Analyses of Adsorption Kinetics Using a Stirred-Flow Chamber: II. Potassium–Calcium Exchange on Clay Minerals

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ABSTRACT

Potassium–calcium adsorption kinetics on a Llano vermiculite and an Arizona montmorillonite were studied using a stirred-flow technique. Various experiments were conducted to distinguish between (i) instantaneous equilibrium and time-dependent reactions, and (ii) solution-concentration-dependent kinetic models vs. those that are independent of solution concentration. These experiments included varying the flow rate and influent concentration and stopping the flow for a period of time. It was found that K–Ca exchange on montmorillonite was too rapid to be measured with the stirred-flow technique, while exchange rates on vermiculite could be ascertained. Adsorption kinetic parameters should be included in transport models to more accurately predict the fate of ions in soils dominated by vermiculitic and micaceous clay minerals.

POTASSIUM IS AN ESSENTIAL ELEMENT for plant growth and is a dynamic ion in the soil system. Soil K can be divided into four major phases: solution, exchangeable, fixed, and structural (Sparks and Huang, 1985). To fully understand the physical chemistry of soil K and to predict its fate with time, one must have a knowledge of the rates and mechanisms of K reactions.

The application of kinetics to soil surface reactions, however, is arduous and has often been limited by the difficulty in separating the solution from the solid phase quickly enough to measure rapid reactions (Sparks, 1989). Also, problems of correctly interpreting experimental results and comparing different kinetic methods have not been solved.

Kinetics of K adsorption on clay minerals have been studied using various methods: batch, stirred batch, vortex batch, and miscible displacement (Keay and Wild, 1961; Jardine and Sparks, 1984; Ogwada and Sparks, 1986). The rate of K adsorption on vermiculite was reported to be much slower than on kaolinite, regardless of the experimental method (Ogwada and Sparks, 1986). Similar results were obtained by Jardine and Sparks (1984), who found K adsorption to be slowest on vermiculite, followed by montmorillonite and kaolinite.

Bar-Tal et al. (1990) presented mathematical solutions of the mass-balance equation in combination with equilibrium and kinetic models. They also proposed experimental tests to distinguish between three types of models: (i) instantaneous equilibrium, (ii) kinetic models in which the adsorbed fraction is a function of solution concentration, and (iii) kinetic models in which the adsorbed fraction is independent of the solution concentration. The objective of this study is to determine the utility of different experimental tests (under specific experimental conditions) for distinguishing between kinetic and instantaneous equilibrium processes using a stirred-flow technique for vermiculite and montmorillonite clays.

MATERIALS AND METHODS

A Llano, Texas, vermiculite and an Arizona montmorillonite obtained from the University of Missouri Source Clays Depository were used in this study. The clays were fractionated by standard procedures (Jackson, 1969), based on a gravimetric method, to an equivalent diameter of 1 to 2 μm. The cation-exchange capacity (CEC) of the Llano vermiculite and the Arizona montmorillonite as determined by Ba–Ca exchange was 210 and 105 cmol kg^{-1}, respectively. These values are in good agreement with published values (Foster, 1963; Sparks and Jardine, 1984).

Prior to the equilibrium and kinetic studies, the clays were made homoionic with respect to Ca by saturating four times with 500 mol m^{-3} of Ca(ClO$_4$)$_2$. The excess salt was removed by repeated washing with deionized water until the electrical conductivity (EC) of the supernatant was near that of the deionized water. Complete saturation of the exchanger was tested by replacing the sorbed Ca with Ba. Perchlorate salts were used in both kinetic and equilibrium studies to minimize CaCl$^+$ formation (Sposito et al., 1981). Calcium and K concentrations were measured in solution using atomic absorption spectrophotometry.

Equilibrium Studies

A batch technique was used for the equilibrium studies on both clay minerals. Triplicate 0.5-g samples of Ca-saturated clay were placed in cleaned, tared, 100-mL polycarbonate centrifuge tubes. Then 20 mL of solutions of varying KClO$_4$ and Ca(ClO$_4$)$_2$ concentrations but of a constant total concentration (20 mol m^{-3}) were added to each tube. Equivalent fractions of K or Ca in the mixed solutions varied from 0.05 to 0.95 with a ClO$_4$ concentration of 20 mol m^{-3}. The tubes were shaken on a reciprocal shaker for 24 h, at which time equilibrium was attained.

