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**RECOVERY OF GOLD AND SILVER FROM WASTE
PRINTED CIRCUIT BOARDS**

PhD thesis abstract

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Introduction

Due to the technological progress of the last decades, there is a keen interest for gold and silver used in printed circuit boards and high-performance connection systems. An accelerated development of industries producing electrical and electronic equipment (EEE) led to generation of large quantities of waste, which includes waste printed circuit boards (WPCBs). Cost-effective processing of WPCBs includes recovery of gold and silver that although exist in small concentration (approx. 0.03%) represents 80% of the profit resulting from the recovery of metals.

Considering the complex composition of WPCBs and economic potential of these secondary metal sources, it is necessary to use preliminary stages in the recovering technology of gold and silver aiming the collection, sorting and processing of the electronic waste leading to the separation of different categories of components. It is also important that the research and implementation of hydrometallurgical processes that allow selective extraction of metals with formation of secondary flows with controlled chemical composition, which, by further processing can lead to obtain in an efficient way metals or alloys. For this reason, we've appealed to use dissolution environment with thiosulfate, thiourea and thiocyanate in the presence of Fe^{3+} or Cu^{2+} , which dissolving selectively the silver and base metals allowed the separation of the residue, with high concentration of gold from these WPCBs materials. However, these environments have the disadvantage that the regeneration of the leaching solution is not cost-effective due to degradation of ligands during the extraction of metals, which becomes more emphasized as the concentration of the metal increases. Therefore, we used FeCl_3 in HCl leaching environment, which is more stable and easier to renew using electrochemical oxidation.

Electrochemical processes leads to higher performance compared to the chemicals as they can be done with lower consumption of reagents and energy. Also, the electrochemical way has the advantage that, the oxidation on the anode allows the parallel electro-extraction of base-metals, from leaching solutions, at the cathode.

For the extraction of gold from secondary flows, obtained in the preconcentration step, it is necessary to use strong oxidizing medium which allows the dissolution of gold with low environmental impact. Using hydrogen peroxide fits for this purpose because in acidic media, it is a strong oxidant able to oxidize even gold, being in the same time environmentally friendly and cheap reactant. The process with hydrogen peroxide also has the advantage that

during process are formed secondary products, which can be recycled for the regeneration of the leaching media.

The present PhD thesis approaches an actual research topic, related to environmental protection aiming to bring a series of original contributions in the field of complex gold and silver recovery from two types of WPCBs: one containing lower concentrations of base metals in which gold and silver is in the form of thin films accessible to dissolving environment and a second type in which gold and silver are mainly in electronic components which has to be separated and further processed.

Keywords:

Printed circuit boards, electrical and electronic equipment, solubilization of gold and silver, recovery of gold and silver, electroextraction, leaching systems, ligands, thiourea, thiosulfate, thiocyanate, chemical-electrochemical process, hydrogen peroxide, hydrochloric acid, silver cementation, environmental impact assessment.

LITERATURE OVERVIEW

1. DISSOLUTION PROCESSES OF GOLD AND SILVER FROM WASTE

Due to the highly positive oxidation potential of Au and Ag there are few substances (aqua regia, fluorine, persulphates etc.) which can directly oxidize these metals. Dissolution of Au and Ag can be achieved by oxidation combined with complexation. Thus, their oxidation potential is more negative, their oxidation can be achieved in the presence of complexing agents. Most commonly used reagents for combined dissolution of Au and Ag are [35]: *aqua regia*, *solution of NaCN/KCN in the presence of O₂ (air)*, *tiosulphates*, *tiourea in the presence of O₂ (air)*, *mixture of halogens with O₂ (air)*, *halogens in aqueous media*.

1.1. Solubilization of gold and silver with copper-ammonia-thiosulfate system

Dissolution of Au in the Cu(II)-S₂O₃-NH₃- O₂ system is a complex process, comprising complexing equilibrium, precipitation and redox disproportionation [42, 43]. The most important step in dissolving gold from WPCBs is its oxidation in the presence of Cu(II), when occurs the oxidation of Au to Au⁺ in parallel with reduction of Cu²⁺ to Cu⁺ [41, 43-44]. Thiosulfate ion with Au⁺ forms a very stable coordinative compound. The redox equilibrium between Au and Cu²⁺ moves to solubilization of metallic Au, with increasing rate as the concentration of thiosulphate is higher.

The speed and efficiency of dissolution of Au is influenced by the thiosulphate counter ion from the salt used, the best results were obtained with calcium and ammonium thiosulphate [43- 45]. Having regard to the complexity due to reduced stability of thiosulphate, there are attempts to replace it with more stable ligands, such as thiourea and thiocyanate [50].

1. 2. Dissolution of gold and silver in the presence of thiourea

Thiourea forms very stable complexes with Ag and Au and is more stable in presence of oxidants than thiosulphate. Thus, when thiourea is used, instead of Cu^{2+} Fe^{3+} can be used, which is a stronger and more effective oxidant [39, 51]. Compared with other dissolving methods, this has the advantage that gold can be oxidized only to Au^+ due to the steric impediment. Therefore, not having Au^{3+} , extracting gold from the solution consumes three times less energy. On the other hand, higher stability of thiourea leads to much lower consumption of reagents whether we have alkaline or acidic media [39, 52, 53].

1. 3. Mediated electrochemical dissolution of gold and silver

Mediated electrochemical dissolution (MED) of gold and silver involves solubilization of them through a redox-mediator couple. MED allows regeneration of the oxidant by direct anodic oxidation without additional consumption of reagents. Mediators used mostly are the ions of the transitional metals or halogens [54].

From the results presented in the literature it is shown that the most efficient mediator in MED for Au and Ag are Cl_2/Cl^- and ClO^-/Cl^- , respectively. High oxidizing potential of Cl_2 and of ClO^- , respectively the ability of Cl^- to form very stable complexes with noble metals leads to a rapid dissolution process [54, 56].

2. OBTAINING GOLD AND SILVER FROM THE LEACHING SOLUTIONS

2. 1. Recovery of gold and silver by cementation

Classic method of extraction for Au and Ag in ore leaching solution is the cementation. This procedure is based on the ability of reactive metals to reduce ions of more noble metal to metal. Due to high chemical inertia of Au and Ag, these can be cementated by a number of metals, most important examples being Al, Zn, Fe, Cu [7, 60-64].

2. 2. Recovery of gold and silver by electroextraction

Electroextraction is a very effective method for recovering noble metals because it allows obtaining selectively Au and Ag with low energy consumption and without additional reagents. Since electroextraction is a cathodic method, MED of Au and Ag from minerals or WPCBs can take place simultaneously in the same reactor. Using this method yields for recovery of Au and Ag is very high, their concentration in the depleted solution is below 0.1 ppm [71]. From experimental research it was observed that using electroextraction combined with ultrasonication increases the efficiency of Au and Ag recovery [71-75].

EXPERIMENTAL RESULTS

3. SELECTIVE DISSOLUTION OF METALS FROM WPCBS USING FeCl_3 AND CuCl_2 BASED REDOX SYSTEMS

The *Aim* of these experiments 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 in HCl solutions.

The efficiency of these leaching systems was compared on the basis of the extent of leaching of individual metals and total metal dissolution, considering the involved redox equilibrium.

3. 1. The influence of oxidant concentration on overall metal dissolution

To evaluate the influence of oxidant concentration on the dissolution of metals from WPCB, leaching tests were performed using five different concentrations of FeCl_3 and CuCl_2 in the range of 0.1-1.6 M. The redox reactions for the involved species and their standard reduction potentials, calculated based on thermodynamic data [79, 81, 74], are the following:



Commonly, the redox potentials for both oxidants are more positive as their concentration is higher. It is well known that this favors the dissolution process of metals, as a result the rate of metal dissolution increases considerably with the increase of oxidant concentration.

As it can be seen in Fig. 3.1, this dependency is more pronounced in the case of FeCl_3 and less for CuCl_2 . Hence, an increase of oxidant concentration by 16 times (0.1-1.6 M) enhances the global dissolution degree 2.6 times for FeCl_3 and 1.5 times for CuCl_2 . This can

be easily explained by considering the different standard reduction potentials of $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Cu}^{2+}/\text{Cu}^+$, Cu^{2+}/Cu redox systems.

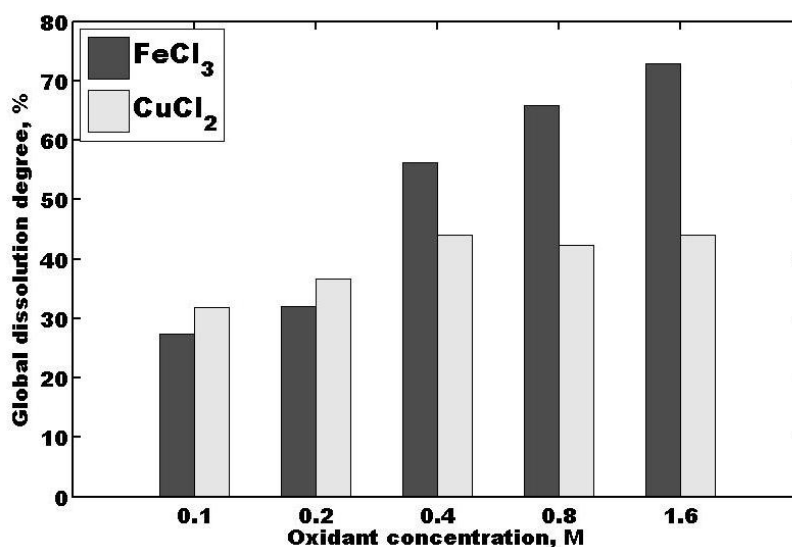


Fig. 3.1. Global dissolution degree of metals in 1 M HCl using FeCl_3 and CuCl_2

As a result, at the same oxidant concentration Fe^{3+} is a more powerful oxidizing agent than Cu^{2+} or Cu^+ in both chloride and chloride free mediums, due to the higher redox potential. However, the experimental results show that at low oxidant concentrations (0.1-0.2 M) it appears that CuCl_2 is more efficient oxidant in the dissolution of metals than FeCl_3 . As for higher oxidant concentrations than 0.2 M, FeCl_3 turns out to be more efficient because the dissolution of metals with Fe^{3+} is not hindered by the formation of a solid phase like in the case of CuCl_2 .

