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Evaluation of Natural Phillipsite and Chabazite as Cation Exchangers for Copper and Zinc

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ABSTRACT

Chabazite and phillipsite, two zeolites widespread in many volcaniclastic deposits in central-southern Italy, were evaluated as cation exchangers for the removal of copper and zinc from aqueous solution. Equilibrium and kinetics of copper and zinc exchange reactions for sodium were investigated in order to verify the selectivity and the uptake rate of both zeolites for these heavy metals. Thermodynamic quantities, such as equilibrium constant, K_a, and $\Delta G°$, as well as rate constant, K, were computed, and they showed that Na-chabazite displays a moderate

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selectivity and a favorable kinetics for copper, whereas in all the other cases uses in wastewater treatment are not recommended.

Key Words. Chabazite; Phillipsite; Ion exchange; Copper; Zinc

INTRODUCTION

Large areas of Italy are covered by thick pyroclastic deposits which arose during the last million years through the intense activity of several volcanoes along the Thyrrenian border of central-southern Italy. After the emplacement the volcaniclastic material, ranging in composition from trachyte to phonolite, was involved in minerogenetic processes through the interaction of its highly reactive glassy matrix with hot fluids. Chabazite and phillipsite were the most widespread authigenic phases formed. Both minerals, except in a few deposits, are almost everywhere present as coexisting phases, representing 50–80% of the whole rock (1).

These materials are currently employed for the production of dimension stones in the building industry (1.5 million tons in 1996) (2). Only a small part of the entire production (about 50,000 tons/year) is employed for other purposes, for instance, in soil amendment and as admixture in animal feeding. On the other hand, the peculiar features of zeolites as cation exchangers make these materials potentially very interesting from a technological point of view, especially in environmental protection (3).

Two main facts attracted the attention of the scientific community to natural zeolites as a valid tool for environmental purposes:

1. The occurrence of cation selectivity sequences which can be very useful in the selective removal of pollutants in the presence of interfering cations (4)
2. Their availability as huge outcroppings all over the world, which makes their cost very low (5)

In order to evaluate Italian zeolites as possible cation exchangers in the removal of toxic cations from wastewaters, a long-time investigation was initiated some years ago. It has already examined the behavior of phillipsite and chabazite for ammonium, lead, chromium, and cadmium (see citations in Ref. 3).

The present study continues this investigation by extending the study to copper and zinc, two metals for which literature data (6–12) do not appear sufficient to evaluate if chabazite and phillipsite act as proper cation exchangers.

EXPERIMENTAL

Zeolitic samples employed in the present study are from two different volcanic districts. One comes from the Riano quarry, near Rome, and belongs to the formation of the so-called *Yellow tuff of Via Tiberina* (YTVT), characterized by a constant prevalence of chabazite over phillipsite besides containing other minor phases, either crystalline or amorphous (1). Actually, the selected sample can be considered fully chabazitic. The second comes from a quarry in Marano, near Naples, and belongs to the formation of *Neapolitan yellow tuff* (NYT), a volcaniclastic deposit of great economic interest in the *Phlegraean* ("burning") *Fields*. Unlike YTVT, this volcanic formation is characterized by the constant presence of high grades of phillipsite along with subordinate chabazite and other minor phases (13). The NYT sample selected was frankly phillipsitic.

The zeolite content of both materials was determined by using the water vapor desorption method, based on estimation of the amount of water vapor adsorbed by the samples owing to various heat activation cycles (14).

Pure zeolite phases were obtained from the parent rocks by the usual enrichment techniques (15). No chemical and structural changes were recorded after the enrichment treatment. Purity was checked using a Philips PW 1730-3710 automatic powder diffractometer and an x-ray Gandolfi camera (Philips PW 1729). Hand-picked selected crystals were subjected to EDS microanalysis (Link AN 10000S apparatus linked to a Cambridge TP 250 scanning electron microscope). Water content was determined by thermogravimetry (Netzsch STA 409 thermoanalyzer).

