

XPS and FTIR study of the influence of electrode potential on activation of pyrite by copper or lead

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Abstract

Activation of pyrite by either copper or lead ions and subsequent xanthate adsorption on activated surfaces were studied in aqueous solutions of pH 5, 6.5 and 9 under different electrochemical conditions using X-ray Photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). At pH 5, the copper concentration on the surface of pyrite increased strongly when the electrode potential was changed towards cathodic direction. At low activation potentials ($E_h \leq +100$ mV), a change in the chemical state of sulfur on the surface was observed by XPS proposing formation of a copper-containing surface sulfide phase. In electrochemically-controlled xanthate adsorption, the behavior of copper-activated pyrite resembled that of chalcopyrite (CuFeS_2). The results indicate that activation of pyrite by copper at pH 5 can be controlled by the potential of the mineral. At pH 9, the copper content on the surface was independent of the potential of pyrite and no changes were observed in chemical state of sulfur if compared to unactivated pyrite in the potential region -100 to $+400$ mV (SHE). In the case of pyrite activation by lead, no changes were observed in sulfur spectra at either pH 5 or 9 at different electrode potentials. The concentration of lead on the surface increased at pH 5 when potential was changed towards cathodic direction. All lead present at the surface of pyrite was concluded to be in the form of lead(II)-oxygen species and no evidence of exchange between lead and iron was found. Both adsorbed xanthate and dixanthogen were observed on the surface of Cu-activated pyrite after activation at cathodic potentials (-100 to $+50$ mV) and subsequent treatment in either ethyl or amyl xanthate solution of pH 5 or 6.5 at potential region $+350$ to 550 mV (standard hydrogen electrode, SHE). In a similar experiments with Pb-activated pyrite, only a faint indication of the adsorbed collector species was found proposing that lead rather depresses than activates pyrite. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Valuable base metal sulfides are generally recovered from ore deposits using flotation processes. Because pyrite (FeS_2) is the most abundant sulfide mineral in the earth's crust and being usually associated with other sulfide minerals, its

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efficient separation is in many cases crucial for the performance of the flotation processes. Selective separation of sulfides is a particularly challenging task when processing complex ores because mutual interactions between different sulfides in the mineral slurry have also to be considered. Electrochemical control in the activation and xanthate conditioning stages has shown to play an important role in the selective flotation of sulfide minerals from complex ores [1]. Although activation is commonly used intentionally to enhance the subsequent collector adsorption and hence, to make a particular mineral more floatable, the mineral can also be inadvertently activated by the presence of other minerals during grinding, conditioning and flotation stages.

Wang [2] has extensively discussed the activation of pyrite by copper using mainly theoretical and indirect experimental methods, while a few surface analytical studies have been previously reported in the literature, e.g. [3,4]. Recently, we reported some preliminary XPS and FTIR experiments where both copper and lead activation was discussed [5]. In this work, we have studied in more detail the influence of electrode potential on the activation of pyrite by either copper or lead in both acidic and alkaline aqueous solutions.

2. Experimental

FeS₂ crystals were single crystal pieces cut from a large single crystal specimen (approximate size 6 × 6 cm) originating from the Ural area, Russia. Elemental composition of the sample was checked with X-ray fluorescence analysis showing only small amounts (<0.1%) of arsenic, copper, cobalt, zinc and antimony as minor impurities. Before each activation experiment, a piece of FeS₂ crystal (approximate surface area 0.5 cm²) was wet polished with SiC grinding paper (600 Mesh), washed with pure deionized water (18 MΩ cm) and introduced as wet to the electrochemical cell. A three electrode cell (volume 250 ml) with an Ag/AgCl/KCl reference electrode connected to a Pine AFRDE5 potentiostat was used for polarization of the pyrite sample. All potentials in this paper are referred to the standard hydrogen elec-

trode (SHE) scale assuming that the potential of Ag/AgCl/KCl electrode is +220 mV versus SHE. After introduction to the electrochemical cell, the mineral sample was first kept at a fixed reductive potential of -250 mV for 10 min to obtain a better defined starting point for subsequent activation treatments. This potential value was chosen to be just above the lower stability limit of pyrite at pH 5, which is more critical than pH 9 in this context. The activation reagent was then added and the potential of the sample was immediately adjusted to the desired value. After a treatment time of 15 min, the mineral was quickly rinsed with pure water to prevent precipitation of the electrolyte during drying, and introduced to XPS spectrometer.

