XRD-investigations of the mechanism of lithium sorption from the separated liquid of the Pauzhetskaya geothermal power plant (Kamchatka) by modified zeolites

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Abstract. The process of extracting lithium ions from the separated liquid of the Pauzhetskaya Geothermal Power Plant by modified zeolites of the Yagodinsky deposit of Kamchatka region has been experimentally studied. The four most characteristic reflexes at 2θ, deg.: 25.68, 27.11, 27.43 and 27.68 were singled out on the basis of the study of the solid phase composition of the modified sorbent on the X-ray diffractometer RIGAKU Ultima-IV (Japan). It has been established that there occurs displacement of the position of the reflexes with a change in the interplanar distance and a change of the peak width value at the semi-height (FWHM) in the process of modification. The predominant mechanism is the ion exchange \( \text{H}^+ \rightarrow \text{Me}^+ \): the calcium and magnesium ions that have been preserved in the zeolite structure during acidic treatment are exchanged for sodium and potassium ions \( \text{Me}_2^+ \rightarrow 2\text{Me}^+ \). The total sorption capacity of the modified sorbent during sorption from an technogenic solution under dynamic conditions is 0.31 mmol/g.

Key words: sorption, sorption capacity, zeolite, lithium, XRD investigations.

1. Introduction
Of great interest at present are the questions associated with the extraction of lithium from hydromineral raw materials. It is proposed to use the freshly precipitated double aluminum and lithium hydroxide \([1-3]\) as a sorbent. This interest is due to the fact that the composition and properties of amorphous \( \text{Al(OH)}_3 \) which coprecipitates with lithium ions have not been sufficiently studied; the parameters of the technological process of the reproducible obtainment of double hydroxide have not been described. The problem is still more complicated with regard to the precipitation of double aluminum lithium hydroxide in the porous material phase \([4, 5]\).

The aim of this paper is to study the composition and properties of the sorbent obtained by precipitating aluminum lithium hydroxide for zeolite with the use of powder X-ray diffraction analysis.

2. Materials and methods
Natural zeolite was chosen as a carrier for double aluminum lithium hydroxide. The comminuted zeolite tuff with particle sizes of 0.25-0.5 mm was placed in a 10 mm diameter column. The height of the sorbent layer was 140 mm.

Solution, representing the mixture of aluminum and lithium chlorides with concentration of aluminum 5.4 g/l, the lithium 0.7 g/l and solution speed 4 ml/min was passed through columns with sorbents. Then columns were shut and kept within 24 hours at a room temperature. In 24 hours 2% solution of ammonium hydroxide was passed through columns. Columns were shut and kept within 24
hours again and washed by water up to a stable value of pH and aluminium and lithium ions absence in washing waters. The double hydroxide aluminum and lithium precipitated in sorbent phase. Before the sorption sorbents were washed with 0.01 M hydrochloric acid and then with water. Sorption from natural solutions was carried out by downflow method at the rate of 1 ml/min. Desorption was carried out using 0.02 M of hydrochloric acid. After that the sorbent was unloaded from the column, dried at a room temperature, after which it was pounded in an agate pestle. Subsequently it was dried in a drying cabinet at a temperature of 60–65 °C during 8 hours.

The X-ray diffraction analysis was performed on Rigaku Ultima IV diffractometer (Japan) (Cu Kα). The X-ray generator operated at a power of 40 kW and 30 mA, the scanning speed was 1.0 degree/min, with a pitch of 0.02 degrees, in an angular range of 3 to 50 degrees (2 theta). The obtained diffractograms were analyzed in accordance with the Rietveld method [5] using PDXL software operating on a personal computer. The crystal phases were identified using the ICDD data base – International Center of Diffraction Data for Inorganic Substances.

3. Results and discussion
The quantitative analysis by the Rietveld method has shown that the zeolite tuff of the Yagodninsky deposit consists of 88% of clinoptilolite-Na, clinoptilolite-Ca and mordenite. Mordenite has an orthorhombic structure, while clinoptilolite-Na and clinoptilolite-Ca have a monoclinic structure. Other phases are represented by anorthite, albite, cristobalite, while the share of secondary phases accounts for about 12%. Biotite and muscovite are determined in the form of single inclusions.

