

*Electrochemistry*

## Methods of Processing of the Gold-Containing Refractory Sulfide Ores and the Concentrates

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**ABSTRACT.** Alternative methods of processing the refractory gold-sulfide ores and concentrates were worked out. The gold-containing refractory sulfide ores of chalcopyrite, pyrite, barite-polymetallic, quartzites, copper-zinc, antimonite were used in the research. As a result of investigation, the optimal conditions of gold leaching by means of thiourea method from the above-mentioned ores and concentrates with 85-90% gold extraction were established. Investigations were carried out on electrochemical leaching of refractory gold-containing sulfide ores and concentrates. We used the acid chloride electrolyte, which contained thiourea as a selective complex-maker for precious metals. The leaching proceeded in conditions of “soft” oxidative mode yielding up to 87% of gold without isolation of molecular chlorine avoiding environmental pollution. The new technological scheme of gold leaching satisfies modern ecological and economical requirements. The reactor designed for the electrochemical leaching of refractory ores and concentrates was tested and patented. © 2017 Bull. Georg. Natl. Acad. Sci.

**Key words:** thiocarbamide method, electrochemical processing, gold-containing ores, flotation tails, barite-polymetallic ore, thiourea

Analysis of literary data shows that in gold mining the main method of gold extraction from ores and concentrates is cyanidation, which is not cost-effective in case of the refractory sulfide ores. Neutralization of cyanide solutions is also a serious problem. On the other hand, application of nontraditional methods are related to number of difficulties: requires multistage operations, is power-consuming and do not always provide high yield [1]. Therefore, it is very important to develop environmentally and eco-

nomically acceptable methods for processing the refractory sulfide minerals allowing to solve the problem of efficient exploitation of natural resources with reduced environmental load.

The problem of processing the refractory gold sulfide raw materials including industrial residues is also topical in Georgia. In the course of years a huge amount of flotation tailings contain tens of tons of gold and several hundred tons of silver were accumulated on the territory of Madneuli Mining Plant,

creating an environmentally hazardous situation. Due to lack of efficient technologies they are not being processed and represent the source of air pollution and contamination of water bodies.

As a result of several years of investigations some scientists came to a conclusion that in comparison to cyanide technologies the thiourea method is an alternate and more competitive one meeting modern requirements of ecology and economy with its small toxicity, kinetic activity, selectivity relative to the noble metals, moderate cost [2].

The main reagent in the thiocarbamide process is thiourea (Thio) or  $\text{CS}(\text{NH}_2)_2$ . For dissolution of gold the acid solutions of thiourea are used, in which trivalent iron sulfate is introduced as an oxidizer. The process of dissolution of gold in thiourea can be represented by the most probable reaction as follows [2].

$\text{Au} + n\text{Thio} + \text{Fe}(\text{Thio})_2^{3+} \rightarrow \text{Au}(\text{Thio})_2^{+} + \text{Fe}(\text{Thio})_n^{2+}$   
Where  $n$  appears to be equal to 4. The process of dissolution of silver is carried out in a similar way.

We performed the experimental work on using the thiourea method for recovery the precious metals from the following sulfide gold ores and industrial residues: quartzite; tailings of copper-pyrite ore of Madneuli Deposit; barite-gold containing concentrate; the residues of copper-zinc ores; tailings from flotation of barite-polymetallic ore of Madneuli deposit and the residues of vacuum-thermal processing of gold-containing antimony ore deposit of Zopkhito, mountainous Racha (Georgia).

Optimum conditions for leaching gold and silver from fine quartzite (Au - 1.38 g/t, Ag - 5.7 g/t) with the solutions of thiourea ( $\text{CS}(\text{NH}_2)_2$  - 0.5%,  $\text{H}_2\text{SO}_4$  - 0.4%,  $\text{Fe}_2(\text{SO}_4)_3$  - 0.3%) were established. When duration of the process was 8-10h., S : L = 1 : 3, intensity of mixing pulp - 200rev/min. and the temperature 18-25°C, the extraction of gold and silver in solution was 90% and 60%, respectively [3].

