



ELECTROCHEMICAL GOLD EXTRACTION FROM THE RESIDUES OF VACUUM-THERMAL TREATMENT OF GOLD-CONTAINING ANTIMONY ORES

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The method for gold extraction from the residues of vacuum-thermal treatment of the concentrate of gold-containing antimony ore of Zopkhito (deposit) has been established by eco-friendly electrochemical method. The effect of main technological parameters on the process of electrochemical leaching of the residues has been studied in the presence of a selective ligand, thiourea, in chloride system and optimal conditions of leaching have been established providing for the gold extraction from gold-containing residues by 82-90 % in the conditions of so-called “soft” oxidation without release of molecular chlorine at the anode and eco-contamination. Continuous technological process of electrochemical leaching of the residues of gold-containing antimony ore and electrochemical reactor for realization of this process are proposed.

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the cinder. Gold-extraction to a high extent from the gold-containing cinder of this type is possible by hydro-metallurgical methods.

Hydrometallurgical cyanide process^{1,2} has been widely used in to extract precious metals from gold-containing raw material. The method is characterized by high toxicity, high costs and low selectivity. Further, the disposal of cyanide solutions presents serious environmental problems.

INTRODUCTION

The most important way to meet the increasing demand for non-ferrous, noble and rare metals is to enhance the efficiency of the processing of the raw materials. To achieve this, it is necessary not only to improve the existing technologies but also to find new, atom-efficient and eco-friendly metallurgical processes. Complete extraction of valuable components from gold-containing antimony ores and their concentrates of Zopkhito deposit (Mountainous Racha) poses a serious challenge.

Most of gold-containing antimony ores are resistant to the common process of gold extraction-treatment with cyanide. One of the reasons of this resistance is a presence of finely-impregnated gold in sulfide mineral of arsenic and antimony. Further, antimonite sulfide destroys cyanide.

The goal of our research involves development of a process for the recovery of gold from the resistant antimony ores of Zopkhito deposit (Mountainous Racha)

In Table 1, chemical composition of the concentrate of Zopkhito ore is presented.

The concentrates of Zopkhito deposit was subjected to vacuum-thermal process at high-temperature vacuum plant (10⁻⁵ MPa, 400-600 °C), in F. Tavazde Institute of Metallurgy and Materials Science. As a result of vacuum – thermal treatment of the concentrate, antimony sulfide (Sb₂S₃) and high-purity antimony are produced and whole of gold (already shorn of protective sulfide layer) remained in

Hydrochlorination method³ is considered as one of the real alternatives of the cyanide process of treating of the residues of vacuum-thermal treatment of gold-containing antimony ore. It was shown⁴ that in concentrated chloride solutions, the normal potential of Cl₂/Cl⁻ electrode is more positive (1.242 V) than that of Au³⁺/Au electrode (1.012 V) which allows metallic gold to be oxidized by molecular chlorine, dissolved in the solution:



The system Cl₂-NaCl-HCl-H₂O, which contains 0.5 M HCl and is characterized by the highest value of redox potential, was used by us to treat gold-containing quartzites by the method of electrochlorination leaching.⁵ The process of electrochemical leaching of gold-containing raw material proceeds at the anode by generation of molecular chlorine which oxidizes gold with the formation of an anionic complex [AuCl₄]⁻ with dissociation constant value of $K=1.2 \times 10^{-12}$ (pK=11.2).⁶ Because of negative charge, the complex cannot migrate to the catholyte and consequently is unable to discharge at the cathode with the formation of metallic gold and remains in the anolyte. Therefore the process of gold extraction from the solution by this method requires the additional operations which hinder the leaching process. Another disadvantage lies in the necessity of high redox potential (higher power consumption) and environmental contamination by excess molecular chlorine, separated at the anode in the course of leaching.

Table 1. Chemical composition of the concentrate of Zophito gold-containing ore

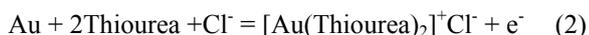
Au, g ton ⁻¹	Ag, g ton ⁻¹	Sb, %	Fe, %	Al, %	Cu, %	As, %	SiO ₂ , %	Pb, %	Ni, %
4.5	1.2	6.0	5.0	5.0	0.2	1.5	75	0.1	0.1

Table 2. Chemical composition of the residue of vacuum-thermal treatment of the concentrate of gold-containing antimony ore of Zopkhito deposit

Au, g ton ⁻¹	Ag, g ton ⁻¹	Sb, %	Fe, %	Al, %	Cu, %	As, %	Si, %	Pb, %	Ni, %
5.5	2.0	1.0	2.0-5.0	5.0	0.02	0.7	67-70	0.1	0.1

Investigations were carried in aqueous solutions containing chlorides of alkali metal and ligands which form strong complexes with gold with an aim to enhance the efficiency of the electrochemical process and to make it more eco-friendly. It has been reported⁷ that lower is the standard redox potential of the aqueous solutions of gold-complex, stronger is the gold-complex. The thermodynamic ease of the oxidation of gold is indicated by the reduction in the redox potential of the complex-forming ligand on its addition to the system. The ease of oxidation finally depends on the kinetic parameters of the process.

