

SURFACE CHEMISTRY INVESTIGATIONS OF PYRITE BEFORE AND AFTER TREATMENT BY DIFFERENT REAGENTS

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ABSTRACT. In order to produce high-grade copper concentrates, the depression of pyrite, accompanying the copper sulfide minerals has a significant role. In the practice of the processing plants, it is most often performed in an alkaline media, using CaO. The subsequent activation of pyrite is usually accomplished by H₂SO₄, which adversely affects the processing equipment. After its treatment with CaO; after subsequent activation by H₂SO₄, and after mechanical treatment of the depressed pyrite, X-ray photoelectron spectroscopy (XPS) for the purpose of studying the surface chemistry of pyrite in its natural state, was performed. Positive results were obtained for the possible application of mechanical activation of depressed by CaO pyrite, as a substitute for the aggressive sulfuric acid.

Keywords: surface chemistry, depressed pyrite, activated pyrite, H₂SO₄, mechanical treatment

ИЗСЛЕДВАНИЯ ВЪРХУ ПОВЪРХНОСТНАТА ХИМИЯ НА ПИРИТ ПРЕДИ И СЛЕД ОБРАБОТКАТА МУ С РАЗЛИЧНИ РЕАГЕНТИ

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РЕЗЮМЕ. Съществено значение за получаването на висококачествени медни концентрати има депресията на пирита, съпътстващ медните сулфидни минерали. В практиката на ОФ тя най-често се извършва в алкална среда, с помощта на CaO. При последващата активация на пирита обикновено се използва H₂SO₄, което оказва неблагоприятно въздействие върху съоръженията. Проведена е рентгенова фотоелектронна спектроскопия РФС (x-ray photoelectron spectroscopy – XPS), за изучаване на повърхностната химия на пирита в естествено състояние; след третирането му с CaO; след последваща активация с H₂SO₄ и след механична обработка на депресирания пирит. Получени са положителни резултати за възможното прилагане на механична активация на депресиран с CaO пирит, като заместител на агресивната сярна киселина.

Ключови думи: повърхностна химия, депресиран пирит, активиран пирит, H₂SO₄, механична обработка.

Introduction

In order to produce a high-grade copper concentrate, the depression of pyrite, accompanying the copper sulfide minerals has a significant role. In the processing plants practice, the depression is most often performed in an alkaline medium, using lime (CaO). In many cases, a subsequent activation of the depressed pyrite is necessary, with the purpose of further processing and usually H₂SO₄ is used as an activator. Application of H₂SO₄ as an activator of the pyrite, has an adversely effect on both equipment in the processing plants and on the environment.

In order to optimize the processes of pyrite processing and recovery, one of the main ore minerals in the Chelopech Cu-Au deposit, investigations were carried out to determine the chemical composition on the surface of the mineral in its natural state and after treatment by CaO, subsequent activation by H₂SO₄, and after mechanical treatment of the depressed pyrite. The study of surface chemistry of pyrite before and after treatment with different reagents and subsequent mechanical activation was performed using X-ray

photoelectron spectroscopy (XPS). Furthermore, the possibilities of applying the mechanical desorption as an activator of depressed by CaO pyrite, as a substitute for the aggressive sulfuric acid used in practice, was investigated.

Materials and methods

For the purpose of the conducted examinations, two polished square sections (plate), with size 1x1x0.5 cm, cut out of massive pyrite ore from the Chelopech Cu-Au deposit were prepared. Pyrite plates have the identical mineral composition, fine-grained and microporous structure. Optical microscopy in reflected light and quantitative X-ray microanalysis was performed to determine the chemical composition of the mineral and the content of impurities.

The optical studies of the pyrite polished plates were performed using MEIJI MT 9430 polarizing microscope, equipped with a DK 3000 digital camera. Quantitative electron microprobe analyses were performed to determine the chemical composition of pyrite and its inclusions from gangue minerals. The analyses were performed using a scanning

electron microscope (SEM) JSM-6010 Plus/LA, with an EDS spectrometer, at the UMG "St. Ivan Rilski". The accuracy of X-ray spectral analyses is in the range of $\pm 1\%$.

The laboratory experiments were conducted to study the surface chemistry of pyrite after treatment with different reagents - treatment with an alkaline solution of lime (CaO); activation with H_2SO_4 of lime-depressed pyrite ($\text{CaO} + \text{H}_2\text{SO}_4$); mechanical activation of CaO-treated pyrite. The experiments were performed according to the following sequence and procedure:

- A solution of 1000 ml of distilled water and 0.98 g of CaO is prepared in a beaker. The pyrite was carefully placed at the bottom of the container.

