

**On the change in the physical-chemical and flotation properties of sphalerite and chalcopyrite under nanosecond electromagnetic pulses**

I. Zh. Bunin, I. A. Khabarova, M. V. Ryazantseva, E. V. Koporulina  
Research Institute of Comprehensive Exploitation of Mineral Resources RAS, Moscow

[bunin\\_i@mail.ru](mailto:bunin_i@mail.ru), [xabosi@mail.ru](mailto:xabosi@mail.ru)

High-voltage nanosecond pulses effectively change phase composition of a surface, electrochemical, physical-chemical and flotation properties of chalcopyrite and sphalerite: the increase of positive values of electrode mineral potential promotes the rise of anionic collector (xanthate) sorption and flotation of these minerals.

*Key words: chalcopyrite, sphalerite, nanosecond electromagnetic pulses, sorption, flotation*

**Citation:** Bunin, I. Zh, I. A.Khabarova, M. V.Ryazantseva, E. V.Koporulina (2012), On the change in the physical-chemical and flotation properties of sphalerite and chalcopyrite under nanosecond electromagnetic pulses, *Vestn. Otd. nauk Zemle*, 4, NZ9001, doi:10.2205/2012NZ\_ASEMPG.

The effect of high-power (high-voltage) nanosecond electromagnetic pulses (HPEMP) on chemical and phase surface composition, structural-chemical, electrophysical, electrochemical, physical-chemical and flotation properties of sulphide minerals (pyrite, arsenopyrite, pyrrhotite and pentlandite) has been studied in the made researches [Chanturiya et al., 2006–2008, 2011a; Chanturiya et al., 2011b; Bunin et al., 2002; Ivanova et al., 2008; Ryazantseva, 2009; Khabarova, 2011]. In this paper the new experimental data about the HPEMP effect on morphology, chemical and phase surface composition, electrochemical, sorption and flotation properties of chalcopyrite and sphalerite are presented.

**Materials and research technique.** The researches were spent on monomineral samples of chalcopyrite and sphalerite from Second Soviet deposit (Dalnegorsk ore field, Primorye Territory) with size of particles in the ranges – 100 +63  $\mu\text{m}$ . The data about chemical composition and impurity contents in researched sulphide tests, received by atomic emission spectroscopy with inductive-connected plasma (ICP-AES), are presented in the table.

**Table.** Chemical composition of chalcopyrite and sphalerite

Specimen	Cu	Fe	Zn	S	Pb	Ca	Mn	Mg	As
	Mass percent								
CuFeS <sub>2</sub>	28.54	27.54	1.91	29.17	3.19	0.70	0.044	0.01	0.006
ZnS	0.286	4.08	>50.00	29.30	6.61	0.19	0.129	0.02	0.153

High-voltage nanosecond pulses treatment of minerals was made on original laboratory plant (IPKON RAS, [Chanturiya, 2006; Bunin, 2009]). The pulse duration did not exceed 10 ns, amplitude of intensity of electric component of the field strength made approximately  $\sim 10^7$  V/m, energy in a pulse was equal to 0.1 J; and pulses repetition frequency was 100 Hz; range of variation of total dose of electromagnetic pulse influence constituted the interval from 0.1 kJ to 1.5 kJ (total  $10^3$ – $1.5 \cdot 10^4$  pulses).

The morphology, sizes and elemental composition of neoformations on sulphide surfaces have been studied by analytical electron microscopy (SEM/EDX, LEO 1420 VP – INCA Oxford 350). Features of mineral surface relief on meso(nano)-scale (less than 100 nm) have been studied by scanning probe microscopy (SPM – AFM, INTEGRA Prima, NT-MDT) in semi-contact mode.