On the basis of experiments,⁸ thiourea was chosen as selective ligand for complexation with gold. Thiourea is characterized by penetration into internal sphere of complex compounds of some heavy metals with the formation of new strong complex compounds.⁹ By the addition of thiourea in chloride system redox potential of the solution is reduced from 1.0 to 0.4 V. Such low redox potential of the system leads to electrochemical leaching of gold from ores under the so-called "soft" oxidative conditions and does not involve release of chlorine at the anode and consequent environmental contamination,^{8,10} Under the experimental conditions, polarization of gold and its passage into the solution phase take place in the anode area. As a result a cationic complex with thiourea, $[\text{Au}(\text{Thiourea})_2]^+$ is formed with a dissociation constant, $K = 10^{-23}$ ($\text{p}K = 22$)⁷ by the reaction:

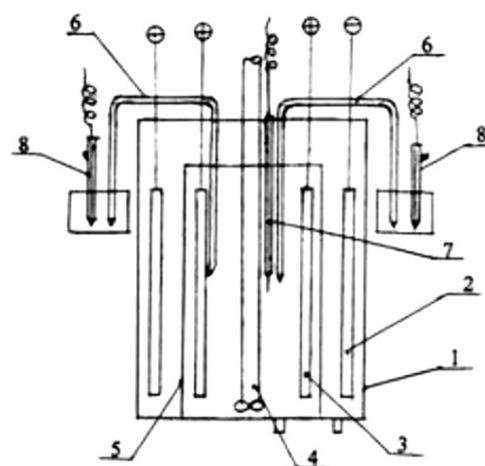


The cationic complex of gold with thiourea is considerably more stable than the anionic chloride one which is due to low (0.38 V) standard potential of the reaction (2). Along with it, due to the presence of positive charge, migration of the cationic gold complex into cathode area and its discharge at the cathode results in the formation of metallic gold. The above-mentioned process of electrochemical leaching considerably simplifies the passage of gold from the ore to the solution and its subsequent extraction since these processes are performed in the same electrochemical apparatus.

EXPERIMENTAL

The main components of the samples of the residues of vacuum-thermal treatment of the concentrate of gold-containing antimony ore of Zopkhito deposit, which were subject of this study, are given in Table 2.

The process was carried out at pilot plant of our elaboration (Fig. 1).

**Figure 1.** Scheme of stationary electrolyzer

1-electrolyzer body; 2-cathode; 3-anode; 4-mixer; 5-diaphragm; 6-electrolytic key; 7-Pt-electrode; 8-Ag/AgCl reference electrode

The anode cell is located at the center of the plant. Graphite was used as the anode and carbon-fiber material, which is characterized by high reaction surface, was used as the cathode. The diaphragm consists of thermally treated perchlorovinyl cloth. In the anode cell, the suspension was the intensively agitated. The process proceeded under potentiostatic regime. Redox potential, anode potential (φ_a), temperature and electrolysis conditions were controlled. Silver chloride electrode was used as a reference one. The potentials were recalculated in terms of potential of normal hydrogen electrode. At the end of the experiment the spent suspension was filtered, the sediment was washed by plumping, dried and the gold content was determined by atomic-absorption spectrometer.

The experiments were performed to establish the effect of electrolyte composition and of process parameters on the indexes of gold extraction by electrochemical method from the residue of vacuum-thermal treatment of the concentrate of gold-containing antimony ore.

RESULTS AND DISCUSSION

Experimental results are given in Table 3. It was observed that with an increase in the concentration of thiourea in the electrolyte, the degree of gold extraction enhances and attains a maximum in the concentration range of 0.5- 0.6 M, which corresponds to the lowest redox potential of the system.

Experimental results (Table3-III) indicated that at the absence of KCl anodic extraction of gold is characterized by low indexes and an addition of 0.5 M of KCl to the solution resulted in considerable increase of gold extraction. Addition of small amounts of Na_2SO_3 and Na_2S , which exerts the catalytic influence on the process¹¹, caused further increase in the degree of gold extraction.

Temperature has a pronounced effect on the indexes of the gold extraction. It is well-known³ that thiourea-containing solution is stable at 25-30 °C, therefore, the experiments were performed in this temperature range. As is seen from Table 3-IV, the temperature variation in the range of 22-27 °C has a negligible effect on the indexes of gold extraction but attains a value of ~90 % at 30-32 °C.

