Investigation of the Mechanism of Interaction at the Hydrothermal Conditions of Zeolite – Cubic Analcime with the Li^+, Mg^{2+}, Sr^{2+} and Fe^{3+} Ions

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Analcime and clinoptilolite are among the most abundant zeolites in nature. During recent decades natural analcimes and clinoptilolites, also synthetic modified analcimes have been investigated as potential and innovative substances, possible to use for the immobilization of radioactive waste, molecular catalysis and other purposes. However, natural analcimes like many natural rocks are contamined with various impurities (about 30 %), which significantly reduces their sorption possibilities and possibilities of their using in such chemical technologies as catalysis, fractioning of hydrocarbons and other. In this article the stability of cubic analcime at the hydrothermal conditions at 180 °C temperature in solutions of various concentrations, containing Li^+, Mg^{2+}, Sr^{2+} and Fe^{3+} ions has been examined. These processes have grand signification for the formation of ion-exchanged analcimes, its sorption properties and also if ions have been immobilized in analcime structure. It has been established, that as result of interaction between cubic analcime and lithium chloride solutions the formation of new compounds: lithium silicate and silinaite occurs. At the same hydrothermal conditions the interaction between cubic analcime and chloride solutions, containing Sr^{2+}, Mg^{2+} and Fe^{3+} ions pass without formation of new compounds, and only with interposition of these ions in the structure of cubic analcime.

Keywords: cubic analcime, ions exchange, analcime structure, hydrothermal conditions.

1. INTRODUCTION

Natural analcimes and clinoptilolites have been examined to immobilize radionuclides, such as strontium, cesium and neptunium, which exist in the high level radioactivity wastes [1 – 3]. The stability of zeolitic structure minerals at the hydrothermal conditions in various solutions, ion-exchange reactions and changes of properties have grand significance in immobilization, sorption and catalysis processes [4, 5]. However, the natural zeolites are contaminated by big quantities of impurities and this limit the possibilities of their practical utilization. The studies of formation of zeolitic structure minerals and its stability are complicated by a grand variety of Si/Al ratio, quantities of H_2O and introduced ions. Meanwhile, it is noted [6], that in many cases of zeolites, Na^+ ions of crystal lattice may be exchanged by Li^+, K^+, NH_4^+, Ag^+, Ca^{2+} and Mg^{2+} ions at high temperature.

Among the most frequently studied natural zeolites, clinoptilolite was shown to have high sorption selectivity for certain heavy metal ions such as Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} [7]. It was determined [8], that the metals uptake is favored at higher temperature, since a higher temperature activates the metal ions for enhancing adsorption at the coordination site of zeolites. However, the processes of interaction of zeolites such as analcime with the waste waters, containing Mg^{2+}, Sr^{2+}, Fe^{3+} and Li^+ ions at the hydrothermal conditions have been investigated poorly.

It is important to note that the sorption capacities of the adsorbents vary, depending not only on the characteristics of the individual adsorbent and the concentration of adsorbate, but also on the extent of chemical modifications.

Analcime, which has been formed at hydrothermal conditions in magmatic rocks, may be attacked by various solutions. It has been noted [9, 10], that at hydrothermal conditions Na^+ ions of analcime may be exchanged easily by K^+ ions from solution with formation of leucite. However, the genesis of analcime still is the aim of large scientific discussion [11 – 14]. Authors [1] have determined that the solubility and stability at the hydrothermal conditions at 90, 125, 175 and 225 °C temperature of two analcimes of different chemical composition depend on Si/Al ratio, however, the crystallographic system of analcimes has not been indicated.

There is no data about stability of different crystallographic systems analcimes in various solutions at hydrothermal conditions. However, authors [15] affirm, that small and middle-sized cations such as Li^+, Ag^+, Ca^{2+} and others can occupy the positions of oxygen atoms or water molecules in the tetrahedral coordination of analcime structure and that in this case the parameter of cubic lattice reduces from 13.67 Å of initial Na-analcime to 13.50 Å of Li-exchanged analcime.

The change of analcime lattice parameters and modification of its crystalline structure may significantly change the sorption properties of analcime.

