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An Equilibrium Ion-Exchange Study on the Removal of NH_4^+ Ion from Aqueous Effluent Using Clinoptilolite

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ABSTRACT

The present work concerns an equilibrium study of naturally occurring clinoptilolite as an ion-exchange medium; the clinoptilolite has been used for the removal of the NH_4^+ ion from a model aqueous effluent of the Landfill Leachate Assisted Froth Flotation (LLAFF) process. The other principal cations involved were sodium and calcium, and the anion was chloride. A number of experimental tests with constant ionic strength in solution were conducted; these were performed to further validate the feasibility of using clinoptilolite to remove NH_4^+ ion from the LLAFF effluent. The experimental data obtained were well described by the law of mass action. A binary-component equilibrium study revealed a value for the binary separation factor $\alpha_{NH_4^+, Na^+}$ of 5.5; this value was relatively unaffected by the total salinity under the

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experimental conditions. Values for the intra-particle diffusion coefficient and the maximum ion-exchange capacity were also obtained; the latter was affected by total salinity. Results from the binary-component and multicomponent studies have revealed the selectivity of clinoptilolite for ammonium over other cations under the compositional conditions of the model LLAFF effluent: The selectivity sequence is $K^+ > NH_4^+ > Na^+ >> Ca^{2+}$. The factors that influence the selectivity of clinoptilolite for NH_4^+ in LLAFF effluent have been ascertained; in particular, it has been found that small quantities of Ca^{2+} in the effluent have a deleterious effect on both selectivity toward ammonium and ammonium ion-exchange capacity.

Key Words: Ion-exchange equilibrium; Clinoptilolite; Ammonium ion removal; Aqueous effluent; Mass action; Separation factor; Competing cations; Selectivity sequence.

INTRODUCTION

Landfill plays a major part in solid-waste disposal. In addition, landfill leachate treatment is well recognized as one of the problematic issues in the operation of sanitary landfills.[1] A significant amount of research has been devoted to the removal of major pollutants containing BOD, COD, and ammoniacal nitrogen by various kinds of treatment process.

Hall[2] investigated a new concept for the disposal of landfill leachates: The Landfill Assisted Froth Flotation (LLAFF) process. Instead of trying to remove the pollutants from the waste stream, this process exploits the organic compounds in leachate, which have similar structures to the conventional surface-active materials used in froth flotation. Thus, it can achieve relatively high recovery during coal floation, as well as remove most of the biodegradable and nonbiodegradable organic substances and total suspended solids. However, liquid waste derived from the LLAFF process contains relatively high ammoniacal nitrogen concentrations that require further treatment. Typically, these concentrations are in the range 50 to 500 mg/L.[3]

A number of treatments involving biological, chemical, or physicochemical processes, or a combination of these, have been developed to remove high concentrations of ammoniacal nitrogen.[4–10] Although each of these unit processes has unique advantages in achieving the established process objectives, each technology also has weaknesses to a greater or lesser extent in terms of their economic, environmental, or technical liability.

This research has been conducted as an extension of the work reported in Ref.[2] and has been designed primarily to investigate a potentially low-cost technology for reducing the ammonia concentrations remaining in the liquid waste derived from the LLAFF process; these should be reduced to a level that complies with the discharge limit set by the wastewater treatment company.

A review of recent ammonia removal processes has revealed that a naturally occurring zeolite, clinoptilolite, has high selectivity for the ammonium ion and some heavy metals.[11–17] Owing to its capacity for the selective removal of NH_4^+ ions, clinoptilolite has a wide range of applications in both water and wastewater treatment. In a previous study, a dynamic investigation of NH_4^+ removal from NH_4Cl solution was carried out using packed-beds of clinoptilolite in up-flow mode.[18] In this way, the feasibility of using clinoptilolite for the removal of NH_4^+ ions from the LLAFF process effluent was established. The present work builds on this study by providing fundamental information on the adsorption equilibria between the NH_4^+ ion present in the effluent and the clinoptilolite ion-exchange surface, under the conditions of the expected composition of the LLAFF process effluent. A compositional analysis of LLAFF effluent is presented in Appendix A.

MODELS OF EQUILIBRIUM ION-EXCHANGE ISOTHERMS

In the most thorough previous treatment of this system, Shallcross and coworkers have attempted to fit standard one-component adsorption models such as Langmuir and Freundlich to their data[15,16] in order to obtain equilibrium ion-exchange isotherm models. However, the applicability of the Freundlich model in describing the equilibrium binary ion-exchange isotherms is questionable. On the one hand, when fit to experimental data, this model imposes no intrinsic limit on the adsorption of the cationic species by the zeolite. On the other hand, it is generally accepted that the cation adsorption capacity of zeolite is limited by the number of exchange sites available. This idea is discussed and supported in reference.[15] In this sense, the single-component Langmuir model is more applicable because a limit on adsorption is imposed. However, the Langmuir model itself fails to account for the true nature of the ion-exchange as a binary, displacement-adsorption process. This involves at least two species, whose relative proportions and hence concentratrions alter.

Since ion-exchange is a phenomenon involving chemical equilibria, the law of mass action may be applied. Mass action is intrinsically a more satisfactory model, since it is based on an equilibrium exchange process between two or more species, and it also imposes a limit on maximum uptake. This is the modeling approach followed in the present work. The generalized equation for cation-exchange by an exchanger is described as follows:

$$b \cdot A^{+a} + aB \cdot Z_b \Longleftrightarrow bA \cdot Z_a + aB^{+b}$$

where a and b are the valences of ions A and B, respectively, and Z is the exchange site on the surface of the solid. The mass-action model for ion-exchange with constant separation factor is expressed in Eq. (2).

EXPERIMENTAL METHODS AND PROCEDURES

In this work, a number of equilibrium tests were carried out to investigate the exchange of ammonium ions on the surface of clinoptilolite. The solid material was pretreated in order to transform the exchangeable sites completely to the Na-form. It was also important to ensure that ion-exchange equilibrium had been achieved. Contact time was set at five days; under normal circumstances, this time is more than adequate to achieve equilibrium.

Materials

Natural clinoptilolite was obtained from the ECOSOLVE Company. The manufacturer provided quantitative compositional information for the material, based on XRD analysis. It was determined to contain three major zeolite minerals: 58% clinoptilolite, 9.6% heulanite, and 6.0% stilbite; the remainder consisted of feldspar, quartz, and illite/mica. The relative amounts were determined by ECOSOLVE using the software package Siroquant, which gives a quantitative phase analysis of minerals based on XRD analysis. The diffraction patterns of the three minerals are rather similar, so the analysis is made under conditions where errors are likely to be higher than normal. Nevertheless, the analysis is sufficiently reliable to establish a definitive composition of the material. Further property specifications were provided, as shown in Table 1. The grain sizes were found to lie in the range 1.02 to 2.04 mm, with an average size of 1.93 mm.