The cation-exchange capacity (CEC) of phillipsite and chabazite was determined by the cross-exchange method (16). Two 1-g zeolite samples, placed on Gooch filters, were percolated at about 60°C up to exhaustion (assumed as the condition when the concentrations of eluted cations attained the value present as impurity in the ingoing solution) with 0.5 M NaCl or KCl solutions, prepared by using Carlo Erba reagent-grade chemicals. In order to assure complete exchange, zeolites were furtherly eluted with sodium or potassium solutions prepared by using the relevant chlorides displaying purity higher than 99.999% (Aldrich Chemical Company). The obtained monocationic forms (Na^+ or K^+) were then reexchanged under the same conditions with potassium and sodium, respectively. Collected eluates were analyzed by atomic absorption spectrophotometry (AAS) using a Perkin-Elmer AA 2100 apparatus. Na^+ and K^+ concentrations in the eluates of the second exchange cycle were used to calculate the mean CEC values. The experimental techniques used in such determinations allowed us to ascertain that the zeolite samples in their original composition and in their sodium form displayed practically the same CEC.

Sodium forms of both zeolites were allowed to react at 25 ± 0.1°C in Teflon-lined stainless steel vessels with solutions containing different amounts of Cu^{2+} or Zn^{2+} and Na^+ at 0.1 total normality, prepared from reagent-grade Carlo Erba $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $NaNO_3$. Reversibility tests of the ion exchange were performed following the recommendations of Fletcher and Townsend (17). The solid-to-liquid ratio was fixed at 1/100 and the reaction time at 3 days, which was shown to be sufficient for attaining equilibrium. The pHs of the reacting systems were recorded at the end of the reaction time and ranged between 4.3 and 5.5. Cu^{2+} and Zn^{2+} concentrations or contents were measured either in the liquid phase or in the solid phase. In the former case titrations with EDTA were performed using murexide as the indicator for copper and xylenol orange for zinc (18). In the latter case zeolites were chemically dissolved, and Cu^{2+} and Zn^{2+} concentrations in the solutions were measured by AAS. To determine without doubt which amount of the total cation-exchange capacity of the two zeolites was available for Cu and Zn exchange, samples of Na-exchanged chabazite and phillipsite were contacted with 0.1 N Cu^{2+} or Zn^{2+} solutions for 1 week, substituting the exhausted solution by a fresh one every 12 hours.

In kinetic runs, Na-exchanged phillipsite or chabazite tuff, ground to a fineness lower than 150 μm, was contacted with 10.0 mN Cu or Zn solutions at a solid-to-liquid ratio of 1/1000. Released Na^+ concentrations were measured in solution at fixed times by AAS.

COMPUTATION OF THERMODYNAMIC PARAMETERS

The procedure used to compute equilibrium constants (K_a) and free energies (ΔG°) of exchange reactions is reported in Ref. 19. According to it, given a generic exchange reaction:

$$z_B A^{z_A}_{(s)} + z_A B^{z_B}_{(z)} \rightleftarrows z_B A^{z_A}_{(z)} + z_A B^{z_B}_{(s)} \qquad (1)$$

where A and B are two cations, z_A and z_B are the valencies of A and B, and subscripts (s) and (z) denote solution and zeolite phase. Calculations were performed as follows:

1. Equivalent fraction in solution (A_s, B_s) and in the solid (A_z, B_z) were obtained from the "smoothed" isotherm
2. The ratios between the ion activity coefficients in mixed solutions were evaluated from the mean ionic activity coefficients calculated

by the method proposed by Ciavatta (20) and corrected by Glueckauf's equation (21)

3. Selectivity coefficients (K_c) were calculated as

$$K_c = \frac{A_Z^{z_B} a_B^{z_A}}{B_Z^{z_A} a_A^{z_B}} \tag{2}$$

where a_A and a_B are A and B activities in solution

4. Equilibrium constants (K_a) and standard free energies of exchange per equivalent of exchanger ($\Delta G°$) were calculated as follows, according to the Gaines and Thomas approach (22):

$$\log K_a = 0.4343(z_B - z_A) + \int_0^1 \log K_c \cdot dA_z \tag{3}$$

$$\Delta G° = -\frac{RT}{z_A z_B} \ln K_a \tag{4}$$

RESULTS AND DISCUSSION

Characterization of the Materials

Table 1 reports the chemical compositions along with the crystallographic formulas calculated on 24 and 32 oxygens for chabazite and phil-

