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Hydrosodalite ion exchange in saturated $Ca(OH)_2$ solution

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The possibility of substituting Na^+ ions contained in pure hydrosodalite crystal structure with Ca^{2+} ions in saturated $Ca(OH)_2$ solution has been examined in the temperature range from 25 °C to 95 °C. It was found that temperature strongly influences the hydrosodalite ion exchange: upon increasing temperature only by 5 °C (from 25 to 30 °C) Ca^{2+} the time required for Ca^{2+} ions to be incorporated within the hydrosodalite crystal structure is reduced by the factor of 3. With the increase of temperature from 45 °C to 65 °C almost all the Ca^{2+} ions, initially contained in the $Ca(OH)_2$ solution, become incorporated in the hydrosodalite structure after 5 min However, high temperature has an adverse effect on the sorption process (Ca^{2+} ions will not be incorporated within the hydrosodalite structure before 10 min have elapsed). Partly reversible ion exchange reactions of hydrosodalite are characteristic at temperatures higher than 30 °C). The structure of hydrosodalite crystals remains stable when performing ion exchange reactions at 25–95 °C temperature.

Key words: *hydrosodalite; ion exchange*

1. Introduction

Zeolites form a group of minerals of a micro-porous structure containing hydrated aluminosilicates of alkaline metals and alkaline earth ones. Their crystal lattices are composed of $[Si(Al)O_4]^{4-}$ tetrahedrons [1]. An important property of zeolites is the capacity of their chemical composition to vary with regard to crystal radii (form and size), pore size and their configuration. A rather easy chemical modification of zeolites creates broad possibilities to perform controlled changes to the structure and to the properties. These parameters can be altered by synthesis, by ion exchange or by other methods [2–5]. Thus, zeolites display an unusually broad application range in industry and agriculture, where they are used for water softening, ammonia removal

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from waste water, concentration removal of radioactive isotopes from radioactive waste. Besides, zeolites are used for nuclear waste transportation. Radiation has no influence on zeolite stability [6, 7].

Gualtieri and Aprea [8] investigated the possibility of substituting of Na^+ ions with K^+ ions in the structure of hydrosodalite crystals. The chemical formula of hydrosodalite with K^+ ions is $K_6[AlSiO_4]_6 \cdot 7.8H_2O$. It is obtained from $Na_6[AlSiO_4]_6 \cdot 8H_2O$, which is a synthetic modification of natural sodalite containing additional water molecules. It should be noted that the symmetry of the hydrosodalite changes after insertion of K^+ ions.

By exploiting ion exchange with nitrate solutions of appropriate metals for 24 h, Kendrick, Dann et al. [9, 10] from $Na_6[AlSiO_4]_6 \cdot 8H_2O$ obtained hydrosodalites of alkaline and earth-alkaline metals having the formula $M_6[AlSiO_4]6 \cdot 8H_2O$ (M = Li, Na, K, Mg, Ca, Sr). Alkaline or alkaline–earth metal ion substituted hydrosodalites possess a cubic sodalite lattice with the space group *P*43*n*; its parameters vary from 0.88 to 0.92 nm. Reference [11] presents relevant data regarding the possibility of realizing hydrosodalite ion exchange using different cations, such as Cd^{2+}, Cu^{2+} Zn^{2+}, Ag^{2+}, and Pb^{2+}.

There have been few references in the established literature to the question of ion exchange in zeolites, especially with regard to the substitution of Na^+ ions with Ca^{2+} ions. This has much relevance, because zeolites having calcium ions are quite universally applied in concrete technologies [12, 13].

The aim of the paper was to investigate the possibility of substituting Na^+ ions contained in pure hydrosodalite crystal structure with Ca^{2+} ions in saturated $Ca(OH)_2$ solution.

