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PROCESSING OF COPPER ANODE-SLIMES FOR EXTRACTION OF METAL VALUES

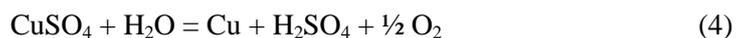
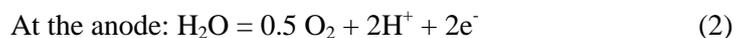
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Processing of anodic slimes from an Egyptian copper electrorefining plant, exhibiting high contents of copper, lead, tin and silver has been presented. The proposed hydrometallurgical process consists of two leaching stages for extraction of copper with $\text{H}_2\text{SO}_4 - \text{O}_2$ and silver with thiourea – Fe^{3+} . Pyrometallurgical treatment of the leaching solid residue for production of Pb-Sn soldering alloy was proposed. Parameters affecting both the leaching and smelting stages were studied.

Key words: anode slimes, leaching, copper, silver

INTRODUCTION

Considering the depleting reserves of primary mineral resources for the extraction of metal values, every effort should be made to process secondary sources such as slag, slimes etc. Electrolytic refining of copper is carried out in Jumbo-cells where a series of cathodes, which are made of pure copper and insoluble lead anodes rest in a steel tanks. Metallic copper is deposited at the cathodes, while the water molecules are decomposed at the anode to produce oxygen. Sulphuric acid is regenerated in the solution which is used to leach copper again (Landsberg, 1977; Subbaiah et al., 1986; Mahadavi and Ditze, 1996). The electrolysis of copper may be described by the following equations:



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Anode slimes are collected from the bottom of the electrolytic cells during the refining of copper. There are two different kinds of slimes depending on the sources from which they are obtained. The first one produced during the processing of copper concentrate which exhibits a relatively high gold, silver, tellurium and selenium content, and the second one produced during the processing of recycled scrap has a higher lead, copper, tin and silver content. This work focuses on processing of anodic slimes obtained from an Egyptian copper electrorefining plant which is characterized by a high content of copper, lead, tin and silver.

Several methods have been attempted for recovery of copper from slags and anodic slimes. These methods can be differentiated into: a) pyrometallurgical processing which includes roasting in the presence of oxidizing agent, sulfate-roasting and soda-ash process (Ying, 1983; Swayn et al., 1993; Hughes, 2000, Filipov et al., 2000), b) hydrometallurgical processing of anode slimes were carried out using different leachants. Chlorination, nitric acid and sulphuric acid (Gill, 1980; Holmes, 1981; Everett, 1994; Petrov, 1999) are used most frequently.

Among the methods of the processing of copper anode-slimes, two of them have been successful on an industrial scale, namely roasting and pressure leaching (Gaylarde and Videla, 1995).

The by-production of sulphuric acid is the troublesome aspect of roasting process because the economic marketing of sulphuric acid depends strongly on site location. Furthermore, even though the gas emission regulation are respected, harmful SO_2 may be released. The advantages of the roasting process are: simplicity, low costs when compared to other processes, and also the fact that know-how is available worldwide. On the other hand, pressure leaching results generally in high degree of extraction which together with the fact that wastes can be confined as stable solids. Hydrometallurgical processing of copper anode slimes has the following advantages: capital costs are relatively low when compared to those for a smelter, process may be applied to small and large operations, air pollution by sulfur dioxide is eliminated, equipment may be designed and installed in modules.

In this investigation sulphuric acid pressure leaching was chosen from various hydrometallurgical methods to process the copper-anode slimes for extraction of copper. The decopperized slimes are then enriched in lead, tin, and silver.

Many hydrometallurgical processes were reported for extraction of noble metals, among them, cyanide (Hoffmann, 1991; McClincy, 1990) and thiourea leaching (Schulze, 1984). The later seems to be effective for silver extraction due to its high complexing ability. Thiourea leaching has been performed in hydrochloric sulfuric and nitric acid media. Dissolution of gold and silver up to 97% was reported in a solution containing $20 \text{ g/dm}^3 \text{ HCl}$, $0.20 \text{ g/dm}^3 \text{ H}_2\text{O}_2$, and 100 g/dm^3 thiourea.

