

Mechanism of Nonoxidizing and Oxidative Pyrrhotites Leaching

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Abstract

Pyrrhotite is one of the main component of sulfide ores. As a result, its behavior has a significant influence on the course of metallurgical processes and on the extraction of non-ferrous metals. There is no definitive description of the mechanism of chemical reactions occurring during nonstoichiometric iron sulfides dissolution. In some studies on pyrrhotite dissolution, pyrite formation is assumed, in others -the elemental sulfur is assumed to form. The aim of this study is to clarify the mechanism of chemical reactions of pyrrhotites dissolution in non-oxidizing acids during oxidative bacterial leaching. In this work, different methods of analyses have been used - scanning electron microscopy, micro X-ray spectral, X-ray diffraction, Mössbauer and IR-spectroscopy analysis. It has been established that acid pyrrhotite dissolution in the non-oxidative conditions proceeds in stages. At first, low-sulfur pyrrhotite dissolution occurs with the transition of iron ions to solution and hydrogen sulfide with simultaneous formation of the sulfur-rich iron sulfide in the residue from the leaching. Pyrrhotites oxidative bacterial leaching proceeds in two stages. In the first stage the pyrrhotites are enriched with iron and then the low sulfur sulfides dissolve with formation of iron sulfate (Fe^{2+}). The proposed mechanism in this work for sulfide oxidative bacterial leaching can predict the parameters and the results of the process.

Key words: Pyrrhotite, Oxidative and Non-oxidative conditions, Solution, Bacterial leaching

Introduction

Pyrrhotite belongs to a class of nonstoichiometric compounds with a sufficiently broad range of homogeneity at low temperatures. Depending on the composition of pyrrhotite, its thermodynamic and technological characteristics change. From the thermodynamic characteristics of nonstoichiometric pyrrhotites that have been adequately analyzed in the literature (Vaniukov et al, 1991, 1978), it follows that the equilibrium dissociation pressure of iron sulfides increases continuously with increasing sulfur content in them, i.e., pyrrhotite properties are constantly modified with changes in Fe/S ratio. The same character of composition and pyrrhotite properties change should characterize their behavior in the process of hydrometallurgical processing.

Peters (Peters E., 1978) found that with a sulfur content increasing within the pyrrhotites homogeneity region, the stability in aqueous solutions increases. For transfer of iron from more sulphurous pyrrhotite into the solution takes a lot of acidity and higher oxidation potentials, rather than the dissolution of low sulfur pyrrhotite Fig. 1.

Thermodynamic analysis shows that sulfur is able to form hydrogen sulfide, elemental sulfur, and even the anion SO_4^{2-} at the dissolution of iron sulfides. Author (Droppers D. J. et al., 1995) showed that in the process of leaching pyrrhotite concentrate by the nitric acid solution, elemental sulfur forms. Anodic oxidation of metal sulfides under a steady flow of oxygen influences the process. At first, higher sulfur sulfide forms, which is then dissolved with the formation of elemental sulfur or sulfate ion. Autoclave dissolution of copper sulfides is accompanied on the first stage by the formation of higher sulfur sulfide.

