Research of combined reagent schemes of activation leaching of gold from oxidized ores of the Malmyzh field

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Abstract. The results of studies of the cyanide and an alternative methods for leaching gold and silver from oxidized ores of the Malmyzh field are presented. The possibility of recovering gold and silver from oxidized porphyry copper ores by thiosulfate solutions in agitation and percolation modes without intensifying the process – heating the solutions and adding copper ions – has been shown. Also, in a separate cycle – copper leaching with low-concentration sulfuric acid-sulfite solutions with additional opening of the silicate matrix with ammonium hydrofluoride – has been studied. The possibility of using ammonia-thiosulfate leaching in percolation mode has been investigated.
Keywords: Malmyzh field, oxidized ores, gold, silver, copper, cyanide leaching, ammonia-thiosulfate leaching, sulfuric-sulfite leaching.

1 Introduction

The most efficient and common method for leaching gold and silver from oxidized and non-refractory primary ores is cyanide leaching. But, along with cyanides, thiosulfate leaching from poor, off-balance and cyanide-resistant ores is also used abroad. This is especially true for ores with a high silver content. Thiosulfates are considered one of the most promising low-toxic solvents for noble metals. The reviews [1, 2] have shown quite fully that thiosulfate leaching of valuable metals from ores is very promising, because has a lower negative impact on the environment in contrast to cyanides, which are highly toxic compounds. The process for recovering valuable metals in thiosulfate leaching is similar to that for cyanidation.

In the technology of processing noble metal ores from a large number of known solvents, thiosulfate salts are ecologically safer, since they are easily biodegradable [3]. This circumstance is reflected in the legislative acts of a number of European countries, the USA, Australia. Abroad, this process is used in a number of factories in the USA and Mexico [4]. In Uzbekistan, for the complex recovery of copper, gold and silver from tailings, heap leaching with an ammonium thiosulfate reagent was carried out at Almalyk Mining Plant [5]. Pilot-industrial and semi-industrial tests were also carried out in relation to carbonaceous ores. In Russia, studies of thiosulfate leaching were carried out at the Irgiredmet Institute, TsNIGRI (the Central Geological Research Institute for Nonferrous

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and Precious Metals), MISiS (the Moscow Institute of Steel and Alloys), and others [6, 7]. It was noted that to intensify the thiosulfate leaching process, it is recommended to add copper ions and heat the solution to 80 ° C [8], however, an increase in temperature above 60 ° C leads to a significant decomposition of the reagent while an introduction of copper sulfate into the solution significantly activates the decomposition of thiosulfate [9].

The authors investigated the possibility of agitation and percolation leaching of gold and silver from oxidized ore at the Malmyzh field with an ammonia solution of sodium thiosulfate, without using process intensification – heating the leaching solutions and adding copper ions, implying the presence of copper in the ore and its partial transition into solutions during leaching. To compare the degree of leaching, cyanide schemes were used as benchmarks.

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2 Methodology of Experimental Study

This work presents the results of a study of the processes of leaching of gold, silver and copper from samples TP-05S-O and TP-06S-O of oxidized porphyry copper ore from the Malmyzh deposit.

The laboratory sample TP-05S-O was taken from the ore interval of the AMM-052 well drilled at Svoboda site of the Malmyzh ore field for laboratory studies of its technological properties. The sample includes oxidized ores, mainly represented by entirely orchedized diorite-porphyrites completely disintegrated to sandy loamy clay. The sample is made up of 1/4 of the core of the AMM-052 borehole taken in the interval of 30.0-42.0 m.

The laboratory sample TP-06S-O was taken from the ore interval of the AMM-100 well drilled at Svoboda site of the Malmyzh ore field for laboratory studies of its technological properties. The sample includes only oxidized ores represented by highly fractured orchedized diorite-porphyrites. The sample is made up of 1/4 of the core of the AMM-100 borehole taken in the interval of 29.4-39.4 m. The ore body is represented by intensely limonitized and clayed diorite-porphyrites. A detailed mineralogical study of schlichs of gravity concentration is given in [10].

