

RESEARCHES ON THE ELECTROLYTE PURIFICATION AND THE USEFUL ELEMENTS RECOVERY IN THE COPPER ELECTROLYTIC REFINING PROCESS

Ioşez JUHASZ,* Ion CONSTANTIN, Vasile HOTEA, Elena POP and Mihaela PODARIU

North University of Baia Mare, Mineral Resources and Environment Faculty, Materials Science and Engineering Department
Victor Babeş 62A, Baia Mare, 430083, Roumania

Received August 30, 2007

This work presents the impurities behaviour (Sb, As, Bi) during the electrolytic refining process of the copper and after the lab experiments, the establish of the optimal current density was aimed, to provide a proper quality deposit, also the establish of the steps number for the electrolytic extraction and the limit concentration of the copper for each of the stages, the establish of the discharging degrees of the main impurities, contained by the electrolyte. The quality of the cathode copper is mainly expressed by its purity and it is the essential parameter in the electrolysis process. The quality of the cathodic deposit depends on very many technological parameters-factors, among which can be mentioned: the composition of the anodes and the electrolyte, the current density, the electrolyte temperature, the circulation capacity of it, the mother-cathodes quality, admixture of surface active matter, etc.

INTRODUCTION

Although it is a well-known procedure and it is industrial applied, the electrolytic refining is so far the main method for obtaining high purity copper.

Throughout the years, the procedure has been improved in order to increase the techno-economical performances, especially the electrolytic copper quality, although it hasn't been totally improved. The quality of the cathode copper is mainly expressed by its purity and it is the essential parameter in the electrolysis process. The quality of the cathodic deposit depends on very many technological parameters, among which can be mentioned: the composition of the anodes and the electrolyte, the current density, the electrolyte temperature, the circulation capacity of it, the mother-cathodes quality, admixture of surface active matter, etc. Most of these technological parameters can be controlled and maintained into some strict limits, so that they cannot considerably affect the quality of the cathodic deposit.

Large fluctuations can be produced in the electrolyte composition as a result of the pollution load increasing of the raw material and implicit of the anodes.

Under these conditions there is the tendency of impurities such as stibium, arsenic, bismuth, nickel, cobalt and others, to concentrate in the electrolyte, in time, till the exceeding of their critical concentration, thus appearing the possibility of their deposition at the cathode by/through electrochemical reduction (Ni, Co) or as floating mud (As, Sb, Bi).¹

The estimated distribution of the main impurities between the anodic mud and the electrolyte is shown in Table 1.

The elements from the Vth group are more electronegative than copper, they are mostly electrochemical diluted in electrolyte and they store in it. On that account they are considered to be the most noxious impurities for the electrolyte refining process.

Their noxiousness is high not because of the fact that they could deposit in the same time with the copper ions (this is possible only at low concentrations under 10g/L Cu in electrolyte) but because they could participate to a series of secondary reactions in the electrolyte, forming a large range of insoluble compounds. These compounds determine the floating muds appearance. The risk of the cathode deposit

* Corresponding author: Phone: 00-40-36-2401265, E-mail: j_joska@yahoo.co.uk

pollution increases this way, mainly with As and Sb, by the secondary precipitation of these elements compounds directly on the cathodic surface.

To avoid phenomena like these, a purification process of the electrolyte is often practiced and it

consists of a permanent filtration of a part of the electrolyte and the replacement of about 0.1 – 0.5 m³ cathodic Cu electrolyte/t with fresh, unpolluted electrolyte.³

Table 1

The distribution of the impurities in the electrolytic refining process.²

The element	% in anodic mud	% in electrolyte
Au	>98	<1
Ag	98	2
Se and Te	98	2
Pb and Sn	98	2
Sb	60	40
As	25	75
Ni and Co	5	95
Fe	<1	>99

THE Sb AND As BEHAVIOUR IN THE ELECTRO-REFINING PROCESS

The As behaviour and mainly of the stibium in the electro-refining process is very complex and interdependent of other elements concentrations

from the copper anodes. Baltazar and Claessens, for example, established the following correlations between the As and Sb proportions that pass through/into the electrolyte and some of the elements contained by the anodes:⁴

$$\%As \text{ (in electrolyte)} = 80[(1-e^{45A})] \quad (1)$$

$$\%Sb \text{ (in electrolyte)} = 49,03-159,87 B+10,46 C \quad (2)$$

In which: % As, % Sb represent the As percentage and Sb respectively, that passes from the anode into the electrolyte;

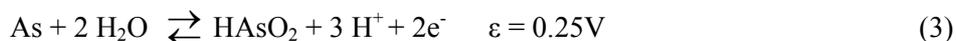
A, B – the As concentration percent and Sb respectively, in the anodes;

C – the concentration ration of the As/(Sb+Bi) in anode.

