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NH₄⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ exchange for Na⁺ in a sedimentary clinoptilolite, North Sardinia, Italy

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Abstract

Recent findings of clinoptilolite-bearing volcanoclastic deposits in northern Sardinia promoted a study aimed at evaluating the cation exchange properties of this zeolite in view of a possible future utilization of the parent rock.

Isotherms of NH₄⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ exchange for Na⁺ at 25°C and 0.1 total normality were obtained and the related thermodynamic quantities K_a and ΔG^0 computed. The maximal exchange level was in any case less than 100% for each cation investigated. Good selectivities were recorded for NH₄⁺ and Pb²⁺, whereas clinoptilolite proved to be unselective for Cu²⁺, Zn²⁺ and Cd²⁺. The cation selectivity sequence NH₄⁺>Pb²⁺>Na⁺>Cd²⁺>Cu²⁺≈Zn²⁺ was obtained.

The results are discussed in the light of literature data, and contrasting performances of various clinoptilolites were ascribed to different cationic compositions of the minerals, due to different mineralogical conditions, which were proved to affect both cation exchange capacity and selectivity. This led to the conclusion that any practical utilization of a clinoptilolite-rich rock as cation exchanger should be preceded by basic studies on representative samples from the deposit under examination. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ammonium; Cadmium; Cation exchange; Clinoptilolite; Copper; Lead; Zinc

1. Introduction

Large occurrences of clinoptilolite-bearing rocks have been found recently in the northern part of Sardinia, Italy [1–4]. These deposits, spread over an area of several hundreds of square kilometers in the Logudoro region, are characterized by an outcropping succession of volcanoclastic and

epiclastic terms. The zeolitized volcanoclastic facies, ranging from 10 to 20 m in thickness, are represented by welded rhyolitic–rhyodacitic ignimbrites, whereas the zeolitized epiclastic terms, averaging about 5 m in thickness, are constituted by a smoothly welded fluvial–lacustrine deposit. Both types of occurrence are clinoptilolite-rich with zeolite contents ranging from 30 to 60% in the volcanoclastites and from 40 to 80% in the epiclastites [5].

Currently, the use of clinoptilolite-rich rocks

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for environmental protection is a matter of active investigation all over the world, especially in connection with the removal of ammonium from municipal sewage and radionuclides, i.e. Cs and Sr, from wastes of nuclear power plant stations [6]. Clinoptilolite is potentially able to remove other noxious and toxic cations, but the literature on this subject is limited and poorly coherent [7–13], which prevents one at present from drawing conclusions on a more general utilization of this zeolite for environmental purposes.

With the objective of finding possible applications of the Sardinian clinoptilolite resources, a research program has been initiated with the aim to better understand the behavior of the zeolite contained in the parent rock as a cation exchanger. More specifically, the present study is dealing with the exchange equilibria of the pre-exchanged Na-form of the Sardinian clinoptilolite with some hazardous cations, such as NH_4^+ , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} .

2. Experimental

2.1. Materials and their characterization

The material investigated was collected at Orvitoro (near Sassari) from an outcrop belonging to the epiclastic deposit (see above). The rock mineralogy was investigated by X-ray powder diffraction (Philips PW1730). The zeolite grade was obtained through the reference intensity ratio (RIR) procedure [14].

Pure clinoptilolite was separated from the parent rock by enrichment processes, based on the greater friability and lower density of the zeolite relative to other rock constituents [15]. The purity of the separated specimen was checked using an X-ray Gandolfi Camera. The chemical analysis of clinoptilolite was performed by electron microprobe analysis (Cameca SX50). The water content was measured thermogravimetrically (Netzsch STA 409 thermoanalyzer).

2.2. Ion exchange

The cation exchange capacity (CEC) of clinoptilolite was measured using the cross-exchange

method, based on the evaluation of the exchangeable cations by elution of the zeolite with a 0.5 M NaCl or KCl (Carlo Erba reagent grade) solution [16]. The concentration of the outgoing cations was measured by atomic absorption spectrophotometry (AAS, Perkin Elmer 2100).

