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Research Paper

Arsenic behavior in the autoclave-hydrometallurgical processing of refractory sulfide gold-platinum-bearing products

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Abstract

Among various types of gold-bearing ores a special place belongs to the ores, which contain gold finely-dispersed in sulphide minerals, mostly in arseno-pyrite and pyrite. Autoclave-hydrometallurgical processing technologies for such raw materials seem to be of a particular interest for study. However, autoclave oxidation of sulfide-arsenic material results in significant amounts of technological solutions with high concentrations of arsenic, iron and sulfuric acid.

This article represents the studies of how arsenic behaves in autoclave oxidative leaching of a refractory sulphide gold-platinum-bearing concentrate. We studied how the composition of arsenic-bearing solutions in autoclave leaching (acidity, concentration of iron and arsenic) influences the depth of arsenic precipitation when neutralized with calcium-containing reagents, which allows converting the maximum amount of arsenic together with iron in the form of iron arsenate into a stable long-term storable precipitation.

Keywords: *Refractory Sulphide Gold-Bearing Ores; Arsenic; Autoclave Oxidative Leaching; Neutralization; Iron Arsenate; Arsenic-Bearing Precipitation.*

1. Introduction

Currently, the share of gold, recovered from technologically simple gold ores, is steadily decreasing, which necessitates more efficient processing of refractory sulphide gold-bearing materials. One of the ways to intensify the liberation process of refractory sulphide gold-bearing ores is their autoclave-hydrometallurgical processing [1-4].

The autoclave treatment of pyrite-arseno-pyrite gold-bearing raw materials involves oxidation of arsenic and iron sulfide compounds at elevated temperatures and pressures, which destructs sulfide minerals and ensures a high level of gold recovery upon a subsequent sorption cyanidation of the autoclaved solid residue [5-7]:

$2FeS_2+7O_2+2H_2O=2FeSO_4+2H_2SO_4$;

$4FeAsS+13O_2+6H_2O=4FeSO_4+4H_3AsO_4$.

Autoclave oxidation of sulfide-arsenic material generates large amounts of technological solutions with high concentrations of arsenic, iron and sulfuric acid. The composition of autoclave solutions depends on the composition of gold-bearing ores and characteristics of their autoclave processing [5,6].

When purified from impurities, those autoclave leaching solutions are used as recycle water, while surpluses are wasted into the surface watercourses. Since arsenic is a toxic impurity, it is undesirable to accumulate it in recycle liquids, and arsenic concentration in the wasted waters should not exceed the maximum permissible values [7], [8].

Since autoclave solutions have sulphate, iron and arsenic in their composition, a promising method to remove arsenic from the technological cycle is joint precipitation of arsenic together with iron during neutralization of the solution with calcium-bearing reagents to form iron arsenate, stable and long-term storable in the tailing pond [7-12].

Thus, it is critical to study how characteristics of autoclave oxidative leaching of refractory sulphide gold-planinum-bearing products influence arsenic pass to the liquid phase of the pulp and how the composition of resulting solutions (acidity, iron and arsenic concentration) influences the depth of arsenic precipitation when neutralized with calcium-bearing reagents.

2. Research methods

We used the Parr laboratory autoclave plant to conduct experiments and study how characteristics of autoclave oxidative leaching of pyrite-arseno-pyrite gold-bearing raw materials influence pass of iron and arsenic to liquid products. The chemical-mineralogical analysis (see results in Table 1), made by means of CamScan S4 scanning electron microscope with an energy dispersive spectrometer and ISIS Oxford Instruments micro-assay system, shows that the test refractory material contained 40% of pyrite, 13% of arseno-pyrite.

