



The Main Features of the Natural Sulphides Surface Modification Under the Impact of High-Power Electromagnetic Pulses

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Abstract

Surface changes in naturally occurring metal sulphides (pyrite, arsenopyrite, sphalerite, chalcopyrite, galena and molybdenite) due to the treatments from high – power electromagnetic pulses (HPEMP) at varying times were studied using XPS. Analysis of the obtained results revealed common patterns and differences in surface transformations. The transformations were found to include two main stages. The first stage were observed at low treatment intensities (up to $N \sim 10^3$ pulses). At this stage formation and accumulation in the surface layer of the nonstoichiometric sulphide phase, oxides and hydroxides, as well as elemental (polysulfide) sulphur and / or metastable sulphur species (thiosulfate, sulphite) were observed. The second stage ($N \geq 3 \cdot 10^3$ pulses) is characterized by the removal of sulphur species and renewal of the mineral surface (sulfidization).

The application of HPEMP treatment to improve flotation selectivity is supported by single-mineral flotation tests. Changes in floatability as a result of HPEMP treatment are principally explained by surface phase changes.

Keywords: natural sulphides surface state, XPS, high – power electromagnetic pulses (HPEMP)

Introduction

The application of innovative methods in mineral processing industry has generated considerable interest in recent year. These methods involves the use of concentrated streams of energy for beneficiation and extraction of valuable components from ore/concentrates: electron and ion beams, laser and microwave irradiation, plasma jets and arches, high-power electromagnetic pulses (HPEMP) etc. (Chanturiya et al., 2008, Chanturiya et al., 2011, Chanturiya et al., 2011 a, Kingman and Rowson, 1998, Grou et al., 2012, Bochkaryov et al., 2011). This paper is focused on the effect of high-power nanosecond electromagnetic pulses on the surface state and flotation properties of natural metal sulphides.

Materials and methods

In this study, sulfide minerals sourced from Russia were used: pyrite (FeS_2), arsenopyrite (FeAsS), chalcopyrite (CuFeS_2), sphalerite (ZnS), galena (PbS), and molybdenite (MoS_2). The origin of the minerals and their chemical composition (Vista CCD Simultaneous ICP - AES, Varian) are listed in Table 1.

The minerals were dry-ground in a porcelain mortar and the size class $-100+63 \mu\text{m}$ was separated by sieving. Distilled water ($\text{MeS}/\text{H}_2\text{O} = 10/1$) was then added to the samples before they were treated with HPEMP and dried in a vacuum to minimize reaction between their surfaces and the atmosphere after the HPEMP-treatment.

HPEMP-treatment of the samples was performed on a lab scale in air by a series of pulses between 5 to 10 ns long. The electrical field component was 30 kV with a pulse frequency

of 100 Hz. The pulse energy was approximately 0.1 J and the integral treatment pulse number varied from $5 \cdot 10^2$ to $1.5 \cdot 10^4$ pulses. Pulse parameters were kept constant and the number of pulses was controlled by varying the treatment duration between 5 s and 150 s.

The X-ray photoelectron spectra were recorded with an Axis UltraDLD (Kratos) spectrometer irradiating the samples at an operating pressure of 10^{-8} Torr by monochromatized $\text{AlK}\alpha$ radiation (1486.6 eV) at 150 W. The pass energy applied was 160 eV for survey spectrum registration, and 20 eV for multiregion spectrum registration. The spectrometer's energy scale was precalibrated using $\text{Au } 4f_{5/2}$, $\text{Cu } 2p_{3/2}$, $\text{Ag } 3d_{5/2}$ photoelectron lines at 83.96, 932.62, and 368.21 eV (to 0.05 eV), respectively, and metal films prerefined by an ion gun.

Results and discussion

XPS results

Analysis of data collected from XPS demonstrated that interactions between sulfide surfaces and HPEMP are governed by some common patterns. This interaction process can be divided in two stages. Each of the stages has its own distinctive features. The first stage was observed to occur at low treatment intensities, up to 10^3 pulses. It is characterized by oxidation of metal atoms with the accumulation of sulfur - rich (metal deficient) sulfide phase, oxides and hydroxides. Table 2 presents the accumulation of oxidized metal phases resulting from the interaction of mineral surfaces and HPEMP. Chalcopyrite and sphalerite are very good examples (Table 2) of this oxidization phase. When the shortest treatment duration of 5 s ($0.5 \cdot 10^3$ pulses) is applied to chalcopy-

Tab. 1. Chemical analysis of the samples (%)

