



STUDYING THE PROCESS OF DEPOSITION OF ANTIMONY WITH CALCIUM CARBONATE

Omarov Kh. B, Absat Z. B, Aldabergenova S. K, Siyazova A. B, Rakhimzhanova N. J and Sagindykova Z. B
Karaganda State University named after academician E.A. Buketov, Karaganda, Kazakhstan
E-Mail: aseka557793@gmail.com

ABSTRACT

Industrial production of copper solutions, in addition to the basic components (Cu, Ni), contain undesirable impurities which include arsenic and antimony. The work is devoted to studying the process of withdrawal of antimony from copper electrolyte with calcium carbonate, which is present in nature as a known mineral and in many cases is waste. Studies of the precipitation of antimony with calcium carbonate from copper-containing sulfuric acid solution was carried out by probabilistic and deterministic planning of the experiment. For the identification of solid precipitation X-ray analysis was used. The studies determined the optimum conditions for precipitation of antimony from copper-containing highly acidic solution in which antimony precipitates the most: Ca:Sb ration - 2:1, the temperature to 25 °C, the content of sulfuric acid in the copper electrolyte – 100 g/l, the duration of process from 45 minutes to 60 minutes. The use of calcium carbonate to clean technology solutions allows you to bring the content of antimony to the optimum content.

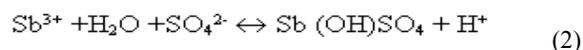
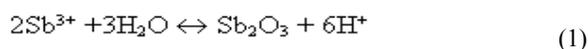
Keywords: copper production, electrolyte, antimony, calcium carbonate, copper, calcium antimonite.

INTRODUCTION

Production of copper takes the leading position in non-ferrous metallurgy in Kazakhstan. The main volumes of balance reserves of copper are concentrated in Karaganda and East Kazakhstan oblasts of Kazakhstan.

Industrial production of copper solutions, in addition to the basic components (Cu, Ni), contain undesirable impurities which include arsenic and antimony.

Antimony in the electrolysis of copper is the most harmful impurity. High concentrations of antimony may be deposited with copper on the cathode. Moreover, this element in the electrolyte are often hydrolyzed to form "floating" sludge:



"Floating" sludge is represented by sparingly soluble compound of Sb (V), Sb (III). This floating gelatinous sludge in the electrolyte in the form of small flakes easily deposited on the cathode and reduces its quality [1-3]. The content of such impurities (As, Sb, etc.) in the electrolyte reduces the conductivity of copper. The higher conductivity of copper results in less power losses in the conductors. For qualitative and complete recovery of copper and nickel from solutions, the prior deposition of these impurities is required.

In studies [4-6] of the process of cleaning the copper electrolyte from arsenic and bismuth with calcium carbonate, results of research have shown that especially effective cleaning process from arsenic (~ 85%), and bismuth (~ 40%) according to precipitant occurs at a sufficiently low acidity level of copper-containing electrolyte (~ 60 g/l of sulfuric acid). However, in factory conditions, the concentration of sulfuric acid in the copper

electrolyte in average is 100 g/l and above, it implies that the pre-neutralization with known methods of processing the copper production or the need to increase the amount of precipitating agent - calcium carbonate is required.

MATERIALS AND METHODS

In this study, the process of cleaning the copper electrolyte with calcium carbonate from the antimony contained in the copper electrolyte additionally was researched, which has a theoretical and practical interest.

Other methods of extracting antimony from solutions of the electrolytic refining of copper by sorption complex ions are also known [7]. To study the deposition of antimony calcium carbonate, we carried out research on the probability-determination planning of experiment on four levels. The factors taken: Ca: Sb (X_1) (0.5:1; 1:1; 1.5:1; 2:1); Temperature, °C (X_2) (25,40,55,70); sulfuric acid concentration in g/l (X_3) (80,100,120,140); duration of experiment, min. (X_4) (15, 30, 45, 60) and multiplier of dosing precipitator (X_5) (1,2,3,4) [8].