In this paper the processes of Na^+ ion (ion radius $r = 0.117$ nm) exchange at the hydrothermal conditions at 180 °C temperature of pure synthetic analcime in the chloride solutions, containing small cations: Li^+ ($r = 0.094$ nm), Mg^{2+} ($r = 0.072$ nm), Fe^{3+} ($r = 0.067$ nm) and Sr^{2+} ($r = 0.126$ nm) [16] have been examined.

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2. MATERIALS AND METHODS OF INVESTIGATION

2.1. Materials

Amorphous $SiO_2 \cdot nH_2O$ with specific surface area $S_a = 1300$ m^2/kg by Blaine and ignition losses – 25.33 % was used. Ignition loss of materials was determined by heating the substance at 1000 °C temperature.

Al containing components were used:

a) $Al(OH)_3$ pure – gibbsite ($S_a = 105$ m^2/kg by Blaine);

b) γ-Al_2O_3 (I) was obtained by heating up $Al(OH)_3$ at 475 °C temperature for 4 hours;

NaOH solution (concentration $c = 11$ mass %) was obtained by dissolving NaOH particles in distilled water.

Reagents: $LiCl \cdot H_2O$, $SrCl_2 \cdot 6H_2O$, $MgCl_2$, $FeCl_3$.

2.2. Methods

Analcime was synthesized from the mixtures $Na_2O : Al_2O_3 : SiO_2$ (molar ratio $4 : 1 : 6$) in fluoroplastic vessels in the autoclave "Lampart". The NaOH solution was additionally diluted to achieve 5.0 water/solid ratio.

Hydrothermal synthesis of analcime in unstirred suspensions has been carried out under the saturated steam pressure at 180 °C temperature; the duration of isothermal curing was 7 hours. The products of the synthesis have been filtrated, rinsed with ethyl alcohol to prevent carbonization of material, dried at a temperature of 30 °C ±5 °C and sieved through a sieve with a mesh width of 80 μm.

The synthesis product has been examined by of X-ray diffraction, thermal analysis and FT-IR spectra analysis.

The X-ray powder diffraction (XRD) data were collected with a DRON-6 powder X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu K_α radiation and graphite monochromator, operating with voltage 30 kV and emission current of 20 mA. The step-scan covered the angular range $5° – 70°$ (2θ) in steps of $2\theta = 0.02°$. Diffraction curves were additionally recorded in step times 1.0 s and step size of 0.01° (2θ) from 2° to 10°. For diffraction profile refinement under the pseudoVoid function and for description of the diffractional background under the 3rd degree Tchebyshev polynom, we used a computer program X-fit. The reliability of method – 98 %.

Crystallite size of the materials was estimated using XFIT programme and Williamson-Hall method.

Simultaneous thermal analysis (STA: differential scanning calorimetry – DSC and thermogravimetry – TG) was also employed for measuring the thermal stability and phase transformation of synthesized products at a heating rate of 15 °C/min, the temperature ranged from 30 °C up to 1000 °C under air atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt-Rh were used.

The processes of ion interaction with cubic syngony analcime were examined in the lithium, strontium, magnesium and iron chloride solutions, in which oxide: Na_2O molar ratios were 0.03; 0.05; 0.07 and 0.10 at the hydrothermal conditions at 180 °C temperature. The analyzed mixtures were prepared by adding to 1 g of cubic analcime calculated necessary quantity of solid chloride and water for obtaining interaction mixture, in which water/solid ratio was 5.0. The interaction of lithium ions with cubic syngony analcime also was examined in more concentrated solutions, in which the molar ratios of $Li_2O : Na_2O$ were 0.2 – 0.4. The composition of obtained products has been determined by X-ray, IR spectra, SEM and EDS analysis.

IR spectra have been recorded with the help of spectrometer Perkin Elmer FT–IR system Spectrum X. Specimens were prepared by mixing 1 mg of the sample in 200 mg of KBr. The spectral analysis was performed in the range $(4000 – 400)$ cm^{-1} with spectral resolution of 1 cm^{-1}.

Scanning electron microscopy (SEM) (Oxford ISIS Leo 440 i, UK) coupled with energy dispersive X-ray spectrometry (EDS) of the samples was performed using a accelerating voltage of 20 kV and a working distance of 10 mm for SEM observation and a 200 s accumulation time for EDS analysis.

3. RESULTS AND DISCUSSION

Analcime stability in cubic crystallographic system has been analyzed under hydrothermal conditions at 180 °C temperature in solutions containing monovalent, bivalent and trivalent ions.

