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ION EXCHANGE PROPERTIES OF GEORGIAN NATURAL ZEOLITES

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Abstract. Ion exchange properties of Georgian analcime, phillipsite and scolecite have been studied. The exchange capacity of analcimes is higher for sodium cations, decreasing in the following series: $Na^+>K^+>Ag^+>NH_4^+>Ca^{+2}>Sr^{+2}>Li^+$, the selectivity sequence for the sodium-enriched form is $NH_4^+>Ag^+>Li^+>Ca^{+2}>K^+\sim Sr^{+2}$. For phillipsite ion exchange isotherms prove the high selectivity towards NH_4^+ and K^+ depending on the origin of zeolite: $K^+>NH_4^+>>Ca^{+2}>Mg^{+2}$ for samples with comparatively low content of potassium, and $NH_4^+>K^+>Na^+>>Ca^{+2}>Mg^{+2}$ for samples with high K-content. For scolecite selectivity sequences depend on temperature and flow rate, at low temperatures and under static conditions the selectivity sequence is $Sr^{+2}>Ba^{+2}>Rb^+>Ca^{+2}>Cs^+>K^+>NH_4^+>Na^+>Mg^{+2}>Li^+>Cd^{+2}>Cu^{+2}>Mn^{+2}>Zn^{+2}>Co^{+2}>Ni^{+2}$.

Keywords: ion exchange, analcime, phillipsite, scolecite.

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Introduction

Natural zeolites are widely used for environmental cleanup from pollutants, including extraction of toxicants from drinking and waste water. Georgia is rich in zeolites [1], reserves of the Dzegi-Tedzami clinoptilolite deposits exceed 36 million tons, production reached a peak (100 thousand tons per year) in time for the elimination of the consequences of the Chernobyl disaster. Sorption, ion exchange, catalytic and other properties of the Georgian heulandite-clinoptilolite from said deposits and other manifestations are well studied, and this material as well as its modifications, have application [2]. Phillipsite-containing Eocene rocks were discovered in Georgia firstly, at the northern fringe of the Akhaltsikhe depression, along with other zeolites (analcime, laumontite, mordenite, *etc*.), and then in the Gurian range. Among the zeolites known on the territory of Georgia, analcime is rather widespread: an abundance of analcime connected with volcanic-sedimentary rocks is observable in the Middle-Eocene rock masses of the Achara-Trialeti folded system, beginning with Mtskheta district, including the Borjomi valley and westward in Bagdadi and Vani districts; analcime-containing stratified rocks are known in Western Georgia in the deposits of Jurassic carbonaceous and colored suites of Kutaisi area, as well as analcime from a basaltic geode (environs of Tbilisi), analcime crystallized in the chemical way (sedimentary rocks from Kutaisi environs), and analcime of diagenetic origin (said volcanic-sedimentary rocks from the Akhaltsikhe deposit). Scolecite is also widespread, but there is only one manifestation perspective for industrial applications, located near the village of Kursebi.

An important role for application of natural zeolites and their modifications plays the ion exchange capacity, mainly depending on the content of aluminum in their crystal lattice. Despite the small size of entrance windows (2.6 Å) and narrow channels, analcime is still used as an ion exchanger and its transition metal containing forms as catalysts [3]. Recently, attention has been paid to the synthesis of analcime [4]. Phillipsite is used for ammonia adsorption [5] and removal of various heavy metals from waste waters [6], the calcium-enriched phillipsites are found to exhibit the ability to sorb humic acids [7]. Application of scolecite is not so wide comparing to cliniptilolite and other common zeolites, but natural scolecite from India has been found as an effective catalyst for the one-pot synthesis of 2,4,5-triarylimidazole derivatives *via* a three component reaction using benzyl or benzoin, aldehydes and ammonium acetate [8]. In Sudan, scolecite was successfully tested for removal of heavy metal ions from industrial wastewater [9] using its comparatively high ion exchange capacity.

The purpose of this study was to evaluate ion exchange properties of natural zeolites of Georgia with a relatively low Si/Al ratio – the analcime (IUPAC formula $|Na_{16}(H_2O)_{16}|$ $[Al_{16}Si_{32}O_{96}]$-ANA), phillipsite ($|K_2(Ca,Na_2)_2(H_2O)_{12}|$ $[Al_6Si_{10}O_{32}]$-PHI), and scolecite belonging to the natrolite group $|Na_{16}(H_2O)_{16}|$ $[Al_{16}Si_{24}O_{80}]$-NAT, general formula for a hydrated calcium silicate $CaAl_2Si_3O_{10}\cdot 3H_2O$.