2. Materials and methods

Pure hydrosodalite was synthesized from reagents: NaOH (Delta Chem., Czech Rep.), $Al(OH)_3$ (POCh S.A., Poland); amorphous $SiO_2 \cdot nH_2O$ (Krasny Khimik Sankt Petersburg, Russia; loss on ignition – 23.5 %). The molar ratios of the starting materials $Na_2O:Al_2O_3:SiO_2:H_2O$ – 2:1:2:10 were chosen based on the results of previous experiments [14, 15]. Low-temperature (105 °C) zeolite synthesis was performed in the unstirred suspension: isothermal curing was of 2 h duration. The final product was filtered, dried at ca. 60 °C and sieved through a 80 μm mesh sieve.

Ion exchange reactions were performed in an unstirred suspension: 100 cm^3 of saturated $Ca(OH)_2$ solution obtained from 98% CaO (POCh S.A., Poland) was filled up with 2 g of zeolite. The experiments were repeated three times, from which the average ion concentrations were evaluated. The sediments in the solution were observed to carbonize and to form $CaCO_3$, which remains in the synthesis products in all investigated cases. It is known [16] that the concentration of Ca^{2+} ions decreases when the temperature of the solution increases. Thus, as the temperature increased from 25 °C

to 95 °C, the corresponding concentration decreased from 0.81 to 0.50 g/dm^3. Ion exchange experiments at 25, 30, 45, 65 and 95 °C lasted 60 min.

The concentration of sodium and calcium ions in the solution was determined (with 97% accuracy) by the atomic absorption spectroscopy with the aid of a Perkin-Elmer Analyst 4000 spectrometer. Each calculation was made 3 times; the data declined no more than 3.5 % from the mean value. After ion exchange, the hydrosodalite was characterized by instrumental as well as chemical analysis methods.

The X-ray powder diffraction data were collected with a DRON-6 X-ray diffractometer, having the Bragg–Brentano geometry, using Ni-filtered CuK_α radiation and a graphite monochromator, operating at 30 kV and with the emission current of 20 mA. The step-scan covered the angular range 2–70 ° (2θ) in steps of $2\theta = 0.02$ °.

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

IR spectra were recorded with a Perkin Elmer FT-IR System spectrometer. For the IR analysis, 1 mg of the substance was mixed with 200 mg of KBr and compressed in a forming press under vacuum.

3. Results and discussion

Ion exchange reactions in pure hydrosodalite occur in the same way both, at 25 °C and at 30 °C, since the shapes of the curves describing the Ca^{2+} ion concentration in the solution are similar (Fig. 1). It should be noted that at 25 °C the equilibrium amount (0.49 g/dm^3) of Ca^{2+} ions is incorporated in the hydrosodalite crystal lattice within 30 min of sorption because after this time its change is rather small (0.51 g/dm^3 in 1 h) (Fig. 1, curve 1).

Moreover, at 30 °C, when the Ca^{2+} ion concentration in the initial solution was 0.68 g/dm^3, it decreased to 0.45 g/dm^3 after 5 min of sorption (Fig. 1, curve 2). The concentration of Ca^{2+} ions after 1 h decreased by the factor of 3 and was equal to 0.24 g/dm^3. Clearly, temperature strongly influences the ion exchange processes in hydrosodalite: if the temperature is increased by 5 °C, the time required for inserting the Ca^{2+} ions into the hydrosodalite crystal structure is reduced by the factor of 3 (from 30 min to 10 min).

In order to investigate the influence of temperature on the ion exchange capacity, the tests were performed at higher temperatures. At 45 °C and 65 °C, the Ca^{2+} ions were incorporated into the hydrosodalite crystal structure much faster than at 25 °C or 30 °C. After first 5 min of the ion exchange, the Ca^{2+} ion concentration in the solution

was 0.006 g/dm^3 (at 45 °C) and 0.002 g/dm^3 (at 65 °C), i.e., nearly all the Ca^{2+} ions were incorporated into the hydrosodalite structure (Fig. 2, curves 1, 2).