Some researchers (Kusnierov et al., 1993; Kucha and Cichowska, 2001) have reported that, thiourea is very effective in the recovery of noble metals from copper concentrates which are especially refractory to cyanidation. An industrial application of thiourea leaching has been reported in New South Wales (Deschenes and Ghali,

1988), where thiourea leaching shows a good potential application to treat sulphide concentrates.

A low toxicity of thiourea compared to cyanide is always mentioned as one of the motivations for developing the research in the field.

MATERIAL

Anode slime samples were collected from the bottom of the electrolytic cells during the electro-refining of copper. These samples were sieved through a 2.0 mm sieve to remove large inclusions of copper and other foreign material present in the slime.

A representative sample of the feed slime was analysed for Cu, Pb, Sn, Zn, Ni, Fe, As, Sb, SiO₂, MgO, and Ag using atomic absorption, spectrophotometer. The chemical analysis is given in Table 1.

Table 1. Chemical analysis of representative sample of studied anode-slime

Chemical constituents	Weight percent (%)
Cu	18.57
Pb	15.3
Sn	9.8
Ag	0.46
Ni	0.94
Fe	1.72
Sb	1.30
As	0.49
Zn	0.74
S	9.22
SiO ₂	8.51
CaO	1.54
MgO	0.82

EXPERIMENTAL

A schematic diagram of the experimental apparatus shows the one-dm³ glass reactor with baffles used for the leaching tests. The cover of the reactor had four ground-glass parts, which contained a Friedrich's condenser, sampling device, oxygen dispersion tube and glass impeller. The impeller was inserted through the center part by means of a Chesapeake stirrer connection and was driven by a Fisher mixer. The entire reactor assembly was clamped into place in water bath which was heated with a temperature controller and held to within ± 0.1 °C of the desired temperature.

In each test a 100 g sample of the ground anodic slime (-0.075 mm) was leached with 1 dm³ solution of sulfuric acid of known concentration. The leaching tests were

conducted at different temperatures for various leaching time and with the admission of variable rates of oxygen as oxidizing agent for copper dissolution. Samples of 5 cm³ liquor were taken for subsequent analysis using atomic absorption technique to determinate the dissolved copper concentration.

At the end of the leaching experiment the slurry was then filtered using water suction pump, through A-No-42 Whatman filter paper and washed thoroughly with hot distilled water, dried at 110 °C, and then ground to minus 0.075 mm. The decopperised slime has been analysed for Pb, Sn, and Ag.

