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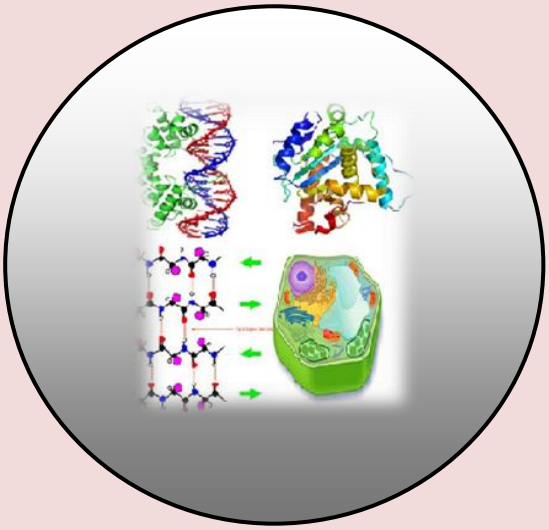

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RESEARCH PAPER

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Thermal Characteristics of Natural Zeolite- Scolecite of Georgia

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ABSTRACT

Some physico-chemical investigation of scolecite of Georgian origin and its modified forms (treated with HCl and NH_4Cl) has been carried out in order to determine feasibility of their practical application. Content of zeolite phase (initial sample 60-65%) and stability of scolecite towards its treatment with ammonium chloride (up to 3 N) and hydrochloric acid (up to 1 N) have been established with X-ray analysis. Complete stability of micro-porous crystalline structure of scolecite up to 450°C has been shown by thermal analysis. Chemical composition and structure of scolecite has been established. High content of zeolite phase in scolecite bearing rocks of Georgia determines the perspective of its extraction. Results of the investigation of thermal characteristics of the initial and modified forms of scolecite condition feasibility of their application in the production of adsorbents and nano-materials.

Keywords: Natural Zeolite, Scolecite and X-Ray Analysis.

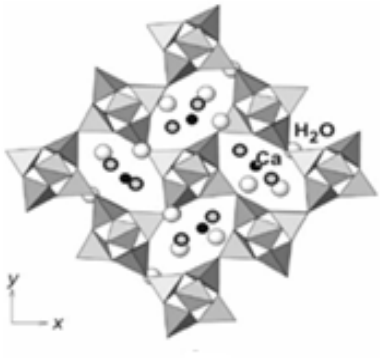
INTRODUCTION

Natural zeolites are characterized by well developed and ordered micro porous crystalline structure, molecular-sieve, adsorptive and ion-exchange properties that conditions the perspective of their practical application (Tsitsishvili et al. 1985; Tsitsishvili et al. 2001). Natural zeolites are successfully used in such technological processes where the application of synthetic zeolites is not economically approved. Special attention is paid to the inexpensive, unique by their properties minerals which simultaneously possess selective, ion-exchange and adsorptive properties and are associate with modern actual problems of wasteless technology and environmental protection (Mumpton, 1999). Taken into account a great perspective of application of natural zeolites, investigation of physico-chemical properties of natural zeolites of Georgia becomes necessary. In the presented work, the results of some physico-chemical properties of low-silicon containing Georgian zeolite of hydrothermal origin - scolecite (SCO) and its modified forms are given in order to prove feasibility of its practical application that will contribute to the rational application of national wealth, such an actual problem at present (Urotadze et al, 2001; Beliavskaia et al. 1986). Scolecite sample under investigation was taken from the granite deposit in the vicinity of village Kursebi (Kutaisi region, Georgia). According to the X-ray analysis, content of zeolite phase in the sample is about 60-65% (Tsitsishvili et al, 2003; K. Siva Prasad et al. 2005).

Idealized formula of unite cell of scolecite is as follows: $Ca_8(Al_{16}Si_{24}O_8)$ $24H_2O$, share of free volume – 0.31 cm^3/cm^3, dimensions of free apertures – 2.6x3.9 A in 8-member rings (Brek D. 1976).
By its chemical composition (%)- SiO_2-46.24; Al_2O_3-26.41; Fe_2O_3-0.04; CaO-12.2; Na_2O-1.2 and K_2O - 0.46 this zeolite is close to the theoretical formula of this mineral (Batiashvili et al,1985; Skhirtladze, 1991).

a.

