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THE EFFECT OF AUROFERROUS PYRITES NON-STOICHIOMETRY ON THEIR FLOTATION AND ADSORPTION PROPERTIES

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The attempt to explain the differences in sorption and flotation properties of auroferrous pyrites of several deposits from positions of inconstancy of iron to sulfur proportion (non-stoichiometry) has been undertaken. The effect of natural pyrites non-stoichiometric composition on their surface ability to oxidation, as well as, on the correlation between sulfite- and sulfate-ions in liquid phase during pyrite flotation has been shown. It has been found, that the collector chemisorption on pyrites with a non-stoichiometric composition has increased. The sulfur/iron ratio in natural auriferous pyrites correlates with their flotation properties at the range of pH 9-12.

Key words: auroferrous pyrite, flotation, adsorption

INTRODUCTION

The study of geochemical peculiarities of great number of pyrites from various types of deposits (Korobeynikov et al. 1993) has shown, that the pyrites of any origin always contain gold. The gold content varies from $n \cdot 10^{-6}$ up to $n \cdot 10^{-3}$ %. The pyrites from gold ore deposits are characterized by a wide range of admixed elements. Gold, silver, copper, lead, zinc and arsenic are concentrated in the elevated amounts and differ by maximal inaccuracy of statistical distribution parameters. The basic reasons of mineral differences in both semi-conductive and physical characteristics are

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isomorphous presence of these impurities in pyrite structure and the stoichiometry deviation of the main components (iron and sulfur).

Flotation models (Avdochin and Abramov, 1989) without taking into account the crystal-chemical minerals singularities, elements-impurities, structural defects of natural sulfides are unsuitable to explain the flotation-depression conditions. The efforts to discover the relationships between physical characteristics and impurity composition of natural pyrites on one hand, and their flotability and sorption properties on the other were undertaken (Krasnikova, Krasnikov, 1978; Eliseev et al. 1979). However, the results of these studies were not completely conclusive. The studies of auroferrous pyrite and arsenopyrite selective flotation have shown that copper and gold isomorphous admixtures have the dominant effect on the mineral properties (Chanturiya et al. 1997, 1998).

The idea of the correlation of physicochemical solid-state properties of sulfide minerals with their flotability and electrochemical aspects of sulfide flotation has been studied by Woods and Richardson (1986), as well as, Hamilton and Woods (1984). The investigation of the surface compounds composition during the pyrite flotation showed, that dixanthogen is a main form of buthylxanthate adsorbed on the pyrite surface. However, the presence of metal-xanthate compounds and their formation conditions are not full accepted (Leppinen et al. 1995; Brandsaw 1997).

The influence of gold-content factor on the pyrite properties is connected with increasing the structural defects when gold is concentrated by a mineral. Raising the arsenic admixture contents and forming the acceptor sulfide vacancies when gold is introduced into the crystal lattice are next reasons (Tauson et al. 1996). The electro-physical characteristics of auriferous pyrite samples vary in broad range. The specific resistance and thermo-electromotive force can have different values inside of one mineral aggregate. The conductivity sign is connected with the "shut-off zone" formation.

It is considered that balance change at the S^{2-} vacancies formation causes an increase of n-type conductivity and on the other hand, the Fe^{2+} vacancies formation results in the p-type conductivity. The modification of pyrite crystalline structure is accompanied by transferring from the p to n conductivity. It is known, that the acceptor centers formation in hydrothermal pyrite, when substituting of divalent iron by univalent gold, causes its affinity to the electron. According to the Lewis acids and bases theory, the auriferous pyrites should reveal acidic properties.

Thus, all the gold-containing FeS_2 natural crystals in greater or smaller degree are defective. These crystals often contain cationic or anionic vacancies with non-stoichiometric composition. In the presented work on attempt to correlate the sulfur/iron ratio in natural auriferous pyrites with their flotation properties has been undertaken.

MATERIALS AND EXPERIMENTAL METHODS

Pyrites from five deposits have been examined. The data on the contents of iron, sulfide and free sulfur, donor (Cu) and acceptor (As) impurities in the samples are given in the Table 1. The true formulas of mineral pyrites have been calculated from the iron and sulfide sulfur analytical ratio.