It has also been observed (Table 3-VI-VII) that the size of ore particles and ratio between solid and liquid phases has a pronounced effect on the index of gold extraction. In particular, in the case of large-size particles (0.16 mm) the index of gold extraction is greater (~86 %). Similarly, smaller is the solid: liquid ratio, greater is the degree of gold extraction (Table 3-VI). This observation may be explained by current distribution in pulp area during the course of electrochemical process.

It is well-known¹² that thiourea system is stable at anode potential of ~0,6 V. At higher potential the anodic oxidation of thiourea takes place. Therefore electrochemical process of ore leaching was carried out in potentiostatic regime where a rigid control of anode potential was maintained. As the experiments show (Table 3-VIII), the indexes of gold extraction attain maximum value at anode potential = 0.5 ± 0.05 V and is ~84 %.

Thus the optimum condition for the maximum extraction of gold (82-90 %) from the concentrate is the use of solution containing 0.5 M KCl + 0.5 M Thiourea + 0.03 M Na_2S , in potentiostatic regime, $\varphi_a = 0.5 \pm 0.05$ V, $T = 22-32$ °C, grinding degree = 0.16 mm and $\text{pH} < 1$.

Based on the experimental results, a continuous technological process for the extraction of gold from the residue (or ore concentrate) of vacuum-thermal treatment of gold-containing antimony ore of Zopkhito deposit was developed and an electrochemical reactor was created. The electrodes for the reactor were made of highly-developed surface carbon-fiber material, which are characterized by high efficiency especially in solutions containing electro-active components in low concentration (Fig. 2).

The reactor operates in the following manner: the pulp is supplied to the reactor and immediately after switching of a mixer the catholyte is fed to cathode cell. When anode and cathode cells are filled by the solutions, constant current of optimal parameters is supplied to the reactor. After a definite time the control of the composition of anolyte and

catholyte drain is carried out. On attaining of optimal composition an adjustment of maximum rate of the solutions supply is carried out by corresponding control. Thus putting of the reactor into stationary regime of operation is completed.

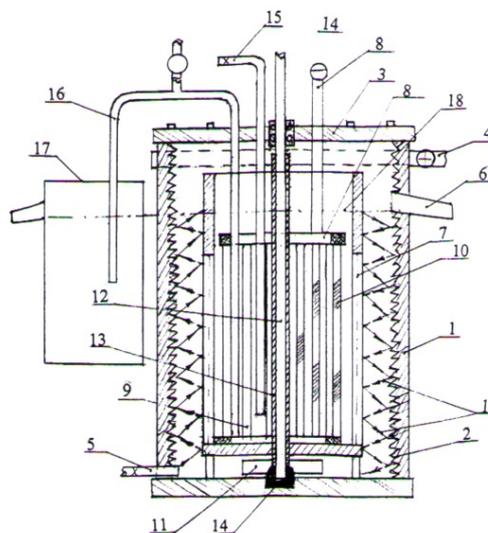


Figure 2. Electrochemical reactor

1-reactor body-graphite anode; 2-anode operating surface; 3-reactor cover; 4-current leading rim; 5-pulpsupplying branch pipe; 6-pulp discharging chute; 7- diaphragm-cathode cell; 8-cathode cassette with current lead; 9-cathodes; 10-carbon material tightly reeled up on the cathode; 11-pump-mixer; 12-pump driving shaft; 13-pump shaft isolating pipe enclosure casing; 14-pump shaft bearings; 15-catholyte supplying pipe; 16-siphon drain for spent catholyte; 17-inter-mediate vessel; 18- solution level; 19-trajectory of pulp circular movement

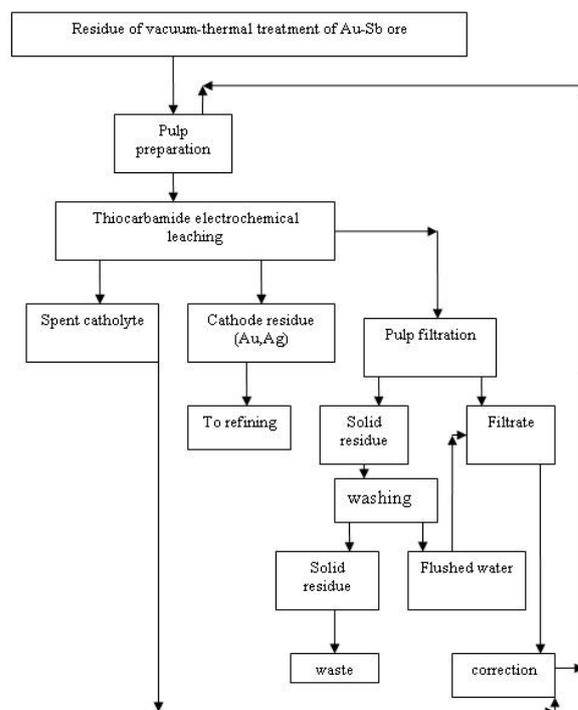


Figure 3. Basic technological scheme of electrochemical leaching of the residue of vacuum-thermal treatment of gold-containing antimony ore