Fig. 1. a. Fibrous zeolite - scolecite molecules

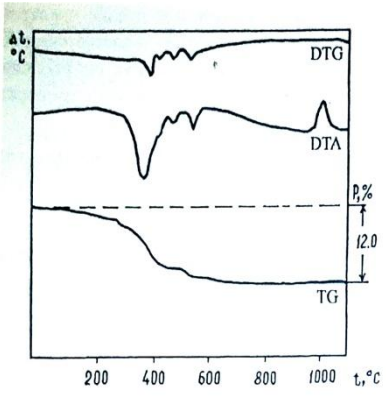


b.

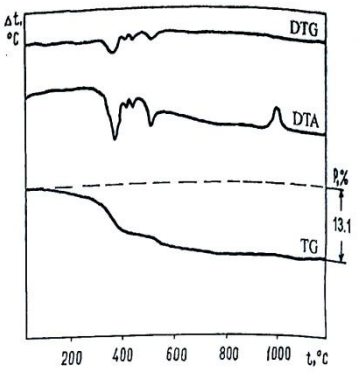
b. Structure of scolecite (black dots – cations of Ca; white circles-water

MATERIALS AND METHODS

We carried out physico-chemical investigations of the scolecite sample, namely rentgenographic and thermographic studies.
According to the diffraction data, at the beginning of the effect the heated sample of scolecite was amorphous, at the end – at 1040°C, new structural phase was formed.
Study of water vapor adsorption over scolecite was made by the exsiccater method at room temperature, at the P/P_s=0.4.
The sample was preliminary activated by heating at 300°C. Calculation of adsorption value (mmol/g) was done by the method of weighing.
As a result of investigation, adsorption capacity of scolecite is a=2.9 mmol/g and V=0.052 cm^3/m.
We have also carried out thermographic investigations of the given zeolite-scolecite.
The study was carried out on thrivatogeraph of the Hungarin firm "Paulik, Paulik, Eerbey" sensitivity of galvanometer: DTA, DTG-1/5, TG-200, T-1330. Thermoneutral aluminum oxide Al_2O_3 served as a control. Sample weight was 400-420 mg.
The samples were heated at two rates: 10°C/min and 5°C/min. The results are given on Fig.2 (a and b).



a.



b.

Fig. 2. Thermal curves of scolecite from Kursebi, Georgia; In air heating: a. 10°C/min; b.5°C/min

At heating the sample by 10°C/min rate (Fig. 2, a), the curve shows three endo-effects and an exo-effect; the curve of DTG- shows four effects and the weight loss at the temperatures 380, 410, 450, and 520°C. On the curve of DTA at 410°C the endoeffect is given as trace.

At heating of the sample by the 5°C/min rate (Fig.2, b) the curve of DGA clearly shows the effect (410°C). Comparison of DTA, DTG curve and TG show that all four effects are conditioned by liberation of water in four stages: the first portion of water is lost in 166-400°C temperature interval with the maximum loss at 380°C. The first endo-effect directly passes into the second endo-effect with its maximum at 410°C, which in its turn passes to the third endo-effect with maximum at 450°C.

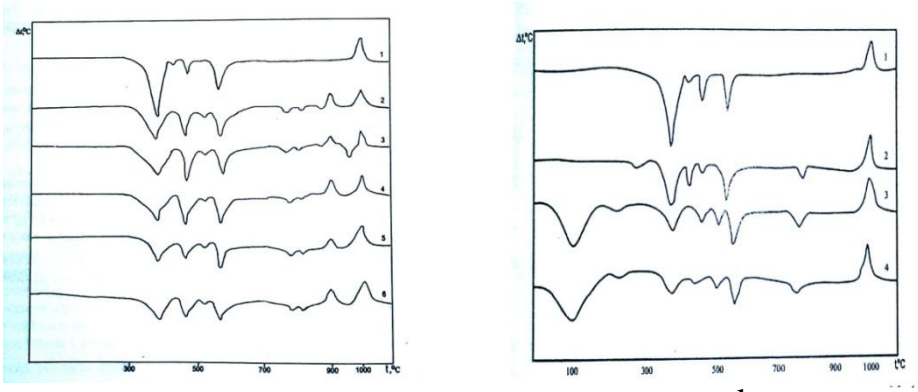
The second and the third endo-effects are characterized by low intensity. The fourth endo-effect is more intense, and is observed in 480-650°C temperature interval with maximum at 520°C. Exo-effect observed at 1000°C is conditioned by structural changes of the sample, since in the section of this effect the weight loss is not observed, what is evidenced by the data of X-ray analysis.