To establish the optimal regimes and parameters of leaching in laboratory conditions, testing for agitational leaching of precious metals from ore was carried out with the solutions of sodium cyanide at a concentration of C_{NaCN} – 0.15%, 0.35%, 1.0% and 3%, sodium thiosulfate 5-aqueous at a concentration $CN_{a2S2O3x5H2O}$ – 20%, 10%, and 5%. An aqueous ammonia solution was added to the sodium thiosulfate solutions until its concentration C_{NH4OH} was 10%, 5%, 3%, and 1% by volume. Conditioning of the pulp to pH> 9.5 during cyanide leaching was carried out by adding alkali – NaOH. The concentration of sodium cyanide in solutions was found titrimetrically. The concentration of elements in solutions, in initial samples and in samples after leaching was found by the atomic absorption method according to the guidelines approved by the Academic Council for Analytical Methods (NSAM).

3 Results and Discussion

Preliminary experiments have shown the fundamental possibility of direct leaching of non-ferrous and precious metals from the oxidized ore of the Malmyzh field using cyanide, ammonium-thiosulfate and sulfuric-sulfite solutions.

The results of the analysis of samples for the content of precious elements in them are presented in Table 1.

Table 1. Results of atomic absorption analysis of the samples under study.

Sample	Content			
	Au, g/t	Ag, g/t	Cu, %	Fe, %
TP-05S-O	0.84	5.01	0.082	10.56
TP-0S-O	0.81	0.56	0.089	12.2

3.1 Agitation cyanide and ammonia-thiosulfate leaching

In agitation mode, testing was carried out on samples of oxidized ore after its crushing to a class of -0.074 mm (60%), with a ratio of S:L = 1:2, the contact time of the phases being 4 hours per 1 stage. Leaching solutions were prepared immediately before the experiment. The results of the study of the process of agitational leaching of metals from ores with cyanide and thiosulfate solutions during stage 1 are presented in Tables 2 and 3.

Table 2. Results of agitational leaching from sample TP-05S-O

TP-05S-O		pH	Recovery, %			
Scheme			Ag	Au	Cu	Fe
1	C_{NaCN}=0,15%	>9.5	95.7	92.5	9.7	0.07
2	C_{NaCN}=0,35%	>9.5	95.7	96.1	11.8	1.08
3	C_{NaCN}=1,0%	>9.5	92.9	87.0	10.6	1.56
4	C_{NaCN}=3%	>9.5	95.1	98.7	10.1	1.85
6	$C_{Thios /NH4OH-20/10 (\%)}$	10.1	93.1	91.5	2.09	0.00
7	$C_{Thios /NH4OH-10/5 (\%)}$	9.8	93.1	90.5	1.84	0.00
8	$C_{Thios /NH4OH-5/3 (\%)}$	8.6	90.4	55.6	0.99	0.00
9	$C_{Thios /NH4OH-5/1 (\%)}$	6.0	91.2	13.3	7.12	0.02

Table 2 shows that the leaching of gold and silver with cyanide solutions of various concentrations from TP-05S-O sample provides approximately the same effect and ranges from 87.0% to 98.7% for gold, and 92.9-95.7% – for silver. The recovery of copper did not exceed 11.8% at a concentration of C_{NaCN} = 0.35%. With an increase in the concentration of cyanides in the solution, the iron yield increases – from 0.07% at C_{NaCN} = 0.15% to 1.85% at C_{NaCN} = 3.0%.