The object of investigation is selected to be an electrolyte solution of copper produced by Corporation Ltd. "Kazahmys Smelting" with a known content of the following components: copper 36,87 g/l free sulfuric acid 100 g/l arsenic 8,45 g/l bismuth 0,192 g/l, and antimony 0,64 g/l.

Experiments were performed in a thermostated reaction cell capacity of 150 ml with stirring. A portion of calcium carbonate taken in the required ratio to antimony was introduced into the electrolyte solution of copper at a predetermined temperature. The temperature of the water bath was maintained with accuracy of ± 2 °C.

The deposition of antimony from a copper-bearing sulfate solution under continuous stirring was conducted with a duration dictated by the condition of the matrix.

After a predetermined time, the solid phase was separated from the solution by vacuum filtration.



The content of antimony remaining in the filtrate was determined by atomic absorption spectrometer AA

140 companies Varian (Australia). Solid pellets were subjected to X-Ray analysis.

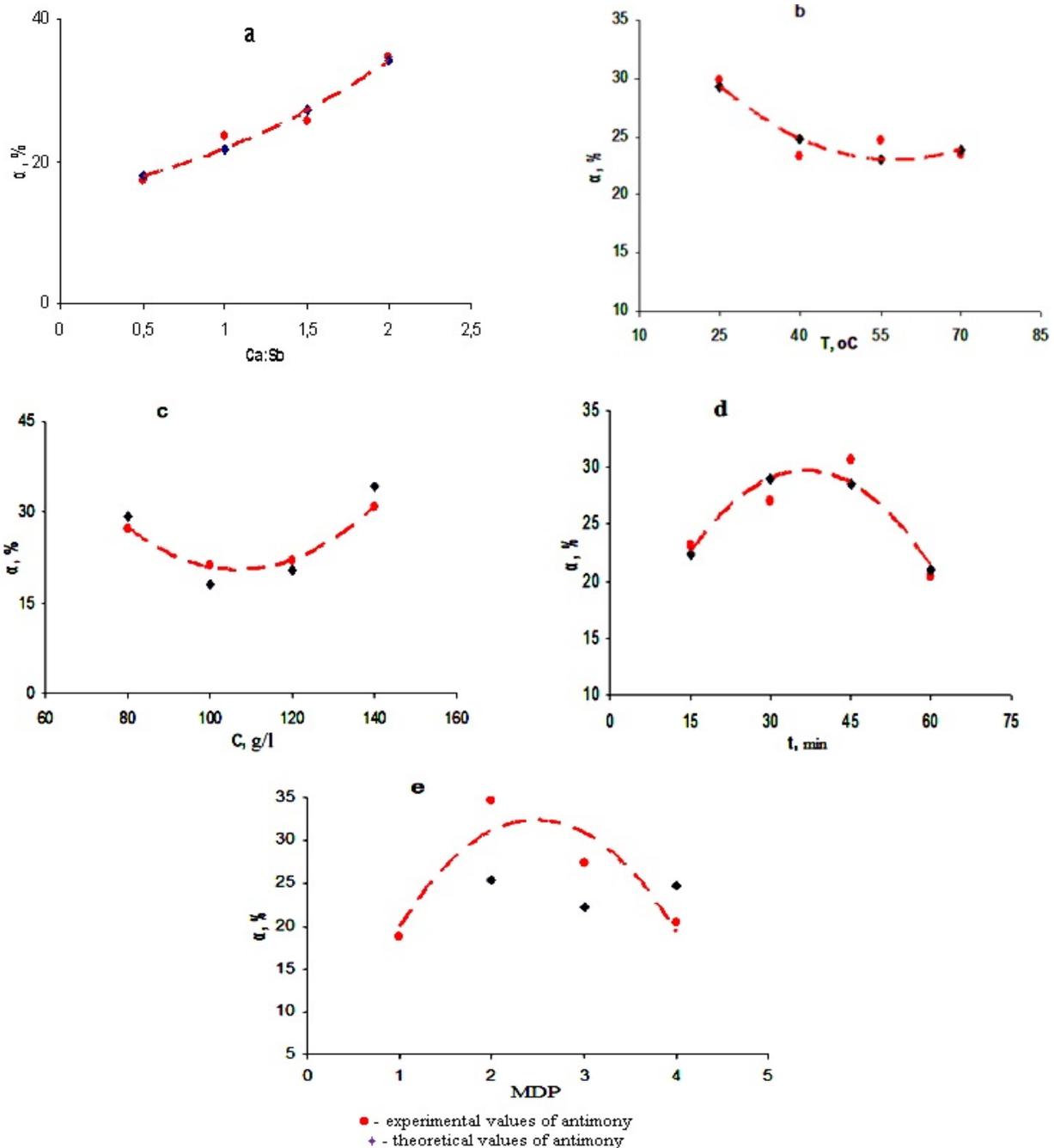


Figure-1. (a, b, c, d, e). Private antimony deposition depending on various factors.

RESULTS AND DISCUSSIONS

As a result of our data sample we received the following: dependence on the degree of partial deposition of antimony on these factors, and the calculated theoretical values of the degree of deposition of antimony, which are shown in Figure-1 (a, b, c, d, e).

Private functions are approved by correlation coefficient and its significance given in Table 2, according to which, only a fifth partial dependency relationship (a function of multiplicity of dosing the precipitant to antimony) was insignificant and, as required, is eliminated.



The experimental conditions and results for the deposition of antimony (α) shown in Table-1.