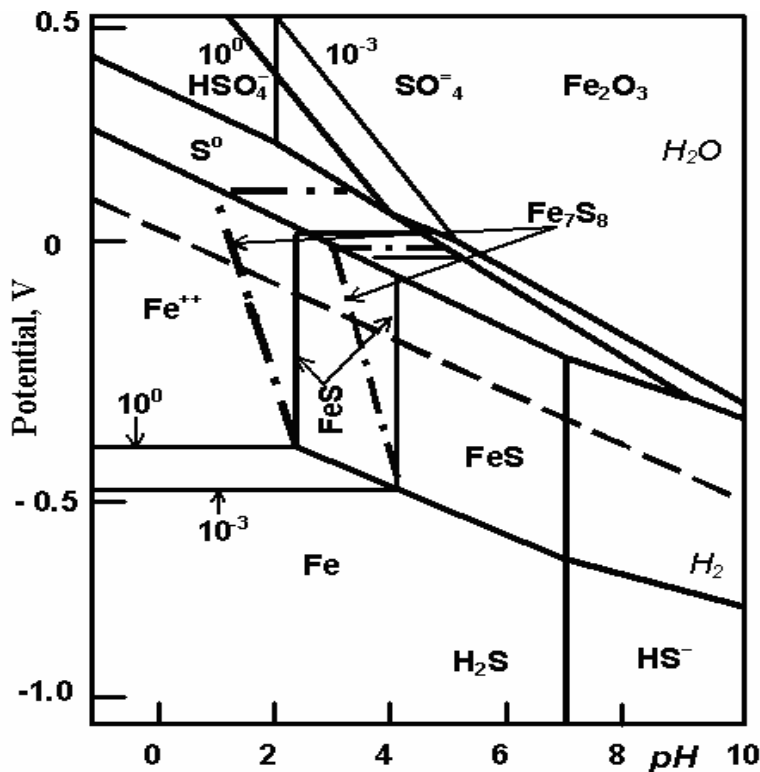


Figure 1 - «Potential – pH» diagram of the Fe-S-H₂O system.

Dissolution of chalcocite in ferric chloride solutions is preceding stadia. Initially, the reaction proceeds with the formation of covellite and then covellite is dissolved to form elemental sulfur. Covellite also forms during the bacterial leaching of chalcocite.

Experimental methods

(a) The pyrrhotite behavior during acid leaching: Most theoretical studies of the iron sulfides properties and behavior were carried out with natural pyrrhotite and iron sulfides, obtained by synthesis of iron and sulfur or iron sulfide precipitation from aqueous solutions.

We decided to study the behavior of the synthetic pyrrhotite during dissolution, derived from natural pyrite. The results obtained on the samples of synthesized pyrrhotite from pyrite to a greater extent will meet the demands of production, since, as such, pyrrhotite is obtained by heat treatment of pyrite bearing materials.

Initial materials: For the study of dissolution mechanism, pyrrhotites were obtained by thermal decomposition of pyrite, followed by homogenization of calcine at 800 °C for 7 days Table 1, as well as products of thermal decomposition of pyrite concentrates without further homogenization.

Roast-dissociation of pyrite concentrate for pyrrhotizing was carried out in a nitrogen atmosphere in a quartz reactor. In pyrrhotizing cinder various amounts of undecomposed pyrite was obtained.

Table 1 - The composition of homogenized pyrrhotites

№ of test	The iron content in pyrrhotite		The pyrrhotite chemical formula	Magnetic susceptibility, units SI x10 ³
	%, at.	%, mass		
1	47.3	60.7	Fe _{0.901} S	2
2	46.95	60.35	Fe _{0.885} S	2190
3	46.7	60.2	Fe _{0.877} S	1640
4	46.3	59.7	Fe _{0.862} S	1390
5	46.1	59.5	Fe _{0.855} S	1250

Table 2 - The condition of pyrite concentrate thermal dissociation and the characteristics of dissociated products

№ of test	Dissociation condition		Iron content in pyrrhotite, % at.	The pyrrhotite chemical formula	The part of pyrite in calcine, %
	T, K	τ, min			
6	1073	60	48.6	Fe _{0.945} S	7.8
7	973	60	47.5	Fe _{0.905} S	9.2
8	1073	20	47.7	Fe _{0.91} S	9.7
9	973	20	46.6	Fe _{0.873} S	13.7
10	1093	40	48.2	Fe _{0.93} S	6.0
11	953	40	47.6	Fe _{0.91} S	14.1
12	1023	68	48.2	Fe _{0.93} S	7.3
13	1023	12	46.6	Fe _{0.871} S	11.1
14	1023	40	47.8	Fe _{0.916} S	11.4
15	1023	40	48.0	Fe _{0.923} S	11.7

Results and discussion

The pyrite content in the original pyrite concentrate was 97.5 %. Size of the initial trial sample is 0.07-0.01 mm in Table 2. Dissolution was carried out with samples in 1-5 Table 1 in 0.1 N hydrochloric acid and sulfuric acid at 293 K for 100 hours. Consumption of acid was from 20 to 120 % from the theoretically required amount for complete pyrrhotite dissolution.

