

Advances in Pulsed Power Mineral Processing Technologies

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Abstract: In Russia and globally, pulsed power technologies have been proposed based on the conversion of energy into a short-pulsed form and exposing geomaterials (minerals, rocks, and ores) to strictly dosed high-power pulsed electric and magnetic fields, beams of charged particles, microwave radiation, neutrons and X-ray quanta, and low-temperature plasma flows. Such pulsed energy impacts are promising methods for the pretreatment of refractory mineral feeds (refractory ores and concentration products) to increase the disintegration, softening, and liberation performance of finely disseminated mineral complexes, as well as the contrast between the physico-chemical and process properties of mineral components. In this paper, we briefly review the scientific foundations of the effect of both high-power nanosecond electromagnetic pulses (HPEMP) and dielectric barrier discharge (DBD) in air on semiconductor ore minerals (sulfides, rare metals minerals) and rock-forming dielectric minerals. The underlying mechanisms of mineral intergrowth disintegration and changes in the structural and chemical states of the mineral surface when exposed to HPEMP and DBD irradiation are discussed. The high performance and potential limitations of pulsed energy impact and low-temperature plasma produced by DBD treatment of geomaterials are discussed in terms of the directional change in the process properties of the minerals to improve the concentration performance of refractory minerals and ores.

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1. 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 [1]. To unlock finely disseminated mineral complexes, along with state-of-the-art grinding technology [2], non-mechanical selective disintegration methods are promising, providing disintegration along interphase boundaries through the formation of defects, microcracks, and electrical breakdown channels as a result of exposure to high-energy radiation of various physical origins on the geomaterials [1,3–16].

In recent years, to achieve 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 [2], radiation [3,4], ultrasonic, electrochemical [3,5], electropulse [3,10,11,13], and plasma [12,14–16] impacts. Research conducted at the Institute of Comprehensive Exploitation of Mineral Resources Russian Academy of Sciences (ICEMR RAS) [1,3–5,17–23] showed, for the first time, that the nonthermal action of high-power nanosecond electromagnetic pulses 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.

The second section of this paper presents an overview of the most significant research and practical developments in the industry applying high-energy impacts in the concentration and deep processing of complex ores. Examples are given of the implementation of various methods for processing minerals, ores, and concentrates, including accelerated electron flow [24–26], microwave (UHF) [6,8,9,27–31] and laser [32] treatment, high-intensity magnetic [33,34] and electric (HVP) [6–11,35,36] fields, high-power nanosecond electromagnetic pulses [1,3–5,23,37–39], and low-temperature plasma of dielectric barrier discharge [16,40–43], enabling a higher performance of the concentration processes for refractory mineral feeds.

In the third section of the paper, the underlying (dominant) mechanisms of mineral intergrowth disintegration and changes in the structural and chemical state of the mineral surface when exposed to high-power nanosecond electromagnetic pulses and dielectric barrier discharge irradiation are discussed. The high performance and possible limitations of the pulsed energy impact (HPEMP) and low-temperature plasma (DBD) treatment of geo-materials are discussed in terms of the directional change in the process properties of minerals to improve the process performance of refractory minerals and ores.

Thus, the study purposed examines present applications of pulsed power methods in the processing of complex ores and deep processing of mineral raw materials, including a more careful consideration of the mechanisms behind the effect of high-power nanosecond electromagnetic pulses and dielectric barrier discharges in the pretreatment of refractory ores and concentration products.

2. High-Energy Methods for Pretreatment of Finely Disseminated Mineral Complexes

Analysis of energy consumption in the processes of crushing and grinding mineral feeds indicate relatively low energy consumption rates by intermediate (0.3–0.5 kWh/t) and fine (0.8–1.2 kWh/t) crushing and high by fine (18–20 kWh/t) and ultra-fine (80 kWh/t and above) grinding [1,2,44]. In the concentration processes of mineral feeds, the central role of disintegration is to complete unlocking of mineral intergrowth with the liberation of mineral grains for their subsequent separation according to their physical and physicochemical properties. The transition to selective disintegration is to manage the process in such a way that disintegration occurs not along the random directions of compressive forces, but along the boundaries of mineral grains as a result of the development of shear and tensile loads at their boundaries [1–5,10]. These requirements are met in dynamic autogenous mills, vibroinertial cone crushers, gas-jets, spring mills for fine and ultrafine grinding (by Mekhanobr–tekhnika, Russia), and high-pressure roller mills (roller presses) [1,2,8,9,45], providing energy and resource savings, higher mineral recovery, and high-grade products.

To achieve the most complete disclosure of finely disseminated mineral complexes of ferrous, non-ferrous, rare, and precious metals, non-mechanical energy impact-based methods appear to be highly promising, contributing to the selective disintegration of minerals along interfacial boundaries through the formation of microcracks and breakdown channels without excessive regrinding, and thus minimal energy consumption. In their pioneering studies, I.N. Plaksin and other researchers at ICEMR RAS and the Siberian Branch of the Russian Academy of Sciences demonstrated that ionizing effects (accelerated electrons, neutrons, gamma rays, etc.) do affect the physical, mechanical, and physicochemical properties of minerals [1,3–5,12,13,35,46–48].

2.1. Applications of Accelerated Electron Energy in the Concentration Processes of Polymetallic Ores

The use of energy from accelerated electrons for the intensification of ore pretreatment and primary mineral processing is of high practical relevance [24,25,44]. Radiation technology based on the use of electron accelerators in the energy range of 0.2–2.5 MeV [49] is characterized by high process safety, energy efficiency, high processing rates, reduction of thermal and chemical pollution, reduction of production areas, long service life of the process equipment, high product grades, and high process availability [44,49].

When semiconductor minerals (sulfides, oxides) and dielectrics (quartz, calcite) are exposed to a concentrated energy flow of accelerated electrons, the main factor determining the efficiency of mineral complex weakening and disclosure is the difference in the ability to accumulate and release charge by semiconductor minerals and dielectric minerals [50–52]. Conductive minerals are characterized by the predominance of the charge drain over the charging process, or the establishment of an equilibrium between the influx and the drain of the charge, where no charge accumulation occurs. In a mineral substance with specific conductivity $\sigma > 10^{-8}$ S/m, the charge is distributed over the particle surfaces, while in a low-conductivity environment, the charge is distributed in the volume of the particle itself [50].

In high-resistance dielectrics excess charge is accumulated and then discharged, and the electrical discharge propagates along the breakdown channels in a self-oscillating (pulsating) mode [50–52], causing the formation of microcracks that propagate in the mineral with each discharge pulse. This leads to a decrease in the strength of the mineral matrix material by two to three orders of magnitude.

As a result of preliminary (prior to grinding) treatment of ferruginous quartzites, polymetallic and gold-bearing ores with an accelerated electron flow, a 1.2- to 2-fold increase in the ore's grinding performance was achieved with a 2-fold reduction in energy consumption and a simultaneous improvement in the intergrowth disclosure performance [24,25,44,53]. Irradiation with accelerated electrons in the range of 0.2–0.8 Mrad of refractory pyrite-arsenopyrite gold-bearing gravity concentrate (particle size less than 500 μm) obtained from the Nezhdanino ore in Yakutia, Russia, led to an increase in gold and silver recovery in the sorption cyanidation circuit by 23.3% and 26.8%, respectively, and an absolute recovery of 74.5% and 48.6%, respectively [26]. Treating the concentrate with water or acid before irradiation activated the disintegration process of the mineral complexes by accelerated electrons, bringing an increase in the recovery of precious metals by 7.7% (Au) and 5.7% (Ag) compared to dry feed [26].

For this energy impact treatment, the energy consumption is from 5 to 10 kWh per ton of concentrate (particle size less than 500 μm), or ~ 1.1 kWh per 1 g of additionally recovered gold. This is 1.7 to 2.5 times lower than during mechanical grinding to a particle size class of $-50 \mu\text{m}$ [3,4].