Separation of the supernatant from the clay slurry was carried out using a procedure developed by Sposito et al. (1981). Both the equilibrium concentrations of K and Ca in the supernatant and the adsorbed quantities of both ions were determined. The adsorbed K and Ca were displaced by equilibrating the clay three times with 25 mL of 500 mol m^{-3} BaCl$_2$. Before adding the displacing solution, the mass of the entrained equilibrium solution in each tube was determined. The final amounts of adsorbed Ca and K were calculated by subtracting the quantity of cations in the entrained solution from those determined by displacement.

Kinetic Studies

The stirred-flow chamber first described by Carski and Sparks (1985) and modified by Seyfried et al. (1989) was used in the kinetic study. The operation of the apparatus is fairly simple, but careful protocol must be followed for reproducibility and time zero must be accurately determined for the system as detailed below.

A magnetic stirring star was placed in the chamber above the rubber plunger. Then a 0.2-μm Gelman metricel membrane filter (Gelman Sciences, Ann Arbor, MI) was placed beneath the outlet port to prevent any loss of the exchanger. A small amount (0.25 ± 0.01 g montmorillonite or 0.50 ± 0.01 g vermiculite) of dried clay was loaded into the reaction chamber. A volume of 5.5 ± 0.05 mL (in montmorillonite experiments) and 5.9 ± 0.1 mL (in vermiculite experiments) of 10 mol m^{-3} Ca(ClO$_4$)$_2$ was added using a hypodermic syringe while trying not to displace any of the exchanger. The clay slurry was mixed using the magnetic stirrer for a short time, and any air present was displaced by slowly pushing up the rubber plunger. Thus, a known constant volume of solution was diluted or washed out. This volume was maintained throughout the adsorption reaction and was determined by weighing the filled chamber

A peristaltic pump was used to maintain various flow rates ranging from 0.5 to 4 mL min^{-1} and a LKB Ultra II 2070 fraction collector (LKB-Produkter AB, Bromma, Sweden) was used to collect effluent fractions at desired time intervals. The magnetic stirrer was utilized to ensure adequate mixing in the reaction chamber, and the stirring speed was kept to a minimum to reduce abrasion of the adsorbent. A plastic scraping device was placed on top of the stir star to prevent clogging of the filter. The 10 mol m^{-3} Ca(ClO$_4$)$_2$ solution was pumped into the chamber for 15 to 20 min to ensure a known initial concentration. Then the tubes were disconnected from the chamber, washed with 0.005 M HCl, rinsed with deion-

ized water, dried, and then reconnected to the fraction collector. The cleaned tube connecting the source solution to the chamber was then washed with source solution, filled up, and finally connected to the stirred-flow chamber. Time zero was defined when the first drop entered the first tube of the fraction collector.

A blank curve was determined for a known chamber volume, using the same initial chamber solution and source solution as was previously described for the clay samples, but without clay in the chamber. This curve was used to calculate adsorbed quantities. All experiments were done in duplicate.

Data Handling and Analyses

The Langmuir model and the modified Gapon model (Sposito, 1977) were found to best describe the equilibrium data for the Llano vermiculite and the Arizona montmorillonite, respectively. The modified Gapon model, as given in Eq. [1], was used to model K exchange with Ca on the Arizona montmorillonite under equilibrium conditions

$$q_K/2q_{Ca} = K_G \, a_K/a_{Ca}^{1/2} \qquad [1]$$

where q_K and q_{Ca} are the quantity of adsorbed K and Ca, respectively (cmol kg^{-1}), a is the activity of the cation in the solution (mol m^{-3}), and K_G is the Gapon selectivity coefficient (m^3 mol^{-1})$^{1/2}$.

The Langmuir model was used to describe the adsorbed amount of K as a function of its solution concentration under equilibrium conditions for the Llano vermiculite:

$$q_K = q_{Kmax}C_K/K + C_K \qquad [2]$$

where q_{Kmax} is the maximum adsorption capacity for K on the clay mineral (cmol kg^{-1}), C is the concentration of K in the solution phase (mol m^{-3}), and K is a coefficient (mol m^{-3}).

The mass-balance equation given in Eq. [1a] of Bar-Tal et al. (1990) was used to interpret data obtained using the stirred-flow chamber.

The data obtained from the equilibrium exchange study were modeled using the GLM and NLIN programs (SAS Institute, 1983). The procedure DO2BBF of the NAG library (Numerical Algorithms Group, 1984) was used to solve Eq. [1] and [2] in combination with Eq. [1a] of Bar-Tal et al. (1990), using known experimental conditions (flow rate, exchanger mass, initial concentration, and CEC) to predict concentration change vs. time, assuming instantaneous conditions using the stirred-flow chamber.