Nitrogen purging was performed for 10 minutes to prevent the dissolution of oxygen in acid

before leaching. After leaching, samples dried in a vacuum to prevent their oxidation, were subjected to X-ray diffraction and electron microscope analysis. At the same time with the help of scanning electron microscope was study the nature of samples surface changing during of dissolution.

The mechanism of chemical reactions of dissolution of the samples [nonhomogenized pyrrhotite 6-15 in Table 2 after thermal decomposition of pyrite concentrate were studied by leaching in hydrochloric acid solution (100 g/l), done with an excess of 20 % acid, at a temperature of 363 K and for a duration of 2 hours. Leaching was carried out in flasks with reflux condenser and magnetic stirrer. The amount of dissolved iron from pyrrhotite was calculated from the results of chemical analysis of solutions and residues from leaching. The composition of pyrrhotite in the residues from leaching was determined by the well-known Arnold equation (Arnold R.G., 1962).

The results of the study on partially dissolved pyrrhotite, by the scanning electron microscope at Fig. 2 and 3, show that the dissolution does not occur uniformly from the surface deep into the grain, and anisotropic leaching takes place. The micrographs indicate a fiber leaching. At the significant degree of leaching (above 80 %), residues have a highly developed surface. The outlines of the initial pyrrhotite particles are retained.

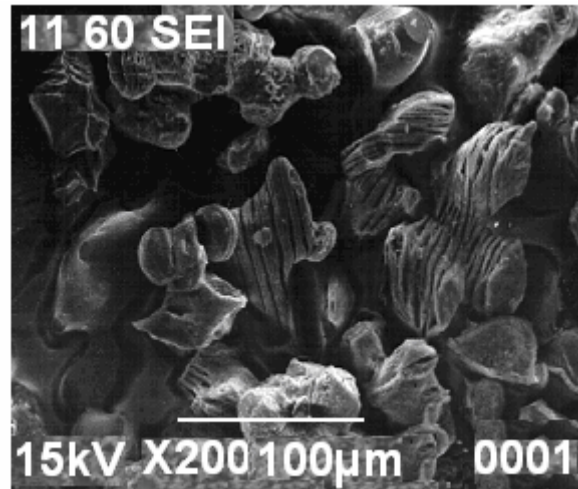


Figure 2 - Photomicrographs of synthesized pyrrhotite residues from leaching.

Thus, it is concluded that the dissolution of pyrrhotite in the initial stages of the specific surface reaction increases because of its anisotropic dissolution.

Comparison of micro X-ray spectral analysis results of the initial synthetic pyrrhotite and cakes from leaching show (Luganov V.A. et al., 2006, 2000), that the in the leaching pyrrhotite composition is changing in the process, with decreasing "Fe/S" ratio in the depth of grain. *This is obviously* due to the changing composition of the solid phase - reaction from the surface into the interior of the particles is accompanied by depletion of the reacting sites of iron (the enrichment of sulfur). Moreover, the uneven sulfur content as a function of depth was observed with sharp rise of the sulfur content in some parts of the particles. This can be explained by the irregularity of the dissolution of initial pyrrhotite particles during dissolution through the pores. As seen in scanning electron micrographs, the dissolution of pyrrhotite occurs in layers.

Preparation of samples for the electron microprobe analysis includes grinding of samples. It is likely that during grinding the hollow fibers are filled with more fragile and soft components of

the residue from leaching. These components may be either pyrite or elemental sulfur.

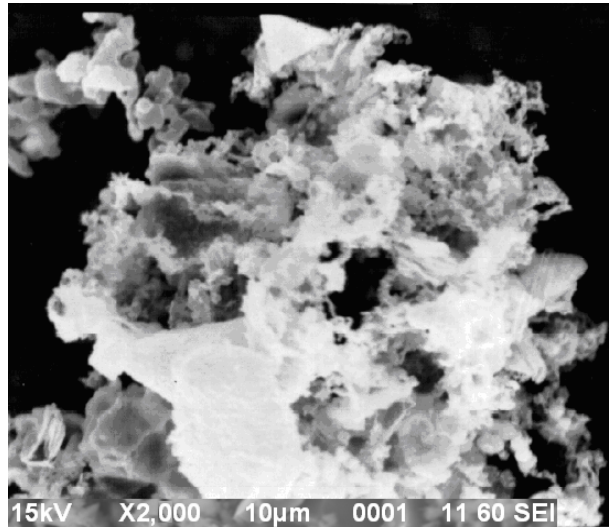


Figure 3 - Electron micrograph of the cakes from the leaching Magnification.