A fresh electrolyte solution was bubbled with nitrogen gas (99.999%) for 30 min before each experiment. Either copper or lead ions were added to the solution as Cu(NO₃)₂ or Pb(NO₃)₂ to obtain a concentration of 10⁻⁴ M. Although copper is usually added as copper(II)-sulfate in real flotation processes (e.g. activation of ZnS with copper), nitrate salts were used in this work, because lead(II)-sulfate is only sparingly soluble. To minimize the number of different anions in the solution, sodium nitrate was used as a basic electrolyte (concentration 0.05 M). The pH of the solution was adjusted with either HNO₃ (pH 5) or NaOH (pH 9). All these reagents were of analytical grade.

Sodium ethyl or amyl xanthate was used in adsorption experiments. Commercially available xanthates were purified in a usual manner by dissolution in acetone followed by precipitation with petroleum ether before each series of measurements.

The XPS experiments were carried out with PHI 5400 electron spectrometer equipped with monochromatized AlKα ($h\nu = 1486.6$ eV) X-ray source and hemispherical electron energy analyzer. Calibration of the energy scale of the spectrometer was performed using Au4f_{7/2} (binding energy BE = 84.0 eV) and Cu2p_{3/2} (BE = 932.7 eV) photoelectron lines. The spectrometer includes a possibility to cool samples with liquid nitrogen (T ≈ 130 K) before evacuation and during the measurement to prevent evaporation of

volatile species from the sample surface in ultra high vacuum ($p \sim 10^{-7}$ Pa) [6].

A Nicolet 740 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector was used to record the infrared spectra. The internal reflection method was applied using Specac's 10-reflection ATR accessory placing the pyrite plate tightly against a germanium internal reflection plate. Preparation of pyrite samples and the electrochemical treatments were identical to that used in the XPS experiments described above except larger pyrite samples (2 cm^2) were used in the FTIR studies.

3. Results and discussion

3.1. Activation of pyrite by copper

At pH 5, the amount of copper on the surface increased strongly when the electrochemical potential of pyrite decreased, which can be clearly seen from the Cu/Fe atomic ratio presented in Fig. 1. According to XPS, most of the copper was in the formal oxidation state +1. However, a small and potential independent contribution of Cu(II) species was also observed in the Cu2p spectra. The existence of Cu(II) species has been earlier explained by Voigt et al. [3] to be due to mixed iron and copper hydroxides formed on the surface even in the acidic pH region.

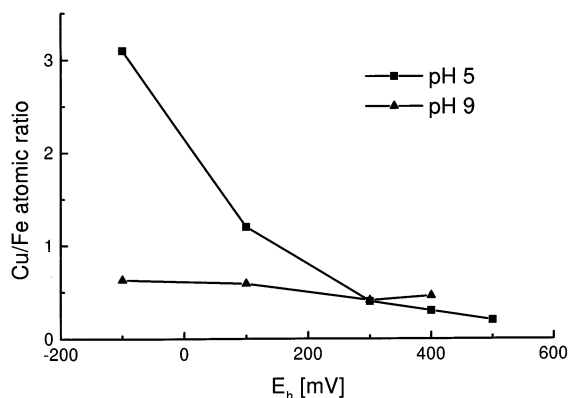


Fig. 1. Measured Cu/Fe atomic ratios as a function of activation potential. Pyrite sample was treated for 15 min in aqueous solution containing Cu^{2+} ions.

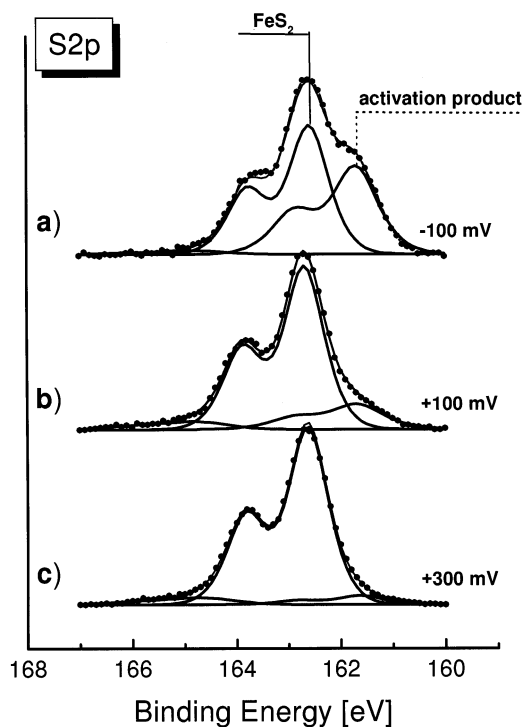


Fig. 2. Sulfur 2p photoelectron spectra of pyrite sample activated with copper in pH 5 aqueous solution for 15 min at potentials -100 mV (a), $+100 \text{ mV}$ (b) and $+300 \text{ mV}$ (c).