At heating of scolcite by 10°C/min rate, the weight loss equals 12.0%, while at heating by 5°C/min rate, weight loss equals to 13.1%.

For obtaining the modified forms of scolecite, the initial sample was treated by ammonium chloride and hydrochloric acid solutions of the same concentrations. Modification was carried out at room temperature, by the triple processing; the ratio of amounts of zeolite and the solution was 1:10. The results of the thermal analysis of hydrogen forms are given in Tables 1 and as their DTA curves on Fig. 3. The thermograms of the samples treated with NH_4Cl solutions are identical and differ from those of the initial sample:

Table 1. Data of the thermal analysis of scolecite treated with ammonium chloride and hydrochloric acid at different concentrations (rate of heating 10°C).

Scolesite Sample	TGA				DTA			
	Treated with ammonium chloride		Treated with hydrochloric acid		Treated with ammonium chloride		Treated with hydrochloric acid	
	Mass total loss, %	Temperature °C	Mass total loss, %	Temperature °C	Type of reaction	Temperature °C	Type of reaction	
Initial form	12.0	380, 410, 450, 520	12.00	380, 410, 450, 520	Endo-	380, 410, 450, 520	Endo-	380, 410, 450, 520
					Exo-	1000	Exo-	1000
Treated with 0.1N H_4Cl	16.9	380, 450, 480, 540, 770, 820, 870	---		Endo-	380, 450, 480, 540, 770, 820, 870	---	
					Exo-	900, 1000		
Treated with 0.25N NH_4Cl	17.3	380, 450, 480, 540, 770, 820, 870, 950	0.25	280, 380, 410, 450, 520, 750	Endo-	380, 450, 480, 770, 820, 870, 950	Endo -	280, 380, 410, 450, 520, 750
					Exo-	900, 1000	Exo-	1000
Treated with 1N NH_4Cl	17.9	380, 450, 480, 540, 770, 820	13.90	100, 220, 380, 450, 500, 550, 750	Endo-	380, 450, 480, 540, 770, 820	Endo -	100, 220, 380, 450, 500, 550, 750
					Exo-	900, 1000	Exo-	1000
Treated with 3N NH_4Cl	18.1	380, 450, 480, 540, 770, 820	14.10	100, 220, 380, 450, 500, 550, 750	Endo-	380, 450, 480, 540, 770, 820	Endo -	100, 220, 380, 450, 500, 550, 750
					Exo-	900, 1000	Exo-	1000
Treated with 5N NH_4Cl	16.7	380, 450, 480, 540, 770, 820	---		Endo-	380, 450, 480, 540, 770, 820	---	
					Exo-	900, 1000		



a **b**

Fig. 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.