TABLE 1
Chemical Analyses (left) and Formulas (right) of Natural Chabazite and Phillipsite

	Chabazite	Phillipsite		Chabazite	Phillipsite
SiO_2	50.14	52.03	Si	8.47	11.45
Al_2O_3	17.75	17.52	Al	3.54	4.54
Fe_2O_3	0.15	0.13	Fe	0.02	0.02
MgO	0.63	0.17	Mg	0.16	0.06
CaO	5.75	3.76	Ca	1.04	0.89
Na_2O	0.30	1.88	Na	0.10	0.80
K_2O	4.43	6.43	K	0.95	1.81
H_2O[a]	20.85	17.00	H_2O	11.75	12.48
			O	24	32
Si/Al	2.40	2.52			
Na/K	0.10	0.44			
E%[b]	2.39	1.11			

[a] Ignition loss.

[b] Percent balance error, 100[(Al + Fe) − (Na + K + 2Ca + 2Mg)]/(Na + K + 2Ca + 2Mg).

lipsite, respectively. Analyses refer to average values obtained by at least 15 points per sample (3 point analyses on 5 different crystals of the same sample). Analyses with balance errors (see footnote *b* Table 1) higher than 4% were discarded. The small differences in the Si/Al ratio displayed by the two zeolites can be ascribed to the slight difference in composition between their precursor glasses. The extraframework cations present in both zeolites to the highest extent are K and Ca, with a typically higher Na content in phillipsite.

CEC values measured on pure phases were 3.37 meq/g for chabazite and 3.30 meq/g for phillipsite. These values are consistent with those calculated by summing Na, K, Ca, and Mg equivalents obtained from the chemical analyses (see Table 1) and relating this sum to 1 gram. These values are 3.38 meq/g in both cases. The mean zeolite content of the parent rocks are:

- YTVT contains 75% zeolite. Such an amount is totally made up by chabazite
- NYT contains 50% zeolite. Such an amount is mostly made up of phillipsite with a few percent chabazite

Ion Exchange Equilibria in Chabazite

Figures 1 (solid line) and 2 show the ion-exchange isotherms for the pairs Na^+/Cu^{2+} and Na^+/Zn^{2+} in chabazite, respectively. We make the following observations:

1. The two exchange reactions appear reversible inasmuch as direct- and back-exchange runs give results that can be fitted by a single curve.
2. The exchange isotherm for the equilibrium $2Na^+ \rightleftarrows Cu^{2+}$ (Fig. 1, solid line) lies above the diagonal for the copper equivalent fraction in solution ($X_{Cu(s)}$) lower than about 0.25, whereas it lies beneath the diagonal in the range $0.25 < X_{Cu(s)} < 1.00$.
3. The exchange isotherm of the equilibrium $2Na^+ \rightleftarrows Zn^{2+}$ lies considerably beneath the diagonal over the whole composition range (Fig. 2).
4. The total cation-exchange capacity of chabazite is available for copper exchange, which does not occur for zinc exchange. In the latter case the exhaustive procedure of exchange reported in the Experimental Section gave rise to a final zinc equivalent fraction in zeolite ($X_{Zn(z)}$) equal to 0.83 (Fig. 2).

The above results appear to be strongly supported by the literature data. Barrer et al. (23) report an upper exchange limit of 85% for cesium on

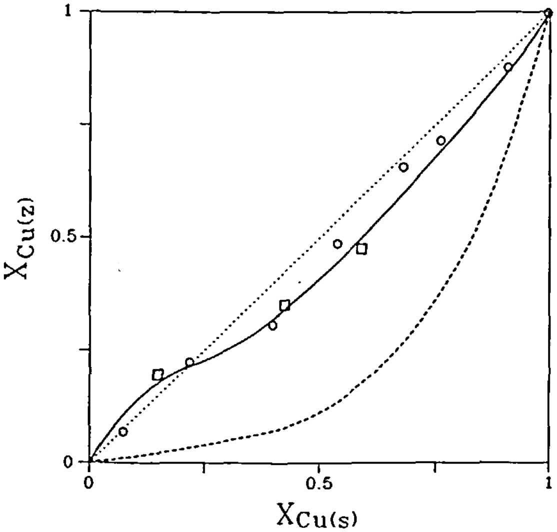

FIG. 1 Isotherm at 25°C for the exchange of Cu into Na-chabazite at 0.1 total normality. Circles = forward points; squares = reverse points. Dashed line refers to the exchange isotherm from Barrer and Sammon (6). $X_{Cu(s)}$ = copper equivalent fraction in solution; $X_{Cu(z)}$ = copper equivalent fraction in zeolite.

