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Physico-Chemical Properties of Acid Modified Forms of Scolecite

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ABSTRACT

Adsorption of water vapor on scolecite of Georgian origin and on its acid modified forms has been studied. According to the obtained data, treatment of the samples with the hydrochloric acid solutions of different concentrations (0.05N, 0.1N, 0.25N, 1N, and 3N) lowers the adsorption capacity of scolecite. Increase in the concentration of acid (0.05N -0.25N) causes changes in the adsorption capacity and comparatively high adsorption ability scolecite exhibits when treated with 0.2 N acid; further increase in the acid concentration decreases the adsorption capacity. Correspondingly to the increase of the acid concentration, silicate module is increased that is legitimate as a result of dealumination caused by the acid. At treating of scolecte with 3N hydrochloric acid, practically complete exclusion of sodium and potassium cations from the exchangeable positions of the structure takes place and these cations are noticed only as traces in the solid phase. As for the calcium cations, 11 % of its initial amount remains in the solid phase that is caused by the strong bond between the calcium cation and oxygen of the zeolite framework.

Keywords: Natural Zeolites, Scolecite, Adsorption, Acid Modification of Zeolite and Ion-Exchange.

INTRODUCTION

Natural zeolites are characterized with quite developed, organized micro-porous structure. They have high perspectives for their practical application as molecular-sieve adsorbents and ion-exchangers. For the last years, great attention has been paid to the investigation of the physical-chemical properties of the fibrous zeolites such as natrolite, mesolite, and scolecite. These zeolites are widely used in such technological processes where application of synthesized zeolites is not economically feasible.

Tetrahedral chains of natrolite type are characteristic for fibrous zeolites that determine their zeolite properties. In the structures of fibrous chain type zeolites, the chains are connected together like spirals.

As the physical-chemical properties of scolecite are less studied, investigations in this field are of great concern. The above zeolites have identical framework structural composition but differ in the composition of the elemental cell; natrolite contains Na^+ cations, scolecite mostly Ca^{2+} cations and in mesolite both Na^+ and Ca^{2+} cations are found. Furthermore, cations and water molecules occupy different positions, two sodium cations are arranged at the edges of the channels and calcium cations are in the center s of the channels. In scolecite, additional water molecules occupy the places of sodium cations. In natrolite, $Na_2(H_2O)_2$ is replaced with $Ca(H_2O)_3$ that causes change in symmetry from Fdd2 to F1d1 (Glauco Gottaedi et al. 1985; Osipova et al. 2020).

According to X-ray analysis, zeolite phase content in scolecite rock of Georgian origin is 60-65% and based on the data of the chemical analysis its chemical composition in oxide form (%) has been established: SiO₂-46.24, Al₂O₃- 26, 41, Fe₂O₃-0.04, CaO-12.21, Na₂O-1.20, K₂O-0.24, H₂O-13.42. Georgian scolecite is close to the standard samples by the composition (according to the Hudson institute of mineralogy: SiO₂-45.94, Al₂O₃- 25, 99, CaO-14.29, H₂O 13.78) (<u>http://webmineral.com/data/Scolecite.shtml#.Xxa2QW0zaUk</u>; Tsitsishvili et al. 2003; Shiva K. Prasad et al. 2005).



Figure 1. (a). Clinographic view of the chain of fibrous zeolite (b). The structure of scolecite.

MATERIALS AND METHODS

Adsorption of water vapor on scilecite of Georgian origin and on its acid modified forms has been studied by the method of dessicator (Uotadze, et al. 2003, Uotadze S.L., et al. 2001). The zeolite was dehydrated at 250-300 $^{\circ}$ C for 4 hours. Constant water vapor pressure (P/P_s=0.04) in the dessicator was provided with sulfuric acid of certain concentration.

The adsorption was carried out at room temperature. After detention of the sample in the dessicator for 100-120 hours, adsorption value (in mol/g) has been determined according to the gained weight. Based on the results of the experiment, the adsorption capacity of scolecite has been determined and it equals 2.9 mmol/g, V=0.052cm³/g. Adsorption of acid modified (H-form) scolecite samples against water vapor has also been studied.

Modification of zeolite implies increase of sizes of micro pours up to effective pours by processing of crystals with acid that causes expel of aluminum and increase of Si/Al ratio. Influence of aggressive medium often causes partial disruption of aluminum silicate framework and formation of transitional pours.

