



ECO-SAFE METHOD FOR PROCESSING OF TECHNOLOGICAL RESISTANT ANTHROPOGENIC MINERAL RESOURCE

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The possibility of gold extraction from the concentrate obtained by secondary enrichment of flotation tails of Madneuli gold-containing barite-polymetallic ore has been studied. Such concentrate contains the gold in the mineral in finely-impregnated form and is considered as difficult-to-process material. It was shown that by the use of $\text{Fe}_2(\text{SO}_4)_3$ as an oxidizer in thiourea acidic solution, the concentrate preliminary milling and roasting at $400\text{ }^\circ\text{C}$ is necessary for the 90 % extraction of gold. By electrochemical method, the 90 % extraction is reached at the system "soft" oxidation in the conditions of Red/Ox potential of 0.4 V in temperature range of $25\text{-}35\text{ }^\circ\text{C}$.

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INTRODUCTION

The problem of gold extraction from resistant anthropogenic mineral resources may be considered as the most important ones which face modern gold-mining industry. Complex multistage schemes of enriching of mentioned ores do not allow the extraction of the ultra-dispersed gold in full measure. Therefore, in the most cases such mineral resources cannot be processed economically and ecologically-acceptable criteria.

Among anthropogenic waste, the enriched tails of the majority of sulfide ores, as the source of noble metals, are of significant interest. Moreover, their storage has a severe impact to the environment. The flows of natural and artificial leaching appear in underground and surface water.

The problem of processing of the above-mentioned mineral resources is topical for Georgia also. In tailing dumps of Madneuli Mining-Processing Combine up to 120 million tons of anthropogenic mineral resource is collected among which up to 27 million tons are flotation tails of enriching of sulfide mineral (barite-polymetallic and chalcopyrite) which contain more than 10 tons of gold and up to 120 tons of silver. Processing of such mineral by profitable technology is a prospective problem and hence investigations in this direction is topical.

EXPERIMENTAL

The objects of our research were gold-containing flotation tails of processing of barite-polymetallic ore. They contain 0.5 and 1.8 g ton^{-1} of gold and silver respectively.

In addition, Cu, Zn, Pb, S, Fe, Cd and Al_2O_3 are also present in amounts varying from 0.02 to 1.7 %. These tails contain 80-90 % quartzite, 3-6 % barite, 3 % pyrite, 3 % alunite 22 % kaolin, 1 % sericite and 2-3 % iron hydroxides. On the basis of mineralogical composition of those tails the procedure for secondary flotation enriching was selected. Flotation was carried out at laboratory flotation machine of mechanical type and at the test bench of flotation machine. Flotation of primary tails of barite-polymetallic ore was carried out by technological scheme presented in figure 1.

The tails were crushed in a wet mill for 5 min at a ratio of L:S = 1:1. Thereafter the suspension was delivered to a flotation machine of mechanical type where the flotation was performed in a the presence of collector ,butyl xanthate (60 g ton^{-1}) and foaming agent T-80 (50 g ton^{-1}). Reagents were delivered twice, at beginning of the process and after 10 min. Flotation duration was 18-20 min. Cleaning was performed by butyl xanthate (20 g ton^{-1}) and foaming agent T-80 (50 g ton^{-1}). Cleaned general concentrate was dried in a thermostat, crushed and sieved. Determination of elements concentration in enriching products was carried out by atomic absorption method. In table 1 the composition of secondary enriching flotation tails of barite polymetallic ore of Madneuli deposit is presented.

Table 1. Chemical composition of secondary concentrate of flotation tails of barite-polymetallic ore.

Au, g ton^{-1}	Ag	Zn %	Cu %	Fe %	S_{Tot} %	S_{SO_4} %	Ba, %
2.53	25.8	0.46	0.57	4.45	4.4	4.25	7.9

For gold extraction from flotation tails of secondary enriching of barite-polymetallic concentrate the researches were carried out by means of electro-chlorination and of chlorination by gaseous chlorine as well as by concentrate treatment by thiourea solutions.