In the stirred-flow method, the effluent concentration is a directly measured quantity from which the adsorbed quantity can be estimated indirectly (Schnabel and Fitting, 1988; Sparks, 1989). The estimation of the adsorbed quantity is based on the effluent concentration measured with the clay, compared with the blank (without clay). The adsorbed quantity is the accumulative difference between the concentration of adsorptive collected in the blank sample and the experiment with clay, plus the difference in the concentration of adsorptive in the chamber between the blank and an experiment with clay. These values are calculated using the following relationship:

$$q(t_i) = \frac{\Sigma[(C_{nc} - C_c)J\Delta t] + [c(t_i)_{nc} - c(t_i)_c]V}{M} \qquad [3]$$

where $q(t_i)$ is the quantity of ion adsorbed at time t_i (cmol kg^{-1}), c is the concentration of K in the chamber (mol m^{-3}), t_i is the end of sample-collection period i (min), Δt is the length of the collection period (min), V is the volume of solution in the chamber, M is the mass of clay in the chamber, and nc and c denote no clay and clay in the chamber, respectively.

The calculation of the first term on the right-hand side of Eq. [3] is based on measured data. For the second term on the right-hand side of Eq. [3], however, there is a need to estimate the chamber concentration at specific times. This estimation can be done if the kinetic model is known (Schnabel and Fitting, 1988), or it can be obtained using average concentration values between two short time increments. The latter method was used in this study and is fairly close to the real values when relatively short time increments are used (Schnabel and Richie, 1987).

RESULTS AND DISCUSSION

Equilibrium Study

Increasing K concentration in solution from 0 to 19.85 mol m^{-3} increased the amount of adsorbed K on the Arizona montmorillonite from 0 to 0.53 cmol kg^{-1} (Fig. 1). The shape of the K–Ca isotherm for the Arizona montmorillonite is in agreement with published data, using similar ionic strengths (Jensen, 1973; Theiller and Sposito, 1988). The modified Gapon model (Eq. [1]) was used successfully to describe K adsorption on montmorillonite as a function of its solution concentration ($R^2 = 0.997$) (Fig. 1). The K_G value was 2.78 ± 0.009 (L mol^{-1})$^{1/2}$.

The isotherm for K sorption on Llano vermiculite shows decreasing affinity for K with an increase in K solution concentration (Fig. 1). The Langmuir equilibrium model (Eq. [2]) was used successfully to describe K adsorption on vermiculite (Fig. 1) with a K value of 3.1 ± 0.39 mol L^{-1} (residual sums of squares [RSS] = 0.0167).

Kinetic Study

The results of the kinetic study for K adsorption on the Arizona montmorillonite and Llano vermiculite, along with predicted and stopped-flow data, using the stirred-flow chamber, are presented in Fig. 2 and 3. The predicted data for the two clays were calculated assuming an instantaneous equilibrium and solving the mass-balance equation (Eq. [1a], Bar-Tal et al., 1990) in combination with Eq. [1] or [2] for montmorillonite and vermiculite, respectively. The predicted effluent concentrations for montmorillonite successfully described the observed effluent concen-

trations, indicating that K–Ca exchange is too rapid to be distinguished from instantaneous equilibrium using the stirred-flow method under the conditions of influent concentration $C_i = 20$ mol m^{-3} and flow rate $J = 1$ mL min^{-1} (Fig. 2).

In contrast to the Arizona montmorillonite, a comparison of the observed and predicted effluent concentrations for the Llano vermiculite indicates the possibility of nonequilibrium conditions (Fig. 4). The difference between predicted data, assuming instantaneous conditions, and observed data is larger than the experimental deviations. The maximum difference between the observed and predicted data occurred 5 min after beginning the experiment.

Bar-Tal et al. (1990) suggested that stopping the flow of adsorptive for a sufficient time period before equilibrium is established should result in an observed drop in effluent concentration if nonequilibrium conditions exist. As shown in Fig. 3, flow of adsorptive was stopped for 60 min after 5 mL of effluent were collected. After renewing the flow, a drop in K concentration occurred at the 6- and 7-mL increments with the Llano vermiculite, indicating nonequilibrium conditions exist in the chamber. However, this was not the case with the Arizona montmorillonite (Fig. 2), indicating instantaneous equilibrium.