- The solution is agitated for 20 minutes with a mechanical stirrer at 300 rpm until a pH of about 12 (12.3-12.5) is reached.

- The pH of the solution was determined with the laboratory pH meter, the pyrite plate was removed and analyzed with XPS.

- H_2SO_4 is added dropwise to the CaO alkaline solution (pH of about 12), containing the depressed pyrite plate in it, and then the solution is agitated to a pH of about 9, the plate is removed and studied by XPS.

- The pyrite plate is again treated with an alkaline solution of CaO in the manner described above.

- A mechanical activation of the pyrite plate depressed by CaO was performed and subjected to XPS.

X-ray photoelectron spectroscopy (XPS) was conducted in order to determine the surface chemistry of pyrite in its natural state and after its sequential treatment by different reagents - treatment with alkaline solution of CaO; activation with H_2SO_4 of pyrite treated by CaO; mechanical desorption of CaO-depressed pyrite.

The XPS analyses were performed on a Kratos Axis Supra spectrometer with a monochromatic $\text{AlK}\alpha$ source. Each analysis started with a survey scan from 0 to 1200 eV pass energy of 160 eV at steps of 1 eV with 1 sweep. For the high resolution analysis the number of sweeps was increased, the pass energy was lowered to 20 eV at steps of 100 meV.

The $\text{C}1s$, $\text{O}1s$, $\text{Fe}2p$, $\text{Cu}2p$, $\text{S}2p$, $\text{Ca}2p$ photoelectron lines were recorded and the obtained spectra were discussed. The $\text{C}1s$ photoelectron line at 284.6eV was used for calibration of recorded spectra.

All data were recorded at 90° take-off angle. High resolution spectra were collected with pass energy of 20 eV.

The obtained spectrum of the $\text{Ca}2p$ photoelectron line was deconvoluted into components using the XPSPEAK 4.1 program.

In order to reduce the possibility of mineral oxidation in air or liquid medium, all studies were carried out on pyrite plates, but not on pyrite fractions.

Results and Discussion

Optical microscopy investigations

Optical observations show that pyrite plates have an identical mineral composition and are made of pyrite aggregates with grainy and microporous structure. In reflected light under a microscope, in some parts of the pyrite aggregates, pyrite grains with fine zonal structure, with an alternation of light and dark zones were observed. Zonal structure of the pyrite is related to variation in the Cu content, incorporated into the pyrite structure.

Pyrite aggregates are microporous, the size of the pores and cavities varies from several μm to about 500 μm , and in some parts of the polished sections reaches even more (Fig. 1, 2). In some places in the cavities and pores in the matrix of grained, microporous pyrite fine inclusions of copper sulfosalt minerals are found such as enargite (Cu_3AsS_4) (Fig. 2) and tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$). Gangue non-metallic minerals in the form of inclusions in the pyrite are represented by kaolinite and barite, filling some pores, voids or cracks in the pyrite aggregates (Fig. 2).

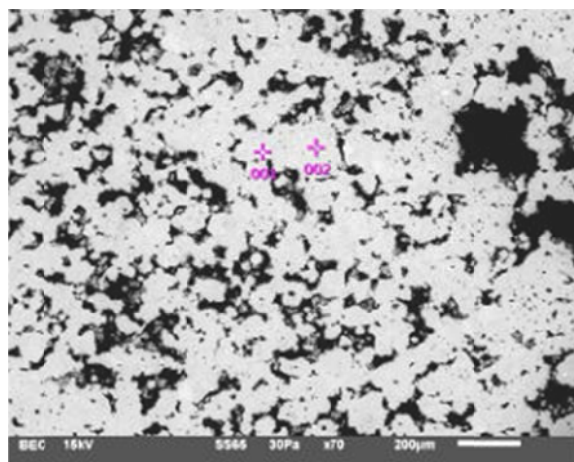


Fig. 1. Pyrite (pale grey), microporous aggregates. Backscattered electron image, SEM, Scale bar - 200 μm

The performed quantitative X-ray microanalyses showed, that pyrite composition is close to the theoretical one (Fe - 46.55%, S - 53.45%). Most of the analyzed pyrite grains contain an isomorphic impurity of Cu, which content varies and reaches 1.4% (Table 1).