Table 1: Chemical Composition of the Refractory Gold-Bearing Concentrate

Mass fraction of the component, %											Au, g/t	PGMs, g/t
As	Fe	S	Cu	K	Ca	Zn	Pb	Mg	Sb	Mn		
6,03	24,54	23,65	0,106	0,931	0,528	0,091	0,031	0,394	0,02	0,05	35	0,1

The primary solutions used to study the neutralization process were liquid phases of oxidized pulps of pyrite-arseno-pyrite ores concentrates, with the ores taken from various deposits: As: 0.5-5.5 g/l; Fe: 11-23 g/l; and H_2SO_4: 20- 60 g/l. The solutions were neutralized at the temperature of 60-90°C, mechanically mixed with calcium neutralizers (limestone/lime), and the pulp was constantly aerated to facilitate the oxidation of ferrous iron. The neutralizer was fed in small portions; with pH of the pulp recorded and the mixing time lasting for 40-60 minutes. The neutralized pulps (pH>7) were stored in glass jars, and samples of the liquid phase were periodically taken in order to determine their chemical composition.

3. Research results

Table 2 shows influence of autoclave oxidative leaching (AOL) on arsenic and iron distribution in the autoclave pulp.

Table 2: Influence of AOL Conditions on Arsenic Distribution in the Autoclave Pulp

№	Liquid–Solid Ratio	t, °C	P_{O2}, atm	Time of libera-tion, min	Consum-ption,% of the concentrate		Residue yield,%	Content in solution, g/l				Recovery, %	
					$CaCO_3$	H_2SO_4		Fe (II)	Fe (III)	As	H_2SO_4	Fe	As
1	6,0	190	7,2	43	0	0	67,1	1,45	22,5	1,73	35,6	64,4	33,7
2	6,0	200	7,2	30	0	0	74,5	1,09	19,1	1,95	42,7	52,5	19,7
3	6,0	225	7,3	20	0	0	3,0	0,77	10,1	1,86	51,0	30,4	19,2
4	2,2	190	7,2	120	0	0	70,4	0,61	56,2	13,1	97,0	57,5	50,3
5	12,0	190	7,2	40	0	0	82,7	1,14	3,33	0,51	30,9	40,3	12,4
6	5,0	190	7,2	87	9,6	0	82,0	2,51	18,4	2,89	38,7	58,0	30,0
7	5,0	190	7,2	59	19,2	0	96,4	1,68	16,9	2,11	29,9	48,6	22,5
8	5,0	190	7,2	88	38,4	0	146,7	2,51	4,55	0,25	19,3	20,1	1,20
9	6,0	190	7,2	44	0	30	60,9	2,11	29,3	4,24	77,9	71,8	29,6
10	6,0	190	7,2	60	0	90	36,8	1,30	49,0	14,8	117	97,5	98,0

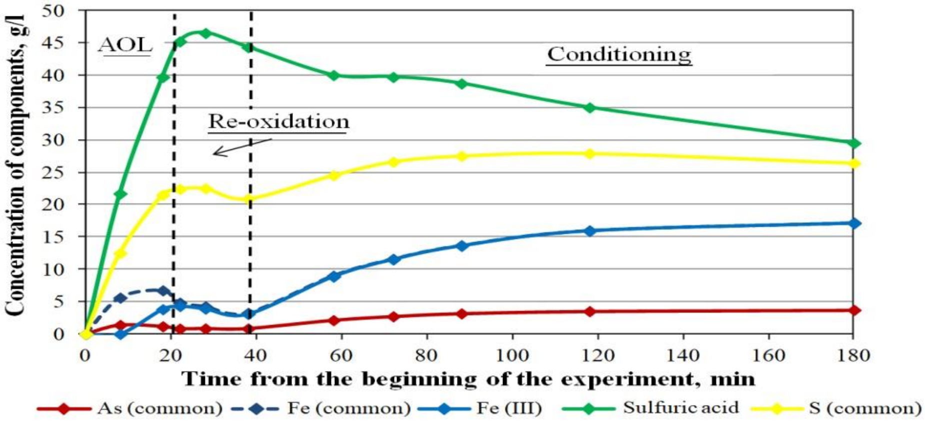


Fig. 1: Influence of Autoclave Product Processing Operations on the Composition of the Liquid Phase of the Pulp.

Under normal AOL conditions (experiment № 1, Table 2), ~ 30% arsenic and ~ 65% iron passes into solution. An increase in the temperature of autoclave liberation from 190 to 225°C reduces dissolution of arsenic by ~ 20% and of iron by ~ 30% (experiments №1-3), with simultaneous increase in the autoclave pulp acidity and the yield of the solid.