RESULTS AND DISCUSSION

We have used electro-chlorination method earlier at processing of gold-containing secondary quartzite with gold extraction up to 85 %.¹ Advantages of this method lies in the

fact that generation of the oxidant, chlorine, is performed directly in the process of concentrate leaching. In electro-chlorination an intensification of mineral opening is carried out at the expense of its dissolving in cracks and structural imperfections and oxidation of sulfide sulfur.

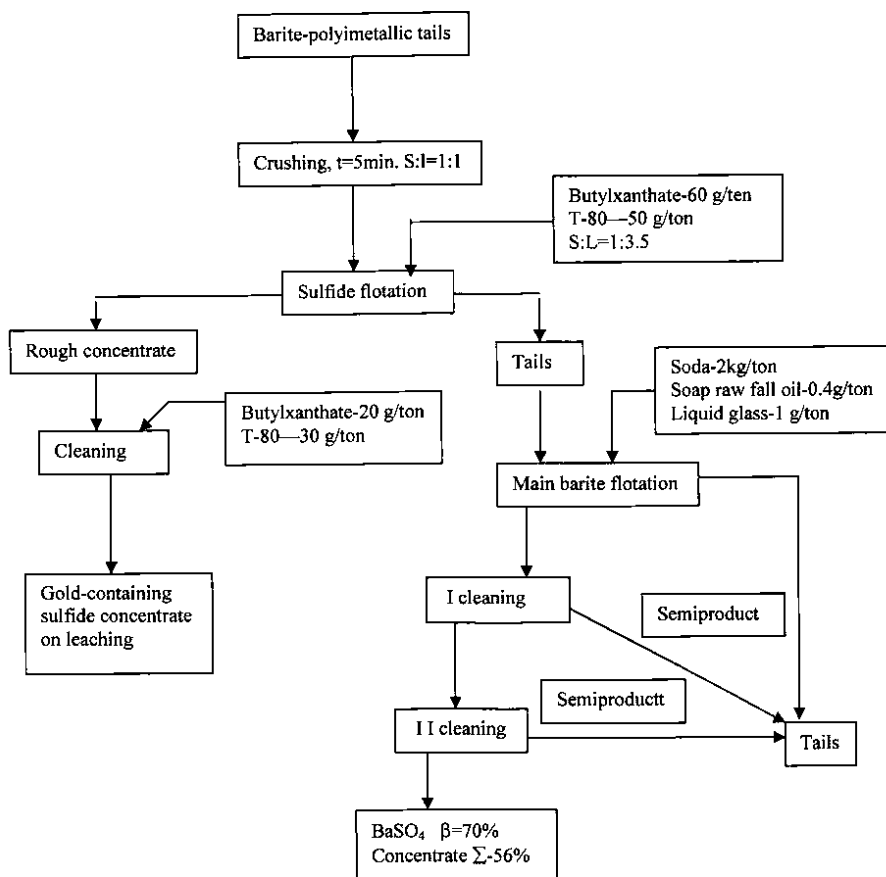


Figure 1. Scheme of flotation of primary tails of barite-polymetallic ore.

This process allows the access to deeply impregnated gold. The method was also tested at leaching of gold-containing concentrate of secondary enriching of barite tails. Their chemical composition is presented in table 1.

Electro-chlorination of the concentrate of the tails secondary enriching was performed by the procedure described previously for researches on treatment of gold-containing secondary quartzite.¹ The results are given in table 2.

As evident from table 2, leaching duration has no unambiguous regular effect on the process of extraction of gold and other components from the concentrate. The results remain within experimental reproducibility. Low gold extraction may be explained by incomplete opening of sulfide mineral. The comparison of the results obtained at leaching of mentioned concentrate by chlorination as well as by electro-chlorination methods are partly indicative of thereof (Table 3).

