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LOW-TEMPERATURE ATMOSPHERIC PLASMA IN THE COMPLEX PROCESSING OF HARD-BENEFICIATION MINERAL RAW MATERIALS

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ABSTRACT – This report provides a brief overview of the main results of theoretical and experimental studies of the processes for the induced structural modification of the surface state, physicochemical and technological properties of non-ferrous and noble metals minerals when exposed to high-power electromagnetic pulses and discharge low-temperature plasma. The main results obtained to date in the field of application of low-temperature plasma from a high-power (high-voltage) pulsed-periodic nanosecond spark discharges (HPEMP) and dielectric barrier discharge (DBD) in air under normal conditions in mineral processing processes reviewed. The high efficiency and possible restrictions of application of the pulsed energy impacts and low-temperature plasma treatment of geomaterials (minerals, rocks and ores) are demonstrated in order to improve the processing efficiency of the difficult-to-enrich mineral raw materials.

Keywords: Sulfide Minerals, Low-Temperature Plasma, Disintegration, Flotation.

INTRODUCTION

In the primary processing of refractory ores and anthropogenic mineral feeds, a significant share (30–35%) of valuable mineral loss is associated with mineral intergrowth (up to 40%) and fine (finer than 10 µm) particles Chanturiya [1]. Energy costs for grinding range from 30 to 60 kWh per 1 t and higher [1,2]. To opening finely disseminated mineral complexes, in addition to state-of-the-art grinding technology, pulsed-power (non-mechanical) selective disintegration methods are promising, providing disintegration along interphase boundaries through the formation of intergranular microcracks, electrical breakdown channels, and other types of defects as a result of exposure to high-energy radiation of various physical origins on the geomaterials [1–3]. To achieve maximum efficiency of selective disintegration of finely disseminated mineral complexes of non-ferrous, rare and noble metals, as well as surface modification controlled change (chemical modification) of the surface properties of minerals, extensive research has been carried out on the applications of energy impacts, such as mechanochemical, ultrasonic, radiation [2,4], electrochemical [1,3,5], electropulse-discharge [3,6,7], and plasma [8–11] impacts.

The aim of this work was to briefly comparatively analyze the impact of two types of nonequilibrium electrical discharges (high-power electromagnetic pulse (HPEMP [1,3,5,12]) and dielectric barrier (DBD [9–11,13]) discharges in air at atmospheric

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pressure) have on the structural state, mechanical (microhardness), and physical chemical surface properties of the target minerals from sulfide ores of non-ferrous and noble metals and some other types of refractory ores.

EXPERIMENTAL

In our comprehensive studies the electromagnetic discharges pulsed treatment of mineral samples was carried out on original laboratory generators equipments (ICEMR RAS; FON, Ryazan). The conditions for processing of mineral samples by high-voltage nanosecond pulses are given in [14]; the parameters of the generator of high-voltage sub-nanosecond pulses initiating a dielectric barrier discharge in air at atmospheric pressure are given in [15].

The nanosecond electromagnetic 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 $(0.5\text{-}1)\times10^{7}$ V/m, time range of the pulsed treatment of the mineral samples is $t_{treat.}$=10-150 s.

We consider different modes of the existence and development of a dielectric barrier discharge (DBD) and low-temperature DBD plasma (LTP-DBD) upon a change in applied stress and the frequency of pulse repetition. We establish the following 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 ~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 15 kHz. The range of change in the duration of the DBD-treatment of the samples is $t_{treat.}$=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.

RESULTS AND DISCUSSION

High-power electromagnetic pulses and pulse-periodic high-voltage discharges

The main idea of using high-energy effects (pulsed-power technologies) to improve the processing efficiency of the difficult-to-enrich mineral raw materials is to selectively break up mineral intergrowths and provide free access of lixiviant solutions to finely dispersed precious metal particles. This technique creates proper conditions for maximum concentration of mechanical stresses or energy promoting host rock disintegration sufficient for effective "unsealing" of valuable components. The application of *nonthermal* [16] HPEMP effect in dressing of resistant polymetallic ores (for example, sulfide gold-bearing ores) appears attractive as this technique results in a selective disintegration of the fine disseminated mineral complexes through the creation of electrical breakdown channels and intergranular microcracks, a significant increase in precious metal recovery, helping reduce both energy consumption and the cost of products [1,3,5,12]. When exposed to HPEMP, effective softening of finely disseminated mineral complexes and selective unlocking of mineral intergrowths is achieved due to the following mechanisms [3,5,12]: - formation of electrical breakdown channels in the host mineral matrix containing micro- and nanoparticles of valuable components, and the formation of zones of induced fracturing around the channels as these grow in the mineral medium; - cracking of mineral aggregates due to the occurrence of thermomechanical stresses at the boundaries of intergrowth of mineral components with different thermal and electrical properties during local pulsed heating; - absorption of the energy of pulsed electromagnetic radiation by particles of noble metals and semiconductor ore minerals carriers (skin effect) [3], as well as in the process of autoelectronic emission from the surface of sulfides [17].