3. 2. The influence of oxidant concentration on individual metal dissolution

Since the WPCBs have a very complex composition it is also important to evaluate the influence of oxidant concentration on the individual dissolution of the metals. Therefore the individual dissolution degree was determined for each metal at the studied oxidant concentrations (0.1-1.6 M). Table 3.1. contains the individual dissolution degree for Zn, Ni and Cu while Fig. 3.2. and Fig. 3.3. for Ag and Pb.

Table 3.1. Individual dissolution degree of Zn, Ni and Cu in 1 M HCl at different FeCl₃ and CuCl₂ concentrations

Oxidant concentration, M	Individual dissolution degree, %				
	Zn		Ni		Cu
	FeCl ₃	CuCl ₂	FeCl ₃	CuCl ₂	FeCl ₃
0.1	93.3	92.5	18.1	26.9	52.8
0.2	93.2	89.3	22.1	33.7	71.1
0.4	95.3	71.6	51.1	43.9	91.9
0.8	95.1	64.1	65.2	43.5	90.7
1.6	94.2	64.1	74.9	45.3	90.8

The results show that the dissolution degree of Zn and Ni varies in opposite direction with the increase of oxidant concentration. For Zn the dissolution rate is decreasing while for Ni it is increasing with the increase of CuCl₂ concentration. As for FeCl₃ the dissolution degree for both metals increases with the increase of oxidant concentration.

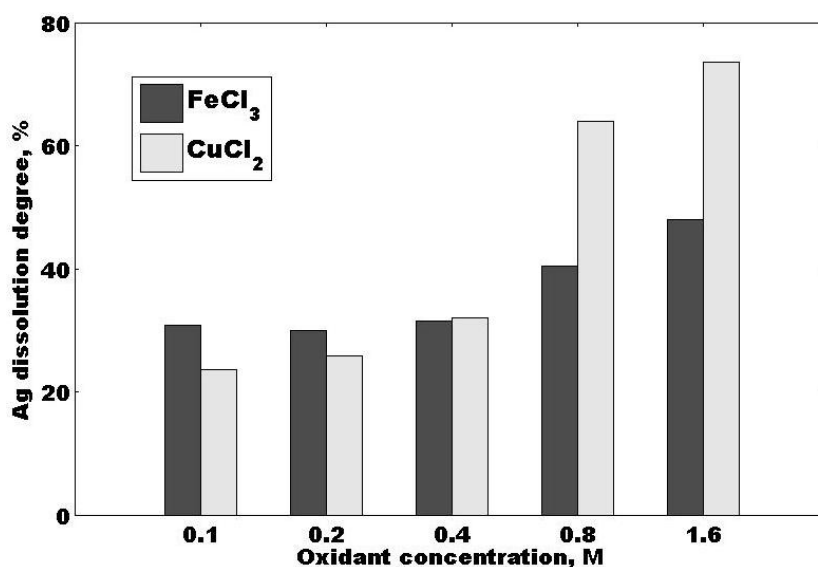


Fig. 3.2. Individual dissolution degree of Ag in 1 M HCl at different FeCl₃ and CuCl₂ concentrations

Comparing the dissolution degrees in the case of Ag and Pb, it can be observed that there are significant differences between the two oxidants, due to the fact that Ag can be reduced by the cemented copper as well, while Pb can be cementated only on more reactive metals like Ni and Zn.

Differently from the previous metals the standard reduction potential of Au⁺ (1.15 V) and Au³⁺ (0.93 V) in the presence of chloride ions is still higher than the ones obtained for the oxidants, as a result the chemical dissolution of gold is not possible in these experimental

conditions. In consequence to achieve higher gold dissolution degrees it is necessary to use a more efficient ligand than chloride ions.

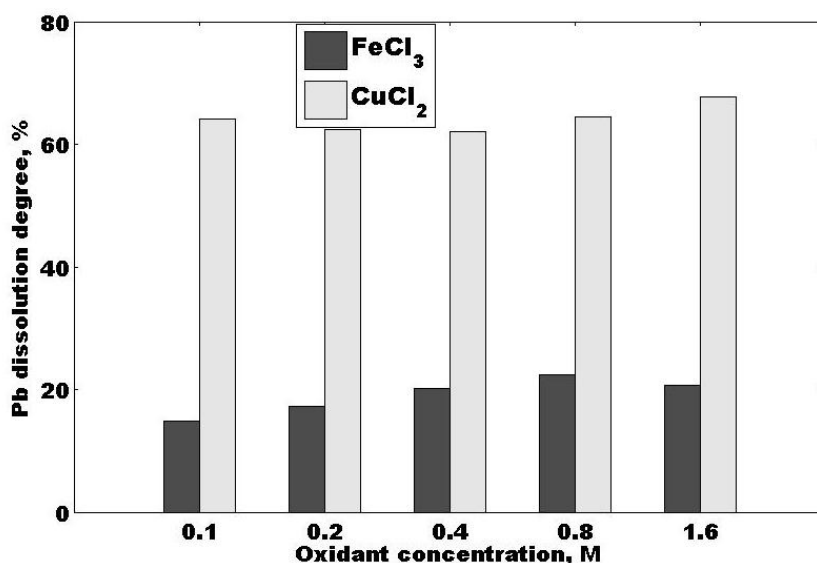


Fig. 3.3. Individual dissolution degree of Pb in 1 M HCl at different FeCl₃ and CuCl₂ concentrations

3. 3. The influence of thiourea, thiosulfate and thiocyanate concentration on metal dissolution

As it was discussed earlier the dissolution rate of the metals is dependent on the difference between the redox potential of the metals and the leaching agents. Therefore, according to the Nernst equation the presence of different ligands can change the rate of metal dissolution by modifying the redox potential of the metals and the leaching agents through the complexation of the electroactive species. Thus, based on the available literature data, thiourea, thiosulfate and thiocyanate were identified as the most appropriate ligands for the dissolution of noble metals [35]. As it can be seen, from the overall dissolution degrees in Table 3.2, 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 3.2. Global dissolution degree in 1 M HCl at 0.2 M oxidant and different ligand concentrations

Ligand concentration, M	FeCl ₃			CuCl ₂		
	NH ₄ SCN	Na ₂ S ₂ O ₃	CS(NH ₂) ₂	NH ₄ SCN	Na ₂ S ₂ O ₃	CS(NH ₂) ₂
	Global dissolution degree, %					
0	32			37		

0.1	51	59	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 the results from Table 3.2. and Fig. 3.1. it seems like 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.

The data from Table 3.3, indicate that the dissolution degree of gold is very different in the case of FeCl₃ and CuCl₂ with the exception when thiosulfate was used.

Table 3.3. Gold dissolution degree in 1 M HCl at 0.2 M oxidant and different ligand concentrations

Ligand concentration, M	FeCl₃			CuCl₂		
	NH₄SCN	Na₂S₂O₃	CS(NH₂)₂	NH₄SCN	Na₂S₂O₃	CS(NH₂)₂
	Gold 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 is due to the fact that Cu²⁺/Cu⁺ decreases more the concentration of the ligands, since forms more stable complexes than Fe³⁺/Fe²⁺. Therefore, it is possible that the amount of free ligands, remained in the solution, is smaller than the required for the further complexation of gold.

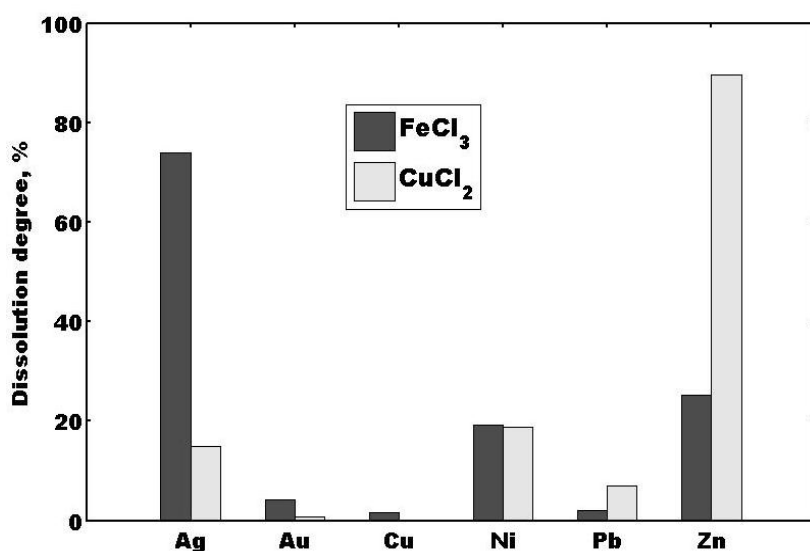


Fig. 3.4. Individual dissolution degree of metals in 1 M HCl at 0.2 M oxidant and 0.5 M $CS(NH_2)_2$