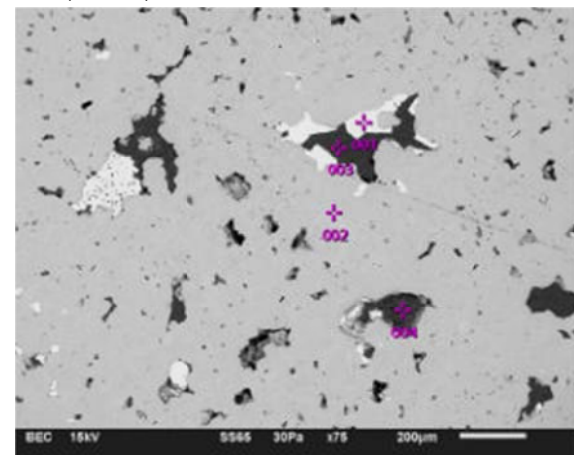


Fig. 2. Pyrite (pale grey), with inclusions of kaolinite (black), barite (white, microporous), enargite (white). Backscattered electron image, SEM, Scale bar - 200 μm

Table 1.

Electron probe microanalyses of pyrite

Analysis №	Element (wt %)			
	Fe	Cu	S	Σ
1	47.05	-	52.95	100.00
2	46.44	0.73	52.83	100.00
3	45.93	1.23	52.85	100.01
4	45.46	1.40	53.14	100.00
5	46.33	0.32	53.34	99.99

Crystallo-chemical formulas of pyrite:

1. $\text{Fe}_{1.01}\text{S}_{1.99}$; 2. $(\text{Fe}_{1.00}\text{Cu}_{0.01})_{1.01}\text{S}_{1.99}$;
 3. $(\text{Fe}_{0.99}\text{Cu}_{0.02})_{1.01}\text{S}_{1.99}$; 4. $(\text{Fe}_{0.98}\text{Cu}_{0.03})_{1.01}\text{S}_{1.99}$;
 5. $(\text{Fe}_{1.00}\text{Cu}_{0.01})_{1.01}\text{S}_{1.00}$

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is an extremely sensitive and non-destructive method for studying the surface chemistry of solids, because it allows obtaining information for the chemical composition and states from the surface layer with a thickness up to 5 nanometers.

X-ray photoelectron spectroscopy was performed on untreated pyrite plate in its natural state and after its subsequent treatment with different reagents.

The registered Fe2p XPS spectra of untreated pyrite and after subsequent treatment (Fig. 3) are typical for the mineral pyrite (FeS_2). The Fe2p spectra has a very strong peak at 707 eV that is typical for Fe^{2+} in the crystal lattice of pyrite (Fig. 3) (Eggleston et al., 1996; Nesbitt et al., 1998; Derycke et al., 2013). The S2p peak is located at 162.5 eV and corresponds to the disulfide ion (S_2^{2-}) in the pyrite (FeS_2) crystal lattice (Chatuverdi et al., 1996; Nesbitt et al., 1998). Some amount of isomorphous impurity from Cu, which replaces Fe^{2+} in the crystal lattice of the mineral, is present due to a low presence of Cu2p spectra. These results coincide with the data from the performed quantitative electron probe microanalysis of pyrite showing the content of structural impurities of Cu, reaching to 1.4% (Table 1).

On the surface of the pyrite there is a small amount of iron hydroxides – Fe^{3+}OOH (goethite) (a peak with binding energy of 531.5 eV in the O1s spectrum) and iron oxides. The presences of sulfate or sulfur have not been found.

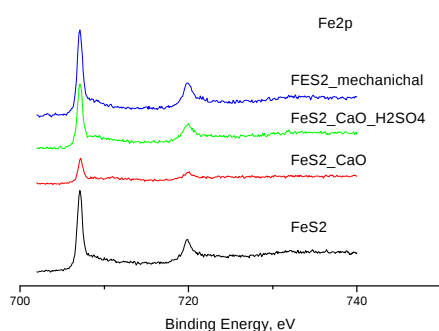


Fig. 3. Fe (2p) XPS spectra of the pyrite surface before and after treatment by CaO, CaO + H_2SO_4 , and after treatment by CaO + subsequent mechanical activation

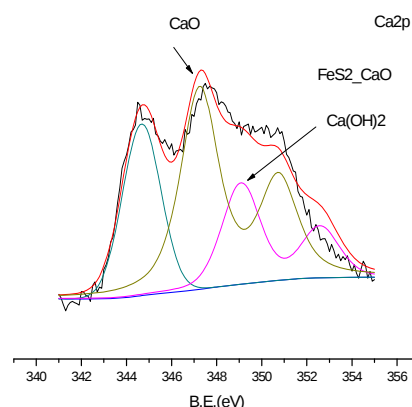


Fig. 4. Ca (2p) XPS spectrum of the pyrite surface after treatment by CaO

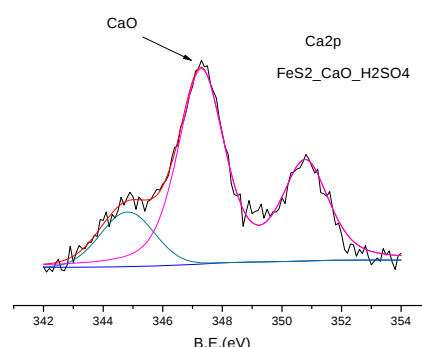


Fig. 5. Ca (2p) XPS spectrum of the pyrite surface after treatment by CaO + H_2SO_4 .