Table 3. Research of technological process of gold extraction by electrochemical method from the residue of vacuum-thermal treatment of gold-containing antimony ore of Zopkhito deposit

#	Composition	Red/Ox potential, V	ϕ_a , V	T, °C	τ , hours	pH	Solid:Liquid ratio	σ , mm	I, A	U, V	W, Vt	Au recovery %	Remarks
I	0.5 M KCl + 0.35 M ThiO	0.435	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.007	0.7	0.0049	77	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.421	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.012	1.1	0.0132	81.8	potentiostatic regime
	0.5 M KCl + 0.65 M ThiO	0.419	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.017	0.75	0.0075	81.2	potentiostatic regime
II	0.5 M KCl + 0.5 M ThiO	0.423	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.012	1.1	0.0132	81.8	potentiostatic regime
	0.9 M KCl + 0.5 M ThiO	0.450	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.01	0.9	0.009	79.8	potentiostatic regime
	1.3 M KCl + 0.5 M ThiO	0.466	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.0081	0.8	0.0065	70.9	potentiostatic regime
III	0.5 M ThiO	0.454	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.031	1.83	0.057	63.6	potentiostatic regime
	0.5 M NaCl + 0.5 M ThiO	0.431	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.006	0.85	0.05	76.1	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO + 0.024 M Na ₂ SO ₃	0.453	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.017	1.57	0.027	83.2	potentiostatic regime
IV	0.5 M KCl + 0.5 M ThiO + 0.03 M Na ₂ S	0.438	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.04	1.75	0.07	82.9	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.422	0.4±0.05	22 °C	4	<1	1 : 3	-0.063	0.012	1.1	0.0132	81.8	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.427	0.4±0.05	27 °C	4	<1	1 : 3	-0.063	0.012	1.1	0.0132	81.8	potentiostatic regime
V	0.5 M KCl + 0.5 M ThiO	0.461	0.4±0.05	30-32 °C	4	<1	1 : 3	-0.063	0.016	1.1	0.0176	89.9	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.420	0.4±0.05	25 °C	2	<1	1 : 3	-0.063	0.057	1.25	0.071	80.4	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.427	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.011	0.9	0.01	81.8	potentiostatic regime
VI	0.5 M KCl + 0.5 M ThiO	0.430	0.4±0.05	25 °C	5	<1	1 : 3	-0.063	0.012	1.1	0.0132	81.8	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.426	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.012	1.1	0.0132	81.8	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.415	0.4±0.05	25 °C	4	<1	1 : 5	— ²² — ²³	0.012	1.1	0.0132	72.7	potentiostatic regime
VII	0.5 M KCl + 0.5 M ThiO	0.42	0.4±0.05	25 °C	4	<1	1 : 3	-0.05	0.01	0.95	0.0151	81.8	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.429	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.012	1.1	0.0132	81.8	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.458	0.4±0.05	25 °C	4	<1	1 : 3	-0.16	0.141	1.79	0.25	85.5	potentiostatic regime
VIII	0.5 M KCl + 0.5 M ThiO	0.426	0.4±0.05	25 °C	4	<1	1 : 3	-0.063	0.012	1.1	0.0132	81.8	potentiostatic regime
	0.5 M KCl + 0.5 M ThiO	0.518	0.5±0.05	25 °C	4	<1	1 : 3	— ²² — ²³	0.0136	1.65	0.022	83.6	potentiostatic regime

Thio=Thiourca

In the course of ore leaching in anode area the gold dissolving and the formation of the cathionite complex with thiourea takes place. The complex after migration through filtering, thermally treated perchlorovinyl diaphragm enters in cathode area where gold is discharged at the cathode, manufactured from carbon-fiber material and free ligand-containing solution is returned to anode area for pulp preparation.

The continuous technological scheme of the process of electrochemical leaching of the residue of vacuum-thermal treatment of the concentrate of gold-containing antimony ore is presented (Fig.3).

Thus on the basis of experimental results it may be concluded that the efficient processing of residue of vacuum-thermal treatment of gold-containing antimony ore of Zopkhito deposit is possible by 82-90 % gold extraction by electrochemical method using chloride electrolyte to which thiourea - selective complex former with gold is added. The process proceeds in the conditions of so-called "soft" oxidation without release of molecular chlorine and environmental contamination.

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