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	Deposit	Fe	Cu	Zn	Pb	Mo	S	As	Sb	Ca	Si	Al
ZnS	Dalnegorskoe (Primorye)	4.08	0.27	> 50	6.61	–	29.30	0.05	–	0.19	–	–
CuFeS ₂		27.54	28.54	1.19	3.19	–	29.17	0.01	0,08	0.70	–	–
PbS		1.41	0.09	8.75	56.71	–	15.60	0.045	0.08	0.24	–	0.18
MoS ₂	Sorskoe (Khakassia)	2.83	0.04	0.05	0.31	37.15	20.07	0.03	–	2.69	6.84	5.31
FeS ₂	Darasun (Transbaikal)	40.61	1.29	0.28	0.88	–	49.89	0.69	1.17	0.78	–	0.99
FeAsS		30.79	0.02	–	0.01	–	19.60	40.30	0.04	0.18	–	0.17

Tab. 2. Surface atomic concentration of oxidized and native sulfide on chalcopyrite (Fe2p) and sphalerite (Zn2p3/2) after HPEMP treatment (measured by XPS)

Tab. 2. Stężenie powierzchniowe utlenionego i naturalnego siarczku na chalkopirycie (Fe2p) i sfalerycie (Zn2p3/2) po obróbce HPEMP (mierzone metodą XPS)

N·10 ³ , pulses	Fe 2p (CuFeS ₂)			Zn 2p3/2 (ZnS)	
	Fe-S (CuFeS ₂)	CuFeS ₂ bulk	Fe _x O _y + FeOOH	Zn-S (ZnS)	Zn-O Zn-O-Zn(OH) +ZnSO ₄
0	13.0	6.6	80.4	69.8	30.2
0.5	9.6	5.9	84.5	53.7	46.3
1.0	7.5	5.2	87.3	24.9	74.1
3.0	9.8	5.4	84.4	-	100.0
5.0	8.7	6.1	85.0	45.4	54.6

rite, the Fe 2 p line indicates a drop in the signals emitted by the iron locked in the bulk mineral structure, accompanied by an increase in the signal emitted by iron oxides and hydroxides.

Common Patterns of Change in Sulfide Surfaces

A similar occurrence is observed on the sphalerite surface. At 0.5·10³ pulses, the Zn 2 p sphalerite spectrum indicates a decrease of 23% (69.8 to 53.7) in the surface state of the un-oxidized sulfide (Table 2). It was also observed that an increase of zinc oxides accompanied the decrease of zinc sulfides (53.7 to 24.9%) as a result of HPEMP treatment above 10 s (10³ pulses).

The first stage attracts particular attention due to the chemical transformations of the surface sulfur atoms. The surface sulfur atoms transform either to S_n²⁻/S⁰ or to metastable compounds of sulfur and oxygen (S₂O₃²⁻, SO₃²⁻). The findings (Table 3) indicate two different surface (sulfur) behavior patterns. The first is the chalcopyrite surface “generating” elemental sulfur S⁰, and the second being thiosulfate accumulation on the surface of a galena sample treated at 10³ pulses. An increase of elemental sulfur concentration (164.0 eV) to 9% (Table 3), along with a 1.2-fold drop of the S₂²⁻ species surface concentration (%), were observed under HPEMP treatment of chalcopyrite (10³ pulses). Similar results were observed with pyrite and arsenopyrite. S 2 p galena line demonstrates a larger shoulder at 161.9 eV (Table 3) at the beginning of the treatment (0.5·10³ pulses is equivalent to a 5 s treatment). In other words, S 2 p fitting clearly indicates an increase in the thiosulfates’ contribution from 24.6% to 32.3 % under HPEMP treatment of galena (Table 3).

As mentioned above, the interaction included two stages. The second stage occurs at 3·10³ to 5·10³ pulses. The main distinctive feature of this stage is thermal removal of elemental S⁰/polysulfide S_n²⁻ sulfur, if the aforementioned sulfur

state accumulation was detected in the previous stage. Table 3 presents evidence that a 30 second HPEMP-treatment results in thermal removal of elemental sulfur (164.0 eV) from chalcopyrite, pyrite, and arsenopyrite surfaces.

Another interaction that can occur during the second stage is the transformation of metastable sulfur into its original (sulfide and disulfide species) state (galena, Table 3). However, this is (both cases) accompanied by an increase in the components attributed to the sulfide state in metal and sulfur XPS lines.

Main Differences in the Surface Alterations

In addition to the similarities identified, XPS data also reveals certain differences in surface behavior. Those differences are primarily related to the mechanism of surface sulfur chemical state change. It was found that pyrite, chalcopyrite, and arsenopyrite accumulate sulfur only as S⁰ or S_n²⁻ increases. It should be noted that the increase in elemental sulfur concentration (at. %) in chalcopyrite and pyrite surfaces is approximately 10%, while arsenopyrite is close to 5%. Chalcopyrite is the only mineral whose surface forms elemental sulfur, rather than accumulating it when treated with 10³ pulses (Table 3).

