

ION-EXCHANGE BETWEEN NH_4^+ SATURATED ZEOLITES AND ESSENTIAL CATIONS OF THE SOIL SOLUTION (K^+ , Na^+ , Ca^{2+} , AND Mg^{2+})

FRANTIŠEK KOVANDA, HELENA KUSÁ, DAVID KOLOUŠEK

*Department of Solid State Chemistry,
Institute of Chemical Technology,
Technická 5, 166 28 Praha, Czech Republic*

Received April 23, 1996.

Cation-exchange reactions between NH_4^+ saturated zeolites and solutions containing essential cations occurring as main cations in natural soil solutions (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) were studied. Natural clinoptilolite and two synthetic zeolites (P_C and phillipsite) prepared by hydrothermal alteration of power station fly ashes were used as zeolites and saturated with NH_4^+ in a NH_4Cl solution ($c = 5 \text{ mol l}^{-1}$). K^+ and Ca^{2+} yielded the best cation-exchange in the case of all three zeolites. The equilibrium isotherms of ion-exchange reactions were measured in concentration limits usual for real soil solutions. The obtained results indicate that the NH_4^+ ions might be relatively quickly released to the soil solution after the application of NH_4^+ saturated zeolites to the soil. The exchange occurs preferably with K^+ ions (and also with Ca^{2+} in the case of the P_C zeolite) present in the soil solution.

INTRODUCTION

Zeolites are alumino-silicate minerals with specific crystal structure containing non-skeletal cations that can be exchanged for other cations from a surrounding medium under certain conditions. This property of zeolites can be utilized to remove unwanted cations such as those of heavy metals, NH_4^+ , etc. from municipal waste waters (Hagivara and Uchida [1], Colella and Aiello [2], Ciambelli et al. [3]). Natural zeolites are very often used for this purpose because of the economic point of view, but synthetic zeolites can be prepared by hydrothermal alteration of fly ashes at comparable costs (Koloušek et al. [4]). In addition, phillipsite prepared by this method is 2.5 times more effective in removing NH_4^+ from water solutions than natural clinoptilolite (Kovanda et al. [5]).

The application of zeolites to waste water purification processes supposes, of course, that the question of the consequent utilization of the used up zeolite should be solved. If the zeolite was used to remove ammonium ions, its application in agriculture as a cheap nitrogen fertilizer seems to be the most promising, because the NH_4^+ ions can be easily released to the soil system as a result of ion-exchanging reactions. The releasing process of NH_4^+ and other cations was studied by Lewis et al. [6], Pirela et al. [7], Weber et al. [8], and Sopková et al. [9]. The zeolites containing adsorbed nutrients are often recommended by advertising

media as slowly releasing fertilizers. Nevertheless, the releasing of NH_4^+ to the soil is a complicated process strongly affected by the kinetics of ion-exchanging reactions between the zeolite and the soil solution and by conditions under which a dynamic equilibrium in the system can be established and it is the goal of this paper to enlighten this process by studying the ion-exchanging reactions between zeolites containing adsorbed NH_4^+ and solutions of cations that are present in natural soil solutions in significant concentrations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}).

Natural clinoptilolite from the Slovak locality Nižný Hrabovec and two synthetic zeolites, P_C and phillipsite, prepared by hydrothermal alteration of power plant fly ashes were used to the experiments. Clinoptilolite $(\text{Na,K})_6(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$ is a mineral with a monoclinic symmetry, belonging to the heulandite group. Its structure consists of so called 4-4-1-1 heulandite units (two above each other positioned five-membered rings of tetrahedra connected through its four corners - Gottardi and Galli [10]). P_C is a synthetic zeolite with cubic structure of the gismondine type (Hansen et al. [11]) and the contents of its unit cell can be expressed by the formula $\text{Na}_x\text{Al}_x\text{Si}_{16-x}\text{O}_{32} \cdot y\text{H}_2\text{O}$ ($3 \leq x \leq 8$) and can be prepared by hydrothermal alteration of fly ashes in an alkaline medium in the presence of sodium ions. Its secondary construction unit are doubled four-membered rings of Si, Al, O tetrahedra. Phillipsite $\text{K}_2(\text{Ca}_{0.5}\text{Na})_4(\text{Al}_6\text{Si}_{10}\text{O}_{32}) \cdot 12\text{H}_2\text{O}$ is a mineral

which can be easily prepared by hydrothermal alteration of glassy precursors (including fly ashes) in mixed aqueous solutions of sodium and potassium hydroxides or carbonates. According to its structure, phillipsite belongs to the same class of zeolites as the P_C zeolite; a different arrangement of the doubled four-membered rings of Si, Al, O tetrahedra is the only difference between the two structures (Gottardi and Galli [10]). The number of exchangeable cations is directly proportional to the number of Al atoms in the unit cell of zeolites. According to this fact, the P_C zeolite and phillipsite should have a higher ion-exchanging capacity than clinoptilolite because of their lower Si/Al ratio, but clinoptilolite has larger structural pores and is more resistant against higher temperatures and lower pH values.