The results of interaction between cubic analcime and lithium chloride in initial mixtures with $Li_2O : Na_2O$ mole ratios $0.03 – 0.1$ are presented in Fig. 1.
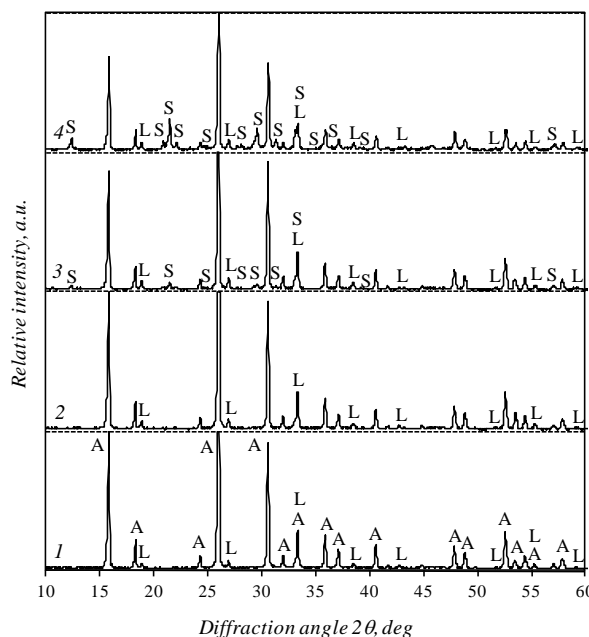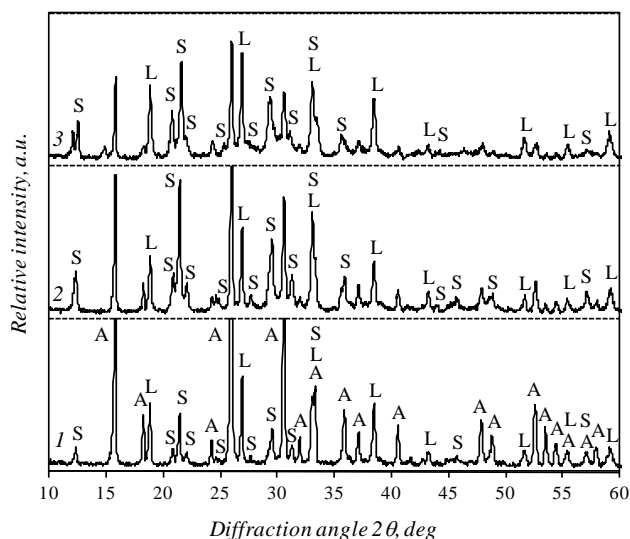

Fig. 1. X-ray diffraction patterns of the synthesis products obtained when molar ratios $Li_2O : Na_2O$ were: 1 – 0.03; 2 – 0.05; 3 – 0.07; 4 – 0.1. Indexes: A – cubic analcime; L – lithium silicate Li_2SiO_3; S – silinaite $LiNaSi_2O_5 \cdot 2H_2O$