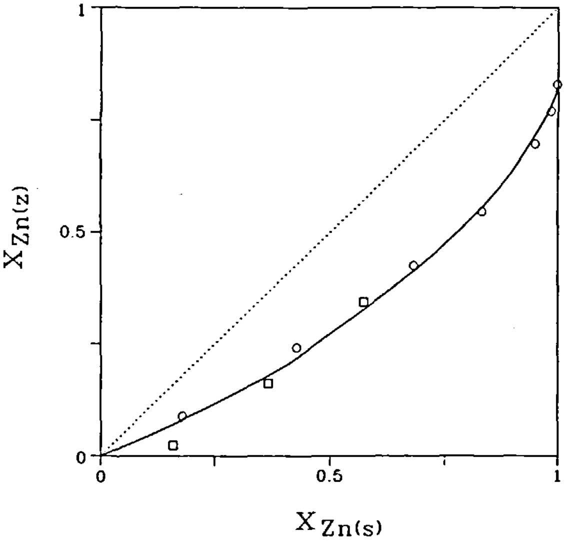

FIG. 2 Isotherm at 25°C for the exchange of Zn into Na-chabazite at 0.1 total normality. Symbols as in Fig. 1.

Na-chabazite and the presence of an inflection point in the isotherm for lead exchange for sodium at about the same conversion of the exchanger. This latter finding is confirmed by Torracca et al. (24) who reported an upper exchange limit of slightly higher than 80% for potassium and ammonium exchange in Na-chabazite. These findings may be interpreted by considering that in chabazite slightly more than 80% of the cation sites are located in the large ellipsoidal cage (sites C2–C4) and the rest are located in the C1 site in the small D6R cage (25). The cation sites of the large ellipsoidal cage are favorable to lead, potassium, ammonium, and cesium, while the C1 cation site is unfavorable, but attainable, to lead and not attainable at all to cesium for steric reasons, or for ammonium and potassium in the experimental conditions chosen. Torracca et al. (24) reported that chabazite undergoes complete exchange for potassium at 0.5 or higher total normality.

The practical coincidence of the zinc upper exchange limit (83%) with the ammonium, potassium, and cesium upper exchange limits may be interpreted in the same way, and thus it appears that the C1 cation site is not available for zinc exchange. The upward concavity of the zinc exchange isotherm accounts for the poor selectivity for zinc of cation sites located in the ellipsoidal cage. Such poor selectivity could result from either the higher dehydration energy of zinc or from difficulties in assuming the proper coordination typical of the considered cation site, namely in assuming the right position between the sites of the framework bearing monovalent negative charges. On the contrary, the inflection point in the copper-exchange isotherm (Fig. 1) at about $X_{\mathrm{Cu(z)}} = 0.28$ cannot be interpreted in terms of site selectivity (6) and does not appear related to the percentage of various cation sites present in chabazite. Actually, Pluth et al. (10) found all Cu^{2+} and water molecules to be in the large cage, perhaps as hydration complexes with Jahn-Teller distortion. Thus, this selectivity reversal might depend on the fact that differently charged cations are in competition with each other. To test this hypothesis the isotherm of Fig. 1 (solid line), representing the $2Na^+ \rightleftarrows Cu^{2+}$ equilibrium at 0.1 total normality, has been compared with the isotherm obtained for the same equilibrium at 0.5 total normality by Barrer and Sammon (6) (the dashed curve in Fig. 1). It can be seen that the curves largely differ from each other; nevertheless, the two exchange isotherms, subjected to the proper mathematical manipulations in order to calculate the thermodynamic quantities (19), give rise to K_a values very close to each other (0.085 for the former and 0.079 for the latter), demonstrating that the shape of the isotherm can be a source of misleading interpretations. The great discrepancy between the two curves of Fig. 1 may be qualitatively explained by considering that the shape of an ion-exchange isotherm is strongly affected in the case of heterovalent ion exchange by the total concentration in solution and that an increase in dilution results in a higher selectivity for the cation of higher valence (26–28).