EXPERIMENTAL PART

Materials

Natural clinoptilolite from the Slovak locality Nižný Hrabovec and two types of synthetic zeolites obtained by hydrothermal alteration of fly ashes resulting from the combustion of lignite were used in the experiments. One of them, the P_C zeolite, was prepared from fly ashes from the heating station in Strakonice (Czech Republic), the other one, a zeolite of the phillipsite type, from fly ashes from the power plant in St. Geertruidenberg (the Netherlands). The alteration was realized in a pilot-plant scale with 2 metric tons of ashes within 4 hrs at 145 °C. The alternating solution was an aqueous NaOH ($c = 2.5 \text{ mol l}^{-1}$) solution in the case of the P_C zeolite or a mixture of KOH and NaOH solutions in the case of phillipsite. The solid product was filtered and partly washed (the pH value of an extract prepared from the product and distilled water in the ratio 1:10 was 12). Because of this high alkalinity, the partly washed product was further washed with diluted hydrochloric acid and finally with distilled water. This way the remaining hydroxides were removed so that the pH value of the extract decreased to 6.

In the next step, the zeolites were saturated with ammonium ions in a NH_4Cl ($c = 5 \text{ mol l}^{-1}$) solution. 5 kg of the respective zeolite were stirred in 10 l of the NH_4Cl solution for 24 hrs. The zeolite was filtered afterwards and the whole procedure was repeated 6 times to reach maximum saturation. The zeolite was then washed with distilled water until the NH_4^+ could not be detected in the filtrate any more. The adsorbed amount of NH_4^+ was determined by distillation with a NaOH solution. The obtained values related to zeolites dried for 4 hrs at 105 °C were 1.223 mmol g^{-1} for natural clinoptilolite, 1.901 mmol g^{-1} for synthetic phillipsite, and 3.842 mmol g^{-1} for synthetic P_C zeolite.

Ion-exchange reactions

Ion-exchange reactions between NH_4^+ saturated zeolites and solutions containing essential cations occurring as main cations in natural soil solutions (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) were followed in a batch arrangement - mixtures of zeolites with the respective solutions were shaken in plastic vessels at a constant temperature. The solutions were prepared by dissolution of the respective nitrates of p.a. quality in distilled water, starting concentrations of K^+ , Na^+ , Ca^{2+} , and Mg^{2+} cations were 50, 60, 190, and 50 mg l^{-1} , resp. These concentrations were chosen so that the resulting equilibrium concentrations of the respective cations corresponded with the concentration limits usual in natural soil solutions. The times necessary to establish the equilibrium were found empirically at 22 °C and were 3 days for the P_C zeolite, 4 days for synthetic phillipsite, and 6 days for natural clinoptilolite and the univalent cations K^+ and Na^+ and approximately twice as long for Ca^{2+} and Mg^{2+} . The equilibrium isotherms of ion-exchanging reactions were measured at the same temperature for all three zeolites and at 0 and 10 °C for the P_C zeolite in addition. Different amounts of the NH_4^+ saturated zeolite were shaken with 150 ml of the respective solution for times necessary to establish the equilibrium, the zeolite was filtered away and the concentration of the respective cation in the filtrate was determined by AAS in the case of metallic cations and by the FIA method in the case of the NH_4^+ cation.