Identification of the mechanism of dissolution was carried out based on the results of dissolution of homogenized and nonhomogenized samples of pyrrhotite in Table 3 and 4, followed by mathematical processing of the results.

Table 3 - The results of homogenized samples

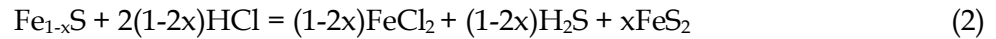
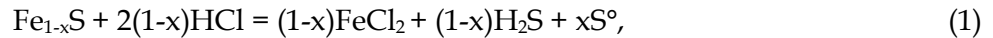
№ of test	The dissolution rate α (%) and pyrrhotite composition in the residues							
	α	comp.	α	comp.	α	comp.	α	comp.
Dissolution in sulfuric acid								
1	10.0	Fe _{0.893} S	15.0	Fe _{0.885} S	25.0	Fe _{0.877} S	30.0	Fe _{0.877} S
2	10.0	Fe _{0.877} S	14.0	Fe _{0.877} S	22.0	Fe _{0.87} S	26.0	Fe _{0.87} S
3	8.0	Fe _{0.877} S	12.5	Fe _{0.87} S	14.0	Fe _{0.87} S	26.0	Fe _{0.862} S
4	5.0	Fe _{0.862} S	10.0	Fe _{0.862} S	12.0	Fe _{0.855} S	22.0	Fe _{0.855} S
5	4.0	Fe _{0.855} S	8.0	Fe _{0.855} S	10.0	Fe _{0.855} S	18.0	Fe _{0.855} S
Dissolution in hydrochloric acid								
1	15.0	Fe _{0.885} S	25.0	Fe _{0.877} S	32.0	Fe _{0.877} S	40.0	Fe _{0.877} S
2	12.0	Fe _{0.877} S	20.0	Fe _{0.87} S	25.0	Fe _{0.862} S	34.0	Fe _{0.862} S
4	10.0	Fe _{0.855} S	14.0	Fe _{0.855} S	16.0	Fe _{0.855} S	25.0	Fe _{0.855} S

X-ray diffraction analysis of residues from leaching shows that with increasing degree of pyrrhotite dissolution the composition remains unchanged - they are enriched with sulfur through the formation of higher sulfur pyrrhotites. For example, the composition of pyrrhotite Fe_{0.901}S, after dissolution, transforms into a Fe_{0.885}S and then into Fe_{0.877}S. Sulfur content in pyrrhotites (samples 4 and 5, Table 2) gets enriched up to the composition of Fe_{0.855}S. Changing the leaching conditions any further does not add sulfur to Fe_{0.855}S in the residues of pyrrhotite leaching (Mc. Namara I. N. et al., 2005).

Nature of the changes in the composition of pyrrhotite in the residues of leaching is similar for dissolution in sulfuric and hydrochloric acids. However, higher dissolution is achieved in hydrochloric acid. With more complete dissolution of pyrrhotite, the x-ray results show higher

sulfur intensities. This may be due to the formation of elemental sulfur (or pyrite).

For forms of sulfur in the residues of leaching Table 4, we calculated the mass balance over the possible dissolution reaction with formation of elemental sulfur or pyrite:

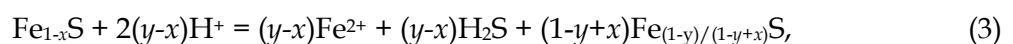


By calculation, iron extraction into solution for the two cases was accounted for by comparing the composition of pyrrhotite, and ratio between pyrrhotite and pyrite in the original sample. Comparison of the two calculated values with experimental results in Table 4 show that the total dissolution process proceeds in accordance with equation (1), i.e. with the formation of elemental sulfur. Radiographic studies of cakes 6 - 15 also confirm the formation of more sulfur than the original sample pyrrhotite in the residues from leaching. Peaks corresponding to elemental sulfur are occurring in the sulfuric acid pyrrhotite dissolution, as well.