X-ray patterns shown in Fig. 1 suggest that after 7 hours of hydrothermal exposure at 180 °C temperature, new compounds form in the initial cubic analcime and LiCl mixture. In the cases of $Li_2O : Na_2O$ mole ratios of 0.03 and 0.05, lithium silicate (d – 0.469; 0.331; 0.270; 0.234; 0.209; 0.177; 0.165; 0.156; 0.147; 0.141; 0.135 nm) emerged as a new compound after hydrothermal processing without
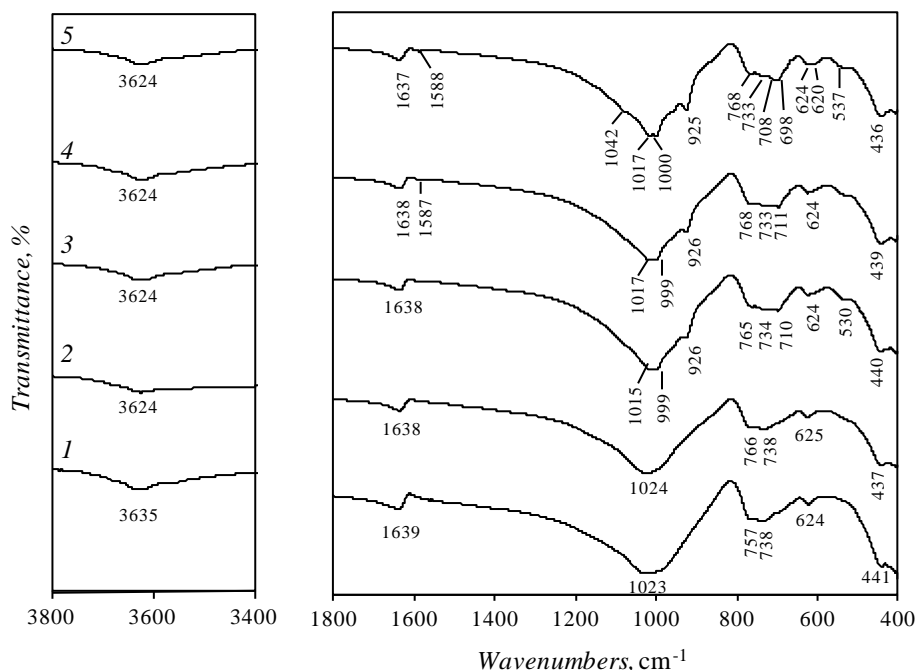
**Fig. 2.** IR spectra of: 1 – cubic analcime; 2, 3, 4, 5 – products with molar ratios $Li_2O : Na_2O$ 0.03; 0.05; 0.07; 0.1

Fig. 3. X-ray diffraction patterns of the synthesis products obtained when molar ratios $Li_2O : Na_2O$ were: 1 – 0.2; 2 – 0.3; 3 – 0.4. Indexes: A – cubic analcime; L – lithium silicate Li_2SiO_3; S – silinaite $LiNaSi_2O_5 \cdot 2H_2O$

cubic syngony analcime (Fig. 1, curves 1 and 2). An increase in $Li_2O : Na_2O$ mole ratios to 0.07 and 0.1 results in X-ray pictures showing peaks characteristic of cubic syngony analcime, lithium silicate and another new compound, namely silinaite (d – 0.714; 0.424; 0.414; 0.402; 0.359; 0.357; 0.284; 0.269; 0.161; 0.155 nm) (Fig. 1, curves 3 and 4). X-ray diffraction reflection intensities of the newly-formed compounds increase as the mole ratio in $Li_2O : Na_2O$ grows, while intensities of the main diffraction reflection peaks characteristic of the cubic analcime are visibly decreasing.

The formation of new compounds and changes in the analcime structure are verified by the product's IR spectrograms. With $Li_2O : Na_2O$ mole ratio of 0.07, IR spectrogram (Fig. 2, curve 4) shows the emergence of

silinaite-characteristic 1042, 1000, 926, 708, 698, 620 and 537 cm^{-1} frequency peaks, the character of Si–O–Si linkage band at (710 – 770) cm^{-1} frequency range alters significantly. Also, a new peak at deformational δHOH bending frequency range (1588 cm^{-1}), which may be attributed to lithium silicate, has been identified.
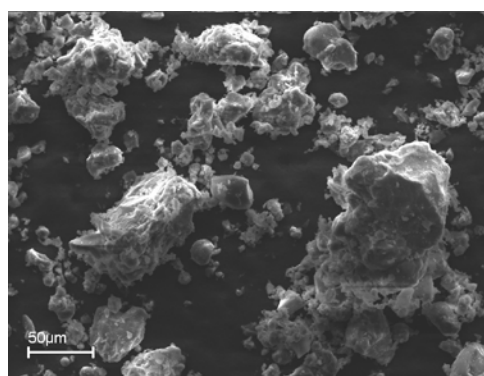
a
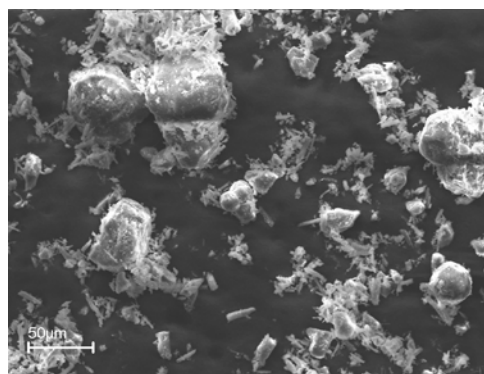
b