Diffractograms of samples of the initial and modified zeolite tuff are presented in figure 1, those of the sorbent that has undergone a sorption and desorption cycle are presented in figure 2.

The most characteristic peaks are placed in an angular range of 25 degrees to 32 degrees (2-theta). We singled out the four most characteristic reflexes at 20, deg.: 25.68, 27.11, 27.43 and 27.68 and carried out a comparison of the absolute intensities of the main diffraction maxima (figures 3, 4). The presence of peaks 27.11, 27.43 testifies to the content of mordenite in the initial zeolite tuff – in the region of peaks 25.68 and 27.68 there occurs the overlap of the peaks corresponding to clinoptilolite-Na and clinoptilolite-Ca for mordenite peaks. In the graph (figure 3) one can clearly see an increase in the intensity of reflexes of the modified zeolite at 20 being equal to 27.11 and 27.43 deg. corresponding to the mordenite content of the initial zeolite tuff, but the greatest reflex is observed at 20=27.68 deg.

Figure 1. Diffractograms of the initial and modified zeolite tuff
Figure 2. Diffractograms of the initial zeolite tuff and the modified one which have undergone the sorption and desorption cycle
When carrying out a comparison of the diffractograms of the initial and modified zeolites which have undergone the sorption and desorption cycle (figure 4) within the above-mentioned range, we should note that the greatest reflex intensity increase is observed at angles 2θ, deg.: 25.68 and 27.68.

Changes occur in the diffractograms of sorbent samples in the process of modification. The greatest parameter changes were noted at $2\theta=27.43$ deg.; the reflex position shifts towards the larger angle by 0.15 deg., while the interplanar distance decreases by 0.0172 Å. Also the peak width at semi-height decreases by 0.19 deg. Reflex displacement towards the smaller angle by 0.02 deg. is observed at $2\theta=27.11$ deg., the interplanar distance increases by 0.0015 Å, and the peak width considerably decreases at semi-height by 0.52 deg. In the process of the sorption-desorption cycle these changes are less pronounced. On the whole, the above-described changes in the position of the diffraction fringes, changes of the interplanar distances and peak width at semi-height are not essential during zeolite tuff modification, which is also true of carrying out the sorption and desorption cycle with the use of the initial zeolite tuff sample and the modified one – this testifies to the stability of the crystalline structure.

**Figure 3.** Absolute intensities of the main diffraction maxima of the initial and modified zeolite tuff

**Figure 4.** Absolute intensities of the main diffraction maxima of the initial and modified zeolite tuffs that have undergone the sorption and desorption cycle

During the sorption of lithium from the technogenic solution it has been established that the alkali metals contained in the technogenic solution: lithium, sodium and potassium are absorbed by the sorbent, while the alkaline earth metals: calcium and magnesium are displaced from the sorbent. Two types of exchange occur: first, the exchange of lithium ions for hydrogen ions in the structure of double aluminum lithium hydroxide $\text{H}^+\rightarrow\text{Li}^+$ and exchange of sodium and potassium ions for hydrogen ions in the structure of zeolite $\text{H}^+\rightarrow\text{Me}^+$; second, the calcium and magnesium ions that have been preserved in the zeolite structure during acidic treatment are exchanged for sodium and potassium ions $\text{Me}^{2+}\rightarrow2\text{Me}^+$. The total sorption capacity of the modified sorbent during sorption from the technogenic solution under dynamic conditions is 0.31 mmol/g.

As a result of the desorption of 0.01 M with a hydrochloric acid solution the lithium extraction accounts for 71.1%, the concentration factor by lithium is equal to 2.02, but the molar ratio $(\text{Na}^++\text{K}^+)/\text{Li}^+$ goes down to 15.8, whereas in the initial solution $(\text{Na}^++\text{K}^+)/\text{Li}^-$ it is 67.8. Consequently, enrichment of the solution with lithium cations takes place.
Conclusion

On the basis of the laboratory research it has been established that for concentrating lithium from hydromineral raw materials it is recommended to use sorbents obtained by the directional modification of the zeolite tuff of the Yagodinsky deposit of Kamchatka region.

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