Experimental

Analcimes from Chachubeti plot of the Tedzami deposit (A-Cha) and from Gelati manifestation in Western Georgia (A-Gel), phillipsites from Akhaltsikhe deposit in Southern Georgia (P-Akh), from Tsinaubani manifestation (P-Tsi), and from the upper plot of the Shukhuti deposit in Guria region (P-Shu) [10], and scolecite from the basalt deposit of village Kursebiin Eastern Georgia (S-Kur) have been used in this study as powdered samples (0.063-0.1 or 0.5-065 mm), washed in distilled water (solid : liquid =1:20, 3-5 times) and dried at 100-110°C. Characterization of samples including zeolite type according to the IUPAC Nomenclature, zeolite phase content in raw material and after washing, as well as separation of magnetic fraction, and main impurities based on XRD data is given in the Table 1. X-ray powder diffraction patterns were obtained from a DRON-4 diffractometer, employing the Cu-Kα line and scanning at 1° per minute.

The chemical composition was calculated on the basis of elemental analyses for the unit cells that contain the number of oxygen atoms, which is defined by the type of zeolite: ($[Al_xSi_yO_{96}]$ for analcimes, $[Al_xSi_{1y}O_{32}]$ for phillipsites, and $[Al_xSi_yO_{80}]$ for scolecite). Elemental analysis was carried out using a Spectromom 381L plasma spectrometer and a Perkin-Elmer 300 atomic absorption spectrometer. Chemical composition of the investigated zeolites is listed in the Table 2 in terms of the empirical formulas $(Na_{2a}K_{2b}Ca_cMg_d)Me_e[Al_xSi_yO_z]\cdot nH_2O$, where $Me = {}^{1}/_{3}Fe^{+3}$, $½Cu^{+2}$, $½Mn^{+2}$, *etc*.

Temperature-controlled ion exchange reactions in static conditions with different solid : liquid ratios and ion concentrations have been carried out in a shaking water bath (Grant Instruments OLS26 Aqua Pro) using water solutions of chlorides of ammonium and alkali (Li, Na, K, Rb, Cs), alkaline earth (Ca, Mg, Sr) and transition (Cd, Cu, Mn, Zn, Co, Ni) metals, as well as a silver nitrate solution. Evaluation of ionic concentration both in solid and liquid phases for calculation of the ion exchange isotherms was based on results of elemental analyses. Sodium-, potassium-, *etc*. enriched forms have been prepared in 1N solutions of corresponding chlorides with a solid : liquid ratio of 1:10, at 80°C under stirring, until the cationic composition of the zeolite was changing.

Table 1

Characterization of zeolite samples.

Sample	*Zeolite type*	*Phase content (%)*	*Main impurities*	*Colour*	*Density (g/cm^3)*
A-Cha	ANA	70/95	chlorite, montmorrilonite	greenish-grey	1.88
A-Gel	ANA	75/90	chlorite, montmorrilonite	yellow-grey	1.86
P-Akh	PHI	60/90	heulandite, pyroxene, clay minerals	grey	1.58
P-Tsi	PHI	65/90	heulandite, pyroxene, clay minerals	grey	1.53
P-Shu	PHI	80/95	heulandite, clay minerals	yellow-grey	1.57
S-Kur	NAT	90/90	calcite, quartz	whitish	1.74

Table 2

Chemical composition of the zeolites.

Sample	*Empirical formula*	*Si/Al*
A-Cha	$(Na_{9.25}K_{2.25}Ca_{1.25}Mg_{0.95})Me_{0.30}[Al_{16.2}Si_{32.0}O_{96}]\cdot 18.4H_2O$	2.00
A-Gel	$(Na_{10.8}K_{1.50}Ca_{0.65}Mg_{0.40})Me_{1.0}[Al_{15.4}Si_{33.0}O_{96}]\cdot 15.7H_2O$	2.14
P-Akh	$(Na_{1.32}K_{0.68}Ca_{0.80}Mg_{0.20})Me_{0.3}[Al_{4.30}Si_{11.3}O_{32}]\cdot 10.0H_2O$	2.63
P-Tsi	$(Na_{1.36}K_{0.70}Ca_{0.70}Mg_{0.32})Me_{0.1}[Al_{4.20}Si_{11.5}O_{32}]\cdot 11.2H_2O$	2.74
P-Shu	$(Na_{1.3}K_{2.0}Ca_{0.30}Mg_{0.25})Me_{0.1}[Al_{4.50}Si_{11.8}O_{32}]\cdot 11.4H_2O$	2.62
S-Kur	$(Na_{0.70}K_{0.20}Ca_{6.75}Mg_{0.00})Me_{0.20}[Al_{15.6}Si_{24.0}O_{80}]\cdot 15.6H_2O$	1.54