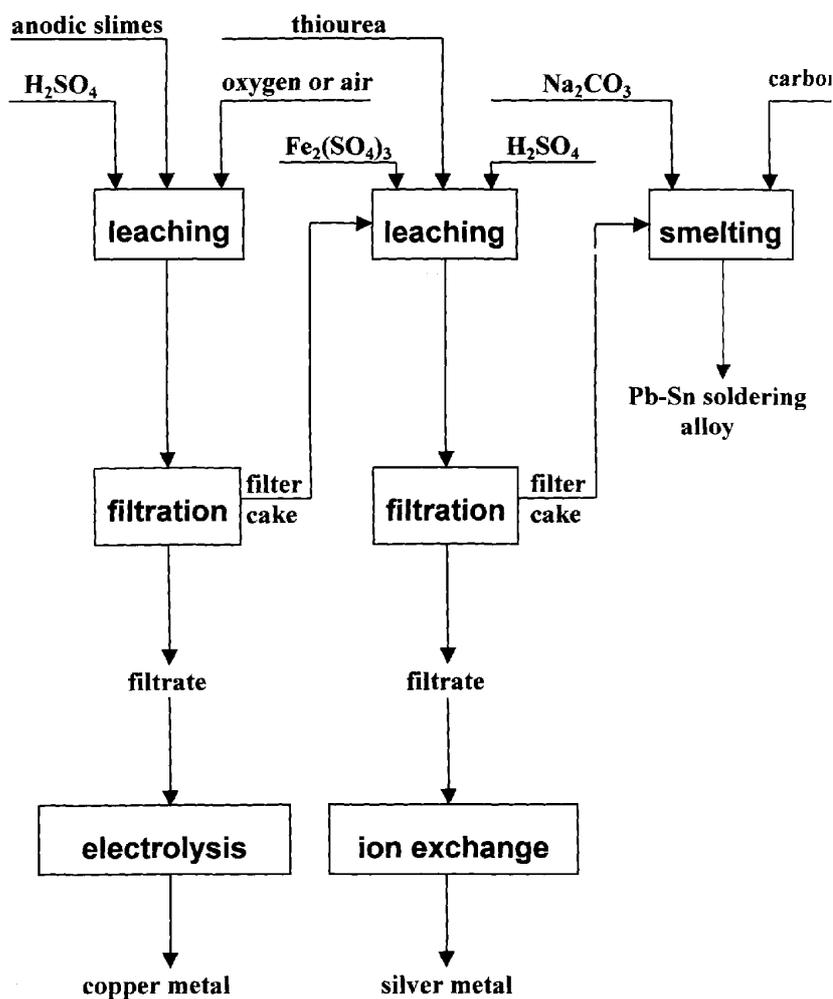


Fig. 1. The flowsheet of the process of utilization of anodic slime for production of Cu, Ag and Pb-Sn soldering alloy

Forty-gram samples of the decopperised slime were leached with 1 dm³ of solution containing different amounts of acidified thiourea and ferric ion as oxidant. The slurry was agitated with a magnetic stirrer at various agitation speeds. Various factors such as temperature, leaching time, and thiourea concentration were examined to determine the optimum operating conditions for silver dissolution.

Liquid samples were analysed using atomic absorption for determination of dissolved silver. The decopperised-silver free residue enriched in lead and tin could be a feed for the production of Pb-Sn soldering alloys.

Fifty-gram samples of decopperised, silver-free residue was mixed in proper proportions of sodium carbonate and carbon and smelted in a graphite crucible at different temperatures and time for production Pb-Sn soldering alloy.

The aim of this investigation according to the flow-sheet illustrated in Fig. 1, is to investigate and optimize the parameters influencing the dissolution of both copper and silver as well as those affecting the production of soldering alloys.

RESULTS AND DISCUSSION

EXTRACTION OF COPPER

EFFECT OF TEMPERATURE

Figure 2 shows that the copper extraction rate increased with the increase of temperature in the range 65-85°C. Further increase in temperature had a little effect on copper extraction.

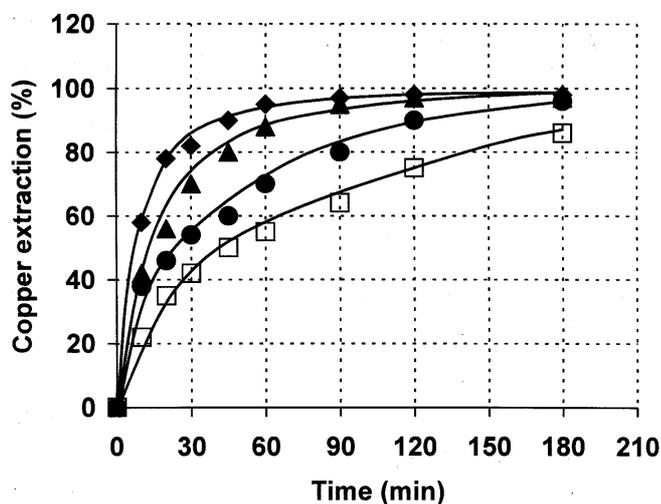


Fig. 2. The effect of temperature on the leaching rate of copper from anode slime by oxygenated 0.5 M H₂SO₄, particle size -75 μm

Applying the following equation:

$$1-(1-\alpha)^{1/3} = -kt \quad (5)$$

where α = fraction reacted, k = a constant for the reaction rate and t = leaching time. Figure 3 shows that the plot of $1-(1-\alpha)^{1/3}$ versus t over the studied temperature range consist of a series of straight lines indicating that the sulphuric acid leaching of anode slimes is chemically rate-limited.

