Scientific Annals, School of Geology, Aristotle University of Thessaloniki Proceedings of the XIX CBGA Congress, Thessaloniki, Greece	Special volume 100	81-87	Thessaloniki 2010

CONTINUOUS EXTRA-FRAMEWORK Na^+ RELEASE FROM GREEK ANALCIME-RICH VOLCANICLASTIC ROCKS ON EXCHANGE WITH NH_4^+

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Abstract: The continuous extra-framework cations release from Greek analcime-rich rock sample was studied, upon ammonium acetate exchange experiments (agitation time 0.25-720 hours), using atomic absorption spectrometry. The analcime-rich material was examined by X-ray powder diffraction, scanning electron microscopy equipped with energy dispersive micro-analytical system and atomic absorption spectrometry. Its sorption ability was measured using the Ammonium Acetate Saturation method. The monovalent cations K^+ and Na^+ after 720 hours, show only 7 and 10% of exchange, respectively. No steady state achieved for Na^+. The bivalent cations Ca^{2+} and Mg^{2+} show better exchange, 97% for Ca^{2+} and 62% for Mg^{2+}. The calculated rate of ion-exchange was 0.01 ppm/h for K^+ and Mg^{2+}, while 0.13 ppm/h for Na^+ and Ca^{2+}. The recorded behaviour on the multi-component ion-exchange system and the linear release of Na^+ over NH_4^+ observed at a slow rate of ion-exchange, can allow us to propose studied analcime-rich rock as a potential material for waste-water purification and pet litter.

Keywords: tuffs, cation exchange capacity, selectivity, potential uses.

1. Introduction

The analcime structure is made up of linked tetrahedral units proscribing three on-connected channels (Szostak, 1992). Analcime has a relatively compact structure compared with other zeolites and has an idealized unit cell of $Na_{16}(Al_{16}Si_{32}O_{96})16H_2O$ (e.g., Meier et al., 1996; Baerlocher et al., 2001). The cubic unit cell is composed of four-, six-, and eight-membered oxygen rings that form three non-intersecting channels with pore openings of 2.6 Å. These channels encompass 24 small cavities, of which 16 are occupied by sodium cations (Saha, 1959). Analcime has maximum cation exchange capacity 4.9 meq g^{-1} (Sherman, 1978). Small pore zeolites, such as analcime, can constitute a basis for possible future technical innovations in selective adsorption and heterogeneous catalysis (Cheng et al., 2000).

High quality natural zeolites have many applications in industry, agriculture and the environment (e.g., Mumpton, 1978; Pond and Mumpton, 1984; Dyer, 1988; Tsitsishvili et al., 1992; Misaelides et al., 1993; Holmes, 1994; Ming and Mumpton, 1995; Misaelides et al., 1995a,b; Filippidis et al., 1996; Godelitsas et al., 1996a,b; Bish and Mind, 2001). The great majority of these applications employs their cation exchange capabilities and involves the replacement of the existing extra-framework cations with other cations from the surrounding environment. Due to the favourable ion-exchange selectivity of natural zeolites for certain cations, these minerals have been studied for potential use in the treatment of nuclear, municipal and industrial wastewaters and acid mine drainage waters. It is of economic importance that natural zeolites are used in their natural state so that expensive purification is avoided.

The aim of this work is to study the outgoing cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) of analcime-rich volcaniclastic rocks during cation exchange with NH_4^+. The NH_4^+ was selected as the cation of choice as the affinity of zeolites for this cation has led to it being exploited for multiple applications such as in waste water treatment, pet litter and aquaculture. It is also used in the recognized AMmonium Acetate Saturation (AMAS) method (Bain and Smith, 1987) for the determination of the sorption ability of zeolites. Studies to evaluate how a natural zeolite exchanges with a single-cation or a multi-cation solution often use the Na- exchanged form of the zeolite, which has been shown to lead to higher cation exchange capacities (Yang et al., 1997). Results of these studies however are not applicable where the zeolite will be used in its natural form. Also, most published ion-exchange data on natural zeolites involve the exchange of two cations only. Little attention has been paid to the problem of understanding multi-component ion-exchange equilibrium, despite the fact that ion-exchange processes in natural systems, generally involve more than two ions. In this paper, the exchange of the extra-framework cations Na^+, K^+, Ca^{2+} and Mg^{2+} found in the natural zeolite with a solution of ammonium acetate (NH_4AcOH), as the source of NH_4^+ cations, is studied. Greek analcime-rich rock was selected due to its high zeolite content in order to study its different rates of exchange, while the results of this work are directly connected to the potential applications of the particular Greek zeolite bearing-rock.