More interesting observation was that in the S2p spectra, a new well defined chemical state of sulfur at binding energy (BE) 161.6 eV was evident when the activation potential was 100 mV or lower (Fig. 2, spectra a and b). The S2p spectrum at 300 mV (Fig. 2, spectrum c) resembles that of pure pyrite. Based on the interpretation presented earlier in the literature [6,7] the main component at BE 162.6 eV is the pyrite bulk signal, whereas the small components observed at approximate BEs 161.5 and 164.7 eV are due to pyrite surface states and oxidized pyrite, respectively. The intensity ratios of the three components in the spectrum c in Fig. 2 are in agreement with those observed for pure pyrite. The BE of the new sulfur state is typical for different copper sulfides (e.g. chalcocite Cu_2S , chalcopyrite CuFeS_2) [8]. Because the Fe/S atomic ratio remained practically constant (varies between 0.47 and 0.49) when the concentration of copper changed, a new phase is very probably of chalcopyrite-type in

which the Fe/S ratio is the same as in pyrite. At the same time, electron neutrality is attained because the reduction of copper is compensated by the oxidation of iron when chalcopyrite is formed. This conclusion was further supported by the results obtained after treating copper-activated pyrite in aqueous ethyl xanthate solution. In that experiment, a pyrite sample was first activated at -100 mV and then treated in 10^{-4} M ethyl xanthate solution for 15 min at $+400$ mV before introduction to the electron spectrometer. Sample cooling [6] was necessary in this case because ethyl xanthate is known to oxidize to dixanthogen on the surface of pyrite [4,6,9] or chalcopyrite [4,10] under these conditions and dixanthogen has such a high vapor pressure that it would evaporate quickly from the surface to the ultra high vacuum at room temperature. The measured S2p, O1s and C1s photoelectron spectra indicated clearly that dixanthogen was the main adsorption product under these experimental conditions. When the same sample was remeasured after warming up the sample to room temperature, dixanthogen was no longer detected on the surface, but O1s and C1s emissions still consisted of components, which are characteristic to chemisorbed ethyl xanthate. The FTIR experiments carried out under similar conditions during this work and earlier [5] are in agreement with the XPS results and interpretation. Both chemisorbed ethyl xanthate and dixanthogen has been earlier observed on chalcopyrite surfaces with both FTIR and XPS methods [10,11], but not unequivocally on the surface of massive pyrite [5,12,13] or chalcocite [14] surfaces. Hence, it may be concluded that copper activated pyrite surface has changed to a chalcopyrite-like surface although it is impossible to verify its exact structure from the experiments carried out here.

The effect of activation potential on the surface properties of pyrite was studied separately using FTIR-ATR spectroscopy. In these studies, activation was carried out at one potential and treatment with sodium amyl xanthate at another potential.

When copper activation was carried out at open-circuit potential (about $+400$ mV), the intensity of the IR peaks of xanthate adsorption

products were very weak after xanthate treatment at -250 to $+550$ mV. At a more cathodic activation potential, $+50$ mV, amyl xanthate adsorption was much stronger after xanthate treatment at $+150$ to $+550$ mV indicated by typical IR adsorption bands of diamyl dixanthogen at 1261 and 1027 cm^{-1} (Fig. 3). In this case, no adsorption products were observed at potentials lower than $+150$ mV.

After activation at $+50$ mV, it was interesting to note that IR peaks of copper amyl xanthate (1181 , 1157 cm^{-1}) appeared in xanthate treatment at $+350$ to $+550$ mV. In this potential range both dixanthogen and copper xanthate were present at the surface of pyrite. Consequently, the electrochemical behavior of xanthate adsorption on copper-activated pyrite resembles that of chalcopyrite presented in the earlier study of Leppinen et al. [11] also showing two surface products at higher potentials. This finding is in agreement with the interpretation of XPS results of this work showing the formation of new sulfide phase at low activation potentials.

