Investigation of oxide films removal process from the ore pulp particle surface during its ultrasonic treatment

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This work was carried out with the aim of experimentally determining the parameters of the ultrasonic treatment process in which oxide films will be removed from the surface of sulfide particles —pyrrhotite, pentlandite, pyrite, etc. in the pulp. Analysis of literature sources and previous studies has shown that there is a lack of experimental data to determine the parameters of ultrasonic treatment process, which would provide the removal of oxide film from ore pulp particle surface. The studies were carried out on a mounted reactor, which is a sealed ore pulp reactor with an ultrasonic vibration concentrator and a working tool (emitter) immersed in it. Water cooling was provided on the outside of the reactor. The experiments were carried out at an ultrasonic vibration frequency of 22 kHz ± 1.65, intensities of 7.2, 11, 21 and 28 W/cm^2, for 15 minutes. The maximum power consumption by the generator was 400 W, acoustic power — 200 W, radiation power — 120 W, with a power control range of 30–100%. The work used samples of sulfide ores from the Shanuch copper-nickel deposit (Kamchatka Krai), subjected to crushing, grinding to 100% control class –0.1 mm and classification on a sieve screen. As shown by studies of ultrasonic exposure on a mounted laboratory reactor using an ultrasonic technological apparatus of the “Volna” type, model UZTA-0.4/22-OM, and microscopic studies using an ore polarizing microscope POLAM R-312, the parameters of the ultrasonic exposure process, in which oxide films will be removed from the surface of the ore particles of the pulp; with minimal grinding of the ore particles, radiation intensity is 21 W/cm^2, the process duration is from 15 minutes, the reduction in the control class –0.1 mm was 12.2%.

Key words: ultrasonic treatment, ore pulp, laboratory installation, ultrasonic technological apparatus, oxide films, mechanical activation.

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Introduction

Ultrasound treatment of the ore slurry can be considered as an option to remove oxide films [1, 2]. Dispersion of oxide, surface films from the mineral part of the ore slurry during ultrasonic treatment takes place mainly under the action of cavitation. The process of destruction of coatings and films is also influenced by the pulsation and oscillations of non-slamming vapor-gas bubbles, secondary effects arising in the pulp during the propagation of ultrasonic waves of finite amplitude in it — acoustic currents, radiation pressure and the sound-capillary effect [3–5]. Acoustic flows in turn cause intensive pulp mixing, thereby abrasively cleaning the surface of ore particles from mineral contaminants [6]. At the same time, according to the authors [4, 7], mechanical scrubbing, treatment with chemical reagents, and heat treatment do not provide a sufficient degree of removal of oxide films from the surface of sulfide minerals, especially from films located in defect channels and microcracks. These processes are expensive, time-consuming and energy-intensive.

The formation of ultrasonic cavitation, acoustic flows, their impact on ore pulp is possible at certain parameters of the sounding process — frequency of oscillations, intensity of radiation, duration of the process, temperature of the environment [8, 9]. In this regard, the purpose of the work is to experimentally determine the parameters of ultrasonic treatment process, at which oxide films will be removed from the ore pulp particles surface with minimal grinding of ore particles. Process parameters include irradiation intensity, duration and ore size distribution.