Ammonium chloride (analytical reagent grade) was obtained from Fisher Scientific with a stated purity of 99.8% and was used as supplied. Sodium chloride (analytical reagent grade) was obtained from BDH with a stated purity of 99.5% and was used as supplied. Calcium chloride (analytical reagent grade) was obtained from Fisher Scientific in the form of anhydrous lumps and was used as supplied. All solutions were prepared using single-distilled water.

Table 1. Properties of clinoptilotite as provided by supplier.

Property	Value
Ion-exchange capacity	160 meq/100 g
Surface area	6,300 m^2/g
Packing density	0.85 g/cm^3
Total pore space	0.468 cm^3/g
Solid density	2.27 g/cm^3
Void volume	32.5%

Analysis of Data

Ammonia concentration in solution was measured using an ammonia electrode, in conjunction with a digital pH/mV meter. The electrode was supplied by Russell pH limited (model 95-5129) and was standardized using 0.1 M ammonium chloride solution. Measurements in the range 4×10^{-6} M up to 1.0 M ammonia are the most reliable. The electrode measurements are not affected by sample color or turbidity. Anions, cations and dissolved species other than volatile amines do not interfere with the electrode. The concentration of sodium in solution was determined by atomic absorption spectroscopy. The concentration of calcium in solution was then determined by subtracting the sum of the concentrations of ammonium and sodium ions from the total equivalent concentration (sometimes referred to as the total salinity, which was fixed for each set of tests); electrical neutrality requires the sum equivalent concentrations of cations in solution to be equal to the total salinity (concentration of chloride anions). In general, the total salinity level may have an effect on ion-exchange behaviour, particularly if it varies over a wide range in values. Note that in preliminary work, we determined calcium ion directly by atomic absorption spectrophotometry. In the test cases, the analysis yielded good agreement with the value determined by difference. The latter method was therefore adopted for all reported measurements.

The mole equivalent fraction of ammonium in the solution phase was determined as the concentration of ammonium divided by the total solution equivalent concentration (i.e., concentration expressed as moles of monovalent positive or negative charge). Solid-phase loading of ions was determined simply as the molar equivalent depletion from solution (solution volume times drop in equivalent concentration) per unit mass of solid. The mole equivalent fraction of ammonium in the solid phase was determined as the adsorption loading of ammonium on the surface of clinoptilolite divided by the total ion-exchange capacity (determined as the maximum adsorption level of NH_4^+ at the total salinity level). Mole equivalent fractions for the other species were determined in a similar way.

Methods

A series of NH_4Cl concentrations were prepared as follows. The total salinity in the solution, defined as the total molar equivalent concentration of ions, was kept constant at either 0.011 N or 0.16 N. The former is equivalent to 11.11 meq/L (or 200 mg/L) of NH_4-N, which is the expected concentration of NH_4^+ in the effluent from LLAFF in the absence of other species. The latter value represents the expected total ionic strength of the LLAFF effluent. Details of the initial compositions used for the binary equilibrium tests at total salinity 0.011 N are summarized in Table 2. 11.11 meq/L ammonium solution was mixed with 1.0 M sodium chloride solution in an appropriate quantity along with distilled water, in order to create the initial compositions shown.

The natural clinoptilolite was first washed in distilled water to remove particulate impurities and then preconditioned in strong brine (0.87 M) for 60 min, in order to transform the surface-exchangeable sites completely to the Na^+ form. The clinoptilolite was then rinsed three times with 50 mL of deionized water. The ion-exchange isotherm was constructed as follows: 2 g quantities of preconditioned, wet zeolite particles were weighed into small sample bottles and placed in contact with 50 mL of solution containing both exchange cations (i.e., NH_4^+ and Na^+). They were subsequently stored at room temperature with vigorous shaking at 300 oscillations/min for about

Table 2. Equilibrium tests with total normality 0.011 N.

Run	Initial proportion between NH_4^+|Na^+	Initial concentration of NH_4^+ mg/L (meq/L)	Initial concentration of Na^+ mg/L (meq/L)
1	10%|90%	20 (1.11)	230 (10)
2	25%|75%	50 (2.78)	192 (8.35)
3	40%|60%	80 (4.44)	153.2 (6.66)
4	50%|50%	100 (5.56)	127.6 (5.55)
5	75%|25%	150 (8.33)	64 (2.78)
6	80%|20%	160 (8.89)	51 (2.22)
7	90%|10%	180 (10)	25.6 (1.11)
8	100%|0%	200 (11.11)	0 (nil)

30 min; we estimated that this was enough to remove the effect of the solid-liquid boundary layer and to ensure diffusion-controlled conditions. Sampling the solutions at 10 min intervals during trial runs revealed this time was sufficient to establish equilibrium. These solutions contained varying initial proportions of NH_4^+ and Na^+ (see, for example, Table 2). It was important that the solutions, although having different relative amounts of NH_4^+ and Na^+ ion, should have a constant total normality (N) and thus allow meaningful results. This is because ion-exchange performance is also, in general, a function of total ionic normality (also known as ionic strength, or salinity).[19] A similar procedure was employed when calcium was additionally present. Following the test, solid and liquid were separated by filtration through Whatman paper grade 541 and vacuum assistance and the filtrates were analyzed for ammonium and/or sodium ion. In order to determine the effect of contact time on the dynamic uptake of the ammonum ion, the test described above was repeated for a number of identical batches using only NH_4^+ ion at a concentration of 200 mg/L. At a certain time, the particles were separated from the solution and the latter analyzed for ammonium. The same technique was also used to determine the equilibrium influence of solution pH on ion-exchange capacity; in these tests, the pH was adjusted prior to shaking.

At equilibrium, the concentrations of NH_4^+ and Na^+ in the solution and solid phases were analyzed to determine the distributions of NH_4^+, Na^+ and Ca^{2+} between the phases. An isotherm was then plotted, which records the equivalent fraction of the exchanging ion in solution (A_S) against that in the zeolite (A_Z), where: $X_{NH_4} = A_S =$ final equivalent concentration of NH_4^+ in solution/[final equivalent concentration of all ions]; $Y_{NH_4} = A_Z =$ moles equivalent NH_4^+ adsorbed on zeolite/moles equivalent total ions adsorbed on zeolite (ion-exchange capacity). See above for details of the measurement.

