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RECOVERY OF COPPER BY ELECTROLYSIS OF SOLUTIONS OBTAINED FROM THE SOLUBILIZATION OF POLYMETALLIC CONCENTRATES FROM WPCBs

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The waste printed circuit boards (WPCBs) were shredded in a Retsch SM2000 cutting mill to the size of 1 mm, and the non-metallic, lighter part was gravitationally separated into a stream of water. The polymetallic concentrate thus obtained was subjected to a solubilization process by means of a Fe^{3+} / Fe^{2+} *redox process, the solution was analyzed by XRF and subjected to electrolysis with a copper sulphate electrolyte, highlighting the kinetics of the electrolytic deposition process and the distribution of the other elements in the electrolyte, the cathode deposit and the anodic deposition.*

Keywords: WPCBs, polymetallic concentrate, redox process, electrolysis.

1. Introduction

The problem of waste management is also manifested in Romania more and more acutely because of the increase in their quantity and diversity, as well as their negative impact, even more pronounced, on the environment. Urban and industrial development of localities, as well as the general increase in the standard of living of the population, lead to the production of more and more waste [1, 2].

In the last decades, the huge amount of waste from electrical and electronic equipments (WEEEs) has created particular problems due to insufficient storage facilities and high levels of hazardous substances for the environment [2, 3]. Electric and electronic products have seen an increase in their use throughout the world. The lifecycle of electrical and electronic devices that are indispensable to our lives has steadily decreased due to the development of new models and their introduction on the consumer market [3, 4]. The evaluation of electronic waste through the recovery process is very important to minimize potential environmental hazards. Therefore, these processes allow materials of

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economic value from WEEEs (metals and plastics) to be used in the production process as well. At the end of the recovery process, not only solid waste quantities are reduced but also natural resources protected [4, 5].

The WEEEs has an important economic potential due to the content of metals and precious metals. Characterization of these wastes and the experimentation of different techniques are of paramount importance for the development of an environmentally friendly recycling system. In recent years, a large number of investigations have been conducted to address the problem of WEEEs and to develop appropriate recycling techniques [6-9]. According to Cui and Zhang [10], recycling of these types of waste can be divided into three main stages: a) mechanical disassembly pretreatment: selective removal of hazardous and valuable components, required for subsequent operations; b) concentration: increase concentration of desirable materials using mechanical and/or metallurgical processing and c) refining: metallurgical treatment and purification of desirable materials. The complexity and heterogeneity of WEEE are the main obstacles to the recovery of metals from these type of waste. For the recovery of metals various treatment options are proposed based on conventional mechanical, physical, pyrometallurgical and hydrometallurgical processes [10-13].

The extraction of non-ferrous metals from the waste of electronic equipment in many cases requires a pretreatment of them because the metals are generally covered with different plastics or ceramics. This process ensures the exposure of the metals of interest to the action of the solubilizing reagents and thus facilitates their efficient extraction [14].

A first step of this pretreatment is disassembly by removing dangerous components such as capacitors, batteries, resistors. The next step is the physical separation that pre-concentrates valuable metals, thus increasing the economic potential of waste and docility to recycle [15]. By mechanically pretreating the metals are concentrated in one fraction and the polymers and ceramics in another.

The most commonly used methods for obtaining these concentrates are shredding, classification and separation (based on density, weight, magnetic properties, etc.) [16]. In order to effectively reduce the size of these types of waste, it is necessary to perform shredding in devices with cutting action or active [17]. The metallic fraction is then subjected to electrochemical processes for recovery. In this paper is proposed a solubilisation procedure for recovering copper from WPCBs by means of a Fe^{3+} / Fe^{2+} redox process, which is an economic (low cost of ferric sulphate) and ecological (the recovery of ferric sulphate) procedure. According to the literature, the waste of printed circuit boards contains about 40% metals, 30% plastic and 30% ceramics. Typical metal waste in WPCBs consists of copper (20%), iron (8%), tin (4%), nickel (2%), lead (2%), zinc (1% 2%), gold (0.1%) and palladium (0.005%) These materials are valuable and can be recovered by appropriate technologies [18].

2. Materials and methods

In the experiment, WPCBs were shredded at -1 mm in a Retsch SM2000 cutting mill and subjected to a gravitational grading process in an ascending stream of water to separate the non-metallic part.