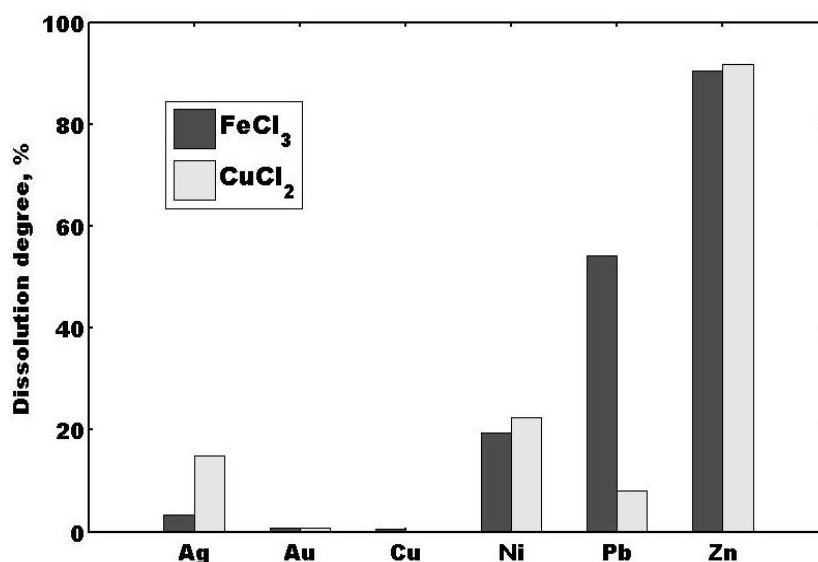


Fig. 3.5. Individual dissolution degree of metals in 1 M HCl at 0.2 M oxidant and 0.5 M $Na_2S_2O_3$

The presence of ammonium ions, in the experiments with thiocyanate, has a benefic effect on both ligand stabilization and metal dissolution. Therefore, in contrast with the other two ligands, Fig. 3.4, Fig. 3.5, 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.

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 except 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 $\text{CS}(\text{NH}_2)_2$ 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.

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

The aim of the study was to find the optimal operating conditions for the dissolution of base metals (Cu, Ni, Zn, Pb) from WPCB in acidic FeCl_3 in order to obtain a gold rich residue and a leaching solution from which metals or alloys can be obtained by electroextraction.

The optimal values of the operating parameters were identified based on the maximum amount of dissolved metals at different combinations of solid/liquid ratios and oxidant concentrations. 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. Other performance evaluation criteria were the efficiency factor, recirculation flow rate and rotation speed of the perforated drum.

4. 1. The influence of solid: liquid ratio on the leaching process

The influence of solid: liquid (S:L) ratio on the dissolution of metals was studied in the range of 1:8 – 1:64 (g:mL) using an acidic 0.21 M FeCl_3 solution. Fig. 4.1, shows that the amount of dissolved metals 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.

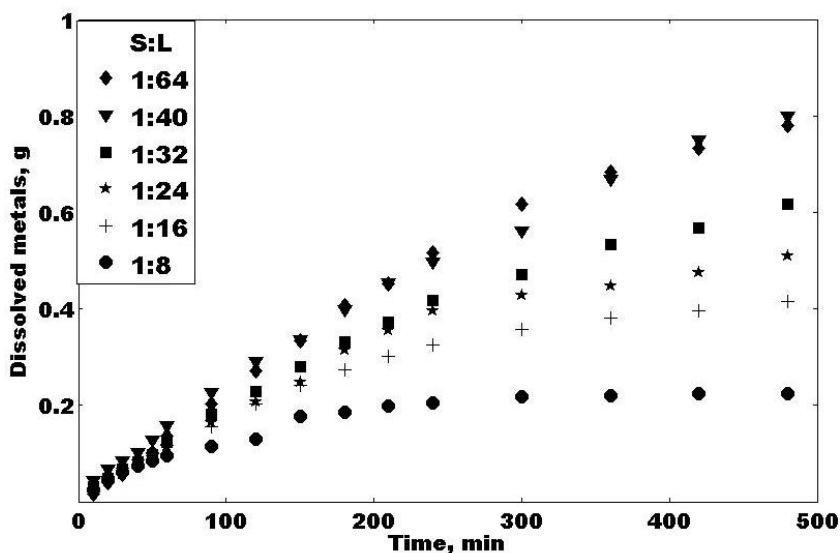


Fig. 4.1. Amount of dissolved metals at different S/L ratios in 0.21 M FeCl₃ and 0.3 M HCl

It seems like at constant volume of leaching solutions the use of higher FeCl₃ concentrations can improve significantly the dissolution rate of metals. Fig. 4.2. shows that the leaching rate, at the S:L ratio of 1:8, increases almost 10 times by increasing the oxidant concentration 8 times. Furthermore, it can be observed that from the 0.64 M FeCl₃ concentration upwards the S:L of 1:8 becomes more efficient than the other ones at 0.21 M FeCl₃ concentration. It is also important to note that the higher dissolution rate at the S:L of 1:8 and 0.64 M FeCl₃ was achieved using an amount of FeCl₃ three times smaller than the one used in the experiment with the S:L of 1:64 and 0.21 M oxidant concentration.

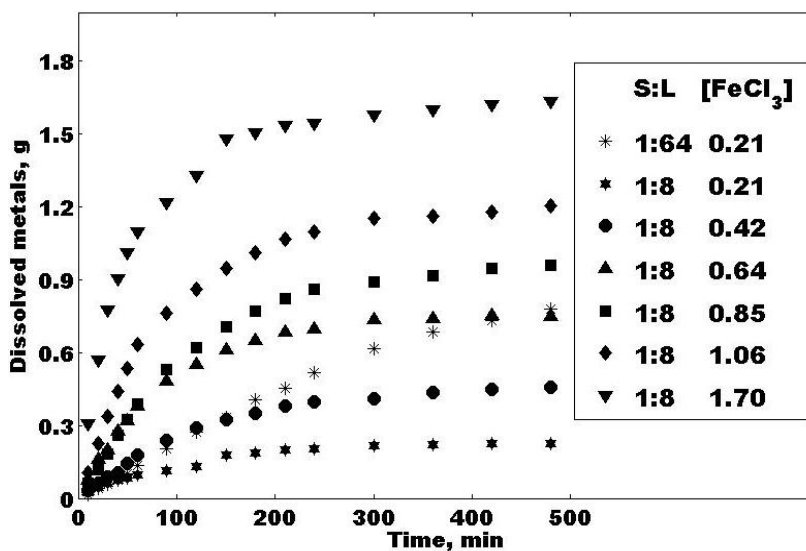


Fig. 4.2. Amount of dissolved metals at different S/L ratios and FeCl₃ concentration in 0.3 M HCl solution

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 $FeCl_3$, Fig. 4.3.

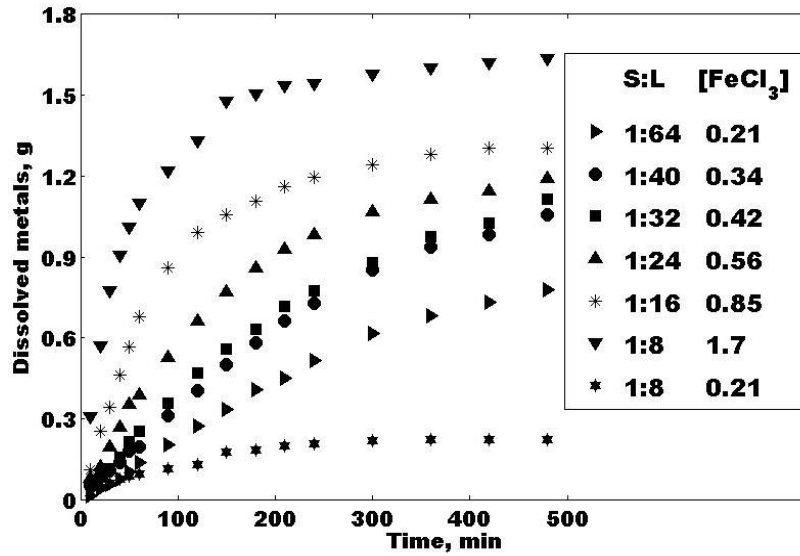


Fig. 4.3. Amount of dissolved metals at 11.07 g $FeCl_3$ dissolved in different volume of 0.3 M HCl solutions

4. 2. Mathematical modeling of the leaching process

Since there are many possible combination of $FeCl_3$ quantities and S:L ratios a mathematical model was developed and implemented in MATLAB in order to determine the dependency of the metal dissolution rate on the operating parameters.