Radiation thermal effect (RTE) treatment of minerals, such as granite, quartz, and magnetite create alternating temperature stresses, which, upon reaching the ultimate strength of a mineral, cause their softening and disintegration [53,54]. Simultaneously, during RTE, the action of accelerated electrons on sulfide ores and minerals is combined with low-temperature (≤ 300 °C) phase transformations of iron-bearing sulfides into magnetic oxides—hematite and magnetite [55,56]. RTE treatment of polymetallic pyrite ore from the Rubtsovo deposit (Fe-16.8%, particle size less than 3 mm, Altai Territory, Russia) at a temperature of 400 °C (electron accelerator ILU-10 with an electron energy of up to 3–5 MeV and a power output of up to 50 kW), resulted in magnetic fraction yields at the subsequent dry magnetic separation stage of 47.4%, compared to as low as $\sim 2\%$ under conventional thermal heating. Recovery of non-ferrous metals (Cu, Pb, Zn) into the magnetic fraction was 85–90% [57].

RTE treatment (ILU-6, electron energy up to 2.5 MeV) of ferruginous bauxite samples from the Vezhayu-Vorykva deposit (Komi, Russia), resulted in ferromagnetic phases forming in bauxites, which can significantly improve the magnetic separation performance of the aluminum and iron components and improve the selectivity of the recovery of rare and rare earth elements [58].

Exposure to accelerated electrons stimulates oxidative processes on the surface of iron-containing sulfides, as evidenced by a positive change in the potential and a decrease in sulfur on the surface of pyrite particles [51]. Pretreatment of arsenopyrite increased flotation activity and xanthate sorption [51]. For pyrite and arsenopyrite, the optimal doses of radiation were found in [59], which ensured the selectivity of flotation of iron and arsenic sulfides with a difference in recovery of about 50%.

2.2. Applications of Microwave Energy in Mineral Processing

Sources of high-power pulsed microwave radiation are capable of creating extremely strong electromagnetic fields (on the order of 1 MeV/cm) in the accelerating units of electron-positron linear colliders [27,29]. The pulsed nature of microwave radiation (as a heat source with the density q , W/m²) can significantly affect the structure and properties of heterogeneous materials and, in particular, earth materials (minerals, rocks, ores) consisting of components with very different mechanical, electrical, and thermal properties (for example, rocks with a high linear expansion coefficient and a low Young's modulus).

When exposed to microwaves, the disintegration of mineral feeds occurs due to quick ($\sim 10^{-5}$ – 10^{-3} s) and non-homogeneous heating of samples from ambient temperature to hundreds of degrees; therefore, microwave treatment is classified as thermal exposure. At the same time, significant thermomechanical stresses arise at the interfaces, exceeding the ultimate strength of the mineral and leading to cracking of the ore [27–30,33]. During conventional mechanical grinding energy is spent to a large extent on the breakdown of gangue, when a mineral feed treated by microwaves is ground, breakage occurs along the interfaces, impurities, intergrowths, and other defects. Also, the effect of weakening as a result of microwave exposure can be achieved through rapid evaporation of the water contained in the pores of the rock, when the saturated vapor pressure inside the pores exceeds the ultimate strength of the rock [27,60,61].

The microwave method offers several advantages [27–30,62]: volumetric transformation of the applied microwave energy into thermal and mechanical energy with a penetration depth of 0.1–1 m in the meter wavelength range; the possibility of processing mineral feeds with a particle size of more than 2–3 mm; a high heating rate up to 10^6 – 10^8 °C/s at high power levels at the optimum frequency, providing thermal shock and the transition from ductile fractures to more energetically favorable brittle fractures; low energy losses due to friction and heat removal to the surrounding structures; availability of industrial-grade generators and other high power equipment (50–300 kW and higher), capable of providing an hourly throughput of up to 10–50 tons of mineral feed; non-contact delivery of fracture energy into the rock with high (up to 70%) efficiency. The microwave power transfer coefficient for a sample exposed to the electric field's maximum is 95% [60,62], making it possible to heat the sample to a temperature of several hundred degrees in a few seconds by applying microwave radiation with a power output of 600 W at a continuous magnetron operating frequency of 2.45 GHz.

Preliminary microwave treatment (especially in the pulse mode [63]) significantly reduces the strength of mineral intergrowth, improving the unlocking performance of valuable minerals in the process of mechanical grinding and their recovery from refractory mineral feeds. Experiments on samples of sulfide copper-nickel ores from Norilsk Region, Russia, the effect of weakening mineral complexes when exposed to pulsed electromagnetic fields in the meter range with a field strength of 0.3 MW [64] was established. For ores containing up to 8% of copper and nickel, the grinding time was reduced by 8–10%, and for low-grade ores (Cu, Ni 0.8%) by 24–34% combined with lower energy consumption for grinding and lower wear of the grinding mills. As a result of the research conducted at the Institute of Nuclear Physics and the Institute of Geology and Geophysics of the Academy of Sciences of Uzbekistan [65], ICEMR (IPKON) RAS, and the Institute of Geosphere Dynamics RAS [66], it was shown that microwave treatment of sulfide ores and middlings contributes to a significant increase in gold recovery by cyanidation and concentration.

The main disadvantages of this method are high power consumption (from 10 up to 100 kWh/t) and the negative impact of high temperatures, which, under certain processing parameters, cause the possible closure of microcracks and breakdown channels formed during the exposure. This sintering of mineral particles, due to melting, pre-determines the insufficiently high concentration performance.

2.3. Laser Technology for Mineral Processing

In [67,68], the effect of laser radiation in pulsed and continuous modes on finely disseminated mineral complexes of noble metals (aluminosilicates from alluvial deposits) was examined. The analysis of rapid thermal (thermodynamic) processes, structural phase transitions and the accompanying phenomena in earth materials when irradiated with a defocused laser beam with a diameter of 2–5 mm showed the possibility of unlocking, extracting, and coarsening valuable mineral particles and forming spherical agglomerates on the surface of gold minerals due to the thermocapillary mechanism [69]. High-intensity electromagnetic exposure during laser treatment of mineral samples from anthropogenic products with ultrafine and colloid-ion gold inclusions (Gaifon deposit, Khabarovsk Territory, Russia) caused defragmentation of minerals due to high-speed melting and subsequent crystallization upon cooling. As a result of pulsed laser treatment, submillimeter spherical granules formed, and ultrathin gold films as a result of continuous treatment [67]. In [32,67,68], process designs were proposed for the concentration and recovery of submicron and ultrafine gold from technogenic placer products by using exposure to laser radiation.

The high-power fiber lasers from 3 to 10 kW leave other laser types behind in all commercially significant characteristics. According to [32], high-power fiber lasers penetrate into mining process flows owing to low energy consumption, simple operation and high endurance.

2.4. Magnetic-Pulse Technology for the Softening and Disintegration of Ferruginous Quartzites

The magnetic-pulse treatment (MPT) to weaken ferruginous quartzites in the slurry feed, prior to mechanical grinding [33] is based on using the phenomenon of magnetostriction in ferromagnetic mineral grains (magnetite) as a result of a high-intensity electromagnetic field [33,34]. During magnetostriction, the shape of magnetite grains changes, which, in the presence of rigid bonds with neighboring components of the mineral complex, leads to mechanical stresses reaching their maximum at the boundaries of the intergrowth between magnetite and quartz, magnetite and hematite, etc. This contributes to the emergence and development of defects at the intergrowth boundaries of magnetite grains with neighboring grains and, as a result, leads to the weakening of the intergrowth. According to [33,70] and estimates in [71], MPT of ferruginous quartzites, although it does not completely destroy intergranular bonds between magnetite and quartz grains, causes softening of mineral complexes, which makes it possible to reduce energy consumption in the grinding of iron ore and improve the concentration performance.

The findings presented in [72] indicate that magnetic pulse treatment practically did not change the particle size distribution of magnetite ore. However, despite this fact, the process performance of the subsequent magnetic separation of ore minerals and their intergrowth with rock-forming minerals improved: the recovery (grade) of iron increased from 81.3% (42.1%) before MPT to 87.7% (44.4%) after MPT.

During full-scale trials of a magnetic-pulse ore processing unit, before feeding the ore to the mill, the feed was treated by MPT by passing the slurry through a dielectric pipe segment with a system of electromagnetic coils installed, which generated alternating electromagnetic field pulses with a frequency of 1–12 Hz. The pulse duration was ~3 ms; high-frequency circuit discharge frequency ~5 kHz; radiation thermal power 1.5–2 kW; and power consumption of the MPT unit ~5 kW [70]. The full-scale trials showed that MPT of ferruginous quartzites makes it possible to increase the grinding yield by 4.4% and, during the subsequent magnetic separation of the ground product, increase the recovery of iron by 2% without sacrificing the concentrate grade, and increase the overall separation performance by 3.3% [70]. In general, for this energy impact treatment, the energy consumption is from 3 to 5 kWh/ton of ferruginous quartzites [33].