The resulting polymetallic concentrate was analyzed by three successive XRF analyzes (X-Ray Fluorescence) and the mean of the values was the following: Cu - 61.537 wt.%; Zn - 16.597 wt.%; Sn - 7.247 wt.%; Ni - 6.807 wt.%; Pb - 3.720 wt.%; Fe - 1.623 wt.%; Ag - 0.606 wt.%; Bi - 0.520 wt.%; Ti - 0.362 wt.%; Sb - 0.297 wt.%; Cr - 0.288 wt. %; Pd - 0.039 wt; Au - 0.038 wt.%, the difference is the nonmetallic material in proportion of 0.320 wt.% [19].

The polymetallic concentrate was subjected to the electrolysis process using copper cathodes at current densities of 25, 30 and 35 mA/cm^2. All experiments were performed in an electrolytic cell with the dimensions: 80x80x150 mm, with an effective volume of 1000 ml, made of Plexiglas. The cathode was made of copper and the anode from a platinum titanium grill. The dimensions of both electrodes were 70x60x1 mm. These investigations aim at the separation of copper from the polymetallic concentrate and the determination of copper deposition kinetics.

To find out informations on the electrolysis copper separation process, the aqueous solution containing cationic species (Table 1) resulting from the chemical dissolution of electronic waste (WPCBs) was subjected to investigations using cyclic voltammetry and chronoamperometry [19]. For this purpose a cell of 25 cm^3 was used for the tests, the process was conducted at room temperature under stationary conditions. The recordings of cyclic voltammetry (platinum electrode and counterelectrod and a silver reference electrode) and chronoamperometry (copper electrode) were performed using PARSTAT 4000 potentiostatic equipment (Princeton Applied Research). Several scanning speeds ranging from 5 -20 mV / s were applied for a potential range between -1.5 and + 1V / Ag ref.

3. Experimental results and discussion

The polymetallic concentrate, with the chemical composition given in the materials and methods section, was subjected to solubilization in a Fe^{3+} / Fe^{2+} redox system, and the solution was analyzed by XRF (Table 1 and Fig. 1).

Table 1

Chemical composition of the solution after solubilization of the polymetallic concentrate

Element	**Fe**	**S**	**Cu**	**Sn**	**Zn**	**Cr**	**Ag**	**Ni**	**Pb**	**Al**	**Ti**	**V**
Concentration, [g/l]	2.47	4.238	60.32	7.11	8.42	0.03	0.6	5.89	3.51	1.91	0.12	0.005
Stat. error	0.14	0.47	0.2	0.69	0.4	6.12	0.38	2.5	0.21	16.8	11.1	2.3