Increased concentration of the solid in the AOL pulp (with other characteristics remaining unchanged) from L/S=12:1 to 2:1 leads to an increased acidity of the pulp and increased recovery of arsenic into solution from 12 to 50% (experiments № 4-5). Adjustment of the autoclave pulp acidity by adding limestone or sulfuric acid (experiments № 6-10) confirms that increased concentration of sulfuric acid (artificially added to leaching) promotes recovery of arsenic and iron into solution, while limestone, on the contrary, suppresses this process.

In order to increase gold recovery and reduce the burden on the sorption cyanidation process (reduction of the solid phase mass delivered from the autoclave), the oxidation process scheme includes re-oxidation (exposure of the pulp to the autoclave leaching temperature) and autoclave pulp conditioning (exposure of the pulp to atmospheric pressure and high temperature). Those two stages added to processing of beneficiation concentrates of refractory gold-bearing ores result in significant changes in the composition of the liquid phase of the oxidized ore. In the course of re-oxidation iron is hydrolyzed, which decreases iron concentration in the solution and increases the yield of the autoclave cake. Conditioning allows us to dissolve most of the basic ferrous sulphates that precipitated during hydrolysis at the stage of autoclave leaching and re-oxidation. When the pulp is conditioned, iron passed into solution accompanied by dissolution of arsenic (Figure 1).

We have established that precipitation of arsenic in neutralization of ferrous sulfate and arsenic-bearing solution has three well-marked stages:

1) st: intensive precipitation of the bulk of arsenic, with the pH range of 1.5-1.8;
2) nd: reduction of arsenic concentration in the solution to minimum values (pH=3.5-5.0);
3) rd: partial reverse pass of arsenic into the solution (pH>5,0).

The composition of the primary solution at the initial neutralization stage (pH<2.0) practically does not affect the behavior of iron and arsenic (Fig. 2). Within the pH range of 0.2-1.3, the neutralization of acid is accompanied by generation of gypsum, while the concentrations of arsenic and iron in the solution remain practically unchanged. Within the pH range of 1.3-2.0, most of iron and arsenic contained in the solution precipitates out: for the primary solution with arsenic and iron contents of 0.53 and 18.40 g/l, respectively, the residual arsenic concentration was 0.006 g/l; for the solution with arsenic and iron content of 1.13 and 22.50 g/l - 0.005 g/l; for the solution with arsenic and iron content of 1.68 and 13.70 g/l - 0.007 g/l; for the solution with arsenic and iron content of 3.60 and 14.15 g/l - 0.09 g/l. In the solid phase samples, taken for the pH range of 1.3-2.0, iron was found as basic ferrous sulphate. X-ray phase analysis of these precipitates does not detect arsenic; however its content is 1.5-3.0%, which proves its co-precipitation with a finely-dispersed X-ray amorphous iron-bearing phase.

We found out that changes in the ratio of iron/arsenic concentrations in the primary solution does not change the pattern of the arsenic precipitation, but rather determines the depth of arsenic precipitation within the pH range of 3.5-5.0 (Fig. 3). The value of the minimum arsenic concentration within this pH range was determined by the ratio of iron/arsenic concentrations in the primary solution: thus, the ratio of Fe:As=3-4 corresponded to a residual arsenic concentration of 0.5 mg/l; for the ratio of Fe:As=5.5 a residual arsenic concentration made 0.25 mg/l and for the ratio of these two components in the initial solution 8 and above a residual arsenic concentration did not exceed 0.05 mg/l [13].

