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Physicochemical peculiarities of Georgian scolecite

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Abstract

Physico-chemical investigation of Georgian scolecite has been carried out to study the adsorption of water vapor on it and its modified forms (treated with HCl and NH_4Cl); their thermal and ion exchange properties against mono (Li, Na, NH_4, K, Cs, and Rb), divalent (Sr, Ba Ca, Mg) and transition (Cd, Cu, Mn, Zn, Co and Ni) metal cations. Treatment of the scolecite samples with different concentrations (0.05N, 0.1N, 0.25N, 1N, and 3N) of HCl changes its adsorption capacity, and scolecite exhibits comparatively high values when treated with 0.2 N acid.

Scolecite's thermal analysis shows the stability of its microporous crystalline structure up to 450°C, which conditions the feasibility of its application as an adsorbent and nanomaterial.

The structure of scolecite, the charge and size of the cations (both in the hydrated and dehydrated state), and cation concentration in the solution (0.1N, 0.3N, 0.5N, 1.0N, and 1.5N) determine the order of selectivity of scolecite against monovalent, divalent, and transition metal cations. Dynamic Exchange Capacity (DEC) values for the above cations on scolecite have been calculated.

Keywords: Natural zeolite; Scolecite; Ion exchange; Molecular sieve; Thermal property; Adsorption

1. Introduction

Scolecite, a tectosilicate mineral, is a hydrated calcium silicate with the chemical formula $CaAl_2Si_3O_{10}·3H_2O$. It is isostructural with mesolite and natrolite by the same aluminosilicate framework and usually occurs as acicular (needle-like) and fibrous aggregates. As a secondary origin hydrothermal mineral, scolecite occurs with other zeolite deposits of low-temperature alteration of basalts and related rocks, gneisses, and amphibolites, on top of the calcium zeolites heulandite, stilbite, and epistilbite. The mineral was first described by the German chemists and mineralogists Gehlend A.F. and Fuchs J.N. in 1813, and its name is derived from the Greek word σκώληξ (sko-lecks), meaning "worm" [1,2].

By X-ray analysis, scolecite appears to have a monoclinic crystalline structure that is usually colorless or white, transparent to translucent, with a white streak and a silky luster in fibrous specimens. In the structure of fibrous zeolites, the chains are linked together like spikes [3]. The fibrous zeolites (scolecite, natrolite, and mesolite) have different compositions of the elementary cells, scolecite contains mostly Ca^{2+} cations, natrolite Na^+ cations, and mesolite both Ca^{2+} and Na^+. In scolecite, the Na^+ cations are replaced by additional water molecules. Fig.1 shows the structure of scolecite, where black dots represent Ca^{2+} cations and white circles represent water molecules.

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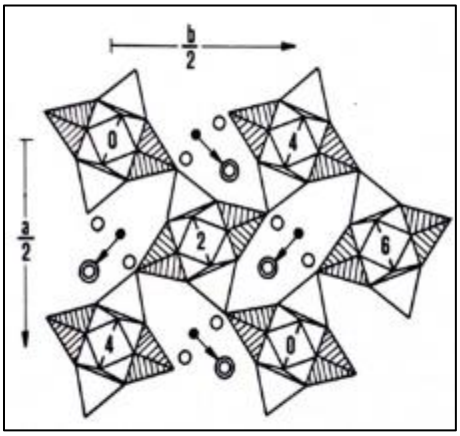


Figure 1 Structure of scolecite

Open channels in the scolecite structure and their sizes allow water and large ions to move within the framework, enabling scolecite to act as a chemical sieve.

The physical-chemical properties of scolecite are less understood, so research in this area is of great interest.

The scolecite sample under investigation was taken from the granite deposit of the village Kursebi (Kutaisi region, Georgia). According to X-ray analysis, zeolite phase content in the above scolecite rock is 60-65% and has the following composition (%) in oxide form: SiO_2-46.24, Al_2O_3- 26, 41, Fe_2O_3-0.04, CaO-12.21, Na_2O-1.20, K_2O-0.24, H_2O-13.42. With such composition, it is close to the standard samples from the Hudson Institute of Mineralogy: SiO_2-45.94, Al_2O_3 - 25, 99, CaO-14.29, H_2O 13.78 [4,5,6].

2. Material and methods

2.1. Experimental

The desiccator method has been used to study the adsorption of water vapor on the scolecite and its acid-modified sample. The zeolite, dehydrated at 250- 300 ºC for 4 hours, was placed in the desiccator with concentrated sulfuric acid for 100-120 hours. The acid provided constant water vapor pressure ($P/P_s=0.04$) in the desiccator. The weight gain of scolecite determines the adsorption value (in mol/g) on it.