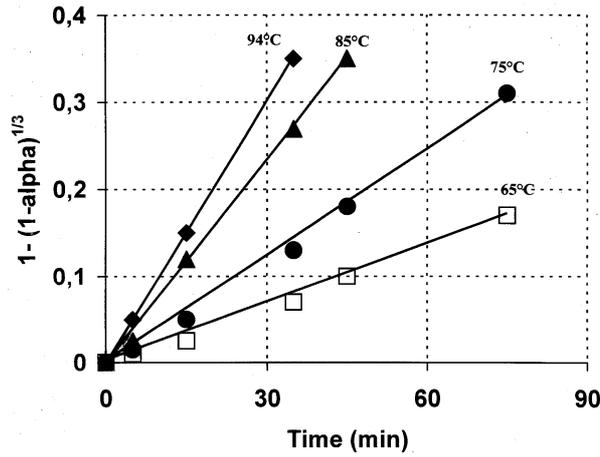


Fig. 3. Kinetic analysis of experimental data of copper leaching (as in Fig. 2).

From the slopes of linearised isotherms in Fig. 3, plot rate constants were determined at given temperatures. The activation energy E_A is determined from Arrhenius plot given in Fig. 4.

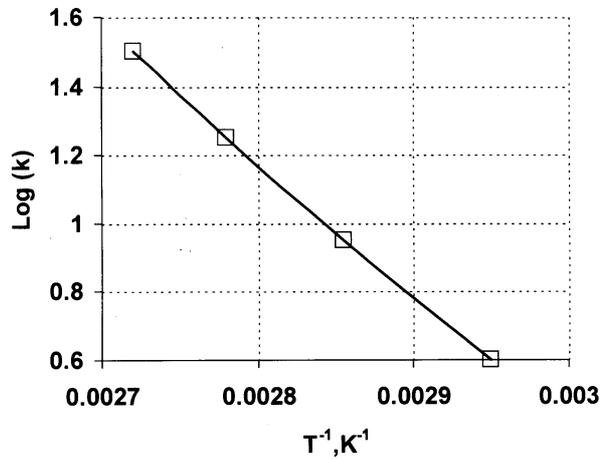


Fig. 4. Arrhenius plot for the copper leaching with oxygenated H_2SO_4 . Parameters as in Fig. 2.

$$\text{Slope} = -E_A/RT \tag{7}$$

The value calculated for the activation energy is 69 kJ/mol which indicates surface chemical control.

EFFECT OF ACID CONCENTRATION

Figure 5 shows that copper extraction increases when the acid concentration increases from 0.02 M to 0.5 M. A further increase in the acid concentration resulted in practically no increase of copper extraction which may be due to the fact that the solubility of oxygen at high acid concentration is low in comparison with its solubility at low acid concentration. Figure 6 illustrates the relation of pH of the leach solution and extraction which indicates that the percentage of the metal uptake increases with increasing pH up to pH 4-5 and thereafter it is more or less constant in the pH range investigated.

