large enough at the concentrations of 1.7 M, in order to allow for a gram of $FeCl_3$ to dissolve a larger amount of Me than at lower concentrations. In fact, Figure 5 shows that according to $f_{met/ox}$ the most appropriate oxidant concentration for the dissolution of Me is 0.64 M even if the dissolution rate is not the highest at this concentration.

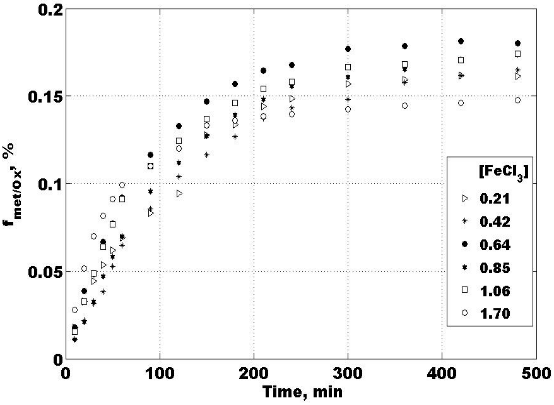

Figure 5. $f_{met/ox}$ vs. time at the S:L ratio of 1:8 using different $FeCl_3$ concentration and 0.3 M HCl solution

CONCLUSIONS

The experimental results proved that acidic $FeCl_3$ solutions are efficient leaching agents for the dissolution of base metals from WPCBs. It was found that the amount of dissolved metals, at constant oxidant concentration, increases significantly with the decrease of S:L ratio reaching a maximum at the value of 1:40. The influence of $FeCl_3$ concentration was also tested at fixed S:L ratio, which revealed that the leaching process is faster if instead of a high volume of leaching solution a lower one is used but at higher oxidant concentration.

Based on the concentration profiles it was also concluded that higher S:L ratios can use more efficiently the same amount of oxidant than lower ones. The mathematical expression for the dependency of the dissolution rate on the S:L ratio and $FeCl_3$ concentration was obtained by using a kinetic model developed in Matlab.

The validated rate equation shows that the Me dissolution rate is approximately minus first order respect to the S:L ratio and 3.3 order respect to the amount of $FeCl_3$. The value of the apparent rate constant at 25 °C was determined and found to be $1.97 * 10^{-4}$ $g^{-2.33} * min^{-1}$, which also confirms the suitability of acidic $FeCl_3$ solutions for the leaching of base metals. The efficiency factor defined in this work along with the dissolution rate lead to the conclusion that the best performances can be obtained at the S:L ratio of 1:8 and 0.64 M $FeCl_3$ concentration.

EXPERIMENTAL SETUP

The leaching tests were carried out in a batch reactor with recirculation which is equipped with a perforated rotating drum instead of an agitator. However, the studies regarding the influence of S:L ratio and oxidant concentration on the dissolution process presented in this work, were performed in unstirred conditions. All experiments were carried out at room temperature using 5 g of WPCB samples which were inserted in the rotating drum of the reactor. During the experiments the reactor was hermetically sealed in order to prevent the influence of air (O_2) on the oxidation of metals. The leaching solution was prepared by using ferric (III)-chloride (Fluka), 32 % HCl solution and double distilled water. The chemical composition of the WPCB samples (Table 1) was obtained by atomic adsorption spectroscopy after aqua regia mineralization. The same analytical method was used to determine the concentration of metals in the leaching solutions and in the residue at the end of the experiments.

Table 1. Chemical composition of WPCBs

Components	**Ag**	**Au**	**Cu**	**Sn**	**Pb**	**Zn**	**Fe**	**Ni**	**Solid residue**
	wt. %								
WPCB generally	0.02	0.01	20	4	1.9	2	8	2	62.07
WPCBs samples	0.02	0.02	16	6.5	1.9	5.5	-	-	70.06

It is obvious from the data shown in Table 1 that the samples contain only a few of the metals present in the WPCBs and in different concentrations. This limitation was necessary because Cu, Sn and Pb have the most important influence on the recovery of precious metals. It is well known that the extraction of high purity Au or Ag is not possible if the solution contains Cu. Furthermore the dissolution of Sn and Pb (solder) is crucial in the separation of electronic components from the other parts of the WPCBs. Moreover if the leaching of Cu, Sn and Pb occurs efficiently in these experimental conditions than there is no doubt that the more reactive base metals like Ni, Fe will be dissolved with high performances.

ACKNOWLEDGEMENTS

Prof. Chován Tibor, University of Pannonia, Veszprém, Hungary and Prof. Árpád Imre-Lucaci, Babeş-Bolyai University, Cluj-Napoca, Romania, are gratefully acknowledged for discussions which have stimulated the development of the research activity here reported.

The authors also 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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