The spectral assignments of the characteristic peaks of copper ethyl xanthate are given in the literature [11,15]. As only the hydrocarbon part is different it can be assumed that the interpretation is valid also for amyl xanthate. The bands at 1181 and 1119 cm^{-1} are due to asymmetric vibrations of C–O–C and S–C–S groups whereas the band at 1025 cm^{-1} is due to the stretching vibration of S–C–S group.

When copper activation was carried out at pH 9, the concentration of copper on the surface was practically independent on the potential of pyrite and about 40% of total copper was formally in the Cu(II) oxidation state. Because the Fe2p spectra also showed a strong Fe(III) contribution it is reasonable to conclude that pyrite surface was covered by both copper and iron hydroxides or oxyhydroxides. This conclusion is further supported by the O1s emission which consisted of two components at binding energies 530.0 and 531.2 eV which are typical values for oxide and hydroxide type oxygen, respectively [13,16]. If compared to corresponding experiments at pH 5, the total concentration of oxygen on the surface was approximately double at pH 9. According to

Wang [2], in the alkaline pH region, the formation of iron (and copper) hydroxides on the surface prevent the direct contact between Cu^{2+} ions and pyrite surface.

No change in the chemical state of sulfur was observed at activation potentials below +400 mV proposing that although copper is stabilized on the surface, all sulfur still remains bonded to iron in pyrite lattice. At +500 mV, pyrite itself was not stable any more and oxidized sulfur species (sulfate, elemental sulfur and metal-deficient sulfide or polysulfide) were also detected.

3.2. Activation of pyrite by lead

Lead $4f_{7/2}$ signal at 138.3 eV was observed after treatment of pyrite sample in lead(II)nitrate solution at pH 5. The concentration of lead (Pb/Fe ratio, Fig. 4) increased when the pyrite potential decreased. Although the general behavior was similar to copper activation, the Pb/Fe ratio was approximately 10–20% of the Cu/Fe ratio at every particular potential studied. No changes in the shape of either sulfur or iron spectra were observed as a function of potential. Taking into account the binding energy of surface lead and

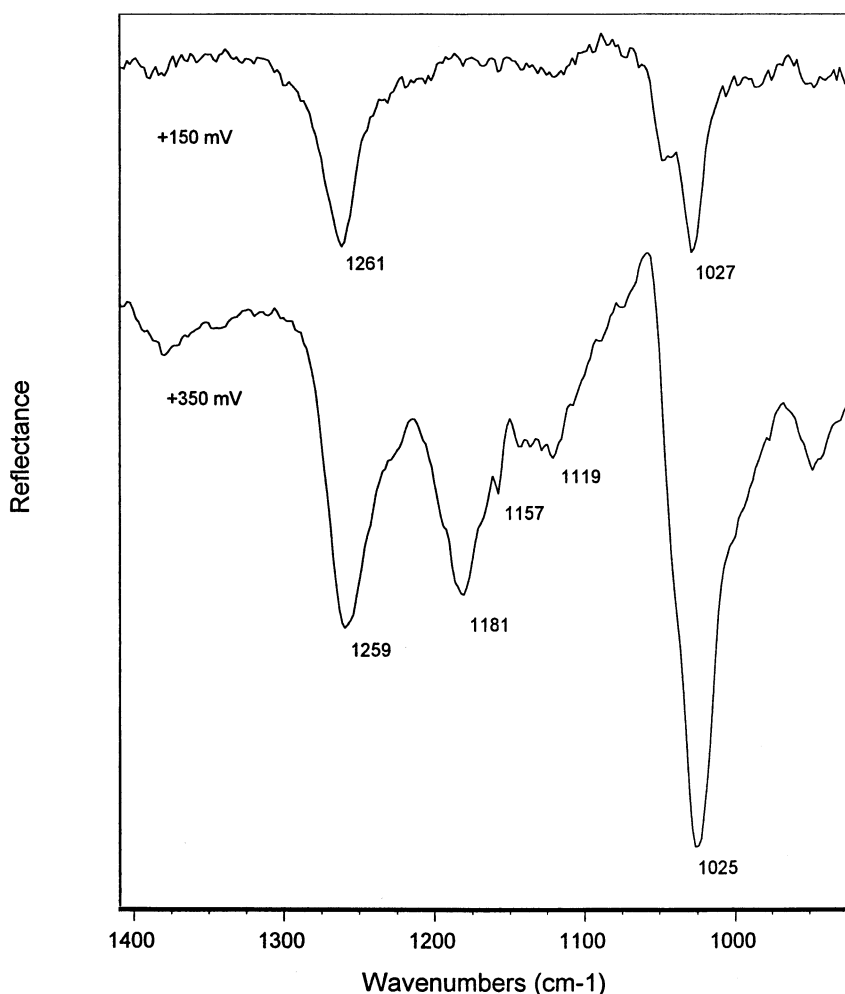


Fig. 3. FTIR spectra of pyrite activated by 6×10^{-5} M CuSO_4 solution (pH 6.5) at +50 mV. The sample was subsequently treated in 6×10^{-5} M potassium amyl xanthate (pH 6.5) at different potentials.