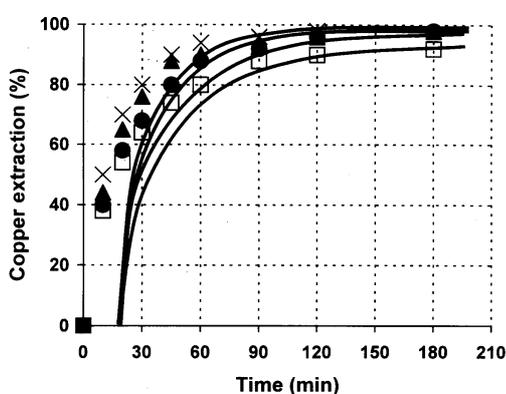


Fig. 5. The effect of H_2SO_4 concentration on the leaching rate of copper with oxygenated solution at $85^\circ C$. Particle size $75\mu m$

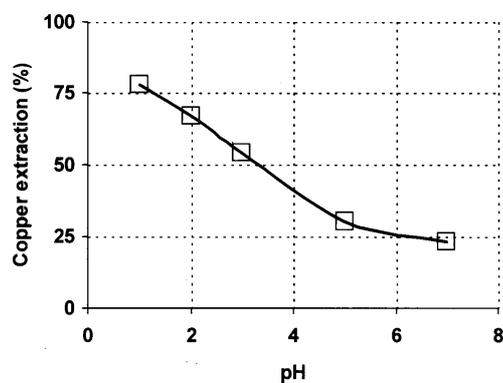


Fig. 6. The effect of pH on the copper extraction at $85^\circ C$. Particle size $75\mu m$

EFFECT OF OXYGEN FLOW RATE

Figure 7 shows the results of leaching $75\mu m$ diameter anode slime in $0.5 M H_2SO_4$ under various oxygen flow rate. It is concluded that under the experimental conditions used the higher the oxygen flow rate, the higher extraction of copper.

It was determined that the leaching of anodic slime in sulphuric acid under oxygen pressure led to extraction of copper (97%) under the following leaching conditions: temperature: $85^\circ C$, sulphuric acid concentration: $0.5 M$, oxygen flow rate: 1 bar, leaching time: 90 min, and particle size: $75\mu m$.

EXTRACTION OF SILVER

This section represents the experiments conducted for the silver extraction from decopperized slime residue. The variables influencing the potential of acidified thiourea solution as leaching agent are: thiourea concentration, temperature, leaching time, Fe^{3+} concentration as oxidant. The previously decopperized slime residue is ground to $-0.075 mm$ and then leached by acidified thiourea solution.

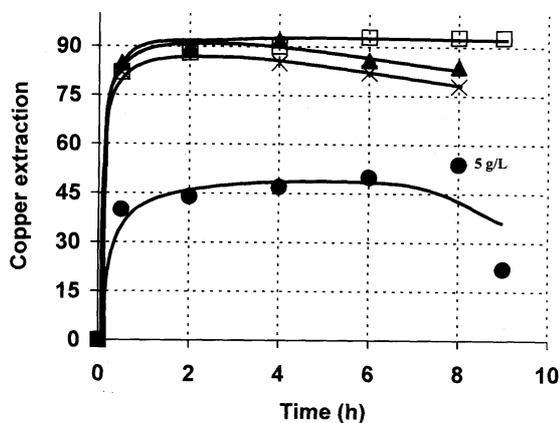
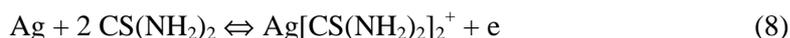


Fig. 7. The effect of thiourea case concentration on the leaching rate of Ag. Temperature 25°C, solid/liquid ratio equal to 0.1. Fe³⁺ concentration 5g/dm³

EFFECT OF THIOUREA CONCENTRATION

In an acidic solution of thiourea, the dissolution of silver proceeds according to the following reaction:



This is a reversible reaction with an electrode potential of 0.352 V at 25 °C on a fresh silver surface and 0.41 V on a passivated surface. According to Fig. 7, the silver extraction increases with the increase of the thiourea concentration and reaches its maximum recovery (90%) at 10 g/dm³ thiourea concentration. The increase of the thiourea concentration up to 10 g/dm³, produces an increase in the silver extraction, especially in the initial leaching period (0.5 h). There is however, a decrease in silver extraction with the increase of thiourea >20 g/dm³. It may be due to that the thiourea is less stable at higher concentrations and decomposes.