RESULTS AND DISCUSSION

Experiments aimed at the determination of time necessary to establish equilibrium in ion-exchanging reactions indicated that the concentrations of ions in the solution had been stabilized before all ammonium ions originally adsorbed on the zeolite were exchanged even though a sufficient amount of metallic ion was still present in the solution and a further exchange was theoretically still possible. The maximum exchange of ammonium ions was found with minimum amounts of zeolite (0.02 g in 150 ml of the solution). The best exchange observed under these conditions was that of NH_4^+ for Ca^{2+} . The Ca^{2+} ions occupied more than 90 % of exchangeable positions in the P_C zeolite or in natural clinoptilolite but not more than 64 % in phillipsite. A somewhat smaller extent of the exchange was found for NH_4^+ and K^+ cations. The K^+ ions occupied 80 % of exchangeable positions in the P_C zeolite, 84 % in natural clinoptilolite, and 56% in synthetic phillipsite. The Na^+ ions occupied 40 % of exchangeable positions in the P_C zeolite, 60 % in natural clinoptilolite, and 55 % in synthetic phillipsite. The Mg^{2+} ions did not occupy more than 50 % of exchangeable positions in any of the three

zeolites. These results are in good agreement with relationships defined for ion-exchanging reactions on the basis of experiments with natural and synthetic zeolites (Chelishchev et al. [12], Breck [13]). According to these relationships, a zeolite shows a higher capacity for cations with higher charge under comparable conditions and larger cations with lower hydration ability enter more easily the zeolite if their charges are equal.

The equilibrium isotherms of ion-exchanging reactions between NH₄⁺ saturated zeolites and solutions of cations present in significant amounts in soil solutions were determined within concentration limits usual for soils of the Czech Republic. The obtained equilibrium concentration limits were 5 - 50 mg l⁻¹ for K, 20 - 40 mg l⁻¹ for Na, 20 - 150 mg l⁻¹ for Ca, and 20 - 50 mg l⁻¹ for Mg. Figure 1 shows equilibrium isotherms of the ion-exchange between NH₄⁺ saturated zeolites and a solution containing K⁺ ions with starting

concentration 50 mg l⁻¹. The coordinates in figures 1-3 represent relative concentrations. Concentrations in the liquid phase are related to the starting concentration of the respective cation in the solution, concentrations in the solid phase represent the ratios between the actual and the maximum attainable concentration of the cation in the zeolite. The distribution of K⁺ between the solid and the liquid phase was well balanced in the case of synthetic phillipsite and slightly in favour of the solid phase in the case of synthetic P_c zeolite and natural clinoptilolite which indicates that the sorption of potassium ions and the release of ammonium ions to the solution would be preferred under these conditions. All three zeolites showed a negative selectivity against sodium ions (see figure 2) - a larger portion of Na⁺ was found in the liquid phase after the equilibrium had been established under similar conditions. A slightly lower degree of exchange of Na⁺ in the case of the P_c zeolite in comparison with