A point of interest is the slope of the stopped-flow curves from 6 min on. For the Llano vermiculite, when flow was stopped, effluent concentration increased more quickly than when flow was continuous (Fig. 3). Thus, the K effluent concentration under the latter conditions was lower after 15 min than when flow was stopped. This phenomenon was due to the maximum amount of K that can be adsorbed on the Llano vermiculite. When the flow is stopped, more K is adsorbed initially, compared with the continuous run. Therefore, when a larger quantity of K was adsorbed at the beginning of the experiment (stopped-flow experiment), a smaller quantity was adsorbed later.

Using more than one flow rate is another way to distinguish experimentally between equilibrium and nonequilibrium models (Bar-Tal et al., 1990). Flow rates of 0.5, 1, 2, and 4 mL min^{-1} were used with the Llano vermiculite, and 1 and 2 mL min^{-1} with the Arizona montmorillonite. Other flow rates could not be used for studying montmorillonite due to clogging
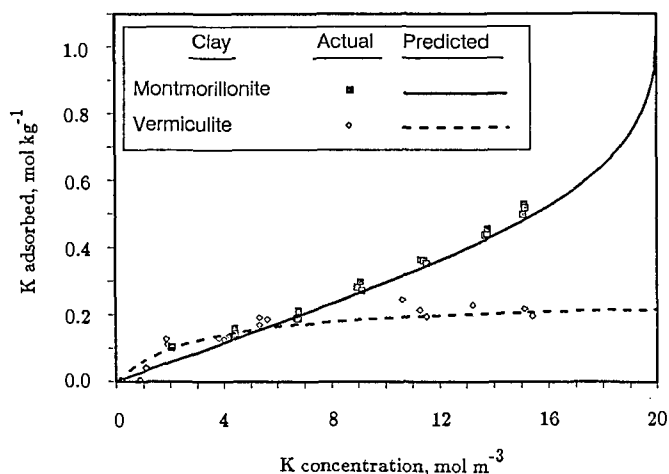

Fig. 1. Potassium adsorption on Ca vermiculite and Ca montmorillonite along with predicted curves using the Langmuir model for vermiculite and the Gapon model for montmorillonite.
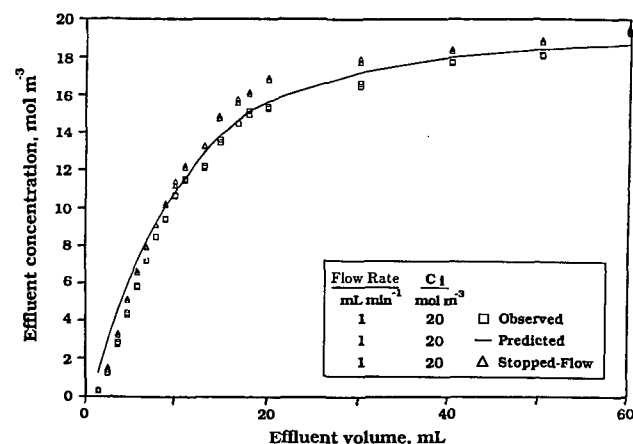

Fig. 2. Comparison of predicted and observed effluent concentration, and the stopped-flow experiment, as a function of time using montmorillonite. C_i = influent concentration.
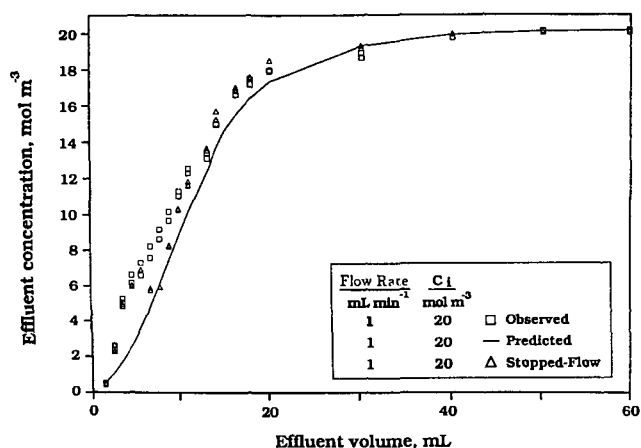
Fig. 3. Comparison of predicted and observed effluent concentration, and the stopped-flow experiment, as a function of time using vermiculite. C_i = influent concentration.