The study of ion exchange in dynamic conditions was carried out on washed and dried (250°C during 3-4 h) samples (0.5-0.65 mm) introduced in a glass column (diameter of 20 and length 200 mm); 500 mL of aqueous solutions of metal chlorides of concentrations 0.1, 0.3, 0.5, 1.0, 1.5 and 3.0 N passed through the column with flow rates 5, 10 and 15 mL/min; periodical sampling (0.1 mL) took place at the outlet of the column. Concentration of ions in starting solutions and samples was determined on "Tsvet-3006" ion chromatograph and Shimadzu ion chromatograph CDD-10Avp/10Asp equipped with conductivity detector. Content of metals in zeolite after the ion exchange treatment was calculated on the basis of elemental analyses.

Results and discussion

According to determined chemical composition of prepared sodium-enriched forms of analcimes, the Si/Al ratio remains unchanged compared with that of the natural samples, the cationic composition of the A-Cha sample can be expressed as $(Na_{12.5}K_{0.3}Ca_{0.65}Mg_{0.95})Me_{0.20}$, compensating the negative lattice charge of –16.2; qualitatively the same results are obtained for the second sample. Thus, the ion exchange results in significant removal of potassium (*approx.* 90%) ions and partial removal of calcium (*approx.* 50%) ions, Mg^{+2} ions are not involved in the process; the total ion exchange capacity for raw analcimes is in the range of 3.2-3.6 meq/g, and *approx*. 4.1 meq/g for washed samples, higher than 3.9 meq/g reported by Sherman, J.D. and comparable with 4.3 meq/g for the ideal structure taking into account zeolite phase content [11]. Sodium-enriched form of the A-Cha sample was used for study of the ion exchange equilibrium with participation of monovalent (Li^+, K^+, NH_4^+, Ag^+) and bivalent (Ca^{+2}, Sr^{+2}) ions.

The ion exchange equilibrium can be qualified using isotherms – a graphical representation of the correlation between the equilibrium and experimental terms at constant temperature. According to Zagorodni's definition, the most common ion exchange isotherm represents solidarity between ionic composition of two phases: the ion exchange material and solution, the isotherm is a function $C_Z = f(C_S)$, where C_Z is concentration of the ion in zeolite, and C_S is its concentration in solution; the shape of isotherm contains information about selectivity towards ions participating in the ion exchange [12]. The ion exchange isotherms obtained experimentally on analcime (equilibrium at 20°C justified by constant concentration of solution, a solid : liquid ratio of 1:20) are shown in Figure 1.

According to Breck's classification [13], the ion exchange isotherms for $Na^+ \leftrightarrow NH_4^+$ and $Na^+ \leftrightarrow Ag^+$ reactions are of the ***a***-type, and sodium-enriched form of analcime demonstrates high selectivity towards NH_4^+ and Ag^+ ions due to reducing of the hydration energy and increase in the activity coefficient during the transition in the solid phase.

In the case of K^+, the isotherm is of the ***c***-type pointing out the dependence of the selectivity on the degree of saturation – at small concentration potassium removes sodium from zeolite. Leucite ($K[AlSi_2O_6]$) is easily prepared with the use of $Na^+ \leftrightarrow K^+$ ion exchange reaction, but no transformation of analcime in ammonioleucite as mentioned in [14] were observed despite a comparatively high temperature of the ion exchange process.

For Li^+, Ca^{+2}, and Sr^{+2}, the ion exchange isotherms are of the ***b***-type, testifying small selectivity of sodium-enriched zeolite. Thus, the selectivity sequence for the sodium-enriched form derived from the ion exchange isotherms is as follows: $NH_4^+ > Ag^+ > Li^+ > Ca^{+2} > K^+ \sim Sr^{+2}$.