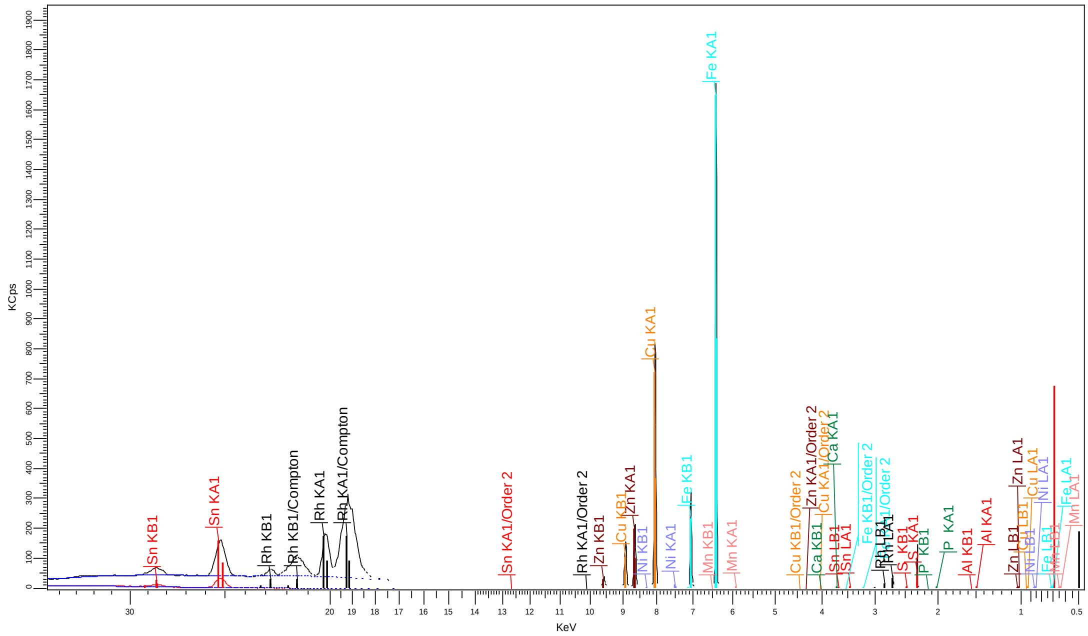

Fig. 1. The XRF spectrum of the solution obtained by solubilizing the polymetallic concentrate

In the chromoamperogram (Fig. 2), the initial area is highlighted, from the first seconds after the application of the potential step, when the drop of the cathodic current goes to slightly lower values (from about 50 mA/cm^2 to 28 - 32 mA/cm^2), followed by an intermediate region (between 10 – 250 sec.), for which the current variation may be associated with the nucleation and deposit growth processes, and finally the area for which the current value has a quasi-consensus value associated with the metal electrodeposition.

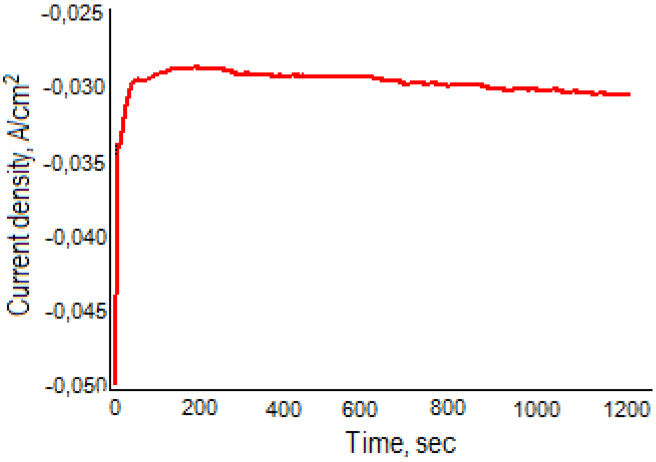

Fig. 2. Chronoamperograms on copper substrate at a constant reduction potential of -0.800 V / Ag ref.

Cyclic voltametry tests in the solution (pH adjusted at 0.5) have identified catodic peaks at ~ -0.3V/Ag ref. ascribable to Cu reduction [19]. Chrono-amperometry tests at constant potential E = -0.800V/Ag ref. up to 20 min. resulted in compact cathode deposits. The EDX analysis is presented in Fig. 2.

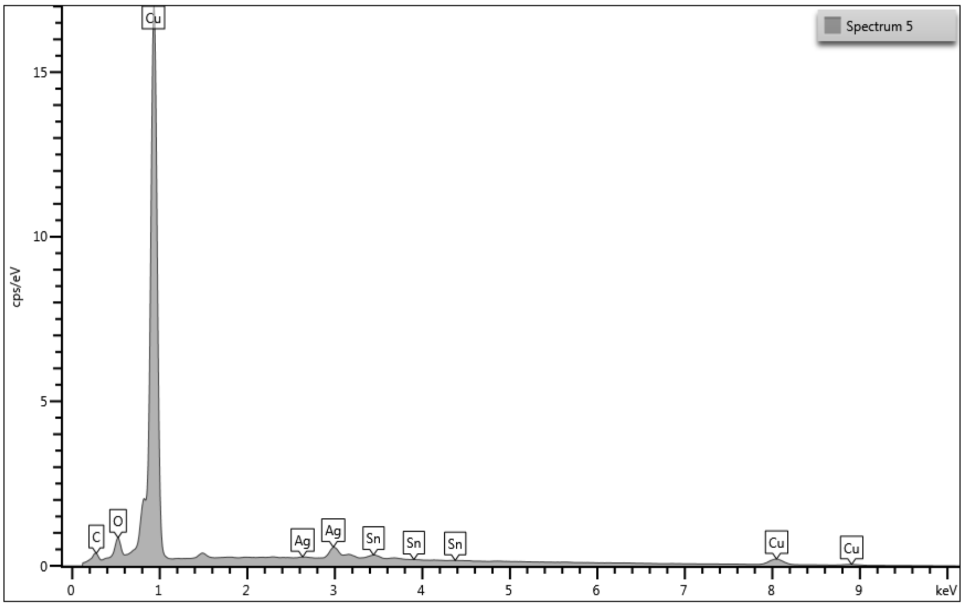

Fig. 3. EDX analysis of electrodeposited layer at -0.8V / Ag ref. on Cu substrate for 1200 sec