Fig. 5. The effect of flow rate on K effluent concentration as a function of effluent volume for montmorillonite. C_i = influent concentration.

of the chamber filter. This clogging reduced the mixing and made maintenance of constant flow rates difficult. Curves of effluent concentration vs. effluent volume (1 and 2 mL min^{-1}; not shown) do not overlap for the Llano vermiculite (as was previously observed with an instantaneous model [Bar-Tal et al., 1990, Fig. 2]). The faster the flow rate, the higher the effluent concentration through the first 10 mL (Fig. 4). The difference between the slowest and fastest flow rates was larger than the experimental deviation. The trend of increasing concentration with increasing flow rate was consistent from the beginning to about 20 min. In contrast to the Llano vermiculite, there was no significant difference between the two flow rates used for the Arizona montmorillonite (Fig. 5). The difference between the various flow rates in the Llano-vermiculite experiment was due to kinetic effects. As the flow rate increases, nonequilibrium conditions in the chamber will occur for longer periods.

Consequently, through the use of flow-rate and stopped-flow experiments, it was found that an instantaneous-equilibrium model is appropriate to describe K–Ca reactions on the Arizona montmorillonite using the stirred-flow chamber. Therefore, the stirred-flow method and experimental conditions described
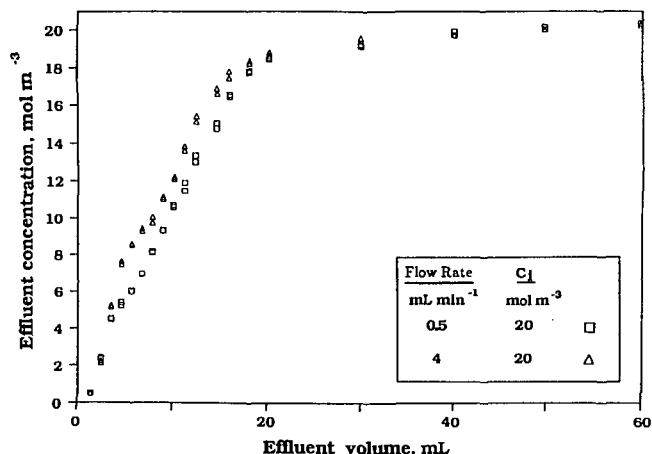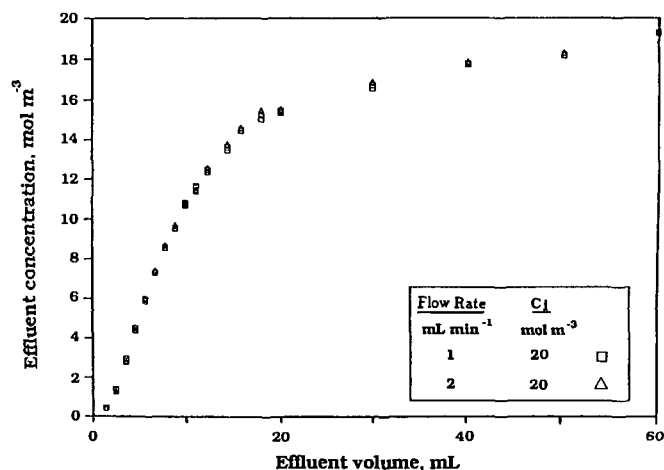
in this study cannot be used to obtain kinetic parameters for montmorillonite. However, predictions of effluent K concentration for vermiculite deviate significantly from the observed data. Also, stop-flow and flow-rate tests indicate nonequilibrium conditions are present inside the chamber. Hence, kinetic processes can be studied using the stirred-flow chamber with a Llano vermiculite clay.

Bar-Tal et al. (1990) also suggested tests to distinguish between two types of kinetic models using the stirred-flow method: kinetic models where the adsorbed amounts are dependent on solution concentration, and those that are independent of solution concentration. Two influent K concentrations and four flow rates were used for this purpose in their study. These tests are analyzed by plotting the adsorbed fraction vs. time and effluent volume.