To study the adsorption of acid-modified (H-form) scolecite against water vapor, a three-fold treatment of the sample with hydrochloric acid (in 1:10 relation) of different concentrations at room temperature has been carried out. The treatment increased the sizes of micro-pores up to the effective ones. This caused the expulsion of aluminum and increase of Si/Al ratio; the sample was washed and dried first on air and then at100 ^{o}C.

The maximum adsorption capacities of the scolecite samples (treated with different concentrations of hydrochloric acid) against water vapor are given in Table 1.

Table 1 Water vapor adsorption (a) and its volume (V) on the initial and acid-modified samples of scolecite ($P/P_s=0.04$; at room temperature)

Concentration of HCl, N	**a. Mili mole/gr**	**V, cm^3/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

Treatment of scolecite with 0.25N HCl shows the highest adsorption capacity. Further increase of the acid concentration causes a decrease in adsorption capacity. The development of the transitional pores in the partially amorphous phase of the crystalline structure of scolecite associated with the internal change is the reason for the change in water vapor absorptivity. Unshielded cations representing active adsorption centers on the cation explain low values of adsorption capacity against water vapor on the given forms. The removal of unshielded cations from the modified zeolite reflects its adsorptive properties [7].

A comparison of the adsorptive values of the initial scolecite and its H-forms shows the relationship between the decrease in the volume of the porous structure and the increase of the silicate module. Table 2 gives the change in the chemical composition of the treated samples.

Table 2 Change in the chemical composition of scolecite treated with the hydrochloric acid of different concentrations

Components	Initial sample	0.1N	1N	3N
Si	21.60	23.00	25.00	25.10
Al+Fe	14.00	12.60	11.00	10.90
Ca	8.70	6.50	2.90	1.00
Na	0.90	0.60	0.30	0.02
K	0.40	0.30	0.20	0.01
H_2O	20.80	19.20	17.20	16.80

Dealumination of scolecite caused by its treatment with high concentration hydrochloric acid increased the sample module. The decrease in the cation part of the scolecite structure after being treated with acid is explained by the replacement of hydrogen ions into the structure. At treating the sample with 3N HCl solution, sodium cations remain only as a trace in the structure. Large potassium cations are also gradually released from the structure. Displacement of the calcium cations existing in the exchangeable positions takes place gradually depending on the increase of the acid concentration, and at 3N HCl, only 11 % of the initial cations remain in the solid phase. This is explained by the strong bonds between the oxygen and calcium cations of the zeolite framework [7].

The nature of existing water in the zeolite, its dehydration process, the stability of the crystalline framework, and the phase transformation have been studied by the method of thermal analysis to determine the stability of the initial and modified (with 0.1 N, 0.25 N, 1.0 N, and 3.0 N HCl and NH_4Cl; ratio 1:10) forms of scolecite as a function of temperature.

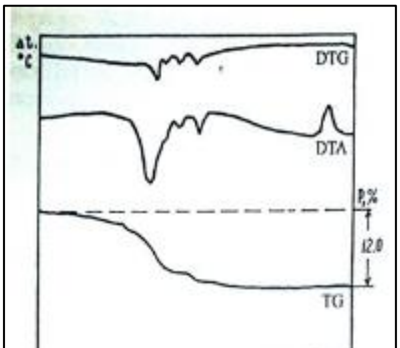


Figure 2 Differential thermal (DTA) and thermogravimetric (DTG) curves of the initial form of scolecite; rate of heating 10 °C/min

DTA curve shows three endo effects caused by the dehydration process taking place in four steps; the process of amorphous state formation begins at 500 ºC; one exo effect at 1000ºC is caused by the structural changes in the zeolite as the dehydration is not noticed in this interval. DTG curve exhibits four weight loss effects at 380, 410, 450, and 520°C, respectively. The total mass loss by 10°C rate of heating up to 1000°C of the initial form of scolecite was 12% by mass.