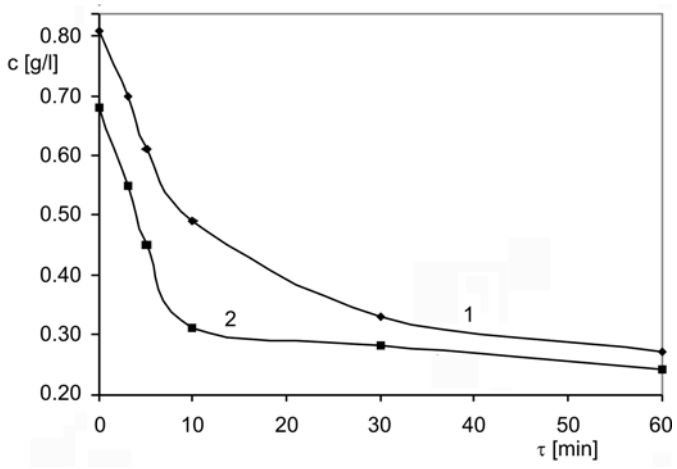

Fig. 1. Time dependence of Ca^{2+} concentration in solution at 25 °C (1) and 30 °C (2)

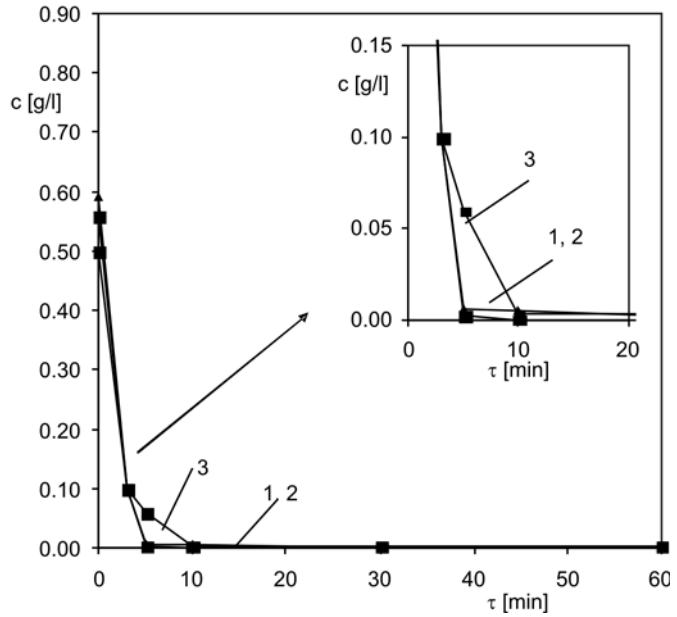

Fig. 2. Time dependence of Ca^{2+} concentration in solution at: 45 °C (1), 65 °C (2), and 95 °C (3)

The results demonstrate also that high temperatures adversely affect the sorption. At 95 °C, the reactions of ion exchange were observed to be slower than those at lower temperatures, because the equilibrium amount of Ca^{2+} ions was incorporated in the

hydrosodalite structure only after 10 min (Fig. 2, curve 3). The main reason for this is that the considered temperature (namely 95 °C) is close to the formation temperature of hydrosodalite itself. Thus, the duration time does affect essentially the ion exchange, its largest part occurs during the first 3–5 min of each experiment.

It was determined that during Ca^{2+} ion adsorption, Na^+ ion desorption proceeded simultaneously. However, at 25 °C desorption of Na^+ ions was almost unchanged: after 3 min the concentration increased only up to 0.0125 g/dm^3 and remained constant during the experiment (Fig. 3, curve 1).