When the electric current passes, the ions are migrated and discharged to the electrodes. At the cathode, the Cu^{2+} (- 0.34 V) ions are reduced because they have lower reduction potential than the H_2O^+ (0 V) ions, and the anode oxidizes the water molecule with lower oxidation potential than the SO_4^{2-} (+ 2.00 V).

Cathode (-) $Cu^{2+} + 2e^- \rightarrow Cu^0$ $(- 0.34V)$ (1)

Anode (+) $2H_2O \rightarrow O_2 + 4H^+_{aq} + 4e^-$ $(1.23V)$ (2)

Total reaction:

$$2CuSO_4 + 2H_2O \rightarrow 2Cu + O_2 + 2H_2SO_4 \qquad (3)$$

The results of the electrolysis tests are shown in Table 2 and illustrated in Figs. 4, 5 and 6.

Table 2

The variation of copper concentration in solution during electrolysis based on cathode current density at a voltage per cell of 2.0 V

Time [min]	**Copper in solution [g/l]**					
	25 mA/cm^2		***30 mA/ cm^2***		***35 mA/ cm^2***	
	g/l	Extraction yield, %	g/l	Extraction yield, %	g/l	Extraction yield, %
0	60.32	0.00	60.32	0.00	60.32	0
15	57.00	5.50	53,00	12.14	48.54	19.53
30	54.55	9.57	48.02	20.39	39.98	33.72
50	53.00	12.14	36.65	39.24	28.75	52.34
70	49.51	17.92	29.22	51.56	15.00	75.13
85	47.41	21.40	20.11	66.66	7.00	88.40
100	44.44	26.33	13.41	77.77	3.00	95.03
115	42.12	30.17	8.57	85.79	1.50	97.51
135	37.54	37.77	3.50	94.20	0.80	98.67
150	35.28	41.51	3.02	94.99	0.20	99.67
165	31.95	47.03	2.14	96.45		
185	28.00	53.58	0.98	98.38		
215	22.89	62.05				
235	18.00	70.16				
250	15.00	75.13				
285	10.00	83.42				
300	6.00	90.05				
335	4.00	93.37				
365	2.50	95.86				
385	2.00	96.68				

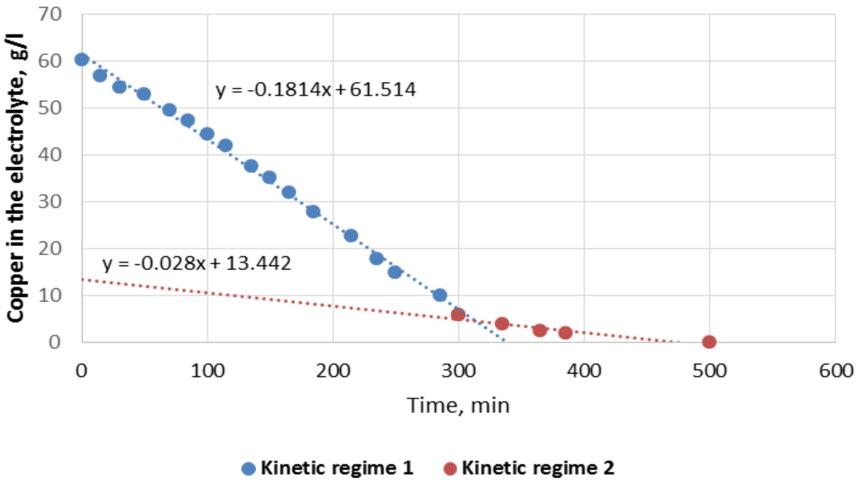

Fig. 4. The variation in time of the concentration of copper in the electrolyte at a current density of 25 mA/cm^2