As evident from table 3, five-hour chlorination treatment of enriching tails in acid solutions gives lesser gold extraction than electro-chlorination treatment in the same conditions. This difference is more appreciable in alkaline solutions.

As evident from the data of table 1, concentrate, obtained by enriching of tails of barite - polymetallic ore, contains all components practically only in the form of sulfates. It may be suggested that among them non-soluble sulfates (Ba, Ca etc.) may be also presented which do not interact with oxidants (including anode ones) as well as with acids, bases and which may cause the gold passivity.

Hence, obtained results show that concentrate of tails of barite-polymetallic ore belongs to the group of rather resistant minerals and gold extraction by chlorination and electro-chlorination methods doesn't exceed 40-50 % which is indicative of the limit of capability of those methods for concentrate of given type.

Table 2. Effect of duration of electro-chlorination leaching of concentrate of flotation tails of enriching of barite - polymetallic ore.

No.	Duration, h	Power consumption, A h ⁻¹	Red/Ox potential, mV	Extraction degree of components, %				
				Au, g ton ⁻¹	Ag, g ton ⁻¹	Cu	Zn	Fe
1	2.5	8.15	675.0	48.5	61.0	61.0	58.0	46.0
2	2.5	5.32	880.0	-	57.0	38.0	36.0	42.0
3	5.0	10.75	688.0	40.6	57.0	43.0	40.0	38.0
4	5.0	11.5	805.0	48.5	57.0	46.0	48.0	42.0
5	8.0	22.33	855.0	54.4	65.0	67.0	69.0	38.0

Experimental conditions: electrolyte - NaCl-150 g L⁻¹; sample-200 g; temperature - 30 °C; pH - 0.5

Table 3. Chlorination and electro-chlorination treatment of concentrate of flotation tails of enriching of barite-polymetallic ore.

No	Systems	Process	pH	Red/Ox, mV	Degree of component extraction, %				
					Au, g ton ⁻¹	Ag, g ton ⁻¹	Zn	Cu	Fe
1	NaCl+HCl	Electro-chlorination	0.5±0.05	1052±50	48.6	85.0	73.0	67.0	54.0
2	NaCl+HCl	Chlorination	0.5±0.05	1069±45	40.7	85.0	77.0	63.0	50.0
3	NaOCl	Electro-chlorination	11±0.05	663±45	58.0	96.0	73.0	27.0	25.0
4	NaCl+NaOH	Chlorination	11±0.05	683±35	31.0	70.0	75.0	14.0	17.0

Experiment duration 5 h, temperature 40 °C.

It is suggested that concentrate resistance is caused by physical depression of gold by non-soluble barium sulfates. For gold extraction from gold-containing concentrate of barite tails the researches were also carried out by means of thiocarbamide solutions. This method was tested by authors of the work at leaching of secondary quartzite and high degrees of gold extraction were obtained (83 %).² Researches, performed on thiocarbamide leaching of concentrate of barite tails at room temperature, did not give desired results. Gold extraction degree slightly increased in comparison with above-mentioned methods and comprised 66 %, but the index is as yet low. Preliminary leaching of concentrate by solution of sulfuric acid at 70-80 °C causes the increase of gold extraction degree only by 3-4 % and comprised 69.8 %.

Table 4. Effect of roasting temperature on gold extraction degree from concentrate of barite tails at pre-treatment and at no-treatment.

No.	Roasting temp., °C	Degree of gold extraction without pre-leaching by sulfuric acid, %	Degree gold extraction at pre-leaching by sulfuric acid, %
1	400	89.2	82.3
2	500	86.4	72.0
3	600	88.0	79.7
4	700	75.6	73.6
5	800	86.3	66.5

Experimental conditions: roasting duration 2 h, sample 20 g, leaching duration- 4 h, S:L=1:5, concentration: Thiourea 2 %, Fe₂(SO₄)₃ 1 %, H₂SO₄ 1 %.