These relations show off that the As and Sb weights passing into the electrolyte depend, besides the concentrations of these elements in the copper anodes, on the concentrations on the Pb and Bi from the anodes.

Sb and As are the impurities with the greatest influence upon the electrolytic refining process, mainly because they can't be highly discharged nor in the previous phase of heat refining.⁵

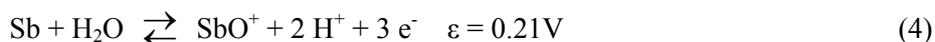
As can exist in the acid solutions of electrolyte either as pentavalent as like H₃AsO₄ or trivalent as HAsO₂ or AsO⁺. Though most of the As from the electrolyte (90-95%) is pentavalent, the initial As according o the electrochemical reaction:⁶



Afterwards, the trivalent arsenic is oxidized to the pentavalent state, in solution, in the presence of the copper ions and oxygen. The pentavalent arsenium has a great influence on the trivalent ions of stibium and bismuth forming stibium arsenates (SbOHAsO₄ or SbAsO₄) and bismuth arsenates (BiAsO₄). These are insoluble in the electrolyte.

Therefore, the pentavalent arsenium plays an important role in the Sb and Bi partial elimination in the anodic muds.

In the first phase, Sb as As, too, resolve in the electrolyte in the trivalent state:⁷



Further on, the oxidation of the trivalent stibium is slower than of the arsenium. Arsenium really oxidizes preferential, maintaining most of

the stibium in the pentavalent state in electrolyte. The trivalent stibium oxidizes easily to the pentavalent state failing the trivalent arsenium.

Most of the pentavalent stibium hydrolyses as Sb_2O_5 . This is the main cause of the floating muds that can lead to the cathodic deposits pollution. The floating muds are actually undefined and they are made up of amorphous compounds formed by the arsenium and bismuth arsenates precipitations.

All of these phenomena increase the risk of the cathodes poisoning with arsenium, stibium, bismuth and not only, through occlusions of floating mud or through the insoluble compounds precipitation directly on the cathodic surface.⁸

TESTING PLANT AND TECHNIQUE EQUIPMENT

The testing researches were carried out in a lab installation, which main components are: the cell, the rectifier, the electrolyte circulating pump, the thermostat, the ammeter, the electronic millivoltmeter and the gas suction hood. The cell was made up of PVC and the warm water supplied by the thermostat is circulated through the double walls of the cell, in order to maintain the temperature between the limits $\pm 1^\circ\text{C}$.

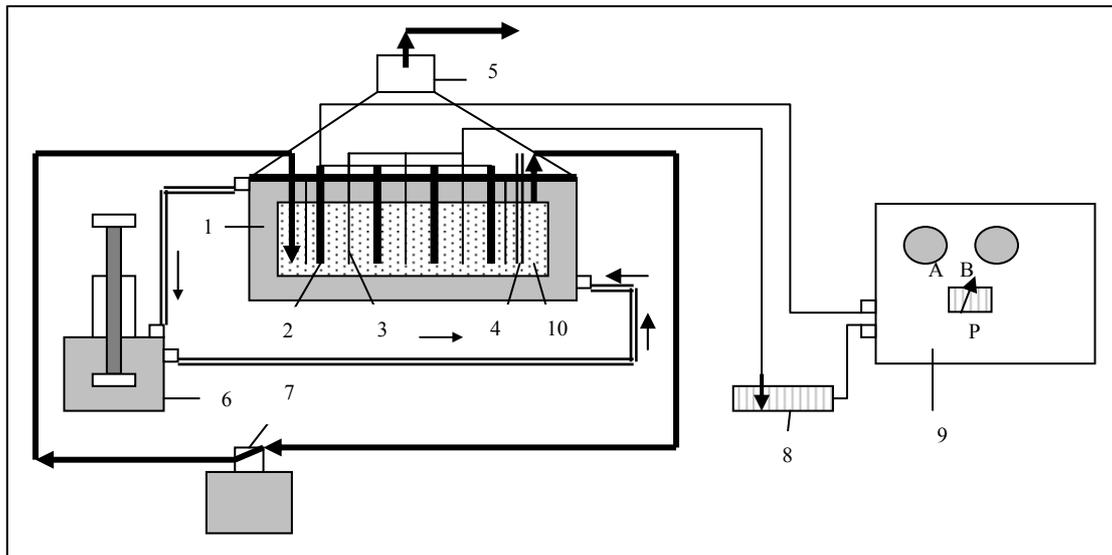


Fig. 1 – The testing plant scheme.

