

## Some molecular-sieve peculiarities of natural zeolite of Georgia

Nana Osipova, Tamar Kvernadze, Nino Burkiashvili \*, Leila Japaridze, Tsiala Gabelia and Eter Salukvadze

*Ivane Javakhishvili Tbilisi State University, P.Melikishvili Institute of Physical and Organic Chemistry, Tbilisi, Georgia.*

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### Abstract

Ion exchange property of fibrous zeolite scolecite of Georgian origin has been studied against mono (Li, Na, NH<sub>4</sub>, K Cs and Rb), divalent (Sr, Ba Ca, Mg) and transition (Cd, Cu, Mn, Zn, Co and Ni) metal cations. Selectivity series of the above cations for scolecite have been compiled.

The structure of scolecite, charge and size of the cations (both in hydrated and dehydrated state) and cation concentration in the solution (0.1N, 0.3N, 0.5N 1.0N and 1.5N) greatly influence on the ion-exchange property and selectivity order of scolecite. Dynamic Exchange Capacity (DEC) values for the studied cations on scolecite have been calculated.

Kinetics of ion exchange in dynamic conditions for the above cations has been studied. Analysis of the obtained data shows that the external diffusion processes have influence on the establishment of equilibrium between the ions on the surface and in the micro porous structure of scolecite. The time of dynamic exchange equilibrium is directly proportional to the cation radii.

**Keywords:** Natural zeolites; Fibrous zeolites; Scolecite; Selectivity series; Ion exchange property; Dynamic exchange capacity

### 1. Introduction

Natural zeolites are characterized by a highly developed and ordered micro porous crystalline structures, molecular sieve adsorption and ion exchange properties [1]. Ion-exchange reactions characteristic for zeolites determine the prospects for their successful practical application in multi-tonnage technological processes, extraction of valuable non-ferrous metals from waste water, for waste and potable water treatment against environmentally toxic cations of various metals [2, 3, 4]. Currently, the environment is saturated with various pollutants, including such life-threatening chemical elements as cesium, strontium, lead, cadmium, etc. Therefore, it becomes necessary to study the selectivity of absorption of various metal cations by the ion exchangers in order to identify the most suitable ones for the optimal extraction of the cations.

Basically, natural zeolites of sedimentary origin, showing a clearly pronounced selectivity with respect to the certain cations, are used for this purpose [5]. The behaviors of these minerals in ion exchange processes depend on a number of factors, primarily on the structural features of a particular zeolite. The completeness and selectivity of the exchange are determined by penetration of analyzed cations in all positions of the zeolite framework where the cations of the mineral have the sieve exchange effect.

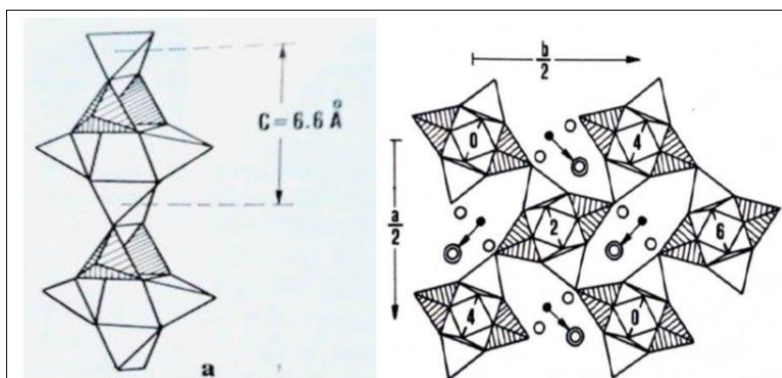
\* Corresponding author: Nino Burkiashvili

Important factors determining the exchange behavior of zeolites are also: 1) the nature of the cation, its charge and size in the hydrated and dehydrated forms; 2) temperature; 3) the concentration of the cation in the solution; 4) the nature of the anions associated with the cations in the solution; 5) the nature of the solvent [6].

Application of synthetic zeolites in the above industrial fields is not economically feasible. Therefore, particular importance is given to the inexpensive, unique mineral in its property such as scolecite of Georgian origin, which simultaneously exhibit selective, ion-exchange and adsorptive properties closely related to modern topical problems of waste-free technology and environmental protection [7].

The aim of our study was investigation of the less studied, low-siliceous, fibrous natural zeolite - scolecite of Georgia.