The electrical strength of minerals can significantly (by tens of times) decrease due to the presence of inhomogeneities (microdefects), especially in the form of electrically conductive microimpurities (such as micro- and nanoparticles of noble metals), which greatly facilitates the development of breakdown channels due to an increase in the electric field strength in the areas of localization of inhomogeneities. Therefore, the formed channels will predominantly bind metal impurities to each other and to the surface, which significantly increases the efficiency of subsequent processing of mineral samples with chemical agents. Effective damage to the treated material occurs if the total energy released in an individual particle is sufficient to sublimate the substance in the breakdown channel (the transition of a substance to a plasma-like state), and the time during which it is released is significantly less than that required for heat transfer and heat dissipation in the surrounding areas. For the formation of a sufficient number of channels, the action of a large number of pulses is required (N_{imp}=10^3–10^4). With repeated exposure to partial discharges in solid dielectrics, due to the development of dissipative processes, dendrites are formed tree-like fractal structures, whose branches are areas of discontinuity (damage) in the material destroyed from pulse to pulse.

The theoretical inferences were proved by commercial tests (ICEMR RAS and TSNIGRI), the maximal exposure of gold-bearing products under the HPEMP effect is supposed for sulfides less 200 – 100 µm in size, and the effect of the breakdown channel formation and selective disintegration increases when the wet feed is treated. The available porous moisture with acid and alkaline reaction positively influences the HPEMP treatment efficiency, intensifies the opening of a rebellious material. The noble metal (Au, Ag) recovery increment ranges from 2 to 40 % depending on a raw material type at the reduced power consumption [3]. The using of technological gold-bearing samples pre-treatment by HPEMP with nanosecond front and duration results in a gold recovery increase during cyanidation of rebellious ores by 4 – 12 % as a whole, by 10 – 30 % for gravity concentrates, 5 – 45 % for flotation concentrates, by 30 – 80 % from tailings of concentration mills.

The pulsed-periodic nanosecond discharges treatment of fine disseminated Au and PGM-bearing ores provides the maximum effect when is applied prior to fine ore grinding processes, followed by flotation process or gravity concentration of raw mineral materials in Knelson concentrator. The recovery increments (%) for platinum, palladium and gold at all three tests (min – max): Pt 32.37 – 66.86; Pd 12.09 – 52.18; Au 11.2 – 74.75 were gained for the products of copper-nickel ore processing (Krasnoyarsk region deposit), processed in Knelson gravity concentrator with regard to the modes of the preliminary HPEMP treatment followed by mechanical grinding. The maximum noble-metal recovery increment (in Knelson concentrator) has been obtained under the HPEMP effect (1.6 s), followed by 15 min grinding. The increase in the noble-metal recovery deals with no increase in the product yield, but with the higher grade parameter (*K* is the metal concentrating coefficient), which is calculated as a ratio of metal content in a product after separation and metal content in a feed. The principal effect of the recovery increment for Au and PGM due to the maximum mineral opening along the joint boundaries, namely, due to the sharp reduction in number of mineral aggregates (joints) because a variety of electric breakdown channels are formed and the host mineral matrix weakens under the local contrast heating [3].

According to microhardness and spectroscopic studies (FTIR) [5,14], exposure to nanosecond HPEMP causes a decrease in the microhardness (Vickers, HV) of the rock-forming minerals of kimberlite rock—calcite, olivine, serpentine —by 40-66%, and in quartz, nepheline, aegirine, field spars (eudialyte concentrate minerals) by 30% due to the breakage of chemical bonds and microstructure of surface layers, formation of defects at various structural levels (dislocations, microcracks, incomplete surface microbreakdowns), disordering and amorphization of the surface. The effect of weakening of the rock-forming minerals of diamond-bearing kimberlites when exposed to HPEMP can be relevant to ensuring the integrity of diamond crystals in ore grinding processes by reducing the residence time of kimberlite rock in autogenous mills [14].