Clinoptilolite was exchanged into its sodium form by percolation with a 0.5 M NaCl solution, prepared using a Carlo Erba reagent-grade chemical, up to complete elution of the parent cations (K^+ , Mg^{2+} , Ca^{2+}). In order to minimize the amount of K impurities in the zeolite, the elution was improved using a solution made from extra-pure NaCl (Aldrich Chemicals, purity: 99.999%).

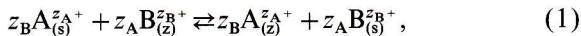
Cation exchange isotherms were obtained by allowing the sodium form of clinoptilolite to react at $25 \pm 0.1^\circ\text{C}$ in sealed PVC test tubes with solutions containing varying amounts of Na^+ and one of the cations NH_4^+ , Cu^{2+} , Zn^{2+} , Cd^{2+} or Pb^{2+} at a total normality of 0.1. The solutions were prepared starting from reagent-grade Carlo Erba NH_4Cl , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and NaNO_3 . Reversibility tests of ion exchange were performed following the recommendations of Fletcher and Townsend [17]. The solid-to-liquid ratio ranged from 1/70 to 1/100. The reaction time was fixed at 3 days, which was proved beforehand to be sufficient for reaching equilibrium.

The ingoing and outgoing cations were measured either in the liquid or in the solid phase. In the former case, titration with EDTA was used for the heavy metals [18], whereas ammonium was determined using the classic Nessler procedure [19]. The possible presence in the solution of other cations, coming from the solid phase, was checked by AAS. Solids were analyzed by dissolving them in HF/HClO_4 . The concentrations of the various cations in the solutions thus obtained were measured by AAS.

To measure the maximal exchange level, i.e. the portion of the total CEC that was available for cation exchange, Na-exchanged clinoptilolite was allowed to react with 0.1 N solutions of the various cations for 1 week, substituting the exhausted solution for a fresh one every 12 h.

Equilibrium constants K_a and standard free energies of exchange ΔG^0 were calculated with a

computer program utilizing a standard procedure [16]. Accordingly, given a general cation exchange equation:



where A is a cation of valence z_A , B is a cation of valence z_B , and subscripts s and z denote solution and zeolite respectively; the selectivity coefficient K_c is defined as:

$$K_c = \frac{X_{A(z)}^{z_B} a_B^{z_A}}{X_{B(z)}^{z_A} a_A^{z_B}}, \quad (2)$$

where $X_{A(z)}$ and $X_{B(z)}$ are the equivalent fractions of the cations A and B in the zeolite, and a_A and a_B are the activities of A and B in solution. Experimental data from the 'smoothed' isotherms, normalized beforehand, i.e. divided by the maximal level of exchange obtained, and activity coefficients in solution, computed with the help of a procedure after Ciavatta [20] and Glueckauf [21], served to calculate K_c , from which, according to Gaines and Thomas [22], K_a and ΔG^0 were computed as follows:

$$\log K_a = 0.4343(z_A - z_B) + \int_0^1 \log K_c dX_{A(z)} \quad (3)$$

$$\Delta G^0 = -\frac{RT}{z_A z_B} \ln K_a. \quad (4)$$

3. Results and discussion

3.1. Materials characterization

The quantitative XRD analysis demonstrated that the Orvitoro epiclastite is mainly constituted by clinoptilolite with minor contents of feldspar, opal CT, quartz and mica (Table 1). Table 2 gives the chemical composition and the formula, based on 72 oxygen atoms, of pure clinoptilolite, sepa-

Table 2
Chemical analysis of Orvitoro clinoptilolite^a

	Chemical composition (wt%)	Calculated formula ^b	
SiO ₂	63.36	Si	28.96
Al ₂ O ₃	12.90	Al	6.95
MgO	1.29	Mg	0.88
CaO	3.10	Ca	1.52
BaO	0.09	Ba	0.02
Na ₂ O	1.39	Na	1.23
K ₂ O	2.16	K	1.26
H ₂ O	15.71	O	72.00
		H ₂ O	23.94

^a Average values of at least 20 spot analyses.