2.5. Pulsed Power Technology for Mineral Processing

The most important direction in the development of advanced, cutting-edge processes is the pulsed power technology, based on the principle of converting the energy of an electric and/or a magnetic field into a pulsed form with the exposure of the mineral feed to dosed high-power pulsed electric and magnetic fields (as well as beams of charged particles, neutrons, and X-ray quanta). One of the applications of the pulsed power technology is the treatment of mineral feeds with ultra-strong pulsed electro-magnetic fields.

In Russia, pulse power processes were first proposed by the Institute of High Current Electronics, Siberian Branch, Russian Academy of Sciences (IHCE SB RAS) Tomsk, the Institute of Electrophysics of the Ural Division of the Russian Academy of Sciences (IEP UD RAS), Yekaterinburg [73], and the Northern Energetics Research Centre-Branch of the Federal Research Centre “Kola Science Centre of the Russian Academy of Sciences” (NERC KSC RAS) [35].

When applied to the processes of breakage and disintegration of building materials, rocks, and ores, the performance of the pulsed power technology is determined by the manifestation of two main processes when a high voltage pulse is applied to a solid dielectric (semiconductor) [10,35,36], which in the vast majority of cases is placed in a liquid medium (Figure 1). These processes include electrodynamic fragmentation and electrohydraulic breakage (grinding).

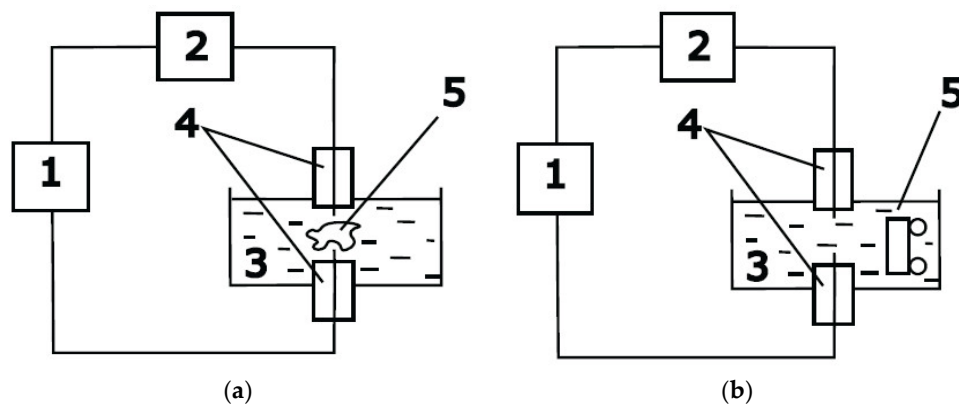


Figure 1. Schemes of (a) electropulse and (b) electrohydraulic technologies; presented in the paper [36]: 1—high-voltage pulse generator, 2—switchboard, 3—discharge chamber filled with liquid, 4—electrode system, 5—technology specimen. Adapted with permission from Ref. [36]. Copyright 2019, Publishing House of the Ural University

In the former case, high-voltage breakdown [74,75] of a condensed medium (geo-material) is accompanied by the emergence of a plasma channel that disintegrates the material along the interfaces due to mechanical tensile stresses [76]. In the latter case, solids are destroyed by shock displacements of the liquid (waves) arising during the development and collapse of cavitation pockets during the passage of an electric discharge through the liquid phase (the Yutkin effect [77]). The breakage mechanism of processed samples, depending on the ratio between the electropulse (EP) and electrohydraulic (EH) components of the electropulse breakdown process, is controlled by the electrical strength of the solid and liquid phases of the medium and the parameters of the pulsed action. The conditions for the transition from one type of breakage to another are determined by the steepness of the leading edge of the pulse (τ_{tr}) and the pulse amplitude U_{imp} [35]: at $\tau_{tr} \leq 100$ ns and $U_{imp} \geq 250$ –300 kV, the EP effect is observed; at $\tau_{tr} > 100$ ns and $U_{imp} < 250$ –300 kV, the EG effect is observed.

2.5.1. Electrohydraulic Disintegration Process

Presently, of all the types of energy effects discussed in this paper and tested in practice, electrohydraulic disintegration (ED) of building materials, rocks, and ores is the one the most widely used globally, implemented as part of high-throughput plants [35,78,79], and full-scale commercial applications [80].

Electrohydraulic (ED) mineral processing, so-called selective crushing, is based on the action of shock waves generated during the electrical breakdown of a liquid on solids (dielectrics, semiconductors, and conductors) placed in the liquid [77]. Brittle intercrystalline fracture of mineral complexes occurs along the boundaries of intergrowths between valuable minerals and the rock-forming matrix due to alternating compression and tension forces formed in solids when shock waves are reflected from solid-liquid interfaces [81]. Under ED exposure, the following forces arise [35,36]: a powerful shock pulse with a discharge energy of up to 80 J, volumetric cavitation microexplosions [82], ultrasonic and electromagnetic radiation, changes in the chemical composition of the medium due to erosion of the electrode material, and the destruction of water molecules in the discharge channel. In the case of cavitation breakage of polymineral intergrowths, the release of nano- and microparticles of noble metals occurs as a result of the interaction of mineral particles with collapsing cavitation bubbles formed from shock loading of liquid heated to the boiling point, into which the particles were placed [82].

The disintegration (crushing) process of the ground particles by shock waves arising from electrical breakdown of the liquid becomes efficient when the pulse duration (τ_{imp}) is less than or equal to the double travel time of a sound wave with speed v in a particle sized d [81]: $\tau_{\text{imp}} \leq 0.5d/v$; $d = 100 \mu\text{m}$; $v = 8000 \text{ m/s}$ (speed of sound in pyrite) $\tau_{\text{imp}} \sim 10^{-9} - 10^{-8} \text{ s}$, which indicates the need for high-voltage (50–250 kV) nanosecond pulses [39,73,81]. In general, for this energy impact treatment, the energy consumption is from 3 to 5 kWh/ton of ores, concentrates, and tailings of enrichment.

In their detailed review, Wei Huang and Yumeng Chen [10] concluded that the mechanisms of selective breakage (disintegration) of rocks and ores in the process of high voltage pulsed electrodynamic and electrohydraulic treatment, despite many years of research by Russian and international scientists, is still debatable and requires further scientific and process research.

The following technological results demonstrate the possibilities of using the ED method for pre-treatment of refractory mineral raw materials. At IEP UD RAS, a unit was developed for electrohydraulic processing of mineral feeds by nanosecond pulses of positive polarity with an amplitude of up to 250 kV, a pulse repetition rate of 300 Hz, an energy in the discharge channel of 3 J, and a power consumption of 5 J/pulse [81]. As a result of nanosecond breakdown of water containing suspended gold-bearing pyrite particles from the Uchaly tailings storage facility (D90 74 μm , Au 2.2 g/t), gold recovery was 60% higher (from 17% to 87%) with an energy consumption of $\sim 4 \text{ kWh/t}$ [81,83].

Pre-treatment in continuous mode (pilot laboratory machine throughput up to 120 kg/h of solid mineral feed) of refractory gold ore from the Albazino deposit (Au 13 g/t, sample particle size $-0.2 + 0.1 \text{ mm}$) by a series of electrohydraulic shocks (total 40 EH pulses) with an energy of 3.2 kJ/dm^3 in an acidic 2% solution of H_2SO_4 followed by thiourea leaching made it possible to improve gold recovery from 65–75% in control runs to 95% after ED treatment [84].

One of the most significant recent developments in Russia is the electrohydraulic plants by the ElectroHydroDynamika Group (NPF EGD, St. Petersburg): EGD-10 for processing mineral samples up to 10 kg on a lab scale (Figure 2a), and the modular EGD-10 for pretreatment of ore and anthropogenic mineral feeds prior to concentration in a full-scale industrial setting (Figure 2b) [79].