Scolecite, characterized by the idealized formula  $\text{Ca}_8(\text{Al}_{16}\text{Si}_{24}\text{O}_{80}) \cdot 24\text{H}_2\text{O}$  is a calcium analog of natrolite, they have identical framework structural composition but differ in the composition of the elemental cell; natrolite contains  $\text{Na}^+$  cations, scolecite mostly  $\text{Ca}^{2+}$  cations. 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 centers of the channels. In scolecite, additional water molecules occupy the places of sodium cations and  $\text{Na}_2(\text{H}_2\text{O})_2$  is replaced with  $\text{Ca}(\text{H}_2\text{O})_3$  [1, 8, 9]. The chemical composition of scolecite in oxide form (%) -  $\text{SiO}_2$ -46.24,  $\text{Al}_2\text{O}_3$ -26.41,  $\text{Fe}_2\text{O}_3$ -0.04,  $\text{CaO}$ -12.2,  $\text{Na}_2\text{O}$ -1.2,  $\text{K}_2\text{O}$ -0.46 is close to the composition of the corresponding theoretical formula of the mineral (according to the Hudson institute of mineralogy:  $\text{SiO}_2$ -45.94,  $\text{Al}_2\text{O}_3$  - 25.99,  $\text{CaO}$ -14.29,  $\text{H}_2\text{O}$ -13.78) [10, 11, 12].



**Figure 1** Fibrous zeolite structure

a) Clinographic view of the chain; b) Structure of scolecite (black dots –cations of Ca, white circles-water)

Scolecite sample was taken from the granite deposits (Georgia). According to the X-ray analysis, carried out on Dron-2 diffractometer (radiation of the spectral line corresponding to  $\text{Cu-K}\alpha$ , scanning speed 1 deg/min), the zeolite phase content in the rock appeared to be 60-65% [11].

Unlike the work [5], where the selectivity of zeolite was determined by the total change in the free energy of the corresponding interacting ions with the zeolite phases and the solution, in our investigation to compile the selectivity series we used the method of dynamic exchange capacity (DEC) values used in chromatography [13].

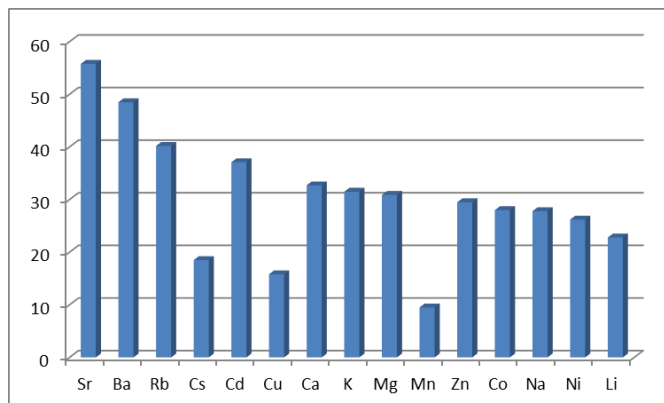
## 2. Material and method

### 2.1. Experimental

Investigation of ion-exchange properties of the studied zeolites has been carried out under dynamic conditions. Scolecite sample has been crushed; a fraction of 0.5-0.65 mm has been loaded into a 20 cm long glass column with an internal diameter of 2 cm. The weight of the sample loaded into the column was 50 g. Ion exchange on zeolites was carried out using the chloride solutions of the studied cations of different concentrations (0.1–1.5N). The flow rate of the solution through the column has been 5 ml/min. At different time intervals, 10  $\mu\text{l}$  samples have been taken from the filtrate. Qualitative and quantitative determination of the cations in the samples was carried out by ion chromatography on the device of mark SHIMADZU.

For the experiment, 0.5-1.5 N aqueous solutions of chlorides of the following metals have been prepared: Cs, Rb, K, Na, Li, Ba, Sr, Ca, Mg, Cu, Cd, Mn, Co, Zn, Ni. The acidity of the solutions was pH 5. 500 ml of each solution has been passed

through a layer of zeolite at the rate of 5 ml/min. In every 2-3 minute interval, a sample of the filtrate has been taken to determine the corresponding cation in it. After the complete washing of 500 ml solution out of the column, the portion (%) of the retained and not-retained cations by scolecite has been calculated. The obtained data are given in Fig. 2.



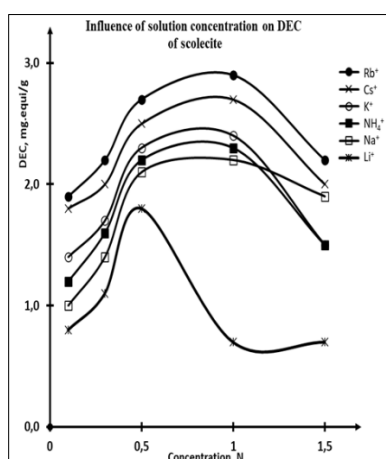
**Figure 2** Percent content of some retained metal cations on scolecite

Based on the obtained results of the ion exchange process on scolecite, dynamic exchange capacity values have been calculated. It was found that scolecite exhibits certain selectivity to mono valent cations with a large radius (Table 1).