Threefold treatment of scolecite was done with hydrochloric acid of different concentrations (starting from 0.05N to 3N) at room temperature; relation of the solid phase and hydrochloric acid was 1:10, after washing of the released solid phase, the sample was first dried on air and then in thermostat at 100 $^{\circ}$ C.



Figure 2. Adsorption capacity of scolecite (against water vapor) depending on the concentrations of hydrochloric acid.

Table 1. Water vapor adsorption on initial and acid modified samples on scolecite o	f
Georgian origin (P/P _s =0.04; at room temperature).	

Concentration of the solution, N	a, Mili mole/gr	V, cm³/gr
0.05	2.05	0.036
0.1	2.42	0.041
0.25	2.51	0.046
1.0	1.25	0.028
3.0	0.87	0.01
Initial sample	2.9	0.052

The presented in the table data give information about the maximum adsorption capacity of the scolecite sample against water vapor depending on the different concentrations of hydrochloric acid. According to the above data, scolecite exhibits the highest adsorption ability in case of treatment with 0.25N HCl. Further increase in the hydrochloric acid concentration causes decrease in adsorption capacity. Change of water vapor adsorptivity on scolecite samples is caused by the development of the transitional pours in the partially amorphous phase of its crystalline structure that is related to the internal change in the scolecite structure. Low values of adsorptive capacity against water vapor on the cation forms are explained by the fact that the active adsorption centers on the given forms represent not shielded cations; when modified with acid, first the not sielded cations are removed from the zeolite structure that is reflected on the adsorptive properties of the modified zeolites.

Comparison of the adsorptive values of scolecite and its H-forms proves the regularity about the decrease of volume of the porous structure depending the increase of the silicate module. Change in the chemical composition of the samples treated with hydrochloric acid of different concentration has been proved on the bases of the chemical analysis.

Components	Initial sample	0.1N	1 N	3 N			
Si	21.60	23.00	25.00	25.10			
Al + Fe	14.00	12.60	11.00	10.90			
Са	8.70	6.50	2.90	1.00			
Na	0.90	0.60	0.30	0.02			
К	0.40	0.30	0.20	0.01			
H ₂ O	20.80	19.20	17.20	16.80			

Table 2. Change in the chemical composition of scolecite treated with the hydrochloricacid of different concentrations.

As it can be seen from the table, increase of scolecite module is noticed according to the increase in hydrochloric acid concentration that is a result of dealuminization caused by action of the acid. Deficiency of the cations (conditioned by partial decationization of scolecite crystals when treated with acid) is caused by the introduction of the equivalent number of hydrogen ions into cation part. Release of the not shielded sodium cations from the crystalline structure takes place simultaneously of the increase of the acid concentration and at treatment with the 3N solution remains as a trace on the solid phase. Large cations of potassium are also gradually expelled from the structure. As for the not shielded calcium cations in the exchangeable positions, their displacement from the crystalline structure gradually takes place depending on the increase in the acid concentration and 11 % of the initial cations are noticed in the solid phase at treatment with 3N acid solution. The fact is explained by strong bonds existing between oxygen and calcium cations of the zeolite frame. It is also noticeable that the treatment with 0.1N hydrochloric acid causes significant dealumination of scolecite that is related to the high content of aluminum in its composition and is conditioned by the existence of weak Al-O bonds compared to that between Si-O. Further increase of hydrochloric acid concentration does not greatly affect the expel of aluminum remained in the solid phase.

RESULTS

Certain changes are noticed in the structure of scolecite when treated with hydrochloric acid; particularly, formation of transitional pours the sizes of which increase at increase of hydrochloric acid concentration and formation of macro pours.

Also, treatment with acid affects the structural changes taking place at amorphization of the zeolite. Adsorptive capacity of the initial sample of scolecite against water vapor (2.9 milli.mol/g) decreases at treatment with HCl. Scolecite exhibits higher adsorptive ability (2.51 milli.mol) at treatment with 0.25N HCl. In case of low concentrations (0.05N and 0.1N), the adsorptive capacities are 2, 05 and 2.42 milli. mol/g, correspondingly. Further increase in the solution concentration causes decrease in adsorptive abilities (at 3N and 1N HCl 0.87 and 1.25 milli.mol/g, correspondingly). Decrease in adsorptive ability at high concentration of hydrochloric acid (3N HCl) is caused with the partial disruption of the zeolite structure.

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