1- double-walled electrolytic tank for heating; 2- anode; 3- cathode; 4- thermometer; 5- hood; 6- thermostat; 7- the electrolyte peristaltic recirculating pump; 8- rheostat; 9- rectifier; 10- electrolyte; \Rightarrow electrolyte circuit; \equiv heating water circuit; $—$ wires.

The cell working capacity is of 2 L electrolyte and has the intermediate space (L x l x H) of 250 x 110 x 100 mm.¹⁶

MATERIALS AND EXPERIMENTAL PROCEDURE

The electrolyte was kept in a continuous recycling by means of the peristaltic pump, with a capacity of $5\text{ cm}^3/\text{min}$, so that the whole electrolyte volume from the cell to be circulated in 6–7 hours. Four anodes of Pb – Sb 6% alloy and three cathodes made of industrial motherboards were used. The electrodes were powered from a direct current rectifier, equipped with finely and hardly adjusting rheostats that allow the current intensity to be kept at the present pre-values. The cell was placed under a negative pressure hood, in order to remove the acid aerosols and the possible gas seeps in the electro-winning process.

Because of the oxygen released, acid aerosols are formed at the anodes, and besides this, the arsenate hydrogen is possible to be released, at a very low concentration of copper.

Under these conditions it is necessary to place the cell under a hood in order to absorb the noxious insults and neutralize them before the gas emanation in the atmosphere.

We used acid solutions of copper sulphate as electrolyte in the experimental researches, which were obtained through the dilution of the industrial electrolyte from the copper refining with the washing waters derived from the same process, with the chemical composition: (in g/L) 27.8 Cu, 0.78 Fe, 0.16 As, 0.11 Sb, 1.04 Ni, <0.001 Bi, 104.3 H_2SO_4 .

The current efficiency calculation was based on the formula:⁹

$$\eta = \frac{100 \cdot \Delta m}{k \cdot I \cdot t}, \text{ in \%} \quad (5)$$

where: k – is the copper electrochemical equivalent

$$k = 0.329 \cdot 10^{-3} \text{ g/A} \cdot \text{s}$$

I – the current strength, in A

t – the electrolytic time, in sec.

Δm – the quantity of the extracted copper from the electrolyte, in g

The quantity of the extracted copper from the electrolyte was determined function of the copper concentration in the initial electrolyte and the copper concentration in the final electrolyte.

The following parameters were adopted and maintained constantly, in order to carry out the experiments: the electrolyte temperature: 45 ± 2 °C and the electrolyte circulating flow: $5 \text{ cm}^3/\text{min}$.

In the first testing set we aimed to establish the best current density to obtain a compact cathode deposit, with a fine grained structure. For this purpose, we used current densities between 150 and 250 A/m^2 with a 25 A/m^2 pass and we viewed the copper concentration to be not decreased under 10 g/L .

The preliminary tests proved that close by this concentration, the cathodic deposit tends to oxidize and become powdery, without adherence to the cathodic surface. The current efficiency was determined in order to establish the best current density and the quality of the deposit was analyzed both visual and microscopically.

In a second experimental set we aimed to establish the limit of the copper concentration in the electrolyte and starting with that, the deposit becomes powdery and we also aimed the impurities behavior under contained by the initial electrolyte. For this end, the required time for the copper concentration decreasing with 5 g/L was theoretical calculated and after that time, a cathode was replaced with a new one and the electrolyses process was continued. After each cathode replacing there were taken electrolyte tests to be analyzed.

The total electrolyte capacity destined to the copper extraction and purification (Q) is calculated function of the annual production capacity (C , in t), the real fund of annual time (F_r , in days) and the specific electrolyte volume required for the refining process (v , in m^3/t electrolytic copper), according to the following relation:¹⁰

$$Q = \frac{1000 \cdot C \cdot v}{F_r \cdot 1400}, \text{ in L/min.} \quad (6)$$

The specific electrolyte volume destined to the refining process is of $0.1 - 0.5 \text{ m}^3/\text{t}$ cathodic copper and depends of the electrolyte pollution load. For example, for an annual production capacity of $25,000 \text{ t Cu/year}$ and a 330 days period of time and a value $v = 0.3 \text{ m}^3/\text{t Cu}$, results an electrolyte capacity of 16 L/min , required by the refining process.