Potassium butyl xanthate (BX) sorption on mineral surface has been determined on residual concentration of collector by UV-spectrophotometry [Chanturiya and Vigdergauz, 1993] on Shimadzu UV-1700 spectrophotometer. The IR-spectra of diffuse reflection of mineral powders have been taken

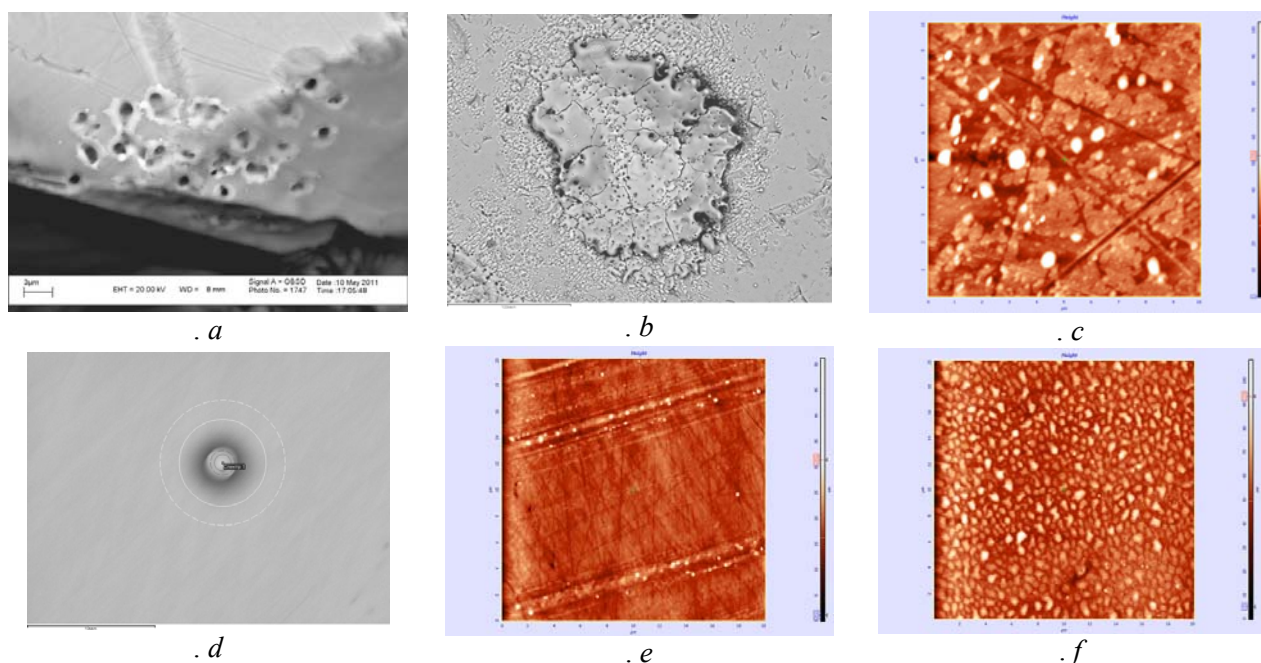
off in a range of wave numbers  $400\text{ cm}^{-1} - 4000\text{ cm}^{-1}$  with the sanction  $4\text{ cm}^{-1}$  using IR-Fourier spectrophotometer (Shimadzu, IRAffinity-1) with the diffuse reflection modulus (DRS-8000).

Electrochemical properties of minerals (electrode potential;  $E$ , mV) have been determined by method of potentiometric titration with the simultaneous control of mineral potential and pH [Chanturiya and Shafeev, 1977; Shafee et al., 1973]. pH-value has been changed by submission of a lime solution, interval of pH was 5.5-11. Working electrodes (approximately  $10 \times 10 \times 5\text{ mm}$ ) have been made of clean chalcopyrite and sphalerite. A comparison electrode was silver-chloride sated electrode. The dependence of electrode minerals potential from pH has been investigated previously for the raw chalcopyrite and sphalerite samples, then the minerals have been subjected to electromagnetic pulse processing and the measurements have been spent repeatedly.

Flotation activity of chalcopyrite and sphalerite has been estimated on output of a mineral in froth product, while potassium butyl xanthate (BX) (30 g/t) and methylisobutylcarbinol (MIBC) were used as reactants at pH 9.5 (CaO). Flotation experiences have been made in the laboratory flotation machine with volume 20 ml with mineral specimen 1 g with grade fineness particle  $-100 + 63\text{ }\mu\text{m}$ . Interaction time with reactants was 1 minute, flotation time was 2.5 minutes. The mean square error of measurements did not exceed 5 %.