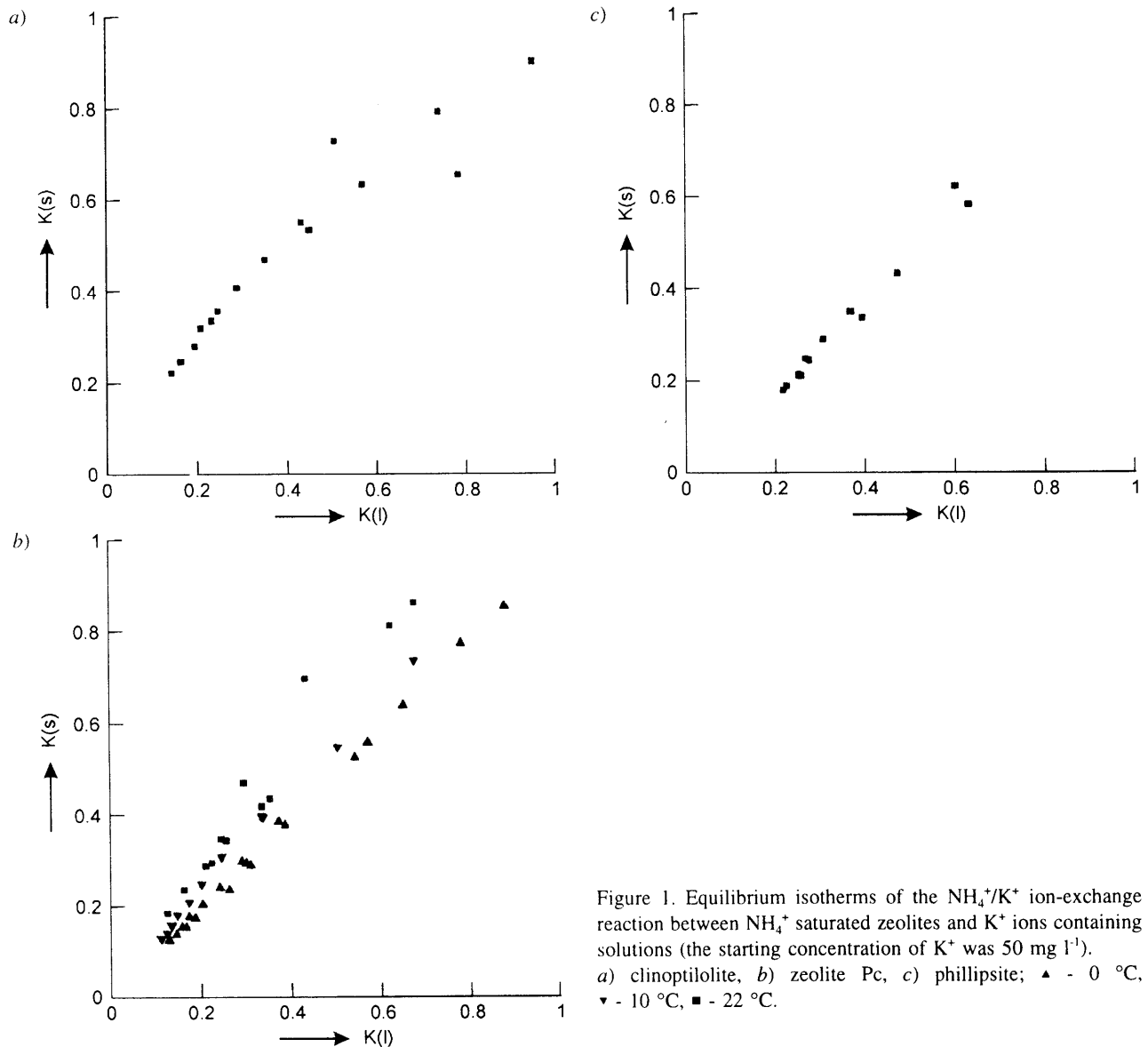


Figure 1. Equilibrium isotherms of the NH₄⁺/K⁺ ion-exchange reaction between NH₄⁺ saturated zeolites and K⁺ ions containing solutions (the starting concentration of K⁺ was 50 mg l⁻¹). a) clinoptilolite, b) zeolite P_c, c) phillipsite; ▲ - 0 °C, ▼ - 10 °C, ■ - 22 °C.

