Role of the carbonate impurities on the surface state of pyrite and arsenopyrite under treatment by high power electromagnetic pulses (HPEMP): oxidation of 50-100 μm size particles.

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Abstract. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Transmission Electron Microscopy (TEM) have shown the variation of surface phase compositions of carbonate bearing pyrite and arsenopyrite as a result of the combined action of chemical oxidation and thermal processes after the treatment by high power electromagnetic pulses (HPEMP). The monitoring of the surface phase composition allowed to determine the correlation between the treatment conditions, the surface phase composition, and the flotation yield. Thus, HPEMP treatment may be regarded as a tool controlling the surface composition and the sorption ability of flotation collector onto minerals surface, and therefore, allowing to control the hydrophobic-hydrophilic surface balance. It was confirmed in this study that the flotation of pyrite with xanthate as a result of the influence HPEMP may vary depending on the presence of impurities such as calcite.

1. Introduction

Gold-bearing sulphides are significant contributors to overall world gold production. Flotation is the principal process for pre-concentration of the sulphides, for subsequent smelting, roasting or hydrometallurgical treatment [1]. It is often found that gold is associated mainly with arsenopyrite or pyrite in a sulphide ore: therefore, the pyrite/arsenopyrite separation would be of interest. Arsenopyrite has very similar properties to pyrite and the selective separation of these minerals using xanthates as collectors is problematic. When the arsenopyrite needs to be separated from pyrite, the former is usually depressed. It is noted that the boundary between flotation and depression of arsenopyrite is marked by the X−/X2 reversible potential [2]. The formation of ferric−hydroxide−arsenate species seems to inhibit the oxidation of xanthate ions into dixanthogen causing depression of arsenopyrite at Eh−pH conditions of dixanthogen stability[3-5].

Regulating the oxidation state of the pyrite and arsenopyrite by the addition of oxidants (such as H2O2, KMnO4, MnO2 and HClO) or reductants (sodium sulfide, sulfite and dithionite) is the key to selective separation using xanthate as collector at high pH. KMnO4 is the preferred oxidant and when
used as an arsenopyrite depressant is coupled with a control of the redox potential at between 400 and 500 mV \([3, 6, 7]\)). The precise control of the redox potential was found to be essential in order to prevent depressing the pyrite also.

Another way of modifying mineral properties of sulphides is to create “energetic impacts”. A strong interest in this method was shown recently \([8, 9]\). The method consists in using high power electromagnetic pulses (HPEMP). This was applied successfully for the selective disintegration of fine-grained mineral complexes for the break out of precious metals inclusions followed by their subsequent extraction in leaching solutions.

Also the possibility of applying this treatment method for selective separation of pyrite from arsenopyrite by flotation in neutral pH environment was observed \([10 -12]\]). It was found that the flotation of pyrite with xanthate after HPEMP treatment may vary, depending on the presence of metal impurities (such as Co, As, Ni, Cu) that have a possible influence on the electrical properties of pyrite. Calcite is another mineral impurity that can modify sensitively the flotation behaviour of pyrite. From this follows the importance of studying the effect of impurities on the surface properties of pyrite. For this purpose, the X-ray Photoelectron Spectroscopy (XPS) and infrared spectroscopy were used as the most powerful tools for investigating the surface state of iron sulfides \([13]\).

This work aims at further understanding of the arsenopyrite and pyrite flotation chemistry with xanthates, and of the surface oxidation of arsenopyrite and of pyrite in the presence of impurities such as calcite. In this work we examined the role of the carbonate impurities on the surface state of pyrite and arsenopyrite during oxidation under treatment by HPEMP. Solid characterizations (DRIFTS, XPS, TEM) were used to ensure a complete understanding of the reactional paths.

2. Materials

Two natural mineral samples used in the present study came from the Darasun ore field (Chita region, Russia). Both the minerals were characterised by X-ray diffraction, ICP-MS, electron microprobe, MEB and TEM analyses. The chemical compositions of pyrite and arsenopyrite used here are presented in Table 1. Minerals were found to contain about 9.3-955% impurities.

| Sample | Fe% | S% | As% | Cu% | Sb% | Pb% | Zn% | Ca% | Al% | P% | Coppm | Bippm |
|--------|-----|----|-----|-----|-----|-----|-----|-----|-----|----|-------|-------|
| FeS₂   | 40.61 | 49.89 | 0.69 | 1.29 | 1.18 | 0.88 | 0.28 | 0.78 | 0.09 | 0.03 | 141.7 | 104.00 |
| FeAsS  | 30.79 | 19.60 | 40.30 | 0.02 | 0.04 | 0.01 | nd  | 0.18 | 0.53 | 0.02 | 0.01 | 40.20 |

Specimens of both the sulfides contain calcite CaCO₃, quartz SiO₂, kaolinite Al₂Si₂O₅(OH)₄. The electron microscope microanalysis of the pyrite specimen reveals Cu, Sb, and As bound with sulfide inclusions of tennantite-tetrahedrite group (Cu₁₂As₄S₁₃ – Cu₁₂Sb₄S₁₃) minerals with appreciably variable Cu, Sb and As ratio. Arsenic in FeS₂ specimens is also bound with arsenopyrite (FeAsS); Pb is bound with galena (PbS), pure or rich in impurities (Sb, Cu, As, Ag) and berthonite CuPbSbS₃ (pure or with As impurities). Zn is bound with sphalerite (ZnS) in association with grey copper ore and pyrite. In pyrite specimens Bi-Te mineral inclusions were found, specific for gold-ore deposits: bismuthinite Bi₂S₃ (inclusions up to 90 µm), tetradymite Bi₂Te₂S (up to 35 µm) and tellurobismuthinite Bi₂Te₃ (up to 10 µm).

