Comparative study on high-voltage nanosecond pulses and dielectric barrier discharge effects on surface morphology and physico-chemical properties of natural pyrrhotite

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Abstract. In this paper we used analytical electron microscopy, potentiometric titration (electrode potential measurements), sorption and flotation measurements and other methods to study changes in the surface morphology, electrochemical, and physicochemical properties of the natural pyrrhotite exposed to nonthermal action of the repetitive nanosecond high-power electromagnetic pulses and low-temperature plasma of dielectric barrier discharge in air at atmospheric pressure. As a result of exposure to high-voltage nanosecond pulses, a sharp shift in the electrode potential of pyrrhotite to the region of negative values caused a decrease in the sorption of the anionic collector on the mineral, a decrease in the hydrophobicity of the surface and flotation of the mineral was due to an increase in the content of oxidized ferric iron on the mineral surface. Dielectric barrier discharge treatment caused the shift of the electrode potential to the region of negative values (~60 mV) in the range of pH 9.7–12, which causes the effect of a decrease in the sorption and flotation activity of pyrrhotite. The advantages of using the short-term (10–30 seconds) energy impacts for structural and chemical modification of the surface and physicochemical properties of sulfide minerals of iron are shown.

1. Introduction

Pyrrhotite is the predominant mineral in sulfide copper-nickel ores of deposits in Russia and the world. This polymorphic sulfide mineral of iron (Fe₃S₈₋₁) degrades the quality of copper and nickel concentrates. Also, the need to solve the problem of utilizing the increased content of sulfur dioxide in the metallurgical processing arises.

The use of electromagnetic pulse effects (electric discharge technologies [1–6]) as preparatory operations preceding the flotation process makes it possible to increase the efficiency of the flotation separation of sulfide minerals with similar physicochemical properties due to the directed (contrast) change in the phase composition and physicochemical properties of the sulfides surface [1, 5, 6].

In this paper, we carried out a comparative study of the mechanisms of nonthermal action of high-power nanosecond electromagnetic pulses (HPEMP [3, 4]) and low-temperature plasma of dielectric barrier discharge (DBD [7, 8]) in air at atmospheric pressure effect on the structural, physicochemical, and flotation properties of pyrrhotite. For this purpose, we used analytical electron microscopy (SEM–EDX), potentiometric titration (electrode potential measurements), sorption and flotation experiments and other methods.
2. Experimental

2.1. Minerals
We used in our experiments the pyrrhotite samples extracted from copper-nickel pyrrhotite-containing ore (Norilsk deposit, Russia). Chemical composition of mineral samples, wt.\%: Fe 59.75, S 39.15, Cu 0.04, Ni 0.03. The pyrrhotite samples were represented by individual grains ~0.16±0.08 mm in size and plane-parallel polished sections with 10×10×4.5 mm in size.

2.2. Research Technique
Electromagnetic pulse treatment of mineral samples was carried out on laboratory generator equipments (IPKON RAS; FON, Ryazan). The conditions for processing of pyrrhotite samples by high-voltage nanosecond pulses are given in [9]; the parameters of the generator of high-voltage sub-nanosecond pulses initiating a dielectric barrier discharge in air at atmospheric pressure – in [8].

The nanosecond pulse generator (HPEMP) operates at a frequency of 100 Hz (pulse repetition rate), the output pulse amplitude is ~25 kV, the duration of the leading edge of the pulse varies from pulse to pulse within 2–5 ns, and the pulse duration varies within 4–10 ns. Video pulses of a bipolar shape are generated, pulse energy ~0.1 J, electric field strength in the inter-electrode gap is (0.5–1)·10⁵ V·m⁻¹, time range of the pulsed treatment of the mineral samples is \( t_{\text{treat}} = 10–150 \) s.

We consider different modes of the existence and development of a dielectric barrier discharge (DBD) upon a change in applied stress and the frequency of pulse repetition. We establish the operating parameters of pulses that initiate a discharge at which the greatest changes in the structural-sensitive properties of minerals are observed: the length of the leading edge of a pulse is 250–300 ns, the length of pulse is 8 µs, the electrode voltage in the barrier discharge cell is 20 kV, and the frequency of pulse repetition is 16 kHz. The range of change in the duration of the DBD-treatment of the samples is \( t_{\text{treat}} = 10–150 \) s. The flow of a discharge current in a discharge cell was limited by one dielectric layer, and the sizes of the electrodes exceeded the length of the inter-electrode space (~5 mm). In the process of the low-temperature plasma processing of minerals, the gas temperature in the working zone of the discharge cell of the barrier discharge did not exceed the temperature of the dielectric barrier and remained on the order of room temperature during 10–60 s. Samples of minerals were exposed to a pulsed barrier discharge in two different ways, namely: (i) macro-samples of minerals were placed in the discharge, so that the working surfaces of the samples were located on the surface of the dielectric barrier. (ii) The mineral particles of the crushed samples were separated from the dielectric barrier by a small air gap, therefore, the mineral particles could move over the barrier during the discharge process.

The surface pyrrhotite structure and qualitative chemical surface composition of minerals were studied via analytical scanning electron microscopy on a LEO 1420VP (EDX Oxford INCA Energy 350 raster electron microscope), and a scanning electron microscope Hitachi Tabletop Microscope TM 4000 Plus. We measured the electrode potential (\( E \), mV) of pyrrhotite by potentiometric titration with simultaneous monitoring of the potential of the mineral and the pH of the medium (pH 5–12). The effect of HPEMP-irradiation on the flotation activity of pyrrhotite was assessed by the yield of minerals into the foam product in the presence of the following flotation reagents: butyl xanthate 50 mg/L, sodium dimethylthiocarbamate 150 mg/L, and methyl isobutyl carbinol at pH 10.5. Flotation experiments were carried out in a laboratory flotation machine with a 20 ml chamber on weighed portions of 1 g of minerals with ~100±63 µm in size. The agitation time with the reagents was 1 min, and the flotation time was 2.5 min.