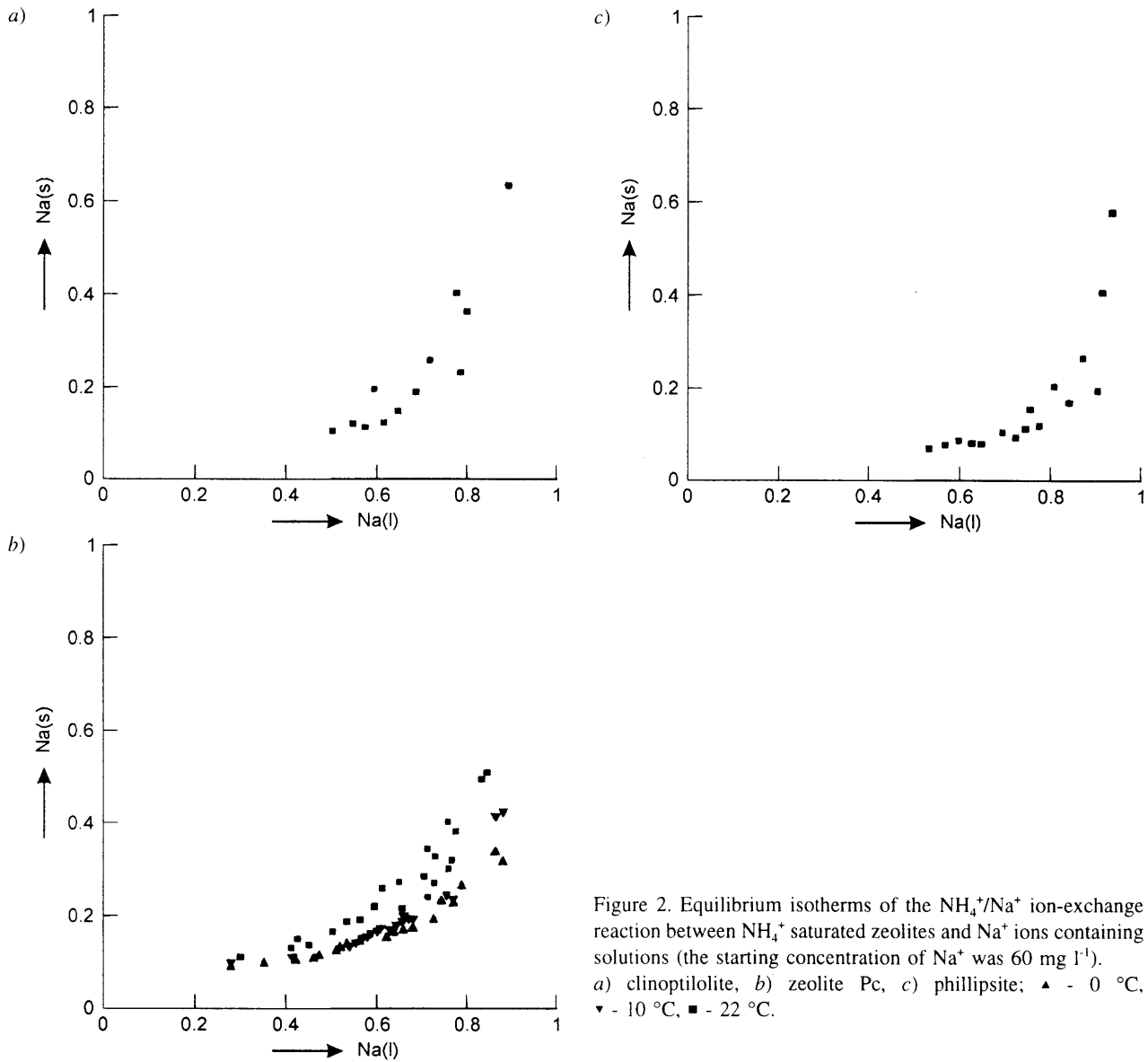


Figure 2. Equilibrium isotherms of the $\text{NH}_4^+/\text{Na}^+$ ion-exchange reaction between NH_4^+ saturated zeolites and Na^+ ions containing solutions (the starting concentration of Na^+ was 60 mg l^{-1}). a) clinoptilolite, b) zeolite Pc, c) phillipsite; \blacktriangle - 0°C , \blacktriangledown - 10°C , \blacksquare - 22°C .

natural clinoptilolite and phillipsite could be explained by the fact that a full saturation of this zeolite with NH_4^+ ions could not be achieved even after repeated saturation attempts - roughly 10 % of the exchangeable positions remained occupied by Na^+ ions. These Na^+ ions were exchanged simultaneously with the NH_4^+ ions, the ratio of ammonium to sodium ions released to the solution remaining the same as that in the solid phase. The equilibrium isotherms of ion-exchanging reactions between NH_4^+ saturated zeolites and Ca^{2+} ions are shown in figure 3. In contrast to natural clinoptilolite and synthetic phillipsite, the P_C zeolite showed a positive selectivity against the calcium ions - the NH_4^+ ions were released to the solution and the extent of the exchange increased slightly with increasing temperature. A similar

effect of temperature was also observed at the exchange of NH_4^+ for K^+ and Na^+ in the case of this zeolite (see figures 1 and 2). The worst and fully non-specific ion-exchange was found between NH_4^+ saturated zeolites and solutions containing the Mg^{2+} ions. The amount of NH_4^+ ions released in the equilibrium state was usually 10 - 20 % in this case and did never surpass 50 % of the exchangeable ammonium ions. None of the three studied zeolites was selective against magnesium ions under the above mentioned conditions.

Equilibrium isotherms of the above mentioned exchange-reactions were measured under experimental conditions similar to those than can really be expected in the soil (temperature, concentration of ions in soil solutions). It is probable, that after the NH_4^+ saturated