For the law of mass action in ion-exchange equilibrium involving monovalent species, we can write:

$$NH_4^+{}_{(liq)} + Na^+{}_{(sol)} \Longleftrightarrow NH_4^+{}_{(sol)} + Na^+{}_{(liq)}$$

for which

$$K_{eq} = \frac{[NH_4^+]_{sol}/[NH_4^+]_{liq}}{[Na^+]_{sol}/[Na^+]_{liq}} \tag{1}$$

The separation factor (α) for an equilibrium ion-exchange of NH_4^+ ions with Na^+ ions on the clinoptilolite surface was calculated using the following relationship, in the case of binary mixtures:[20]

$$\alpha_{NH_4^+,Na^+} = \frac{(Y_{NH_4}/X_{NH_4})}{(Y_{Na}/X_{Na})} = \frac{Y_{NH_4} \times (1 - X_{NH_4})}{(1 - Y_{NH_4}) \times (X_{NH_4})} \tag{2}$$

By multiplying the numerator and denominator of Eq. (2) by the ratio of ion-exchange capacity to solution total equivalent concentration, it can be seen that the separation factor is equal to the equilibrium constant K_{eq} for mass-action equilibrium, i.e., $K_{eq} = \alpha_{NH_4^+, Na^+}$.

Similar relationships can be written for other pairs of ions. If one of the exchanging species is divalent, such as calcium, the equilibrium can be written as

$$Ca^{2+}{}_{(liq)} + 2Na^{+}{}_{(sol)} \Longleftrightarrow Ca^{2+}{}_{(sol)} + 2Na^{+}{}_{(liq)}$$

for which

$$K_{eq} = \frac{[Ca^{2+}]_{sol}/[Na^{+}]_{sol}^{2}}{[Ca^{2+}]_{liq}/[Na^{+}]_{liq}^{2}} \tag{2a}$$

Regardless of the valency of exchanging ions, the definition of separation factor expressed in Eq. (2) remains valid. Multiplying Eq. (2) (written for the case where one ion is divalent) by the ratio of ion-exchange capacity to solution total equivalent concentration and inspection of Eq. (2a) leads to the result: $K_{eq} = \alpha_{Ca^{2+}, Na^+} [Na_{sol}^{+}]_{liq}/[Na_{sol}^{+}]$.

In multicomponent mixtures (i.e., ternary component mixtures in this work), the second equality in Eq. (2) clearly does not apply.

Unless otherwise stated, all tests were performed at an ambient temperature of approximately 20°C and under conditions of natural pH (i.e., that which pertains following equilibration with water at neutral pH).

RESULTS AND DISCUSSION

Conditioning of the Clinoptilolite

Measurements on the maximum adsorption level of ammonium ions onto clinoptiloloite (i.e., the ion-exchange capacity) from a 200 mg/L solution of ammonium ions (i.e., 11 meq/L) revealed that the brine preconditioning process was able to increase the ion-exchange capacity from 0.19 meq/g to 0.22 meq/g. The unit cell formula for clinoptilolite is $(Na_4K_4)(A_{l8}Si_{40}O_{96}) \cdot 24H_2O$, indicating that the unconditioned, naturally occurring material contains both potassium and sodium as exchangeable ions. Since replacement of potassium by sodium increases ion-exchange capacity, this would suggest that the clinoptilolite material has a greater affinity for the potassium ion than the sodium ion. Such an observation agrees with previous studies.[15,23–25]

Effect of Final NH_4^+ Concentration on the Ion-Exchange Capacity

The results of the analysis of the adsorption isotherm of NH_4^+ on clinoptilolite are presented in Figs. 1 to 3. In Fig. 1, the maximum adsorption level of NH_4^+ onto clinoptilolite (i.e., the ion-exchange capacity) was equal to 0.22 meq/g of ammonium ion when the solution contained 100% NH_4^+; this was measured at a low total ionic strength, equal to 0.011 N. Watanabe et al.[27] have reported a value for natural zeolites (containing clinoptilolite and mordenite) of 0.34–0.36 meq/g at an ionic strength of 0.001 N, rising to 1.2 mmol/g at 0.01 N. This latter figure agrees with the manufacturer's reported value of 1.6 meq/g (Table 1). Hagiwara and Uchida[28] report an ammonium ion-exchange capacity for a processed mordenite (zheobarb) of 1.78 meq/g. However, Jama et al.[29] have suggested that maximum ammonium ion-exchange with clinoptilolite in the sodium form is only partially complete. Even at 0.1 N ammonium ion, they report a figure of 68%. In addition, Murphy, Hrycyk, and Gleason[30] report much lower values for clinoptilolite sourced in the western states of the United States ranging between 0.06 and 0.14 meq/g, with higher figures at higher ammonium feed

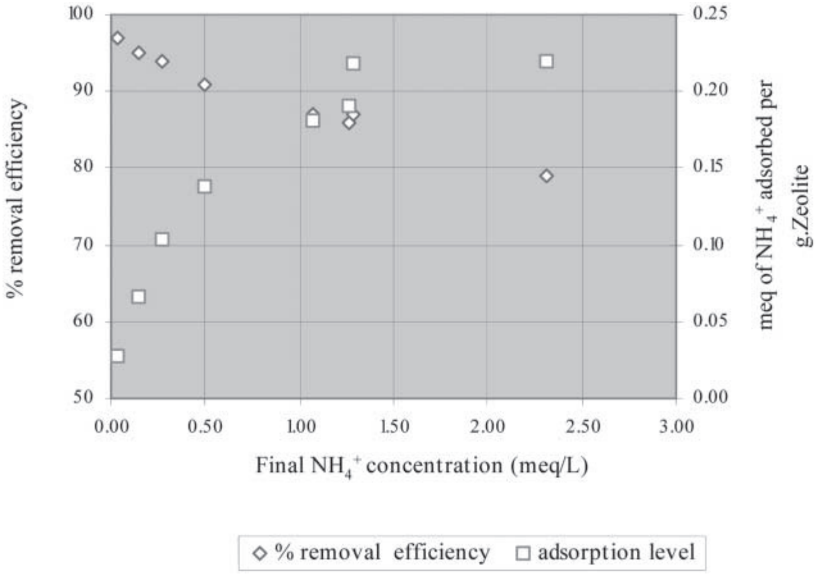

Figure 1. Ammonium removal efficiency and adsorption level.

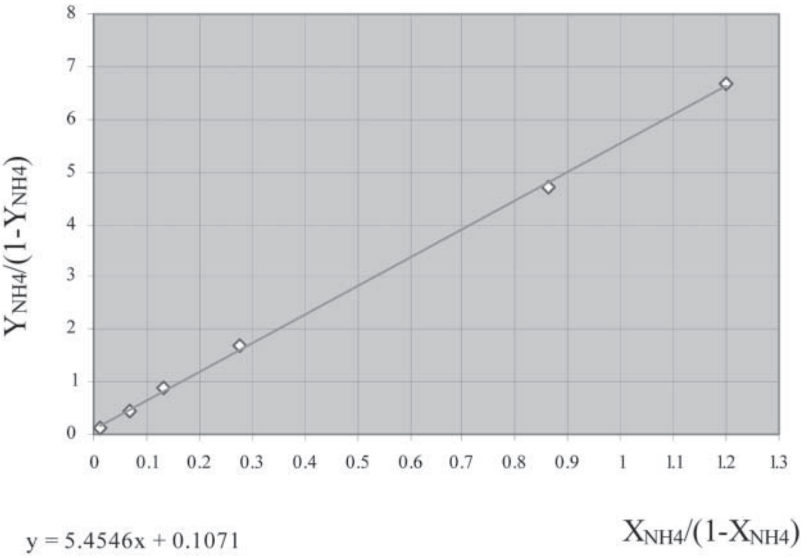

Figure 2. Determination of separation factor $\alpha_{NH_4^+,Na^+}$ with a salinity of 0.011 N.

