

Kinetics of Calcium–Magnesium Exchange on Soil Using a Stirred-Flow Reaction Chamber

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ABSTRACT

Ion exchange reaction kinetics may significantly affect effluent concentrations under both laboratory and field conditions. One limitation to the study of exchange reaction kinetics has been the lack of appropriate methods. A stirred-flow method that uses a constantly stirred reaction chamber with constant, steady inflow of the reactant solution and outflow of reactants and products was tested. The method allows for continuous sampling and accommodates a wide range of soil particle sizes. The basic assumption of a well mixed solution in the chamber has not been tested, however. That assumption was tested over a wide range of flow rates and found to be applicable. The measurable reaction rates using the stirred-flow method were estimated using a simple empirical equation that allowed the use of the reaction half-time ($t_{1/2}$) to describe reaction rates. Values of $t_{1/2}$ of 3 min and greater were detectable while a 0.3 min $t_{1/2}$ was not detectable under the experimental conditions. Calcium–Mg exchange on a Nordya sandy loam (Typic Rhodoxeralf) soil from Israel was investigated. Measured effluent concentrations were compared with values calculated assuming no adsorption preference for Ca or Mg, and assuming local equilibrium between adsorbed and solution phases prevailed. Effluent concentrations were accurately predicted when the reaction direction was from equilibrium with Ca solution to equilibrium with Mg, but not for the reverse. These results suggest that either the local equilibrium or the nonpreference assumption was not appropriate. Flow rate reduction and stopped-flow experiments indicated that local equilibrium prevailed. Equilibrium exchange isotherms obtained using the chamber indicated a preference for Ca over Mg.

ION EXCHANGE has been extensively studied by soil scientists (Thomas, 1977). Nutrient cations and

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heavy metals are subject to exchange reactions in soils and soil constituents. Knowledge of ion exchange in the context of moving soil water is important in the study of soil fertility, salinity management, and pollution control.

Models used to describe ion transport commonly assume that exchange reactions are sufficiently rapid that local equilibrium between adsorbed and solution phases can be assumed (Valocchi, 1985). The vast majority of work on ion exchange to date has been with equilibrium relationships. Several researchers have, however, suggested that reaction kinetics may not be sufficiently rapid for the local equilibrium assumption to be valid (e.g., Selim et al., 1976; Lai and Jurinak, 1972). Nonequilibrium behavior during transport through porous media (soils) can result from physical interactions with the media and/or exchange reaction kinetics (Nkedi-Kizza et al., 1984).

One of the problems encountered in kinetic studies has been the development of appropriate methods (Sparks, 1985; Harter, 1986). One method that has shown some promise is the stirred-flow method (previously referred to as modified miscible displacement) proposed by Carski and Sparks (1985). Some of the potential advantages of the method are that reaction rates are independent of the physical effects of porous media, the same apparatus can be used to measure both equilibrium and kinetic parameters, continuous (or incremental) measurements allow monitoring of reaction progress, experimental conditions such as flow rate and soil mass are easily manipulated, and the procedure is suitable over a wide range of textures and colloidal particle sizes.

The stirred-flow method has not been widely used for soils, however, and investigation into its applicability is needed. For example, quantitative analyses of the results using this method are generally based on the assumption that the soil-solution mixture is sufficiently well mixed that no diffusion gradient exists in the bulk solution. This assumption, however, has

not, to the authors' knowledge, been tested. In addition, questions concerning the accuracy and rates of reaction that can be measured with the method need further investigation.

The purpose of this study was to investigate the applicability of a slightly modified version of the stirred-flow chamber introduced by Carski and Sparks (1985) to the study of ion exchange reactions in soil. To that end we tested the basic assumption of well mixing and then applied the method to Ca-Mg exchange on an Israeli soil.

MATERIALS AND METHODS

Theory

Analysis of flow through the stirred-flow reaction chamber is based on the following equation of mass balance

$$(C_i - C_e)J = V_c \partial C/\partial t + M \partial S/\partial t \quad [1]$$

where

C_i	= influent concentration,	mol m ⁻³ ;
C_e	= effluent concentration,	mol m ⁻³ ;
C	= chamber concentration,	mol m ⁻³ ;
J	= flow rate,	m ³ s ⁻¹ ;
t	= time,	s;
V_c	= chamber volume,	m ³ ;
S	= amount adsorbed,	mol kg ⁻¹ ; and
M	= soil mass,	kg.

