Influence of High-Power Electromagnetic Pulses on the Structural-Chemical and Physicochemical Properties of Rare-Earth Minerals

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Abstract
The investigation of the structural-chemical state and sorption properties modification of columbite and eudialite surface under the impact of high-power nanosecond pulses (HPEMP) was performed using XPS and FTIR. It was defined that preliminarily treatment of rare-metal minerals with high-power nanosecond pulses is promising tool for the directional changes in their physicochemical and structural-chemical properties as it was confirmed by the increasing of mineral’s sorption activity.

Keywords: columbite, eudialite, high – power electromagnetic pulses, XPS, FTIR

Introduction
The flotation of rare earth minerals is important for the economic recovery of rare earth minerals from their ores. Flotation is a key step in the industrial production of RE materials, understanding the process of RE flotation will facilitate improvement in the flotation recovery and more efficient production of RE s for their numerous applications. Systematic studies on RE flotation are urgently required, the research presented in this study id directed toward the better understanding the RE minerals flotation regularities.

Materials and methods
The mineral samples of columbite and eudialite used in this study (size fractions - 100 + 63 µm) contained about 98% of the studied mineral according to XRD results.

The treatment of minerals samples by high-power nanosecond video pulses [1] was carried out in air atmosphere under standard conditions and the following electro physical parameters of the impulse treatment: \( \tau \approx 1 - 5 \text{ ns} \) – pulse front, \( \tau \approx 50 \text{ ns} \) – pulse duration, \( U \approx 25 \text{ kV} \) – pulse amplitude, \( E \approx 10^7 \text{ V/m} \), pulse repetition rate is 100 Hz, pulse energy \( \approx 0.1 \text{ J} \), processing time \( t \) of mineral samples were varied from 10 s to 150 s. Before electromagnetic pulse treatment, the concentrate samples were wetted with distilled water with ration of solid to liquid respect to \( S: L = 5: 1 \) according to recommendations [2].

X-ray photoelectron spectra were obtained on a Versa Probe II spectrometer (ULVAC-PHI; Material Science and Metallurgy Collective Center) at NITU MISIS using monochromatic Al Ka radiation with an energy of 1486.6 eV; power X - ray source \( \approx 50 \text{ watts} \). The XPS spectra were recorded in the constant transmit energy mode of the analyzer, which was 160 eV for the recording of survey spectra, and 29.35 eV for recording the spectrum of Si 2 p. The survey spectrum was recorded with a step of 1.0 eV, the high resolution spectrum of the 2 p line of silicon – with a step of 0.1 eV.

To eliminate the effect of charging the samples the registration of spectra was performed using double neutralization. The obtained spectra were calibrated by the binding energy of the low-energy component in the spectrum of 1 s electrons of carbon atoms (C 1s line) of hydrocarbons adsorbed on the sample surface; The binding energy of this component was assumed to be 285.0 eV. To obtain qualitative and quantitative information on the composition of the surface of minerals, the spectra of individual lines of elements were fitted according to standard procedures using the Casa XPS program.

The technique of the adsorption experiment was as follows: a 0.5 g mineral was placed in the cell of a laboratory flotation machine and agitated in distilled water for 3 minutes \( (S: L = 1: 20) \), then the pH was adjusted to the required value \( (\text{NaOH} - \text{pH} 9.0 (\text{NaOH}); \text{Flotinor sm 15} - \text{pH} 3.5 (\text{H}_2\text{SO}_4); \text{CH}_3(\text{CH}_2)_6\text{C(O)N(H)OH} - 6.0 (\text{HCl}) \) and the reagent was added (300 mg / l), the contact time with the collector – 3 minutes, after that the solid phase was separated by filtration, washed with a tenfold volume of distilled water and dried in air.

IR spectra were obtained in the wavelength range from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) (spectral resolution 4 cm\(^{-1}\)) using an Fourier transform spectrometer (IR – Affinity, Shimadzu) and the diffuse reflectance attachment (Diffuse IR, Pike Technologies). For each sample, at least five spectra were obtained; the number of scans was 50 for each spectra.

Results and discussion
XPS
Table 1 presents the experimental results of the columbite (manganocolumbite) surface chemical composition changes as a result of pulsed energy impact; the chemical composition was determined by the survey XPS spectra. The compo-
sition of the mineral surface before and after the treatment was characterized by the presence of Nb, O and Fe atoms in an amount sufficient to analyze their chemical and valent state by XPS.