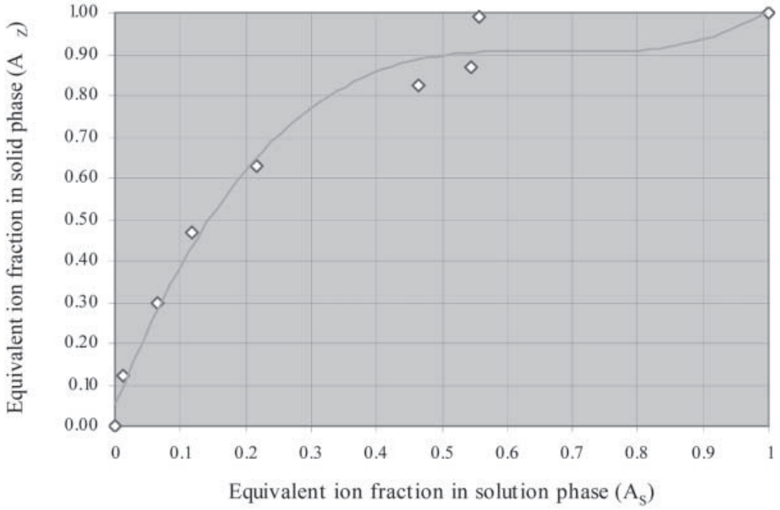

Figure 3. Generalized ion-exchange isotherm for exchange of NH_4^+ and Na^+ on clinoptilolite.

concentrations. Clearly, the place of origin of the material has a significant influence on ammonium exchange capacity.

Figure 2 represents a direct plot of Eq. (2). In order to find the value of separation factor, we find the best straight-line fit of the form $y = ax + b$. It is clear that the data can be fit well by the mass action model, with a value for the separation factor $\alpha_{NH_4^+, Na^+}$ of 5.53. Moreover, the value of the intercept b is small at 0.1071, indicating the best-fit line passes close to the origin. This value was used to obtain the curve-fit to the data in Fig. 3, which adequately passes through the measured points. Jama et al.[29] have reported separation factors for binary ion-exchange involving ammonium and either sodium, potassium, or calcium. The factors vary with ammonium equivalent fraction. For sodium, values range from 4 to 9, in broad agreement with this work. Hagiwara and Uchida[28] report a value for $\alpha_{NH_4^+, Na^+}$ on zheobarb of 4.75 at salinity of 0.13 N and 4.97 at a salinity of 0.21 N. Shallcross and coworkers have reported separation factors (termed selectivity coefficients in their work) in a range of values between 0.5 and 4.[15] However, these values were not obtained by direct application of the mass-action model.

Figure 1 also indicates that the percentage efficiency of NH_4^+ removal (defined as the amount removed divided by the amount initially present) decreases with an increase in final NH_4^+ concentration; this is consistent with the ion-exchange surface becoming increasingly saturated with ammonium ion.

Effect of Contact Time

It was found that 50% and 75% of final NH_4^+ uptake on clinoptilolite occurred within the first 15 and 60 min, respectively. The rate of uptake was essentially negligible after 4 hrs. Booker[11] has reported rapid rates of adsorption during the first 10 min of batch tests. Many researchers have reported that, in zeolite ion-exchange, the rate-controling step is the diffusion process through the internal porosity of the ion-exchange particles.[19,22] Additionally, it can be expected that there will be some resistance caused by the mass-transfer of ions through the boundary layer of fluid surrounding the particles, and the Nernst layer of oriented water molecules close to the particle surface; the significance of this resistance is influenced by the Reynolds number of the external fluid and the cation concentration. The effect of this resistance is, however, lumped into the final value of diffusion coefficient.

In the case of the present study, the very high surface area of the material in Table 1 is indicative of a high degree of internal porosity. Therefore, it can be expected that the rate of ion-exchange depends principally upon the diffusion of cations, water molecules or cation-water complexes through the zeolite framework. Vermeulen's approximation[11] expresses fractional attainment of equilibrium with time:

$$X = [1 - \exp(-D\pi^2 t/r^2)]^{0.5} \tag{3}$$

where $X =$ fractional attainment of equilibrium, $D =$ diffusion coefficient (m^2/s), $t =$ time (sec) and $r =$ particle radius (m). In this case, r was specified by the manufacture as 1.93 mm (see Table 1).

To determine fractional attainment of equilibrium, we determined the ammonium uptake as a fraction of the total final uptake after 5 days. Equation (3) may be rearranged into a linear relationship with respect to time: a plot of $-\ln(1 - X^2)$ vs. time has a slope of $D\pi^2/r^2$. A good best-fit straight line is indeed obtained in Fig. 4, with a correlation coefficient of $R = 0.983$. The values of x range from 0.4 to 0.7 over the first hour of contact. Note that the line does not pass through the origin as expected, but uncertainties exist regarding zero time for the experiment. Aside from systematic experimental errors, the experiment cannot begin in precisely the way required to match the boundary conditions in Vermeulen's analysis. We have simply preferred

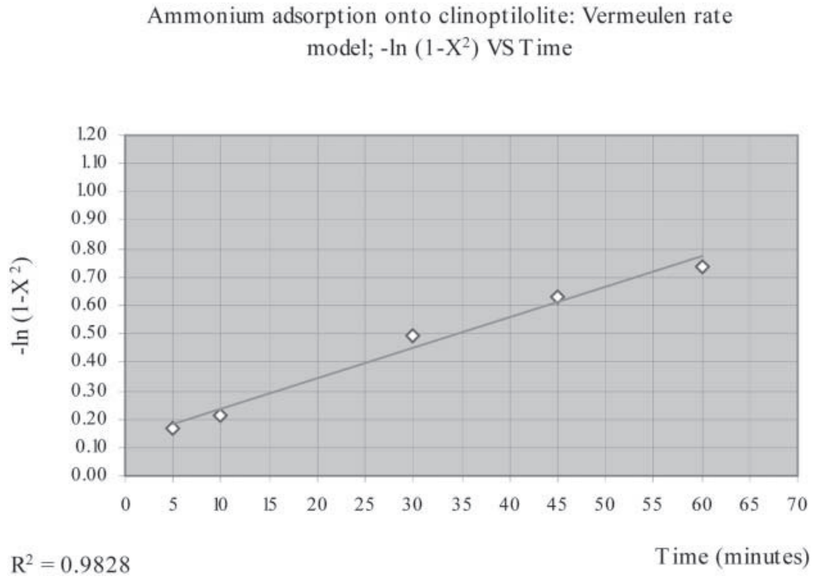

Figure 4. Rate test results fitted to model of Vermeulen's approximation.

to find the best-fit straight line (with arbitrary intercept); the linearity supports the validity of the Vermeulen approximation.