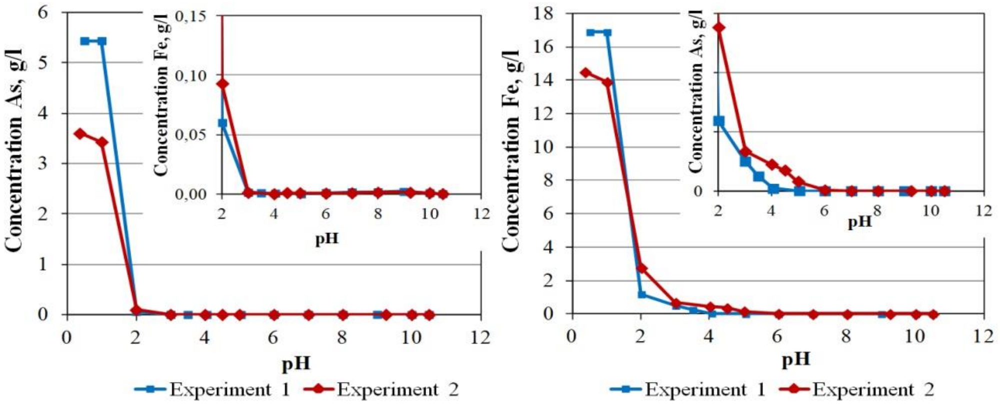
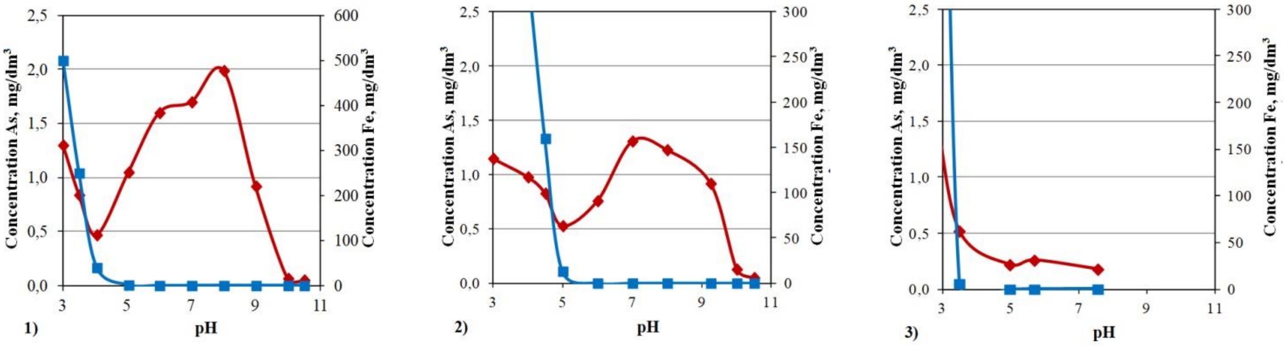


Fig. 2: Concentrations of Iron and Arsenic at Different Ph Values during Neutralization of the Liquid Phase of the Oxidized Pulp.

Concentration in the primary solution, G/Dm^3: Fe - 16,9; As -5,4

Concentration in the primary solution, G/Dm^3: Fe - 14,5; As -3,6

Concentration in the primary solution, G/Dm^3: Fe - 11,1; As - 2,02



Concentration in the primary solution, G/Dm^3: Fe - 13,7; As - 1,68

Concentration in the primary solution, G/Dm^3: Fe - 22,5; As - 1,13

Concentration in the primary solution, G/Dm^3: Fe - 18,4; As - 0,53

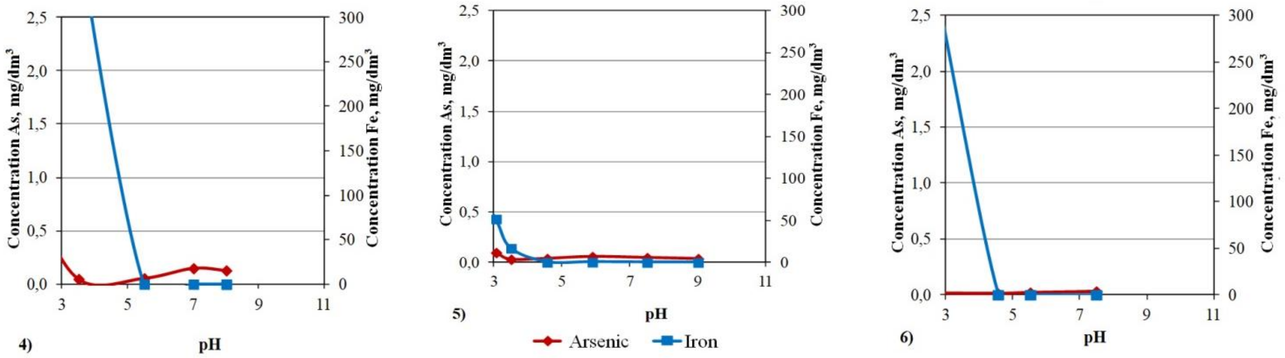


Fig. 3: Influence of the Composition of the Primary Solution on Co-Precipitation of Iron and Arsenic.