The total cathodic surface of the copper extracting (S) will be established function of the total electrolyte capacity (Q), of washing water flow (V_0 in L/min), if these are used in this phase of the process, of the gradient of copper concentration that has to be realized ($\Delta C = C_1 - C_2$), of the estimated current efficiency and of the current density, according to the relation:¹¹

$$S = \frac{(Q + V_0) \cdot \Delta C}{60 \cdot \eta \cdot k \cdot D}, \text{ in m}^2 \quad (7)$$

where: $k = 0.329 \cdot 10^{-3} \text{ g/A} \cdot \text{s}$

If the electrolyte flow destined to the refining process is 10 L/min and the washing water flow is 25% from the electrolyte flow, for a gradient of concentration of 15 g/L , current efficiency 90% and current density 175 A/m^2 , results a total cathodic surface of approximately $96,5 \text{ m}^2$.

The number of the electrolyte tanks from the first step: $N = S/S_c$ (S_c is the total surface of the cathodes from an electrolytic tank). If $Q + V_a < q$ then the electrolytic tanks from the first step are serialized from the electrolyte circulation point of view and, if the inequality is opposite, the electrolytic tanks are placed in line.

THE STUDY AND ANALYSIS OF THE CATHODIC DEPOSIT AND REMNANT

The morphological study of the cathodic deposit and of the remnant was realized by the use of the Reichert UnivaR optical microscope (from Germany) on-line coupled with a Hitachi KPF1 digital webcam, in order to take up the microscopic pictures and their processing on the computer. The chemical analyses of the electrolyte from the copper sulphate acid solutions and of the remnant electrodeposited on the bottom of the electrolytic tank were determined with the atomic absorption spectrometry GBC 932 AB PLUS (Australia).

RESULTS AND ARGUMENTS

In the first experimental set it was aimed to establish the copper limit concentration from which the significant codeposit of Sb and As from the electrolyte arises.

In a second experimental set the Sb and As elimination test from the electrolyte was aimed, related to the copper concentration from the residual electrolyte.

The experimental conditions and the results are shown in Table 3 (Annex 2).

In order to outline the lowest copper concentration in the electrolyte, where the codeposition on the precipitation of the present impurities starts from, many experiments of deposition in a one single step of electrowinning were done. Analyzing the findings we found out that the decreasing of the copper concentration till 6.45 g/L does not determine a meaningful modification of the As, Ni and Fe concentration.

On the other hand, it can be observed a decreasing of the Sb concentration, when the copper concentration decreases under the value of 10 g/L. For example, at a final copper concentration of 7.30 g/L, the Sb concentration decreases with about 32.7 %. Also, concerning the quality of the cathode deposit, in all the situations this showed a sputtering and oxidation tendency, process that was stronger according to the lower final concentration of the copper in the electrolyte.

Referring to all these, we appreciate that, till minimum of 9 – 10 g/L Cu there is not any significant decrease of the Sb or As concentration in the electrolyte.

Under these conditions, for current efficiency of 82 – 85% (see Table 2), copper can be partially recovered in solid state, on the cathode collars and partially as a surface oxidized powder.

In Table 3 it can be observed the increasing of the arsenic and stibium elimination grade with the lower residual concentrations of copper. Thus, at copper final concentration of 0.18 g/L, the As elimination was of 56,8% and the Sb one of 73,8%,

reported to the concentration of this electrolysis step and of 79% at the given initial concentration from the used electrolyte.

The lowest values of As and Sb elimination were measured when the copper residual concentration was of 0.98 g/L (exp.7).

In this case the elimination ratios were of 26.6 % (31.25%) for As and of 39.18% (59%) for Sb (the global elimination grades for all the electrolysis steps are given in brackets). In this case, the elimination ratio was 26.6 % (31.25 %) for As and 39.18% (59%) for Sb.

Images of the crystal developed on the cathodic surface and of the cell bottom residues are given in figures 2 and 3. The chemical analysis of the last one is the following: 24.86% Cu, 0.28% As, 0.14% Sb, <0.005% Bi, 0.03% Fe, 0.025% Ni, 20.62% SO₄ anions. The very low concentration of Ni and Fe exclude the possibility of the cathode deposits to be represented by the sulphates of these elements.