Table-1. Plan matrix and the results of the five-factor experiment at four levels of antimony.

	(x ₁)	(x ₂)	(x ₃)	(x ₄)	(x ₅)	α , Sb %	α , Sb %
1	0,5:1	25	80	15	1	15,06	20,21
2	1:1	40	100	30	1	12,53	20,75
3	1,5:1	55	120	45	1	20,18	25,06
4	2:1	70	140	60	1	27,05	33,54
5	0,5:1	40	120	60	2	16,47	13,16
6	1:1	25	140	45	2	48,27	35,68
7	1,5:1	70	80	30	2	36,65	32,27
8	2:1	55	100	15	2	7,02	23,27
9	0,5:1	55	140	30	3	26,31	23,44
10	1:1	70	120	15	3	26,15	16,38
11	1,5:1	25	100	60	3	23,31	22,17
12	2:1	40	80	45	3	41,97	41,40
13	0,5:1	70	100	45	4	11,93	16,21
14	1:1	55	80	60	4	14,93	18,07
15	1,5:1	40	140	15	4	22,13	29,53
16	2:1	25	120	30	4	32,79	40,73

Table-2. Correlation coefficients (R) and their significance (t_r) for private dependency degree of deposition of antimony with calcium carbonate.

Function	R	t_r	Importance
$Y_1 = 3,11x_1^2 + 2,999x_1 + 15,712$	0,97	55,66	important
$Y_2 = 0,006x_2^2 - 0,6903x_2 + 42,83$	0,84	9,06	important
$Y_3 = 0,0094x_3^2 - 2,0035x_3 + 127,48$	0,99	0,71	important
$Y_4 = -0,0157x_4^2 + 1,1471x_4 + 8,755$	0,88	6,61	important
$Y_5 = 3,0056x_5^2 - 18,519x_5 + 50,697$	<0,66	<2	not

Statistical description of the partial dependence is presented by equation of Protodyakonov. For the deposition of antimony with calcium carbonate:

$$Y_n = (3,11x_1^2 + 2,999x_1 + 15,712) \cdot (0,006x_2^2 - 0,6903x_2 + 42,83) \cdot (0,0094x_3^2 - 2,0035x_3 + 132,94) \cdot (-0,0157x_4^2 + 1,1471x_4 + 8,755) \cdot 25,3^{-3} \quad (3)$$

The correlation coefficient of the equation for antimony R = 0.67, and its importance $t_r = 4.14$, error equation $\sigma = 7.76\%$.

Protodjakonova equation, a mathematical model of the process makes it possible to determine the optimal conditions for the implementation of the cleaning process of the copper electrolyte from antimony, with various combinations of existing factors.