Pyrite tailings stockpiled on the territory of Madneuli mining plant (~16 million ton) are finely dispersed sulfide ( $\text{S}_{\text{sum}}$  - 10.7%) materials. They con-

tain non-ferrous and noble metals: Cu - 0.35%, Au - 0.38 g/t and Ag - 3.5 g/t. Given the fact that these metals in the tailings are associated with pyrite, from the tailings the pyrite flotation concentrate was obtained with a yield of 22.2%, containing 1.61 g/t of gold. Gold recovery in the concentrate comprises 89.2%.

For separate extraction of nonferrous and noble metals, it is advisable to submit the pyrite concentrate to oxidative firing (700-800°C) and to treat the obtained dross consistently first by aqueous solution of ammonia, and then by acidic solutions of thiourea.

Extraction of copper and zinc from the dross in the form of complex compound ( $[\text{Me}(\text{NH}_3)_4]^{2+}$  with the use of aqueous solution of ammonia ( $\text{NH}_4\text{OH}$  - 12%,  $(\text{NH}_4)_2\text{SO}_4$  - 8%) is 98%, and extraction of gold by further processing of the dross with acidic solution of thiourea (Thio - 0.4%,  $\text{H}_2\text{SO}_4$  - 0.4%,  $\text{Fe}_2(\text{SO}_4)_3$  - 0.4%) is 88.8% [4].

In Madneuli ores, the barite-gold-containing concentrate attracts special attention with its gold and silver content (Au - 9g/t, Ag - 38g/t). The maximum extraction is achieved with preliminary roasting of the flotation concentrate (500°C) by subsequent processing of the residue with sulfuric acid solution (50 g/l), after which the residue is submitted to thiourea leaching. The optimum conditions of leaching are as follows: duration - 6 hours, S : L = 1 : 5, concentration of the thiourea solution (Thio - 2%,  $\text{H}_2\text{SO}_4$  - 1%,  $\text{Fe}_2(\text{SO}_4)_3$  - 1%). In these conditions the degree of the gold and silver extraction is 94.9% and 97.2%, respectively [5].

The study of processing the flotation concentrate of the copper-zinc sulfide ore of Madneuli deposit containing Cu - 14.5%, Zn - 5.8%,  $\text{S}_{\text{sum}}$  - 29% is of interest. The concentrate also contains 6.8 g/t Au and 8.8 g/t Ag. The solid residue obtained after pyrohydrometallurgical processing of the copper-zinc concentrate enriched by precious metals also contains 14-16g/t gold and 18-20g/t silver. For extraction of these metals the thiourea method was applied. The

results of the study showed [6] that a high degree of extraction of precious metals is achieved after pre-oxidizing roasting of the residues at temperatures of 600 – 700°C for 1 hour, after which the residue is treated with a solution of sulfuric acid to remove residual copper and zinc. Obtained solid residue is leached with an acid solution of thiourea (Thio - 2%, H<sub>2</sub>SO<sub>4</sub> – 1%, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> – 1%) for 4 hours at a ratio S : L = 1 : 5. Under these conditions, the gold recovery is up to 96%, and silver - 70%, although after roasting at 600°C the degree of extraction of silver is higher and is 82.4%, gold – 87.2%. This is due to the fact, that oxidative roasting of silver is optimal at 600°C that ensures the destruction of both simple and complex sulfides of silver and opening of its surface.

For extracting of gold from gold-containing secondary concentrate of barite-polymetallic tailings the thiocarbamid method was also applied. For complete removal of physical and chemical depressants of gold we carried out roasting of the secondary concentrate in the temperature range of 400-800°C and leaching of the residue with the acid solution of thiourea. The best results were obtained with roasting of the grained (-0.16 mm) secondary concentrate of the barite-polymetallic tailings at the temperature of 400°C and leaching without pre-acid treatment of the roasted product with a solution of thiourea (Thio - 2%, H<sub>2</sub>SO<sub>4</sub> – 1%, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> – 1%) with the ratio of S : L = 1 : 5 for 4 hours. In such conditions the degree of gold extraction reaches 89% [7].