The higher concentrations of Sb and As can indicate the presence of some complex combinations of copper arsenates antimonites, arsenides, antimonides type, etc. This is also confirmed by the decreasing of these elements concentration in the electrolyte. The high concentration of the sulphate radical shows that the residue contains besides the metallic copper as surface oxidized powder, copper sulphate and iron and nickel sulphates tracks, too.

Figure 2 reproduces the deposit which, in all the cases was powdery, very oxidized without adherence and besides that, on the cathode surface appeared compounds shaped as large – sized crystals formed by precipitating from the electrolyte, of different cathodes, from clear to green and blue-green.

In time, a part of these get loose together with the copper powdery deposit, and settle down on the bottom of the cell. This process is more substantial when the copper concentration decreases under 1 g/L, as shown in Figure 3.

Table 2

The test data concerning the copper concentration establishment where the impurities codeposit starts from.

No	t [°C]	I [A]	S [cm ²]	D [A/m ²]	V _{el.} [cm ³]	τ [min]	Δm [g]	η [%]	The initial/final electrolyte composition, in g/l						Observation concerning the cathodic deposit	
									Cu	H ₂ SO ₄	As	Sb	Bi	Ni		Fe
1	45	7	400	175	1700	250	29,58	85,63	27,80	104,3	0,16	0,11	<0,001	1,04	0,78	Powdery and rusty on solid base formed in the first period of time
									10,4	137,7	0,16	0,09	0,0015	1,18	0,84	
2	45	7	400	175	1700	260	30,43	84,70	27,8	104,3	0,16	0,11	<0,001	1,04	0,78	idem
									9,90	140,9	0,14	0,09	<0,001	1,20	0,84	
3	45	7	400	175	1700	200	24,17	87,47	27,8	104,3	0,16	0,11	<0,001	1,04	0,78	Solid and hard with sputtering and oxidation tendency
									13,58	137,7	0,15	0,094	<0,001	1,03	0,79	
4	45	7	400	175	1700	300	34,48	83,19	27,8	104,3	0,16	0,11	<0,001	1,04	0,78	Powdery and oxidized without adherence at the deposit formed in the first period of time
									7,30	147,8	0,15	0,074	<0,001	1,03	0,79	
5	45	7	400	175	1700	320	36,29	82,08	27,80	104,3	0,16	0,11	<0,001	1,04	0,78	idem
									6,45	151,6	0,16	0,088	<0,001	1,18	0,84	

Table 3

The test data concerning the electrolyte refining.

No	t [°C]	I [A]	S [cm ²]	D [A/m ²]	V _{electr} [cm ³]	τ [min]	Δm [g]	η [%]	As [%]	Sb [%]	The initial/final electrolyte composition, in g/l						
											Cu	H ₂ SO ₄	As	Sb	Bi	Ni	Fe
6	45	7	400	175	1700	180	10,659	42,85	56,8	73,8	6,45	151,6	0,16	0,088	<0,001	1,18	0,84
									56,8	79	0,18	194,6	0,069	0,023	<0,001	1,17	0,90
7	45	7	400	175	1700	120	10,744	64,79	26,6	39,1	7,30	147,80	0,15	0,074	<0,001	1,03	0,79
									31,2	59	0,98	165,7	0,11	0,045	<0,001	1,11	0,84
8	45	7	400	175	1700	210	16,082	55,42	35,7	57,7	9,90	140,9	0,14	0,09	<0,001	1,20	0,84
									43,7	65,4	0,44	165,7	0,09	0,038	<0,001	1,20	0,91
9	45	7	400	175	1700	180	12,546	50,44	35,7	50	7,73	140,9	0,14	0,09	<0,001	1,19	0,85
									43,7	59	0,35	158,5	0,09	0,045	<0,001	1,21	0,92

In which:

% As – is the As eliminating ratio in the last stage of the refining process and respectively, towards the initial electrolyte used.

%Sb – is the Sb elimination ratio in the last stage of the refining process and respectively, towards the initial electrolyte used.



Fig. 2 – Images of the crystal formed on the cathodic surface (x25).