^b Percent balance error: $100[1 - (Na + K + 2Ca + 2Mg)/Al] = -5.03$.

rated from the parent rock. A peculiar feature of this clinoptilolite sample is the quite high Mg content compared with clinoptilolites from other locations [4].

The data of Table 2 allowed the calculation of the theoretical CEC, which was 2.53 mequiv/g based on the Al content and 2.66 mequiv/g based on the extra-framework cations content. The measured CEC was 2.22 mequiv/g or 2.38 mequiv/g with Na⁺ or K⁺ as eluting cation respectively (see Section 2). These discrepancies, as already pointed out previously [4], are due to failure of complete Ca and Mg replacement for Na or K in the cation exchange experiments. The value of 2.22 mequiv/g was adopted for the study of cation exchange equilibria.

3.2. Cation exchange equilibria

Figs. 1–5 respectively show the isotherms of NH₄⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ exchange for Na⁺ in the clinoptilolite studied. A perfect reversibility of the various exchange reactions was observed, as the experimental points for the direct

Table 1
Quantitative analysis of Orvitoro clinoptilolite-bearing rock

	Clinoptilolite	Feldspar	Quartz	Opal CT	Mica
Amount (wt%)	80(±5)	10(±2)	3(±1)	7(±2)	1(±1)

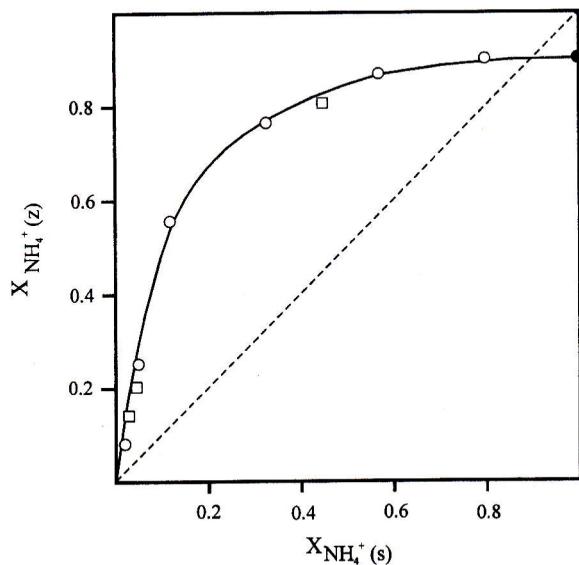


Fig. 1. Isotherm at 25°C for the exchange of NH_4^+ into Na-clinoptilolite at 0.1 total solution normality. $X_{\text{NH}_4^+(\text{s})}$: ammonium equivalent fraction in solution; $X_{\text{NH}_4^+(\text{z})}$: ammonium equivalent fraction in the zeolite. Open circles: forward points; squares: reverse points; filled circle: maximal exchange level.