Registration and subsequent analysis of the Nb 3d, Fe 2p lines showed that the spectral characteristics did not change as a result of the treatment, namely, the Nb 3d 5/2 doublet (BE = 206.9–207.0 eV) corresponded to the state of niobium pentoxide Nb₂O₅ [3]; The position of the Fe 2p3/2 peak (BE = 711.4–711.8 eV) indicated that the chemical state of the iron atoms in the surface layer of the particles of the studied mineral was close to maghemite (γ – Fe₂O₃) or lepidocrocite (γ – FeO (OH)) [4].

The O 1s line (figure 1) was fitted with two components: the first with a binding energy BE ~ 530.0 eV corresponded to structural oxygen in the structure of Nb₂O₅ and γ – Fe₂O₃ (γ – FeOOH); the second contribution with BE ~ 532.0 eV was attributed to silicon and aluminum oxides and, presumably, hydroxogroups adsorbed on the surface of the mineral, oxygen in organic pollutants, and chemisorbed water molecules [5].

The result of the columbite samples electromagnetic treatment for 10–150 s (range from 10³ to 1.5 × 10⁴ pulses) is a consistent increase in the O 1s spectra component with a binding energy of BE ~ 530.0 eV, corresponding to structural oxygen atoms in niobium and iron oxides (Table 2, Fig. 1), and a decreases by 5–9 at.% of the high-energy component with BE ~ 532.0 eV, which characterizes the presence on the mineral surface of SiO₂, Al₂O₃, adsorbed water and functional hydroxogroups (Table 2). Since the surface concentration of Si and Al (at.%) remained constant during the treatment (Table 1), it can be assumed that at long treatment times (1.5–3.0 × 10⁴, 2.5–5.0 min) were accompanied by thermal removal of hydroxo groups and chemisorbed water molecules from the surface of columbite (dihydroxylation – dehydration) due to local temperature increase [6].

**Fig. 1.** O 1 s line of columbite samples before (a) and after (b), (c) the treatment by high – power electromagnetic pulses during 150 s (b) and 300 s (c)

**Tab. 1.** Influence of high-power electromagnetic pulses on the chemical composition of the columbite surface according to XPS results, at. %

| N pulses, 10³ | Nb | Ta | O | Fe | Si | Al | F | Zn | Pb | Th | C |
|-------------|----|----|---|----|----|----|---|----|----|----|---|
| 0           | 1.7 | 0.2 | 54.2 | 5.5 | 6.9 | 3.4 | 1.3 | 0.7 | 1.2 | 0.3 | 24.6 |
| 1           | 1.2 | 0.2 | 53.4 | 5.2 | 7.3 | 3.3 | 1.3 | 0.5 | 1.0 | 0.2 | 26.6 |
| 5           | 1.7 | 0.3 | 22.4 | 4.3 | 6.6 | 2.5 | 1.1 | 0.7 | 1.0 | 0.3 | 28.3 |
| 10          | 2.0 | 0.1 | 51.9 | 4.9 | 5.4 | 3.1 | 1.5 | 0.5 | 1.1 | 0.2 | 29.4 |
| 15          | 2.2 | 0.1 | 48.8 | 8.3 | 5.5 | 2.6 | 2.4 | 0.7 | 1.4 | 0.2 | 25.7 |
| 30          | 2.4 | 0.7 | 53.0 | 6.1 | 5.5 | 2.8 | 1.9 | 0.6 | 1.2 | 0.4 | 23.8 |

**Tab. 2.** Influence of the treatment by high-power electromagnetic pulses on the columbite surface according to XPS, at. %

| N pulses, 10³ | Eₘ = 530.0 eV | Eₘ = 532.0 eV | O 1s |
|-------------|---------------|---------------|------|
|             |Nb₂O₅, Fe₂O₃   | SiO₂, Al₂O₃,  |      |
|             |               | OH, H₂Oadsorbed, O=C_adsorbed |
| 0           | 15            | 85            |      |
| 1           | 15            | 85            |      |
| 5           | 20            | 80            |      |
| 10          | 20            | 80            |      |
| 15          | 25            | 77            |      |
| 30          | 24            | 76            |      |