Ion Exchange Equilibria in Phillipsite

Figures 3 and 4 show the ion-exchange isotherms for the pairs Na^+/Cu^{2+} and Na^+/Zn^{2+} in phillipsite, respectively. The most striking features of the reported isotherms are the following:

1. The exchange isotherm of the pair Na^+/Cu^{2+} on phillipsite displays an evident hysteresis loop inasmuch as direct- ($2Na^+ \rightarrow Cu^{2+}$) and back-exchange ($Cu^{2+} \rightarrow 2Na^+$) runs gave results that could be fitted by two distinct curves over the whole composition range. On the contrary, the $2Na^+ \rightarrow Zn^{2+}$ reaction on phillipsite appears to be reversible.
2. The total cation-exchange capacity of phillipsite is not available for both exchange reactions. Actually, the exhaustive procedure of exchange, described in the Experimental Section, gave rise to a final copper equivalent fraction in zeolite ($X_{Cu(z)}$) of 0.76 and a final zinc equivalent fraction in zeolite ($X_{Zn(z)}$) of 0.73.

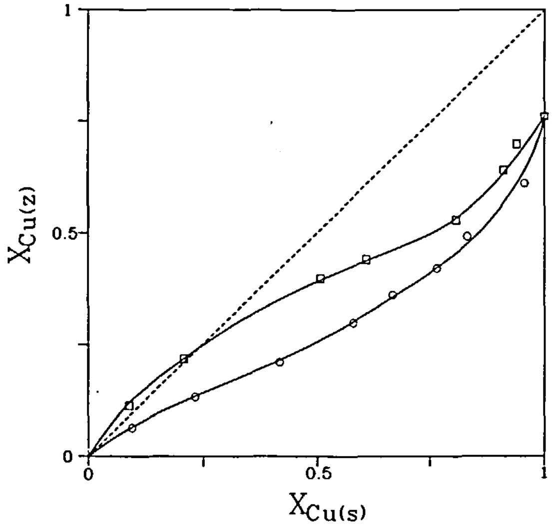

FIG. 3 Isotherm at 25°C for the exchange of Cu into Na-phillipsite at 0.1 total normality. Symbols as in Fig. 1.

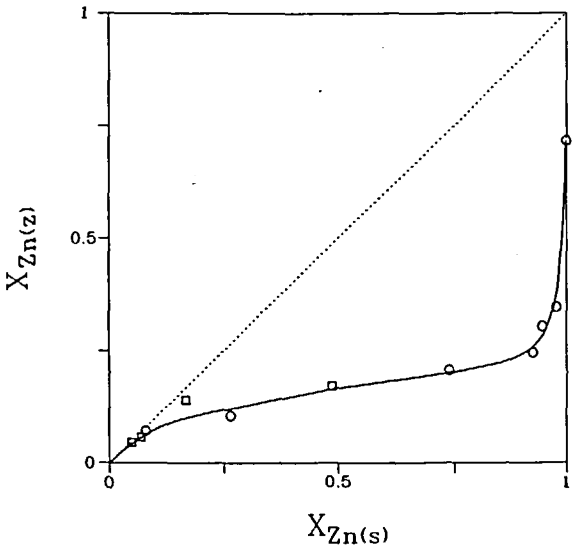

FIG. 4 Isotherm at 25°C for the exchange of Zn into Na-phillipsite at 0.1 total normality. Symbols as in Fig. 1.

3. The exchange isotherms of the equilibrium $2Na^+ \rightleftarrows Zn^{2+}$ lie considerably beneath the diagonal over the whole composition range.
4. The curve for the sodium exchange for copper lies considerably beneath the diagonal over the whole composition range, whereas the curve for the copper exchange for sodium lies above the diagonal for the copper equivalent fraction in solution $X_{Cu(s)}$ and beneath the diagonal in the range $0.25 < X_{Cu(s)} < 1.00$.