Table 5. Voltammetric characteristics of platinum electrode in various systems

No.	Current density mA cm ⁻²	Systems, Red/Ox, V		
		A	B	C
1	0	0.338	0.229	0.270
2	5	1.402	0.382	0.377
3	10	1.398	0.200	0.391
4	15	1.400	0.411	0.393
5	20	1.418	0.417	0.404
6	30	1.558	0.427	0.643
7	50	1.698	0.444	0.648

System A = 0.5 N KCl, B = 0.5 N KCl + 0.5 N Thiourea, C = 0.5 N KCl + 0.5 N Thiourea + 0.5 N HCl

Table 6. Electrochemical treatment of flotation concentrates of tails of barite- polymetallic ore

Parameter	Solution composition, g L ⁻¹		
	KCl-100	KCl-100; urea - 15	KCl-100, thiourea - 18
Red/Ox, V	1.0 ± 0.15	1.0 ± 0.15	0.4 ± 0.04
Gold extraction degree, %	54.0	64.3	87.1

Experimental conditions: *t* - 25 °C; *I_a* - 0.75 A cm⁻²; *m* - 200 g, duration 5 h.

Table 7. Electrochemical treatment of gravitational concentrates of chalcopyrite tails

No.	τ , h	T , °C	Red/Ox, V	Gold extraction degree, %
1	1.0	25.0	0.4 ± 0.04	30.0
2	3.0	25.0	0.4 ± 0.04	55.0
3	5.0	25.0	0.4 ± 0.04	86.0
4	5.0	30.0	0.4 ± 0.04	86.8
5	5.0	35.0	0.4 ± 0.04	87.4

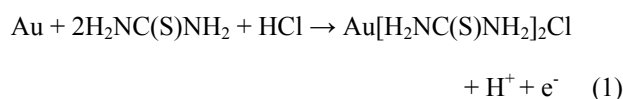
Experimental conditions: KCl 100 g L⁻¹, Thiourea 18 g L⁻¹, I_a 0.75 A cm⁻², m 200 g.

For complete removal of physical and chemical depressants of gold the roasting of secondary concentrate at temperature range from 400 °C to 800 °C and cinder leaching by thiourea solution was performed. After concentrate roasting at 400 °C gold extraction increased to 89 % and at further temperature growth gold extraction degree is slightly reduced.

In following series roasted concentrate was treated by acid before thiourea leaching. Experimental results are presented in Table 4. As evident, gold extraction degree from concentrate, roasted at 400 °C, reduced and comprised 82.3 %. At further growth of temperature reduction of gold extraction degree is more appreciable, at 800 °C this value reduced to 66 %. Experimental results have shown that pre-treatment of cinder by acid is non-productive. Because of the fact that roasting of gold containing concentrate of barite tails at 400 °C gives the best results, in the following series of experiments roasting was carried out in temperature range from 350 °C to 500 °C at additional grinding of concentrate. Results have shown that after roasting at 400 °C and fine grinding of concentrate (0.16 mm) and cinder treatment by thiocarbamide solution, gold extraction degree is notably increases and attains 93.4 %. At temperatures of 350 °C, 450 °C and 500 °C this value is roughly same i.e. 88-89 %

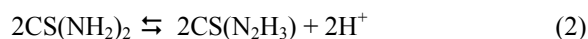
Experimental results have shown that re-grinding and roasting of concentrate is reasonable for complete opening of gold surface which is favorable for efficiency of further operations of gold extraction. But the use of pre-treatment (grinding, roasting) of concentrate under study before leaching with further extraction of noble metals from the solution is associated with a high power consumption.