The nonthermal action of HPEMP starts physicochemical processes (solid-phase chemical reactions) on the surface of sulfide minerals involving the formation of micro- and nanophases in the form of hydrophobic elemental sulfur and various hydrophilic oxygen-containing compounds, which increases the selectivity of the flotation process of sulfides with similar physical and chemical properties [1,5,12,17]. The processes of gas outflow from channels of nanosecond breakdown of semiconductor ore minerals (sulfides, oxides), condensation of matter in the outflowing jet and its deposition on the mineral surface determine one of the possible mechanisms of structural-chemical modification of the surface of earth materials as a result of electromagnetic pulse treatment. When a gas jet exits the breakdown channel into air of normal density, the jet expands, cools down, and conditions form for vapor condensation. As a result of deposition of condensation products, the structural and chemical state of the surface of minerals changes. Another mechanism established in [5,18,19], for the changes in the structural, physicochemical, and process properties of semiconductor ore minerals under the action of nanosecond HPEMPs is the process of direct oxidation of the surface of minerals. This occurs with the active participation of *ozone* formed in interparticle spark electric discharges and/or dissolved in a thin film of water on the surface of mineral particles, with the emergence of insoluble and water-soluble surface formations. The non-thermal effect of nanosecond HPEMP on sulfide minerals causes a contrast change at the micro- and nanostructural level in the chemical and phase composition of the surface of sulfides with similar physical and chemical properties ("pyrite-arsenopyrite", "pyrrhotite-pentlandite", chalcopyrite, and sphalerite), electrophysical, electrochemical, sorption, and flotation properties of the minerals. As a result of short-term ($t_{treat.}$=5 or 10-30 s) electromagnetic pulse pretreatment, the recovery of pyrite, pentlandite, chalcopyrite, and sphalerite into the flotation froth increased by 10–20% compared to the reference samples, while for arsenopyrite and pyrrhotite, on the contrary, it decreased by 10–15%.

Dielectric barrier discharge low-temperature plasma modification of geomaterials

A dielectric barrier discharge (DBD) is a discharge in which the current flow is limited by at least one dielectric layer and the typical dimensions of the electrodes significantly exceed the interelectrode gap [13]. The dielectric prevents the flow of direct current in the system, so harmonic or pulsed supply voltage is usually used to initialize and maintain the discharge [10,11,13,15].

For practical applications, the problem of obtaining a diffuse discharge [20] in air at atmospheric pressure is relevant, as it is more efficient and convenient, since in this case the effect of the barrier discharge plasma spreads uniformly over the largest possible area. During the experiments on the low temperature (LTP-DBD) plasma minerals treatment, the mineral particles were affected by the following factors: a high-strength pulsed electric field, ionic wind, and low-temperature plasma (LTP) products in the form of chemically active compounds, such as ozone O_3, singlet oxygen O_2 ($a^1\Delta_g$), H_2O_2, OH, and nitrogen oxides, as well as the electric charge transfer to the surface of the sample and an increase in the temperature of the dielectric barrier occurred [13,15,21].

The main mechanism of change in the morphology and structural state of the sulfides surface under the influence the effective factors of dielectric barrier discharge (DBD) action, is the destruction of the microcrystalline structure of the mineral surface layers in the process of electrical destruction of thin films (most likely, oxides and hydroxides of metals); this process manifests itself as plasma cleaning of the mineral particles surface from films and secondary phases. In [22] we observed the largest changes in the electrode potential of pyrrhotite (the titration at pH 9.5-12) as a result of short-term plasma mineral pretreatment ($t_{treat.}$= 10 s). The shift of the electrode potential of pyrrhotite to the region of negative values (–60 mV) occurred, which caused the effect of a decrease in its sorption and flotation activity (depression). This fact is very significant for the selective separation (recovery) of pyrrhotite from sulfide copper-nickel ores.

A mechanism is proposed for modifying the acid-base properties of pyrite and arsenopyrite surface as a result of exposure to low-temperature plasma of a dielectric barrier discharge (DBD–LTP) in air under normal conditions. In [10] we found that plasma treatment strengthens acceptor properties and weakens electron donor properties of pyrite surface, as well as weakens acceptor properties of arsenopyrite. As a result, the adsorptive properties of pyrite relative to the electron-donor butyl xanthate grow, and, as a consequence, the flotation activity of the mineral improves. In the case of arsenopyrite, the adsorptive properties and flotation activity decrease. Shortterm plasma pretreatment of minerals ($t_{treat.}$= 30–40 s) resulted in an increase in the selectivity of flotation separation of pyrite and arsenopyrire. In conditions of monomineral flotation, the difference in the recovery of minerals into flotation froth was ~57% (without plasma pretreatment—19%).

CONCLUSION

Low-temperature plasma (HPEMP or DBD in air) processing of geomaterials is a suitable method for adjusting the floatability of sulfide minerals (in particular, iron sulfide minerals). The improved floatability and the differences in the process properties of sulfide minerals can improve the performance of the efficiency of processing of low-grade copper-nickel and refractory pyrite-arsenopyrite gold-bearing ores. Our results testify to practicability and potential of using comparatively brief ($t_{treat.}$= 10-30 s) atmospheric pressure discharge plasma treatment (HPEMP, DBD) in air under standard conditions for the selective disintegration of fine disseminated mineral complexes and structural chemical modification of the physicochemical properties of target minerals from sulfide ores of non-ferrous and noble metals.

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