2. Materials and Methods

Analcime-rich (AR) volcaniclastic rock sample was taken from the Neogene sedimentary Karlovassi basin of Samos island. The basin's volcanic rocks have been extensively zeolitized to give HEU-type, analcime, chabazite, phillipsite and mordenite of which HEU-type and analcime are the most abundant (e.g., Stamatakis, 1989; Hall and Stamatakis, 1992; Pe-Piper and Tsolis-Katagas, 1991; Kantiranis et al., 2004).

The sample was studied in its bulk form, ground (<125 μm) and homogenized. Sample for mineralogical and chemical analyses was ground further in an agate mortar. Chemical analysis of sample was carried out by AAS on a Perkin Elmer 5000 spectrometer equipped with a graphite furnace. Electron probe microanalysis of the studied zeolite phase was performed on polished thin sections of the zeolite-rich rocks by SEM-EDS (Jeol JSM-840: A scanning electron microscope, equipped with a LINK 10000 AN Energy Dispersion Analyser). Corrections were made using the ZAF-4/FLS software provided by LINK. To minimize volatilization of alkalis in the zeolites framework, the electron beam spot size was enlarged and the counting time decreased. Different minerals (micas, carbonates, feldspars) and pure metals were used as probe standards.

The experimental procedure for the cation exchange experiments entailed placing 100 mg zeolite-rich sample (<125 μm) and 10 mL of 1N ammonium acetate (of pH 7.0) solution into screw-top glass tubes. The tubes were sealed and agitated for 0.25, 0.75, 1.25, 2, 4, 6, 8, 12, 18, 24, 36, 48, 72, 96, 120, 144, 168, 192, 216, 240 and 720 h. The mixtures were then centrifuged and the liquor decanted into a 200 mL volumetric flask. The solid was then washed with 10 mL of deionised water three times and the washings were combined with the liquor and the volume adjusted to 200 mL. The concentration of Na^+, K^+, Ca^{2+} and Mg^{2+} cations in this solution was analyzed by AAS on the Perkin Elmer 5000 spectrometer.

The mineralogical composition of the sample was determined by X-ray Powder Diffraction (XRPD) method. The XRPD analysis was performed using a Philips PW1710 diffractometer with Ni-filtered CuK_α radiation on randomly oriented samples. The counting statistics of the XRPD study were: step size: 0.01° 2θ, start angle: 3°, end angle: 63° and scan speed: 0.02° 2θ/sec. Quantitative estimates of the abundance of the mineral phases were derived from the XRPD data, using the intensity of a certain reflections and external standard mixtures of minerals.

In order to determine the sorption ability of the studied zeolite-rich sample, the sample was treated with 1M ammonium acetate (NH_4OAc) aqueous solution, according to the AMAS method. Approximately 125 mg of the <125 μm sample was added to a centrifuge tube with 10 mL of the 1N NH_4OAc solution. The suspension was well shaken, agitated for 24 hours, and then centrifuged. The clear liquid was discarded and the NH_4OAc-saturation procedure repeated 9 times, adding fresh 10 mL of NH_4OAc solution each time. After the completion of the 10-day NH_4OAc-saturation, the excess NH_4OAc was washed with 10 mL of 99% isopropyl alcohol, well shaken, and centrifuged. The clear supernatant liquid was discarded and the procedure repeated five times. The sample then was dried in room temperature. Following the NH_4OAc saturation, the NH_4^+ ions retained by the zeolite-rich sample, are converted using a strong base to NH_3 and analysed by an ammonia electrode. The NH_3 concentration was determined using an Orion potentiometric ammonia gas electrode combined with a Jenway 3045 pH/mV/ion analyser. Each air-dried NH_4^+-saturated sample was placed in a 100 mL Pyrex beaker containing a