The straight-line fit confirms that intra-particle diffusion controls, or plays a major role in, the rate of adsorption. The calculated diffusion coefficient for the adsorption and exchange of NH_4^+ ions onto clinoptilolite is $6.06 \times 10^{-11}\,m^2/sec$ (at 25°C). This figure agrees well with the measurements of Shallcross,[15] who reported values in the range 1×10^{-11} to $1 \times 10^{-10}\,m^2/sec$.

Effect of Solution pH

The pH has a significant effect on the performance of NH_4^+ ion-exchange by clinoptilolite. The experimental results indicate that the performance of clinoptilolite for NH_4^+ removal is favoured by neutral pH, as shown in Fig. 5; extremes in pH lower the removal efficiency. The highest adsorption efficiency was obtained when pH was adjusted within a range between 5 and 8. The NH_4^+ removal efficiency was significantly lowered by increasing solution pH over 9, or decreasing it below 5. The result at high pH can be interpreted in terms of the ammonium dissociation equilibrium: an alkaline pH causes neutralization of the ammonium ion by hydroxyl ion, rendering it

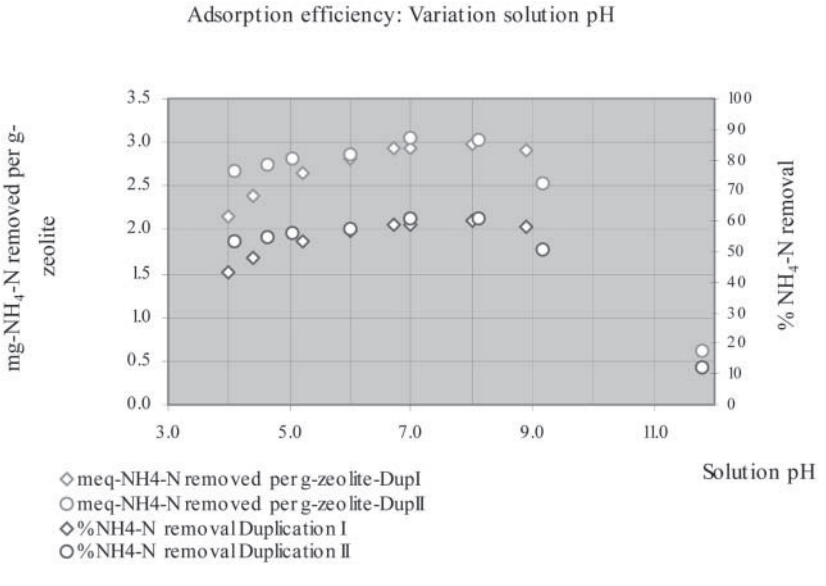

Figure 5. Effect of variation of solution pH on ammonium adsorption efficiency.

uncharged. At low pH, high concentrations of hydrogen ion compete with the ammonium ion for available ion-exchange capacity.

Two-Component Ion-Exchange Equilibrium

Batch experiments using solutions of differing composition were carried out to evaluate the effect of competing cations on the equilibrium capacity of clinoptilolite. Contact time was set at 5 days to ensure complete attainment of the ion-exchange equilibria. Total ionic strength in the solution was chosen to match that of the effluent from multistage froth flotation (0.16 N).

Equilibrium Test Between NH_4^+ and Na^+

In Fig. 6, the data depart somewhat from a straight line. The best-fit line indicates a separation factor $\alpha_{NH_4^+, Na^+}$ of 5.3679, indicating that the exchange pattern for the clinoptilolite is favorable for the removal of NH_4^+ ion from the aqueous effluent. This value also agrees with that obtained at the lower ionic strength in Fig. 3, i.e., 5.5 (see earlier discussion). The value of the intercept b is 0.5468, indicating this best-fit line does not pass close to the origin due to

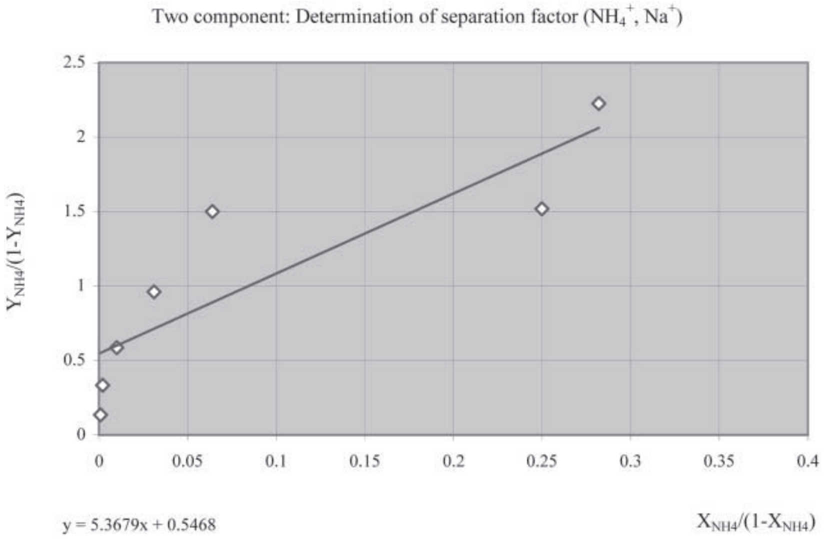

Figure 6. Determination of separation factor $\alpha_{NH_4^+, Na^+}$ at 0.16 N salinity.

the curvature in the data. Thus, the assumption of a constant separation factor is seen to be only approximately true at high ionic strength. According to Breck's classification, the ammonium-sodium ion-exchange conforms to type *a*.[31]

Equilibrium Test Between Na^+ and Ca^{2+}

Since Ca^{2+} ion is divalent, it might be expected that Ca^{2+} is preferentially adsorbed onto the clinoptilolite surface over univalent sodium. Another set of binary ion-exchange experiments were conducted involving Ca^{2+} instead of NH_4^+. The equilibrium separation factor for the Na^+ ion over the Ca^{2+} ion on clinoptilolite, $\alpha_{Na^+, Ca^{2+}}$, is determined in Fig. 7 as 1.9716. According to Breck's classification, the sodium-calcium ion-exchange also conforms to type *a*.[31]