Fig. 4. SEM photos: a – pure cubic analcime; b – after treatment by lithium chloride solution, when molar ratio $Li_2O : Na_2O = 0.1$

After raising $Li_2O:Na_2O$ mole ratio to $0.2-0.4$, the X-rays (Fig. 3) show well crystallized lithium silicate and silinaite X-ray diffraction peaks along with almost twice lower intensity of the main cubic syngony analcime peaks.
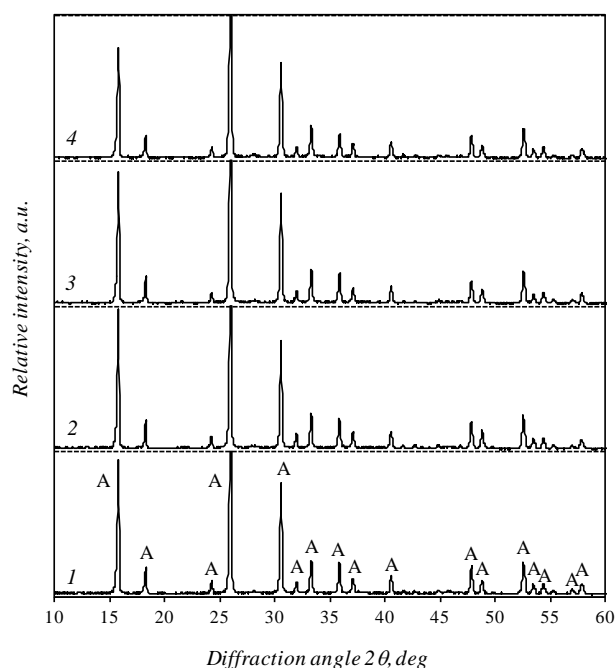
It can be seen from SEM images (Fig. 4) that after ion exchange in hydrothermal conditions in a solution containing Li^+ ions, the shape of analcime crystals changes to form many small needle-shaped crystals.

With the help of an EDS analysis it was established that sodium content in these crystals is 2 % below the levels in pure cubic syngony analcime. Therefore, it is assumed that the needle-shaped crystals are characteristic of the silinaite that is formed as a result of ion exchange.

Results of the research performed implicate that in different concentration solutions of lithium chloride under hydrothermal conditions at 180 °C temperature, changes in analcime structure take place and both sodium and silicon ions are released, which results in the formation of new compounds: lithium silicate and lithium sodium silicate – a silinaite with only small amounts of lithium penetrating into analcime structure.

Analogous analysis has been carried out to investigate the stability of cubic syngony analcime under hydrothermal conditions in solutions containing Sr^{2+} and Mg^{2+} bivalent ions. Solutions have been mixed from $SrCl_2$ and $MgCl_2$, mole ratios of SrO and MgO as compared with Na_2O levels present in analcime were 0.03; 0.05; 0.07 and 0.1.

X-ray diffraction curves (Fig. 5) demonstrate that with the increase in $SrO:Na_2O$ mole ratios, intensities of the main analcime peaks ($d – 0.560; 0.343; 0.292$ nm) in cubic crystallographic system decrease to a remarkable extent. Since no additional peaks have been discovered in X-ray patterns, it is probable that replacement of Na^+ ions with Sr^{2+} ions would not lead to the latter forming any new compounds but rather penetrating into the analcime structure.

It must be noted that when cubic syngony analcime is exposed to a solution containing Sr^{2+} ions, aggregation of small cubic crystallographic system analcime crystals (Fig. 6, field 3) and the formation of large crystals with rather regular edges (Fig. 6, field 2), which differ in their element composition (Table 1), is observed.
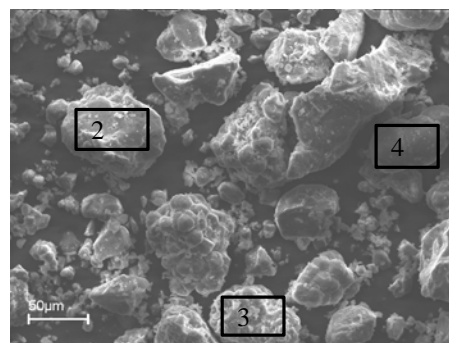
Fig. 6. SEM photo of hydrothermal interaction products between cubic analcime and strontium chloride solution, when molar ratio $SrO:Na_2O = 0.1$