Ground mineral samples were agitated in distilled water in the presence of pH regulator. The liquid phase within the range of pH 6-12 was analyzed for the content of sulfide and sulfite ions. The inverse iodimetric titration and lead nitrate titration at the presence of dithizon methods were used (Lurie, 1984). An amount of elementary sulfur at the mineral surfaces, quantities of adsorbed butyl xanthate under different pH values were analyzed by using UV-spectroscopy with Specord M 40.

Experimental conditions for determination of oxidized and reduced forms of sulfur compounds were as follows: 2 g of -0,16+0, 063 μm mineral sample was mixed with 40 ml of liquid phase than the suspension was conditioned by 10 minutes. The suspension pH regulated with NaOH.

Table 1. Elemental composition and non-stoichiometry of pyrite samples

Sample No	Content					Real formula	Non-stoichiometry: (S/S _{theoretic})	
	Fe	S Sulfide	Cu	As	g/t Au			mg/g S free
1	42,0	45,0	0,2	0,04	10	0,11	FeS _{1,87}	0,94
2	33,2	45,55	3,2	0,01	10	0,33	FeS _{2,39}	1,2
3	41,5	36,6	0,6	0,3	1	0,77	FeS _{1,54}	0,77
4	38,3	33,8	0,8	2,5	40	0,23	FeS _{1,55}	0,78
5	38,7	45,5	0,14	0,1	10	0,19	FeS _{2,05}	1,03

For flotation tests 1g of mineral samples were used. Mechanical flotation cell having 20 ml in a volume was used. Xanthate and frother dosages were 300 and 150 g/t respectively. The conditioning and flotation time was 2 minutes.

RESULTS AND DISCUSSION

The analysis of the studied pyrite characteristics (Table 1) has allowed to classify them according to types which reflects the relations between the structure and composition for non-stoichiometric compounds (Wadsley, 1964). The deviation from a multiplicity of cationic and anionic parts proportions in samples (1) and (5) is connected with the lack of sulfur and iron variable amounts in mineral structure

(deduction). Non-stoichiometry of sample (2) and sample(4) can be explained by admixtures (copper or arsenic) entering the mineral lattice (interpolation). Displacement dominates in the sample (3) which is rich in free sulfur. The iron atoms can be located in sulfur positions becoming vacant during oxidation of S^{2-} to S^0 .

A comparison of the ration of substantial and stoichiometric of sulfide sulfur contents ($S/S_{theoretic}$) and free sulfur amounts on their surfaces has shown the following features. The deviation from a stoichiometry of mineral samples composition strongly influences their surface abilities to oxidation. Therefore, free sulfur is determined at pyrite surfaces (sample 1) and (sample 5) where small deflection from a stoichiometry (0,11 and 0,19 mg/g) existed. On the other hand, samples with considerable excess of sulfur (sample 2) and (sample 3) show a deficit of anionic parts (0,33 and 0,77 mg/g). Influence of gold content on pyrite surface oxidation is marked. Sample (3) (1g/t Au) and sample (4) (40 g/t Au) are characterized by approximately identical deviation from a stoichiometric sulfide sulfur content, however amount of free sulfur on an auriferous sample is 3 times less in this case.

It is known, that when increasing the oxygen concentration and sulfur contact endurance the further oxidation with liberation of mineral surface will be happen (Glazunov,1998).The peculiarity of such processes in the mineral suspension at non-stoichiometry pyrite positions, were observed. The curves in the Fig. 1 and 2 illustrate the variation of the sulfite and sulfate ion concentrations at the mineral suspensions in the range of pH 6-12. Pyrite, with an excess of anionic part is characterized by a formation of sulfites and sulfates in less degree (curve 5, Fig. 1 and Fig. 2). In the case of pyrite with a deficit of anionic components the sulfur is oxidized up to sulfates (curve 1, Fig. 2). Under the equal starting oxygen concentration in liquid phase of sample (1) and sample (5) it is possible to suspect, that pyrites with a shortage of sulfide anions are oxidized up to the highest sulfur oxidation degree (+6), and pyrites with an excess of sulfide anions oxidized up to intermediate degree (+4). This conclusion is correct at the values of $pH > 9$, where the sulfites are rather stable only in alkaline conditions. An anionic part surplus in the sample (2) and its deficit in the sample (4), and also free sulfur amount on their surfaces are considerably higher than the same parameters at sample (5) and sample (1). However, sulfur oxidation in liquid phase is more gentle (curves 2 and 4). In this case a free sulfur surface film on the mineral surface is inconvertible enough and it is not removed during contact to fluid phase. The sample (3) is characterized by the greatest deficit of anionic part and free sulfur content and the sulfur surface is oxidized both to sulfites and sulfates (curve 3, Fig.1 and Fig. 2 respectively). Thus, at the deviation from a proportion multiplicity of cationic and anionic parts in pyrites as can be dedicated (sample 1 and sample 5) the free sulfur is removed from the surface and passes in a liquid phase as sulfur-containing ions with a degree of oxidation (+4) or (+6). The non-stoichiometry of pyrite which aroused by the interpolation of elements-admixtures (samples 2 and 4), causes the formation of an inconvertible free sulfur film on the mineral surface. The