Based on experimental data, the characterization of ion exchange and other properties of studied analcime forms are given in the Table 3, including cation content, cation exchange capacity (CEC), Si/Al ratio, number of water molecules in zeolite cell (*n*), and water adsorption capacity (*V*) at p/p_S=0.40 and room temperature as a measure of "free" volume in zeolite pores and channels after incorporating of different ions.

According to these data, Si/Al ratio varies within the limits of experimental error, and the negative charge of the lattice remains the same. Water content in the cell for sodium-enriched form is increased in comparison with the natural sample, and decreases with increasing cation radius, the latter being noticeable only for fairly high degrees of substitution (K^+, Ag^+, NH_4^+). In general, it is easier to introduce monovalent cations in the microporous crystal lattice of analcimes with exception of lithium characterized by highest hydration energy. Small amount of lithium ions (6.2% of total positive charge) significantly decreases the water adsorption capacity by blocking the entrance windows. The share of the impurity compensating metals Me after ion exchange is reduced (in the case of A-Cha from 1.85% to 1.2% of the total charge, in the case of A-Gel Me becomes immeasurable).

The exchange capacity of natural phillipsites in relation to different ions evaluated using the results of chemical analysis is in the range of 1.5-3.3 meq/g, at least by 30% lower in comparison to 4.5 meq/g of the synthetic sodium phillipsite $Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$ applied for preparation of surfactant-modified material [15]. The cation exchange capacity of sodium-, potassium, and ammonium-enriched forms prepared from natural phillipsites is given in the Table 4; the sample P-Shu, which has nearly the same Si/Al ratio as P-Akh, but is characterized by higher content of potassium and demonstrates the highest capacity not only in relation to potassium.

The cation composition of sodium-, potassium, and ammonium-enriched forms of natural phillipsites is given in Table 5. Impurity compensating metals are removed during ion exchange treatment, bivalent cations are not involved in the process of exchange of monovalent ions.

Ion exchange isotherms for the $Na^+\leftrightarrow K^+$ and $Na^+\leftrightarrow NH_4^+$ reactions belong to the ***a***-type and prove high selectivity towards NH_4^+ and K^+ ions; participation of bivalent ions results in the ***b***- and ***c***-type isotherms. The selectivity sequences depend on the origin of zeolite: $K^+>NH_4^+>>Ca^{+2}>Mg^{+2}$ for the P-Akh and P-Tsi samples with low content of potassium and high content of calcium and magnesium, while for the P-Shu sample with comparatively high content of potassium the sequence is as follows: $NH_4^+>K^+>Na^+>>Ca^{+2}>Mg^{+2}$.

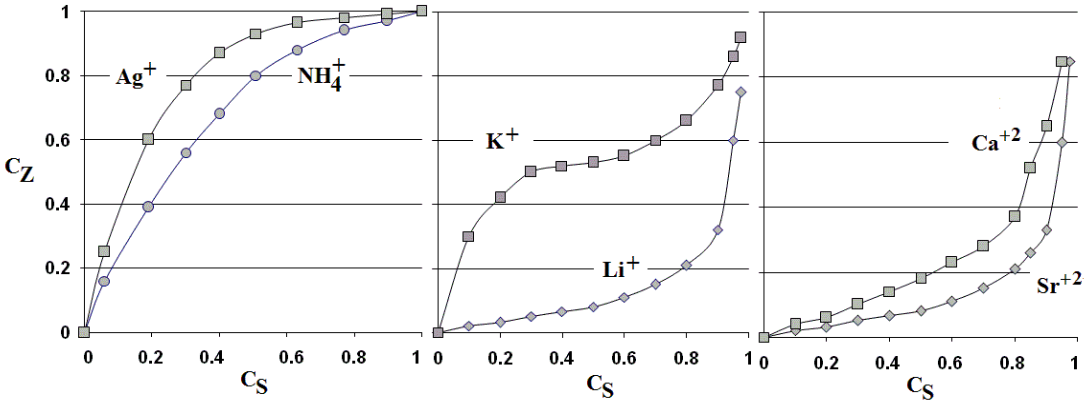


Figure 1. Ion exchange isotherms on analcime.

Table 3

Characterization of analcime cationic forms.

