Journal of Contemporary Issues in Business and Government Vol. 27, No. 1, 2021
P-ISSN: 2204-1990; E-ISSN: 1323-6903
https://cibg.org.au/

Investigation Of Changes In The Concentration Of Metals In The Process Of Bacterial Oxidation Of Flotation Concentrate

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Abstract. The article deals with the behavior of the most important cationic elements, which directly affect the processes of bacterial oxidation of sulfide ores. These are iron, calcium, selenium, arsenic, various modifications of sulfur. In addition to this, data are presented on the appearance of new compounds that promote the dissolution of precious metals, which are selenites, thiosulfates, hydrochloric acid and nitric acid. The main physical and chemical parameters of the studied samples of the bacterial oxidation chain are determined. Possible transformations of the main minerals are established. The tables and figures provide information about changes in the concentration of the main elements during bacterial oxidation. the reasons for changes in the concentration and appearance of new minerals are discussed. The questions of the behavior of organic carbon, the possibility of its activation and the ability to absorb noble metals are covered.

Keywords: sulfides, arsenopyrite, biooxidationation, ferrooxidance, floatation.

1. INTRODUCTION

If we look at the table of chemical elements of DI Mendeleyev, we note that sulfur compounds are characteristic for elements located almost exclusively on the right side of this table, especially for metals of the so-called secondary series of the periodic system. The same can be said about selenium, telluride, arsenic and other compounds. The pronounced affinity of sulfur with heavy metals is manifested in the fact that it forms almost sulfur-free compounds that are almost insoluble in water. In contrast, similar compounds of most light metals (Na, K, Mg, etc.) are established only in the dissolved state in the waters. Chemically, the compounds are often compared with oxygen compounds - simple oxides and oxygen salts. Indeed, in the chemical formulas of these types of compounds there are common features (for example, Cu_2O and Cu_2S, HgO and HgS, Sb_2O_3 and Sb_2S_3, etc.).

As the available X-ray data show, sulfides and similar compounds should be assigned to ion covalent compounds, sometimes with some involvement of a metal bond. Most of them are very different from typical ionic oxygen compounds for a number of very characteristic properties and are much closer to native elements than to oxides and oxygen salts. These differences are due to the properties of the atoms or ions themselves, which are part of sulfide, selenide, telluride, arsenic and antimony compounds.

The phenomenon of polarization leads to the fact that in the crystalline structures there is a significant unification and delocalization of the electrons of neighboring oppositely charged ions, which can be inferred by the metallic luster characteristic of generally typical metals, which is clearly pronounced for most sulfides and similar compounds. With this, the electrical conductivity of most sulfurous, arsenic and other compounds is also easily linked. This explains the sometimes observed lack of metal atoms in comparison with the atoms of non-metals (for example, in pyrrhotite-Fe1-XS), the frequent absence of strict Daltonian relationships in the composition of minerals, etc.

In compounds with S, Se, Te, the metallic properties increase as sulfur is replaced by selenium and tellurium. In the series of the iron family, the enhancement of these properties occurs as we approach Mn to Ni. The same can be seen in the series As, Sb and Bi, where the metallic properties are enhanced as they approach bismuth. Indeed, bismuthine (Bi_2S_3) is characterized by a stronger metallic luster than the antimonite (Sb_2S_3), whereas the auripigment (As_2S_3) is semitransparent and has only a diamond shine [1].

During the geological and technological studies of the Kokpatas deposit ores, a determination was made of the content of dispersed gold in them, taking into account the possible presence of dispersed gold in the oxidation zone in various forms in carrier minerals such as goethite, hydrogoethite, speedite, alunite, and in the zone of basic gold-bearing sulfide mineralization in pyrite , arsenopyrite and carbonaceous matter[3,4].

The main forms of dispersed gold in the sulfide ores of the Kokpatas deposit are its complex with iron, arsenic and sulfur (gold is more concentrated in arsenopyrite), iron and sulfur, iron, copper and sulfur (pyrite), and also probable organo-metallic compounds in the carboniferous subtypes of sulfide ores[5-8].