Table 1. Chemical composition of products (1) and composition of crystals (field 2, 3 and 4, noted in Fig. 6)

Element	Weight %			
	1	2	3	4
O	55.14	55.30	52.15	53.11
Na	9.11	7.63	9.20	9.08
Al	14.27	21.22	12.68	11.03
Si	21.48	15.85	25.97	26.78
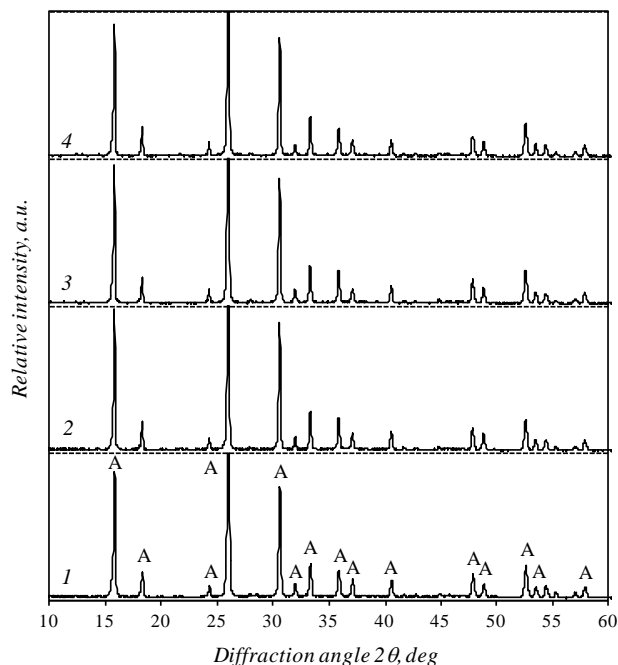
Fig. 7. X-ray diffraction patterns of the synthesis products obtained when molar ratios $MgO:Na_2O$ were: 1 – 0.03; 2 – 0.05; 3 – 0.07; 4 – 0.1. Index: A – cubic analcime


Fig. 5. X-ray diffraction patterns of the synthesis products obtained when molar ratios $SrO:Na_2O$ were: 1 – 0.03; 2 – 0.05; 3 – 0.07; 4 – 0.1. Index: A – cubic analcime

Analogous results have been obtained when cubic syngony analcime was exposed to magnesium chloride solutions under hydrothermal conditions. X-ray diffraction

curves (Fig. 7) show that after hydrothermal exposure to 180 °C temperature for 7 hours a new compound does not form and cubic syngony analcime is the only compound identified.

Therefore, it is probable that an intensive cubic syngony analcime interaction and the formation of new compounds in solutions containing Mg^{2+} ions examined under hydrothermal conditions do not occur.

Structural changes in the analcime are manifested through main analcime peaks (d – 0.560; 0.343; 0.292 nm) consistently shifting to lower diffraction angle fields (Fig. 8). In addition, if exposed to magnesium chloride solutions, the cubic syngony analcime displays changes in the relative intensities of the main analcime diffraction reflection peaks. This leads to a conclusion that when cubic crystallographic system analcime is exposed to magnesium chloride solution under hydrothermal conditions at 180 °C temperature, the analcime undergoes structural changes but retains stable matrix of its structure without any new compounds being formed.
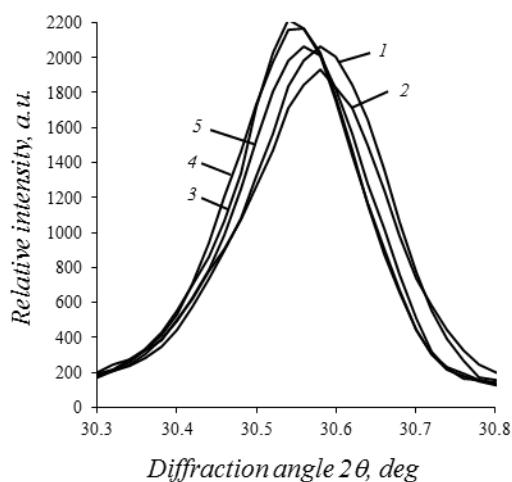
Fig. 8. Intensity of main diffraction patterns (d – 0.292 nm) when: 1 – cubic analcime; 2, 3, 4, 5 – synthesis products when molar ratios $MgO : Na_2O$ were: 0.03; 0.05; 0.07; 0.1