The material balance equations for the leaching process were written considering that the dissolution of metals occurs in a batch reactor by the following reaction:



Based on the mass balance equations the dependency of the amount of dissolved metals on the concentration of $FeCl_3$ can be defined by the following rate equation:

$$r = 1v_{Me} \cdot \frac{dC_{Fe^{3+}}}{dt} = \frac{1}{2} \cdot k \cdot C_{Fe^{3+}}^a \quad (4.2)$$

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

$$r = \frac{1}{2} \cdot k \cdot m_{Fe^{3+}}^a \cdot \frac{M_{Me}}{M_{Fe^{3+}}} \quad (4.3)$$

Also another term V was introduced in (4.3), in order to link the dissolution rate of the metals to the S:L ratio:

$$r = \frac{1}{2} \cdot k \cdot \frac{M_{Me}}{M_{Fe^{3+}}} \cdot m_{Fe^{3+}}^a \cdot V^b \quad (4.4)$$

By including the constants from (4.4) into the apparent rate constant:

$$k_{ap} = \frac{1}{2} \cdot k \cdot \frac{M_{Me}}{M_{Fe^{3+}}} \quad (4.5)$$

The following rate equation is obtained:

$$r = k_{ap} \cdot m_{Fe^{3+}}^a \cdot V^b \quad (4.6)$$

The optimal values for a , b and k_{ap} 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) [96]. Inserting the best fitting values of the parameters into the objective function the following expression was obtained for the dissolution rate of the metals:

$$r = 1.97 \cdot 10^{-4} \cdot m_{Fe^{3+}}^{3.33} \cdot V^{-0.98} \quad (4.7)$$

The amount of dissolved metals calculated on the basis of the above equation gives a good fit to the experimental data Fig. 4.4. The value of the relative error determined on the basis of the mathematical model is approximately 8%.

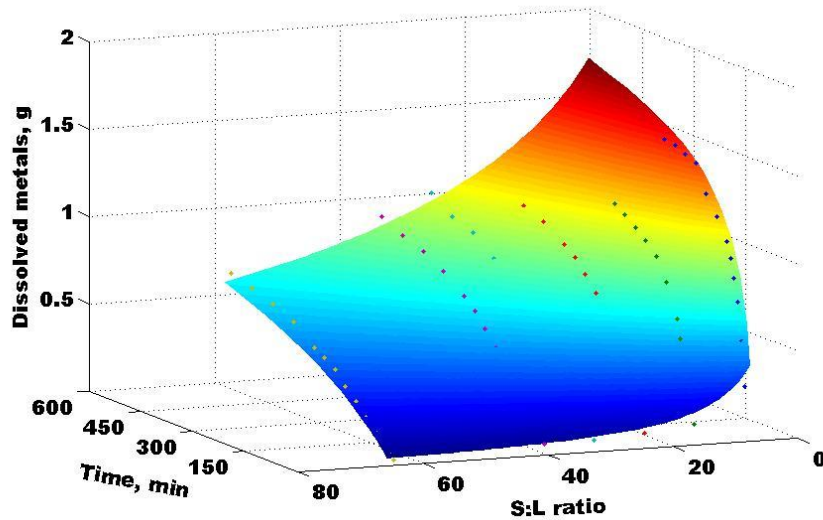


Fig. 4.4. Model vs. experimental data

The values found for $a=3.33$ and $b=-0.98$ sustain the conclusion that the dissolution rate of the metals is more strongly dependent on the amount of $FeCl_3$ used than on the applied 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.

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 efficiency factor ($f_{met/ox}$) was defined as the ratio between the amount of the dissolved metals and total amount of $FeCl_3$ used in the experiment:

$$f_{met/ox} = \frac{\text{Amount of dissolved metals}}{\text{Amount of } FeCl_3 \text{ used}} \quad (4.8)$$

This parameter reveals which $FeCl_3$ concentration and S:L ratio allows to use more efficiently the existing amount of oxidant. In the case of the S:L ratio both parameters give the value of 1:8 as the most suitable for the dissolution of metals. 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. Fig. 4.5. shows that according to $f_{met/ox}$ the most appropriate oxidant concentration for the dissolution of metals is 0.64 M even if the dissolution rate is not the highest at this concentration.

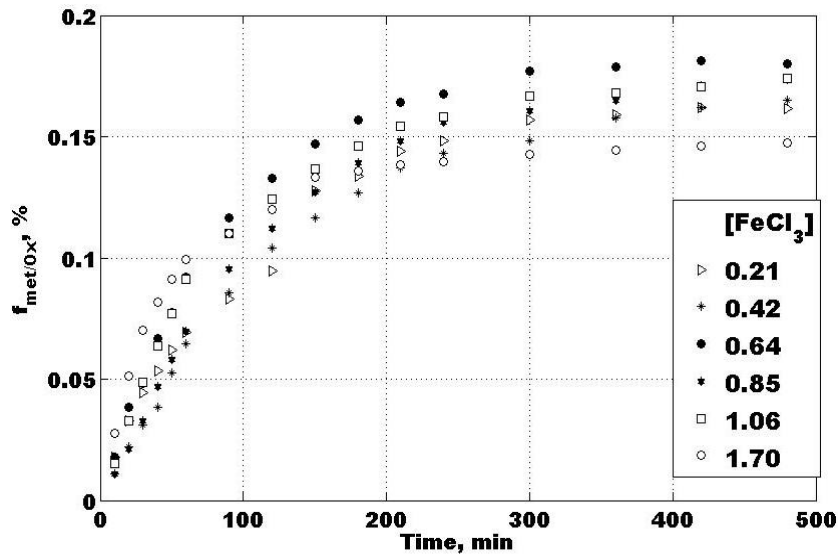


Fig. 4.5. $f_{met/ox}$ vs. time at S/L ratio of 1/8 and different $FeCl_3$ concentrations in 0.3 M HCl

4. 3. Intensification of the dissolution process

Since the process takes place in a recirculating batch reactor, equipped with a rotating drum which contains the WPCB samples, the dissolution rate can be increased significantly by increasing the mass transport of the reactants. This can be accomplished through

increasing the flow rate and/or increasing the rotation speed of the perforated drum. Therefore, solubilization-tests were conducted using three flow rates: 10, 15, 20 mL/min and 3 rotation speeds: 10, 20, 30 rot/min. For other parameters we have used the optimum values already established in the previous studies: 0.64 M FeCl₃ and S/L: 1/8. Other conditions were identical to previous studies, excepting that in this case the testing period was 240 min.

From the evolution of the quantity of dissolved metals in time, at different values of the tested parameters (Fig. 4.6.-Fig. 4.8), it can be observed that the dissolution rate increases with the increasing flow rate and rotation speed. According to the data in Fig. 4.6, the amount of the dissolved metals is 20% higher at 10 mL/min and 10 rot/min than under stationary conditions (with double time), value which increases at 30 rot/min to 37%.

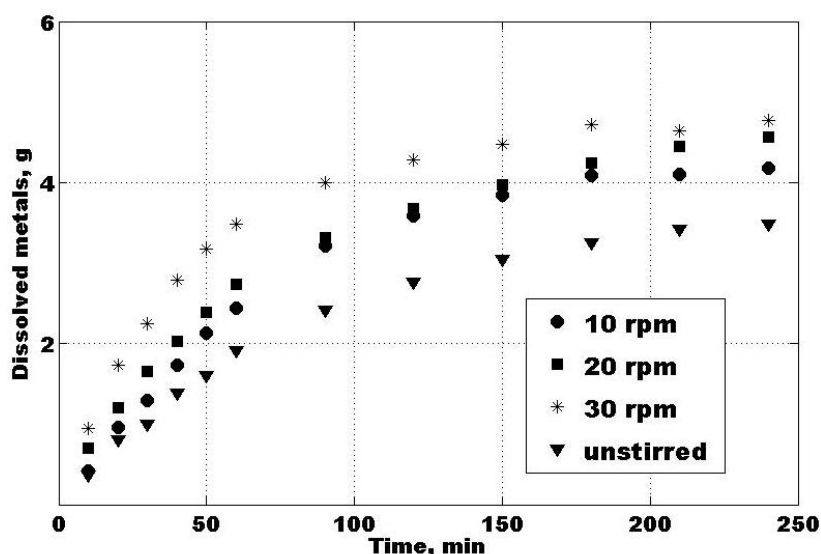


Fig. 4.6. Amount of dissolved metals vs. time in stationary solution and 10 mL/min using different rotation speeds

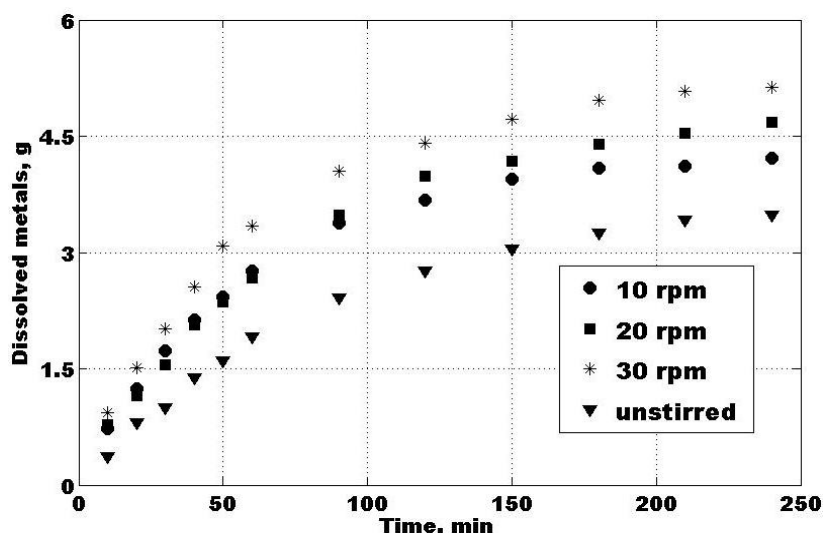


Fig. 4.7. Amount of dissolved metals vs. time in stationary solution and 15 mL/min using different rotation speeds

Furthermore, at the flow rate of 20 mL/min and 30 rot/min (Fig. 4.8), this percentage reaches 55%.