After reaching its minimum, arsenic concentrations growth was declining progressively to the rising ratio of the components concentration in the primary solution, and when the ratio reached 19.9, there was no evidence of growth at all. This can be explained by iron deficiency in case of a low ratio of iron/arsenic concentrations in the liquid phase of the pulp at the second precipitation stage (pH>3.0), which leads to precipitation of calcium arsenate together with iron arsenate. At pH 4.5-5.0, calcium arsenate reacts with carbon dioxide contained in the air to form calcium carbonate, and arsenic passes into solution.

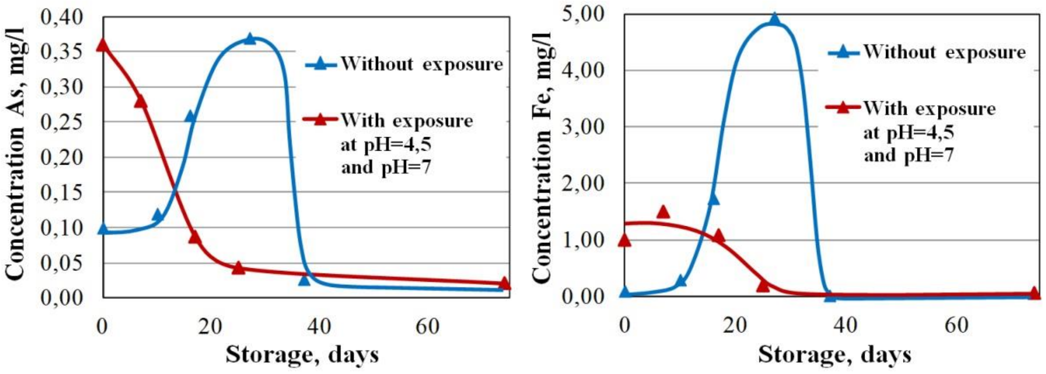
There are several variants of autoclave-hydrometallurgical processing of refractory gold-bearing ores; some offer to filter the pulp after neutralizing the autoclave solution and store the "dry" cake at the tailing pond, while others offer to dump the thickened pulp or non-dehydrated pulp and take the clarified solution from the tailing pond as recycle water.

Throughout the storage of arsenic-bearing products, unstable compounds of arsenic and iron are destroyed. At the same time, other, more stable compounds are formed, making the two elements bound. The conflict of these processes leads to fluctuations in concentrations of these components in the liquid phase of the pulp/stored cake.

We found out that when neutralized at temperatures below 60°C, iron precipitates as amorphous hydroxides and basic sulfates. The x-ray phase analysis of neutralization cakes at 90°C showed that the solid phase of samples contains jarosites - crystalline basic iron sulfates. X-ray phase analysis did not detect any arsenic-bearing phases (iron and calcium arsenates) in neutralization cakes due to their low content.