Besides the significance of the correlation coefficients private functions were determined by the

confidence interval. To find the confidence interval, three repeated experiments and calculation of the reproducibility of the experiment on Cochran's Q test were made.

$$G = 0.37 < 0.8412$$

According to the values of the correlation coefficient and the confidence interval, it can be concluded that both the significance tests are in complete agreement.

The deposition of antimony by calcium carbonate with increasing amounts of injected precipitator characterized as the increase of extraction level of antimony in precipitation in the entire range of the ratio Ca: Sb (Figure-1, a).

With increasing temperature (as shown in Figure-1 (b)) the ability to extract antimony from copper electrolyte drops sharply, due apparently to the acceleration of competing reaction to form calcium sulfite in highly acidic environments. Maximum recovery of antimony calcium carbonate is observed at 25°C.

With increasing the concentration of sulfuric acid in accordance with Figure-1 (c), the deposition of antimony passes through a minimum. When the concentration of sulfuric acid up to 100 g/l the probability of formation of calcium sulfate increases, this is a cause of decreasing the output level of antimony from copper electrolyte. Furthermore, with increasing concentrations of sulfuric acid, the extent of precipitation of antimony decreases because the antimonates gidroantimonaty and calcium are unstable in highly acidic environments. However, a slight increase of its output to a solid precipitation with increasing sulfuric acid concentration from 100 g/l to 140 g/l can be explained by a high adsorption capacity of calcium hydrosulfate to antimony.

The resulting calcium gidroantimonaty according to Figure 1 (d) are unstable in sulfuric acid and a decrease degree of deposition of antimony is observed in the range of from 45 minutes to 60 minutes.

Constantly updated active surface by dosed filing in accordance with Figure-1 (e) increases the extraction of antimony from copper solution. Besides formation of antimonates of calcium, competing reaction of calcium sulfate occurs.

According to the values of the correlation coefficient and the confidence interval, we can conclude that both significance criteria are consistent.

CONCLUSIONS

Based on the analysis results of the study, the optimal conditions for the deposition of highly acid solutions of antimony copper were determined, in which antimony mostly fully precipitates: Ca ratio: Sb - 2:1, the temperature to 25 °C, the content of sulfuric acid in the copper electrolyte – 100 g/l, the duration of the process from 45 minutes to 60 minutes. The presence of solid precipitation of calcium antimonate confirmed by X-Ray analysis in accordance with Figure-2 (a, b).



Color of obtained precipitation from the experiments on the deposition of antimony with calcium carbonate is white.

From X-ray of solid precipitation, captured after the deposition of antimony follows that antimony from

copper electrolyte is precipitated with calcium carbonate in the form of antimonate, composition $\text{Ca}_2\text{Sb}_2\text{O}_5$.