Figures 4 and 5 show the spectra of Ca2p photoelectron line of pyrite after CaO treatment as well as subsequent activation of the depressed pyrite by H_2SO_4 , respectively. The same spectra were compared to the XPS spectrum recorded after mechanical activation of CaO depressed pyrite (Fig. 6).

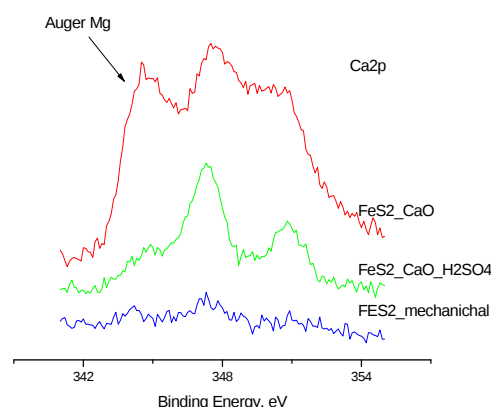


Fig. 6. Ca (2p) XPS spectra of the pyrite surface after treatment by CaO, CaO + H_2SO_4 , and after treatment by CaO + subsequent mechanical activation

The obtained spectra show that after treatment of pyrite with alkaline solution of CaO, a fine coating of CaO and a subordinate amount of $\text{Ca}(\text{OH})_2$ is found on the surface of the mineral (Fig. 4). The presence of CaSO_4 is not observed. The addition of H_2SO_4 leads to the dissolution and complete removal of $\text{Ca}(\text{OH})_2$, leaving a certain amount of CaO,

probably in the voids and pores of the pyrite aggregates. (Fig. 5). After treatment of pyrite by CaO and subsequent mechanical activation by attrition, a clean pyrite surface from hydrophilic phases is achieved, and only traces of CaO have been detected (Fig. 6).

It should be noted, that after pyrite treatment with an alkaline CaO solution, the presence of Mg contained as an impurity in the lime used, is observed over the pyrite surface, so for a better interpretation of the results, the obtained spectra are subjected to deconvolution.

Surface chemistry of pyrite

The surface chemistry of pyrite is affected by a number factors such as oxidation in air or water, temperature, presence of bacteria, concentration of ferric ions Fe^{3+} , particle size, trace element content, mechanical activation when milling, etc. (Paneva et al., 2007).

According to Chatuverdi et al. (1996), the surface properties of the naturally occurring, cube face of pyrite (100) differ from the pyrite surfaces, obtained through mechanical action such as mechanical cutting, crushing, grinding. The crystallographic orientation of the pyrite cuttings it is also very important.

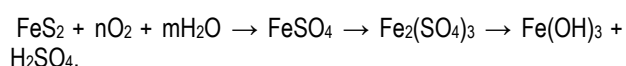
It was found that natural pyrite exhibits structural sensitivity to oxidation, and the octahedral crystal face (111) show greater oxidation potential than pyrite cube crystal face (100) (Guevremont et al., 1998).

Pyrite can be mechanochemically oxidized by intensive grinding, since the mechanical activation during milling leads to an increase in the specific surface area of the pyrite particles and contributes to the formation of hydrophilic phases such iron sulfates, iron oxides and hydroxides.

During the mechanical activation of the pyrite in the initial stage, transformation of the mineral into ferrous sulfate monohydrate is performed, according to the reaction: $\text{FeS}_2 \rightarrow \text{FeSO}_4 \cdot \text{H}_2\text{O}$ (szmolnokite) (Paneva et al., 2007).

Initially, in the first minutes of grinding, ferrous sulfate nuclei are formed, which subsequently form a fine layer on the activated pyrite surfaces. During long-term grinding, the amount of iron sulfate monohydrate formed is increased, as for 36 minutes about 7.1% $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ is formed (Paneva et al., 2007). The oxidation of the pyrite in the initial phase is carried out by oxidation of the sulfur - S^{2-} to S^{6+} .

In natural environment, pyrite exposed to air and in the presence of water is readily oxidized to ferric hydroxide $\text{Fe}(\text{OH})_3$, according to the following scheme:



The ferric hydroxide $\text{Fe}(\text{OH})_3$ is deposited as a gel which is dehydrated and converted to FeOOH (goethite) and/or other iron oxides.