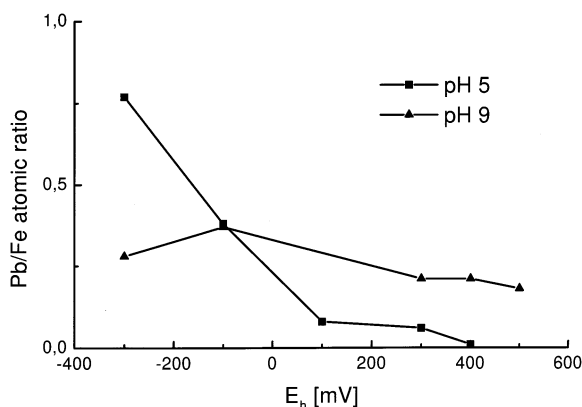


Fig. 4. Measured Pb/Fe atomic ratios as a function of activation potential. Pyrite sample was treated for 15 min in aqueous solution containing Pb^{2+} ions.

the observation that oxygen concentration on the surface increased in line with lead concentration, it seems reasonable to conclude that some lead(II)-oxygen species were formed on the surface. The activation process of pyrite with lead ions presumably takes place through lead surface complexes such as hydroxides or carbonates and no exchange between lead ions and iron in pyrite occurs.

At pH 9, the content of surface lead did not depend on the potential of pyrite. If compared to the results obtained at pH 5, the relative intensity of oxygen and iron(III) signals were much higher proposing that the surface was now covered by oxidized iron and lead species.

Collector adsorption on lead-activated pyrite was studied in an experiment where the activated pyrite sample was subsequently treated in ethyl xanthate solution. The treatment was carried out in the same way as described above for the corresponding experiment for copper activated sample. A remarkable observation was that only a faint indication of characteristic signals of dixanthogen was evident in S2p, O1s or C1s spectra. Furthermore, no big change between samples measured at 130 K and at room temperature was observed indicating that lead-activated pyrite behaves quite differently from copper-activated or pure pyrite, where dixanthogen was the main hydrophobic entity on the surface under the same experimental

conditions. The analysis of O1s and C1s spectra measured at room temperature revealed weak components which could be interpreted to be due to adsorbed xanthate or lead xanthate species on the surface. Unfortunately sulfur emission cannot be used to identify small amounts of xanthate on pyrite because of the overlap of xanthate sulfur and the substrate sulfur signals [6].

The above XPS experiments agree very well with the FTIR experiments carried out for similarly prepared samples. In those experiments, no lead xanthate nor dixanthogen was observed on the lead-activated pyrite surface. The fact that some evidence of these species was found from XPS measurements is probably caused by a better sensitivity of XPS in this particular case. Hence, it seems that lead ions rather depress than activate pyrite. This may be due to passivation of pyrite surface or precipitation of xanthate as lead xanthate which is not adsorbed onto the surface. The latter possibility is supported by the XPS observation that the concentration of lead on the surface decreased more than 50% during xanthate treatment.

4. Conclusions

Both copper and lead species are found on the surface of pyrite after treatment in aqueous solution containing either Cu^{2+} or Pb^{2+} ions. At pH 5, the concentration of surface copper and lead continuously increased when the electrode potential of FeS_2 decreased. At the potential region $E_h \leq 100$ mV, the formation of a new copper-iron-sulfide (chalcopyrite-type) surface phase was observed in the XPS measurements. The interaction between lead and pyrite was much weaker and no new sulfide species was observed. No clear potential dependence in the Cu/Fe or Pb/Fe ratios was observed at pH 9 in the potential range studied in this work.

Because pyrite is usually depressed in real flotation processes, copper activation needs to be prevented. This can be best done using high pH or avoiding low potential during grinding and conditioning. Lead seems to depress rather than activate pyrite under conditions studied in this work.

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