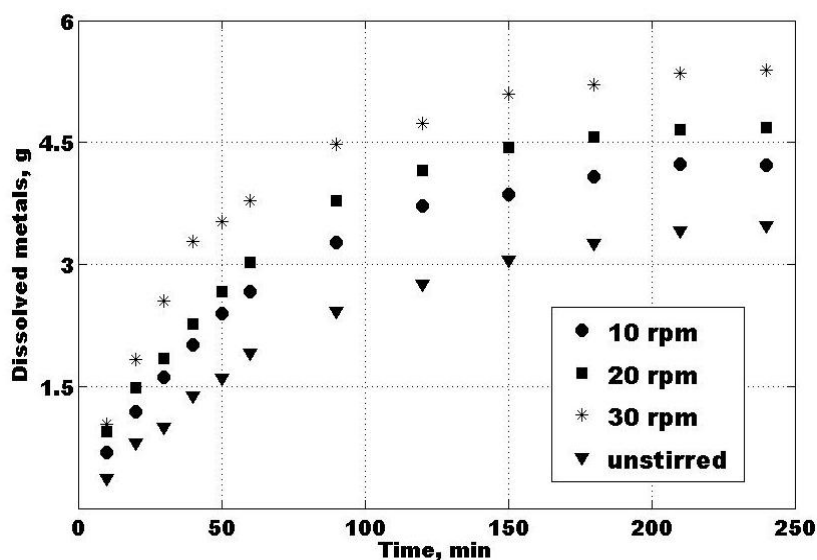


Fig. 4.8. Amount of dissolved metals vs. time in stationary solution and 20 mL/min using different rotation speeds

5. COMBINED CHEMICAL-ELECTROCHEMICAL PROCESS

The aim of this study was to develop a combined chemical-electrochemical process which allows the regeneration of FeCl_3 , through anodic oxidation of Fe^{2+} ions, with the parallel electrodeposition of the dissolved metals from the WPCB samples.

The processes performances were evaluated based on efficiency of metal dissolution, cathodic current efficiency and specific energy consumption.

5.1. Influence of current density and initial concentration of FeCl_3 on the performance of the process

As it's shown in Fig. 5.1 and Fig. 5.2., the dissolution and cathodic current efficiencies were studied, at different current densities and oxidant concentration. From the dissolution efficiency it can be concluded, that by regenerating the oxidant at 4 mA/cm^2 and 0.1 M FeCl_3 the same performance can be achieved as with chemical dissolution at 0.64 M oxidant concentration. Furthermore, at 4 mA/cm^2 and 0.37 M FeCl_3 , for the dissolution process the

yield is 30 % higher than for the chemical process even if the last one operates at a double oxidant concentration than the first one. In contrast, the electrodeposition of metals results in a lower yield (up to 35 %) compared to the values obtained during the dissolution process, even at the most favorable values of current density and oxidant concentration. This value can be reached at a current density of 4 mA/cm² or 8 mA/cm², but because the value for dissolution degree is lower at 8 mA/cm², therefore it is considered that 4 mA/cm² is the best suited value for the global process.

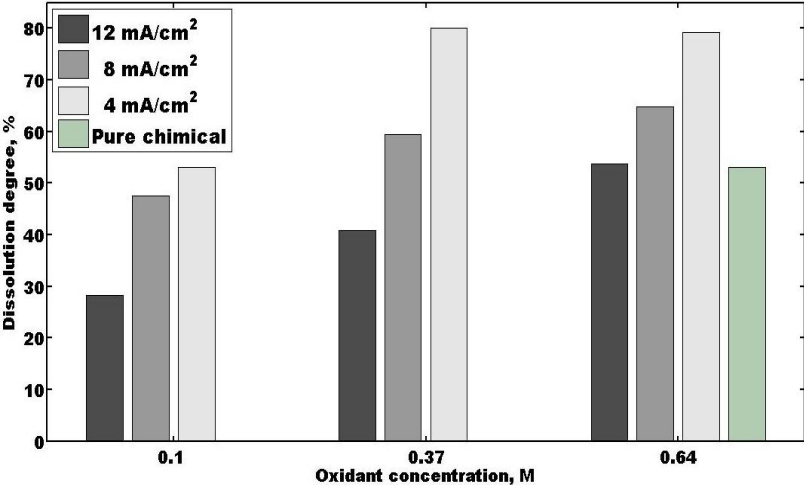


Fig. 5.1. Dissolution efficiency at different current densities and oxidant concentration

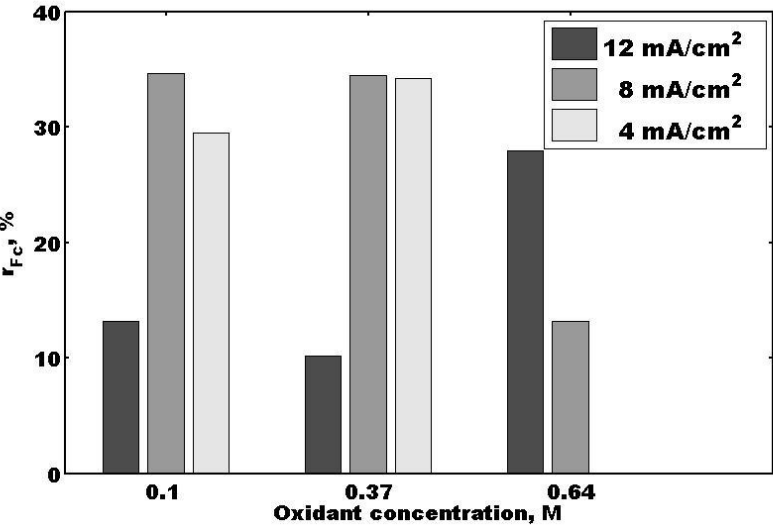


Fig. 5.2. Cathodic current efficiency at different current densities and oxidant concentration

The value of the cathodic current efficiency is limited at 35 % due to the side reactions among which the most important is the reduction of Fe³⁺, thanks to the high standard reduction potential of the Fe³⁺/Fe²⁺ redox couple. At the concentration of 0.64 M FeCl₃ the influence of this secondary reaction on the cathodic process becomes so significant that the

formation of the metallic deposit is not possible. This is also confirmed by the values of the cathodic potentials, Table 5.1, which indicate, at the current density of 4 mA/cm² and 0.64 M FeCl₃, a cathodic process that can only be attributed to the reduction of Fe³⁺ to Fe²⁺. For this reason the electroextraction of metals can take place at more negative values of the cathodic potential.

Table 5.1. Cathodic potential at different current densities and oxidant concentration

i mA/cm ²	FeCl ₃ , M		
	0.1	0.37	0.64
	ε _c , V		
4	-0.66	-0.06	0.28
8	-0.73	-0.21	-0.15
12	-0.74	-0.34	-0.20

Different combinations of current densities and oxidant concentrations favor the formation of metallic deposits with several compositions. Therefore, at 0.37 M FeCl₃ for all current densities a high purity copper deposit, over 91 % (see Table 5.2), was obtained in agreement with the values of the cathodic potentials. Deposits with similar composition were also obtained at 0.64 M FeCl₃ with the exception of 4 mA/cm².

Table 5.2. Cathodic deposit composition at different current densities and oxidant concentration

i, mA/cm ²	FeCl ₃ M	Cu	Pb	Zn	Sn	Fe
		%				
4	0.1	32.57	10.59	0.50	53.83	2.51
	0.37	91.66	0.08	0.51	0.30	7.45
8	0.1	37.08	10.91	0.25	49.92	1.84
	0.37	95.75	0.13	0.79	0.39	2.95
	0.64	93.51	0.09	0.99	0.40	5.00
12	0.1	53.17	7.86	0.28	38.69	0.04
	0.37	95.73	1.17	0.85	2.26	0.31
	0.64	99.50	0.14	0.24	0.12	0.10

In contrast at 0.1 M FeCl₃ a ternary Cu-Sn-Pb alloy was obtained in which the concentration of these metals varies with the current density and electrolyte composition,

Table 5.3. The increase of current density increases the copper concentration and decreases the concentration of tin and lead (Table 5.2).

Table 5.3. Concentration of metals in the electrolyte at different current densities and oxidant concentration

FeCl₃	i,	Cu	Pb	Zn	Sn
M	mA/cm²	%			
0.1	4	32.47	13.75	5.81	47.97
	8	35.57	11.51	4.88	48.04
	12	46.25	8.75	8.24	36.77
0.37	4	67.30	5.75	7.64	19.31
	8	61.01	6.55	8.41	24.04
	12	68.70	9.55	5.47	16.28
0.64	4	70.91	4.79	7.88	16.42
	8	71.38	4.59	7.92	16.11
	12	81.24	5.36	4.61	8.80

The primary anodic reaction, oxidation of Fe²⁺ to Fe³⁺, is strongly influenced by the leaching and cathodic processes which led to the formation of Fe²⁺ ions. Considering the above discussions the highest amount of Fe²⁺ is generated at the current density of 4 mA/cm² and 0.64 M FeCl₃. In consequence the anodic potential has the lowest value at these values of the operating parameters Table 5.4.

Table 5.4. Anodic potential at different current densities and oxidant concentration

i,	FeCl₃, M		
	0.1	0.37	0.64
	ε_a, V		
4	1.33	0.91	0.80
8	1.48	1.45	1.28
12	1.48	1.47	1.43

The values of the cell voltage shown in, Table 5.5, can be explained on the basis of the electrochemical processes and electrode potentials. The increase of cell voltage with the decrease of oxidant concentration can be attributed to the lower conductivity of the electrolyte and to the formation of gas byproducts which temporally block the surface of the electrodes.