The full-scale EGD-10 plant is composed of (Figure 2b) [79] feed unit (1), reactor (2), pulse current generators (3), air discharger (4), capacitor unit (5), material sampling unit (6), water buffer tank (7), water supply pump (8), slurry pump (9). The plant supports continuous loading and processing of feeds with a maximum grain size of 5 mm at a S:L

ratio of no more than 1:2 with a throughput of up to 9 t/h. A closed-loop hydraulic system with circulating process water ensures low water consumption. Maximum installed power is 7 kW/t, and maximum power consumption is 63 kW.

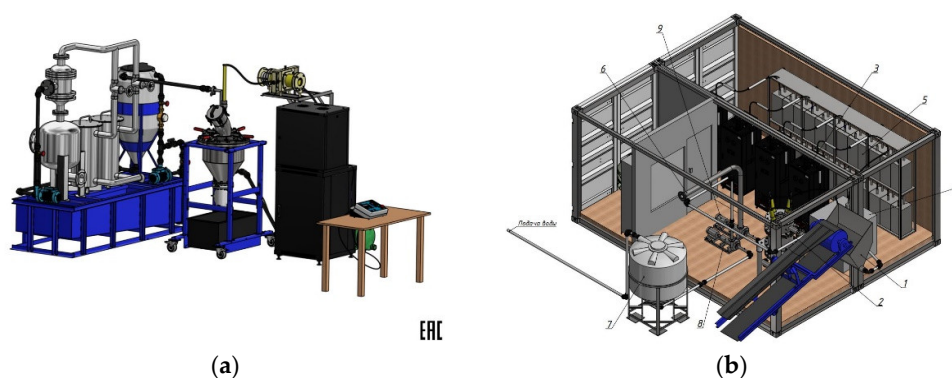


Figure 2. Electrohydraulic installations of the ElectroHydroDynamika Group (St. Petersburg, Russia): (a) laboratory installation EGD-10 and (b) industrial modular installation EGD-10 [79]: 1—feed unit, 2—reactor, 3—pulse current generators, 4—air discharger, 5—capacitor unit, 6—material sampling unit, 7—water buffer tank, 8—water supply pump, 9—slurry pump. Reprinted with permission from Ref. [79]. Copyright 2017–2021, ElectroHydroDynamics

Among global developments, commercial lab scale equipment SELFrag Lab by SELFrag, Switzerland, for the selective fragmentation of composite materials, mineralogical and geological samples using high-power high-voltage electric discharges in a liquid medium is worth noting [78].

In general, the disadvantages of the ED method include significant limitations in the processing of fine mineral products with a particle size of less than 100 micron and a relatively high energy consumption. The need for a liquid medium at a S:L ratio of 1:1 reduces process performance and increases energy consumption. In practice, the uncontrolled change in the ionic composition of the aqueous phase of the slurry causes the formation of oxidation by-products (iron hydroxide films) on the surface of mineral particles, which creates additional energy barriers that prevent the selective disintegration and opening of mineral aggregates and subsequent recovery of valuable minerals.

2.5.2. Advanced Pulsed Power Technology for Dry Mineral Processing

Presently, both global and Russian practice of ore pretreatment and concentration is dominated by the so-called “wet” methods of concentration; for example, flotation, gravity processes, electrohydraulic breakage. Despite the continuous improvements in process management, ore concentration process flows have not undergone radical changes over the past decades. Wet concentration methods, for all their performance, due to the shortage of water all over the world, have the following significant disadvantages [85]: high water consumption, the need for water-sludge circuits, high irretrievable energy costs of moving large water volume, the need for auxiliary energy-intensive equipment, large capital costs involved in the construction and operation of concentrators.

In this context, “dry” concentration processes can become the preferred solution for a number of mineral feeds (“mineral processing technologies of the future”) [85–87]. Promising dry concentration processes, include gravity concentration, magnetic separation [86,87], X-ray radiometric separation (large-sized ore sorting [85]; this technology is planned to be implemented at more than 300 deposits), electrical separation (separation of fine fractions) [85,87], weakening and structural-chemical modification of mineral feeds by high-power nanosecond electromagnetic pulses [1,3–5,17–22,37,38], low-

temperature dielectric barrier discharge plasma [14–16,41–43], and other methods [24,25,44,67,68,71,85–87].

Currently, research is carried out on the use of high-power sources of electromagnetic radiation [73,88] for *nonthermal* impacts on natural and engineered environments of various nature [89]. Research is underway at the Kotelnikov Institute of Radioengineering and Electronics (IRE) Russian Academy of Sciences in Moscow and IHCE SB RAS in Tomsk on nonthermal impacts on biological objects, including living organisms, of high-power nanosecond microwave pulses (radio pulses) [90]. In [91], a mechanism of resonant action for virus inactivation is proposed, based on the transformation of electromagnetic oscillations into acoustic ones. In [92], a hypothesis was put forward about the possibility of using high-power nanosecond electromagnetic pulses with specific frequencies in the microwave range for ponderomotor action on bacteria and viruses to destroy biological objects with known morphological features in the form of nanoprotusions and nanopoints.

Energy impacts of this type belong to the so-called *nonthermal impacts*, since the energy of each pulse is not capable of significantly changing the overall temperature of the object. In [89], the conditions of nonthermal impact of HPEMP on natural and engineered environments of various nature are presented:

- (1) The temperature, T , of the environment as a whole, as well as the temperature of its characteristic relatively homogeneous elements, practically does not change, T_{average} (before the treatment) $\cong T_{\text{average}}$ (after the treatment).
- (2) The strength amplitude of the electric field of the pulse E is much greater than the static breakdown amplitude, $E_{\text{max. imp.}} \gg E_{\text{stat.}}$
- (3) Pulse duration, Δt , is much less than the thermal relaxation time of the medium, $\Delta t \ll \Delta t_{\text{therm.rel.}}$. During a time, much shorter than the typical time to establish the thermophysical properties of the materials making up the environment, local temperature during the impact can be high [89,93].

The method of *nonthermal* exposure to high-power nanosecond electromagnetic pulses [1,3–5,37,38] is used in the processing of refractory, gold-bearing, and polymetallic ores and their concentration products. It is an effective solution for overcoming the physical resistance of ore by unlocking finely disseminated mineral complexes of non-ferrous, rare, and noble metals; thus, increasing the recovery of valuable components in cyanidation [3,4,37,38,94], gravity separation [71], and acid leaching circuits [95–98]. It also increases the contrast of the properties of semiconductor ore minerals (sulfides, oxides) and improves their subsequent separation during flotation due to the formation of hydrophobic and hydrophilic nanoparticles on their surface [1,4,5,17–23,99].

In the preparation of mineral feeds for concentration, the effectiveness of high-power electromagnetic pulses in the processes of selective disintegration is regulated by the following conditions and limitations: predominantly dry or wet (S:L from 5:1 to 3:1) ground feed is processed; the range of change in the mineral particle size is from 100 microns to 2–5 mm.

As a result of the impact of HPEMP on refractory ores and middlings containing finely disseminated particles of noble metals, a sustainable improvement of 5–10% in the recovery of precious metals was achieved, with a decrease in energy consumption and a decrease in the cost of finished products [3,4,37,38,94]. Electropulse treatment of a wet feed intensifies the process of intergrowth unlocking and, depending on the type of mineral feed, provides an increase in the recovery of precious metals between 2% and 40% while reducing the energy consumption [3,38,100].

According to [3,4,38], for a gravitational concentrate of ore from the Nezhdaninskoye deposit exposed to HPEMP, a rather high gain in precious metal recovery was obtained with a minimum energy expenditure of just 3–4 kWh/ton of concentrate being processed and 0.2–0.25 kWh/g of additionally recovered gold. Energy consumption in a process involving the mechanical grinding of ore from 500 μm to 50 μm was about 20–25

kWh/ton of ore and 0.9 kWh/g of additionally recovered gold. This fact indicates that the HPEMP effect provides highly efficient breaking-up of resistant ore products, primarily owing to the partial destruction of mineral complexes and the generation of breakdown channels promoting the access of lixiviant to gold and silver particles.