Jama et al.[28] report a value for $\alpha_{NH_4^+,Ca^{2+}}$ at high ammonium fraction of 20. Similarly, they report a value for $\alpha_{NH_4^+,Na^+}$ of 9 at high ammonium fraction. This would seem to imply a value of $\alpha_{NH_4^+,Ca^{2+}}$ of 2.22. However, taking their data at low ammonium fraction implies a value of over 100. Similarly, Hagiwara and Uchida[28] report that the value of α_{Ca^{2+},Na^+} (the reciprocal separation factor) at 0.1 N salinity is less than one. Qualitatively, at least,

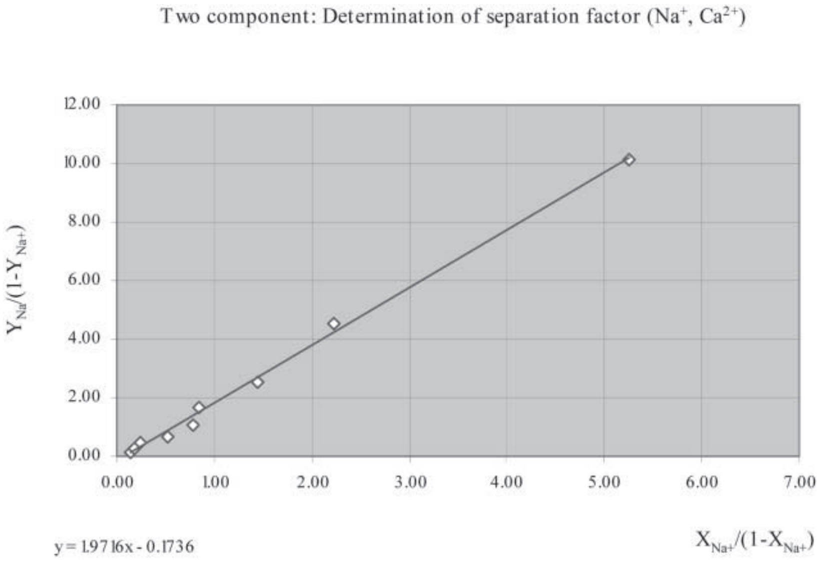

Figure 7. Determination of separation factor $\alpha_{Na^+,Ca^{2+}}$ at 0.16 N salinity.

this all confirms that clinoptilolite shows a strong preference for sodium over calcium.

Note that, in the case of monovalent and divalent exchanging ions, the separation factor is never strictly constant. Nevertheless, it is standard practice to use such values in comparing the ion-exchange selectivity between ions of different type and valence, so we apply the best-fit line analysis already used for the monovalent case. The resulting factor represents an average value over the range of interest. Thus, it is found that clinoptilolite shows a selectivity for Na^+ ions over Ca^{2+} ions. This is discussed further next.

When we combine the separation factor $\alpha_{NH_4^+,Na^+} = 5.3679$ and $\alpha_{Na^+,Ca^{2+}} = 1.9716$, the binary selectivity sequence for pairs of these ions under the total salinity conditions would appear to follow the sequence: $NH_4^+ > Na^+ > Ca^{2+}$.

Multi-Component Ion-Exchange Equilibrium

In view of the binary selectivities just observed, further study was conducted to investigate the possibility that multi-valent cations in the LLAFF effluent might still have deleterious effects on the removal of the NH_4^+ ion during ion-exchange with Na^+ on clinoptilolite. In multicomponent equilibrium tests, the solutions are composed of three major ions: NH_4^+, Na^+, and Ca^{2+} (total ionic strength maintained at 0.16 N, equivalent to that of LLAFF effluent). The molar equivalent ratio of Ca^{2+} (when present) to total Na^+ and NH_4^+ ions was maintained roughly equal to that in the analysis of LLAFF effluent feed, i.e., 1 : 10 (for details of the analysis of the LLAFF effluent, see Appendix A).

A comparison of the maximum NH_4^+ adsorption levels in two- and multicomponent systems (determined at 100% NH_4^+ and 91% NH_4^+: 11% Ca^{2+}, respectively, for a total salinity of 0.16 N and with the clinoptilolite initially conditioned in the sodium form) is shown in Table 3. The results show that the presence of Ca^{2+} ions in the system slightly reduces the maximum adsorbed amount of NH_4^+ ions on the solid phase by 21% from 0.54 to

Table 3. A comparison of maximum adsorption level of ammonium from two- and multicomponent systems (total normality = 0.16 N).

Maximum adsorption level: (meq/g)	Two-component system NH_4^+ and Na^+:	Multicomponent system NH_4^+, Na^+, and Ca^{2+}:
	0.54	0.47

0.47 meq/g. Note also that a comparison of Table 3 with Fig. 1 indicates that the maximum adsorption level of ammonium ions, and thus ion-exchange capacity, increases significantly with total solution salinity; however, the level measured at 0.16 N falls far short of the suppliers value of 1.6 meq/g. See also the discussion in section 4.2.

In a previous study by Ouki and Kavannagh,[13] it was reported that, for calcium concentrations less than 400 mg/L (10 meq/L, as used here), the effect of calcium on the removal efficiency of most metallic ions was negligible for both clinoptilolite and chabazite. On the other hand, a drastic decrease in ammonium removal efficiency was observed when calcium concentrations exceeded 1000 mg/L (25 meq/L). The expected maximum concentration of calcium in LLAFF effluent is thus at the borderline for having a potentially deleterious effect.

The separation factor $\alpha_{NH_4^+,Na^+}$ for the NH_4^+ ion on clinoptilolite, in the presence of both Na^+ and Ca^{2+}, is determined in Fig. 8. From the best-fit straight line, the determined value of $\alpha_{NH_4^+,Na^+}$ equals 1.83 in the presence of Ca^{2+}. The value of the intercept b is −0.00371, indicating the best-fit line

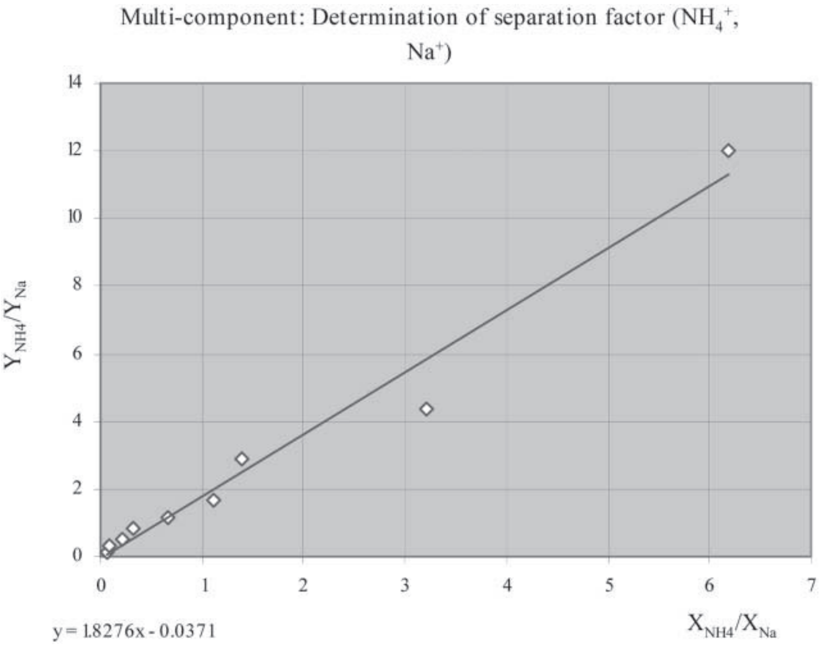

Figure 8. Determination of separation factor $\alpha_{NH_4^+,Na^+}$ in the presence of Ca^{2+} at 0.16 N salinity.