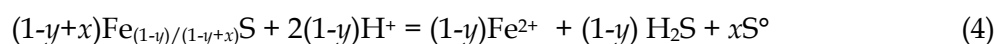
Table 4 - The results of the pyrrhotizing product dissolution

No of test	The initial atomic ratio S / Fe	Test data		Estimated recovery of iron, %	
		iron extraction into solution, %	atomic ratio S / Fe in a cake	by equation (1)	by equation (2)
6	1.13	96.2	2.5	94.1	86.7
7	1.19	93.7	1.7	92.5	80.8
8	1.19	91.8	1.9	92.4	81.3
9	1.26	88.4	2.9	89.1	73.4
10	1.12	94.8	1.9	95.4	86.5
11	1.23	90.3	2.4	88.9	77.3
12	1.14	95.8	2.3	94.4	85.3
13	1.24	91.0	3.5	91.2	75.6
14	1.2	92.3	2.9	91.1	80.6
15	1.19	91.1	2.1	90.9	81.23

Based on the results of X-ray diffraction and micro X-ray spectral analysis of residues from leaching and mass balance calculation results of dissolution of the two possible mechanisms, we can conclude that the initial dissolution is accompanied by changes in the composition of pyrrhotite (an enrichment of sulfur). Dissolution of the newly established higher sulfur pyrrhotite ($\text{Fe}_{0.855}\text{S}$ - $\text{Fe}_{0.862}\text{S}$), comes with the release of elemental sulfur. Thus, the mechanism of chemical reaction process can be represented in the form of the equations of chemical reactions. In the first stage, iron dissolution is occurring with hydrogen sulfide and high sulfurous pyrrhotite formation by the reaction:



where y is greater than x, and is within 0.13 - 0.145. In the second stage of dissolution, the expansion of high sulfurous pyrrhotite occurs with the formation of elemental sulfur, the ferrous iron cations pass in to solution, and the hydrogen sulfide goes to the gas phase:



Thus, the findings indicate the stepwise mechanism of pyrrhotite dissolution and formation of the high sulfurous pyrrhotite and elemental sulfur as a result of the expansion (Luganov V.A. et al., 2000, Mc. Namara I. N. et al., 2005).

(b) The behavior of pyrrhotites oxidative bacterial leaching:

Initial materials: Table 5 shows the composition and Fe/S ratios during the pyrrhotites oxidative bacterial dissolution with natural and synthetic materials (Table 5). Fineness - 0.074 microns.

Table 5 - The composition of initial pyrrhotites

No	Pyrrhotite	d ₁₀₂	Fe %	Fe/S	Fe _{1-x} S
1	Natural	2.058	46.7	0.87	Fe _{0.87} S
2	Natural	2.053	45.9	0.85	Fe _{0.85} S
3	Synthetic	2.049	45.7	0.84	Fe _{0.84} S

Electron microscopic analysis showed that the synthesized pyrrhotite is represented by particles with a smooth surface without visible blisters and pores. There is the formation of the layered structure. Micro X-ray analysis of samples showed a constant ratio of «iron: sulfur» in the depth of the particles. Natural pyrrhotite samples are represented by particles with highly porous surface. X-ray and Mössbauer studies of pyrrhotites allow establishing the simultaneous presence of several structures of pyrrhotites with different lattice parameters. Thiobacillus ferrooxidans bacteria were used in the leaching.

Pyrrhotites dissolution mechanism was studied by conducted tests with the samples 1-3, in Table 5. The weight of samples was 2 grams. Samples were treated with distilled water and 120 ml of culture thiobacillus ferrooxidans, 0,4 g/L of CN and 1 ml of H₂SO₄ in the ratio of S:L = 1:2 and 1:5 while the tests were done for 5 days with stirring. Comparative experiments were carried out by treatment of initial pyrrhotites with water (pH = 5) with no chemicals or bacteria added as control samples. Samples for analysis were collected daily. IR-spectroscopic analysis was performed using FT-IR spectrometer «Avatar - 370 CsI » in the spectral range of 4000-250 cm⁻¹. Samples were ground with liquid paraffin.