Therefore for simplification of technology of processing of resistant sulfide ores and concentrates and for elaboration of eco-safe and highly efficient method of their processing the two methods, electrochemical and thiourea one, were combined. From the viewpoint of electrochemical dissolution of metals the resistant sulfide ores must be considered as system of sulfides in which fine-dispersed gold is impregnated. At the action of electrochemical reactions the electronegative elements of this system will be dissolved primarily. As a result of electrochemical dissolution of sulfides in anode space the destruction of mineral structure and opening of fine-dispersed mineralization of gold proceeds. By selective complex formation with free thiourea, present in the electrolyte, gold will pass to the solution in the form of cation complex (eqn.1).

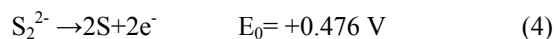
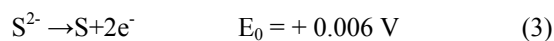


At the cathode the complex discharges and precipitation of metal results. This method provides the electrochemical treatment of resistant sulfide mineral (in the form of suspension or pulp) in chloride electrolyte, containing organic ligand for complex formation, thiourea.^{3,4} Variation of potentials at polarization of Pt - electrode in this solution is presented in Table 5.

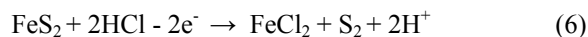
Introduction of thiourea in chloride solution is favorable for reduction of system Red/Ox potential from 0.8-1.2 to 0.35-0.45 V (Table 6). In accordance with,⁵ standard potential of reaction (eqn. 2).



is equal to + 0.42 V. Standard potentials of reactions,⁶



At the values of Red/Ox potentials of electrolyte systems under study (Table 5) passing of the following reactions is highly possible:



In Table 6 the results of the research of gold-containing concentrates of barite - polymetallic flotation by the use of various chloride systems are listed.

As evident, efficiency of gold extraction from given concentrate is attained only from electrolytes containing thiourea as a complex former. It also should be noted that electrochemical treatment of the 3-rd system was performed without ore pre-grinding and roasting of concentrate.

Similar results were obtained at electrochemical treatment of resistant gold-containing gravitational concentrates of chalcopyrite tails in mentioned systems (Table 7).

Conclusion

On the basis of results obtained, it may be concluded that resistant gold-containing flotation tails of enriched of barite-polymetallic ore may be efficiently processed by thiourea method (by grinding and pre-roasting of concentrate) with 94 % gold extraction as well as by electrochemical method (without grinding and pre-roasting of concentrate) with 90 % gold extraction. In the latter case an acid chloride electrode, pH 0.5-2 was used, containing 15-20 g L⁻¹ of selective organic complexing agent for noble metals, thiourea.

The process takes place in the conditions of “soft” oxidation regime, Red/Ox = 0.38-0.42 V, without separation of molecular chlorine and without environmental contamination. It should be noted that the latter method is reassuring, therefore, further the research will be continued in mentioned direction.

References

¹Gvelesiani, J., Gagnidze, Ts. Mamporia, M., Adamia, T., *Sak. Mets. Akad. Matsne, Khimii ser.*, **2006**, 32 (1-2), 167-175.

²Gvelesiani, G., Gaprindashvili, V., Mechurchlishvili, T., Shavgulidze, V., Chagelishvili, R., *Sak. Mets. Akad. Matsne. Khimii ser.*, **2000**, 25 (3-4), 315-328.

³Gagnidze, Ts., Gvelesiani, J., Mamporia, M., *Khsnari okroschemveli sulfiduri nedleulis gadamushavebisatvis, Sakpatenti*, **2011**, 5220.

⁴Gagnidze, Ts., Chagelishvili, R., Khavtasi, N., Nadareishvili, M., International Scientific Conference, *Modern Res. Prospects Use Chem., Chem. Eng. Related Fields*, September, 21-23, **2016**, Ureki, Georgia.

⁵Preisler, P., *J. Am. Chem. Soc.*, **1949**, 71, 2840.

⁶*Spravochnik Khimika*, v.III. Izdat. ”Khimia”. M., **1965**, 750.

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