Plasma treatment of ores, ore concentrates, and mineral feeds is used most often to improve the separation performance of ore minerals and non-metallic gangue, as well as for the “plasma grinding” of ores and processing products to reduce the time of subsequent mechanical grinding and energy costs. The practical application of plasma for directed modification of the structural-chemical and process properties of geomaterials (among other factors) is largely associated with the use of a process (plasma-forming) gas. The power consumption of a plasma-technological reactor with a capacity of 120 kg/h for processing of tin-lead, molybdenum ores and concentrates with a low-temperature plasma flow varies in the range of 50–100 kW [12].

The central role of low-temperature oxygen (Ar-O_2) plasma in processing sulfide minerals with similar physicochemical surface properties, is selective plasma-induced surface oxidation of sulfides from a natural mixture of disseminated mineral particles [12,14,15]. Exposure to plasma leads to a stepwise change in the chemical state of atoms and structural phase transformations on the surface of minerals, the appearance of surface films of oxides (hydroxides) and microdefects, and the reduction and thermal removal of sulfur causing a directed change in the process properties of sulfides and improves their flotation performance [14,15,101–103]. As applied to full-scale production of zirconium oxide (fluoride), oxygen plasma can be used to clean the surface of zircon from organic films and modify its flotation properties [104]. It is also proposed to use oxygen plasma treatment of tantalum oxide films to control their electrical and dielectric properties [105].

Non-equilibrium, low-temperature plasma of dielectric barrier discharge, characterized by high pressure (hundreds of Torr and higher), high electron temperatures (average electron temperatures can reach several electron volts), and low temperature of the process gas (close to the temperature of dielectric barriers) [40] is considered the most precise, efficient, and safe tool for modifying the composition, structure, and properties of the surfaces of various materials, including geomaterials [15,16,41–43,98,106–109]. A dielectric barrier discharge occurs in a gas under the action of an alternating voltage applied to the conducting electrodes, provided that at least one electrode is covered with a dielectric layer on the side of the discharge gap. The discharge can be carried out in oxygen or air at atmospheric pressure, room temperature, and natural air humidity [40,110], i.e., under normal conditions (NIST) and without the use of a special plasma gas. The parameters of HV generators for DBD plasma producing are generally in the range of power 0.5–10 kW, pulses repetition rate initiating discharge—5–50 kHz, pulse voltage—5–20 kV; for effective materials surface treatment, the discharge energy in the range of 0.5–1.5 kJ/m² should be provided [40,110].

3. Dominant Mechanisms behind HPEMP and DBD Effects on Structural, Physico-chemical, and Process Properties of Geomaterials

3.1. High-Power Nanosecond Electromagnetic Pulses

The main idea behind using the impact of high-energy radiation of high-power electromagnetic pulses of nanosecond duration in the processes of disintegration and structural-chemical modification of fine and polydisperse mineral media, such as complex natural composites of dielectric and semiconductor minerals, as well as micro- and nanoparticles of noble metals interspersed in the host mineral matrix, is as described below [3,37,38,111,112].

When the electric intensity of the electromagnetic pulse exceeds the electrical strength of the substance E_{bd} (for example, in quartz $E_{bd} = (2-3) \times 10^7$ V/m), an electrical breakdown develops in the particles of a solid dielectric or semiconductor, accompanied

by the emergence of an electric current (current lacing) in a narrow channel (current filament, or breakdown channel). However, the main discharge current can propagate through the air gaps between mineral particles without affecting their internal volume. This undesirable development can be avoided by using pulses with a short front ($t_{fr} \sim 1$ ns) and amplitude E_A , which significantly exceeds the dielectric strength of the substance in a static field. Under such impact, breakdown along the gas (air) gaps between the particles does not have time to develop, since the ionization time of air molecules ($t_i \approx 10^{-6}$ s) along a narrow and strongly curved streamer propagation trajectory significantly exceeds t_{fr} of the pulse. The main current flow channel will be the less inertial breakdown of a solid dielectric or semiconductor.

When current flows through the current path, the initial release of energy ($\sim 1\text{--}50$ ns) leads to evaporation of the substance, a sharp increase in pressure in the channel, and disintegration of the substance with the formation of a through breakdown channel. At a long (submicrosecond, $t_{heat} \sim 10^{-3}$ s) discharge duration, the released heat begins to be redistributed throughout the volume of the substance and can lead to negative effects: overheating, sintering of particles, melting of the surface of the particles, and closing of the resulting microdamage sites, which further hinders the access of leaching solutions into the mineral particles. Therefore, the duration of high voltage pulses should not exceed $t_{imp} \sim 5\text{--}100$ ns.

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. This greatly facilitates the development of breakdown due to an increase in the electric field strength in the areas of localized 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, 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 a large number of pulses is required. 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 (Figure 3a).

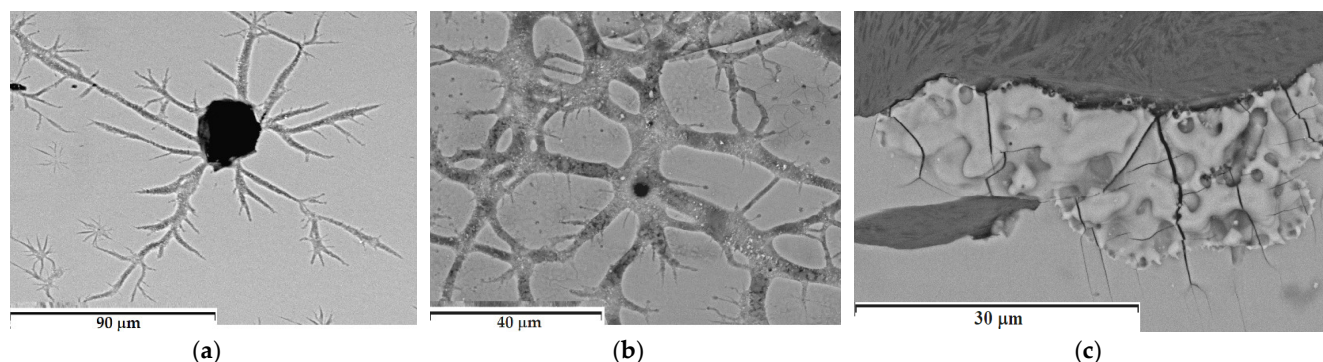


Figure 3. Damaged pyrite surface as a result of exposure to HP EMP. SEM; scale bars: (a) 90 μm , (b) 40 μm , and (c) 30 μm .

An estimate of the power density P [37] required to implement this method of action at an electric field strength of 10^7 V/m gives a value of the order of ~ 100 GW/m², which can be achieved using relativistic high-current electronics devices [88,89]. Figure 4 shows the modular units for continuous treatment of dry and moist (S:L from 10:1 to 5:1) mineral feeds with nanosecond HP EMP developed at ICEMR RAS in cooperation with

the Scientific-Production Enterprise FON, Ryazan: pilot experimental setup with a throughput of 20 kg/h (output voltage amplitude $U_a = 20\text{--}25\text{ kV}$, pulse repetition rate $f = 10\text{--}300\text{ Hz}$) (Figure 4a) and pilot units with a throughput of up to 100–120 kg/h ($U_a = 30\text{--}35\text{ kV}$, $f = 50\text{--}300\text{ Hz}$,) (Figure 4b) and 1 t/h ($U_a = 70\text{ kV}$, $f = 100\text{--}1000\text{ Hz}$) (Figure 4cd).