Potassium adsorption on the Llano vermiculite as a function of time and effluent volume would be better described by a kinetic model that is dependent on solution concentration. This is shown by the adsorption vs. time and effluent-volume data (Fig. 6 and 7). The curves for the first test, using two influent concentrations, are significantly different (Fig. 6). This is in contrast to the overlap of the simulated curve for the kinetic models, which are independent of solution
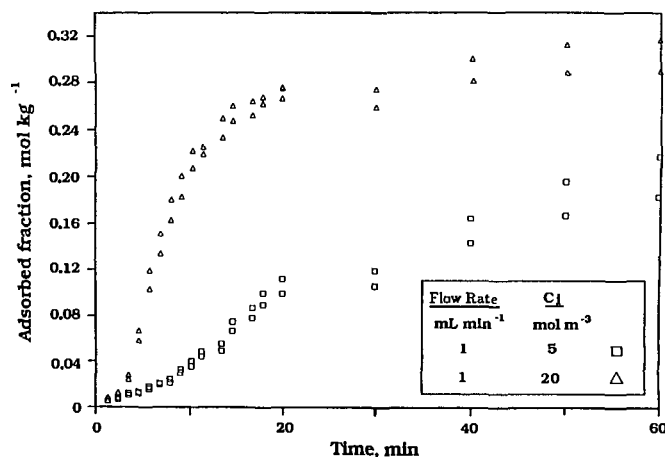

Fig. 4. The effect of flow rate on K effluent concentration as a function of effluent volume for vermiculite. C_i = influent concentration.

Fig. 6. The effect of influent K concentration (C_i) on the adsorbed fraction of K as a function of time for vermiculite.
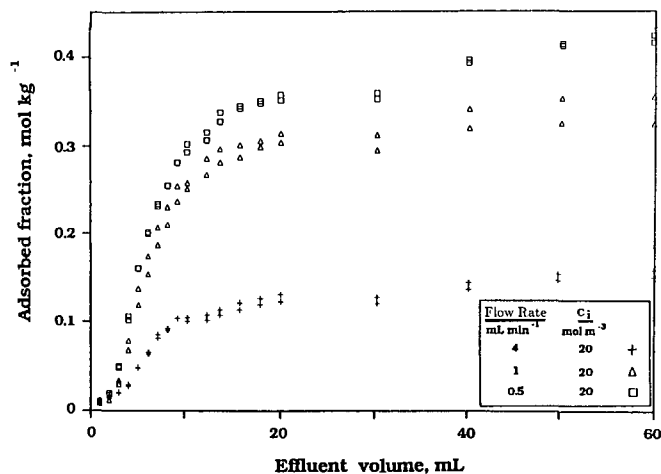
Fig. 7. The effect of flow rate on the adsorbed fraction of K as a function of effluent volume for vermiculite. C_i = influent concentration.

concentration (Bar-Tal et al., 1990, Fig. 4a). In a similar way the second test, using various flow rates, is significantly different (Fig. 7). Again, this is in contrast to the simulated curve from a kinetic model where the adsorbed amount is independent of solution concentration (Bar-Tal et al., 1990, Fig. 4a). Therefore, a kinetic model that is independent of solution concentration is improper for the Llano vermiculite.

CONCLUSIONS

Potassium adsorption on montmorillonite was described by the Gapon exchange model, while the Langmuir adsorption model was used to describe adsorbed K as a function of K concentration in solution. Several experiments suggested by Bar-Tal et al. (1990) were used for the study of K adsorption on the clays, using the stirred-flow method. The experiments help distinguish between three main types of models: instantaneous equilibrium, a kinetic model where the adsorbed amount is dependent on solution concentration, and a kinetic model where the adsorbed amount is independent of solution concentration. The tests were compared with the theoretical analysis presented by Bar-Tal et al. (1990) and showed the following: (i) K–Ca exchange on the Arizona montmorillonite is too rapid to be measured using the stirred-flow technique and 1 to 2 mL min⁻¹ flow rates, and (ii) K-adsorption kinetics on vermiculite are slow enough to be measured with the stirred-flow method. It is also likely that K-adsorption kinetics can be measured on other micaceous clay minerals. These results were anticipated, since the type of clay mineral has a significant effect on the rates of ion exchange. With the stirred-flow technique, diffusion in the bulk solution is substantially reduced. Therefore, the rate of ion exchange will

depend mainly on the structural properties of the clay minerals. Smectites are 2:1 clay minerals where the inner peripheral space is able to swell with adequate hydration and thus allow for rapid passage of ions into the interlayers. However, vermiculite and micaceous minerals have only semiexpansible interlayers, which may impede many ion-exchange reactions. One of the implications of this research is that adsorption-kinetics parameters should be included in transport models dealing with leaching and plant nutrition, particularly if one is studying soils dominated by vermiculitic and micaceous clay minerals.

ACKNOWLEDGMENTS

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