Ion exchange reaction	*Cation content*	*CEC (meq/g)*	*Si/Al*	*n (H_2O/unit cell)*	*V (cm^3/cm^3)*
$(K^+, Ca^{+2}, Mg^{+2})\leftrightarrow Na^+$	$Na_{12.5}K_{0.3}Ca_{0.65}Mg_{0.95}$	4.10	1.90	19.2	0.070
$Na^+\leftrightarrow K^+$	$Na_{7.0}K_{7.5}Ca_{0.6}Mg_{0.9}$	2.0	1.875	18.0	0.050
$Na^+\leftrightarrow Ag^+$	$Na_{8.8}Ca_{0.5}Mg_{0.9}Ag_{5.8}$	1.7	1.90	17.5	0.061
$Na^+\leftrightarrow NH_4^+$	$Na_{9.0}Ca_{0.6}Mg_{0.8}(NH_4)_{5.6}$	1.6	1.90	17.8	0.044
$Na^+\leftrightarrow$ ½ Ca^{+2}	$Na_{10.6}Ca_{1.75}Mg_{0.95}$	0.7	2.00	18.6	0.031
$Na^+\leftrightarrow$ ½ Sr^{+2}	$Na_{11.8}Ca_{0.5}Mg_{0.9}Sr_{0.7}$	0.5	1.90	18.5	0.027
$Na^+\leftrightarrow Li^+$	$Li_{1.0}Na_{12.0}Ca_{0.6}Mg_{0.9}$	0.3	1.95	18.3	0.012

Table 4

Cation exchange capacities of phillipsite cationic forms.

Sample	*CEC of Na-form (meq/g)*	*CEC of K-form (meq/g)*	*CEC of NH_4-form (meq/g)*
P-Akh	1.5	1.9	2.2
P-Tsi	1.7	1.7	2.6
P-Shu	2.0	3.3	3.2

Table 5

Cationic composition of sodium-, potassium-, and ammonium-enriched forms of phillipsite.

Sample	*Na-form*	*K-form*	*NH_4-form*
P-Akh	$Na_{3.5}Ca_{0.16}Mg_{0.24}$	$K_{3.3}Ca_{0.2}Mg_{0.3}$	$Ca_{0.30}\,Mg_{0.25}\,(NH_4)_{3.2}$
P-Tsi	$Na_{3.5}Ca_{0.10}Mg_{0.25}$	$K_{3.2}Ca_{0.15}Mg_{0.35}$	$Ca_{0.15}\,Mg_{0.3}\,(NH_4)_{3.3}$
P-Shu	$Na_{3.6}K_{0.3}Ca_{0.1}Mg_{0.2}$	$Na_{0.1}\,K_{3.9}\,Ca_{0.1}\,Mg_{0.15}$	$Na_{0.1}\,Ca_{0.1}\,Mg_{0.25}\,(NH_4)_{3.7}$

The process of ion exchange on natural scolecite leads to almost total removal of impurity metals and significant removal of sodium and potassium; the cation composition of the products can be expressed by the formula A_aCa_c, where A is a substituting metal. Results of the chemical analysis of the products obtained are indicative of the conservation of the Si/Al ratio. The negative charge of the crystal lattice retains its value of –15.6 for the cell containing 24 silicon and 80 oxygen atoms. The cation exchange capacity of natural scolecite is increasing with the rise of temperature, for monovalent cations these dependencies have different inclinations (Figure 2), resulting in the change of the selectivity sequence from $Rb^+>Cs^+>K^+>NH_4^+$ at temperatures below 70°C, to $Cs^+>Rb^+>NH_4^+>K^+$ for higher temperatures. In the case of bivalent cations the temperature dependence of capacity is linear and can be expressed as $CEC = CEC_{20} + B\Delta t$, where CEC_{20} is the cation exchange capacity at 20°C, empirical coefficient B = (5±0.3) μeq/g°C, Δt = (t – 20)°C, t – temperature of solution (°C). Cation exchange capacity is high for heavy alkali, alkaline earth and transition metals, but there is no strict correlation between capacity and mass or ionic radii of substituting cations [16] (Figure 3).

Low-temperature cation exchange capacity (CEC_{20}) and degree of substitution (expressed as a share of 5.0 meq/g for total substitution of compensating cation of natural scolecite) by different cations are given in Tables 6 (monovalent cations) and 7 (bivalent cations).