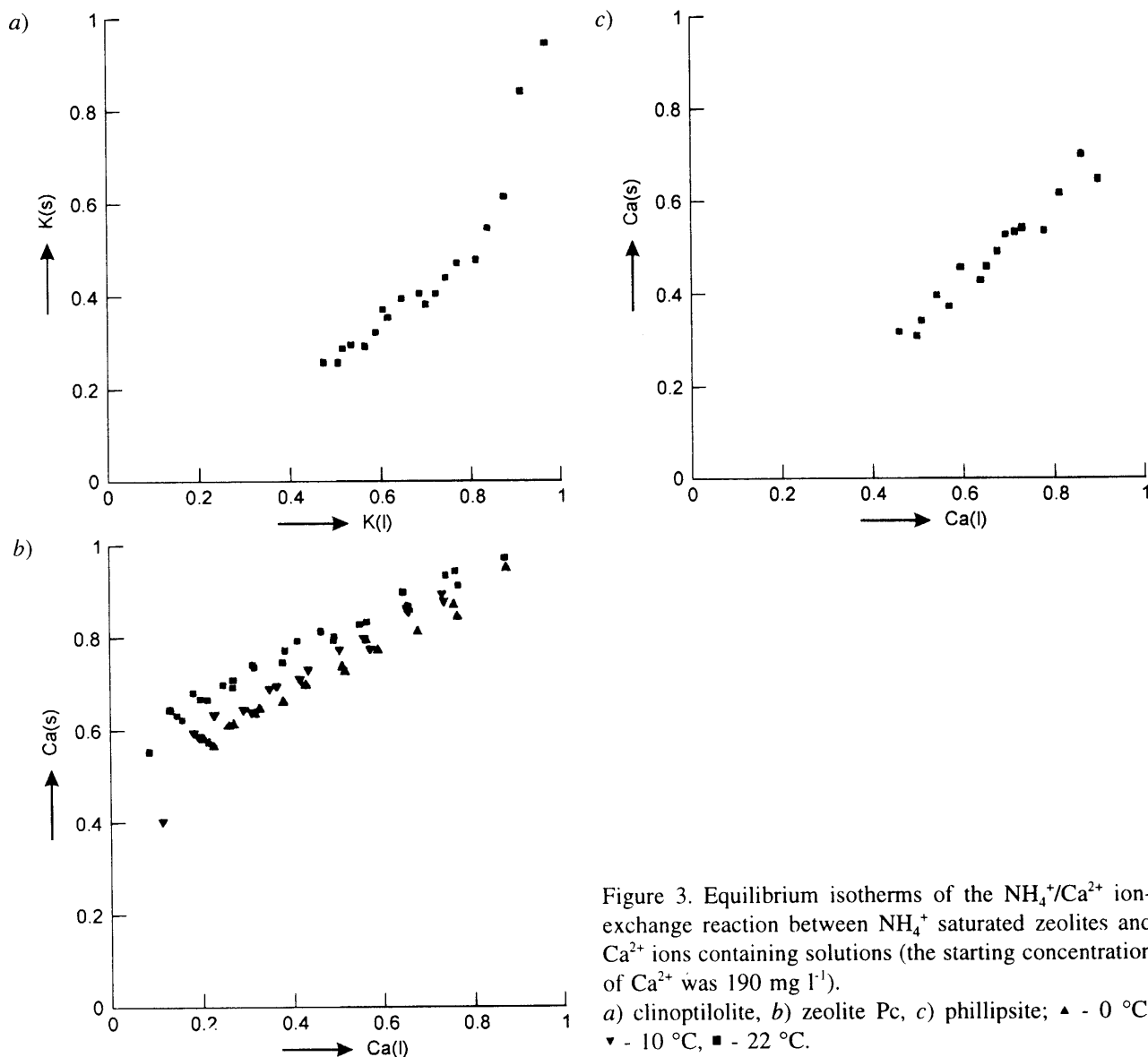


Figure 3. Equilibrium isotherms of the $\text{NH}_4^+/\text{Ca}^{2+}$ ion-exchange reaction between NH_4^+ saturated zeolites and Ca^{2+} ions containing solutions (the starting concentration of Ca^{2+} was 190 mg l^{-1}).

a) clinoptilolite, b) zeolite Pc, c) phillipsite; \blacktriangle - $0 \text{ }^\circ\text{C}$, \blacktriangledown - $10 \text{ }^\circ\text{C}$, \blacksquare - $22 \text{ }^\circ\text{C}$.

zeolites have been applied to the soil, the NH_4^+ ions will be released to the soil as a result of the ion-exchange reactions with K^+ ions (and also Ca^{2+} in the case of the P_C zeolite) present in the soil solution. Consequently, the zeolites saturated with ammonium ions (e.g. in waste water purification processes) can be used as a cheap source of nitrogen in agriculture. The time necessary for the ammonium ions to be released to the soil is relatively short (several days) and the release could probably be accelerated by the decrease of the concentration of ammonium ions in the soil by further processes (nitrification, the uptake of nitrogen by plants etc.). It is evident, that the NH_4^+ saturated zeolites cannot be considered to be a slow releasing nitrogen fertilizer.