3. Experimental Procedure

Minerals were dry ground in a porcelain mortar, and a size fraction of 50-100 µm was selected by sieving. The samples were then wetted in distilled water before being treated by HPEMP and dried in a nitrogen atmosphere to minimize the natural oxidation of the minerals. The untreated wet samples that were dried under nitrogen will be referred to as initial samples in both the cases.

The treatment of the samples by electromagnetic pulses (HPEMP) was carried out in a laboratory unit \([8]\) in air by using a series of pulses with a nanosecond front period between 5 and 30 ns. The
Electrical field component was 30 kV, whereas the frequency of pulses and pulses repetition were set at 100 Hz. The treatment doses varied from 0.05 to 1.5 kJ. The pulses parameters were kept constant meanwhile the treatment doses were controlled by changing the treatment duration.

DRIFT spectroscopy was used to characterize the surface species on the treated mineral particles. The spectra were taken using a BRUKER EQUINOX55 device.

XPS spectra were recorded at room temperature under a pressure of ~10^{-9} mbar using an X-ray photoelectron spectrometer KRATOS Axis Ultra equipped with a monochromatic Al Kα source (1462 eV). The instrument was calibrated using metallic copper (binding energy of 932.62 eV for the Cu3/2 line). The spectra were recorded around the S2p, C1s, O1s and Fe2p lines.

In addition to information obtained from IR and XPS was also used a high-resolution transmission electron microscope (TEM) Philips CM20 (200 kV) equipped with an Energy Dispersive Spectrometer (EDS).

4. Results and Discussion

Surfaces of HPEMP treated pyrite minerals have been studied by DRIFT spectroscopy, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy including microanalysis (TEM/EDS).

DRIFT analysis (figure 1) has shown that, before the treatment, the pyrite surface was represented by a mixture of Fe^{2+}/Fe^{3+} hydrated sulphates (nH_2O=7−9) dominated by melanterite (Fe^{2+}SO_4·7H_2O). Sulphates, observed in spectra, are associated with ferrous (606 cm^{-1} ν_4, 1093 cm^{-1} ν_3), ferric iron (998 cm^{-1} ν_1, 1043 and 1152 cm^{-1} ν_3) and occasionally with both iron oxidation states (1020 cm^{-1}). The weak quantity of ferric oxyhydroxide, probably goethite FeOOH (the massif at 600-700 cm–1 and characteristic absorption band at 794 cm –1 can also be associated with Si-O of quartz), as well as of Ca carbonates (713, 874, 1437 cm –1) and traces of calcium sulfates (1115 cm –1 with a shoulder at 1155 cm–1) were detected.

After the HPEMP treatments (0.05÷1 kJ) of the sample, the mineral surface is strongly "gypsumed" because of FeS_2 oxidation and calcite transformation into gypsum as show the stretching (νOH) at 3548, 3491, 3408, 3244 cm -1 and the bending (δOH) at 1618, 1685 cm -1 vibration of crystal water and also stretching (νSO_4) vibration of sulfate groups at 1137, 671, 606 cm -1 (Figure 1). The chemical oxidation of FeS_2 under HPEMP treatments in the presence of water can provoke a local formation of sulphuric acid, which can react with calcium carbonate impurities to form gypsum according to the reaction:

\[ \text{FeS}_2 + 15/4\text{O}_2 + 9/2\text{H}_2\text{O} + 2\text{CaCO}_3 \rightarrow \text{FeO(OH)} + 2\text{CaSO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2 \]

With consideration for the local surface heating effect [8], it can be assumed that the increase in number of impulses can cause the thermal oxidation and decomposition of pyrite to form a series of final products, such as hematite (Fe_2O_3), magnetite (Fe_3O_4), iron (ferric or ferrous) sulphate (Fe_2(SO_4)_3), FeSO_4 and gaseous sulphur oxides (mainly SO_2) that react with CaCO_3 to form CaSO_4:

\[ \text{CaCO}_3 + \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{CaSO}_4 + \text{CO}_2 \]

Simultaneously, the absorption bands of carbonate group of calcite decreased considerably (1795, 1421, 874, 713 cm–1).

An increased intensity of stretching and bending of OH-groups vibration of the sulphates crystal water is detected on the spectra of pyrite under a high treatment dose (≥1kJ). In addition, the vibration of free water OH groups appears in the spectra (3702 cm^{-1} and 3727 cm^{-1}) at high number of pulses. In the case of arsenopyrite, no considerable variation of DRIFT spectra profile was detected with the increase in number of pulses. But similarly to the pyrite case, bending vibrations of free water molecules were observed. It is essential to mention that gypsum does not form at arsenopyrite surface and that calcite, available in a specimen, undergoes none transformations depicted by IR spectroscopy.