With thiosulfate-ammonia leaching, the recovery of silver is equally high at various concentrations of sodium thiosulfate, ammonia and pH values, and amounted to 90.4-93.1%, which is quite comparable to cyanide leaching with C_{NaCN} = 0.15%. The recovery of gold decreases with a decrease in the concentration of sodium thiosulfate and amounted to 91.5% at a concentration of $C_{Na2S2O3x5H2O}$ = 20%, NH_4OH = 10%, while at a concentration of $C_{Na2S2O3x5H2O}$ = 5%, NH_4OH = 1% it was 13.3%.

Table 3. Results of agitational leaching from sample TP-06S-O

TP-06S-O		pH	Recovery, %			
Scheme			Ag	Au	Cu	Fe
1	C_{NaCN}=0,15%	>9.5	75.0	99.6	3.78	0.05
2	C_{NaCN}=0,35%	>9.5	74.0	98.7	4.45	0.83
3	C_{NaCN}=1,0%	>9.5	71.3	98.6	4.20	1.41
4	C_{NaCN}=3%	>9.5	73.1	98.3	4.31	1.63
6	$C_{Thios/NH4OH-20/10\ (\%)}$	10	74.6	99.4	1.06	0.00
7	$C_{Thios/NH4OH-10/5\ (\%)}$	9.6	71.2	88.5	0.62	0.00
8	$C_{Thios/NH4OH-5/3\ (\%)}$	9.4	66.5	54.8	0.45	0.00
9	$C_{Thios/NH4OH-5/1\ (\%)}$	5.3	74.0	16.0	2.25	0.03

Similar results were obtained for the TP-06S-O sample. The recovery over the entire range of applied sodium cyanide concentrations is the same, and ranges for silver from 71.3% to 75%, for gold from 99.6% to 98.3%. With thiosulfate-ammonia leaching, the recovery of silver is equally high at various concentrations of sodium thiosulfate, ammonia and pH values, and amounted to 66.5-74.6%, which is quite comparable with cyanide leaching with C_{NaCN} = 0.15%. As seen from Table 3, gold recovery decreases with a decrease in the concentration of sodium thiosulfate and amounted to 99.4% at a concentration of $CN_{a2S2O3x5H2O}$ = 20%, C_{NH4OH} = 10%, while at a concentration of $C_{Na2S2O3x5H2O}$ = 5%, C_{NH4OH} = 1% it was 16.0%.

Leaching of gold with a thiosulfate-ammonia solution with a concentration of $C_{Thios/NH4OH}$ 20/10% in terms of the degree of recovery under the same conditions approaches the degree of leaching with a 0.15% cyanide solution. These concentrations are optimal for gold. With regard to copper and iron, under these conditions, the degree of leaching of those metals is minimal. For silver, it is possible to reduce the concentration of sodium thiosulfate and ammonia to minimum values, without losing the percentage of recovery.

3.2 Percolation ammonia-thiosulfate and sulfuric-sulfite leaching

Testing of oxidized ore in percolation mode was carried out in laboratory percolators, using weighed samples crushed to -1 mm class, in two stages. At the first stage, percolation leaching was carried out with ammonia-thiosulfate solutions; at the second stage, an attempt was made to leach copper with a sulfuric acid-sulfite solution with the addition of ammonium hydrofluoride to break open the oxidized "bound" forms of copper. For thiosulfate leaching, 5 drain cycles, for sulfuric acid-sulfite drainage – 17 cycles were applied. The results of the study of the percolation leaching process are shown in Tables 4 and 5.

The degree of leaching of noble metals by ammonia-thiosulfate solutions using the percolation method is not high enough than using the agitation method and, on average, silver recovery decreased by 33% for the TP-05-O sample and 17% for the TP-06-O sample. It should be noted that the recovery of gold during percolation leaching with ammonia-thiosulfate solutions also decreases with a decrease in the concentration of sodium thiosulfate and amounted to 40.12% and 48.24% at a concentration of $C_{Na2S2O3x5H2O}$ = 20%, C_{NH4OH} = 10%, while at a concentration of $C_{Na2S2O3\%x5H2O}$ = 5%, C_{NH4OH}- = 1%, it was 16.19% and 16.26% for TP-05-O and TP-06-O samples, respectively.