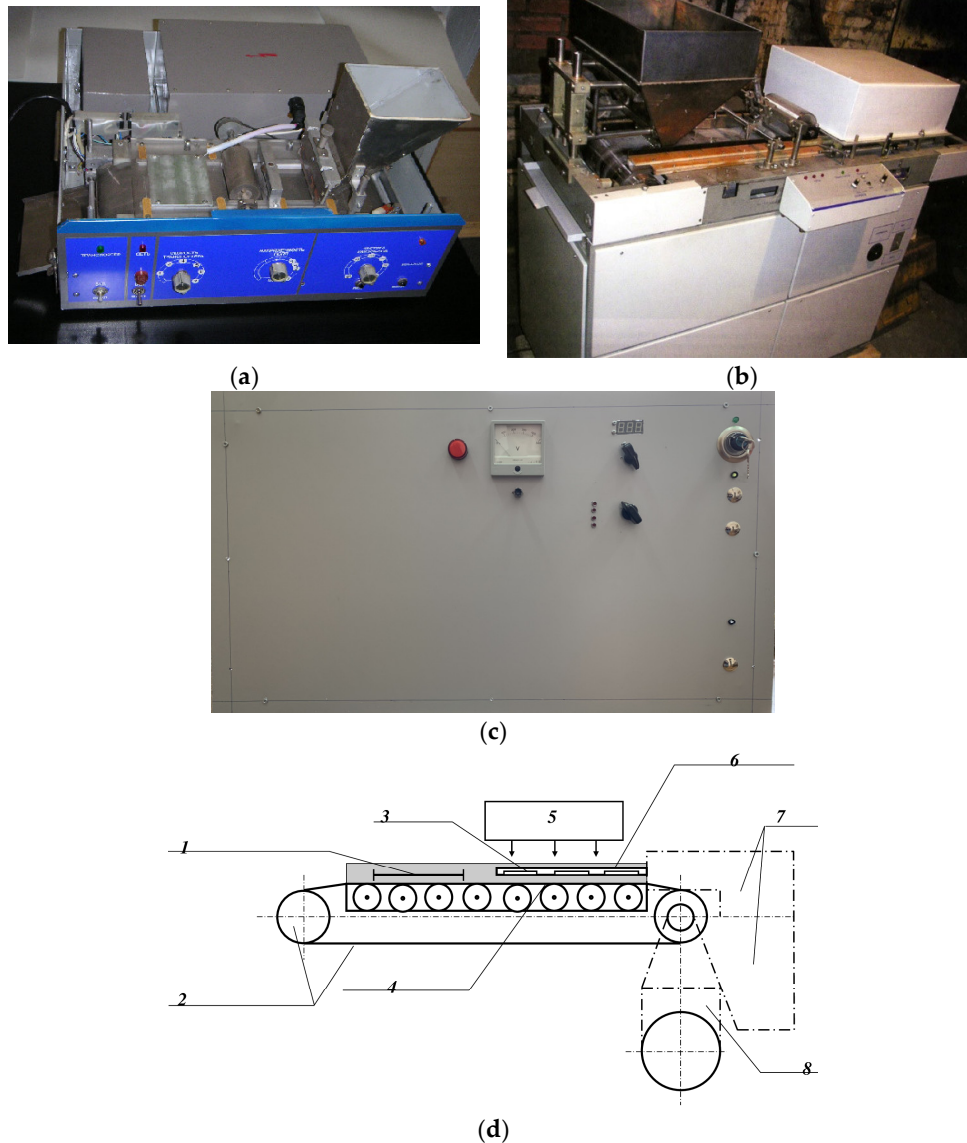


Figure 4. Modular installations for the treatment of mineral products by high-power nanosecond electromagnetic pulses with a capacity of (a) 20 kg/h, (b) 100–120 kg/h; (c) generator of high-voltage nanosecond pulses (U_a up to 70 kV), and (d) structural scheme of the installation with a capacity of 1 ton/h: 1—block for receiving and forming the flow of ore, 2—conveyor for moving the ore flow, 3—electrode system, 4—support plate for electrode system, 5—high-voltage pulse generator with a sharpener block, 6—core and mineral treatment unit, 7—receiver-accumulator for mineral raw materials after HPEMP treatment, 8—conveyor drive.

When exposed to HPEMP, effective softening of finely disseminated mineral complexes and selective unlocking of intergrowth is achieved due to the following [3,4,94,112]: 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 [111] (Fig-

ure 3b); 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 [111,113] (Figure 3c); absorption of the energy of pulsed electromagnetic radiation by particles of noble metals and semiconductor ore minerals carriers (skin effect) [113], as well as in the process of auto-electronic emission from the surface of sulfides [93].

To describe the development of a breakdown in a particle of a dielectric mineral or a semiconductor, it appears most appropriate [3,111] to use an approximation of the avalanche-streamer gas discharge theory by Mick, Loeb, and Roether [114] with photoionization [115] taken into account. The breakdown of a natural dielectric with conductive micro- and nanoscale inclusions by a short high-voltage pulse occurs when an avalanche-like multiplication of electrons accelerated in an electric field occurs. The distribution of electrons in the avalanche becomes anisotropic, and the breakdown channel grows due to the entry into it of the region ionized by the avalanche electrons.

With repeated exposure to HP EMP of an inhomogeneous dielectric medium with finely disseminated metals, electrical breakdowns can develop gradually, from pulse to pulse, at a field strength lower than the electrical strength of a homogeneous dielectric. In the intervals between pulses, relaxation of the energy released in the breakdown channel occurs. One of the main mechanisms for the relaxation of this energy is the formation of microcracks around the breakdown channel due to the expansion of the heated gas in the channel and its outflow from the channel if the latter exits to the sample surface. After the breakdown channel grows to the surface of the particle, the discharge transforms into a surface one (Figure 3a), in an attempt to ensure the neutralization of the electric field in the entire volume of the particle.

The processes of gas outflow from channels of nanosecond breakdown of semiconductor ore minerals (sulfides, oxides), condensation of matter in the outflowing jet (Figure 5a) and its deposition on the mineral surface (Figure 5b) determine one of the possible mechanisms of structural-chemical modification of the surface of earth materials as a result of electromagnetic pulse treatment. In [19,116,117], using pyrite FeS_2 as an illustration, the staged process discussed the outflow of an evaporated substance in the form of a gas consisting of a mixture of monatomic iron and sulfur from a nanosecond breakdown channel, taking into account the condensation of substance vapors. 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.

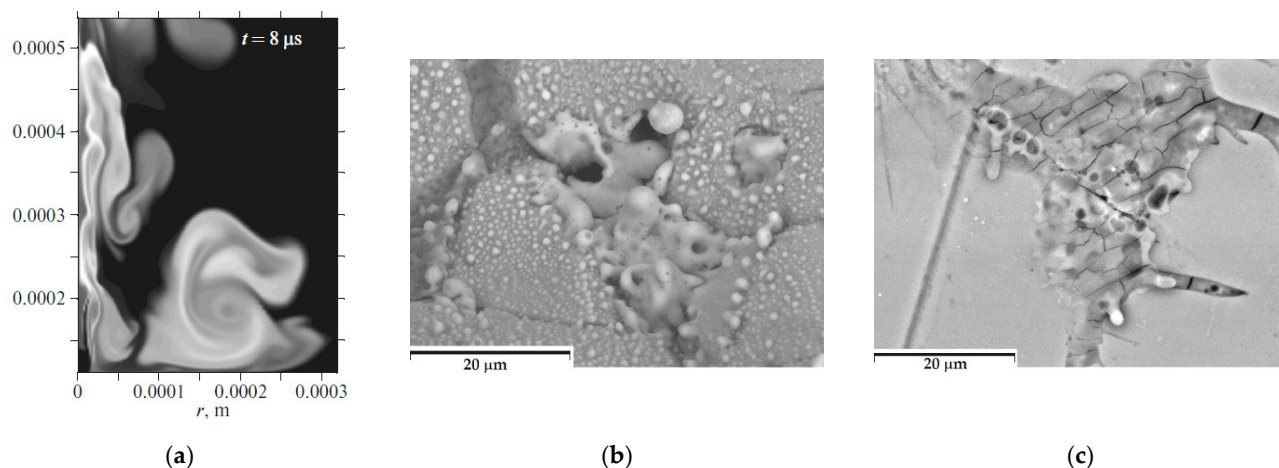


Figure 5. (a) Distribution of condensed matter at the late stage of iron vapor outflow from the nanosecond breakdown channel of sulfide minerals (pyrite); presented in the paper [117]. (b,c) New formations of the iron oxides (hydroxides) on the surface of (b) pyrite and (c) arsenopyrite after treatment by HP EMP ($t_{\text{treat}} = 10\text{--}30$ s). SEM-EDX; scale bars: (b,c) 20 μm .

Another mechanism established in [1,3–5,17–23,99,118], for the changes in the structural, physicochemical, and process properties of semiconductor ore minerals under the action of nanosecond HPMPs 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 (Figure 5b).