Reported Na^+/Cu^{2+} and Na^+/Zn^{2+} exchange isotherms reveal the poor selectivity of phillipsite for copper and zinc. Moreover, phillipsite displays severe restrictions in the occupancy of its six cation sites (29) by these two heavy metal cations. Interpreting the exclusion of copper and zinc from one site or another would require structural analysis. The feeling is that in sedimentary phillipsite the exclusion should not be a matter of cation dimensions compared to structure constraints, inasmuch as in a previous paper (30) it was reported that the exchange of Na- or K-phillipsite, coming from NYT, for Ca does not exceed a calcium equivalent fraction in the zeolite higher than 0.5. It must be pointed out that such a low final Ca content was recorded only for this particular phillipsite. For other phillipsites, either natural or synthetic, higher and even total Ca conversion were recorded. This inhomogeneous behavior accounts for the general difficulty in substituting monovalent cations for divalent cations in a zeolite due to the particular distribution of negative charges on its framework. Accordingly, the incomplete exchange of Na for Cu and Zn might be related to their difficulties in assuming the proper coordination typical of some cation sites in phillipsite.

The presence of a hysteresis loop in the Na^+/Cu^{2+} exchange isotherm is related to a miscibility gap between two solid phases: the Na-phillipsite and the phillipsite having $X_{Cu(z)} = 0.76$, i.e., the phillipsite with the maximum copper content.

Table 2 reports the thermodynamic quantities, calculated according to Caputo et al. (19), compared to similar data for exchange reactions of Na-exchanged sedimentary chabazite or phillipsite for other heavy metal cations.

Ion-Exchange Kinetics

In Fig. 5 the Na^+ concentration released by the Na-exchanged chabazite and phillipsite tuffs owing to exchange with Cu^{2+} and Zn^{2+} are reported as a function of time. The length of the runs (400 minutes) did not allow equilibrium to be attained.

Assuming that Cu^{2+} and Zn^{2+} concentration varies only slightly during the first hour of reaction and that the kinetic order is 2 with respect to the number of available sites for the exchange $(C_0 - C)$ (9), the kinetic equation can be written

$$-(dC/dt) = K(C_0 - C)^2 \tag{5}$$

TABLE 2
K_a and ΔG° of Reported Exchange Reactions Compared with Data Concerning Some Other Relevant Cation Pairs

Zeolite	Cation pair	K_a	ΔG° (kJ/eq)
Chabazite[a]	Na^+/Cu^{2+}	0.085	2.8
Chabazite[a]	Na^+/Zn^{2+}	0.037	4.1
Chabazite[b]	Na^+/Pb^{2+}	4.1	−1.7
Chabazite[c]	Na^+/Cd^{2+}	0.57	0.7
Phillipsite[a]	Na^+/Zn^{2+}	0.005	6.5
Phillipsite[d]	Na^+/Pb^{2+}	22.8	−3.9
Phillipsite[c]	Na^+/Cd^{2+}	0.025	4.6

[a] This work.
[b] Reference 24.
[c] Reference 19.
[d] Reference 30.