**DRIFT**

IR spectra of columbite samples after contact with the collector in the initial state, as well as after treatment by high-power nanosecond electromagnetic pulses are given in figure 2. IR spectra of the sample in the initial state (Figure 2 a) demonstrate the presence of the bands indicating the adsorption of the collector. The presence of an adsorption peak at 1530 cm⁻¹ and 1600 cm⁻¹ indicates the formation of Fe (III), tantalum and niobium on the surface [7, 8], and a weak shoulder at 1670 cm⁻¹ indicates the presence of a physically adsorbed hydroxylic acid [9]. Based on this, capryl-hydroxylic acid is adsorbed chemically on the surface of the mineral, predominantly, with the formation of complex compounds with metal atoms; the amount of physically adsorbed hydroxylic acid is small. A comparative analysis of the IR spectra showed the following changes: the shoulder at 1670 cm⁻¹ identified for the initial sample and corresponding to
the physical sorption of hydroxamic acid transform into the clear band (Figure 2a) for the samples after the treatment by high-power electromagnetic pulses that indicates an increase in the quantity of physically adsorbed collector.

IR spectra of treated and untreated eudialite samples after the contact with Flotinor sm 15 are shown in Figure 2 b. The presence of the bands indicating the adsorption of the reagent were identified: 1350 cm$^{-1}$; 1380 cm$^{-1}$; 1460 cm$^{-1}$; 2850 cm$^{-1}$; 2950 cm$^{-1}$. At the same time, the position of the spectral peaks for the adsorbed Flotinor sm 15 coincides with the spectrum of the pure substance indicating the physical adsorption of the collector.

The calculation of the spectra’s peak areas demonstrates that the preliminary high-power electromagnetic treatment of eudialyte results in the increasing of the Flotinor sm 15 adsorption. The area of the band at 1380 cm$^{-1}$ increases 4.3–7 times (from 0.03 (untreated sample) to 0.124 relative units (10$^3$ pulses) and further to 0.22 (10$^3$ pulses) and further to 0.35 (5 · 10$^3$ pulses).

As a result of studies, it was identified that the use of pulsed energy (high-power electromagnetic pulses) gives a possibility of the minerals technological properties regulation. It was found that usage of high-power electromagnetic treatment of eudialyte before the acid leaching allows to increase the zirconium recovery of 1.7 times and Σ REE – 1.4 times [10]. It is shown that treatment by high-power electromagnetic pulses results to the increasing of the of manganocolumbite sorption activity towards octanohydroxamic acid. The shoulder at 1670 cm$^{-1}$, identified for the untreated sample and corresponding to the physically adsorbed reagent transform in the clear absorption band in the case of the sample that was treated by high-power electromagnetic pulses.

Conclusion

The structural and chemical transformations of the manganocolumbite surface as a result of non-thermal treatment by high-power nanosecond electromagnetic pulses were studied. According to XPS data, at the initial stages at low treatment durations (from 10$^3$ pulses to 5 × 10$^4$ pulses), the surface state of mineral was characterized by the presence of hydroxyl groups and adsorbed water molecules. With the increasing of the treatment duration up to 5 × 10$^4$ – 1.5 × 10$^5$, chemisorbed water and hydroxogroups were removed from the surface of columbite.

With usage of DRIF was defined that treatment by high-power electromagnetic pulses allows to control the physicochemical properties of columbite and eudialyte. The growth of the sorption activity for eudialyte towards Flotinor sm 15 was defined. It was identified that the areas of the bands describing the adsorption of the regent into mineral surface increased on average 4 to 7 times for the samples after the high-power electromagnetic treatment. It is shown that treatment by high-power electromagnetic pulses results to the increasing of the of manganocolumbite sorption activity towards octanohydroxamic acid. The shoulder at 1670 cm$^{-1}$, identified for the untreated sample and corresponding to the physically adsorbed reagent transform in the clear absorption band in the case of the sample that was treated by high-power electromagnetic pulses.

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**Wpływ impulsów elektromagnetycznych dużej mocy na właściwości strukturalne, chemiczne i fizykochemiczne mineralów ziem rzadkich**

Badanie modyfikacji stanu strukturalno-chemicznego i właściwości sorpcyjnych powierzchni kolumbitu i eudialitu pod wpływem impulsów nanosekundowych o dużej mocy (HPEMP) przeprowadzono za pomocą XPS i FTIR. Ustalono, że wstępna obróbka mineralów rzadkich impulsami nanosekundowymi o dużej mocy jest obiecującym narzędziem do kierunkowych zmian ich właściwości fizykochemicznych i strukturalno-chemicznych, co zostało potwierdzone przez zwiększenie aktywności sorpcyjnej mineralu.

**Słowa kluczowe:** kolumbit, eudialyte, impulsy elektromagnetyczne dużej mocy, XPS, FTIR