3. Results and Discussions

3.1. Effect of nanosecond electromagnetic pulses and dielectric barrier discharge on morphology and chemical composition of pyrrhotite surface
As a result of the generation of a pulse-periodic sequence of nanosecond spark discharges (HPEMP) in the air gap between the active electrode and the surface of the processed samples, the formation of ozone occurs with a concentration of at least 0.2 mg/L. This physicochemical process intensifies the processes of sulfides surface oxidation [1, 5, 10, 11]. After exposure to HPEMP \((t_{\text{treat}} = 10–30 \text{ s})\), new formations of complex morphology on the surface of pyrrhotite were found (figure 1 (a), (b)), which can be attributed to new formations of hydrophobic elemental \(\text{S}^0\) and polysulfide \(\text{S}_{n-2}^2\) sulfur, iron oxides and, presumably, insoluble polysulfides. With an increase in the processing time \((t_{\text{treat}} = 50–100 \text{ s})\), we observed the destruction of the surface films, the formation and unification of microtraces (autographs) of the current channels of the spark discharge.

![Figure 1](image1.png)

**Figure 1.** (a, b) SEM-images of new products (probably iron oxides or hydroxides) on a surface of pyrrhotite as a result of HPEMP treatment within 10–30 seconds \((t_{\text{treat}} = 10–30 \text{ s})\). (c, d) Pyrrhotite surface after exposure to a dielectric barrier discharge in air at atmospheric pressure \((t_{\text{treat}} = 30–50 \text{ s})\). Scale bars: (a), (b) 10 μm; (c) 300 μm, and (d) 20 μm.

As a result of processing pyrrhotite samples with a low-temperature plasma of a dielectric barrier discharge, characterized by high electron temperatures and a low temperature of the working gas, as well as the action of a strong electric field, micro-discharges in the DBD cell and ozone formed in electric discharges, the following changes in the surface morphology of sulfide minerals occurred. For pyrrhotite, we observed the formation of microcracks and channels of electrical breakdown (figure 1 (c), (d)), as well as the removal of microcrystalline fragments of mineral matter (micro chips) from the
surface of the samples (figure 1 (d)) due to mass transfer under the action of an electric field, and, possibly, due to the effect of ponderomotive forces.

3.2. Effect of nanosecond electromagnetic pulses (HPEMP) and low-temperature plasma of DBD on electrochemical and technological properties of pyrrhotite

To improve the technology of flotation separation of minerals with similar physicochemical properties, experimental data on changes in the electrochemical properties (electrode potential) and hydrophobicity of the surface of minerals (flotation activity) as a result of energy effects are of great interest. The electrode potential is one of the most important parameters used to assess the electrochemical properties of the surface of minerals, which have a great influence on the process of interaction of mineral particles with flotation reagents [12].

As a result of short-term \( t_{\text{treat}} = 10 \) s treatment of pyrrhotite samples by high-voltage nanosecond pulses, a shift of the electrode potential of the mineral in the direction of negative values occurred. The maximum difference in the values of the electrode potential before and after the electric pulse treatment equal to 73 mV and was achieved in an alkaline medium at pH 10. The minimum sorption of the flotation reagent butyl xanthate (decrease by 17%) on the surface of pyrrhotite was also found under a short-term pulse treatment \( t_{\text{treat}} = 10 \) s. This result is consistent with the experimental data on the effect of HPEMP on the electrode potential of the mineral, namely, a sharp shift in \( E \) of pyrrhotite to the region of negative values caused a decrease in the sorption of the anionic collector on the mineral. Preliminary electric pulse treatment of pyrrhotite for \( t_{\text{treat}} = 10 \) s caused a decrease in the hydrophobicity of the surface and floatability of the mineral in the presence of a flotation reagent (dimethylthiocarbamate), which corresponds to the data on the highest content of oxidized ferric iron on the mineral surface (figure 1 (a)).

Dielectric barrier discharge processing caused an increase in the positive values of the electrode potential of pyrrhotite by 10–65 mV in the range of pH 5–9.5. At pH 9.7–12, the largest changes in the \( E \)-values were established for the mode of short-term \( t_{\text{treat}} = 10 \) s treatment of the mineral. The shift of the electrode potential to the region of negative values \( (E = -60 \) mV) occurred, which causes the effect of a decrease in the sorption and flotation activity of pyrrhotite. Thus, the advantages of using the short-term \( (t_{\text{treat}} = 10–30 \) s) energy impacts for structural and chemical modification of the surface and physicochemical properties of sulfide minerals of iron are shown.

It should be noted that relatively low energy consumption (less than 3–4 kWh·ton\(^{-1}\) of the processed material), technological features of the proposed methods of energy impacts (standard conditions for temperature and pressure, the use of air as a plasma-forming gas), and high efficiency (selectivity) of influence on the functional properties of geomaterials indicate on the prospects of application of nanosecond HPEMP and low-temperature plasma of DBD to the deep processing of refractory sulfide polymetallic ores.

4. Conclusion

The obtained experimental result indicates the advantages of the using of short-term \( (t_{\text{treat}} = 10–30 \) s) electromagnetic pulse treatments (HPEMP and DBD in air under standard conditions) to increase the efficiency of the flotation separation of sulfide minerals with similar physicochemical properties.

On the example of a natural pyrrhotite, we demonstrated the possibility of increasing the efficiency of the structural and chemical modification of the mineral surface and directed (contrasting) changes in the electrochemical, sorption and flotation properties of sulfide minerals by applying electromagnetic impulse effects.

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