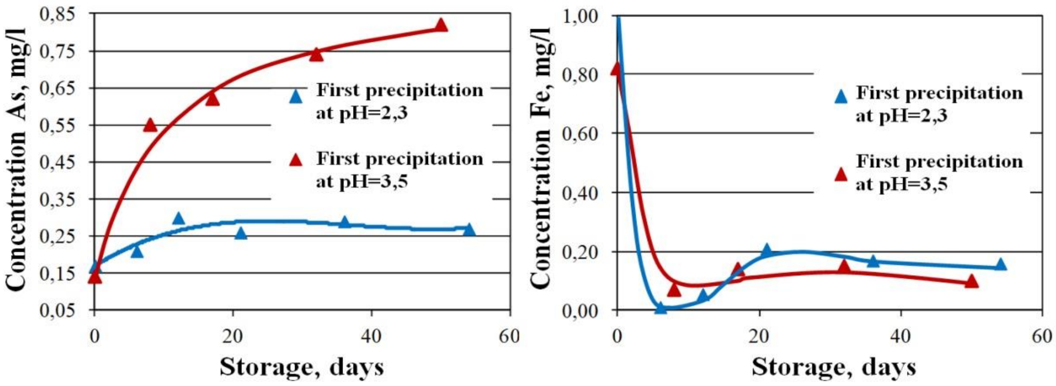
It was found out that with a rapid change in pH of the pulp during neutralization, the proportion of unstable arsenic-bearing compounds, precipitated in the solid phase, increases. When storaged these compounds re-crystallize, with some arsenic and iron passing into the solution. Thus, an increased rate of neutralization can contribute to a declining stability of the solid phase stored in the tailing ponds. Figure 4 shows analysis of the liquid phase during the storage of the neutralization pulps obtained after neutralization of the autoclave solution (As-2.58 g/l, Fe-20.3 g/l, H_2SO_4-37 g/l) with different limestone feed rates.

For pulps obtained after neutralization of the autoclave solution (As-1.68 g/l, Fe-13.7 g/l, H_2SO_4-37 g/l) at high temperatures (90-95°C) with precipitation at different stages, it is typical for arsenic to pass into solution in the initial stages of storage. Further on, the growth in arsenic concentration slows down and a gradual decrease begins. We found out that the lower the pH of the first stage precipitation is, the more stable the solid phase precipitated in the neutralization is (Fig. 5). The most stable long-term storable precipitations were obtained through a stepwise neutralization.



a). b).

Fig. 4: Influence of the Neutralizer Feed Rate (Limestone, at 60°C) on the Subsequent Pass of Arsenic (A) and Iron (B) to the Liquid Phase of the Pulp During Storage



a). b).

Fig. 5: Behavior of Arsenic (A) and Iron (B) During Storage of the Pulp Obtained after Neutralization of the Autoclave Solution for Various Initial Precipitations (T=90°C).

Based on the arguments given above, the most preferable neutralization is a 3-staged neutralization of solutions of autoclave oxidation at 90°C (pH=1.6-1.8; pH=4.0-4.5, duration 0.7-1.0 hours each, neutralizing agent: limestone pulp; adjusting to pH=7.5, neutralizing agent: lime), with a seeding agent for the 1st stage taken from the 2nd neutralization stage, in the amount of 5-7% of the total solid phase.

Given the high pulp filtration rates after the solutions of autoclave leaching of refractory gold-bearing materials are neutralized with calcium-based agents (1.0-1.2 $t/(m^2 \cdot h)$), it is possible to filter the pulp after the second precipitation stage and to feed the filtrate into the final stage of neutralization - adjusting pH to 7.5-8.5. Low content of arsenic in the filtrate, fed into the final stages of neutralization, will ensure required concentration of arsenic in the liquid phase of the pulp wasted into water. The cake received after filtration of the pulp in the second neutralization stage can be used as a seed for a recycled precipitation.

4. Conclusions

An increase in the autoclave recovery temperature from 190 to 225°C reduces recovery of arsenic into solution by 20% and of iron by 30%. Increased concentration of the solid in the AOL pulp (with other characteristics remaining unchanged) from L/S=12:1 to 2:1 leads to an increased acidity of the pulp and increased recovery of arsenic into solution from 12 to 50%, of iron - from 40 to 57%.

Re-oxidation and conditioning of the oxidized autoclave pulp lead to a significant change in the weight of the gold-bearing precipitation (reduction by 30-40%), accompanied by an increase in the concentrations and ratio of iron/arsenic in the liquid phase of the pulp.

The ratio of iron/arsenic concentrations is the main factor determining the value of the residual concentration of arsenic in the liquid phase after neutralization of leaching solutions of arsenic-bearing sulfide concentrates. When purifying arsenic-bearing sulfuric acid solution, the minimum concentration of arsenic can be achieved within the pH range of 3.5-5.0, amounting to 0.25-0.5 mg/l for Fe:As ratio<6 in the primary solution; 0.05 mg/L and less for the Fe:As ratio>8. The most stable long-term storable precipitations are obtained through a stepwise neutralization.

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