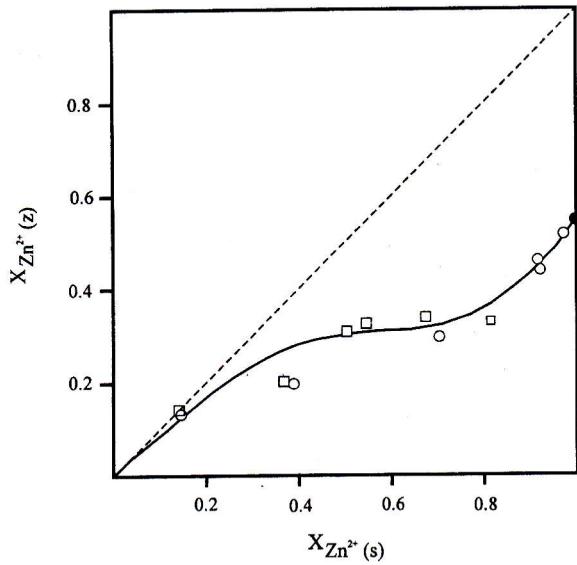


Fig. 3. Isotherm at 25°C for the exchange of Zn^{2+} into Na-clinoptilolite at 0.1 total solution normality. $X_{\text{Zn}^{2+}(\text{s})}$: zinc equivalent fraction in solution; $X_{\text{Zn}^{2+}(\text{z})}$: zinc equivalent fraction in the zeolite. Other symbols as in Fig. 1.

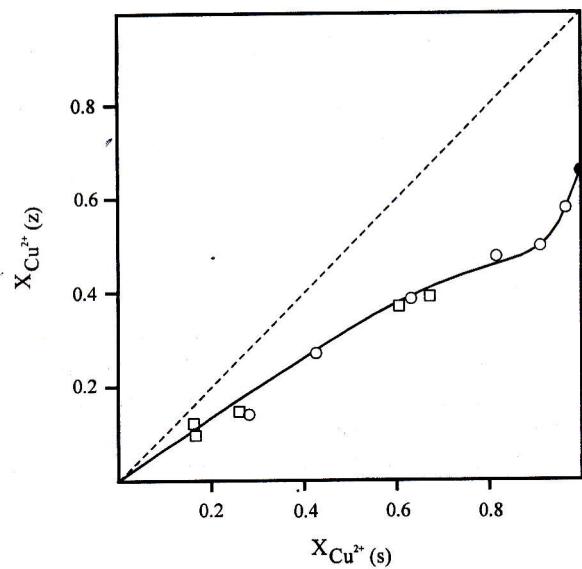


Fig. 2. Isotherm at 25°C for the exchange of Cu^{2+} into Na-clinoptilolite at 0.1 total solution normality. $X_{\text{Cu}^{2+}(\text{s})}$: copper equivalent fraction in solution; $X_{\text{Cu}^{2+}(\text{z})}$: copper equivalent fraction in the zeolite. Other symbols as in Fig. 1.

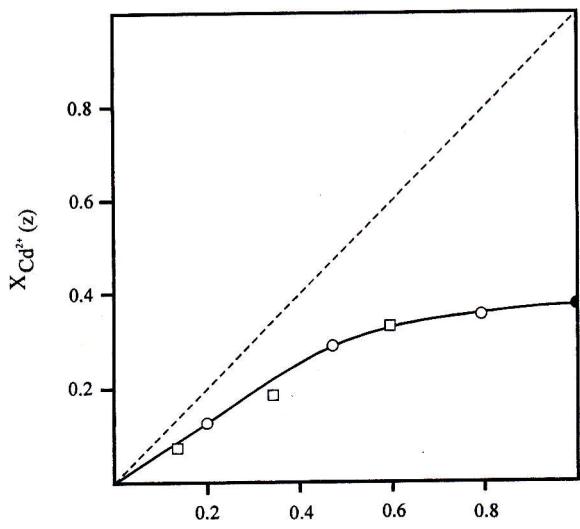


Fig. 4. Isotherm at 25°C for the exchange of Cd^{2+} into Na-clinoptilolite at 0.1 total solution normality. $X_{\text{Cd}^{2+}(\text{s})}$: cadmium equivalent fraction in solution; $X_{\text{Cd}^{2+}(\text{z})}$: cadmium equivalent fraction in the zeolite. Other symbols as in Fig. 1.