EFFECT OF TEMPERATURE

Table (2) presents the effect of temperature using 10 g/dm³ thiourea and 5.0 g/dm³ ferric ion. Extraction of more than 90% silver is reached at both 40°C and 60°C after leaching time of 30 minutes. The silver extraction is improved with the increase of temperature to 40°C where it reaches 93.5% after 4 hrs of leaching.

Table 2. Effect of temperature on silver extraction (S/L = 10%, thiourea. 10 g/dm³, F³⁺ = 5 g/dm³, pH 1-0)

Temperature	Silver extraction		
	30 min	4h	8h
25	80.4	87.3	93.4
40	80.7	93.5	93.4
60	92.2	94.0	92.5

EFFECT OF FERRIC ION

The oxidating effect of ferric ion in the presence of thiourea can be illustrated in the following reaction.



In contact with oxidants such as Fe^{3+} , thiourea may be oxidized in successive stages to form several products. The first is the formation of formamidine disulphide [Schulze, 1984].



In a second irreversible reaction the formamide disulphide yields thiourea and unidentified sulphinic compound which then decompose to yield cyanomide and elemental sulphur. The elemental sulphur created at the end of this decomposition has a detrimental effect by passivating the leachable silver surface and precipitating some silver from solution.

The study of the effect of oxidizing agent shows that there is an equilibrium between thiourea and formamidine disulfide. The leaching efficiency of silver depends on this equilibrium. It indicates that the optimum extraction of silver was 93% using 10 g/dm^3 thiourea and $5.0 \text{ g/dm}^3 \text{ Fe}^{3+}$ in one leach of 4 hrs.

As seen in Fig. 8, an addition of 2 g/dm^3 of Fe^{3+} slightly improves the initial leaching kinetics but results in no real improvement in silver extraction.

Further increase in Fe^{3+} concentration to 5.0 g/dm^3 results in increase of the leaching rate and also increases the extraction of silver to 93.4% for 7 hrs of leaching. It is seen that, the rate of silver dissolution is very rapid in the first 30 min of leaching. For the 5.0 g/dm^3 concentration of the oxidant, 80% of silver was leached in this period. Adding $8.0 \text{ g/dm}^3 \text{ Fe}^{3+}$ in solution caused a significant decrease in silver extraction. When the amount of oxidant is too large, there is oxidation of thiourea and the remaining amount of leachant is less effective for extraction of silver.

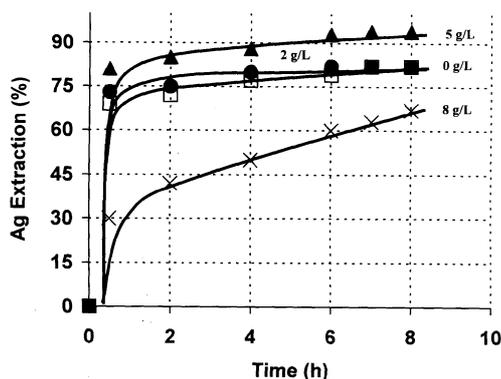


Fig. 8. Effect of Fe^{3+} concentration on the leaching rate of Ag with thiourea

PRODUCTION OF LEAD-TIN SOLDERING ALLOY

After the removal of the copper and silver the slime was then enriched in lead (41.6%) and tin (29.0%). Residues were dried and ground to <0.075 mm and then mixed with different proportions of sodium carbonate and carbon. There were smelted in graphite crucibles at different temperatures and various time intervals. The effects of the following parameters were studied: carbon as reducing agent, sodium carbonate as flux, temperature, and reduction time.

The effects of these variables are illustrated in Tables 3–6. The optimum operating conditions can be summarized as follows: carbon added: 30% by weight of slime added, sodium carbonate: 40% by weight of slime added, temperature: 1100°C, and reducing time: 1-0 hr. Under the above mentioned operating conditions, the lead and tin contents are 53.0% and 33.0%, respectively.