After extraction of the antimony and arsenic in vacuum thermal processing of the gold-containing antimony ores of Zopkhito deposit [8], remains the residue containing 5.5 g/t gold and 12g/t silver. As a result of researches the optimum mode of leaching the finely ground (- 0.4 mm) residue with thiourea was established: composition of the solution -Thio - 0.5%, H<sub>2</sub>SO<sub>4</sub> - 0.8%, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> – 0,8%; duration - 4h., S : L = 1 : 5; speed of the stirrer rotation – 200 rev/min, temperature - 18-25°C. In these conditions the degree of extraction of gold from the residues is 87% [9].

The results of investigation show that for full

opening the gold surface in refractory sulfide mineral with this method regrinding and roasting of the concentrate is advisable, which contributes to the efficiency of the subsequent operations of gold extraction.

However, the use of preliminary roasting of the investigated concentrate before leaching and then removing from the solution the gold is associated with large power consumption.

According to literature [10], the most appropriate method for processing the refractory sulfide ore is the method of hydro-chlorination along with thiocarbamide.

As a method of processing the gold-containing tailings of the refractory sulfide concentrates we chose the method of electrochemical oxidation of sulfides in the ore pulp with the use of various chloride systems, instead of the method of hydrochlorination. The advantage of the method of electrochlorination before hydrochlorination is simultaneous regeneration of the oxidizing agent - molecular chlorine at the anode.

Studies show that the process of electrochemical leaching of the gold concentrate with a high Red/Ox potential of the system (I-II) (Table 1) is accompanied by separation of the molecular chlorine at the anode, which oxidizes the gold directly in the process of leaching producing the anion complex [AuCl<sub>4</sub>]<sup>-</sup> with the constant of instability  $K=5 \times 10^{-22}$  (pK-21.3) [11] in the reaction:



It was established [12] that the use of the electrochlorination method with solution Cl<sub>2</sub>-NaCl-HCl-H<sub>2</sub>O at pH~2, and Red/Ox =1200-1300V provides a high degree of gold extraction (85%) from the ores containing highly dispersed metal nuggets of gold (quartzite) (Table 2). However, the degree of gold extraction from the tails of enrichment of the gold-containing refractory sulfide concentrates by the use of this method does not exceed 54.4% (Tables 1,2)[13].

The reason for the low degree of extraction of gold in systems I–II (Table. 1) is sulfide layer, cover-

**Table 1. Electrochemical leaching of the tails of flotation enrichment of barite-polymetallic and chalcopyrite ores in different chloride systems t-25<sup>0</sup>C; i<sub>a</sub>-0.75A/dm<sup>2</sup>; m<sub>conc</sub>-200g; τ -5h**

	The solution composition, g/l		
	I	II	III
	NaCl-100	NaCl-100, Urea-18	NaCl-100, Thiourea-18
Red/Ox, V	1.0±0.15	1.0±0.15	0.4±0.04
The degree of extraction of gold from barite-polymetallic tails, %	43.2	64.3	87.1
The degree of extraction of gold from chalcopyrite tails, %	54.4	61.5	86.8

ing disseminated gold and complicating the processing of the gold-bearing refractory sulfide ores.

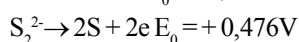
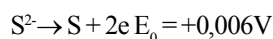
In order to simplify the technology of processing the refractory sulfide ores and concentrates and to create ecologically safe and highly effective method of their processing, studies were conducted towards the use of the method of direct electrochemical leaching without pre-treatment of sulfide concentrate, using non-toxic electrolyte based on chloride of alkali metals in the presence of the organic complex agent - thiourea (Table 1, syst. III) [14].

In chloride solution the thiourea reduces the Red/Ox potential of the system to 0.4V (table 1), which allows leaching in a “soft” oxidizing modes without separation of the molecular chlorine and pollution of the environment with a high degree of gold extraction (Table 1, syst. III) [15].