failure of stoichiometry as a displacement (sample 3) is characterized by considerably major content of free sulfur, however, it dissolves partially as sulfites and sulfates at the fluid phase contact.

The deviation of pyrites composition from a stoichiometric iron to sulfur proportion with formation both cationic, and anionic vacancies testifies to partial crystal lattice destruction. This destruction effects on the adsorbed xanthate forms on the mineral surface. The relationship between chemisorbed form of collector and a proportion of a substantial and idealized content of sulfide sulfur is illustrated in Fig. 3.

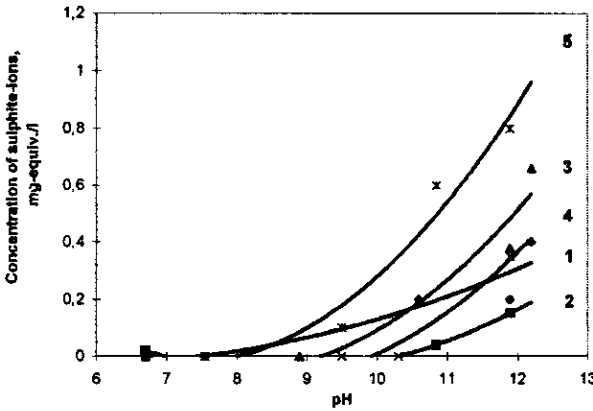


Fig.1. Sulphite-ions concentration in liquid phase of pyrite suspensions as a function of pH
1; 2; 3; 4; 5 – sample number

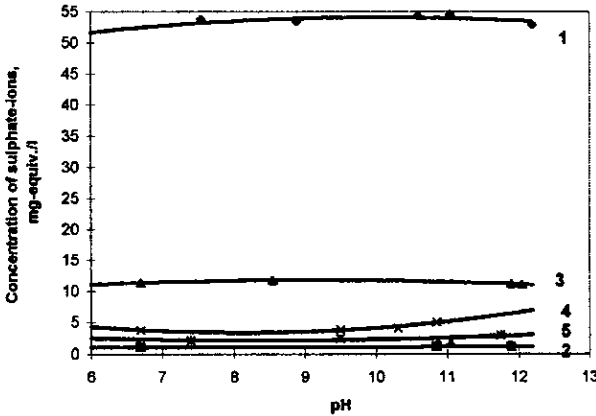


Fig.2. Sulphate-ions concentration in liquid phase of pyrite suspensions as a function of pH
1; 2; 3; 4; 5 – sample number

The non-stoichiometry increase as a result of anionic part surplus or its shortage, results in the increase of chemical sorption. From the collected data such as free sulfur amount and its stability on the mineral surfaces, and a magnitude of the collector chemisorption, it is possible to suspect, that samples with a deviation in iron and sulfur ration will show a different behavior in flotation.

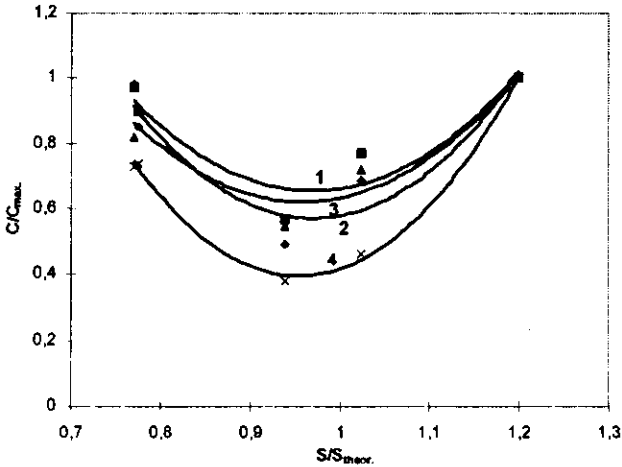


Fig.3. Xanthate chemisorption as a function of pyrites anionic part non-stoichiometry
 1 – pH 9; 2 – pH 10; 3 – pH 11; 4 – pH 12