It was found that on some minerals (galena, sphalerite), there are intermediate products of sulfur oxidation that accumulate on the surface. In the S 2 p region of sphalerite (treated with 10³ pulses), a sizeable peak at 166.8 eV due to sulfite SO₃²⁻ formation was observed, probably through the oxidation of sulfide S²⁻. Polysulfide S_n²⁻ was found as well, but the increase in the S⁰ concentration is approximately 2%, compared to the original sample (Table 3). The same applies for the galena surface as the accumulation of metastable lead sulfate was observed at 10³ pulses. The increase in the elemental sulfur concentration (at. %) is less significant than the increase in thiosulfate. In other words, S 2 p fitting in

Tab. 3. XPS atomic percentage and interpretation of S (2p) of the chalcopyrite and galena samples

Tab. 3. Udział atomowy XPS i interpretacja S (2p) próbek chalkopirytu i galeny

N·10 ³ , pulses	S 2p								
	CuFeS ₂			PbS			ZnS		
	CuFeS ₂ (S ²⁻)	CuFeS ₂ (S ^{2-?})	S ⁰	S-Pb (PbS)	PbS ₂ O ₃	S _n ²⁻	ZnS	S _{2x} ^{2-ox}	SO _x
0	44.7	50.2	-	63.1	24.6	12.3	30.2	69.8	-
0.5	41.3	51.3	-	51.5	32.3	16.1	16.5	38.3	54.8
1.0	42.2	41.5	9.0	56.4	29.1	14.5	28.4	71.6	-
3.0	46.3	45.5	-	65.8	22.8	11.4	48.8	51.2	-
5.0	45.9	47.9	-	45.7	36.2	18.1	100	-	-

Tab. 4. XPS atomic percentage and interpretation of O (1 s) of the arsenopyrite, galena and chalcopyrite samples

Tab. 4. Udział atomowy XPS i interpretacja O (1 s) próbek arsenopirytu, galeny i chalkopirytu

N·10 ³ , pulses	O 1 s							
	FeAsS			PbS		CuFeS ₂		
	Fe _x O _y	FeOOH	H ₂ O _{surface}	∑ PbO + PbOH	H ₂ O _{surface}	Fe _x O _y	FeOOH	H ₂ O _{surface}
0	56.36	36.14	7.50	47.5	52.5	28.7	41.1	30.2
0.5				61.2	38.3	21.8	39.9	41.3
1.0	47.07	30.07	22.22	63.0	37.0	29.4	51.2	19.4
3.0	44.87	31.98	23.15	48.3	51.7	22.2	64.0	13.8
5.0	42.02	23.15	18.26	57.2	42.8	19.8	43.8	36.4

sphalerite and galena clearly demonstrates an increase in the share of metastable sulfur (Table 3). Thus, the process of surface sulfur change is connected to the accumulation of metastable sulfur in galena and sphalerite surfaces treated with 10³ pulses. The chemical state of the surface sulfur in molybdenite remained unchanged under the treatment. S 2p spectra of all treated molybdenite samples were found to be equivalent to each other compared to the untreated sample, with the same contributions to the fitting of the spectra.

Another major difference observed in the response of the minerals with HPEMP involves the hydration/dehydration of the surface during the treatment. It was found that HPEMP results in hydration of arsenopyrite and sphalerite surfaces, irrespective of treatment duration (Table 4, as illustrated by arsenopyrite). Specifically, the concentration of surface oxygen bonded with water molecules (approx. 533 eV) grew approximately 7–12 times in sphalerite and approximately 2.5–3 times in arsenopyrite. HPEMP treatment of galena and molybdenite resulted in surface dehydration. The concentration of water (oxygen bonded with water) dropped approximately 1.5–2 times (Table 4, as illustrated by galena).

Chalcopyrite and pyrite surfaces were first hydrated and then dehydrated. The concentration of water molecules grew 1.5–2 times at the beginning of HPEMP treatment and then dropped dramatically. O 1s spectra provides evidence of dehydration for the chalcopyrite surface after a HPEMP treatment of 10 s (10³ pulses) while a duration of 30 s causes dehydration of the mineral surface. It can also be seen that surface dehydration in chalcopyrite starts at a smaller number of pulses.

Flotation Tests

Recovery of the treated and untreated mineral samples as a function of pulse number is presented in Fig. 1. Test results indicate that HPEMP treatment greatly improves the flota-

tion performance for the majority of the minerals.

The greatest improvement in flotation recovery was observed for pyrite and galena samples. Flotation recovery improvement increased up to 30% for pyrite and approximately 20% for galena. In contrast, arsenopyrite recovery dropped by 10–11% after HPEMP treatment. Therefore, HPEMP treatment has the most positive effect on pyrite versus the most negative effect on arsenopyrite for flotation selectivity. HPEMP treatment clearly improves the recovery of ZnS and CuFeS₂. In untreated samples, the recovery was approximately 74% for both minerals. At the completion of the treatment, sphalerite recovery increased by 14–15% (Fig. 1 a) and the improvement in chalcopyrite recovery was less significant with an average of approximately 12%.