According to the percentage substitution values, the selectivity sequence of studied metals by natural scolecite at low temperatures can be given as $Sr^{+2}>Ba^{+2}>Rb^{+}>Ca^{+2}>Cs^{+}>K^{+}>NH_4^{+}>Na^{+}>Mg^{+2}>Li^{+}>Cd^{+2}>Cu^{+2}>Mn^{+2}>Zn^{+2}>Co^{+2}>Ni^{+2}$. Values of low-temperature capacities relative to the heavy metals correspond to ones obtained in [9] for natural scolecite collected from Bayouda desert, Sudan, but the selectivity sequence is slightly different: $Ni^{+2}> Cd^{+2} > Zn^{+2}$.

The cation exchange capacity under dynamic conditions (DCEC) depends on temperature, concentration of solution, and its flow rate. The temperature dependences shows the same behaviour as in static conditions, including changes in selectivity of ion pairs Rb^+ – Cs^+, and K^+ – NH_4^+. The concentration dependence (Figure 4) show maximum at 1 N solutions, with the exception of lithium presenting the highest substitution when a solution of 0.5 N concentration passes through the column.

The dynamic exchange capacity decreases with increasing flow rate. For monovalent cations this dependence is characterized by inexact extrapolation to CEC values at a zero flow rate. The curves have different slope, the strongest for potassium ions (Figure 5*(a)*), changing selectivity: $K^+>NH_4^+$ at comparatively low flow rates, and $NH_4^+>K^+$ when the solution passes through the column with increased flow rate. In the case of bivalent cations dependence of the dynamic cation exchange capacity on the flow rate is linear (Figure 5*(b)*), and can be expressed as $DCEC=CEC–bv$, where CEC – cation exchange capacity under static conditions at corresponding temperature, empirical coefficient b=(60±10) μeq·min/g·mL, v – flow rate (mL/min).

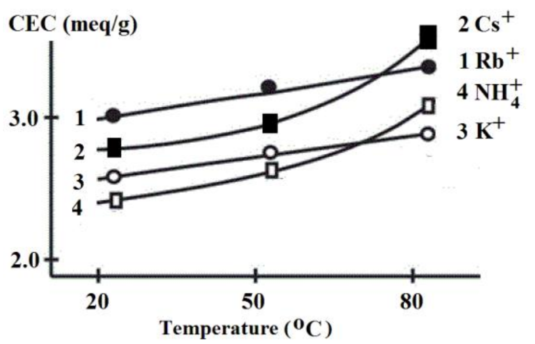


Figure 2. CEC at different temperatures.

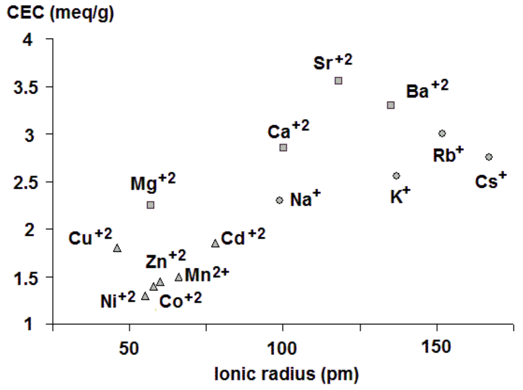


Figure 3. Exchange capacity versus ionic radius.

Table 6

Cation exchange capacity and degree of substitution by monovalent metals in scolecite.

Ion	*Rb^+*	*Cs^+*	*K^+*	*NH_4^+*	*Na^+*	*Li^+*
CEC_{20} (meq/g)	3.0	2.75	2.55	2.5	2.3	1.9
Substitution (%)	60	55	51	50	46	38

Table 7

Cation exchange capacity and degree of substitution by monovalent metals in scolecite.

Ion	Sr^{+2}	Ba^{+2}	Ca^{+2}	Mg^{+2}	Cd^{+2}	Cu^{+2}	Mn^{+2}	Zn^{+2}	Co^{+2}	Ni^{+2}
CEC_{20} (meq/g)	3.55	3.3	2.85	2.25	1.85	1.8	1.5	1.45	1.4	1.3
Substitution (%)	71	66	57	45	37	36	30	29	28	26