Equation [1] is valid if the chamber is sufficiently well mixed that there is no gradient for diffusion within the bulk suspension. This condition, referred to here as the well-mixed condition, implies that $C = C_e$. Subsequent equations will be expressed in terms of the measured parameter, C . The mixing properties of the chamber can be tested using solutions only with no soil present. In this case

$$C = C_i \exp(-Jt/V_c) \quad C = C_i, t = 0 \quad [2]$$

$$C = C_i[1 - \exp(-Jt/V_c)] \quad C = 0, t = 0. \quad [3]$$

All of the variables in Eq. [2] and [3] can be measured independently. These expressions therefore provide a way to test the applicability of the well-mixed condition under experimental conditions of interest. It should also be noted that C varies with Jt , the effluent volume. If the well-mixed condition applies, then plots of C as a function of effluent volume should not depend on J as long as V_c and C_i are constant.

The basic approach used in applying the stirred-flow method to ion exchange was to compare measured effluent concentrations to predetermined equilibrium values. The calculation of equilibrium solution concentrations followed the approach of Lai and Jurinak (1971). The variables C and S are expressed as dimensionless variables such that

$$X = C/C_0 \text{ and,} \quad [4]$$

$$Y = S/CEC, \quad [5]$$

where C_0 (mol m⁻³) is the maximum solution concentration and CEC (mol kg⁻¹) is the cation exchange capacity (assumed constant) of the soil. Assuming the well-mixed condition, and substituting Eq. [4] and [5] into Eq. [1] results in

$$VC_0 \partial X/\partial t = J(C_i - XC_0) - (M)(CEC)\partial Y/\partial t. \quad [6]$$

Since Y is a function of X as well as t , then, from the chain rule,

$$\partial Y/\partial t = (dY/dX)(\partial X/\partial t). \quad [7]$$

The term dY/dX is the slope of the exchange isotherm plot-

ted on a normalized scale. In this study we consider the case of a linear or nonpreference exchange isotherm such that

$$Y = X, \quad [8]$$

although the approach used here may also be applied to nonlinear isotherms (see Lai and Jurinak, 1972).

Substitution of Eq. [7], and [8] into Eq. [6] results in

$$dX/dt + (J/\tau)X = (C_i J)/(C_0\tau) \quad [9]$$

where

$$\tau = V + (CEC)(M)/C_0. \quad [10]$$

The solutions to Eq. [9] of interest are

$$X = 1 - \exp(-Jt/\tau) \quad t = 0, X = 1 \quad [11]$$

$$X = \exp(-Jt/\tau) \quad t = 0, X = 0. \quad [12]$$

All variables in Eq. [10] and [11] can be measured independently. These equations describe effluent concentrations if there is no preference between ions exchanged and if local equilibrium prevails. The term local equilibrium indicates that the reaction is sufficiently rapid that measured effluent concentrations are indistinguishable from equilibrium (see Rubin, 1983, for further discussion of local equilibrium).

Additional calculations were made to establish approximately what reaction rates might be distinguished from equilibrium under the experimental conditions of this study. For practical reasons, the following empirical expression for Y was used

$$Y = X[1 - \exp(-kt)], \quad [13]$$

where k is a rate coefficient (s⁻¹). There are two reasons that Eq. [12] was used. First, it has the property that very slow reactions (small k) approximate the nonadsorbed condition while very rapid reactions (large k) approximate the instantaneous adsorption case. Second, reaction rates can be described in terms of a reaction half-time ($t_{1/2}$) analogous to the half-life used to describe radioactive decay. Values of k can be calculated for $t_{1/2}$ values of interest from the relationship

$$k = (-\ln 0.5)/t_{1/2}. \quad [14]$$

The solution concentration (C) in Eq. [1] given Eq. [13] was obtained for different k values and numerical integration using the NAG library on IBM computers (Gill and Murry, 1978). This provided a semiquantitative analysis of the reaction rates measured with the method.