passes very close to the origin. Despite the presence of Ca^{2+} ions in solution, ion-exchange on clinoptilolite is still favourable for the replacement of NH_4^+ ion in solution with Na^+ ion. However, when the separation factor in the multicomponent system ($\alpha_{NH_4^+,Na^+} = 1.83$) is compared with that for the two-component system determined previously ($\alpha_{NH_4^+,Na^+} = 5.37$), it can be seen that the presence of Ca^{2+} ions seems to have a deleterious effect on the exchange of NH_4^+ ions onto clinoptilolite; under the maximum levels of calcium ion expected in the LLAFF effluent, the separation factor for ammonium/sodium is reduced by a factor 2.93. This result is somewhat unexpected, given that the clinoptilolite shows a preference for the sodium over the calcium. However, we have already observed that the presence of calcium has a deleterious effect on the exchange capacity; one possible explanation is that, as a divalent ion, the calcium has a strong and specific electrostatic shielding effect on the ion-exchange medium. In shielding the negative charges of the exchanger, the ability to exchange ammonium counterions with the sodium ions initially present on the exchanger surface is reduced.

For the multicomponent systems, the equivalent fraction of Ca^{2+} and Na^+ in the solution and solid phases were also analyzed, in order to determine the separation factor between them in the presence of all three ions. Figure 9 establishes α_{Ca^{2+},Na^+}, which equals 0.6214. Thus, $\alpha_{Na^+,Ca^{2+}}$ equals 1.609. Again, the constant b in the best-fit line is -0.3646, indicating the best-fit line does not pass close to the origin. As pointed out previously, the

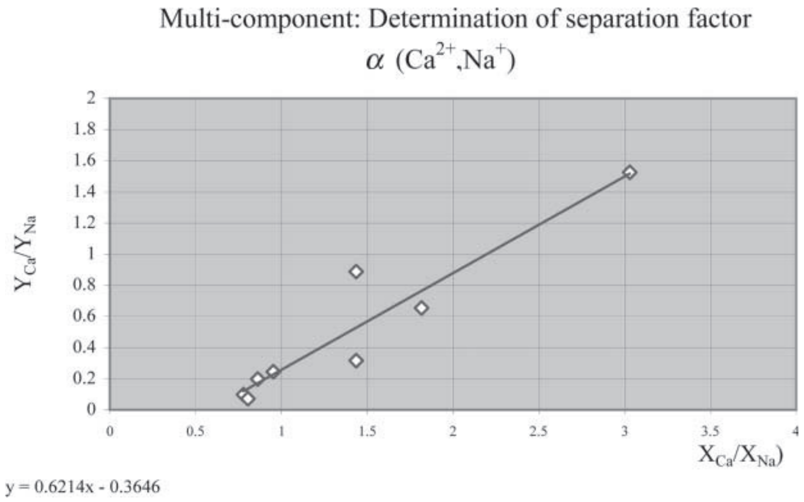

Figure 9. Determination of separation factor α_{Ca^{2+},Na^+} at 0.16 N salinity.

assumption of a constant separation factor is not strictly valid for mixtures of monovalent and divalent ions. The result for separation factor reveals that clinoptilolite is also less inclined to adsorb the Ca^{2+} ion than the Na^+ ion in the presence of ammonium. This result is also consistent with that seen earlier in the binary sodium-calcium case, where $\alpha_{Na^+,Ca^{2+}}$ equals 1.97 (see previous discussion). Referring to the results from multicomponent equilibrium studies, the ion-exchange selectivity sequence of clinoptilolite under typical LLAFF effluent compositions is again $NH_4^+ > Na^+ > Ca^{2+}$. A summary of values for separation factors determined in this work, for binary-component and multicomponent conditions, is given in Table 4 and compared with reported values in the literature.

According to Refs.[13,15,19], the selectivity series of an ion-exchanger is the result of various factors. One factor is the geometrical sieving effect, owing to the framework structure of the zeolite itself. The other factor is the specificity of a surface containing fixed charges for cations; this can be understood in terms of ion hydration energies and radii, and electrostatic bond energies.[13]

A factor that prevents an ion being adsorbed by zeolite is the hydrated ionic size. If the ionic size is greater than that of the pore, the species will be excluded geometrically. According to Table 5, there is no appreciable

Table 4. Separation factors determined under binary and multicomponent conditions (total salinity = 0.16 N; ratio of equivalent added calcium to total salinity held at 1 : 10).

Separation factor determined	Value of separation factor	Values reported in litertaure
$\alpha_{NH_4^+,Na^+}$ in binary component system	5.37 ($\pm$0.7)	4.0–9.0 at 0.1 N[28] 4.75–4.97 at 0.13 N (on zheobarb[27])
$\alpha_{Na^+,Ca^{2+}}$ in binary component system	1.972 ($\pm$0.004)	2.2 – ≈100[27,28] at 0.1 N >1.0 at 0.21 N (on zheobarb[27])
$\alpha_{NH_4^+,Na^+}$ in ternary component system: NH_4^+, Na^+, and Ca^{2+}	1.83 ($\pm$0.03)	Not available
$\alpha_{Na^+,Ca^{2+}}$ in ternary component system: NH_4^+, Na^+, and Ca^{2+}	1.61 ($\pm$0.04)	Not available

Table 5. Hydrated sizes of certain cations.

Cations	Hydrated size (Å)
Ca^{2+}	0.099
Na^{+}	0.097
K^{+}, NH_4^+	0.133

difference in hydrated size amongst the ions of interest in this study (with ammonium slightly larger). Considering that the effective window size of clinoptilolite lies in a range between 3.9 and 5.4 Å, all the cations listed in Table 5 should pass easily through the effective window of clinoptilolite, and therefore ionic sieving cannot explain the selectivity sequence observed.