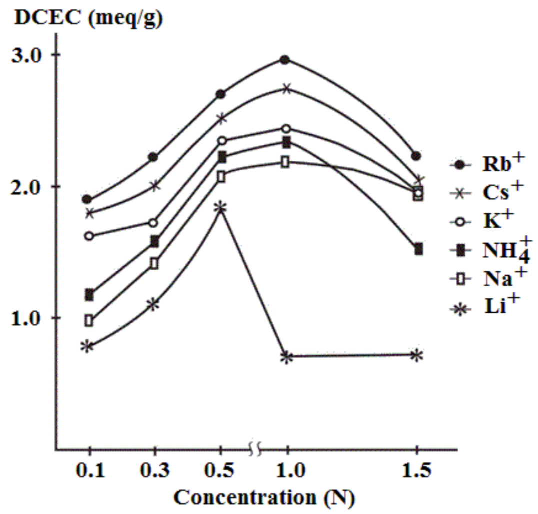
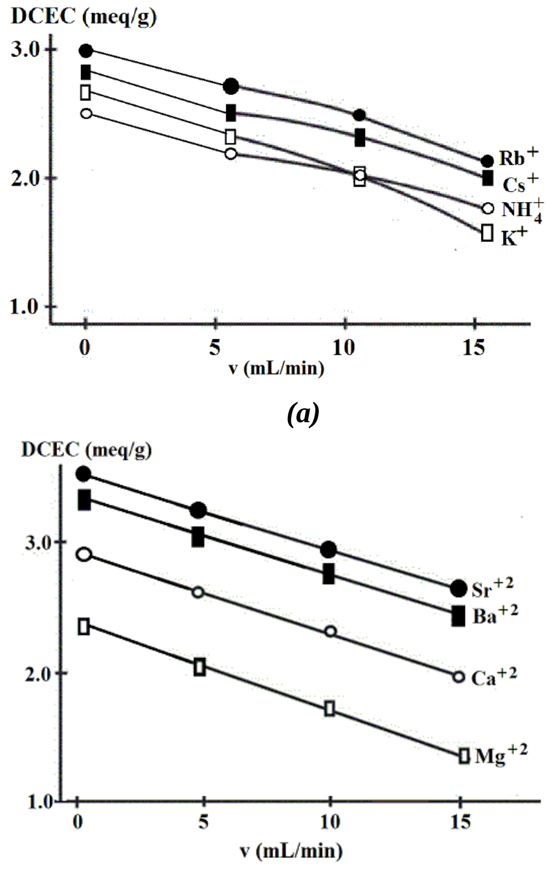


Figure 4. Dynamic ion exchange capacity of Georgian scolecite for monovalent cations at different concentration of solutions.



(a)

(b)

Figure 5. Dynamic ion exchange capacity of Georgian scolecite for monovalent *(a)* and bivalent *(b)* cations at different flow rates.

Conclusions

The exchange capacity of analcimes is higher for sodium cations (4.1 meq/g), decreasing in the following series: $Na^+ > K^+ > Ag^+ > NH_4^+ > Ca^{+2} > Sr^{+2} > Li^+$; the selectivity sequence for the sodium-enriched form is as follows: $NH_4^+ > Ag^+ > Li^+ > Ca^{+2} > K^+ \sim Sr^{+2}$.

The ion exchange capacity of natural phillipsites is up to 3.3 meq/g, ion exchange isotherms prove high selectivity towards NH_4^+ and K^+, however the selectivity sequences depend on the origin of zeolite: $K^+ > NH_4^+ >> Ca^{+2} > Mg^{+2}$ for samples with comparatively low-, and $NH_4^+ > K^+ > Na^+ >> Ca^{+2} > Mg^{+2}$ for high K-content.

The strong temperature dependence of scolecite exchange capacity towards Cs+ and NH_4^+ ions leads to a change in the selectivity sequence: $Rb^+ > Cs^+ > K^+ > NH_4^+$ at temperatures below 70°C, and $Cs^+ > Rb^+ > NH_4^+ \ K^+$ at higher temperatures. The cation exchange capacity under dynamic conditions is the highest for 1 N solutions (0.5 N for lithium), and decreases with increasing flow rate. The total selectivity sequence of studied metals at low temperatures and under static conditions is $Sr^{+2} > Ba^{+2} > Rb^+ > Ca^{+2} > Cs^+ > K^+ > NH_4^+ > Na^+ > Mg^{+2} > Li^+ > Cd^{+2} > Cu^{+2} > Mn^{+2} > Zn^{+2} > Co^{+2} > Ni^{+2}$, at high flow rates (v > 10 mL/min) the selectivity sequence should be corrected swapping potassium and ammonium.

The obtained results showed that Georgian natural zeolites – analcime, phillipsite, and scolecite, can be effectively used as ion exchangers and substitute because of their availability and comparatively low cost can, other synthetic materials in local industrial and environmental applications.

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