Analysis of previous studies

In the institute “Uralmechanobr” researches of ultrasonic method for oxide film removal from the surface of feldspar, glass quartz sands, electrocorundum, silicon carbides, boron, etc. at the frequency of vibrations 15–25 kHz, intensity 2 W/cm^2, duration of the process from 1 to 15 min were given [4, 7]. The best results at removal of iron hydroxide films from the surface of quartz glass sands of Verkhne-Dnepropetrovsk deposit were achieved at the frequency of 20 kHz, duration of oscillations 2–5 min, with the addition of $NaHCO_3$. At the same time, mechanical sand scrubbing took 30-60 min. Experiments have shown that in the beneficiation of electrocorundum, silicon and boron carbides, as well as vein quartz and rock crystal, ultrasonic exposure usually provides significant advantages over chemical scrubbing of these materials and chemical acid treatment of crystal. In this case, ultrasound treatment allows to reduce the duration of the operation to 5–10 min [4, 7]. The Siberian Federal University conducted research on the effect of ultrasonic influence on gold concentrates before cyanidation [10]. Mineral composition — quartz, muscovite, chlorite, etc. Concentrates with gold content of 7.5 g/t (100 microns); 13.5 g/t and 17.5 g/t (70 microns) were exposed in an ultrasonic bath at a total radiation power of 300 W, frequency 35 kHz, duration of 20 minutes. As a result of the experiments, films, contaminants were removed from the surface of ore minerals, oxidation of Fe^{2+} to Fe^{3+} with the formation of oxyhydroxides occurred, the morphology of the surface of ore minerals changed and microchannels, craters, defects were formed on it. The paper [11] presents the results of research on the influence of ultrasonic treatment of pulp on the process of flotation of fluorite ores. Studies have shown that at ultrasonic irradiation adsorption and hydrate layers on the surface of minerals are subjected to changes, the weakest bonds of collectors with the surface of minerals are destroyed. Similar results are presented in [12]. Established, under the action of ultrasound frequency of 22 and 44 kHz, output power of 400 W, duration of 5, 7, 10 min. surface graphitic film is removed from sulfide minerals. Data on intensification of zirconium leaching process from eudialyte concentrate are given in [13, 14]. The study substantiates the mechanism of intensification of concentrate leaching using constant ultrasonic treatment at oscillation frequency of 20 kHz, process duration of 30, 60 and 120 min. consisting in dispersion of colloidal silicate gel, prevention of its precipitate formation on the surface of mineral particles, formation of numerous defects and microcracks on the surface of eudialyte grains up to their destruction. The kinetics of antimony leaching from refractory gold ore using ultrasound was investigated [15]. The results showed that ultrasound increases the leaching rate of antimony from 81.2% to 93.1%. According to the authors [15], intensification of the process under the influence of ultrasound with a frequency of 22 kHz, power 600 W, for 60 min. occurs due to the removal of surface films from the particles, their grinding, the formation of microcracks in them, which facilitates the penetration of leaching acid inside the particles. The authors from Northeastern University (PRC) applied physical dispersion of copper-nickel sulfide ores by ultrasound with a power of 100–400 W, duration of –20 min to weaken heteroaggregation of pentlandite and serpentine to increase the flotation rate. The results showed that ultrasonic power is a key factor affecting the dispersion of pentlandite-serpentine, as well as the change in surface roughness of the minerals. Optimal ultrasonic treatment conditions — 200 W for 3 min [16]. The results of [16] are confirmed by experiments [17, 18], where ultrasound exposure of sulfide ore pulp was carried out with power of 200, 300 W, 50 min, 240 min. Along with experimental studies in 2023 analytical calculation of the optimal value of ultrasonic vibration intensity capable of removing oxide films from the surface of sulfide cobalt-copper-nickel ore particles in order to avoid the creation of passivating effect on their surface was carried out. As shown by the calculations of Iodis V. A. [19], the optimal value of ultrasound intensity lies in the range of 17 to 28 W/cm^2, at the frequency of ultrasonic oscillations of 22000 Hz.

Analysis of literature sources, previous studies showed that the data of experiments to determine the ultrasonic treatment process parameters, at which the oxide films will be removed from the ore pulp particles surface is insufficient.

Materials and methods

Ore

The samples of sulfide ores of copper-nickel deposit Shanuch (Kamchatka Krai) with 60-70% of ore minerals were used in this work. Initial metal content in the ore sample: 3.22% Ni; 0.88% Cu; 0.087% Co; 28.1% Fe_2O_3. The 65 mm ore samples were crushed on a Pulverisette 1 laboratory jaw crusher to a particle size of 10 mm. They were then pulverized in a Pulverisette 5 planetary ball mill to 100% control grade –0.1 mm. The crushed ore was then separated by classification on an "Analysette 3, model PRO" sieve screen. Granulometric composition of ore after grinding: 62.5% — 100 μm; 26.4% — 80–100 μm; 7.8% – 50–80 μm; 3.3% < 50 μm. A microscopic image of the ore pulp particles before ultrasonic treatment, obtained using a POLAM P-312 ore polarization microscope, is shown in **Fig. 1**.