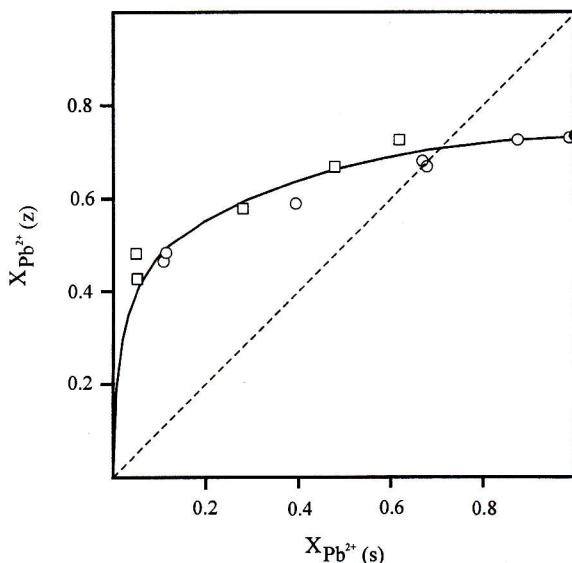


Fig. 5. Isotherm at 25°C for the exchange of Pb^{2+} into Na-clinoptilolite at 0.1 total solution normality. $X_{\text{Pb}^{2+}(s)}$: lead equivalent fraction in solution; $X_{\text{Pb}^{2+}(z)}$: lead equivalent fraction in the zeolite. Other symbols as in Fig. 1.

and back exchange are well fitted by a single curve. Despite the fact that Na-exchanged clinoptilolite contains some residual calcium and magnesium (vide supra), no significant amount of these cations was observed in the liquids after equilibrium, demonstrating that the systems investigated may be considered bicationic.

The maximal exchange levels attained were as follows: NH_4^+ : 90.1%; Cu^{2+} : 66.3%; Zn^{2+} : 53.8%; Cd^{2+} : 37.3%; Pb^{2+} : 74.5%. The failure to attain 100% exchange appears the most striking feature of this set of exchange isotherms.

Fair exchange levels and good selectivities were observed only for NH_4^+ and Pb^{2+} . In the former case, the exchange isotherm lies above the diagonal up to about 0.90 ammonium equivalent fraction in the zeolite, and in the latter case, up to about 0.71 lead equivalent fraction in the zeolite; this indicates a good selectivity towards both cations entering the clinoptilolite framework.

The copper, zinc and cadmium exchange isotherms lie below the diagonal over the whole composition range, regardless of their shape and their cation exchange capability for the specific entering cation, demonstrating a substantial selec-

Table 3
Thermodynamic quantities of investigated equilibria

Cation couple	K_a	ΔG° (kJ/equiv)
$\text{Na} \rightarrow \text{NH}_4$	10.21	-5.72
$2\text{Na} \rightarrow \text{Cu}$	0.11	2.71
$2\text{Na} \rightarrow \text{Zn}$	0.10	2.83
$2\text{Na} \rightarrow \text{Cd}$	0.61	0.61
$2\text{Na} \rightarrow \text{Pb}$	4.40	-1.82

tivity lack of clinoptilolite for each of the above cations. These observations are confirmed by the values of the thermodynamic quantities K_a and ΔG° , computed by processing the exchange isotherms with the procedure reported in the Section 2.1. (see Table 3).

From the data of Table 3 the following selectivity sequence is derived: $\text{NH}_4^+ > \text{Pb}^{2+} > \text{Na}^+ > \text{Cd}^{2+} > \text{Cu}^{2+} \cong \text{Zn}^{2+}$. This sequence may be interpreted on the basis of the Eisenmann theory [23,24]. The high Si/Al ratio of clinoptilolite results in a typical low anionic field that gives rise to good selectivity towards cations of lower charge, e.g. NH_4^+ , and poor selectivity towards cations of higher charge, e.g. divalent cations. The observed preference of clinoptilolite for Pb^{2+} is an exception to this rule, and is due to its lower hydration energy compared with the other three divalent cations [8].

To demonstrate the general behavior of Na-exchanged clinoptilolite towards the investigated cations, the results from the present study are compared with some reliable data from literature.