Experimental Procedures

The soil used was a Nordya sandy loam (Typic Rhodoxeralf) A horizon from Israel. Using standard methods (Page et al., 1982), the pH in CaCl₂, organic matter content (g kg⁻¹), and cation exchange capacity (cmol. kg⁻¹) were found to be 7.3, 14, and 6.25, respectively. The Nordya soil has 98 g kg⁻¹ clay and the abundance of minerals in the < 2-μm fraction is: 2:1 interstratified > kaolinite > mica > chloritized vermiculite.

The stirred-flow reaction chamber used was a slight modification of that described by Carski and Sparks (1985). An influent solution of known composition was pumped at a constant flow rate into a chamber containing a known mass of soil and volume of solution until equilibrium, as judged by equivalence of influence and effluent concentrations, was achieved. The chamber volume was 8.30 mL and the mass of soil used was 1.6 g. The contents of the chamber were continuously stirred with a magnetic stir star resulting in a suspension. Soil was retained in the chamber with a 25-mm diam., 0.2-μm filter, and the effluent was collected with a fraction collector. A plastic scraping device, which rested on the stir star, was added to prevent clogging of the filter.

Mixing in the chamber was tested using solutions only (no soil) with eight runs using flow rates ranging from 0.28 to 2.20 mL min⁻¹ (Table 1). All tests except the 0.83 mL min⁻¹ flow rate were performed by monitoring effluent electrolyte concentration changes by electrical conductivity as chamber solution concentrations changed from 0.01 to 0.50 M CaCl₂ or the reverse. In the 0.83 mL min⁻¹ flow rate test the chamber was initially filled with 0.0256 M Ca(ClO₄)₂ and displaced with the same concentration of Mg(ClO₄)₂. Effluent Ca and Mg concentrations were measured using atomic absorption spectrometry. The effluent solutions were collected in 1.1-mL aliquots. Each run resulted in one effluent concentration curve except the 0.83 mL min⁻¹ run, which resulted in two curves, one for Ca, the other for Mg. The best nonlinear least square fit of each curve to Eq. [2] or [3] was determined using the program NLIN (SAS Institute, 1983), with the Gauss-Newton iteration technique. Fitted and measured V_c values were then compared. The well-mixed condition was assumed to be applicable if there was good agreement between the measured and fitted values, and if the fitted V_c did not change with flow rate.

Six kinetic runs were performed with initial conditions shown in Table 2. The concentration of all solutions was 0.256 M of either Mg(ClO₄)₂ or Ca(ClO₄)₂. For run I soil was initially equilibrated with Mg solution and displaced with Ca solution until equilibrium was achieved. Run II was the reverse of run I. In run III soil initially equilibrated with Mg solution was displaced with Ca solution until equilibrium with that ion was achieved, then displaced with Mg solution back to the initial state. Run IV was identical to II except that the flow rate was reduced to 0.28 mL min⁻¹. Runs V and VI started in equilibrium with Mg and Ca, respectively, and flow was halted for 75 min after 9 mL of effluent were collected. Two effluent curves were generated for runs I, II, and IV, one for Mg and one for Ca (a and b, respectively, Table 2). Four curves were generated for run III because exchange from both Mg to Ca and the reverse were included. Only Mg was monitored in runs V and VI.

An exchange isotherm was determined experimentally us-

ing the same chamber. Nine 0.0256 M solutions of Ca(ClO₄)₂ and Mg(ClO₄)₂ ranging in molar Ca/Mg ratios from 0.9:0.1 to 0.1:0.9 at intervals of 0.1 were made. Determinations for each solution were made in duplicate. The chamber, containing 1.6 g of soil, was filled with solution of the desired ratio. This same solution was then pumped into the chamber at a rate of 0.83 mL min⁻¹ for at least 75 min. After this time both Ca and Mg effluent solution concentrations were found to be within 1% of the influent solution concentration. Preliminary investigations did not reveal a noticeable effect of extending the equilibration time overnight. About 80 mL of 0.50 M BaCl₂ was then added to the chamber at the same rate. The total amount of displaced Mg and Ca was measured as before.