References

1. Hagiwara Z., Uchida M.: In: *Natural Zeolites*, Int. Conf. Tucson 1976, p.463, Pergamon Press 1978.
2. Colella C., Aiello R.: In: *Occurrence, Properties and Utilization of Natural Zeolites*, 2nd Int. Conf. Budapest 1985, p.491, Akadémiai Kiadó Budapest 1988.
3. Ciambelli P., Corbo P., Liberti L., Lopez A.: In: *Occurrence, Properties and Utilization of Natural Zeolites*, p.501, 2nd Int. Conf. Budapest 1985, Akadémiai Kiadó Budapest 1988.
4. Koloušek D., Procházková E., Seidl V., Šmejkalová M.: Czech Patent Application No. 04530-90R, C-01-B-33/34 (1990).
5. Kovanda F., Koloušek D., Seidl V., Procházková E., Obšasníková J.: *Ceramics - Silikáty*, 38, 75 (1994).

6. Lewis M.D., Moore F.D., Goldsbery K.L.: In: *Use of Natural Zeolites in Agriculture and Aquaculture*, p.105, Westview Press, Boulder, Colorado 1984.
7. Pirela H.J., Westfall D.G., Barbarick K.A.: In: *Use of Natural Zeolites in Agriculture and Aquaculture*, p.113, Westview Press, Boulder, Colorado 1984.
8. Weber M.A., Barbarick K.A., Westfall D.G.: In: *Use of Natural Zeolites in Agriculture and Aquaculture*, p.263, Westview Press, Boulder, Colorado 1984.
9. Sopková A., Bubanec J., Černaj P., Šingliar M., Mondík P., Budinská V.: *Chemický průmysl* 68, 145 (1993).
10. Gottardi G., Galli E.: *Natural Zeolites*, Springer Verlag, Berlin 1985.
11. Hansen S., Hakansson U., Landa-Canovas A.R., Falth L.: *Zeolites* 13, 276.
12. Chelishchev N.F., Berenstein B.G., Vorodin V.F.: *Ceolitynovyj tip mineralnogo syria*, Nauka, Moscow 1987.
13. Breck D.W.: *Zeolite Molecular Sieves*, Wiley, New York 1974.

Submitted in English by the authors.

IONTOVÁ VÝMĚNA MEZI ZEOLITY NASYCENÝMI NH_4^+ A HLAVNÍMI KATIONTY PŘÍTOMNÝMI V PŮDNÍM ROZTOKU (K^+ , Na^+ , Ca^{2+} , Mg^{2+})

FRANTIŠEK KOVANDA, HELENA KUSÁ, DAVID KOLOUŠEK

*Ústav chemie pevných látek,
Vysoká škola chemicko-technologická,
Technická 5, 166 28 Praha 6*

Byly sledovány iontově-výměnné reakce probíhající mezi zeolity nasycenými ionty NH_4^+ a roztoky obsahujícími kationty, které se ve významných koncentracích nalézají v půdním roztoku (K^+ , Na^+ , Ca^{2+} a Mg^{2+}). K experimentům byl použit přírodní klinoptilolit a dva syntetizované zeolity (zeolit P_c a phillipsit) připravené hydrotermální alterací elektrárenských popílků. Zeolity byly nasyceny amonnými ionty v roztoku NH_4Cl ($c = 5 \text{ mol l}^{-1}$). U všech tří sledovaných zeolitů probíhala iontová výměna nejlépe v roztocích obsahujících ionty Ca^{2+} a K^+ , poněkud hůře pak v roztocích obsahujících ionty Na^+ . V roztocích obsahujících ionty Mg^{2+} probíhala iontová výměna pouze v malém rozsahu. Rovnovážné izotermy iontově-výměnných reakcí byly změřeny v koncentračních rozmezech, v nichž se uvedené kationty obvykle nalézají v reálném půdním roztoku. Z výsledků měření vyplývá, že po aplikaci zeolitů nasycených ionty NH_4^+ do půdy zřejmě dojde k jejich poměrně rychlému uvolnění v důsledku výměnných reakcí s ionty K^+ a v případě zeolitu P_c rovněž s ionty Ca^{2+} přítomnými v půdním roztoku.