As far as NH_4^+ is concerned, Barrer et al. [25], Bilba et al. [26] and Suzuki and Ha [27] obtained a convex exchange isotherm, which lies abundantly above the diagonal over the whole composition range and attains 100% exchange. The equilibrium constant at 60°C was reported in the former study to be equal to 7.9. On the contrary, Townsend and Loizidou [28] reported an exchange isotherm with an inflection point, denoting a selectivity reversal and reaching 76% as maximal exchange level ($K_a = 5.12$ at 25°C). Howery and Thomas [29], using a column technique, found a ΔG° value of -5.04 kJ/quiv at 30°C, which corresponds to $K_a = 8.53$.

Contrasting data on the Na–Pb pair are also found in the literature. Blanchard et al. [9] reported a convex isotherm attaining 100% exchange and a selectivity of clinoptilolite for lead higher than for ammonium. Chelishchev et al. [7] and Semmens and Seyfarth [8] obtained a 100% maximal exchange level with a sharp selectivity reversal at a lead equivalent fraction in the zeolite of about 0.8. Loizidou and Townsend [10] reported an exchange isotherm whose shape and maximal exchange level (79%) closely resemble those depicted in the present paper, the only difference being a remarkably higher value of the equilibrium constant ($K_a = 21.87$ at 25°C).

Scant and fragmentary data are found in the literature concerning the Na–Cd, Na–Cu and Na–Zn pairs. Loizidou and Townsend [11] reported an exchange isotherm for Cd²⁺ with a different shape than the isotherm obtained in the present study and displaying about 66% as maximal exchange level ($K_a = 0.16$ at 25°C). Data on Cu²⁺ and Zn²⁺, reported by Semmens and Seyfarth [8], cannot be directly compared with those of this investigation, since they were determined in different experimental conditions, whereas in other papers, e.g. Ref. [30], it is just reported that clinoptilolite is unselective for Cu and Zn.

Discrepancies between the data reported in the present study and data from literature appear evident even from the above short review. Different data obtained for a cation pair from different samples of the same zeolite may, in some cases, be ascribed to a different Si/Al ratio, a parameter that may substantially affect cation selectivity, as demonstrated in phillipsite [31]. This seems not to be the case for clinoptilolite, whose Si/Al ratio presents a more limited variation range than phillipsite does [32].

On the other hand, clinoptilolite frequently displays an experimental CEC lower than the calculated one [4,33], but this should not affect selectivity, at least at a first glance. Actually, as a recent crystal chemical and structural investigation of the Sardinian clinoptilolite has demonstrated [4,34], the selectivity can be influenced by the original cationic composition, due to the different origin of the various clinoptilolite samples. In the Sardinian clinoptilolite, calcium and magnesium

occupy two or even three different cationic sites, out of the four sites of the structure [35], which have different energetic features. The consequence is that calcium and magnesium are only partially exchanged, and this accounts for the discrepancy between the experimental and calculated CEC [4]. The occupancy of some sites by residual calcium and magnesium, and therefore the partial unavailability of such sites, can also affect either the maximal exchange level or the general preference of the zeolite for an entering cation, e.g. sodium.

4. Conclusions

Cation exchange features of a Sardinian clinoptilolite confirmed the good selectivity of this zeolite for NH₄⁺ and Pb²⁺, disclosing possible practical applications. On the contrary, the low selectivity for Cd²⁺, Cu²⁺ and Zn²⁺ seems to prevent its use in the treatment of waters containing these polluting cations.

In addition, the results of this investigation, compared with literature data, pointed out the wide variability of the cation exchange properties of clinoptilolite. In particular, it has been emphasized that the cation exchange selectivity of clinoptilolite is markedly dependent on its original cationic composition, as not all the cationic sites in the structure can be made available for cation exchange.

This suggests that it is not possible to draw conclusions of a general or fundamental nature from cation exchange on these types of mineral. Therefore, before any practical application, one should carry out specific studies on representative samples from the deposit that is being examined for its exploitation potential.

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