Therefore, to clarify the reasons for the loss of precious metals, it was necessary to conduct complex studies in the process of bacterial oxidation of the flotation concentrate.

Object and methods of research. The material of the studies was samples of sulfides from the current production cycles of HMP-3 BIOX at 13 points (Table 1).

The purpose of the research was to conduct a series of qualitative and quantitative analyzes of cations and anions of selected samples from BIOX (HMP-3) reactors.

From the incoming samples, liquid and solid phases were separated. A wide range of qualitative and quantitative analyzes for a wide group of metalson the ICP-MS-7500 instrument was carried out with them.

A complete analysis of the object under study can be carried out by observing a certain sequence of detection of individual ions. During the systematic analysis, separate groups of ions were isolated from the analyzed mixture. The separation of ions into groups was performed in a certain sequence. For this, the similarity or difference in the properties of the ions with respect to the action of group reagents was used. The ion groups were subdivided into subgroups, and then within the given subgroup individual ions were separated and detected by characteristic reactions.

For the separation of ions into groups, the following methods were used:

- Precipitation of ions in the form of sparingly soluble compounds;
- Restoration of ions by metals in accordance with their normal oxidation-reduction potentials;
- Elective adsorption of ions and other methods.

The results and their discussion. In this paper, we present the results of chemical and physic-chemical studies of the behavior of certain cations in the bacterial oxidation of the flotation concentrate.

A total of 13 sampling points were selected for the analyzes (Table 1).

From the received samples, the liquid and solid phases were separated and qualitative and quantitative analyzes were carried out for the main chemical elements

Table 1 Characteristics of liquid and solid phases of BIOX samples

№	Name of sample	Density, g/cm^3	The ratio of the solid phase		pH medium
			g	%	
1	Classifier of the upper sink	1.146	135	11.78	8.07
2	Floatation concentrate from the UCS	1.239	252	20.33	8.45
3	Reactor 2-1	1.210	216	17.85	2.05
4	Reactor 2-2	1.195	226	18.91	2.15
5	Reactor 2-3	1.185	114	9.62	2.10
6	Reactor 2-4	1.180	125	10.59	2.08
7	Reactor 2-5	1.175	148	12.59	2.10
8	Reactor 2-6	1.173	139	11.84	2.10
9	CCD-1	1.068			4.26
10	CCD-3	1.145	328	28.64	6.15
11	Feed to Kemix	1.308	486	37.15	9.82
12	Cyanidation Tailings	1.180	253	21.44	11.95
13	Tails of cyanidation cinder				

As can be seen, the density of the selected samples varies from 1.068 to 1.308 g/cm^3, the solid phase ratio is 10.59-37.15% and the pH of the medium is in the range 2.05-11.95. This is due to the time intervals of sampling.

To clarify the mechanism of biooxidation leaching, we investigated the content of calcium ions in sulfide minerals and solutions on the ISP-MS device, which can be part of the anorthite Ca [$Al_2Si_2O_8$] and contained in the ore in quantities up to 0.16%.

In the flotation concentrate, the amount of calcium ions increases to 0.22%, and in oxidation reactors, its amount increases as much as possible, varies from 0.288 to 0.309%, and in the decantation stage it is represented in the amount of 0.267 and 0.23%. A significant increase in the number of calcium cations in leach reactors can be explained only by adding to the pulp crushed $CaCO_3$to maintain the pH of the medium at the optimum level (Figure 1).