TEM qualitative analysis for samples of pyrite, allows confirm in this study the formation of calcium sulphate under HPEMP treatment. As shown in figure 2, peaks corresponding to Ca, S and O are
detected in the EDX spectra and it was confirmed that gypsum is formed in calcite-bearing pyrite samples during HPEMP treatment.

![Figure 1. DRIFT spectra of the untreated and HPEMP treated pyrites samples. Treatment energy of samples: a) 0 kJ, b) 0.1 kJ, c) 0.5 kJ, d) 1.0 kJ.](image)

![Figure 2. (a-b) TEM micrographs and corresponding EDS spectra of elements of gypsum in the pyrite sample after HPEMP treatment (0.05 kJ); (c-f) X-ray images which mapped the location of O, Fe, Ca and S.](image)

In this study, the feasibility was explored for using transmission electron microscope (TEM) in conjunction with energy dispersive x-ray spectroscopy (EDS) to determine the oxygen directly and to quantify the sulfur content of the pyrite. The ability to perform chemical analysis of a sample during observation is an advantage to determine the degree of oxidation of pyrites and their chemical composition based on the detected elements after different treatment dose. In treated minerals, the TEM-EDS measurements show significant alterations in the respective surfaces when different HPEMP treatment were applied. In treated samples, the formation of Fe^{III} species containing oxygen were detected. The pyrite surface shows a layer of modified species with high oxygen content as a function of energy of HPEMP treatment (Figures 3 and 4). The samples of pyrite treated with a dose of 0.5 kJ produces less oxidized pyrite and iron oxide particles than in the samples treated with 0.05 kJ and 1 kJ (Figure 3). That is, there is no pattern of growth of oxide particles with the increase of the energy processing. This may indicate the presence of certain processes and the formation of compounds that protect the particles during the processing of pyrite oxidation [13].

Since we could not explain this result only from infrared spectroscopy or electron microscopy results, we used an additional X-ray photoelectron spectroscopy results presented in a previous paper [12]. As was reported by Chanturiya et al. [11,12] XPS results show considerable qualitative and quantitative changes of the surface layer composition of both the sulphides depending on the treatment conditions. After the treatment the increase of Fe oxidized (FeOy-FeOOH.nH_{2}O - Fe(OH)_{y}.nH_{2}O) was determined for all treated samples of pyrite from Fe2p and O1s lines.

At a treatment dose 0.05 kJ the intensive formation of iron oxide and hydroxide phase was observed in Fe2p and O1s lines. The surface concentration of iron oxides increased 2 times according to the fitting of O1s line. An increase of S° surface concentration from 12.95 % to 23.56 % was observed according to the S2p line [12].
Figure 3. Schematic representation of the results of TEM-EDS analysis of change chemical composition of the FeS$_2$ samples as a function of energy of HPEMP treatments.

A further increase of treatment dose (0.1 kJ) results in an increase of iron sulphates surface concentration. These results corroborate with the surface modification obtained in this paper and confirm the cyclic character of pyrite oxidation as a result of combined action of chemical oxidation and thermal processes after the treatment by high power electromagnetic pulses (HPEMP).

The treatment at 0.5 kJ results in a further increase of Fe sulphide, as well as a decrease of S$^0$ surface concentration (Figure 3). A 1 kJ treatment dose results in an increase of the surface concentration of the oxidation product. The process of elemental sulphur thermal removal was hypothetically discussed previously as an explanation of these results [12].

Arsenopyrite has shown an intensive oxidation at low treatment doses with formation of iron sulphates and As oxides. We have shown [10] that the surface hydration increased 3 times as
compared with the initial sample. An increased sorption activity of HPEMP-processed pyrite at 0.5 kJ and 1.0 kJ in relation to HPEMP-unprocessed mineral was identified. Flotation tests have demonstrated that in the presence of ethyl xanthate, flotation activity of processed pyrite samples increased in average by 18.9% in comparison with the reference sample. On the contrary, the recovery of arsenopyrite decreased from 53.4% (0) to 23.7% (0.1 kJ). For 0.5 kJ and 1.5 kJ modes, arsenopyrite recovery was 36.1% and 29.07%, respectively [10].

5. Conclusions.
The phase composition of pyrite surface underwent significant changes during electric pulse treatment. The TEM study coupled to DRIFT analyses shows a cyclic oxidation way of pyrite surface as a result of combined actions of chemical and thermal action of high power electric pulse treatment. The pyrite activation at low-energy high-pulse treatment (<0.1 kJ) is ensured by the formation of elementary sulphur within a dose range of 0.1 kJ \( \div \) 1 kJ. The arsenopyrite depression is related to an increase in the general hydration of mineral surface during treatment, as well as a change in phase composition and electrophysical surface properties. The significant amounts of gypsum on the surface of the pyrite after HPEMP treatment is linked to the interaction of sulfates ions with the calcite present as impurity in the pyrite.

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