From the endo-effects shown on the DTA curve of the natural scolecite (Fig. 3), the endo-effects with the maximums at 380°C (the increase of concentrations of the solution causes the broadening of this peak and decrease of its intensity) are noted on the thermograms of the modified samples; at 450°C (intensity of the peak increases with an increase of the solution concentration up to 1N , and the further increase in concentration causes the decrease of peak size); at 520°C (shifting of this endoeffect in the higher temperature region of 540°C is noticed with an increase of the solution concentration); with the treatment by NH_4Cl solution of lower concentration (0,1N) additional endoeffect is observed at 500°C which is of low intensity. The mentioned additional endo-effects in high temperature interval within 770-920°C and exo-peak at 900°C, not-characteristic for the initial form apparently is caused by the structural changes in the process of amorphization. The increase in the mass loss attributed to the isolation of ammonia is characteristic for the samples modified with ammonium chloride; the mass loss reaches maximum -18,1% (by mass) when treated the sample with 3N solution. From the noted endo-effects of the initial sample and samples treated with hydrochloric acid, the endo-effect is maintained only at 380°C. However, with increasing the solution concentration its intensity sharply decreases. The low-temperature endo-effect at 100°C of the samples treated with 1 and 3N solution of HCl indicates the formation of macro-pores; but formation of the transitional pores at treatment with diluted hydrochloric acid is confirmed by the corresponding endo-effect of low intensity at 280°C. The sizes of the transitional pores increase with the treatment with the concentrated solutions of HCl that is proved by the displacement of the endo-peak to the lower temperature 220°C region. The loss of water in the low temperature range is high and composes 4,5%. Apparently, formation of the macro and transitional pores, and also the thermal dehydration attrebuted to these pores, causes an increase in the loss of overall mass up to 14% for the samples treated with the solutions of hydrochloric acid. As for the high-temperature endo-effects attributed to the processes of stepped dehydration, the broadening of the corresponding peaks and the displacement in the region of the higher temperature is observed for the modified forms. In addition to this, the acidic treatment of scolecite to the certain degree influences the structural changes in the process of amorphization that is testified by additional endo-effect at 750°C.

RESULTS

On the basis of the investigation, it might be concluded that the total mass loss at heating of Georgian natural zeolite scolecite (initial) is 12% (by mass). The maximum loss of the mass is 18.1% at treating with 3N solution of ammonium chloride. Water is released step by step at different temperatures.

As for the high temperature endo-effect attributed to the process of stepwise dehydration, the broadening and shifting of the corresponding peaks are noted for the modified samples.
Furthermore, acidic treatment of scolecite has an influence on its structural changes during the amorphisation that is explained by the additional endo-effect at 750°C. The exo-peak at 1000°C is noticed for both initial and modified samples of scolecite caused by the structural changes in the zeolite

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REFERENCES

Batiashvili T.V., Mikadze G.A. and Gogishvili V.G. (1985). Some characteristic peculiarities of zeolites of Meskheti (Georgia). Geology, physic-chemical properties and application of natural zeolites, Metsniereba, Tbilisi, 61-67.

Beliavskaia T.A., Bolshova T.A. and Brukina G.D. (1986). Chromatography of inorganic substances, Vishaia Scola, Moscow, 208**.**

Brek D. (1976). Zeolite molecular sieves. Mir, Moscow, 781.

Shiva Prasad K., P.S.R. Prasad and S.R. Sharma (2005). Infrared spectroscopic study of phase transitions in natural scolecite. Indian journal of pure and applied physics, vol.43, pp.79-82

Mumpton, F.A. (1999). *La roca magica:* Uses of natural zeolites in agriculture and industry. Proc. Acad. Sci., USA, v. 96, #7, 3463-3470.

Skhirtladze N.I. (1991). Sedimentary zeolites of Georgia. Tbilisi: Ed. TSU, 144

Tsitsishvili G.V., Andronikashvili T.G., Kirov G.N. and Filizova L.D. (1985). Natural Zeolites, 224.

Tsitsishvili G.V., Urotadze S.L., Ocipiva N.A. and Kvernadze T.K. (2001). Determination of the selectivity of the natural zeolite-scolecite in respect of cations of different metals. Azerbaijan Chemistry Journal, #4, 34

Tsitsishvili G.V., Urotadze S.L., Tsintskaladze G.P., Ocipiva N.A. and Kvernadze T.K. (2003). IR spectroscopy scoecite of Georgia. Ukrainian chemical journal, vol.69, #8, p.101-103

Urotadze S., Sturua G., Chipashvili D. and Burjanadze M. (2001). Radiographic and thermographic investigation of natural zeolite – scolesite deposits of Georgia. Proceedings of the Georgian academy of sciences, vol. 27, #1-2, p.140-143.

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