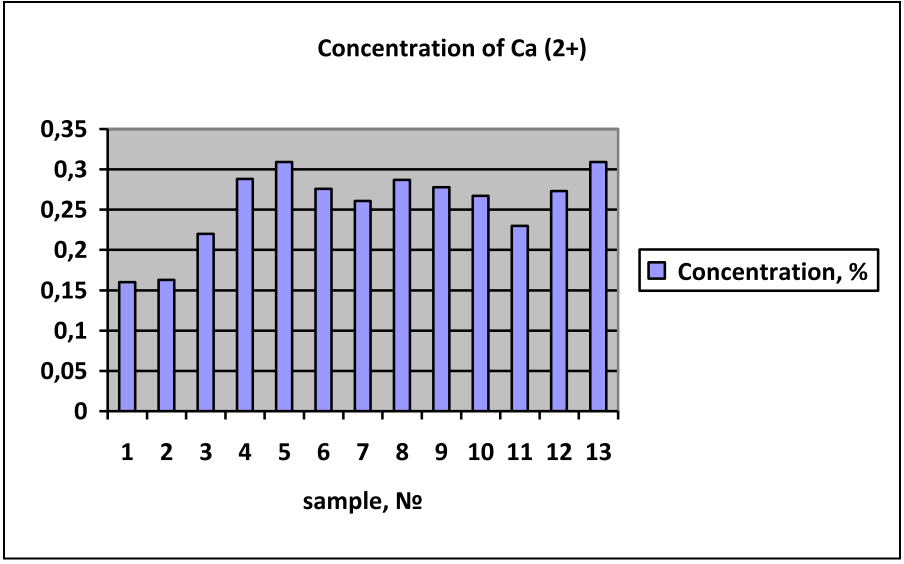

Figure 1. The behavior of calcium ions at different stages of leaching

Iron ions are mainly in the composition of ore minerals - pyrite - FeS_2 and arsenopyrite - AsFeS, and also in the composition of fayalite - $Fe_2[SiO_4]$ (Fig. 2). Content in pyrite: Fe - 46.6%, S -53.4%. Often, pyrite contains very small amounts of impurities: Co(cobaltite pyrite), Ni, As, Sb, sometimes Cu, Au, Ag, etc. The content of the latter elements is due to the presence of mechanical impurities in the form of minute inclusions of foreign minerals, sometimes in a finely dispersed state. In these cases we are dealing essentially with solid pseudo solutions, crystallosols.

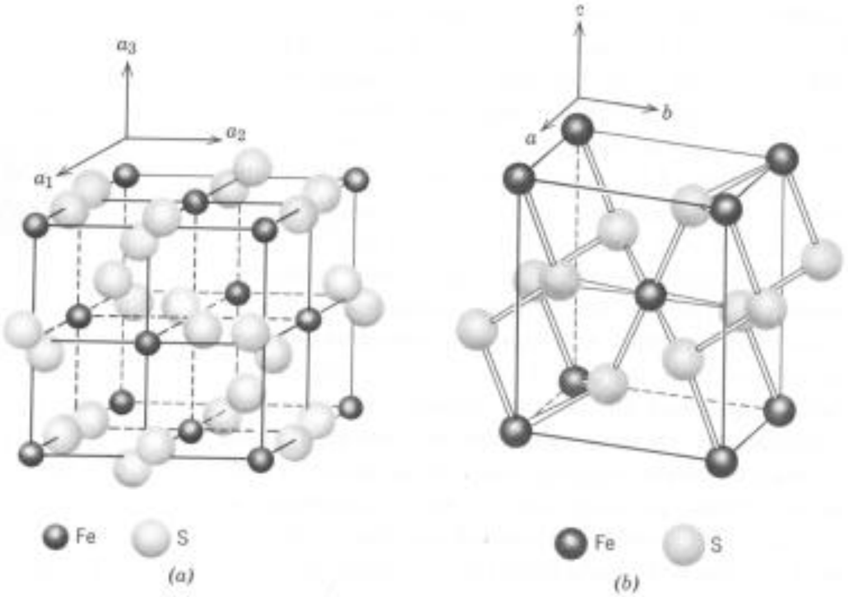

Figure 2. The crystalline structure of pyrite with black (iron) and light (sulfur) spheres.