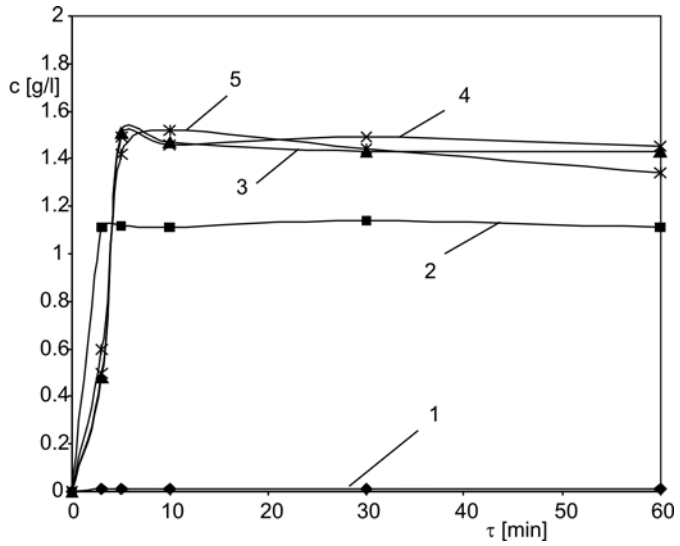

Fig. 3. Time dependence of Na^+ concentration in solution at:
25 °C (plot 1), 30 °C (plot 2), 45 °C (plot 3), 65 °C (plot 4), 95 °C (plot 5)

At higher temperatures, 30 °C, 45 °C, 65 °C and 95 °C, Na^+ ion desorption was more intense. At 30 °C (Fig. 3, curve 2), 1.11 g/dm^3 of sodium ions desorbed from hydrosodalite into the solution after 3 min. Similarly, the concentration of sodium ions in the solution also increased at higher temperatures: after 5 min, the amount of Na^+ ions increased from 1.42 to 1.51 g/dm^3. It can be stated that the equilibrium amounts of Na^+ ions enter from hydrosodalite crystal structure to the solution in 3–5 min.

It was noticed that the quantity of sodium ions desorbed from hydrosodalite structure is higher than that of incorporated Ca^{2+} ions. This was confirmed by chemical analysis which showed that pure hydrosodalite contained: SiO_2 – 34.5%, Al_2O_3 – 31.0%, Na_2O – 16.2%. After ion exchange the Na_2O zeolite composition was: SiO_2 – 34.5%, Al_2O_3 – 31.0%, Na_2O – 8.62%, CaO – 1.97%.

The obtained results were confirmed by structure examinations. The general composition of hydrosodalite is expressed by the formula $Na_{6+x}(SiAlO_4)_6(OH)_x{\cdot}nH_2O$. The ratio $(6 + x):x:n$ denotes the number of sodium ions, hydroxyl anions and water molecules per a unit cell, respectively. One unit cell equals two β cages. The β cages of the

hydrosodalite contain Na^+ cations for the compensation of the negative charge and may host OH^- ions and H_2O molecules. Some sodium cations can be compensated by OH^- anions and these sodium cations can be easily removed by washing hydrosodalite in water. The structure of hydrosodalites is dynamical with respect to the guest molecules in β cages. Sodalite β cages connected by six and four rings, in the centre one β cage in detail displaying the Si–O–Al bond angles, the 4 positions of the Na^+ cations, and the oxygen atoms of 4 water molecules embedded in this cage. Because of this, the kinetic curves of Ca^{2+} adsorption and Na^+ desorption are different, e. g. hydrosodalite adsorbs about 0.55 g/dm^3 Ca^{2+} ions and desorbs about 1.5 g/dm^3 Na^+ ions. It is reasonable to presume that in the hydrosodalite structure some of the desorbed Na^+ cations are compensated by host OH^- ions and H_2O molecules.

In order to determine whether a reversible ion exchange reaction is characteristic of hydrosodalite, the samples after sorption were placed in distilled water. It was determined that Ca substituted hydrosodalite is stable in water at temperatures up to 25 °C (Table 1). In the 65 – 95 °C temperature range, Ca^{2+} ions from the zeolite enter to the liquid phase and achieve their highest concentration (0.222 g/dm^3). During the investigation of hydrolysis isothermal dynamics of this zeolite with prolonged duration the amount of Ca^{2+} ions in the solution was noticed to decrease gradually due to $CaCO_3$ formation and sedimentation.