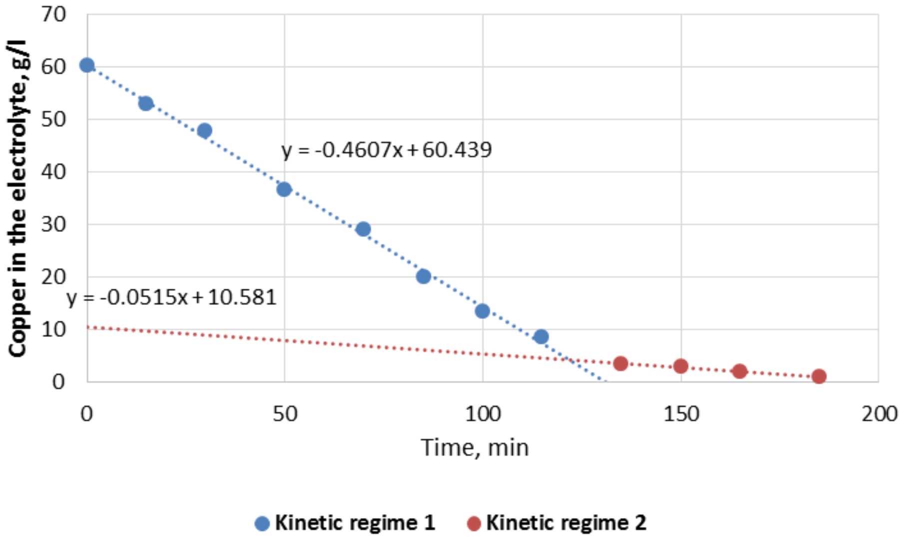

Fig. 5. The variation in time of the concentration of copper in the electrolyte at a current density of 30 mA/cm^2

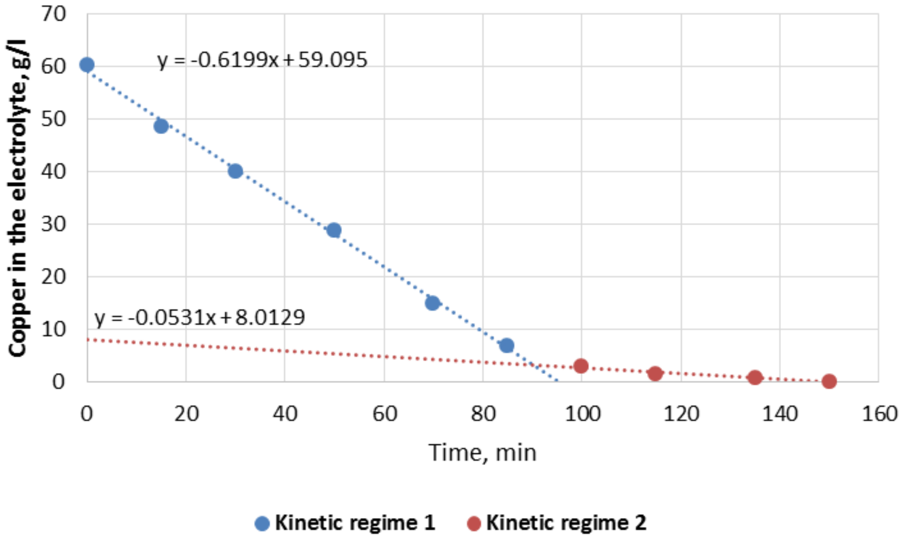

Fig. 6. The variation in time of the concentration of copper in the electrolyte at a current density of 35 mA/cm^2

In all three cases, the kinetic reduction of the copper at the cathode follows a two-stage mechanism. At an initial stage where the copper concentration of the solution is high, the copper reduction respects a linear kinetic regime, the linear form being expressed by equation (4):

$$[Cu^{2+}]_t = [Cu^{2+}]_i - k_0 t \quad (4)$$

The equations determined from the experimental data for the three cases are:

$$y11 = -0.1814x + 61.514 \tag{5}$$

$$y21 = -0.4607x + 60.439 \tag{6}$$

$$y31 = -0.6199x + 59.095 \tag{7}$$

By identifying the coefficients of equation (4) with the coefficients of equations (5), (6) and (7) the values of the speed constants for the copper cathodic reduction reactions are obtained for the three values of the current density:

$$k11 = -0.1814\ (g/l.min) \tag{8}$$

$$k21 = -0.4607\ (g/l.min) \tag{9}$$

$$k31 = -0.6199\ (g/l.min) \tag{10}$$

It is noticed that the deposition rate of copper rises with the increase in the density of the current, but deposits are made more roughly morphologically (Fig. 7) and more impure (other cations begin to decrease the copper concentration below ~ 6g / l, when the deposition potential is approaching that of other cations, the relationship 11).