The non-thermal effect of nanosecond HPMP [89,119] 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. The optimal mode of pretreatment of sulfide minerals with high-voltage nanosecond pulses was experimentally established, and the possibility of improving the selectivity of flotation separation of sulfides was demonstrated [1,4,5,17–23,99,118]. The parameters of the pulses and the processing time of mineral samples are as follows: pulse front duration is $t_{fr} \sim 1\text{--}5$ ns; pulse duration— $t_{imp} \leq 50$ ns; pulse amplitude— $U_A \sim 25\text{--}30$ kV; electric field strength $E \sim 10^7$ V/m; pulse repetition rate $f = 100$ Hz; pulse energy ~ 0.1 J; range of treatment time for mineral samples— $t_{treat} = 5\text{--}50$ s. As a result of 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%.

According to microhardness and spectroscopic studies (FTIR) [95,106,120–122], exposure to nanosecond high-voltage pulses 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 microbreak-downs), disordering and amorphization of the surface. The effect of weakening of the rock-forming minerals of diamond-bearing kimberlites when exposed to HPMP 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 [120,121,123].

According to analytical electron microscopy (SEM–EDX), electromagnetic pulse processing of eudialyte caused damage to the surface of mineral grains with the formation of new relief depending on the processing time: from parallel-fractured at $t_{treat} = 30$ s (Figure 6a) to polygonal-fractured at $t_{treat} = 60\text{--}90$ s (Figure 6b). As a result of spectroscopic studies (FTIR, XPS), the mechanism of structural transformations of eudialyte was established in [95,98,106], associated with the destruction of structural fragments of the zeolite-like silicon-oxygen framework of the mineral, namely, three- and nine-membered silicon-oxygen rings of SiO_4 tetrahedra (Si_3O_9 and/or Si_9O_{27}) [124].

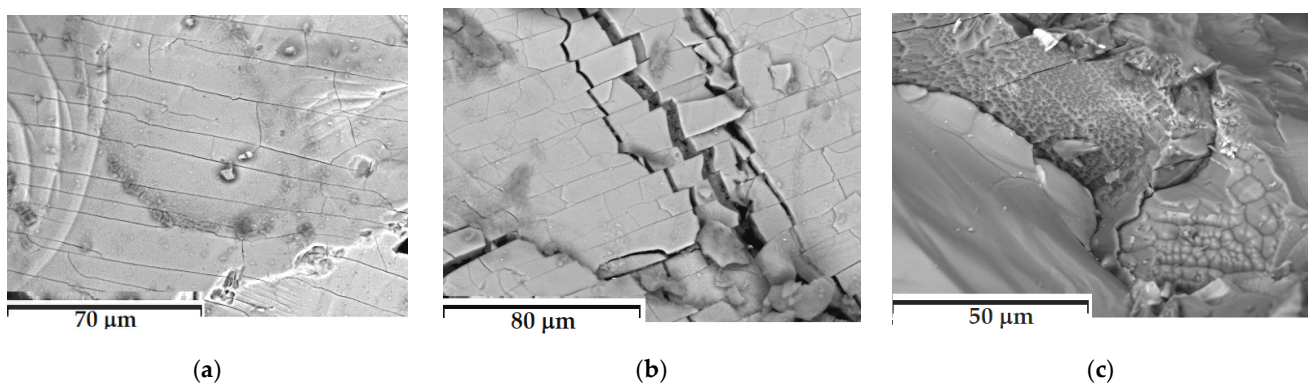


Figure 6. (a,b) Eudialyte and (c) perovskite surface after treatment by HPMP ($t_{treat} = 30\text{--}90$ s). SEM; scale bars: (a) 70, (b) 80, (c) 50 μm .

The results obtained in [106], support the application efficiency of high-power electromagnetic pulses for a directed change in the physicochemical properties and floatability of eudialyte. In all experiments, a decrease in the negative potential of eudialyte leads to an increase in adsorbability of anionic collector and, as a consequence, an increase in the eudialyte recovery to concentrate. As a result of preliminary short-term ($t_{\text{treat}} = 30$ s) electromagnetic pulse treatment of eudialyte rough concentrate and the use of sodium oleate (NaOl) at a consumption of 1000 g/t during its subsequent flotation, the recovery of eudialyte into the concentrate increased by 15% (from 48% at $t_{\text{treat}} = 0$ s to 63% at $t_{\text{treat}} = 30$ s). In combination of NaOl with $\text{Al}_2(\text{SO}_4)_3$ (as a strong eudialyte flotation activator) at a consumption of 500 g/t, eudialyte recovery increased by 4% (from 80% at $t_{\text{treat}} = 0$ s to 84% at $t_{\text{treat}} = 50$ s) [106].

As a result of pretreatment for 3 min with high-voltage nanosecond pulses with $U_A = 25$ kV and subsequent nitric acid leaching of the eudialyte concentrate from the Lovozero deposit, the increase in recovery into the pregnant solution was 9.4% for ZrO_2 and 6.4% for ΣREE [95].

For perovskite (CaTiO_3) from the Afrikanda deposit, Russia, using SEM–EDX, it was found in [109] that the effect of HPEMP ($U_A = 70$ kV, $f = 375$ Hz) was the destruction of the structure of the mineral surface, the formation of deep parallel cracks (Figure 6c) and surface areas with subparallel pyramidal protrusions (Figure 6c). A monotonous decrease in the microhardness of perovskite was observed with an increase in the time of electric pulse treatment from 930 MPa in the initial state to 624 MPa at $t_{\text{treat}} = 150$ s, i.e., $\Delta HV_{\text{max}} = 33\%$. As a result of pretreatment of samples with HPEMP, due to a change in the structural and chemical state of the surface, an increase in hydrophobicity and sorption activity, there was an additional increase in the total recovery of the perovskite monomineral fraction into the flotation froth by ~10–15%: $\varepsilon = 90\%$ ($t_{\text{treat}} = 60$ s) and ~95% ($t_{\text{treat}} = 120$ s) [109].

3.2. Subnanosecond Dielectric-Barrier Discharges

A dielectric barrier discharge (DBD) is a discharge in which the current flow is limited by at least one dielectric layer (Figure 7a) and the typical dimensions of the electrodes significantly exceed the interelectrode gap [40,110]. 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. For practical applications, the problem of obtaining a diffuse discharge 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 [40,110,125,126].

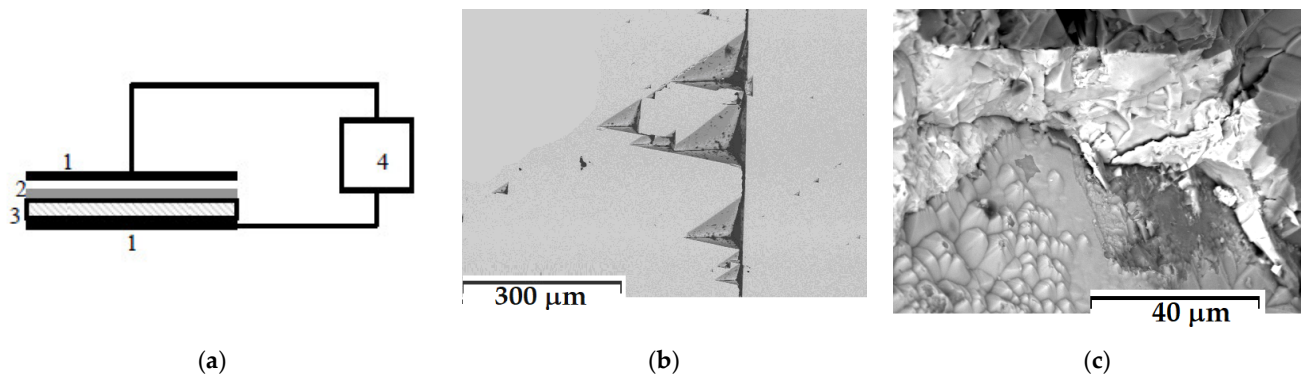


Figure 7. (a) Schematic representation of a cell of a dielectric barrier discharge: 1—flat metal electrodes of plate form, 2—layer of the ground mineral, 3—plate of dielectric, 4—high voltage power supply. Reprinted with permission from Ref. [125]. Copyright 2019, Andreev V.V. (b) Galena and (c) perovskite surface after treatment by DBD ($t_{\text{treat}} = 50$ s). SEM; scale bars: (b) 300, (c) 40 μm .