Since the silica/aluminium ratio in clinoptilolite is relatively high (4.25–5.25), and the volumetric capacity is correspondingly low, the electrostatic field within the zeolite structure is relatively less important, and the electrostatic interactions are not expected to be as important as the hydration free energies. The lower the hydration free energy of an ion, the greater the ease with which its water of hydration may be shed. The ion with the highest free energy of hydration will therefore tend to remain in the solution phase where its hydration requirements can be better satisfied (in outer-complex form), rather than on the surface where it becomes partially unhydrated (in inner-complex form). According to the hydration energies listed in Table 6, the selectivity series for the cations considered is thus expected to be $NH_4^+ > Na^+ > Ca^{2+}$; this sequence is in fact obtained during the multicomponent equilibrium studies under LLAFF conditions.

It can thus be concluded that hydration free energy plays a dominant role in the exchange of NH_4^+ ion onto clinoptilolite, as compared to other factors such as valence (electric-charge) effects and ion-sieving effects.

Table 6. Hydration energies for certain cations; based on Ref.[20].

Cations	Free energy of hydration (KJ/mol)
Ca^{2+}	−403.60
Na^{+}	−111.80
NH_4^+	−103.94

Nevertheless, the presence of Ca^{2+} ion in solution under the LLAFF effluent conditions has a notable and deleterious effect on the selectivity of clinoptilolite for the NH_4^+ ion over the Na^+. It would seem that the calcium is competing for ion-exchange sites. The importance of this effect will depend, in practice, on the levels of hardness (i.e., Ca^{2+} ion) in the effluent.

CONCLUSIONS

A number of equilibrium batch-experiments have been conducted, at laboratory scale, to study the use of clinoptilolite as an ion-exchange medium for the removal of ammonium ions from the aqueous LLAFF process waste effluent. The study has revealed important information about the characteristics and behavior of the clinoptilolite in this application, under the compositional conditions of the LLAFF effluent. The present work has built on our previously reported study,[18] by providing fundamental information on the adsorption equilibria between the NH_4^+ ion present in solution and the clinoptilolite ion-exchange surface, in the absence and the presence of a competing divalent cation. Based on the results of the investigation, a number of conclusions have been drawn.

Data on the equilibrium ion-exchange of NH_4^+ on clinoptilolite has been described well by the law of mass-action; this model is intrinsically more satisfactory than previously reported models, based on single-component Langmuir or unbounded Freundlich adsorption isotherms. Furthermore, the total ionic strength in the solution has a significant effect on the maximum adsorption level of NH_4^+ onto clinoptilolite; the ion-exchange capacity of the material is thus dependent on total salinity. Therefore, the total ionic strength should be kept constant, if meaningful results on adsorption levels are to be obtained that are amenable to comparison.

Binary ion-exchange studies with a total salinity of 0.16 N revealed that ion-exchange on the clinoptilolite surface was highly favorable for the removal of NH_4^+ ions from solution; the separation factor $\alpha_{NH_4^+,Na^+}$ was 5.3679 (although the assumption of a constant separation factor is not strictly valid at this higher salinity). A value of 5.4546 was obtained at a salinity of 0.011 N. Thus, over the range of low values for salinity considered here, the separation factor appears to be relatively independent of salinity. This is reasonable for a pair of monovalent ions. The ion-exchange capacity of clinoptilolite for ammonium was maximized by converting the zeolite surface from a mixture of the Na- and K-forms to the pure Na-form by conditioning with high-strength brine; this reveals that the K^+ ion is preferred by the surface over the Na^+ ion. The highest NH_4^+ removal efficiency was obtained when pH was adjusted between 7.0 and 8.0; this avoids both neutralization of the ammonium ion by hydroxyl ion, and proton saturation of the zeolite surface. The diffusion coefficient for adsorption of NH_4^+ through the porous network of the clinoptilolite granules toward the ion-exchange sites equaled $6.06 \times 10^{-11}\,m^2/sec$ at 25°C ($R = 0.991$), according to the application of Vermeulen's model.[11]

During multicomponent ion-exchange studies, it was found that the presence of Ca^{2+} ions in the system caused a significant reduction in the ammonium/sodium separation factor, $\alpha_{NH_4^+,Na^+}$, of clinoptilolite. In a study where total ionic strength and Ca^{2+} concentration reflected the effluent from LLAFF (with total normality $= 0.16\,N$), the reduction was from a value of 5.37 to 1.83, i.e., by a factor 2.72. Furthermore, the presence of calcium caused a small reduction in the measured ion-exchange capacity for ammonium. The expected maximum concentration of calcium in LLAFF effluent is at the border-line for having a potentially deleterious effect, and careful monitoring of this ion would be required in practice.

The binary separation factor for the Na^+ ion over the Ca^{2+} ion on clinoptilolite, $\alpha_{Na^+,Ca^{2+}}$, was measured as 1. 972. In addition, the separation factor $\alpha_{Na^+,Ca^{2+}}$ when determined in the presence of ammonium ion was 1.61. This demonstrates that clinoptilolite is actually less selective toward the divalent Ca^{2+} ion than toward the monovalent Na^+ ion. Overall, the results of multicomponent equilibrium studies under LLAFF conditions reveal that the selectivity sequence of the considered cations in solution on clinoptilolite is $K^+ > NH_4^+ > Na^+ > Ca^{2+}$. Such a result agrees with previous studies, such as that in Refs.[15,23–25] in which the ion capture series is collectively presented as

$$K^+ > NH_4^+ > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}$$

It is postulated that the ion hydration energies play a dominant role in determining the ion-exchange selectivity of clinoptilolite for the NH_4^+ ion; at least under the LLAFF effluent conditions, this factor dominates over other factors, such as ion-sieving action and ionic valence (electrostatic) effects. Finally, it can be noted as a consequence that high-strength sodium or potassium chloride solution would be effective as a regenerating agent for clinoptilolite ion-exchanger beds being used to treat LLAFF effluent.

APPENDIX A

Analysis of feed and effluent from multistage froth flotation.

Parameters	Feed	4th filtrate
pH (Units)	7.8	8.2
Conductivity (μS/cm @ 25°C)	7,380	9,620
Total sulphur as SO_4	24.5	1,660
Calcium as Ca ion	91.9	171
Magnesium as Mg ion	44.1	103
Sodium as Na ion	555	1,440
Potassium as K ion	352	159
Nickel as Ni ion	0.04	0.12
Chromium as Cr ion	0.04	<0.02
Cadmium as Cd ion	<0.01	0.09
Copper as Cu ion	0.03	0.17
Lead as Pb ion	<0.03	<0.03
Zinc as Zn ion	0.04	0.06
Manganese as Mn ion	0.88	0.20
Iron as Fe ion	2.38	0.19
Nitrogen present as ammonium	404	149
Nitrite as N	<0.1	0.4
Nitrate as N	12	9.1
Chemical oxygen demand	610	420
Biochemical oxygen demand	60	15
Total organic carbon	200	75
Total alkalinity as $CaCO_3$	290	516
Chloride as Cl	810	1,960

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