### Transformation of structural-chemical and morphological properties of chalcopyrite and sphalerite surface under HP EMP-irradiation

Three morphological types of neoformations corresponding to the processes of structural and chemical transformations of the sulphide mineral surfaces due to the HP EMP effect (fig. 1a-c) were revealed on *chalcopyrite* surface by means of analytical electron microscopy (SEM/EDX). The first of these form dense, extended ( $\sim 100\text{ }\mu\text{m}$ ) coatings that are fractured and porous, with local swells of beadlike and irregular spherical shapes that, in some cases, decorate the breakdown channel openings (fig. 1a,b). The second phase, represented by spherical formations with sizes of  $3\text{ }\mu\text{m}$  and lower (fig. 1c), is found mainly near the breakdown regions. Superthin ( $Z \leq 100\text{ nm}$ ) films of the third phase, which hypothetically consist of anhydrous sulfates of copper and can be diagnosed by scanning probe microscopy (SPM-AFM, fig. 1c), uniformly cover the sulphide surface mainly in the regions where the craters and erosion holes of breakdown channels (fig. 1a) and microcracks are localized.



**Fig. 1.** Neoformations on chalcopyrite (a–c) and sphalerite (d–f) surface as a result of HP EMP-irradiation; SEM – EDX (a,b,d), scale bars –  $2\text{ }\mu\text{m}$  (a),  $30\text{ }\mu\text{m}$  (b),  $4\text{ }\mu\text{m}$  (d); AFM (c,e,f), scanning fields:  $10 \times 10\text{ }\mu\text{m}$ , height  $Z \sim 100\text{ nm}$  (c);  $10 \times 10\text{ nm}$ , height  $Z \sim 40\text{ nm}$  (e);  $10 \times 10\text{ }\mu\text{m}$ , height  $Z \sim 90\text{ nm}$  (f)

As against chalcopyrite, essential transformations of *sphalerite* surface morphology (fig. 1d-f) were marked only for samples subjected long electropulse treatment ( $\geq 5 \cdot 10^3$  pulses). Breakdown

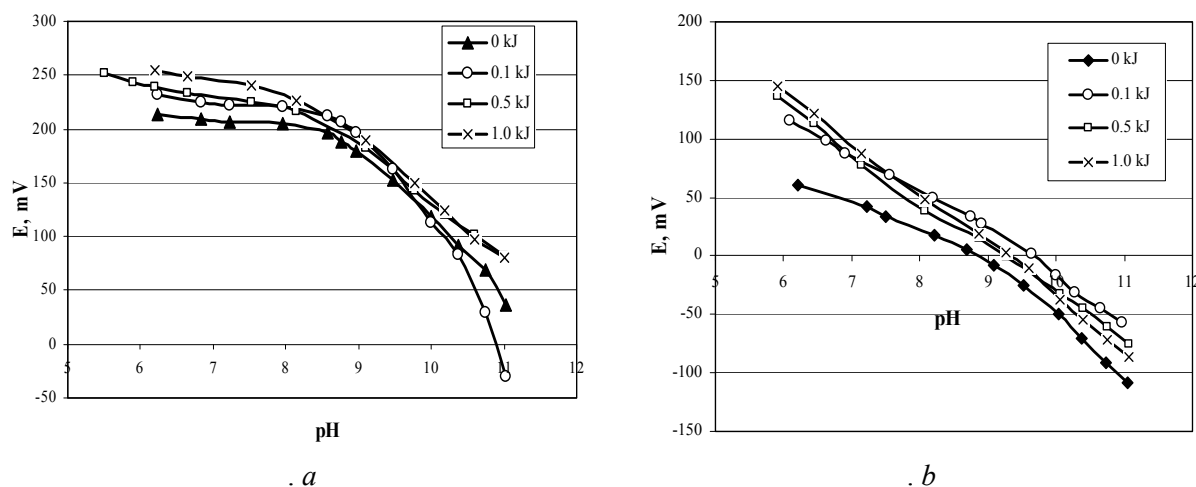
microchannel openings and spherical formations (with sizes of 3  $\mu\text{m}$  and lower (fig. 1d)) located along surface defects (fig. 1e) were revealed on the mineral surface. A pronounced peak corresponding to oxygen has been traced in the X-ray spectrum of a surface from these autonomous phases. With increase of duration of electropulse treatment up to approximately  $2 \cdot 10^4$  pulses, the formation of dense (such as epitaxial) layer of new structured oxide phase (fig. 1f), which hypothetically consists of copper sulfates and oxides (on the data obtained by IR-Fourier spectroscopy), was revealed on sphalerite surface.