Teflon covered stirring bar. Deionised nitrogen-free water (50 mL) was added and the solution was stirred to suspend the sample. The electrode was immersed into the suspension taking care to prevent entrapment of air under the concave tip. By addition of 0.5 mL of 10M NaOH, the NH_3 measurements were taken at constant level achievement. The electrode calibration was performed daily using ammonium calibrating solutions of 10, 100 and 1000 ppm provided by Jenway and hourly using the 10 ppm ammonium solution.

3. Results and Discussion

The quantitative mineralogical composition of the studied zeolite-rich sample is shown in Table 1. Analcime, micas (muscovite and/or illite) and clay minerals (mainly smectite) constitute the microporous minerals of the zeolite-bearing rock. The non-microporous minerals found in studied sample are quartz and feldspars. This classification is based on their ability to sorb cations on their structure. Amorphous material (volcanic glass) was also determined in the sample (10 wt %). The analcime content was determined 71 wt %., while in minor amounts micas (5 wt %), and clay minerals (2 wt %, mainly smectite) were also found. The total microporous mineral content in sample AR was 78 wt %.

Table 1. Quantitative mineralogical composition (wt %) of the studied sample.

Sample	A	M	Cl	TMM	Q	F	Am
AR	71	5	2	78	4	8	10

AR: analcime-rich, A: Analcime, M: Muscovite and/or illite, Cl: Clay minerals (mainly smectite), TMM: Total microporous minerals (Zeolite+M+Cl), Q: Quartz, F: Feldspars, Am: Amorphous.

The chemical composition of the studied zeolite-rich sample is shown in Table 2. AR sample was containing 56.11 wt % SiO_2, while the Al_2O_3 content was measured 18.80 wt %. Low amounts (<0.20 wt %) of TiO_2 and MnO were also found, while the Fe_2O_{3T} content was measured 2.98 wt %. The total percentage of oxides of the exchangeable cations Na^+, K^+, Ca^{2+} and Mg^{2+} was 12.07 wt %, with Na^+ being the main exchangeable cation. Loss on ignition was measured 9.43 wt %.

In Table 3 the measured sorption ability (meq/100g), the theoretical and the expected C.E.C. (meq/100g) of the studied zeolite-rich sample are given. The measured sorption ability was derived experimentally by the AMAS method. The theoretical C.E.C. of the sample was calculated from the quantitative mineralogical composition using values of 454 meq/100g for analcime, 20 meq/100g for muscovite-illite and 100 meq/100g for smectite (Mumpton, 1977; Deer et al., 1992). The expected C.E.C. was calculated from the total extra-framework cations of the contained zeolite, measured by SEM-EDS (Table 4). For the calculations of the theoretical and expected C.E.C. values the results were modified according to the zeolite content of the rock.

The measured sorption ability of the sample was too close to the expected C.E.C., meaning that the main process involving the sorption procedure of the studied sample was the ion-exchange.

Table 3. Values (meq/100g) of measured sorption ability, theoretical and expected C.E.C. of the studied sample.

Sample	Measured sorption ability	Theoretical C.E.C.[a]	Expected C.E.C.[a,b]
AR	334	325[c]	329

[a] Values modified according to TMM content (zeolite+micas+clay minerals) of the sample, [b] Measured from the zeolite micronalysis (by SEM-EDS), [c] Amorphous ability to sorb ions was ignored.