Table 5.5. Cell voltage at different current densities and oxidant concentration

i , mA/cm ²	FeCl ₃ , M		
	0.1	0.37	0.64
	E _b , V		
4	2.12	1.09	0.58
8	2.52	1.88	1.55
12	2.55	2.12	1.85

Since the most important performance criterion in the case of electrochemical processes is the specific energy consumption, this parameter was calculated for both anodic and cathodic processes. Fig. 5.3. and Fig. 5.4 shows that for both processes the smallest values of the specific energy consumption were obtained at the current density of 4 mA/cm². As for the oxidant concentration, it seems like for the dissolution process the concentration of 0.64 M FeCl₃ gives the best performances while for the electrodeposition of the metals the lowest specific energy consumption is found to be at 0.37 M FeCl₃. Considering that the deposition of metals is not possible at 0.64 M FeCl₃ the optimal oxidant concentration for the overall process was chosen to be 0.37 M FeCl₃.

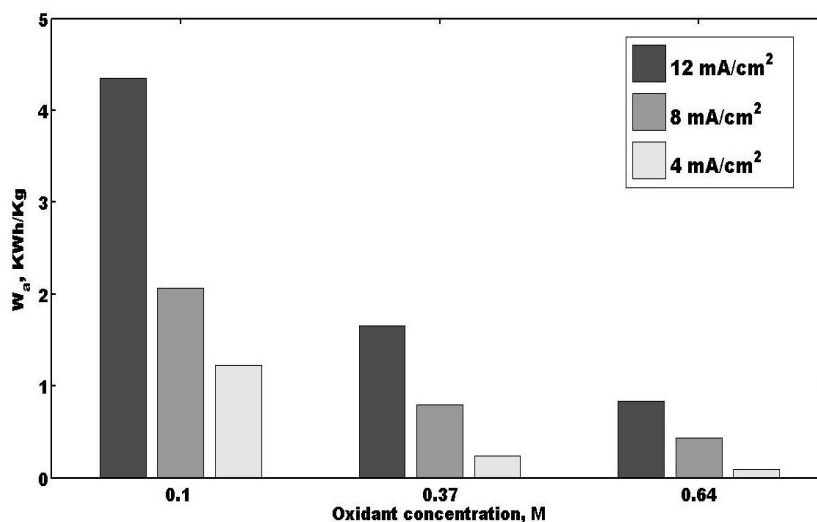


Fig. 5.3. Specific energy consumption for the dissolution process (W_a) at different current densities and oxidant concentration

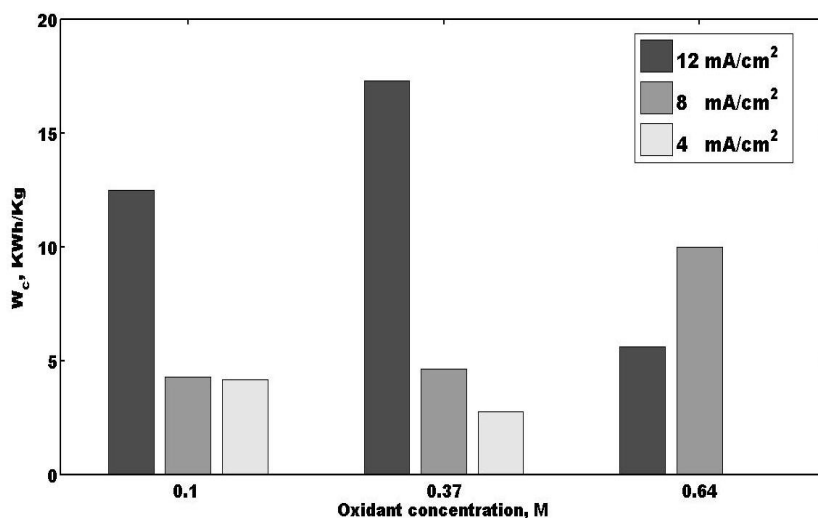


Fig. 5.4. Specific energy consumption for the electrodeposition process (W_c) at different current densities and oxidant concentration

5. 2. Combined chemical-electrochemical process scale-up to 1:10

To separate the gold rich electronic components it was necessary to realize a scale-up of the combined chemical-electrochemical process, allowing the treatment of the entire WPCB not just the parts selected for the previous experiments. The experiments with duration of 12 h were performed at the optimal values of the operating parameters found in chapter 8. The composition of the cathodic deposit in Table 5.6, indicates an increase of copper concentration from 91.66 % (chapter 8) to 99.04 %.

Table 5.6. Deposit composition

Metal	Ag	Cu	Pb	Zn	Sn	Fe	Ni
Concentration, %	0.01	99.04	0.08	0.17	0.55	0.10	0.05

Also it can be noticed, in Table 5.7 that the copper deposit is obtained with a higher current efficiency and lower energy consumption, which means that the scaled-up process improved the performances of the electroextraction of metals.

Table 5.7. Performance parameters of the process

i	ϵ_a	ϵ_c	E_b	r_{Fc}	r_d	W_c	W_a
mA/cm ²	V			%		KWh/Kg	
4	0.87	-0.15	1.33	63.84	90.07	1.75	0.59

The dissolution of metals in the chemical reactor also occurs with a higher performance reaching a dissolution degree of 90.07 %. The sludge obtained in the leaching process has a high copper content (see Table 5.8), as a result increasing the duration of the process can lead to a more efficient recovery process.

Table 5.8. Sludge composition

Components	Ag	Au	Cu	Pb	Sn	Plastic
Concentration, %	0.035	0.104	73.85	11.16	7.8	7.05

It is important to note that the sludge has a gold content ten times higher than the initial WPCB sample and in the case of silver two times higher. Other secondary products of the leaching process are the surface mounted devices and gold rich electronic components. Table 5.9, shows that these solid materials have a gold concentration 30 times higher than the initial sample.

Table 5.9. Composition of SMD and chips

Metal	Ag	Au	Cu	Pb	Zn	Sn	Fe	Ni
Concentration, %	0.02	0.3	14.1	1.26	0.15	0.73	1.72	0.75

6. TREATMENT OF THE SECONDARY STREAMS OBTAINED IN THE PRECONCENTRATION STEP

6.1. Dissolution of gold from the solid residuum using the H₂O₂ – HCl leaching system

The aim of the study was to find the optimal conditions for the dissolution of gold, from the solid residuum obtained in chapter 3, using the H₂O₂ – HCl leaching system.

6.1.1. The influence of H₂O₂ and HCl concentration on the dissolution of gold

The dissolution of gold occurs by the following reaction:



The experimental data shown in Fig. 6.1. indicate that the percentage of dissolved gold increases with the increase of H₂O₂ and HCl concentration reaching a maximum of 26.4 %.

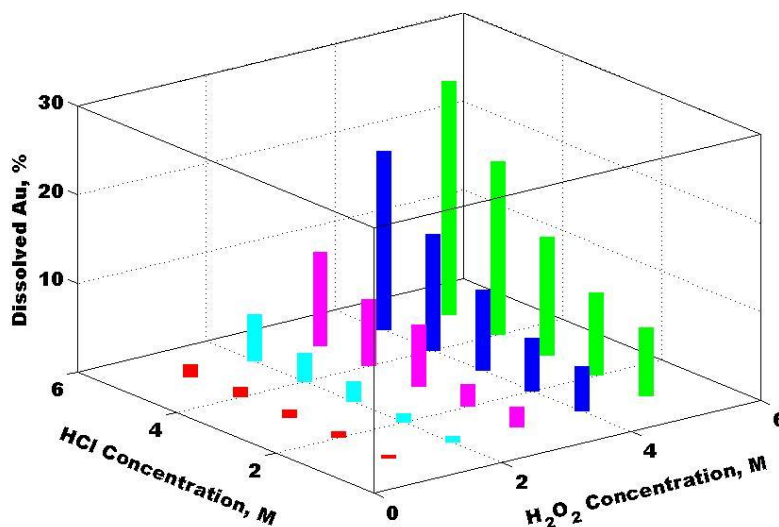


Fig. 6.1. Percentage of dissolved gold vs. hydrogen peroxide and hydrochloric acid concentration

Furthermore, Fig. 6.1. reveals that the dissolution process of gold is more strongly dependent on the H₂O₂ concentration than on the HCl concentration.

In order to establish the most efficient conditions for the use of hydrogen peroxide in the dissolution of gold, an efficiency factor was defined as the ratio between the amount of dissolved gold and the amount of hydrogen peroxide used in the experiment:

$$f_{Au/H_2O_2} = \frac{\text{Amount of dissolved gold}}{\text{Amount of } H_2O_2 \text{ used in the experiment}} \quad (6.2)$$

This factor is very useful because it reveals the experimental conditions where the secondary reactions have the most significant impact on the process. The values of f_{Au/H_2O_2} , Fig. 6.2, show that the highest amount of gold, with the lowest consumption of H₂O₂, is dissolved at 5 M hydrogen peroxide. Similarly an efficiency factor was defined in the case of HCl:

$$f_{Au/HCl} = \frac{\text{Amount of dissolved gold}}{\text{Amount of HCl used in the experiment}} \quad (6.3)$$

Fig. 6.3. shows that $f_{Au/HCl}$ is more strongly dependent on the H₂O₂ concentration leading to the highest values at 4 and 5 M hydrogen peroxide.