On the results of SEM/EDX, AFM and IR-spectroscopy high-voltage nanosecond pulses in a range of electromagnetic effect dose 0.1–1 kJ ( $10^3$ – $10^4$  pulses) result in formation and accumulation of copper sulfate  $\text{CuSO}_4$  in superficial layer of chalcopyrite, and formation and accumulation of zinc sulfate  $\text{ZnSO}_4$  and carbonate  $\text{ZnCO}_3$  on sphalerite surface. The increase of HP EMP effect intensity up to 1.5 kJ results in oxidation of sulfates and formation of copper ( $\text{Cu}_x\text{O}_y$ ) and zinc ( $\text{ZnO}$ ) oxides on sulfide surfaces. Formed micro- and nanophases are located mainly in the regions of sulfide surface heterogeneity (electrical breakdown craters, microdefects, edges and tops of crystals).

#### Effect of HP EMP on electrochemical, sorption and flotation properties of chalcopyrite and sphalerite

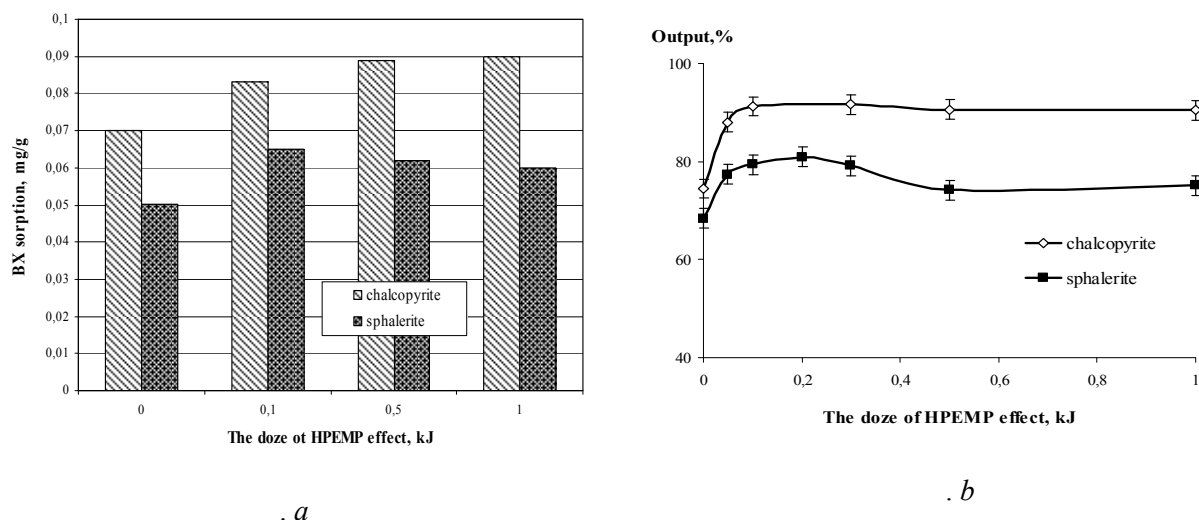
**Electrochemical properties.** The effect of nanosecond electromagnetic pulse processing on electrode potentials of chalcopyrite and sphalerite (fig. 2) is established. The effect of HP EMP resulted in the increase of positive values of electrode chalcopyrite potential in the mean on 25 mV at pH 6–10 (fig. 2a). In alkaline environment at pH 10–11 electrode potential  $E$  of samples processed 0.1 kJ is decreased in the mean on 20 mV; the maximal absolute difference in electrode potential values before and under HP EMP treatment ( $\Delta E = E_{\text{pulses}} - E_0$ ) equal to -69 mV at pH 11. At increase of electropulse effect dose up to 1 kJ the maximum  $\Delta E$  equal to 43 mV at pH 11.