RESULTS AND DISCUSSION

Mixing Tests

The results of the mixing tests are summarized in Table 1. The volume ratio referred to is the ratio of the measured V_c value and that obtained by fitting Eq. [2] or [3] to effluent concentration data. Thus, the volume ratio from a well-mixed chamber would be equal to 1.00. Results were presented in this manner because there were slight differences in chamber volume for some of the runs and it facilitated comparison of results.

Within a flow rate of 0.28 to 2.20 mL min⁻¹ volume ratios were quite close to 1.00 (Table 1). Thus, the best fit V_c agreed with the measured value, and that value was constant over a range of flow rates. Measured and calculated effluent concentrations of Ca and Mg from the 0.83 mL min⁻¹ run illustrated in Fig. 1 also indicate that there is close agreement. The confidence intervals for each estimate, also shown in Table 1, indicate that volume ratios were estimated precisely. It was concluded that it was appropriate to assume that the reaction chamber is well mixed when run under conditions tested.

Reaction Rate Tests

The calculated effluent concentration curves generated for $t_{1/2}$ values of 3 and 30 min are compared to the instantaneous case ($t_{1/2} = 0.0$ min) and the case where no reaction occurs (no soil present) in Fig. 2. A curve with a 0.3-min $t_{1/2}$ was virtually equivalent

Table 1. Chamber mixing tests.

Flow rate, mL min ⁻¹	Volume ratio†	Confidence interval‡
0.28	1.01	0.02
0.55	1.01	0.02
0.55	1.03	0.02
0.83§	1.00	0.01
0.83¶	1.00	0.03
1.10	1.04	0.03
1.10	0.99	0.02
1.10	0.99	0.05
2.20	1.03	0.02

† Best fit V_c /measured V_c .

‡ $\alpha = 0.95$.

§ Fit to Mg effluent concentration.

¶ Fit to Ca effluent concentration.

Table 2. Best-fit τ values for kinetic experiments.

Run no.	Initial sat. ion†	Measured ion	τ	Confidence interval‡
Ia	Mg	Mg	11.35	0.24
Ib	Mg	Ca	11.16	0.36
IIa	Ca	Mg	9.95	0.32
IIb	Ca	Ca	9.24	0.53
IIIa	Mg	Mg	11.05	0.24
IIIb	Mg	Ca	11.52	0.41
IIIc	Ca	Mg	10.31	0.32
IIId	Ca	Ca	10.01	0.60
IVa	Ca	Mg	9.96	0.33
IVb	Ca	Ca	9.78	0.30
V	Ca	Mg	9.38	0.18
VI	Mg	Mg	10.90	0.17

† Initial saturating ion in the chamber.

‡ $\alpha = 0.95$.

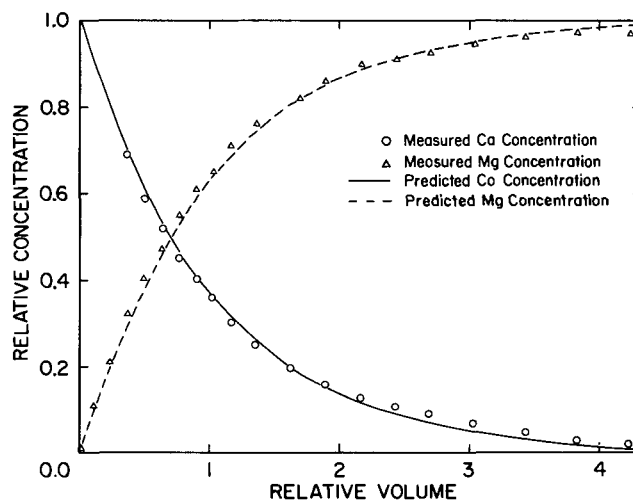


Fig. 1. Simultaneous relative effluent concentrations of Ca and Mg with no soil in the chamber.

to the instantaneous case while the 3-min $t_{1/2}$ curve can barely be distinguished from the instantaneous curve. Thus, the most rapid reactions detectable with the method under these experimental conditions would be characterized by $t_{1/2}$ values between 0.3 and 3 min. Faster reactions (lower $t_{1/2}$ values) would appear instantaneous. Also note that very slow reactions ($t_{1/2} \gg 30$ min) will be indistinguishable from the case of no soil present. Although this approach can be applied to any experimental condition, these numerical limits apply only to the experimental conditions of the study.