However, a wide range of lead-tin soldering alloys is known to depend on the lead-tin ratio.

Table 3. Effect of carbon as reducing agent. Temp. 1100°C, Na₂CO₃ 40%, reducing time 1 hr

% of carbon	Chemical composition								
	Pb	Sn	Cu	Ni	Zn	Sb	As	Al	Ag
10	82.42	2.2	4.2	5.5	0.5	3.3	0.25	0.09	0.32
15	82.30	3.9	1.2	3.9	0.4	6.2	0.5	0.1	0.17
20	80.90	4.0	2.1	4.2	1.0	6.7	0.5	0.1	0.2
30	55.0	31.6	1.5	2.0	0.4	6.8	2.0	0.07	0.15
40	52.7	31.5	1.5	2.5	0.98	7.3	2.0	0.2	0.15

Table 4. Effect of sodium carbonate as flux. Temp. 1100°C, carbon: 40%, reducing time 1hr

Na ₂ CO ₃ %	Chemical composition								
	Pb	Sn	Cu	Ni	Zn	Sb	As	Al	Ag
20	55.0	31.0	1.5	2.0	0.4	6.8	2.0	0.07	0.15
30	53.0	32.5	1.3	2.3	1.1	6.4	2.0	0.09	0.10
40	52.88	33.62	1.5	2.0	0.6	0.6	2.0	0.07	0.10

Table 5. Effect of temperature. Carbon 40%, Na₂CO₃ 40%, reducing time 1hr

Temp. °C	Chemical composition								
	Pb	Sn	Cu	Ni	Zn	Sb	As	Al	Ag
900	44.0	34	1.0	1.7	0.8	0.2	1.7	0.08	0.04
1100	52.8	33.6	1.5	2.0	0.6	0.6	2.0	0.07	0.1
1300	59.0	23.23	1.7	3.3	0.5	9.0	2.1	0.05	0.51

Table 6. Effect of reducing time. Temp. 1100°C, C 40%, Na₂CO₃ 40%

Reduction time	Chemical composition								
	Pb	Sn	Cu	Ni	Zn	Sb	As	Al	Ag
1.0	53	33.24	1.4	2.1	1.3	5.8	1.9	0.03	0.12
2.0	52.8	33.62	1.5	2.0	0.6	0.6	2.0	0.07	0.1
3.0	53.8	32.7	1.2	2.1	0.8	6.3	1.8	0.06	0.12

CONCLUSIONS

About 90% of copper initially present in the anodic slimes with 75 µm in diameter particles dissolved in 0.25 M H₂SO₄ solutions at 85°C under 1 bar oxygen pressure within 90 min. leaching time. The apparent activation energy of 69.0 kJ/mole is characteristic for systems under chemical reaction control.

Thiourea leaching of silver shows a good potential application to treat slimes bearing silver to recover silver where the low toxicity of thiourea compared to cyanide is always mentioned as one of the motivations for developing the research in this field. Almost 93% of silver is extracted using concentration of thiourea of 10 g/dm³, under temperature 60°C in 30 min leaching time.

Smelting of the slimes after leaching of copper and silver at 1100°C in the presence of sodium carbonate 40% and carbon 30% for one hour lead to production of Pb-Sn soldering alloy (Pb: 53.0% - Sn: 33%).

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Opisano przeróbkę szlamów anodowych pochodzących z egipskiego zakładu elektrorafinacji szlamów. Szlamy te posiadają wysoką zawartość miedzi, ołowiu, cyny i srebra. Zaproponowano proces hydrometalurgiczny składający się z dwóch etapów ługowania, czyli ekstrakcji miedzi za pomocą $H_2SO_4-O_2$ oraz srebra w układzie z tiomocznikiem i Fe^{+3} . Zaproponowano także pirometalurgiczny przerób pozostałości po ługowanie w celu otrzymania stopu Pb-Sn. Przebadano parametry wpływające na procesy ługowania i wytopu.