Electrode potential of sphalerite got more positive values at electropulse processing, being increased in the mean on 35 mV (fig. 2b). The absolute difference in values  $\Delta E$  is changed within limits of 12–70 mV, and the maximal value ( $\Delta E = 70 \text{ mV}$ ) was got at pH 6 as a result of preliminary HP EMP processing (1 kJ).



**Fig. 2.** Dependence of the electrode potential of chalcopyrite (a) and sphalerite (b) of pH-values before and after HP EMP-treatment

**Sorption properties.** On the UV-spectroscopy data BX sorption on chalcopyrite and sphalerite surfaces processed by HP EMP is increased (fig. 3a). Maximal BX sorption (increase at 22 %) on chalcopyrite surface is found at HP EMP effect mode  $10^4$  pulses (1 kJ). The maximum of BX sorption (increase at 23 %) on sphalerite surface is found at a mode  $10^3$  pulses (0.1 kJ). Obtained results will be coordinated to the data on electromagnetic pulse effect on electrochemical properties of sulfides: shift of electrode potentials of chalcopyrite and sphalerite in the region of positive values (fig. 2) results in increase of anionic collector sorption on minerals.



**Fig. 3.** Effect of HPEMP-treatment on sorption properties of chalcopyrite and sphalerite surface (pH 9.5; UV-spectrophotometry) (a) and floatability of chalcopyrite and sphalerite at pH 9.5 in the presence of BX (b)

**Flotation properties.** In the field of low intensity of the pulse effect (0.05–0.1 kJ), the rise of chalcopyrite flotability from 75 % to 91.5 % (fig. 3b), owing to the increase of collector amount on sulfide surface and increase of its electrode potential is established. With increase of pulse number, output of chalcopyrite in froth flotation product was not less than 90 %.

The HPEMP treatment (0.2 kJ) resulted in the increase of sphalerite flotability from 69 % (without preliminary pulse processing) to 81.5 % is observed (fig. 3b). The maximal output of the mineral in froth flotation product (increase on 10–12 %) was got at 0.05–0.3 kJ (fig. 3b). This fact is caused by the increase of BX amount on sphalerite surface and shift of electrode potential in the region of positive values. With increase of power effect dose the decrease of mineral output in froth product up to 74 % (0.5 kJ) and 76 % (0.1 kJ) is established.

Thus, on the basis of these experimental data about mechanisms of structural-chemical transformations of chalcopyrite and sphalerite surfaces at the effect of high intensity fields, it is possible to make a conclusion about an opportunity of high-voltage nanosecond pulses application for development of innovation technologies, which directionally modified physical-chemical and technological properties of sulphide minerals.

## Conclusion

1. As a result of made spectroscopical researches of high-voltage nanosecond pulses effect on phase composition of chalcopyrite and sphalerite surfaces, the range of change of electromagnetic pulse influence dose is established and equal to 0.1–1 kJ ( $10^3$ – $10^4$  pulses). At which there is the formation and accumulation of copper sulfate  $\text{CuSO}_4$  in superficial layer of chalcopyrite, and zinc sulfate  $\text{ZnSO}_4$  and carbonate  $\text{ZnCO}_3$  on sphalerite surface. The increase of HPEMP effect intensity up to 1.5 kJ results in oxidation of sulfates and formation of copper ( $\text{Cu}_x\text{O}_y$ ) and zinc ( $\text{ZnO}$ ) oxides on sulphide surfaces.

2. The experimental data showing of the change of electrochemical chalcopyrite and sphalerite properties owing to preliminary electromagnetic pulse treatment of minerals, namely, increase of positive values of electrode sulfide potential are received. It is promotes increase of anionic collector (xanthate) sorption and flotation of these minerals.