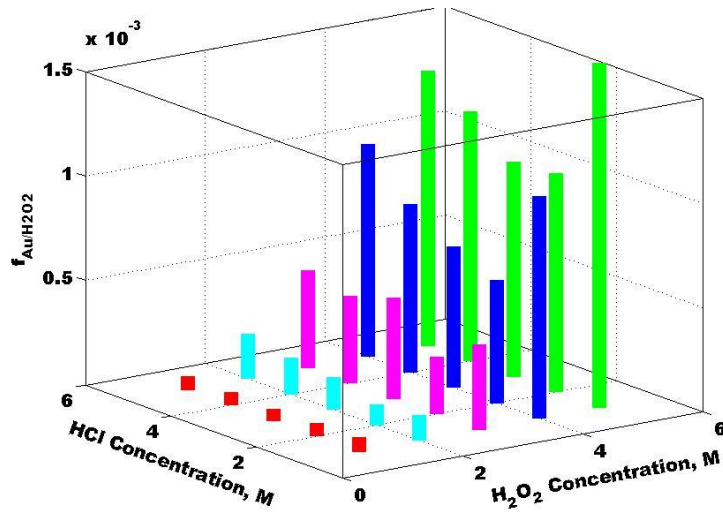


Fig. 6.2. f_{Au/H_2O_2} vs. hydrogen peroxide and hydrochloric acid concentration

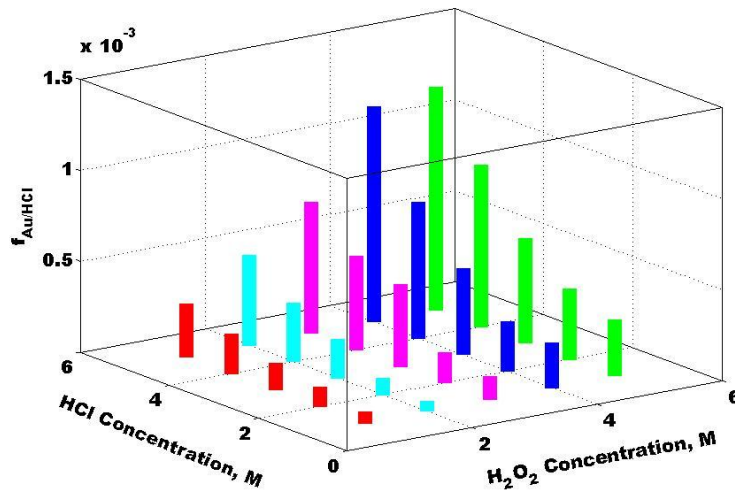


Fig. 6.3. $f_{Au/HCl}$ vs. hydrogen peroxide and hydrochloric acid concentration

Based on the obtained result it can be concluded that the dissolution of gold occurs the most efficiently at 5 M H₂O₂ and 5 M HCl.

6. 2. Gold electroextraction from the leaching solution

The aim of the study was to obtain metallic gold, from the leaching solution (chapter 5.1), through electroextraction using the rotating disc electrode. The same technique allowed the characterization of the mass transport during the electrodeposition of gold.

6. 2. 1. Mass transport characterization during the electroextraction of gold with the rotating disc electrode

The most important parameters which characterize the mass transport during the electrodeposition of gold were calculated on the basis of the limiting currents, Fig. 6.4, using the Levich equation [99, 100]:

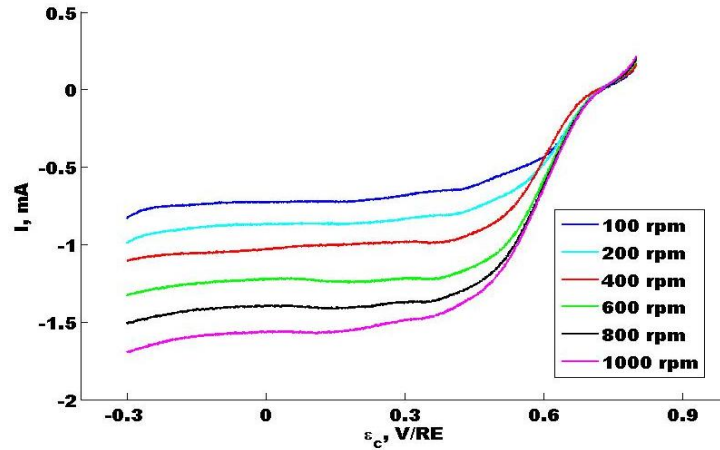


Fig. 6.4. Polarization curves at different rotational speeds in 0.5 g/L gold and 5 M HCl;
 $v=10 \text{ mV/s}$

$$I_L = 0.62 z F C A \nu^{-1/6} D^{2/3} \omega^{1/2} \quad (6.4)$$

where: I_L – limiting current, A; z - nr. of electrons, 3; F – Faraday number, 96486 C; C – concentration of the electroactive species, 2.53 mol/m^3 ; A - electrode surface area, $0.283 \cdot 10^{-4} \text{ m}^2$; ν – cinematic viscosity, $1.1206 \cdot 10^{-6} \text{ m}^2/\text{s}$; D – diffusion coefficient, m^2/s ; ω – rotation speed, s^{-1} ;

The diffusion coefficient can be determined from the slope of $I_L = f(\omega^{1/2})$. According to Fig. 6.5. the limiting current has the following dependency on the rotation speed:

$$I_L = 3.94 \cdot 10^{-4} \omega^{1/2} \quad (6.5)$$

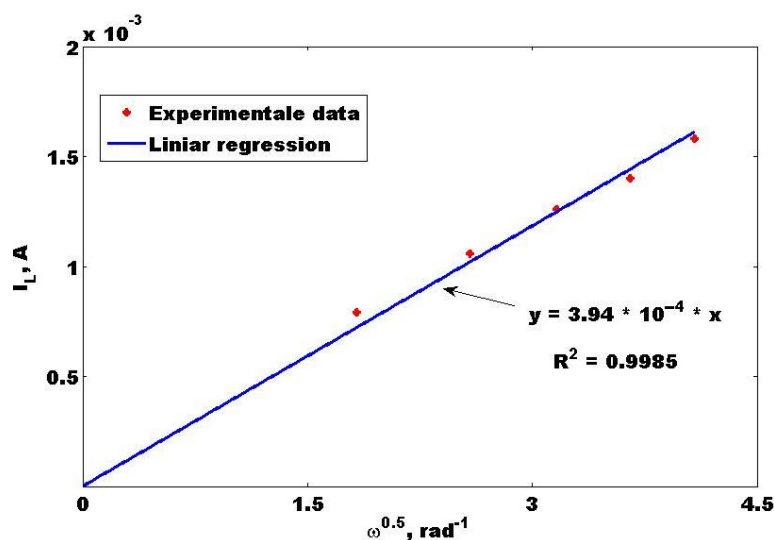


Fig. 6.5. Limiting current vs. rotation speed.

From equation (6.4) and (6.5) the value of the diffusion coefficient is:

$$D = \sqrt{\left(\frac{3.94 \cdot 10^{-4}}{0.62 \cdot 3 \cdot 96486 \cdot 2.53 \cdot 0.283 \cdot 10^{-4} \cdot (1.1206 \cdot 10^{-6})^{-1/6}} \right)^3} \quad (6.6)$$

$$D = 5.53 \cdot 10^{-9} \text{ m}^2/\text{s}$$

Using equation (6.7), (6.8) it is possible to calculate the partial mass transport coefficient and the Nernst diffusion layer thickness:

$$k_m = 0.62 \nu^{-1/6} D^{2/3} \omega^{1/2} \quad (6.7)$$

$$\delta_N = 1.6 \nu^{1/6} D^{1/3} \omega^{-1/2} \quad (6.8)$$

The calculated values for k_m and δ_N at different rotation speeds are presented in Table 6.1:

Table 6.1. Mass transport parameters at different rotation speeds

ω , rpm	I_L , A	$k_m \cdot 10^4$, m/s	$\delta_N \cdot 10^4$, m
200	0.79	2.57	1.58
400	1.06	3.05	1.11
600	1.26	3.38	0.91
800	1.4	3.63	0.78
1000	1.58	3.84	0.70

Based on the results in Table 6.1, it has been decided to perform the electroextraction experiments in galvanostatic conditions applying 85 % of the limiting current obtained at

1000 rpm. As Table 6.2. shows it was possible to extract 40 % of the gold present in the leaching solution in just 4 h. Further electroextraction is not justified since the specific energy consumption is rising as the concentration of gold decreases in the leaching solution, becoming double at the end of the experiments. The same conclusion can be drawn by comparing the other parameters.

Table 6.2. Performance parameters of the electroextraction process of gold

Time, h	i, mA/cm²	ϵ_c, V	ϵ_a, V	E_b, V	Au extracted, %	r_F, %	W, KWh/Kg
1	4.5	0.33	0.8	0.74	12.35	97.87	0.309
2		0.17	0.94	1.06	23.38	92.65	0.396
3		-0.018	1.22	1.48	32.59	86.09	0.518
4		-0.11	1.41	1.73	39.84	78.93	0.648

The deposit was characterized by scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDAX). The EDAX elementary analysis, Fig. 6.6, confirm that the deposit consists of pure gold.