Table 1. The amount of Ca^{2+} ions in solution, g/dm^3

Duration [min]	Temperature [°C]				
	25	30	45	65	95
5	0	0.028	0.125	0.222	0.222
10	0	0	0.037	0.074	0.074
30	0	0	0.019	0.037	0.037
60	0	0	0.005	0.037	0.009

Figure 4 presents the results of X-ray diffraction analyses of hydrosodalite before and after sorption and desorption. The curves show that the diffraction peaks with interplanar distances (*d*) at 0.628, 0.363, 0.281, 0.256, 0.290, 0.174 nm are characteristic of hydrosodalite. The structure of hydrosodalite crystals was observed to be stable because the shape of the X-ray diffraction patterns (Fig. 4, curve 2) did not change when the duration of the experiment was prolonged up to 60 min.

It is important to note that the temperature of the ion exchange process has no effect on hydrosodalite mineral composition (Fig. 5). The peaks of the X-ray diffraction patterns were similar when the temperature varied in the 25 °C to 95 °C range of, i.e., hydrosodalite was predominant.

DSC analysis shows that hydrosodalite is predominant in the products: the endothermic peaks at 130, 143, ~275 °C are characteristic of hydrosodalites (Fig. 6).

$CaCO_3$ decomposes at 755 °C, while the peak at 866 °C corresponds to the transformation of zeolite into anhydrous nepheline $NaAlSiO_4$ (Fig. 6b).

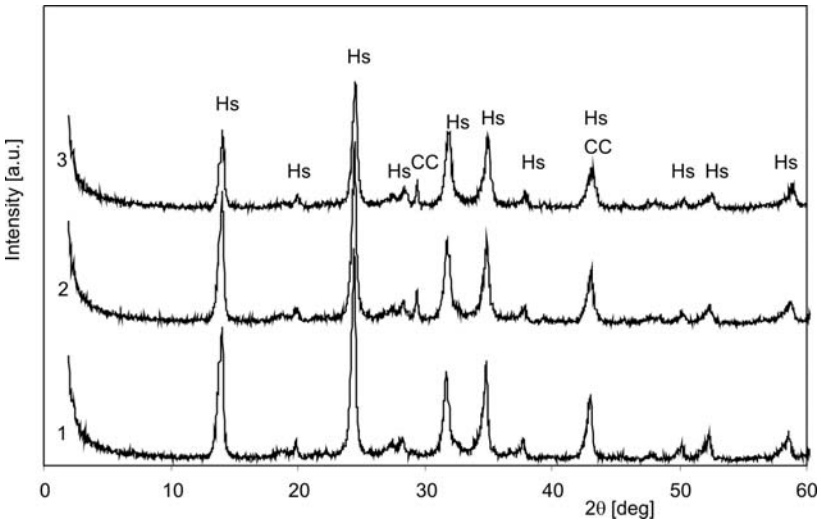

Fig. 4. X-ray diffraction patterns of hydrosodalite, ion exchange carried out at 65 °C for 60 min: 1 – pure hydrosodalite; 2 – after sorption; 3 – after desorption; Hs – hydrosodalite; CC – calcium carbonate