3. For monomineral flotation of chalcopyrite and sphalerite, optimal conditions (range of the HPEMP dose change was from 0.05 kJ to 0.3 kJ) for preliminary electromagnetic pulse processing of sulphides is established and experimentally proved. At which it is essential (in the mean on 10–15 %) raises mineral flotation.

*The authors acknowledge the financial supports from the RFBR (Grant no 11-05-00434-a) and the Program of the Scientific School of Russian Federation (Grant no NSh-220.2012.5) and the Grant from the President of the Russian Federation (Grant no MK-1968.2012.5).*

## References

- Bunin, I. Zh., T. A. Ivanova, V. D. Lunin (2002). Effect of high-energy impacts on the process of dissolution of gold-containing minerals, *Mining Informational and Analytical Bulletin (Scientific and Technical Journal)*, №8, pp.172-176.
- Bunin, I. Zh. (2009). Theory of nanosecond electromagnetic pulses effect on disintegration and breaking-up process of fine-disseminated mineral complexes and noble metals recovery from ores, *Synopsis of Grand PhD thesis*, Moscow, MGRI-RSGPU, 39 p.
- Chanturiya, V.A., R. Sh. Shafeev (1977), *Chemistry of surface phenomena in flotation*, Moscow, Entrails, 191 p.
- Chanturiya, V. A., V. E. Vigdergauz (1993). *Electrochemistry of sulphides. Theory and practice of flotation*, Moscow, Nauka, 206 p.
- Chanturiya, V. A., K. N. Trubetskoi, S. D. Victorov, I. Zh. Bunin (2006). *Nanoparticles in processes for disintegration and breaking-up of geomaterials*, Moscow, ICEMR RAS (IPKON RAN), 216 p.
- Chanturiya, V. A., T. A. Ivanova, I. A. Khabarova, M. V. Ryazantseva (2007). Effect of ozone on physico-chemical and flotation properties of surface of pyrrhotite under the nanosecond electromagnetic pulses treatment, *Journal of Mining Science*, v.43, №1, pp.83–90.
- Chanturiya, V. A., I. V. Filippov, L. O. Filippov, M. V. Ryazantseva, I. Zh. Bunin (2008). Effect of powerful electromagnetic impulses on surface and flotation properties of carbonate-bearing pyrite and arsenopyrite, *Journal of Mining Science*, v.44, №5, pp.518–530.
- Chanturiya, V. A., I. Zh. Bunin, M. V. Ryazantseva, I. V. Filippova, E. V. Koporulina (2011a). Nanosecond electromagnetic pulse effect on phase composition of pyrite and arsenopyrite surface, their sorption and flotation properties, *Journal of Mining Science*, v.47, №4, pp.506–513.
- Chanturiya, V. A., I. Zh. Bunin, M. V. Ryazantseva, L. O. Filippov (2011b). Theory and application of high-power nanosecond pulses to processing of mineral complexes, *Mineral Processing and Extractive Metallurgy Review*, vol.32, №2, pp. 105–136.
- Ivanova, T. A., I. Zh. Bunin, I. A. Khabarova (2008). On the characteristic properties of oxidation of sulfide minerals exposed to nanosecond electromagnetic pulses, *Bulletin of the Russian Academy of Sciences: Physics*, v. 72, №10, pp.1326–1329.
- Khabarova, I. A. (2011). Increase of physics-chemical and flotation contrast properties of pyrrhotite and pentlandite using high-power electromagnetic pulses, *Synopsis of Ph.D thesis*, Moscow, ICEMR RAS (IPKON RAN), 22 p.
- Ryazantseva, M. V. (2009). Mechanism of nanosecond electromagnetic pulses effect on structural-chemical and flotation properties of pyrite and arsenopyrite, *Synopsis of Ph.D thesis*, Moscow, ICEMR RAS (IPKON RAN), 19 p.
- Shafeev, R. Sh., V. A. Chanturiya, V. P. Yakushkin (1973). *Effect of ionization radiation on flotation process*, Moscow, Nauka, 58 p.