Atoms of iron in the composition of sulfide minerals are in a divalent form. In bacterial leaching in oxidation reactors in a sulfuric acid medium, they transform into a solution in the form of sulfates of bivalent and trivalent iron. In the process of bacterial leaching, ferrous iron, forming hydroxides can also precipitate. Sulfide sulfur pyrite is oxidized to sulfate, and ferrous iron is oxidized to the oxide and two products are formed: sulfuric acid ferric and sulfuric acid.

Sulfuric acid iron oxidises pyrite chemically to form ferrous sulfate and elemental sulfur. Ferrous iron is again oxidized by bacteria to the oxide, which can be consumed as a pyrite oxidant.

The leading role in the realization of the transformations considered belongs to thionic bacteria - A. ferrooxidance, oxidizing sulfides and ferrous iron and A. thiooxidance - oxidizing elemental sulfur.

In the absence of thionic bacteria, the oxidants of minerals can in principle be dissolved in water oxygen and ferric sulfate. However, at normal pressure and low temperatures, the oxidation of sulfides with oxygen proceeds at very low rates, and the ferric sulfate in acid medium without iron-oxidizing bacteria is practically not formed (iron remains in its ferrous form).

Thus, in the case of pyrite, the twofold role ofthiobacteria in the leaching of non-ferrous metals is visible: direct participation in the oxidation of sulfides and indirectly by the formation of leaching reagents (ferric sulfate and sulfuric acid).

Bacteria A. ferrooxidance accelerate the oxidation of Fe^{2+} and sulfide minerals several times, in tens, and sometimes even hundreds and thousands of times compared to purely chemical oxidation under the same conditions: arsenopyrite can oxidize 4-8 times faster, chalcopyrite - at 6 -12 times, covellite and bornite - 18 times, pyrite - 1000 times, ferrous iron in acid medium - 200,000 times (compared with oxygenation of air). Elemental sulfur is oxidized with the participation of bacteria in sulfuric acid. The reaction of oxidation of pyrite with oxygen is sometimes recorded in two consecutive stages: first, the oxidation of sulfide sulfur to formferrous sulfate, and then the bacterial oxidation of ferrous iron to the oxide stage. Gold, silver is also often accompanied by sulfide minerals - they occur in the form of fine impregnations in minerals such as pyrite, arsenopyrite, stibnite. After preliminary destruction by thionic bacteria of the crystal lattice of sulfide minerals, the exposed precious metals can be recovered by any suitable solvent.

Quantitative analysis of the presence of iron ions showed its variation in the liquid phase in percentage terms in a large amount, especially in oxidation reactors - from 0.02 to 0.04% (Fig. 3).