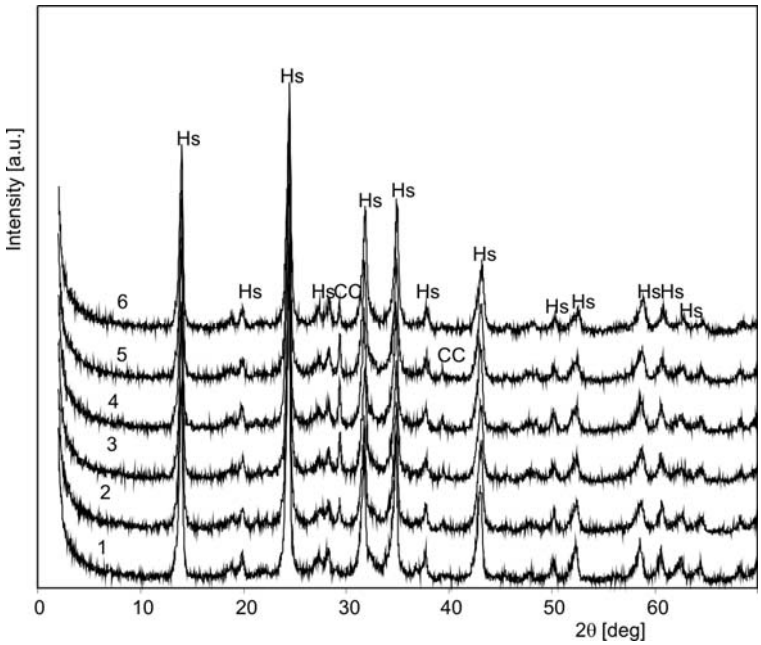

Fig. 5. X-Ray diffraction patterns of hydrosodalite, ion exchange carried out in 60 min, at various temperatures: 1 – pure hydrosodalite, 2 – 25 °C; 3 – 30 °C; 4 – 45 °C; 5 – 65 °C, 6 – 95 °C; Hs – hydrosodalite; CC – calcium carbonate

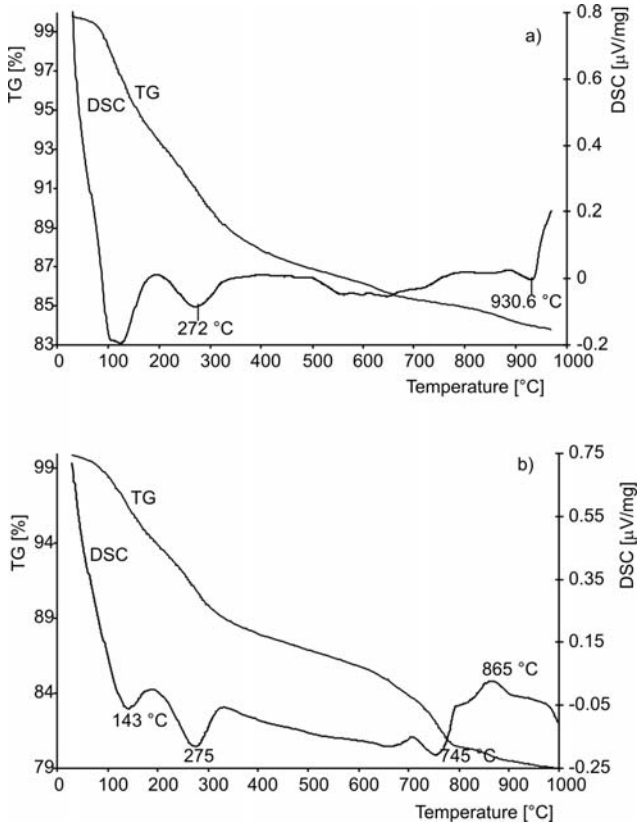

Fig. 6. The results of thermal analyses of hydrosodalite (a) and hydrosodalite after ion exchange carried out at 65 °C for 60 min (b)

Hydrosodalite gradually lost mass in all temperature ranges. Pure hydrosodalite shows lower loss on ignition (16.24%) compared with hydrosodalite after ion exchange (20.99%).