3.1. *The ion-exchange of extra-framework cations for NH_4^+*

The cation exchange behaviour of the zeolite-rich sample was investigated in order to determine which of the exchangeable ions is released first, the rate and the total amount of exchangeable cation occurs at the steady state, and the influence of the multionic system on the exchange behaviour. The SEM-EDS analyses gave accurate zeolite’s chemical formula in the sample (several readings were taken for each zeolite and the average values tabulated in Table 4) providing clear data on how many and what species of potential exchangeable cations are contained in the zeolite structure and also the number of water molecules associated with the zeolite. The positions of both extraframework-cations and water molecules depend on the nature of the exchangeable cations of

Table 2. Chemical composition (wt %) of the studied sample.

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_{3T}	MnO	MgO	CaO	Na_2O	K_2O	LOI	Total
AR	56.11	0.19	18.80	2.98	0.10	0.50	0.94	6.36	4.27	9.43	99.68

AR: Analcime-rich, LOI: Loss of ignition (at 1050ºC for 2 hours).

the zeolites (Armbruster and Gunter, 1991; Gunter et al., 1994). However, the exact structural arrangement in the channels also depends on the specific Si/Al framework distribution and the water content, which is dependent on the water vapour pressure surrounding the sample. Thus, the exchangeable cations and channel water molecules are interdependent. Changes in cation composition cause changes in the amount and structural distribution of water molecules; likewise, changes in channel water content affect the positions of the channel cations (Bish and Boak, 2001).

Table 4. Formulae and total exchangeable cations (ppm) of the studied zeolite.

Sample	Formulae	Total exchangeable cations			
		Na^+	K^+	Ca^{2+}	Mg^{2+}
AR	$(Mg_{0.20}Ca_{0.28}K_{0.58}Na_{14.97})(Fe_{0.15}Al_{15.80}Si_{31.92}O_{96})\cdot 16H_2O$	913	60	30	13

Micas and clay minerals (mainly smectite) found in AR sample also contain alkaline and alkaline earth exchangeable cations. However, due to their small weight percentages in contrast with the zeolite content of the rock, for the purpose of this discussion it is assumed that the cations released originate from the zeolite phase only.

The kinetic curves of AR sample for cation exchange of Na^+, K^+, Ca^{2+} and Mg^{2+} were presented in Figures 1(a)-1(d). Statistical analysis of the data was obtained using Microcal Origin v.6.0 software, while statistical models and correlation coefficients (R^2) were shown in each figure.

The release of Na^+ cations from sample AR (Fig. 1a) was linear with time over the whole 30 days (720h) period studied and a steady state was not reached. However, it is known that analcime, which has a dense structure, non-intersecting channels and small individual cavities, exhibits very limited ion exchange of its Na^+ for other cations. Particularly, at room temperature analcime does not readily exchange, but at elevated temperatures Na can be completely exchanged by other cations such as K^+ and NH_4^+ (Vaughan, 1978). Balgord and Roy (1974) reported that Na-analcime can be completely exchanged by K^+, Ag^+ ,Tl^+, NH_4^+ and Rb^+ cations at elevated temperatures, whereas only small amounts of Sr^{2+}, Mg^{2+}, Ni^{2+} and Co^{2+} move into analcime.

Despite the slow exchange, the sorption ability value of 334 meq/100g obtained, using the AMAS technique, is very close to the expected value of 329 meq/100g calculated from the total percentage of extra-framework cations within the analcime structure (Tables 3 and 4). The very low degree of exchange observed in our experiment is probably due to the fact that AR zeolitic material being contacted with the same ammoniacal solution for 30 days. The AMAS method significantly improves the rate of cation exchange by replacing the solution every 24 hours for 10 days thus encouraging cation exchange by removing any competing cations from solution.

After 30 days (Fig. 1b) the concentration of K in solution was 4 ppm (Table 5) indicating the exchange of only 7 % of K^+ cations found in the aluminosilicate framework (Table 4). Bivalent cations Ca^{2+} and Mg^{2+} show better exchange. The Ca^{2+} concentration achieve a steady state of 29 ppm (Table 5) after 216 hours of agitation (Fig. 1c) indicating an almost fully exchange (97%) of Ca^{2+} cations found in analcime framework (Table 4). On the other hand, Mg^{2+} did not achieve a steady state (Fig. 1d), but after 30 days (720 h) its concentration was 8 ppm (Table 5), indicating the exchange of 62% of Mg^{2+} cation found in the analcime framework (Table 4). No steady state achieved for Na^+ (Fig. 1a) and only a percentage of 10% was exchanged from the structure of analcime (Tables 4 and 5).