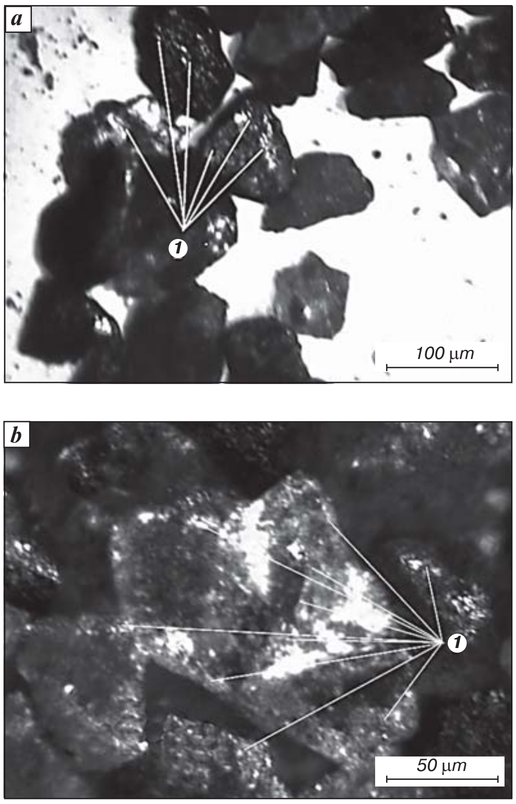

Fig. 1. Microscopic image of ore pulp particles before ultrasonic treatment:
1 – oxide films

Laboratory installation

The setup for the laboratory studies was a steel (12X18N10T stainless steel), sealed reactor with an immersed ultrasonic vibration concentrator and working tool(s) (22 kHz ± 1.65) [20]. The intensity of radiation can be 4.2–35 W/cm^2. The concentrator was connected to an ultrasound generator (type "Volna", model UZTA-0.4/22-OM) [21, 22] through a piezoelectric oscillating system (**Fig. 2**). The maximum power consumed by the generator was 400 W, with a power control range of 30–100%. The acoustic power and efficiency were 200 W, 60%. The volume of the ultrasonic processing chamber to the volume of the cooling chamber was 1 to 5. Circulation was provided by a Kronos 50 Full pump with a capacity of 0.0023 l/s. To ensure a constant ore pulp temperature during the process of 20 ± 0.5 °C, the volume flow rate of cooling water was adjusted depending on the intensity of sonication and ranged from 1 to 2 l/min. To control pulp temperature we used a temperature meter of IRT-4/16 brand (indication resolution of 0.1 °C, measurement error ±0.25%). To study the microstructure of ore pulp particles we used an ore polarization microscope POLAM-R312.

Experiment

Crushed copper-nickel sulfide ore from Shanouch copper-nickel deposit to 100% control grade –0.1 mm was mixed with distilled water at a ratio of 1 to 5, 200 g ore to 1000 g water. Dry grinding in a planetary ball mill leads to oxidation of pyrite, chalcopyrite by mechanoactivation. When the pump was switched on, the pulp filled the ultrasonic treatment chamber and circulated through a closed circuit. Further, by a manual valve, water from the cold water supply system was supplied to the external water cooling chamber at a constant volume flow rate and the ultrasound generator was turned on with the specified radiation intensities — 7.2, 11, 21 and 28 W/cm^2. The duration of sonication was 15 min at atmospheric pressure, at the end of the treatment process pulp samples were taken for microscopy.

Results and discussion

Microscopic images of ore pulp particles before and after ultrasonic exposure are shown in **Figs. 3–6**. As shown by studies of ore pulp particle microstructure after ultrasonic treatment with the intensity of 7.2 W/cm^2 and at the process duration of 15 min. oxide films are not removed from the ore surface. (**Fig. 3**).

Radiation intensity of 11 W/cm^2 partially removes some of the oxide films from the ore pulp. Some of the pulp particles (about 5–7%) are pulverized and form a suspension. The suspension partially covers the pulp particles, which makes it difficult to take pictures and study them (**Fig. 4**).

Fig. 5 shows that ultrasonic treatment at an intensity of 21 W/cm^2 removes most of the oxide films from the ore pulp particles. As studies have shown, 12.2% of the pulp particles are pulverized.

The experiment showed that at an intensity of 28 The experiment showed that at an intensity of 28 W/cm^2, duration of 900 s almost all oxide films are removed from the surface of ore pulp particles. Crushing of particles under the action of ultrasound is ≈ 30-35%.

The degree of particle size reduction of Shanuch deposit (Kamchatka Krai) ore pulp after ultrasound exposure of different intensity, the same duration of 15 min. is presented in **Fig. 7**.

The change in temperature of the crushed ore and distilled water mixture during exposure and external cooling is shown in **Fig. 8**.