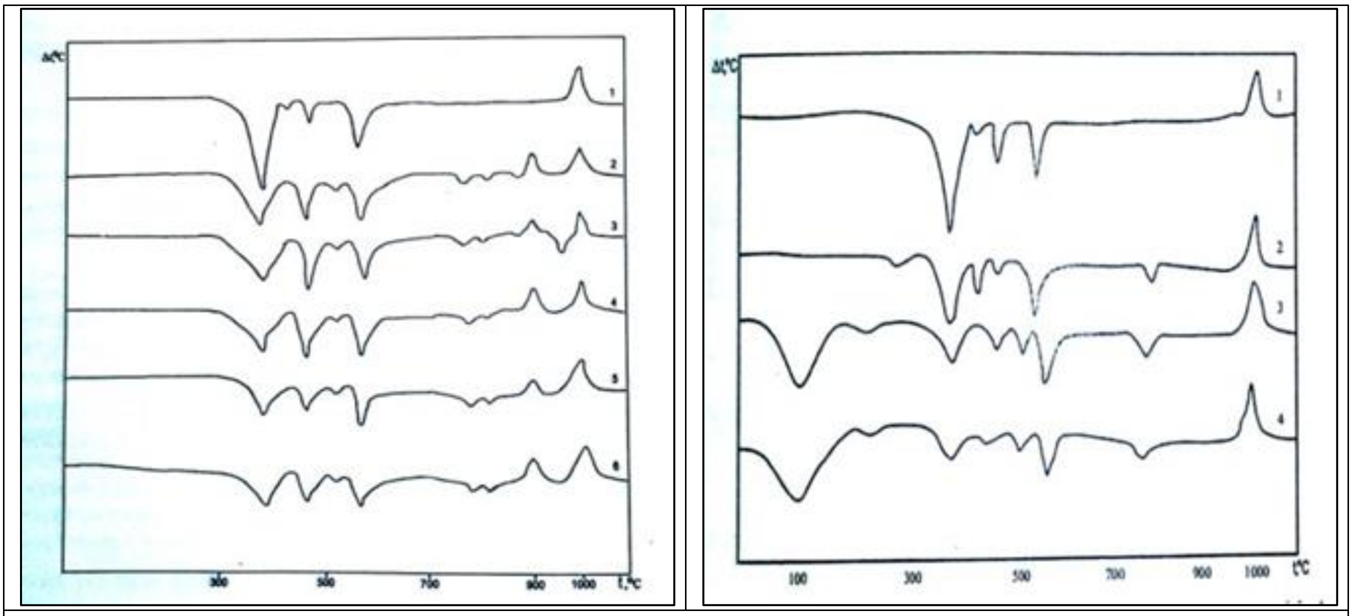


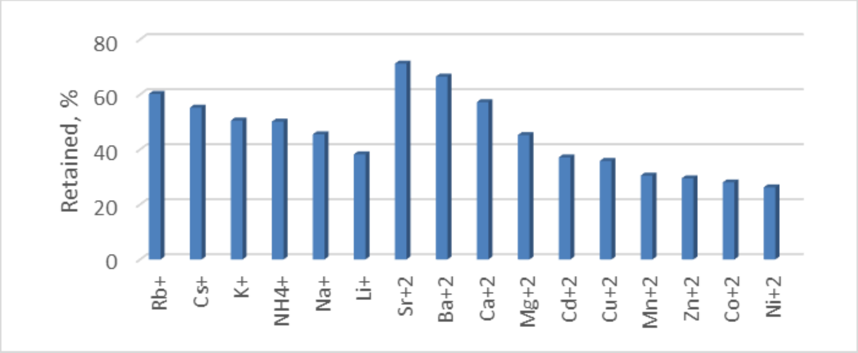
Figure 3 DTA curves of scolecite (rate of heating 10°C/min)

a. treated with NH_4Cl; b. treated with HCl; a.1-Initial; Treated: 2 –0.1 N; 3-0.25 N; 4–1.0 N; 5–3.0 N; 6–5.0 N; b. 1-initial; 2-0.25 N; 3-1.0 N; 4–3.0 N.

When treated with 0.1N NH_4Cl, low-intensity additional endo effects at 500ºC, in the 770-920ºC temperature range, and exo effect at 900ºC are observed. Such peaks are not characteristic of the initial form and are caused by the structural changes in the process of amorphization. The maximum mass loss of 18,1% (by mass) is observed when the sample is treated with 3N NH_4Cl solution.

When scolecite is treated with HCl, the endo effect is at 380ºC; in the case of 1-3N HCl, the endo effects at 100ºC are explained by the formation of macropores, but those at 280ºC are explained by the formation of the transitional pores. Dehydration of the sample at low temperature is about 4.5%, which probably is related to macro and transition pores, which in turn cause the total loss of mass of 14%. Furthermore, an additional endo effect at 750 °C evidences the structural changes in the amorphization process [3].

To study the ion-exchange properties of scolecite under dynamic conditions, 50 g of the crushed (0.5-0.65 mm) sample was loaded into a glass column (20 x 2 cm). 500 ml of 0.5-1.5 N aqueous solutions of chlorides of Cs, Rb, K, Na, Li, Ba, Sr, Ca, Mg, Cu, Cd, Mn, Co, Zn, Ni were passed through the column at a rate of 5 ml/min. The pH of the solutions was 5. 10µl samples were taken from the filtrate at 2–3-minute intervals and analyzed by ion chromatography to determine the portion (%) of cations retained by scolecite. The obtained data are shown in Figure 4.



(concentration of the solution 0.5 N; at room temperature, V=5ml/min)

Figure 4 Percent content of some retained metal cations on scolecite

To establish certain selectivity towards monovalent, divalent, and transition metal cations, dynamic exchange capacity (DEC) values for scolecite were calculated (Figure 5).