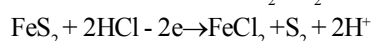
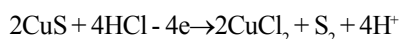
According to [16] the standard potential of the reaction:



The standard potentials of reactions [17]:

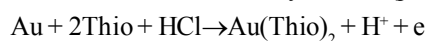


For Red/Ox potentials of the electrolyte system under study (Table 1, syst. III) the following reactions are admissible:



Data in Table 2 confirm the suggestion. Obviously, in conditions of electrochemical leaching the sulfide layer covering the disseminated gold destructs and under action of the thiourea, contained in the electro-

lyte passes into solution in the form of a cationic complex with the constant of instability  $K=10^{-23}(\text{pK}-22)$ :



Together with the gold the main components (Table 2) contained in concentrate pass into solution that can be separated in the form of commercial products.

We used the method of “soft” oxidative mode in the process of electrochemical leaching of the residues of the vacuum-thermal treatment of the antimony gold-containing concentrates. The process of electrochemical leaching was carried out in a cylindrical electrolyzer with central anode cell separated from the cathode space by a diaphragm in potentiostatic mode. Red/Ox potential of the system,  $\varphi_a$  anode potential, temperature, electrolysis conditions were under the control. At the end of the experiment the treated suspension was filtered, the precipitate was washed by repulping, then dried and the content of gold was determined by atomic absorption spectrometer.

The maximum extraction of gold (81-87%) in electrochemical leaching of the residue vacuum-thermal treatment of gold-containing antimony concentrates is achieved in the solution of the composition 0.5M KCl + 0.5M Thio+0.03M Na<sub>2</sub>S, at S : L = 1:3, 0.5±0.05, t = 22-27<sup>0</sup>C and the consistency of grind-0.16mm; pH<1[18].

Based on the research on electrochemical leaching of gold-containing sulfide mineral, closed technology and construction of the electrochemical reactor were elaborated [18].

**Table 2. The degree of extraction of components from flotation tailings of sulfide ore minerals in the process of electro-chlorination.**

Process mode: I - 2.8A; U-3.7V;  $\tau$  -5h. The composition of the solution: NaCl - 150 g/l; pH - 0.5; weight-200 g; temperature – 25<sup>0</sup>C; Red/ox -1052±50mV

№	Concentrate	The degree of extraction of components			
		Au, g/t	Ag, g/t	Cu, %	Fe, %
1	Gold-containing quartzite	85	33	36	21
2	Barite-polymetallic tails	43.2	65	67	48
3	Chalcopyrite tails	54.4	85	63	54

Thus, as a result of the studies it was established that by means of electrochemical method using solutions based on chlorides of alkali metals in the presence of selective complex agent with gold-thiourea, the tails of flotation enrichment of gold-containing re-

fractory sulfide ores and the residue of vacuum-thermal treatment of gold-containing antimony sulfide concentrates can be effectively treated yielding up to 87% of gold without separation of molecular chlorine and environmental pollution in the process of leaching.

### ელექტროქიმია

## ოქროშემცველი ჯიუტი სულფიდური მადნების და კონცენტრატების გადამუშავების მეთოდები

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(წარმოდგენილია აკადემიის წევრის გ. ცინცაძის მიერ)

ჩატარდა კვლევები საქართველოს ოქროშემცველი ჯიუტი სულფიდური მადნების გადამამუშავებლად ციანიდური ტექნოლოგიის ალტერნატიული და მეტად კონკურენტუნარიანი მეთოდების გამოყენებით. დადგინდა, რომ ჯიუტი ოქროშემცველი მადნები წარმატებით შეიძლება გადამამუშავდეს თიოკარბამიდული მეთოდით მათგან 85-90% ოქროს ამოღებით. მხოლოდ ეს მეთოდი, უმეტეს შემთხვევებში, საჭიროებს კონცენტრატის წინასწარ გამოწვას 400-600<sup>0</sup>C-მდე ელუატებიდან ოქროს შემდგომი ამოღებით. კვლევები ჩატარდა აგრეთვე “ჯიუტი” სულფიდური კონცენტრატების პირდაპირი ელექტროქიმიური გამოტუტვის მეთოდის გამოყენებით კონცენტრატის ყოველგვარი წინასწარი დამამუშავების გარეშე “მსუბუქი” დაჟანგვის რეჟიმის პირობებში და კათოდზე ოქროს იმპედროული გამოლექვით. ამ დროს მადნიდან ოქროს ამოღების ხარისხი 87%-ს აღწევს.

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