The results show in Tables 6 and 7 and Fig. 4 and 5 that natural and synthetic pyrrhotites behave similarly. With increase in duration of the experiments from 1 to 5 days, iron content (²⁺) decreases and iron (³⁺) increases. Simultaneously sulfate ion (SO₄⁻²) concentration also increases. The increase of SO₂⁻⁴ concentrations indicates oxidation of sulfide sulfur to sulfur (⁶⁺).

Table 6 - Pyrrhotites composition after leaching with Thiobacillus ferrooxidans

Pyrrhotite	d ₁₀₂	Fe. %	Fe/S	Fe _{1-x} S
Test 1	2.07	47.7	0.91	Fe _{0.91} S
Test 2	2.058	46.7	0.87	Fe _{0.87} S
Test 3	2.058	46.7	0.87	Fe _{0.87} S

Table 7 - The productive solutions composition obtained by leaching with Thiobacillus ferrooxidans

Pyrrhotite	Concentration g/l
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	Duration, days	Fe ²⁺	Fe ³⁺	SO ₄ ²⁻	S ₂ O ₃ ²⁻
Fe _{0,875} S	1	6.7	1.8	19.65	0.13
	3	8.2	0.8	19.6	0.086
	5	8.7	0.6	18.7	0.084
Fe _{0,857} S	1	7.2	1.0	19.1	0.18
	3	8.6	0.6	19.6	0.14
	5	8.1	0.85	18.9	0.084
Fe _{0,855} S	1	6.0	2.2	18.6	0.10
	3	8.0	1.0	18.6	0.08
	5	8.9	0.2	19.2	0.067

The comparison of the initial and treated pyrrhotite IR-spectrogram, Fig. 4 shows that, as a result of pyrrhotites leaching, the wave number shifts to lower frequencies. Initial pyrrhotite is characterized by peaks at 272 and 262 cm⁻¹ Fig. 4a, and pyrrhotite after leaching at 267 and 257 cm⁻¹ Fig. 4c. This shows the weakening link between iron and sulfur in pyrrhotite.

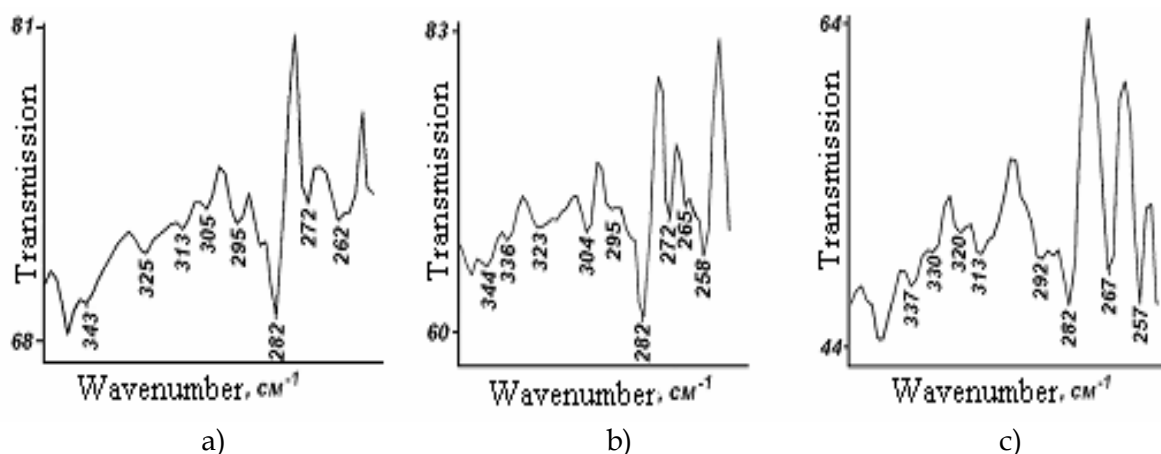


Figure 4 – IR-spectrograms of the initial and processed pyrrhotites
a) the initial natural pyrrhotite, b) pyrrhotite, treated by water c) pyrrhotite after bacterial leaching
X-ray diagrams in Fig. 5 show that the interplanar distance d_{102} of pyrrhotites after treatment has changed.