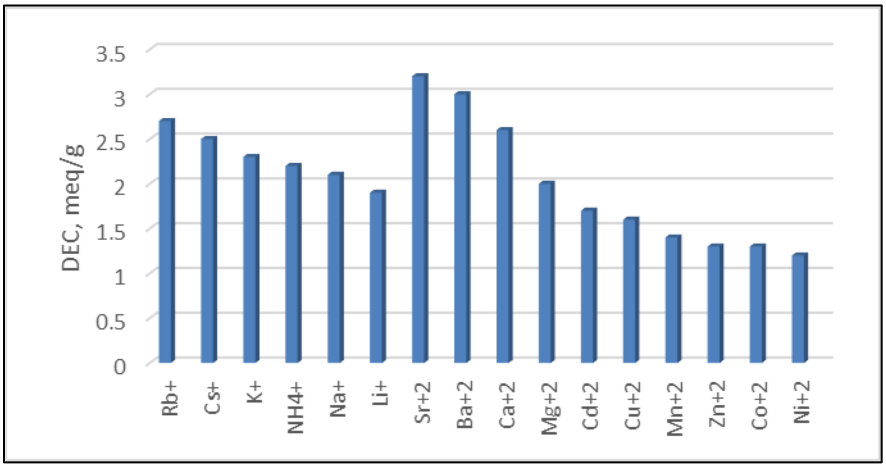


Figure 5 Values of Dynamic Exchange Capacities (DEC, meq/g) of mono, di-valent, and transition metal cations for scolecite (concentration of the solution 0.5 N; at room temperature, V=5ml/min)

Based on the calculated DEC values that are influenced by the solution concentration, the following selectivity series for monovalent cations was established: Rb>Cs>K>NH_4>Na>Li. The higher the concentration of the monovalent cation salt solutions (from 0.1 to 1.5N), the higher the DEC values. A slightly different dependence for Li^+ cation is possibly due to its hydration. Increasing the concentration of the solution up to 2N almost equalizes the selectivity of scolecite for monovalent cations, apparently due to its saturation as a cation exchanger.

Relatively high DEC values are characteristic for divalent cations, especially for large, weakly hydrated Ba^{+2} and Sr^{+2} cations DEC values for which exceed 3 meq/g. The high affinity for the divalent cations and their DEC values are apparently due to the crystalline structure and the arrangement of the cations in different positions. Calcium cations located in the scolecite structure have relatively higher mobility than other cations of the same charge in the ion exchange process. The DEC values decrease as the radius of the counter ion decreases (Figure 5). For the studied scolecite, the following selectivity series for the divalent cations was established: Sr^{+2}>Ba^{+2}>Ca^{+2}>Mg^{+2}.

The percent of the retained transition metal cations on scolecite and their DEC values are given in Figures 4 and 5.

Transition metal cations have relatively low DEC values (1.2-1.7 meq./g) compared to monovalent and especially divalent cations, and the following selectivity series has been established: Cd>Cu>Mn>Zn>Co>Ni.

The selectivity of scolecite for these cations is determined by their cation radius. The larger the radius of the counter ion, the more selective it is. Scolecite shows significantly high selectivity for Cd^{+2} and Cu^{+2} cations. The process of ion exchange of relatively small cations is influenced by the peculiarity of the microporous, crystalline structure of scolecite, the size of the entrance windows, and the distribution of cations in the cavities [8,9].

3. Conclusions

Treatment of scolecite with increasing concentration of HCl causes the formation of transitional and macro pores and increase in their sizes; while treatment of the initial sample with HCl decreases its adsorption capacity against water vapor and the highest value is seen at 0.25N HCl (Table 1). Further increase of HCl concentration causes the decrease of adsorptive abilities, and at 3N HCl, the partial disruption of the zeolite structure occurs.

On heating, the sample undergoes progressive dehydration, and 12% of the total mass from the initial sample of scolecite was lost; in treatment with 3N NH_4Cl solution, the maximum loss of the mass (18.1%) was reached. The endo effect at 750°C is a result of the amorphization of the zeolite sample related to its acid treatment, while the exo peaks at 1000°C in both the initial and modified samples demonstrate their structural changes.

For monovalent cations, scolecite shows selectivity depending on their radius; the larger the radius of the cation, the higher the selectivity toward it (Rb>Cs>K>NH_4>Na>Li). Bivalent cations have higher DEC values than monovalent ones, especially for large, less hydrated Ba and Sr cations (Sr^{+2}>Ba^{+2}>Ca^{+2}>Mg^{+2}). As for the transition metal cations, relatively high selectivity is obtained for the Cd^{+2} and Cu^{+2} cations (Cd>Cu>Mn>Zn>Co>Ni).

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

No conflict of interest to be disclosed.

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