**Table 1** Dynamic exchange capacity (DEC) values of scolecite against mono and divalent cations (concentration of the solution 0.5 N; at room temperature, V=5 ml/min)

	Mono valent cations						Divalent cations			
	Rb <sup>+</sup>	Cs <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	Li <sup>+</sup>	Sr <sup>+2</sup>	Ba <sup>+2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>
Retained, %	60.2	55.2	50.5	50.1	45.5	38.2	71.2	66.5	57.2	45.2
Not retained, %	39.8	44.8	49.5	49.9	54.5	61.8	28.8	33.5	42.8	54.8
DEC, meq/g	2.7	2.5	2.3	2.2	2.1	1.9	3.2	3.0	2.6	2.0

Based on the DEC values, the following selectivity series were established: Rb>Cs>K>NH<sub>4</sub>>Na>Li. It was found that the concentration of the solution affects the DEC values (Fig.3).



**Figure 3** Relationship between the solution concentration of mono valent cations and the DEC values (at room temperature, V=5 ml/min) on scolecite

From the obtained data it follows that an increase in the concentration of the salts, solutions containing monovalent cations from 0.1 to 1.5 N causes an increase in DEC values. A slightly different dependence is noted for Li<sup>+</sup> cation which

is possibly caused by hydration of this cation. Increase the concentration of the solution up to 2N almost equalizes the selectivity of scolecite with respect to monovalent cations. This is apparently caused by the saturation of the scolecite capacity as a cation exchanger.

Under the dynamic conditions, according to the number of adsorbed and non-adsorbed cations on scolecite, relatively high DEC values are characteristic for divalent cations compared to monovalent ones. This is especially evident for large, weakly hydrated Ba<sup>+2</sup> and Sr<sup>+2</sup> cations DEC values for which exceed 3 meq/g. High affinity for the divalent cations and DEC values of scolecite is apparently due to the peculiarity of the crystalline structure and the arrangement of cations in different positions. It is possible to assume that the calcium cations located in the scolecite structure exhibit a relatively high mobility in relation to the cations of the same charge in the process of ion exchange (Table 1). It follows from the table that the DEC values decrease in accordance with the decrease in the radius of the counterion. For the studied scolecite, the following selectivity series Sr<sup>+2</sup>>Ba<sup>+2</sup>>Ca<sup>+2</sup>>Mg<sup>+2</sup> has been established.

The ion-exchange properties of scolecite with respect to the cations of some transition metals and the DEC values were studied as well.

**Table 2** Dynamic exchange capacity (DEC) values of some transition metal cations on scolecite (concentration of the solution 0.5 N; at room temperature, V=5 ml/min)

	Transition metal cations					
	Cd+2	Cu+2	Mn+2	Zn+2	Co+2	Ni+2
Retained, %	37.1	35.8	30.5	29.5	28.0	26.2
Not retained, %	62.9	64.2	69.5	70.5	72.0	73.8
DEC, meq/g	1.7	1.6	1.4	1.3	1.3	1.2

Relatively low DEC values (1.2-1.7 meq./g) have been obtained for transition metal cations compared to monovalent and especially divalent ones. The following selectivity series has been established: Cd>Cu>Mn>Zn>Co>Ni.

The selectivity of scolecite for these cations is determined by the cation radius and the selectivity increases with an increase in the radius of the counterion. Scolecite exhibits significantly high selectivity to Cd<sup>+2</sup> and Cu<sup>+2</sup> cations. Apparently, the process of ion exchange of relatively small size cations are affected by the peculiarity of the microporous crystalline structure of scolecite, the size of the entrance windows, the distribution of cations in the cavities, and others.

Other important factors determining the exchange behavior of scolecite are its kinetic characteristics - time of dynamic equilibrium ( $\tau_2$ ) and the completion time of ion exchange ( $\tau_\infty$ ).