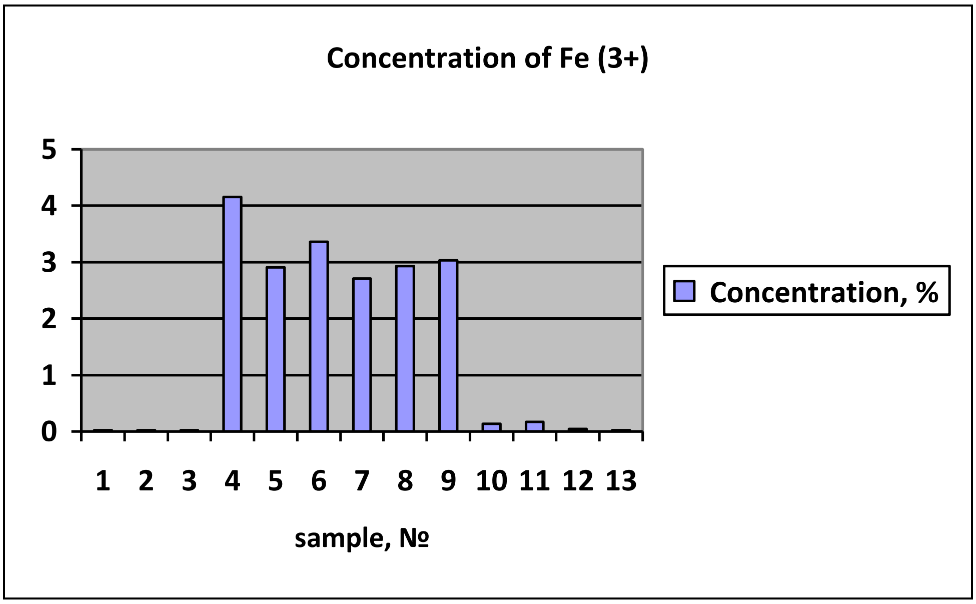

Figure 3. Behavior of iron ions during leaching

Remains of iron hydroxide in the stage of sorption cyanidation in an amount of 7 to 9 g/l, involving in the reactions with sodium cyanate bind some of it and form ferrocyanide, reduces the activity of cyanide.

After the decomposition of pyrite and arsenopyrite, the release dim purities of Ni, As, Sb, sometimes Cu, Au, Ag, etc., with the exception of noble metals, also oxidize and pass into solution. From Fig. 3 that ferric ions are present in an amount of 3.361 to 4.157%, mainly in oxidation reactors. On countercurrent decantation after washing, their quantity decreases to 0.137 and 0.017%. The equation for the oxidation reactions of iron is given below:

$$2FeS_2+7{,}5O_2+H_2O \rightarrow Fe_2(SO_4)_3+H_2SO_4 \quad (1)$$

$$FeS_2+Fe_2(SO_4)_3 \rightarrow 3FeSO_4+2S^0 \quad (2)$$

$$2FeSO_4+0{,}5O_2+H_2SO_4 \rightarrow Fe_2(SO_4)_3+H_2O \quad (3)$$

$$S^0+1{,}5O_2+H_2O \rightarrow H_2SO_4 \quad (4)$$

Also, oxide iron can be detected as Fe^{3+}, $[Fe(OH)]^{2+}$, $[Fe_2(OH)_2]^{4+}$, $[Fe(SO_4)_2]$- ions. The hydrolysis of ferric sulfate at a pH above 2.8 proceeds with the formation of hydroxides, and at a lower pH with the formation of jarosite:

$$Fe_2(SO_4)_3+6H_2O \leftrightarrow 2Fe(OH)_3\downarrow+3H_2SO_4 \quad (5)$$

$$3Fe_2(SO_4)_3+12H_2O \leftrightarrow 2HFe_3(SO_4)_2(OH)_6\downarrow+5H_2SO_4 \quad (6)$$

In the jarosite molecule, instead of the H + ion, there may be other cations NH4+, Na+, K+ depending on the composition of the solutions.

Biochemical schemes of bacterial oxidation of sulfide minerals, especially three-component (Fe, As, S, etc.) are much more complicated, since in this case biochemical processes occur simultaneously with the participation of different enzyme systems (iron and sulfur-oxidizing), and simultaneously biochemical and purely chemical processes.

The most interesting is the demonstration of the behavior of arsenic in the liquid phase (Fig. 4).

Arsenic is mainly concentrated in the composition of arsenopyrite - FeAsS.

$$2As + 3H_2SO_4 \rightarrow As_2O_3\downarrow + 3SO_2 + 3H_2O \qquad (7)$$

$$Fe + H_2SO_4 = FeSO_4 + H_2\uparrow \qquad (8)$$

If the content of arsenic in the ore material was minimal and amounted to 6403.7 µg /l, its content did not change significantly in the composition of the flotation concentrate and amounted to 6376.083 µg/l.