Conclusion

1. X-ray photoelectron spectroscopy was applied to study surface changes in naturally occurring sulfides as a result of HPEMP treatment. There is an indication that sulfide surfaces are induced by the radiolysis products of water and local thermal processes. Further research would be required to determine the impact of radiolysis as a driving factor in surface transformations and the resulting effects on floatability.
2. Analysis of the obtained results revealed principal common features. It was found that the surface changes develop through two main stages. The first stage was observed at a low treatment intensity (up to N ~10³ pulses). At this stage, formation and accumulation in the surface layer of nonstoichiometric sulfide phase, oxides and hydroxides, as well as elemental (polysulfide) sulfur and/or metastable sulfur species (thiosulfate, sulfite) was observed. The second stage (N ≥ 3·10³ pulses) is characterized by

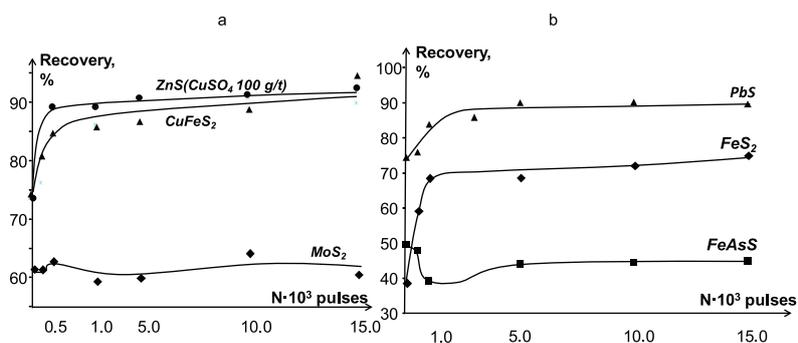


Fig. 1. Floatability of sphalerite, chalcopyrite, molybdenite (a) and pyrite, arsenopyrite, galena (b) as a function of treatment duration (number of pulses)
Rys. 1. Flotowalność sfalerytu, chalkopirytu, molibdenitu (a) i pirytu, arsenopirytu, galeny (b) w funkcji czasu trwania impulsów (liczba impulsów)

thermal removal of sulfur species and renewal of the mineral surface (sulfidization).

3. It was found that the chemical changes of the sulfur on the surface layer of pyrite, arsenopyrite, chalcopyrite included accumulation/formation of S^0 (S_n^{2-}) at the first stage of the transformation, followed by its removal. An increase in the surface concentration of elemental sulfur for pyrite and chalcopyrite was 10–12% while arsenopyrite was approximately 5%. A more complicated chemical change was observed for sphalerite and galena that included formation/accumulation of metastable sulfur species (thiosulfate, sulfite) at the initial stage (up to 10^3 pulses)

and during longer treatment times, the sulphur is reduced back to its initial state (sulfide or disulfide). The increased concentration of S^0 sulfur, compared to the original sample, was only 3% in galena and sphalerite.

4. HPEMP treatment has demonstrated that it can be utilized to alter surface characterizations to improve floatability and provides an option for potential processing applications.

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Efekty modyfikacji powierzchni naturalnych siarczków za pomocą impulsów elektromagnetycznych dużej mocy

Zmiany powierzchni w naturalnie występujących siarczkach metali (piryt, arsenopiryt, sfaleryt, chalkopiryt, galena i molibdenit) w wyniku obróbki impulsami elektromagnetycznymi o dużej mocy (HPEMP) w różnym czasie badano przy użyciu XPS. Analiza uzyskanych wyników ujawniła typowe wzory i różnice w transformacjach powierzchniowych. Stwierdzono, że transformacje obejmują dwa główne etapy. Pierwszy etap obserwowano przy niskiej intensywności działania impulsami (do $N \sim 103$ impulsów). Na tym etapie zaobserwowano tworzenie i akumulację w warstwie powierzchniowej niestechiometrycznej fazy siarczkowej, tlenków i wodorotlenków, a także siarki elementarnej (polisiarczkowej) i / lub metastabilnej (tiosiarczan, siarczyn). Drugi etap ($N \geq 3 \cdot 10^3$ impulsów) charakteryzuje się usuwaniem rodzajów siarki i odnawianiem powierzchni mineralnej (siarczowanie). Zastosowanie obróbki HPEMP w celu poprawy selektywności flotacji jest poparte testami flotacji pojedynczych minerałów. Zmiany flotowalności w wyniku obróbki HPEMP są wyjaśnione zmianami fazy powierzchniowej.

Słowa kluczowe: stan powierzchni naturalnych siarczków, XPS, impulsy elektromagnetyczne dużej mocy (HPEMP)