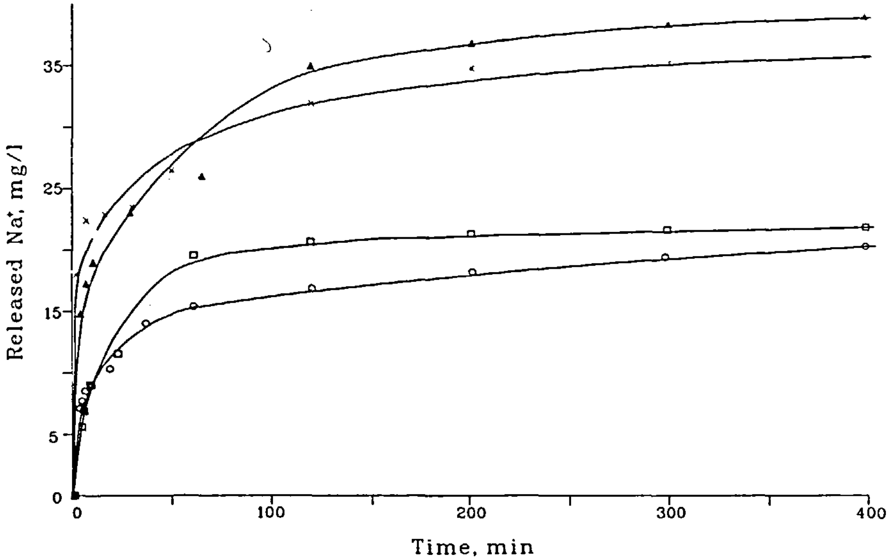

FIG. 5 Kinetics of Cu^{2+} (crosses) and Zn^{2+} (triangles) uptake by Na-exchanged chabazite-rich tuff and Cu^{2+} (circles) and Zn^{2+} (squares) uptake by Na-exchanged phillipsite-rich tuff from 10.0 mN solution at 25°C. Solid-to-liquid ratio = 1:1000.

which on integration gives

$$[1/(C_0 - C)] - \alpha = Kt \tag{6}$$

where C is the amount of copper or zinc taken up by the zeolite tuff or the amount of sodium released at each instant, C_0 is the cation exchange capacity of the tuff, K is the rate constant, and t is time. Considering the boundary conditions $C = 0$ for $t = 0$, it follows that $\alpha = 1/C_0$.

Each set of experimental points in Fig. 5 within the first hour of reaction, when processed according to this model (Eq. 6), yields a straight line, the slope of which represents the rate constant K of the reaction. These values, reported in Table 3 (samples denoted by superscript *a*), do not seem sensibly affected by the type of exchanger (chabazite- or phillipsite-rich tuffs). On the contrary, they are affected by the cations: actually zinc-exchange reactions display rate constants about 40% higher than the corresponding copper-exchange reactions. In the same table some reference values obtained with similar materials but with different cations are also reported. Inspection of Table 3 results in the following conclusions: rate

TABLE 3
Rate Constant K of Exchange Reactions

Tuff	Cation pair	K (L/meq·min)
Chabazite-rich[a]	Na^+/Cu^{2+}	9.1×10^{-4}
Chabazite-rich[a]	Na^+/Zn^{2+}	1.3×10^{-3}
Chabazite-rich[b]	Na^+/Pb^{2+}	1.3×10^{-1}
Chabazite-rich[c]	Na^+/Cd^{2+}	9.4×10^{-3}
Phillipsite-rich[a]	Na^+/Cu^{2+}	8.2×10^{-4}
Phillipsite-rich[a]	Na^+/Zn^{2+}	1.5×10^{-3}
Phillipsite-rich[d]	Na^+/Pb^{2+}	1.3×10^{-2}
Phillipsite-rich[c]	Na^+/Cd^{2+}	1.0×10^{-3}

[a] This work.
[b] Reference 31.
[c] Reference 32.
[d] Reference 30.

constants of the reactions under consideration are much lower than those involving lead, while they substantially compare with those involving cadmium. Even this large difference in rate constants between Pb and Cd, Cu, and Zn might be related to difference in the hydration energies of the various cations. The fact that Cd, Cu, and Zn must lose more molecules of water than Pb might result in their slower kinetics of exchange.

CONCLUSIONS

The results of this study contribute to knowledge of the cation-exchange properties of phillipsite and chabazite, two zeolites widespread in many volcanic areas in Italy. The data reported do not recommend the utilization of phillipsite-rich materials in the removal of copper and zinc from water because of the incompleteness of exchange (reduction of about 25% of either Cu or Zn exchange capacity with respect to the total cation-exchange capacity), poor selectivity, and low exchange rate, especially if compared to other cations, e.g., lead.

These considerations are also valid for chabazite-rich materials as regards zinc. On the contrary, copper removal from water appears possible. The entire cation-exchange capacity of chabazite is available for Cu exchange, and Na-chabazite displays a moderate selectivity for copper at 0.1 total normality at the lowest copper loadings. The dramatic dependence of selectivity for copper on the total concentration of the solution is a strong indication of the sharp increase of this selectivity with the increasing dilution which often occurs in wastewaters.

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