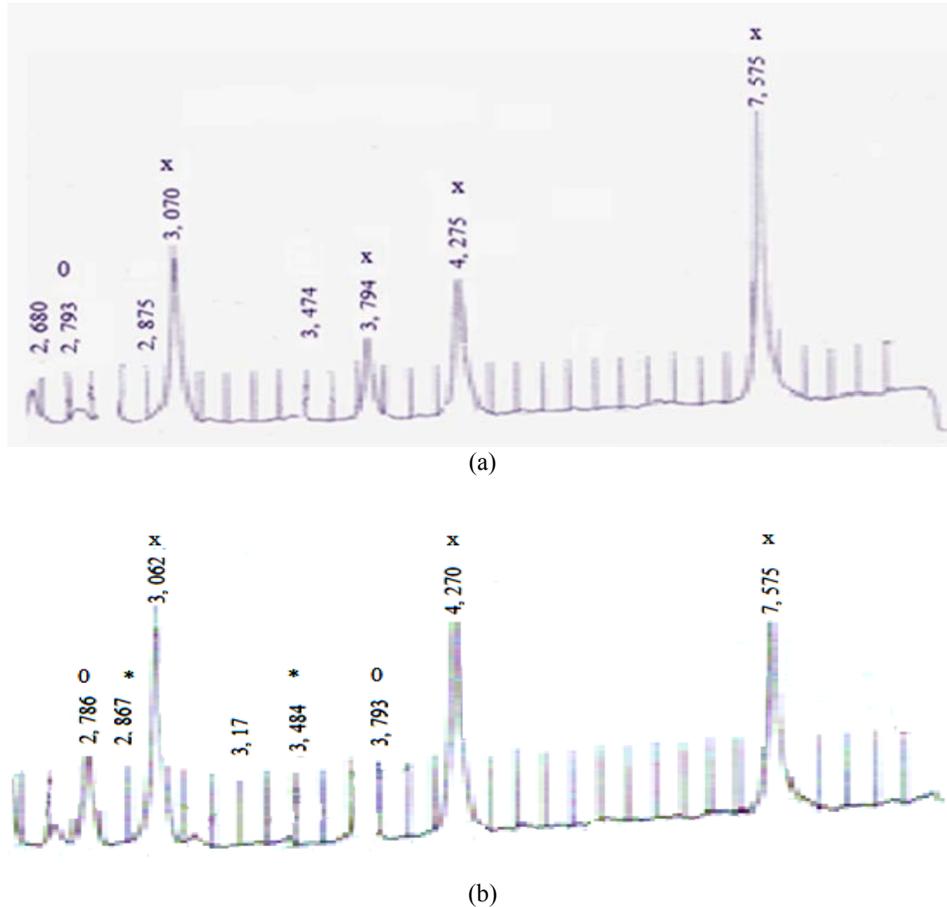


Figure-2. X-ray of solid precipitation formed by deposition of antimony with calcium carbonate, where x - $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, o - $\text{Ca}_2\text{Sb}_2\text{O}_5$; a - 7th experiment; b – twelfth experiment.

Besides antimonate, calcium sulfate precipitation falls, it happens due to the occurrence of a parallel reaction of calcium ions and sulfate ions. Radiographs of solid residues, obtained in a series of experiments, are qualitatively not different.

Thus, for the first time, the process of output of antimony copper electrolyte by calcium carbonate was studied, whereas calcium carbonate meets in the minerals in nature and known in many cases as a waste product. The possibility of using calcium carbonate to clean technology solutions in order to bring the content of antimony to the optimum concentration, which subsequent stages of processing solutions in copper production brings a high quality of copper- and nickel-containing products [9].

REFERENCES

- [1] Utkin N.I. 2000. Production of non-ferrous metals. M: Internet Engineering. pp. 442.
- [2] Soshnikov LA, MM Kupchenko. 1978. Recycling copper electrolytic slimes. M: Metallurgy. pp. 200.
- [3] Livshits L.Ya., Pazukhin V.A. 1958. The behavior of arsenic and antimony in the electrolytic refining of copper. Applied Chemistry, t. XXVII. No.3: 298-309.
- [4] Zhambekov M.I., Absat Z.B. 2003. The purification process of the copper electrolyte from arsenic. Auth. Testimonies. RK #40952 from 27.01.2003y.



www.arpnjournals.com

- [5] Absat Z.B., Tusipbaev N.E. 2012. Cleaning copper electrolyte from contaminants. Proc. Scien. articles Part 1. Almaty: Publishing House «Raritet». pp. 122-123.
- [6] Absat Z.B., Sagindykova Z.B., Omarov H.B. and others. 2009. Patent for innovation №21002 RK. Method of precipitation of arsenic from stock solutions of copper production. Bulletin No. 3.
- [7] Shubinok A.B. 1994. Author's certificate No. 42778 RK. A method of extracting antimony from copper electrolyte. Bulletin No. 1.
- [8] Malyshev V.P. 1994. Probabilistic and deterministic mapping. Almaty: Science. pp. 373.
- [9] Omarov H.B., Zharmenov A.A., Sultanova L.M. and others. 2005. Author's certificate No. 42778 RK. Method processing copper. Bulletin No. 1.