The results of IR spectroscopy analysis (Fig. 7) confirmed the data obtained by X-ray diffraction and thermal analyses. In the IR spectrum of the sample strong absorption band at 3442 cm^{-1} represents the frequencies of hydroxyl groups bound with hydrogen bonds. A narrow absorption band at 3638 cm^{-1} is attributed to water molecule hydroxyl groups that bound with the frame oxygen or with sodium cations. The abovementioned peak dominates in pure hydrosodalite and disappears after sorption (Fig. 7, curve 2). The absorption band at 1667 cm^{-1} is attributed to deformation vibration of water molecules. A broad absorption band at 979 cm^{-1} is attributed to frequencies of (Si, Al)–O bond in tetrahedron along lines that bind $[(Si, Al)O_4]^{4-}$ tetrahedron oxygen atoms with central Si or Al atom. The characteristic hydrosodalite absorption bands are as follows: 987 cm^{-1} – asymmetric atomic vibration, 731, 701, 662 cm^{-1} – symmetrical atomic vibration, – 458, 428 cm^{-1} Si(Al)–O deformation vibration. Multiplicity of IR curve (Fig. 7, curve 2) of Ca^{2+} substituted hydrosodalite is altered

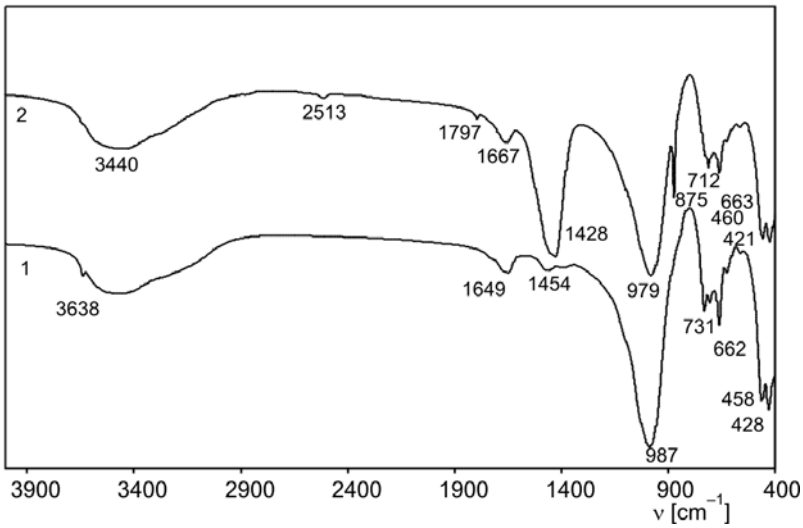

Fig. 7. The IR spectra of hydrosodalite (1) and hydrosodalite after ion exchange carried out at 65 °C for 60 min (2)

instead of three peaks of pure hydrosodalite two peaks at 712, 663 cm^{-1} occurred in the 731, 701, and 662 cm^{-1}. Bands at 2513; 1797; 1428 and 875 cm^{-1} are characteristic of $CaCO_3$.

4. Conclusion

Temperature has a large effect on the process of hydrosodalite ion exchange: upon increasing the temperature by only 5 °C (from 25 to 30 °C), the time required for inserting the Ca^{2+} ions into the hydrosodalite crystal structure is reduced by a factor of 3 (namely from 30 min to 10 min).

At higher temperatures (45 °C and 65 °C), the equilibrium amount of absorbed Ca^{2+} ions from saturated $Ca(OH)_2$ solution also increased: after 5 min of sorption almost all Ca^{2+} ions contained in the solution were incorporated into the structure of hydrosodalite. Meanwhile, high temperature that is close to the temperature of formation of hydrosodalite has a an adverse influence on the sorption process, since the equilibrium amount of Ca^{2+} ions incorporated hydrosodalite structure only after 10 min.

Partly reversible ion exchange reactions of hydrosodalite occur at a higher temperatures (at least 30 °C).

The structure of hydrosodalite crystals was determined to be stable in the 25–95 °C temperature under conditions of ion exchange reactions ($Na^+ \leftrightarrows Ca^{2+}$).

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