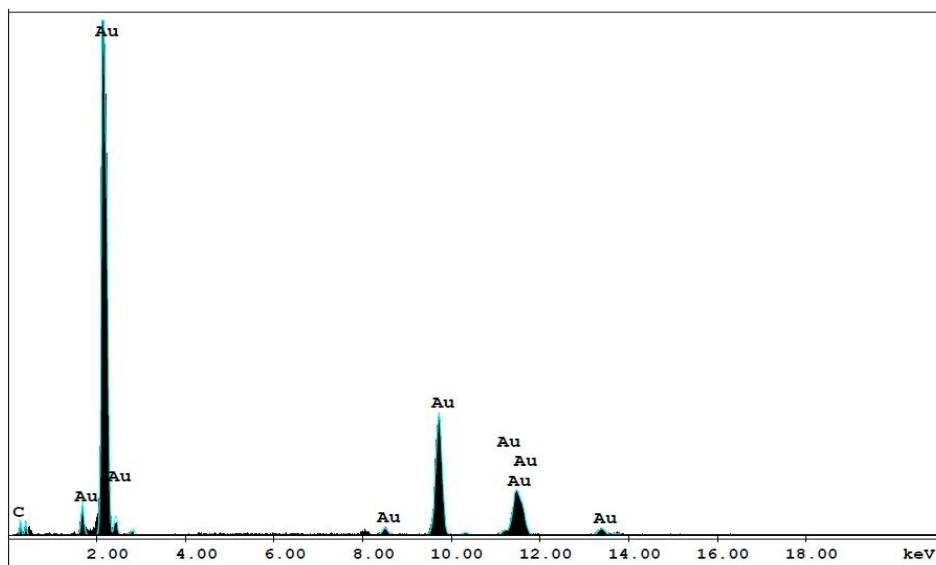


Fig. 6.6. EDAX spectrum of the gold deposit

The SEM image on Fig. 6.7, shows that the deposit contains globular and ‘rice-like’ structures. This can be attributed to the fact that the high current density does not allow the formation of a more uniform deposit. This can be resolved by operating at lower current densities or by using some additives, especially in galvanization of other metals.

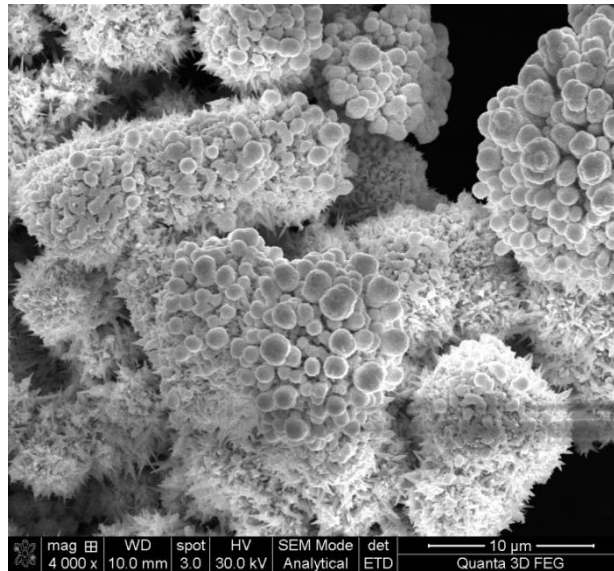


Fig. 6.7. SEM image of the gold deposit

6. 3. Recovery of silver from the sludge obtained in the preconcentration step

The study aimed the recovery of silver, from the sludge obtained in the preconcentration step, through cementation on zinc particles.

6. 3. 1. The cementation of silver on zinc particles

Fig. 6.8 shows that after 5.5 h the amount of silver cemented on zinc represents 53 % of the total silver found in the sludge.

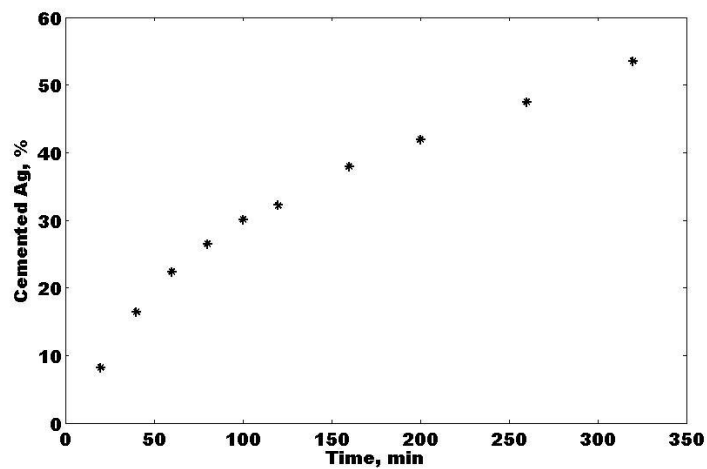


Fig. 6.8. Percentage of cemented silver vs. time

7. ENVIRONMENTAL IMPACT ASSESSMENT OF COPPER AND GOLD RECOVERY PROCESSES FROM WPCBS

The method has a simple structure and is based on data that can be accessed easily. In the first stage all available data relevant to the process are collected. Mass balance is drawn up with all the inputs and outputs of the process. These data are supplemented with data from literature. The environmental impact factors of the components are obtained from the inputs and outputs of the technological process in the second stage of implementation of the method. Finally, the quantities of raw materials and products, with ecological factors, are combined in a set of indices which lead to the global environmental impact. These indices calculated for the studied processes show that they have a relatively low environmental impact.

8. GENERAL CONCLUSIONS

The present thesis deals with a current research topic related to environmental protection aiming to bring a series of highly original contributions in the field of complex gold and silver recovery from various types of WPCBs.

In the first part of the thesis – *The literature survey* - chapters 1-6, the thesis summarizes literature data on the importance of gold and silver; the preliminary recovery processes from wastes; methods of dissolution of gold and silver from WPCBs respectively obtaining them from leaching solutions.

In the literature survey the detailed description of the dissolution media used for leaching gold and silver has been emphasized, respectively on their extraction methods, issues that are discussed in detail in the original contributions part of the thesis.

In the personal contributions part, chapters 7-11, the thesis is aimed at developing efficient methods that lead to obtaining metallic gold and silver.

In Chapter 7, based on literature data, a method has been developed for selective dissolution of metals from WPCBs using FeCl_3 and CuCl_2 redox systems in acidic environment respectively in the presence of complexing ligands: thiourea, thiosulfate and thiocyanate. Experimental results show that the overall efficiency of metal dissolution is higher for CuCl_2 at concentrations lower than 0.2 M, while at higher concentrations of oxidant, FeCl_3 is more effective. The performed studies show the possibility to reduce the oxidant consumption by 50% and to improve the selectivity of the dissolution process by adding to the leaching solution small amounts of thiourea, thiosulfate and thiocyanate. Based on the process flow, elaborated from these experimental studies, it can be concluded that by using the proposed leaching system in the most appropriate sequences, it is possible to dissolve selectively the metals from WPCBs, obtaining a gold rich residue.

Chapter 8 focuses on the optimization of the dissolution process with FeCl_3 in HCl medium using a leaching reactor with perforated rotating drum. Based on the mathematical model developed in Matlab, a mathematical expression was obtained for the dependence of the dissolution rate of metals with the S/L ratio and the concentration of FeCl_3 . It was found that the dissolution rate is approximately of -1 order to the S/L ratio and 3.3 order with respect to the amount of FeCl_3 . The value of the apparent rate constant was found to be $1.97 \cdot 10^{-4} \text{ g}^{-2.33} \cdot \text{min}^{-1}$ at 25 °C. The efficiency factor defined in these studies, together with the

dissolution rate, lead to the conclusion that the best performance can be obtained at an S/L ration of 1/8 and a concentration of 0.64 M FeCl₃.

The studies of dissolution intensification show that the amount of dissolved metals reaches a maximum at 20 mL/min and 30 rot/min, being with 55 % higher than in the case of the steady state process, even if the duration of the experiment was twice shorter.

Combined chemical-electrochemical method developed in Chapter 9, allows the regeneration of FeCl₃ by anodic oxidation of Fe²⁺ ions respectively cathodic electrodeposition, in parallel, of the dissolved metals from the WPCB samples. The studies reveal that the dissolution efficiency is 30 % higher for the combined process at 4 mA/cm² and 0.37 M FeCl₃, than for the chemical one (chapter 8), at a double concentration of oxidant. The implementation of the combined chemical-electrochemical process at a scale of 1:10 allowed the processing of the whole WPCB, not only the parts taken in the previous studies, with separation of gold rich electronic components. A longer processing time, under these conditions, determined an increase of the current efficiency from 35 % to 65 % and a decrease of the specific energy consumption from 2.76 to 1.75 kWh/kg, obtaining a deposit of copper with purity over 99 %.

Chapter 10 proposes an original method for leaching of gold from the residue obtained after the dissolution process presented in Chapter 7. Using 5 M hydrogen peroxide in 5 M hydrochloric acid allowed the dissolution of gold in a proportion of 26.36 % in just 4 h of experiment. Further, using the rotating disk electrode, the electrowinning of gold achieved 40 % at a current efficiency of 79 % and with a specific energy consumption of 0.65 kWh/kg.

Studies on obtaining metallic silver from the sludge obtained in the preconcentration phase, shows that thiosulfate environment is suitable for the dissolution of silver chloride. Using zinc granules for the cementation of silver from this solutions, allowed the extraction of silver in a proportion of 53 % in 5.5 h.

The method developed for obtaining gold and silver allows the recirculation of the leaching solutions in the process respectively the ecological regeneration of the reaction environment with a reduced cost.

From the results of the environmental impact assessment, Chapter 11 it can be concluded that:

- The GEI values obtained for the recovery of copper in the preconcentration step are comparable with the literature data for the recovery of copper in sulfuric acid medium

- By comparing the two methods of obtaining gold, it is estimated that the GEI values for the cyanide process for both inputs and outputs are more than 1.5 times higher than for the process using hydrogen peroxide. GEI values obtained for the two gold recovery processes shows that cyanide process has a much higher environmental impact than the process using hydrogen peroxide.

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