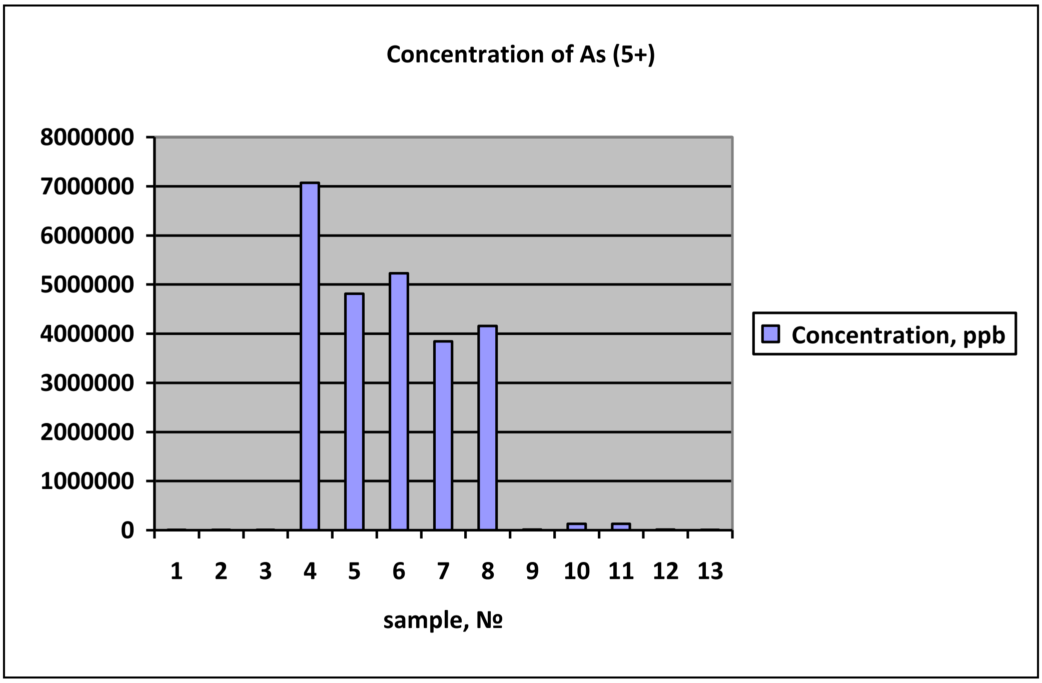

Figure 4. Behavior of arsenic in the process of leaching

However, in oxidation reactors under the action of microorganisms and a sulfuric acid medium, arsenic from arsenopyrite is dissolved in the maximum amount and is released into the liquid phase. Its amount in primary oxidation reactors is much higher and ranges from 7072682.52 to 5227309.06 µg/l than in secondary oxidation reactors (3844466.46 - 4263106.39 µg/l). This fact shows that the bulk of arsenic is oxidized at the very beginning, then, in secondary oxidation reactors, its oxidation is observed. After washing, in the feed of sorption cyanidation, before the sorption cyanidation, the arsenic content also increases in the liquid phase and amounts to 132485.844 µg/l. This is due to the fact that microorganisms are still fixed in under-oxidized arsenopyrite and continue to leach arsenic in the subsequent stages of the process. Possible exposure to sodium cyanide. The presence of arsenic in the cyanidation tails of 11192.3 µg/l and the tail of the cinder, 7310.7 µg/l, demonstrates the presence of unoxidized arsenic.

Among the cations, particular attention is paid to gold, the results of which are shown in Fig. 5. The analysis showed that at the very beginning, colloidal gold in the amount of 141 µg/l is released into the solution at the grinding stage. In flotation, part of this gold disappears, in solution there is only about 80 µg/l. Apparently, gold ions depressed by some types of flotation agents have passed into flotation tailings. Later, in oxidation reactors, the amount of ionic gold in the amount of 60 to 35 µg/l decreases. The rest of the colloidal gold is washed away from the decantation apparatus, passing to the neutralization stage.