SEM image (Fig. 9) shows that under hydrothermal conditions small crystals emerge when the analcime is exposed to solutions containing Mg^{2+} ions.
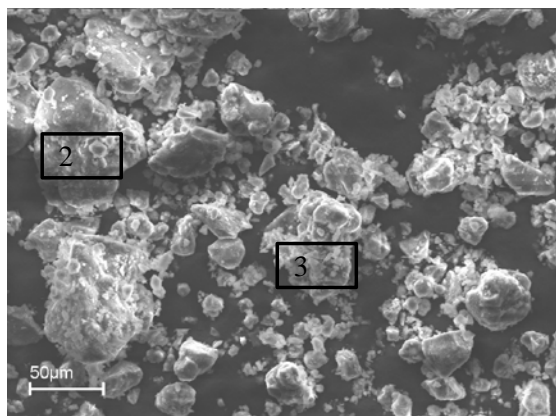
Fig. 9. SEM photo of hydrothermal interaction products between cubic analcime and magnesium chloride solution, when molar ratio $MgO : Na_2O = 0.1$

Results of an EDS analysis (Table 2) confirm that under given conditions only Mg^{2+} ions penetrate into the crystal structure of the cubic syngony analcime.

Results of an EDS analysis have shown that in pure cubic syngony analcime, sodium content totals 10.2 %, while after ion exchange its levels drop ~2.8 % and ~3 % magnesium content is found, thus it is probable that magnesium ions replace Na atoms present in analcime structure in equivalent amounts.

Table 2. Chemical composition of products (1) and composition of crystals (field 2 and 3, noted in Fig. 9)

| Element	Weight, %		
	1	2	3
O	53.74	54.97	58.36
Na	7.37	8.21	6.91
Mg	3.03	2.26	3.04
Al	15.47	11.71	11.75
Si	20.39	22.85	19.94

Analogous occurrences were observed in the investigation of the stability of the cubic syngony analcime in iron chloride solutions containing trivalent iron ions. After 7 hours hydrothermal exposure in 180 °C temperature, X-ray diffraction analysis curves (Fig. 10) of the substance under investigation only showed peaks of initial cubic crystallographic system analcime and no newly-formed compounds were discovered.
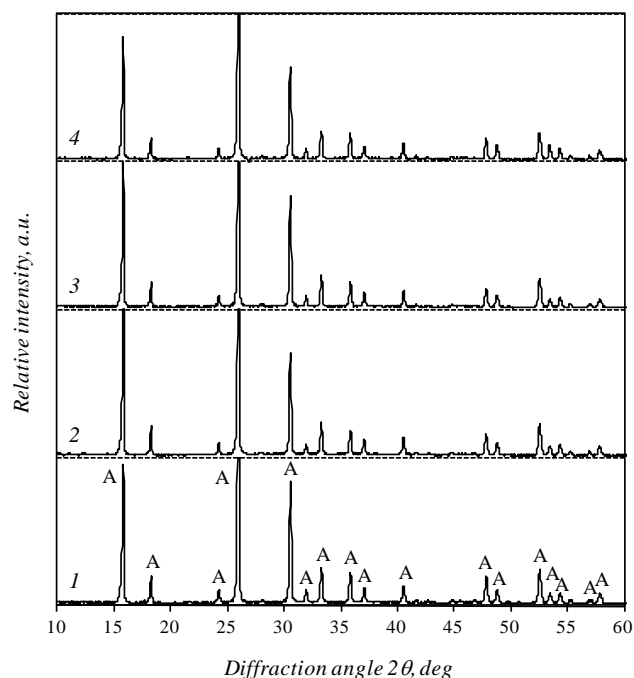
Fig. 10. X-ray diffraction patterns of the synthesis products obtained when molar ratios $Fe_2O_3 : Na_2O$ were: 1 – 0.03; 2 – 0.05; 3 – 0.07; 4 – 0.1. Index: A – cubic analcime