According to Cai et al., (2009) pyrite oxidized easily in air and aqueous media. The oxidized products that are formed on the

pyrite surfaces are different, depending on the pH of the medium, and under alkaline conditions Fe^{3+} oxyhydroxides the only oxidizing product, which is formed on the pyrite surface.

The chemical nature of the phases, deposited on the pyrite surface during the processes of depression, reactivation and flotation of the pyrite, is dependent on a number of factors such as: the type of ore grinding (dry or wet), grain size, reagent type, pH of the medium, dissolved oxygen content, chemical composition and presence of impurities in the pyrite, etc.

In the processing and flotation of copper ores in the processing plants, such as pyrite depressant in alkaline conditions, predominantly lime (CaO) is used. It has been widely accepted that in alkaline conditions pyrite surfaces are mainly covered with hydrophilic species – iron oxides and hydroxides – $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$ or $\alpha\text{-Fe}^{3+}\text{OOH}$ (goethite). However, studies by some authors show, that in alkaline environments on the pyrite surfaces sulfates are often deposited - $\text{Fe}_2^{3+}(\text{SO}_4)_3$ or $\text{Fe}_2^{3+}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (coquimbite) and $\text{Fe}^{2+}\text{SO}_4$ or $\text{Fe}^{2+}\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (melanterite) (Mermillod-Blondin et al., 2005). The ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ on the pyrite surface, depends mainly on the pH of the medium and the particle size, respectively variations in surface chemistry of the mineral particles are observed at different pyrite particle sizes.

It was found that after dry grinding the spatial distribution of oxidation products on the pyrite surfaces is non-uniform. Slightly oxidized zones of several nanometers (nm), located between zones with a higher degree of oxidation with thickness of several tens of nanometers (nm), forming pillar shaped aggregates, are observed. Oxidation products with pillar structure show heterogeneous composition and are built by iron sulfates, hydroxides and hydrated iron oxides (De Donato et al., 1993, 1998; Mermillod-Blondin et al., 2005). Hydrated ferrous sulfates predominate at the base of the pillars, at the top part ferric sulfates dominate, and in the central part there is a skeleton of iron hydroxides and hydrated iron oxides. Many observations on various oxidized pyrite surfaces have confirmed the presence of pillar shaped oxidation products of different thickness amid a quasi un-oxidized pyrite surface.

The published data in the literature for the Ca-bearing species, adsorbed onto lime-depressed pyrite surfaces are contradictory. The phases $\text{Ca}(\text{OH})_2$, CaO, CaCO_3 , CaSO_4 have been established by the different authors (Mermillod-Blondin et al., 2005).

According to Xiaojun and Kelebek (2000), the hydrophilic phases on the pyrite surfaces after treatment with lime are predominantly CaO, CaSO_4 and $\text{Ca}(\text{OH})_2$, but may also include $\text{Fe}(\text{OH})_3$. The same authors carried out studies on a pyrite fraction of 100-200 mesh (149-74 μm). It was observed that on the surface of lime depressed pyrite particles, besides the Ca oxide and hydroxide, a certain amount of CaSO_4 is deposited as a result of the reaction of Ca^{2+} from the solution with SO_4^{2-} ions from the oxidized pyrite surfaces. The pyrite is easily oxidized, with the smaller size of the analyzed pyrite particles favoring the oxidation processes. On the other hand, at a higher pH of the medium, as a result of oxidation of pyrite the deposition of ferric hydroxide $\text{Fe}(\text{OH})_3$ is easily achievable.

The presence of a fine hydrophilic coating on the pyrite reduces the flotation kinetics of the mineral.

The results of the present studies applying XPS, show a fine CaO and Ca (OH)₂ coatings on the pyrite surface during the treatment of a pyrite plate by CaO (Figure 4). Presence of CaSO₄ and Fe (OH)₃ was not observed. With the mechanical activation by attrition, removal of hydrophilic phases on pyrite surface could be achieved, and barely traces of CaO being recorded.

The presented studies on pyrite surface chemistry, before and after treatment by different reagents, were carried out on polished pyrite plates, to limit the possibility of oxidation of the mineral in air and liquid media. In real conditions during the processing and flotation of copper ores in the processing plants, the much smaller size of the pyrite particles and their greater specific surface area will contribute to the formation of oxidation products on the pyrite particles. The obtained positive results related to the use of mechanical treatment as activator of depressed by CaO pyrite, can be confirmed by conducting semi-industrial experiments, with the aim of applying the mechanical activation as a substitute of the commonly used sulfuric acid.

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