In Table 5 the agitation time (h), the cation concentration (ppm), the degree of cation exchange (%) and the rate of exchange (ppm/h) once a steady state has been achieved, were summarized for sample AR.

Taking into consideration all the above data, the order of cation release from AR sample, is: Ca^{2+}

Table 5. Ion-exchange statistics for analcime-rich sample.

Extra framework ion	Na^+	K^+	Ca^{2+}	Mg^{2+}
Agitation time until steady state (h)	No steady state	290	216	720
Concentration at steady state (ppm)	After 720 h: 94	4	29	8
Degree of exchange (%)	10	7	97	62
Rate of exchange (ppm/h)	0.13	0.01	0.13	0.01

$>K^+>>Mg^{2+}>>>Na^+$, while the order of the degree of total cation release, is: $Ca^{2+}>Mg^{2+}>>Na^+\approx K^+$. Furthermore, the rate of ion-exchange was calculated for K^+ 0.01 ppm/h, for Ca^{2+} 0.13 ppm/h, for Mg^{2+} 0.01 ppm/h, while Na^+ exchanged in a constant rate of 0.13 ppm/h (Table 5). Using this rate of ion-exchange, the order for sample AR, is: $Na^+=Ca^{2+}>>K^+=Mg^{2+}$. Dyer and Yusof (1989) suggest a systematic-continuous replacement of Na^+ by NH_4^+ in analcime structure, which reduces the water content of analcime.

The linear release of Na^+ over NH_4^+ observed at a slow rate of ion-exchange in our experiments, can allow us to propose studied analcime-rock as a potential material for waste-water purification and pet litter. Analcime can act as an ion sieve (Barrer, 1950; Barrer and Hinds, 1953; Ames, 1966; Balgord and Roy, 1971; Moroz et al., 1998; Seryotkin et al., 2000; Likhacheva et al., 2002), while Dyer and Yusof (1987; 1989) carried out extensive studies on cation and water self-diffusion, concluding that analcime has the potential for use in the storage and disposal of titrated water.

4. Conclusions

The exchange of the extra-framework cations Na^+, K^+, Ca^{2+} and Mg^{2+} found in Greek zeolite-rich rock was studied in its natural form in order to determine its ion exchange behaviour. It is of great importance to understand the behaviour of a multi-component ion-exchange system, because processes of ion removal in natural systems, generally involve more than two ions. Zeolite-rich sample has analcime content 71 wt %. Na^+ was the main exchangeable cation. Loss of ignition was measured 9.43 wt %.

The exchange of initial cations occurs very slow. Monovalent cations K^+ and Na^+ show over the whole period of the experiments (720 hours), only 7 and 10% of exchange, respectively. No steady state achieved for Na^+. Bivalent cations Ca^{2+} and