Table 4. Results of percolation leaching from sample TP-05S-O

TP-05S-O		pH	Recovery, %			
Scheme			Ag	Au	Cu	Fe
1	$C_{Thios/NH4OH-20/10\ (\%)}$	10.7	60.19	40.12	5.32	0
	$C_{Na2SO3+H2SO4}$	<2.0	2.42	16.40	27.62	45.34
2	$C_{Thios/NH4OH-10/5\ (\%)}$	10.4	60.02	32.18	5.82	0
	$C_{Na2SO3+H2SO4}$	<2.0	2.25	15.45	26.53	54.90
3	$C_{Thios/NH4OH-5/3\ (\%)}$	9.3	50.99	20.02	5.48	0
	$C_{Na2SO3+H2SO4}$	<2.0	2.45	17.83	26.57	35.40
4	$C_{Thios/NH4OH-5/1\ (\%)}$	8.3	54.24	16.19	6.43	0
	$C_{Na2SO3+H2SO4}$	<2.0	2.57	15.92	29.75	45.72

Table 5. Results of percolation leaching from sample TP-06S-O

TP-06S-O		pH	Recovery, %			
Scheme			Ag	Au	Cu	Fe
1	$C_{Thios/NH4OH-20/10\ (\%)}$	10.5	43.69	48.24	2.01	0
	$C_{Na2SO3+H2SO4}$	<2.0	15.03	13.44	36.39	40.02
2	$C_{Thios/NH4OH-10/5\ (\%)}$	10.2	43.55	26.28	2.07	0.00
	$C_{Na2SO3+H2SO4}$	<2.0	15.87	10.53	36.11	42.40
3	$C_{Thios/NH4OH-5/3\ (\%)}$	9.1	47.17	18.35	1.82	0.00
	$C_{Na2SO3+H2SO4}$	<2.0	15.42	14.68	35.90	39.95
4	$C_{Thios/NH4OH-5/1\ (\%)}$	6.1	35.44	16.26	2.32	0.01
	$C_{Na2SO3+H2SO4}$	<2.0	13.81	15.11	37.14	37.69

As one can see (Tables 4 and 5), copper leaching became possible when using a sulfuric acid-sulfite solution with the addition of ammonium hydrofluoride, and amounted to 33.38% for the TP-05-O sample and 38.44% for the TP-06-O sample.

4 Conclusions

Testing carried out on oxidized ores of the Malzhyzh field with a low metal content showed the possibility of direct ammonia-thiosulfate leaching of noble metals without additional intensification of the process: heating the solution and introducing copper ions, and the rate of leaching with thiosulfate solutions is comparable to the rate of leaching of noble metals by cyanide solutions.

Analyzing the data obtained, it can be noted that when using different concentrations of ammonia-thiosulfate solution, it is possible to ensure selective leaching of precious metals and copper from the ore. At the concentration of sodium thiosulfate and ammonia $C_{Na2S2O3x5H2O}$ = 5%, C_{NH4OH} = 1%, mainly silver is recovered, with additional strengthening of the solution to $C_{Na2S2O3x5H2O}$ = 20%, C_{NH4OH} = 10%, mainly gold gets into the solution.

Using a sulfuric acid-sulfite solution with the addition of ammonium hydrofluoride, the possibility of subsequent copper leaching is ensured.

As a result of the study performed on leaching two samples of oxidized ore from weighed portions with sodium thiosulfate solutions of various concentrations, the possibility of selective leaching of gold and silver from them has been shown, which is especially important for the development of an environmentally friendly technology for processing refractory ores with a low precious metal content.

The results of the research performed to study the processes of leaching of precious metals with combined reagents can serve as a basis for creating new technological schemes for the integrated use of substandard mineral raw stock that reduce the use of toxic cyanide solvents.

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