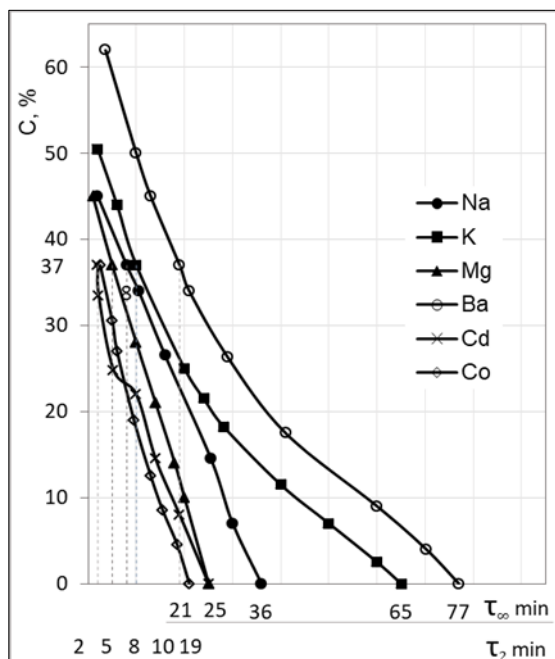
**Table 3** Time of dynamic equilibrium ( $\tau_2$ ) and the completion time of ion exchange ( $\tau_\infty$ ) of some cations on scolecite

Cations	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cs <sup>+</sup>	Rb <sup>+</sup>	Mg <sup>+2</sup>	Ca <sup>+2</sup>	Sr <sup>+2</sup>	Ba <sup>+2</sup>	Cd <sup>+2</sup>	Cu <sup>+2</sup>	Mn <sup>+2</sup>	Co <sup>+2</sup>	Zn <sup>+2</sup>	Ni <sup>+2</sup>
$\tau_2, min$	3	8	10	12	15	18	5	13	19	19	2	1.5	<1	<1	<1	<1
$\tau_\infty, min$	19	36	65	70	67	88	25	40	55	77	25	25	30	21	29	19

The time of dynamic equilibrium ( $\tau_2$ ) characterize the equilibrium of ion-exchange processes taking place on the surface of the zeolite and in its micro-porous structure. The index is determined by pore-diffusion mechanism and takes into account the duration of the initial step ( $\tau_1$ ), when the ion-exchange mainly takes place on the surface of the zeolite and is conditioned by outer diffusion mechanism. The completion time of ion exchange ( $\tau_\infty$ ) corresponds to the establishment of equilibrium between the solution and zeolite phase at simultaneous action of outer- and pore-diffusion mechanism.

Decrease in the concentration of the exchangeable cation in the solution  $C(Z_A^+)$  has an exponential character:  $(Z_A^+) = C(0)exp(-\tau_1/\tau_2)$ , where C(0) is an initial concentration; for the quantitative evaluation of  $\tau_2$ , the time interval when relative concentration of the cation decreases  $\approx 2.7$  times (that corresponds 37% of the initial concentration) has been chosen.  $\tau_2$  and  $\tau_\infty$  parameters for some cations of the ion-exchange process on scolecite are given in Table 3 [14, 15].

For some transition metal cations (Mn, Co, Zn, Ni), an initial step of ion exchange (ion exchange on the surface of zeolite) occurs very fast (in about 10-100 s) and evaluation of  $\tau_2$  is impossible.



**Figure 4** Kinetic Characteristics of ion exchange for some cations on scolecite

Thus, the higher the selectivity toward the cation the faster the dynamic equilibrium is established in the system “zeolite-solution”. The obtained correlation proves that the kinetic curves have a universal character; but selectivity factor has the same influence on ion exchange taking place both on the surface and in the micro porous structure of zeolite.

### 3. Results

On the basis of the obtained results of the investigation of the ion exchange process on scolecite, it has been established that scolecite exhibits certain selectivity toward the monovalent cations with large radius; different relationship is noticed for Li cation, that might be caused by its hydration.

The solution concentration has an influence on DEC values; increase in concentration of the salt solution from 0.1 to 1.5 increases DEC values.

Relatively higher values of DEC for the divalent cations compared to monovalent ones are typical for scolecite. Mostly this is exhibited for large, less hydrated Ba and Sr cations. It is possible to admit that Ca cations, located in scolecite structure shows relatively high mobility for the cations with the same charge in the ion exchange process. The radiuses of these cations determine selectivity of scolecite and a relatively high selectivity is obtained for the cations  $\text{Cd}^{+2}$  and  $\text{Cu}^{+2}$ . Establishment of the exchange equilibrium between the ions on the surface and into the micro porous structure is effected by the outer diffusion process; duration of the establishment of dynamic equilibrium is directly proportional to the radiuses of the cations.

### 4. Conclusion

On the basis of the conducted researches, the following conclusions have been derived:

- Chemical composition of Georgian natural zeolite scolecite and zeolite phase (60-65 %) content in it have been determined.

- Selectivity series of scolecite against some monovalent, divalent, and transition metal cations have been established.
- Dynamic Exchange Capacity values of scolecite for the studied cations have been calculated
- Kinetic characteristics - time of dynamic equilibrium and the completion time of ion exchange have been determined

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## Compliance with ethical standards

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### *Disclosure of conflict of interest*

No conflict of interest.

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