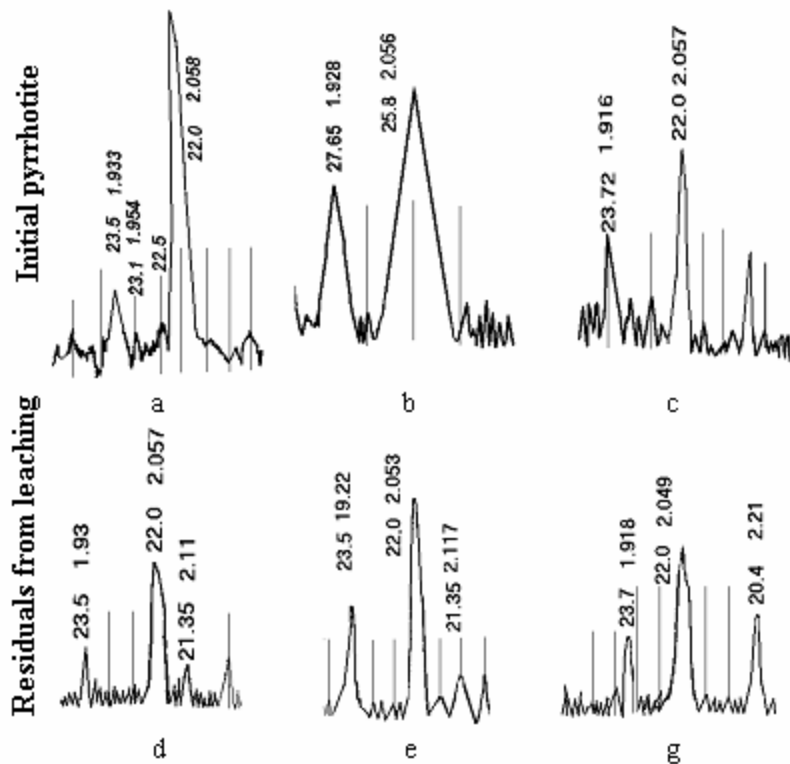


Figure 5 – X-ray diagrams of the initial pyrrhotites and residues of their bacterial leaching

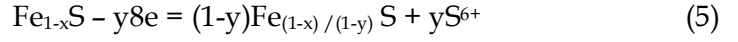
During the leaching of natural pyrrhotites, (1) the interplanar spacing for residues varied from 2.057 to 2.058 Å at Fig. 5a and 5b, and (2) at Fig. 5c and 5d - from 2.056 to 2.053 Å, and for synthesized pyrrhotite (Fig. 5g and 5e) - from 2.057 to 2.049 Å. The calculated interplanar distance for pyrrhotites, the iron/sulfur ratio and pyrrhotites composition before and after treatment, are shown in Table 6.

Analyses of productive solutions in Table 7 show that the sulfur in solution is present as sulfate and thiosulfate forms. And the number of thiosulfate sulfur decreases as the duration of the leaching process increases, i.e. the oxidation of sulfide occurs in stages. The oxidation mechanism to form thiosulfate has not been indicated in pyrrhotite, because its number is several times lower than the sulfate concentration in solution, which seems to be the final product of oxidation.

From these results, it is indicated that the pyrrhotites oxidative bacterial leaching process proceeds in two stages. First - pyrrhotite enriched with iron and sulfur goes into solution in the form of sulfate ions. So, if the initial natural pyrrhotites had the composition $\text{Fe}_{0,87}\text{S}$ and $\text{Fe}_{0,85}\text{S}$, after leaching the composition changed to $\text{Fe}_{0,91}\text{S}$ and $\text{Fe}_{0,87}\text{S}$, respectively. The synthetic pyrrhotite behaves similarly. Its composition has changed from $\text{Fe}_{0,84}\text{S}$ to $\text{Fe}_{0,87}\text{S}$. In this case, the first stage is the preferred sulfur oxidation.