During the experiments in [16,41–43,98,106–109], mineral samples were exposed to a pulsed barrier discharge in two experimental settings (by analogy with [127]): first, mineral particles of the crushed samples filled the gap between the active metal electrode and the dielectric barrier and were separated from the electrode by a small air gap. In this case, free movement of particles above the barrier during the discharge was possible. In the second setting, consolidated mineral samples (crystals, thin sections, polished sections, plates) were placed into the discharge, so that the active surfaces of the samples, controlled during structural studies, were on the surface of the dielectric barrier.

Apparently, in the first case, 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 [128]. In the second case, the indicated barrier discharge radiation effects were supplemented with electric charge transfer to the surface of the sample and an increase in the temperature of the dielectric barrier [16,40,127].

When conducting experiments on the effect of subnanosecond DBD on the structural and physicochemical properties of minerals, the following rational parameters of pulses initiating a barrier discharge were established in [16,42], at which the most significant changes in the structure-sensitive properties of minerals were observed: duration of the leading edge of the pulse 250–300 ns, pulse duration 8 μs , voltage on the electrodes in the barrier discharge cell 20 kV, repetition frequency of the pulses initiating the discharge 16 kHz, LTP treatment time range $t_{treat.} = 10$ –150 s. The dimensions of the electrodes of the DBD discharge cell significantly exceeded the length of the interelectrode gap, which was ~5 mm. The gas temperature in the active zone of the discharge cell did not exceed the temperature of the dielectric barrier and remained on the order of ambient temperature for $t_{treat.} = 10$ –60 s. With an increase in the treatment time of up to 150–300 s, the temperature could rise to 150–200 °C.

As a result of exposure to DBD radiation, the following changes occurred in the surface morphology and structure-sensitive properties of the minerals [16,42]. According to SEM, defects of a regular triangular shape (Figure 7b) formed on the surface of galena samples due to the removal of microcrystalline fragments, most likely due to ponderomotive forces in the region of a strong electric field. On the surface of chalcopyrite, the formation of irregularly shaped defects was observed, and on the surface of sphalerite, microchannels of electrical breakdown formed, bordered by the sinter formation material of oxide (hydroxide) micro- and nanophases. The change in the morphology of the surface of sulfides caused weakening, and a significant decrease in the microhardness of minerals as a whole by 20–30%. Short ($t_{treat.} = 10$ s) treatment of pyrrhotite caused a shift in the electrode potential of the mineral to negative values ($\varphi = -60$ mV, at pH 9.7–12) [41,43,108], which predetermines the effect of reducing the sorption activity of pyrrhotite with respect to xanthate, hence its flotation recovery reduction.

In rock-forming minerals, the following features of changes in surface properties when exposed to DBD were established [16,41]. With increasing plasma treatment time of the quartz samples $t_{treat.} = 10$ –150 s, smoothing of surface irregularities and the formation of microdefects of irregular shape ($\leq 3 \mu m$) occurred. This caused weakening and a monotonous decrease in the microhardness of the mineral from ~1420 MPa up to 1320 MPa in the original and modified at $t_{treat.} = 150$ s states, respectively. The maximum relative change (decrease) in microhardness ΔHV_{max} was ~7%. The contact angle of wetting the quartz surface with water changed nonmonotonically. As a result of short-term exposure ($t_{treat.} = 10$ –30 s), the contact angle increased from 44° to 53°, which indicates an increase in the hydrophobicity of the mineral's surface, while with an increase in $t_{treat.}$, a gradual decrease in the contact angle was observed to initial values at $t_{treat.} = 150$ s. The possibility of modifying the hydrophobicity of quartz by energy impacts [16,122] can be

used in industrial processes for separating the mineral from impurities and selective (reverse) flotation of ferruginous quartzites.

Changes in the surface morphology of eudialyte exposed to DBD ($t_{\text{treat}} = 50$ s) are associated with the formation of defects in the form of imprints of current microchannels of electrical breakdown with a diameter of 1–3 microns and microcracks. With an increase in the treatment time to 100 s, fragmented low-dimensional coatings formed on the grain surface. In the process of forming new surface phases, the minerals associated with eudialyte (nepheline, loparite, aegirine) were broken up, the chemical elements of these minerals moved and precipitated on the surface of eudialyte grains due to barrier discharge factors, such as ion wind, transfer to the surface of electric charge, and low-temperature plasma products [42]. As a result of the barrier discharge action, the surface of eudialyte was weakened, and its microhardness decreased with an increase in treatment time from 790 to 420 MPa at $t_{\text{treat}} = 0$ s and 150 s, respectively ($\Delta HV_{\text{max}} = 47\%$), where after a short ($t_{\text{treat}} = 10$ s) treatment ΔHV was 20% [106].

Short ($t_{\text{treat}} = 30$ s) pretreatment of eudialyte concentrate samples with DBD contributed to the opening and disintegration of mineral particles and increased the recovery of zirconium into the pregnant solution of acid leaching by 4.0% [98].

Changes in the surface morphology of perovskite exposed to DBD ($t_{\text{treat}} = 50$ s) are associated with the formation of defects in the form of intergranular and intragranular microcracks, as well as (as in the case of HPMP treatment) surface areas with pyramidal protrusions (Figure 7c). This caused surface weakening and a decrease in perovskite microhardness with an increase in t_{treat} from $HV = 912$ to 663 MPa at $t_{\text{treat}} = 0$ and 150 s, respectively [109]. According to spectroscopic studies (FTIR), plasma treatment, resulted in an increase in the sorption activity of perovskite with respect to caprylhydroxamic acid. Moreover, the main attachment form of the reagent on the mineral surface modified by DBD was the complex compound, titanium hydroxamate [109,129]. Changes in the structural and physicochemical properties of the mineral predetermined an additional increase in the total recovery of the perovskite monomineral fraction into the flotation froth by ~10–15%: $\varepsilon = 90$ –93% ($t_{\text{treat}} = 10$ –30 s) and ~95% ($t_{\text{treat}} = 100$ s).

The established parameters of pulsed energy impacts and reagent flotation modes [42,95–98,106,109] can be used to improve the flotation performance of eudialyte and perovskite ores. This is confirmed by the results of flotation experiments presented in [106,109]. As a result of the preliminary short-term ($t_{\text{treat}} = 30$ s) electromagnetic pulse treatment of eudialyte rough concentrate, the eudialyte recovery in a flotation increased by 15% (from 48% at $t_{\text{treat}} = 0$ s to 63% at $t_{\text{treat}} = 30$ s). The effect of HPMP and DBD on the physicochemical properties of the perovskite surface represents a shift in the electrokinetic potential towards positive values, an increase in the contact angle ($t_{\text{treat}} = 10$ –30 s), as well as the improved adsorption of the collector and the higher flotation recovery of perovskite by 10–15% [109].

4. Conclusions

The analysis of the research conducted in Russia and the world over the past 10–15 years in the field of practical applications of high-intensity energy effects in the processing of refractory minerals as presented in this paper indicates the theoretical possibility and efficiency of pulsed power technologies.

According to the discussed research findings, compared to all the methods of energy treatment of mineral feeds that precede concentration, the method of exposing gold-bearing and polymetallic ores to high-power nanosecond electromagnetic pulses (HPMP) has significant advantages. This method allows the most rational use of electrical energy (selective destruction occurs without heating the ore) and produces the most complete intergranular disintegration of mineral components, and thus the highest recovery at the lowest energy consumption. The nonthermal action of high-power nanosecond electromagnetic pulses is causing physicochemical processes (due to the occurrence of chemical solid-phase reactions) on the surface of sulfide minerals involving the

formation of micro- and nanophases. Depending on their chemical composition, these neoformations in the form of hydrophobic elemental sulfur and various hydrophilic oxygen-containing compounds, can enhance the contrast of the process properties of minerals, which is effectively used to improve the selectivity of the subsequent flotation separation of sulfides.

The method of plasma-chemical processing of earth materials with low-temperature pulsed nanosecond dielectric barrier discharge (DBD) plasma in air at atmospheric pressure has great prospects for practical applications in the processes of selective separation of semiconductor ore minerals (sulfides, oxides). It creates optimal conditions for enhancing the contrast between the process properties of minerals and reducing the concentrations of toxic flotation agents. However, for the development and design of high-capacity process units and their commercialization, further theoretical and experimental research is needed into the processes of plasma-chemical modification of the surface of geomaterials.

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