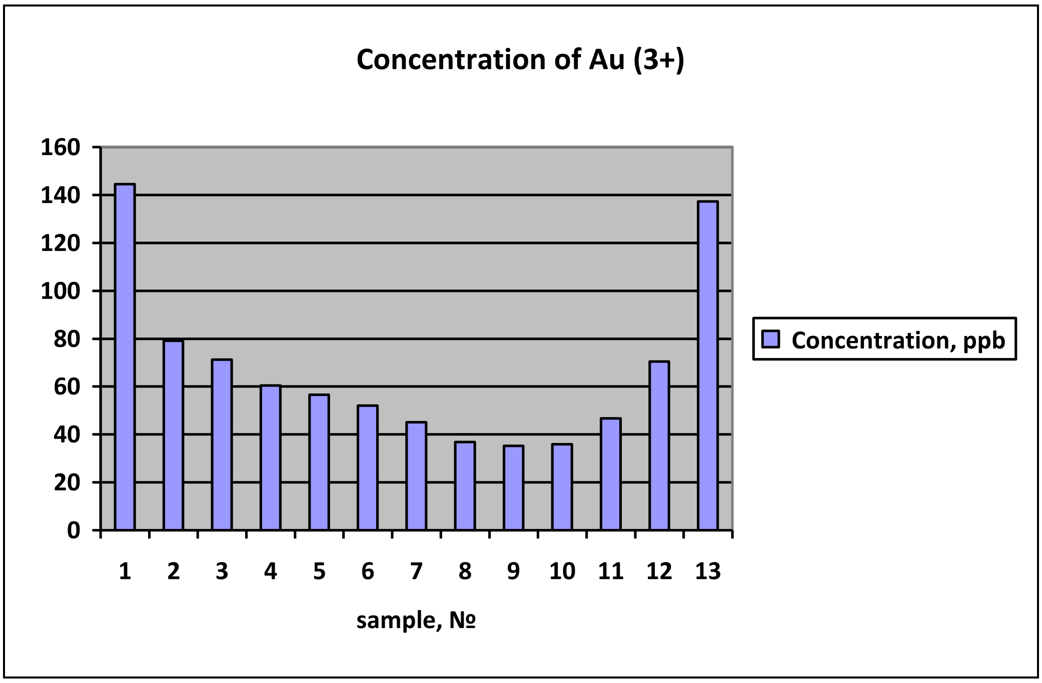

Figure 5. The behavior of gold ions at different stages of leaching

Perhaps chlorine and nitrate ions in a strong acidic medium are capable of forming hydrochloric and nitric acids, which, in the form of royal vodka, can also participate in the dissolution of gold and convert it into a dissolved state. In addition, selenate and sulfate ions were found in the solutions. Mixtures of these ions in an acid medium are capable of dissolving gold in the composition of the ore and also converting it into an ionic form. The equation for the reactions of the above ions is given below:

$$Au + HNO_3 + 4HCl \rightarrow H[AuCl_4] + NO\uparrow + 2H_2O \quad (9)$$

$$2Au + 3Cl_2 \rightarrow 2AuCl_3 \quad (10)$$

$$2Au + Cl_2 \rightarrow 2AuCl \quad (11)$$

$$Au + 3Cl_2 + 2HCl \rightarrow 2H[AuCl_4] \quad (12)$$

$$2Au + 6H_2SeO_4 \rightarrow Au_2(SeO_4)_3 + 3SeO_2 + 6H_2O \quad (13)$$

$$Au + NaNO_3 \rightarrow NaAuO_2 + NO \quad (14)$$

The process of thiosulfate leaching is based on the oxidation of gold by air oxygen in the presence of sodium thiosulfate:

$$4Au + O_2 + 8S_2O_3^{2-} + 4H^+ \longrightarrow 4\left[Au(S_2O_3)_2\right]^{3-} + 2H_2O \quad (15)$$

in acidic medium, or bivalent copper:

$$Au + 5S_2O_3 + \left[Cu(NH_3)_4\right]^{2+} \longrightarrow \left[Au(S_2O_3)_2\right]^{3-} + 4NH_3 + \left[Cu\left(S_2O_3\right)_3\right]^{5-} \quad (16)$$

in an alkaline medium (thiosulfate-ammonia leaching).