During the second stage, iron-enriched pyrrhotite dissolves with the formation of iron sulfate (Fe^{2+}) and sulfate ion. With increase in leaching duration, Fe^{2+} concentration decreases while Fe^{3+} and SO_4^{2-} increases. This confirms that elemental sulfur oxidation by the bacteria occurs into ions of SO_2^{-3} and later in to SO_4^{2-} and iron oxidation by bacteria to Fe^{3+} .

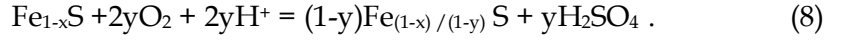
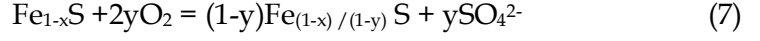
In summary, the mechanism of pyrrhotites chemical transformations during oxidative leaching can be described by the following equation:



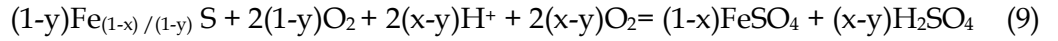
i.e., the sulfur in sulfide is oxidized to sulfate in the oxidation process:



Or in general:



Then the dissolution of low-sulfur sulfide with formation of iron sulfate and sulfuric acid by the following reaction occurs:



The resulting ferrous sulfate - FeSO_4 , oxidized by atmospheric oxygen and catalyzed by bacterial influence converts to $\text{Fe}_2(\text{SO}_4)_3$ by the reaction:

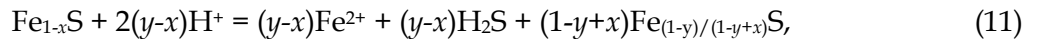


Thus, it was found that in the nonoxidative acid leaching of pyrrhotites (part 'a' of the work), first residues from leaching get enriched with sulfur with formation of high sulfurous pyrrhotite; and in the oxidative bacterial leaching (part 'b' of the work), first sulfur is oxidized and goes into solution in the sulfate form, which leads to increasing of solution acidity.

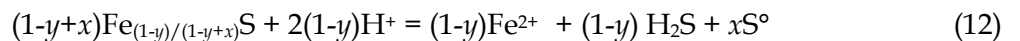
Thus, the pyrrhotites oxidative bacterial leaching proceeds in two stages: (i) - pyrrhotite enriched with iron and sulfur goes into solution in the form of sulfate ions, (ii)- enriched iron pyrrhotite dissolves with the formation of iron sulfate (Fe^{2+}) and sulfate ions.

Conclusion

Thermodynamic analysis shows increased sulfur activity and, therefore, there is an increase in sulfur concentration within the homogeneity region of pyrrhotites stability in aqueous solutions. The transfer of iron from more sulfurous pyrrhotite into the solution requires high acidity and increase in oxidation potentials. During the pyrrhotite dissolution, sulfur can be released in elemental form as well as in the form of SO_4^{2-} ions and hydrogen sulfide. Acid pyrrhotite dissolution in the non-oxidative conditions proceeds in stages: at first, low-sulfur pyrrhotite dissolution occurs with the transition of iron ions to solution and hydrogen sulfide with simultaneous formation of the sulfur-rich iron sulfide in the residue from the leaching by the reaction:

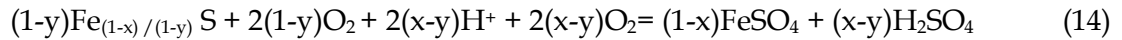
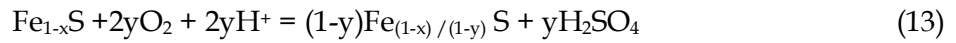


The sulfurous pyrrhotite dissolution follows with formation of hydrogen sulfide and elemental sulfur by the reaction:



Pyrrhotites oxidative bacterial leaching proceeds in two stages: in the first stage the pyrrhotites are enriched with iron, then the low sulfur sulfides dissolve with formation of iron sulfate

(Fe²⁺).



Establishment of mechanism of sulfide oxidative bacterial leaching can predict the parameters and the results of the process.

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