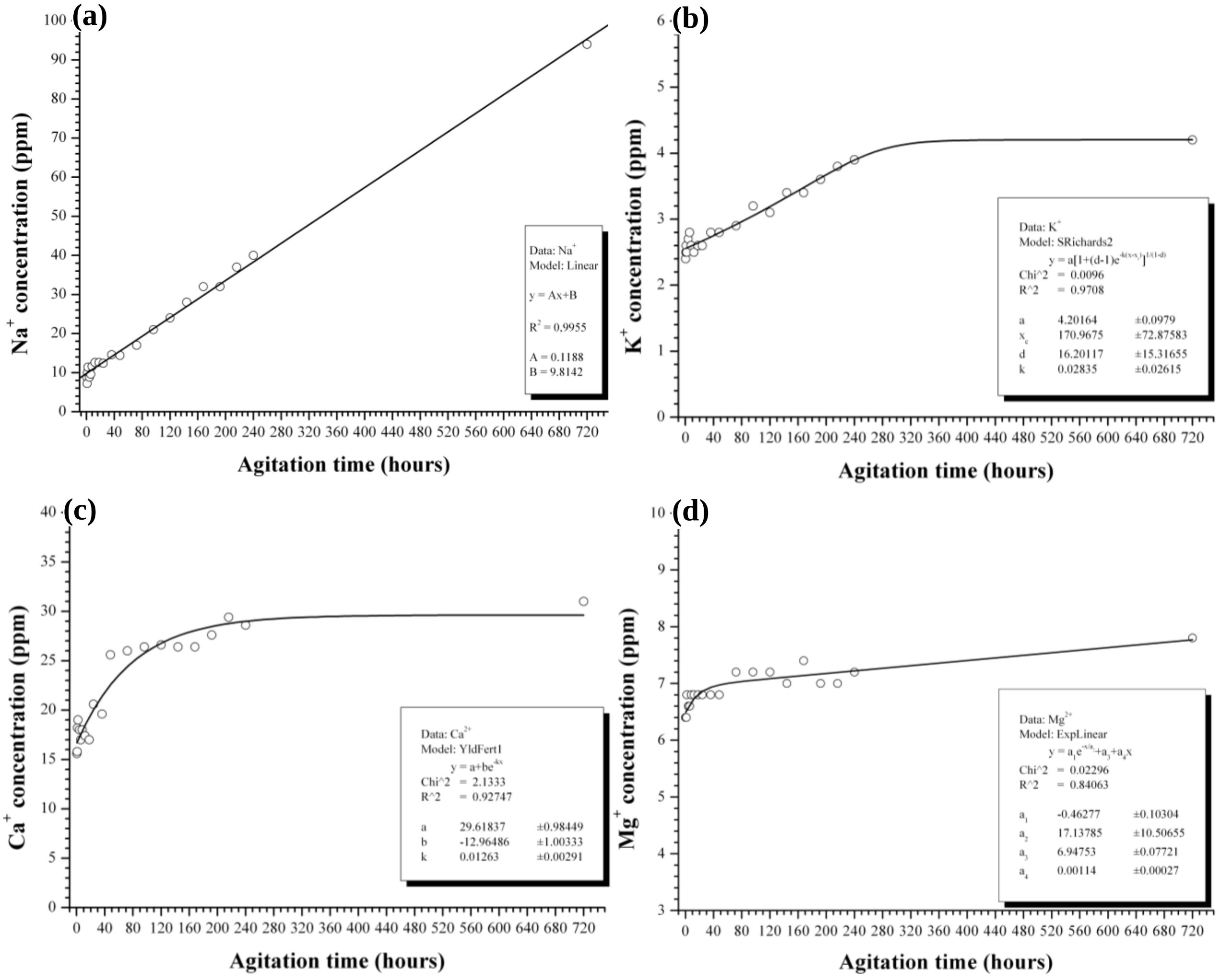

Figure 1(a-d). Kinetic curves of (a) Na^+, (b) K^+, (c) Ca^{2+} and (d) Mg^{2+} for the AR sample.

Mg^{2+} show better exchange. The Ca^{2+} was almost fully exchanged (97%), while Mg^{2+}, despite that did not achieve a steady state after the end of experiments (720 hours), shows an exchange of 62%. The rate of ion-exchange was calculated for K^+ 0.01 ppm/h, for Ca^{2+} 0.13 ppm/h, and for Mg^{2+} 0.01 ppm/h. Na^+ was exchanged in a continuous constant rate of 0.13 ppm/h. Thus, using the rate of ion-exchange, the order for sample AR, is: $Na^+ \approx Ca^{2+} >> K^+ \approx Mg^{2+}$.

The continuous release of Na^+ over NH_4^+ observed at a slow rate of ion-exchange in our experiments, can allow us to propose studied analcime-rich rock as a potential material for waste-water purification and pet litter.

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