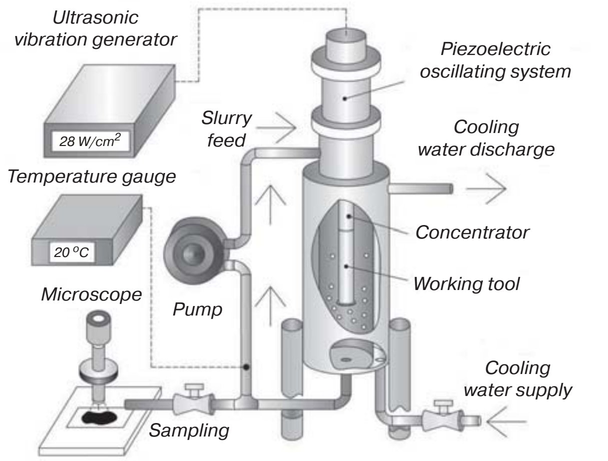

Fig. 2. Laboratory installation for investigation of oxide films removal from ore pulp particles surface during its ultrasonic treatment at 20 °C

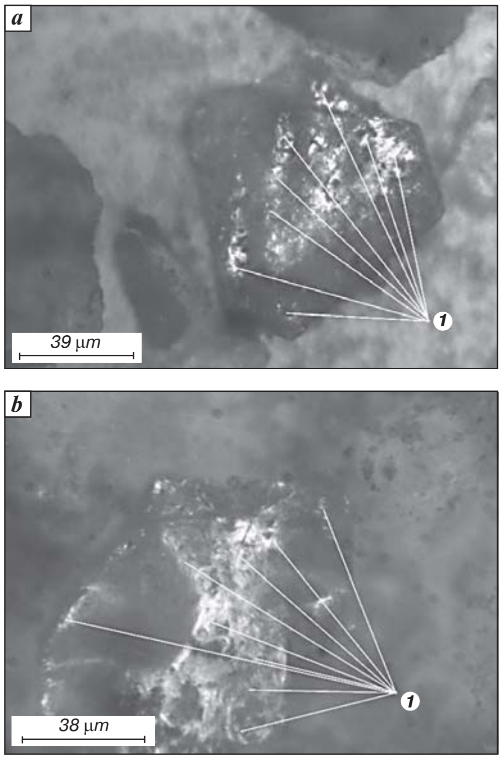

Fig. 3. Microscopic image of ore pulp particles after ultrasound treatment with radiation intensity 7.2 W/cm^2:
1 – oxide films

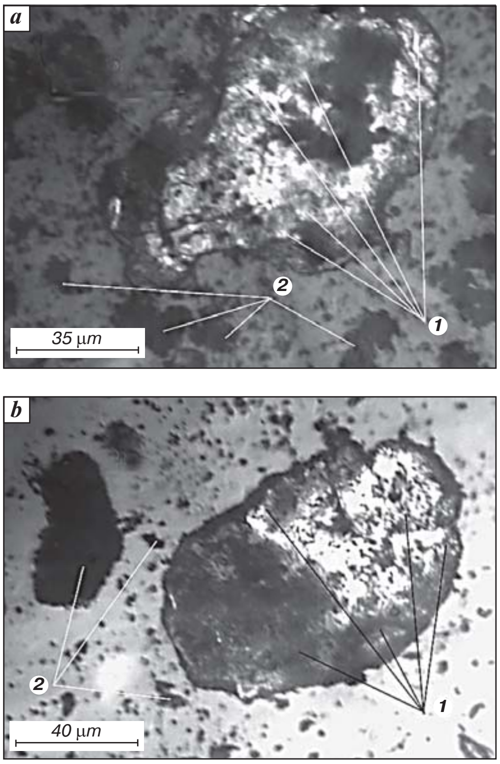

Fig. 4. Microscopic image of ore pulp particles after ultrasonic treatment with intensity 11 W/cm^2:
1 – oxide films, *2* – suspension of crushed particles

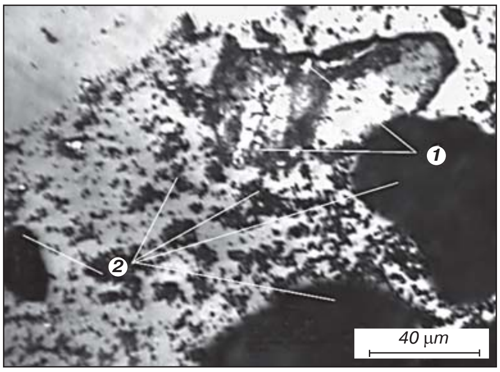

Fig. 5. Microscopic image of ore pulp particles after ultrasonic treatment with intensity of 21 W/cm^2:
1 – oxide films; *2* – suspension of crushed particles