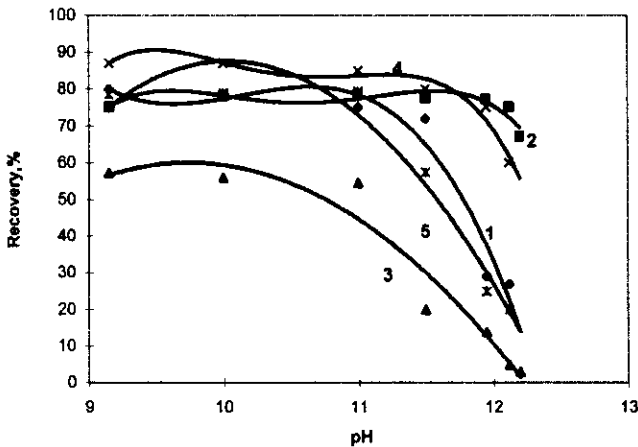


Fig.4. Floatability of pyrite samples as a function of pH, 1; 2; 3; 4; 5 – samples numbers

The analysis of pyrite flotation curves as a function of pH (Fig. 4) has shown, that sample (1) and sample (5) exhibit similar floatation properties. The pyrite recovery was about 80 % in a range of pH 9-11. The further raise of liquid phase alkalinity causes a partial depression. The pyrite recovery do not exceed of 25 % at pH equals 12-12,2 .

Sample (2) and sample (4), with high content of copper, arsenic and gold impurities and high values of non-stoichiometry, were effectively floated even in strongly alkaline conditions at pH 11,8-12,2.

Sample (3), which is rich in surface sulfur and has the most defective crystal lattice resulted in a displacement of sulfide vacancies by iron atoms, is the most responsive to the alkaline depression.

CONCLUSION

The experimental investigations onto geochemical differences and structural irregularities, as well as onto oxidizing, sorption and floatation characteristics of auroferrous pyrites have been performed. It was found, that the deviation from a stoichiometry of the basic components - iron and sulfur can be used for the forecasting technological properties of minerals under hard-to-beneficiate gold ores processing.

The relationship between pyrites non-stoichiometry and their oxidation ability is detected. The minerals having structure close to stoichiometric, are oxidized with transferring sulfide sulfur into sulfite and sulfate ions. Thus, oxidation of pyrite with an excess of anionic part occurs up to a stage of sulfites ions formation, and with a deficit - up to sulfates ions. A limiting stage of oxidation process of pyrite with a maximal deficit of sulfide part is the free sulfur formation.

Pyrites non-stoichiometry caused by the elements-admixtures intrusion results in formation as surplus (donor impurity of copper), and shortage (acceptor impurity of arsenic) of anionic part. The similar non-stoichiometry of iron/sulfur ratio essentially raises the chemisorbed collector content and ensures the pyrites floatability even in strong alkaline solutions.

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V.A.Chanturiya, A.A.Fedorov, T.N.Matveeva, Wpływ niestechiometrii złotonośnego pirytu na właściwości flotacyjne i adsorpcyjne, *Fizykochemiczne Problemy Metalurgii* 34 (2000), 163 –170, (w jęz. ang.)

W pracy podjęto próbę wyjaśnienia różnic w właściwościach sorpcyjnych i flotacyjnych pirytów pochodzących z różnych złóż. Różnice we własnościach pirytu uzależniono od proporcji podstawień atomami żelaza i siarki czyli odstępstwami od stechiometrycznego składu pirytu. Wpływ tej naturalnej niestechiometryczności składu pirytu upatrywano w lepszej zdolności do utleniania, jak również, korelowano ten fakt z stężeniem jonów siarczanowych i siarczynowych w roztworze w trakcie flotacji. Zostało pokazane, że chemisorpcja kolektora wzrasta na pirytach o niestechiometrycznym składzie. Stosunek siarka/żelazo w naturalnych złotonośnych pirytach koreluje dobrze z wynikami flotacji w zakresie pH 9-12.