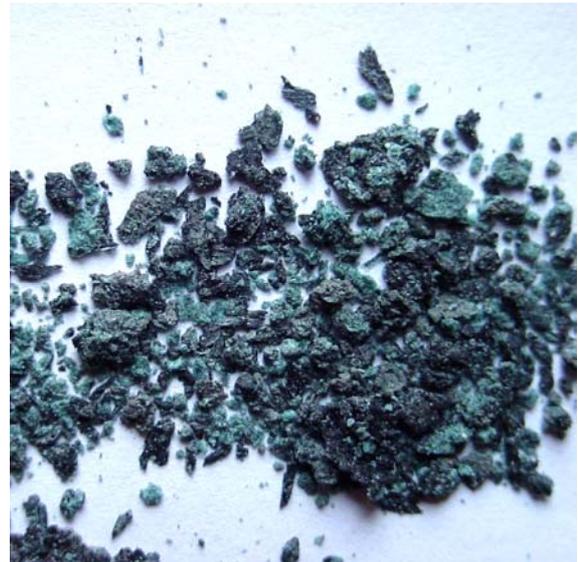


Fig. 3 – Residue deposit on the cell bottom (x25).

CONCLUSIONS

The lab searches regarding the copper extracting and purification of the used electrolyte from the electrolytic refining process led to the following conclusions: during the electrolytic refining process, some of the impurities (such as As, Sb, Ni, Fe, Bi, etc) tend to pass into the electrolyte concentrating in it. Their over limit presence determines the floating muds appearance (solid suspensions in the electrolyte volume) and their possibility to be incorporated into the cathodic mass. As a result, the deposit quality decreases and determines the electrolytical copper to enclose in law marks, inappropriate for some ranges of use.

The trials showed that it is possible to obtain solid cathodic deposits, till a concentration of 18 – 20 g/L copper in electrolyte, with a fine structure and a purity that allows it a directly merchandising. The electro deposition becomes hard under these concentration limits, and for lower concentrations it becomes powdery.

For higher concentrations than 9–10 g/L copper in electrolyte it was discovered that the impurities, with a few exceptions for Sb, do not considerably modify their concentration in the electrolyte. For lower concentrations than 9–10 g/L copper in the electrolyte, the deposit becomes exclusive powdery, shows the surface oxidation tenderly and besides, precipitates of different compounds

(inclusive with As and Sb content) appear on the cathodic surface. Most of the deposits (inclusive the precipitates) get loose from the cathodes and settle down on the cells bottom. The current efficiency decreases very much in this case, mainly if the residual concentration of copper is under 0.35 g/L. Current efficiency about 50-55% resulted from concentrations of 0.35 – 0.45 g/L. In the same time, the As concentration decreases with about 30 – 40% in this stage, and the Sb ones with about 60 – 65% under the conditions of some unadhesive, powdery and rusty deposits and with a great amount of crystals, based on complex compounds of Sb, As, Bi, etc. In the same time, the Ni and Fe concentrations increase with about 15 – 20%.

REFERENCES

1. I. Constantin, "Copper metallurgy", The University Polytechnic of Bucharest, 1989.
2. V.Baltazar and P.L.Claessens, *Met.Soc.Inc.*, **1987**, 211.
3. J.P.Demaerel, *Met.Soc.Inc.*, **1987**, 195.
4. A.K.Biswas and W.G.Davenport, "Extractive Metallurgy of Copper", Pergamon Press, New York, 1976.
5. R.Winand and Ph.Harlet, *Met.Soc.Inc.*, **1987**, 239.
6. J.P.Demaerel, *Met.Soc.Inc.*, **1987**, 199.
7. O.Forsen and C.Lilius, *Met.Soc.Inc.*, **1985**, 353.
8. T.B.Braun, J.R.Rawling and K.J.Richards, *Met.Soc.Inc.*, **1976**, 511.
9. P.L.Claessens and V.Baltazar, *Symposium an Copper Electrorefining*, IMM-GmbH-Germany, Oct. 1980.
10. K.G.Fisher, and R.G.Hughes, *Trans.Inst. Min.Metall.*, **1971**, 80, 250.
11. J.H.Schloen, *Met.Soc.Inc.*, **1987**, 3.
12. K.Toyabe and C.Segawa, *Met.Soc.Inc.*, **1987**, 117.
13. T.Shibata, M.Hashiuchi and T.Kato, *Met.Soc.Inc.*, **1987**, 99.
14. J.L.Delplancke and R.Winand, *Min.Met.and Mat.Soc.*, **1999**, III, 603.
15. R.Winand *Min.Met.and Mat.Soc.*, **1999**, III, 411.
16. Modernize technology to electrolytical refining of copper, *Relansin*, Report of phase, 2004.