However, when exposed to iron chloride solution, X-ray diffraction reflection peaks (Fig. 11) for the cubic syngony analcime have also shifted to lower diffraction angle fields and displayed smaller intensity. Therefore, it is

assumed that iron ions penetrate into the structure of the cubic syngony analcime.
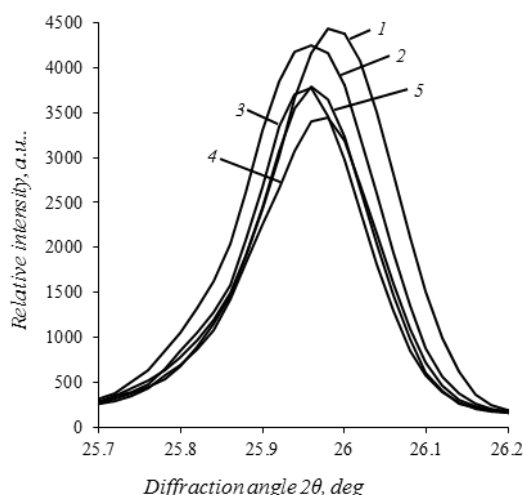
Fig. 11. Intensity of main diffraction patterns $(d - 0.343 \text{ nm})$ when: 1 – cubic analcime; 2, 3, 4, 5 – synthesis products when molar ratios $Fe_2O_3 : Na_2O$ were: 0.03; 0.05; 0.07; 0.1

Results of SEM and EDS analyses (Fig. 12, Table 3) confirm that Fe^{3+} ions are incorporated into the structure of analcime crystals.
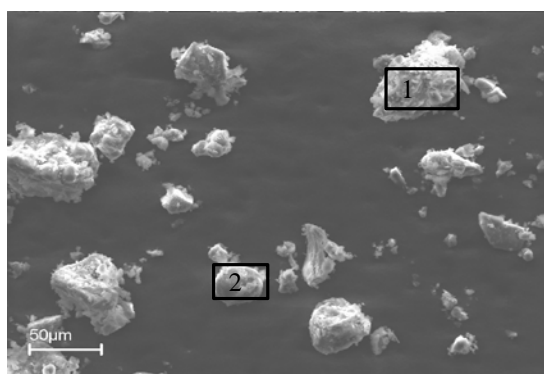
Fig. 12. SEM photo of hydrothermal interaction products between cubic analcime and ferrous (III) chloride solution, when molar ratio $Fe_2O_3 : Na_2O = 0.1$

Table 3. Chemical composition of crystals, noted in Fig. 12

Element	Weight %	
	1	2
O	62.96	59.05
Na	5.97	8.28
Al	13.45	9.90
Si	15.04	21.98
Fe	2.58	0.79

It must be noted that in contrast to pure cubic syngony analcime, sodium levels drop by 4.2 % after ion exchange, while the iron content accounts for 2.6 %. Therefore, it can be assumed that iron ions replace nearly twice the amount of sodium atoms.

4. CONCLUSIONS

To sum up the results of the cubic crystallographic system analcime stability under hydrothermal conditions at 180 °C temperature in different solutions containing monovalent, bivalent and trivalent ions, it can be stated that under given conditions the structure of cubic syngony analcime changes in solutions containing strontium, magnesium and iron ions, however, the carcass composition of crystal structure remains stable and new compounds do not form. It must be noted that magnesium ions replace Na atoms present in the structure of the analcime in equivalent amounts and iron ions replace nearly twice as many sodium atoms. Meanwhile, when the cubic syngony analcime is exposed to different concentration lithium chloride solutions, remarkable changes are observed in the analcime structure, with not only lithium ions penetrating into the crystal analcime structure but also new compounds, including lithium silicate and silinaite, emerging.

The paper is focused on the analysis of ion exchange processes under hydrothermal conditions between the cubic analcime Na^+ ions and smaller ion radius Li^+ $(r = 0.094 \text{ nm})$, Mg^{2+} $(r = 0.072 \text{ nm})$, Fe^{3+} $(r = 0.067 \text{ nm})$ and Sr^{2+} $(r = 0.126 \text{ nm})$ ions in respective solutions. Study results show that the cubic analcime interaction with respective solutions under hydrothermal conditions is not determined by the differences in the size of ion radius. Variations in analcime interaction with a solution containing lithium ions may be attributed to higher alkalinity in the liquid substance under hydrothermal conditions. The selectivity of structure stability of cubic analcime in examined solutions at the hydrothermal conditions has been sustained. It is useful to note, that the mechanism of immobilization and releasing of ions containing in waste waters at the hydrothermal conditions by minerals of zeolitic structure, such as analcime, must be examined in each case separately considering selectivity of these processes.

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