To clarify the decrease in gold concentration in the reactors, additional experiments were conducted with a solid phase separated by filtration. The obtained solid part was fired in a muffle furnace at a temperature of 6500 ° C, the solutions were dissolved in nitric acid, then in hydrofluoric acid, then with aqua regia and the resulting mass was diluted with distilled water. The analysis was carried out on an ICP-MS-7500 instrument, the results of which are presented in Table 2 and Fig. 6.

Table 2 Results of mass spectrometric analysis of samples of sulfide minerals

Name of sample	Dissolved elements, g/t									
	Fe	Ag	Au	As	Zn	Cr	Mg	Al	Mn	Li
Floatation concentrate	58000	1,2	1,00	3500	93,0	140	29000	69000	940	24,0
Reactor 2-3	56000	8,3	4,30	5000	200	110	11000	45000	180	17,0
Reactor 2-6	55000	4,0	5,10	7200	230	190	13000	60000	22,0	18,0
The CCD-3 node	38000	2,0	7,60	3000	230	130	13000	51000	180	22,0

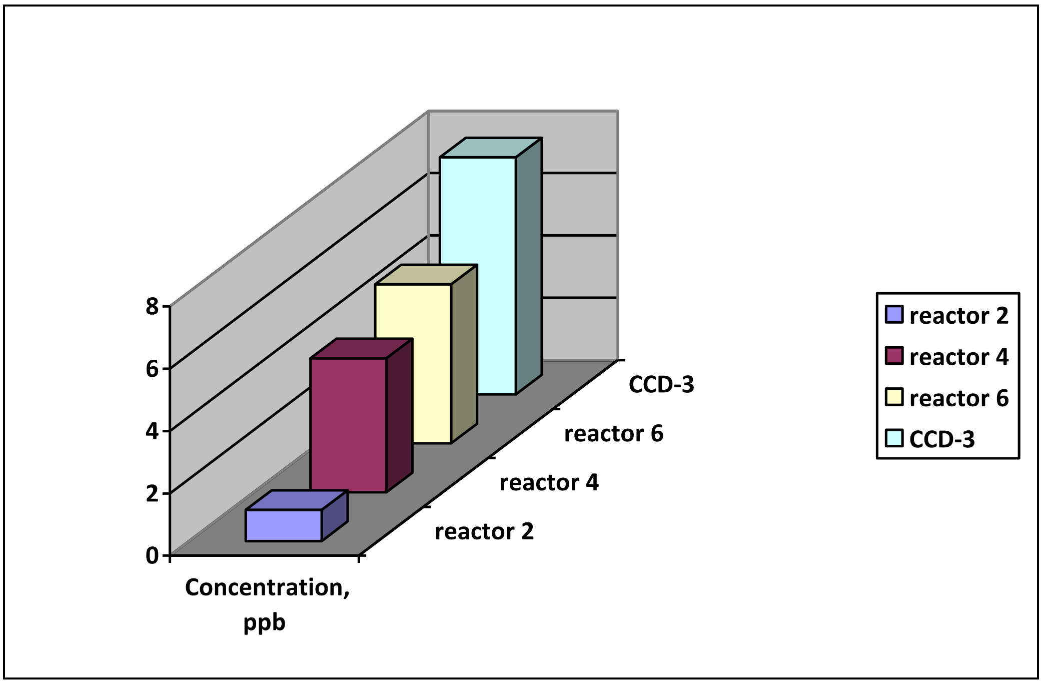

Figure 6.Sorption of gold on organic carbon in different stages of leaching.

In a comparative analysis of the absorption of gold ions in the liquid phase (Table 2, Fig. 5 and 6), a correlation was observed between the absorption of gold ions by amino acids and organic carbon.

CONCLUSION

Thus, the obtained results showed a decrease in the concentration of gold in the reactors of bio-oxidation by its possible dissolution in the formation of new chemical compounds - aqua regia, thiosulfates, selenate ions, chlorine-chloride solutions, free amino acids, absorption in carbonaceous substances and its removal by washing with countercurrent decantation.

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