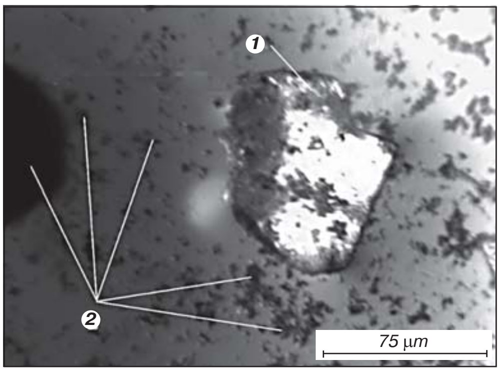

Fig. 6. Microscopic image of ore pulp particles after ultrasonic treatment with radiation intensity 28 W/cm^2:
1 — oxide films, *2* — suspension of pulverized particles

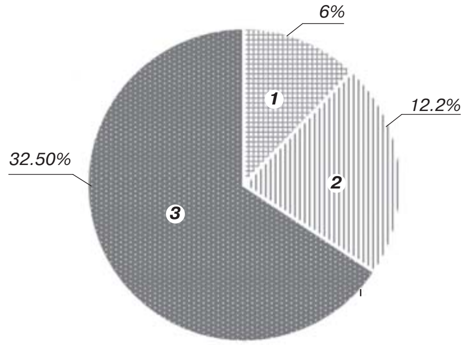

Fig. 7. Degree of ore pulp size reduction after ultrasound exposure, W/cm^2:
1 – intensity 11; *2* — 21; *3* – 28

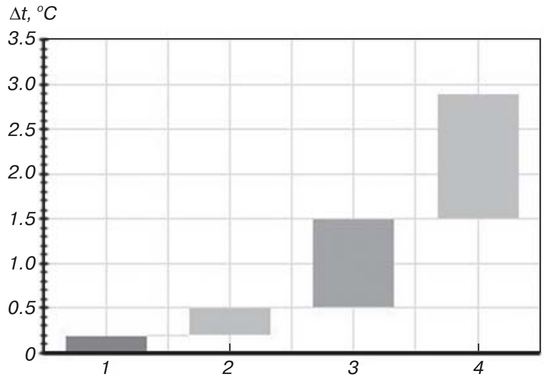

Fig. 8. Change of ore pulp temperature in the process of ultrasound exposure, W/cm^2:
1 – intensity 7.2; *2* – 11; *3* – 21; *4* – 28

Comparison on the basis of estimated calculation and experiments on ultrasonic cleaning of mineral particles surface from oxide films with mechanoactivation showed that this process has higher energy costs. To remove oxide films, the ultrasonic oscillation generator "Volna" [21, 22] should be operated at 60% (21 W/cm^2) of full power. At an ore mass of 200 g and a process duration of 15 min. the energy consumption for processing 1 g of ore will be 0.3 W·hr. Ore particle size distribution after ultrasonic treatment with intensity of 21 W/cm^2: 50.3% — 100 µm; 28.1% — 80–100 µm; 13.4% — 50–80 µm; 8.2% < 50 µm. At mechanoactivation on a planetary mill "Pulverisette 5", power 1300 W, duration of 60 min. power consumption for processing of 1 g of ore will be 0.535 W·hr.

The experiment has shown that due to cumulative jets and acoustic currents appearing in the ore pulp ultrasonic impact can provide removal of oxide films almost without particle grinding, in contrast to mechanical activation, in which most of the particles are crushed. Granulometric composition of ore after mechanical activation for 1 hour in a planetary mill: 37.7% — 100 microns; 33.4% — 80–100 microns; 18.3% – 50-80 microns; 10.6% < 50 microns.

Conclusion

Experimental studies of oxide films removal process from the ore pulp particles surface during its ultrasonic treatment were carried out. Experiments were performed at intensities of 7.2, 11, 21 and 28 W/cm^2, for 900 s, at ultrasonic frequencies of 22 kHz ± 1.65. The samples of sulfide ores from the Shanuch copper-nickel deposit (Kamchatka Krai) subjected to crushing, grinding to 100% of the control grade –0.1 mm and classification on a sieve screen were used in this work.

During the research of ultrasonic treatment with the use of a mounted laboratory reactor with ultrasonic technological apparatus of "Volna" type, model UZTA-0,4/22-OM and microscopic research with the use of ore polarizing microscope POLAM P-312, the parameters of ultrasonic process were determined, providing removal of oxide films from the surface of ore pulp particles with minimum grinding of ore particles and are as follows: radiation intensity 21 W/cm^2, duration of the process from 15 min, with a 12.2% decrease in the control grade of –0.1 mm.

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