$$\varepsilon_{Me/Me^{z+}} = \varepsilon^{0}{}_{Me/Me^{z+}} + \frac{RT}{zF} \cdot \ln a_{Me} \tag{11}$$

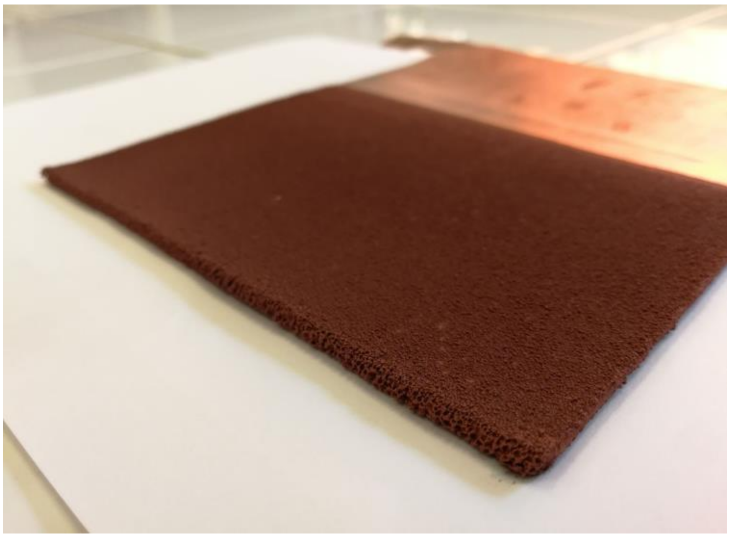

Fig. 7. Coarse deposition of Cu on cathode

At low copper concentrations in the electrolyte, it changes, keeping the linear form but decreasing the deposition rate (relations 12, 13, 14).

$$y21 = -0.028x + 13.442 \tag{12}$$

$$y22 = -0.0515x + 10.581 \tag{13}$$

$$y23 = -0.0531x + 8.0129 \tag{14}$$

Following the same reasoning, the following values are obtained for the reaction velocity constants for copper reduction at the cathode in the three cases of application of the current density.

$$K21 = -0.0280\ (g/l \cdot min) \tag{15}$$

$$k22 = -0.0515\ (g/l \cdot min) \tag{16}$$

$$k23 = -0.0531\ (g/l \cdot min) \tag{17}$$

In this case it is also noted that the deposition rate of copper rises with the increase of the current density.

4. Conclusions

The basis of the experimental work was copper recovery from WPCBs. Copper is the predilection and predominant choice in the electrotechnical industry due to both high electrical and thermal conductivity. For recovery of copper from solid waste, a succession of precursor operations was needed, namely shrreding, gravitational grading, solubilization and filtration.

The polymetallic concentrate obtained by shrreding and solubilization in a Fe^{3+} / Fe^{2+} redox system was analyzed by XRF and EDX. The aqueous solution containing cationic species resulting from the chemical dissolution of electronic waste (WPCBs) was subjected to preliminary experimental investigations using cyclic voltammetry and chronoamperometry.

There are two major cathode peaks at potentials of about -0.305 V/Ag ref. and -0.783 V/Ag ref. and a shoulder at about -0.615 V/Ag ref. At a potential sweep rate of 20, 10 and 5 mV/s, it was pointed out that the cathode peak at a potential of $\approx$ -0.3 V may be associated with the reduction of the Cu species. The slightly more electronegative value of the potential is associated with the presence in solution of other cationic species. Cathodic peak appearing at -0.783 V / Ag ref. may be associated with the reduction of Ni species. Cathode reduction processes for Al^{3+}, Ca^{2+}, S^{2-} ions can not be highlighted on voltamograms from aqueous solutions due to potential limitations.

From the kinetic point of view, the reduction of copper respected a linear regime. The rate of copper deposition rises with the increase in the density of the current, but deposits are more grossly morphological and more impure.

In the end, copper recovery is achieved which can be recycled as a raw material to the thermal refining of copper.

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