These observations could be significantly different for different reaction mechanisms. Equation [13] was not intended as a hypothesized reaction equation, only a convenient expression that could give a rough indication of the magnitude of reaction rates that might be measured with the stirred-flow method under the experimental conditions.

Kinetics Experiments

The results of the kinetic runs are summarized in Table 2. After runs I, II, and III were completed the best fit τ values (Eq. [9]) obtained could be categorized into two groups based on the direction of the reaction. When the initial condition was equilibrium with Mg, the average τ value of 11.27 (SD = 0.21) agreed closely with the calculated value of 11.31. When the initial condition was equilibrium with Ca, the average τ value of 9.88 (SD = 0.46) was significantly lower ($\alpha = 0.95$) and not in close agreement with the calculated value.

This is illustrated in Fig. 3, where predicted curves (using the measured τ value of 11.31) are compared to measured Ca and Mg concentrations for run III, which included both directions. In the first half of Fig. 3, measured and predicted values agreed closely, as they did with run I. However, there was a consistent, systematic discrepancy between measured and calculated effluent concentrations in the second half (Ca to Mg) of Fig. 3 that is very similar to that observed for run II (not shown). The Mg solution concentration rose more rapidly, and the Ca concentration fell more rapidly, than predicted.

One explanation for the observed discrepancy is that Mg did not exchange with Ca rapidly enough to attain local equilibrium. This would result in Mg solution concentrations higher than predicted (due to greater amounts adsorbed). It implies that Ca displaces Mg faster than Mg displaces Ca. Although this result was

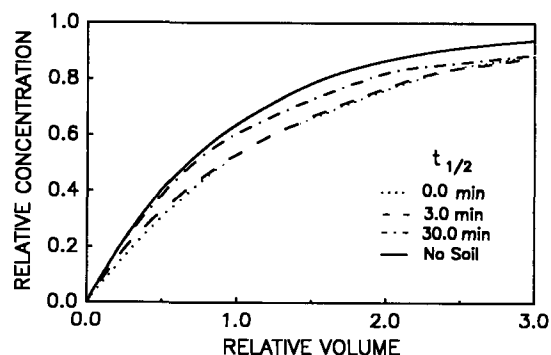


Fig. 2. Effect of $t_{1/2}$ variation on calculated effluent concentration curves. The no soil curve represents conditions of no reaction. Conditions were: $J = 0.83$ mL min⁻¹, $V_c = 8.3$ mL, $M = 1.6$ g, CEC = 0.0482 mol kg⁻¹, and $C_0 = 0.0256$ M.

not expected, there has been other work that suggests that this is possible (Bunzl, 1974; Bunzl et al., 1976).

The above explanation was tested in two different experiments. One was to reduce the influent flow rate to 0.28 mL min⁻¹ or one-third the flow rate of the other runs. This would allow more time for equilibrium to be achieved. If the observed discrepancy in effluent curves is due to disequilibrium, then one would expect the effluent curve results to be intermediate between the previously obtained curves (i.e., τ values between 9.8 and 11.2). However, best fit τ values obtained from this test (run IV) were not significantly different from other, faster runs made in the same direction (run II, IIIc, and IIId) indicating a lack of disequilibrium.

The other experiment was to stop flow of reactant solution into the chamber for a period of 75 min. This was done after about 9 mL (or a relative concentration of 0.6) of effluent had been collected, which was the portion of the curves where the discrepancy was maximal. The time period of 75 min was sufficient for the solution and adsorbed phases to equilibrate. This would result in a solution concentration very similar to the predicted value. Thus, one would expect that Mg concentrations would go down during the stopped period and then gradually rise again. The magnitude of the relative concentration change should be about 0.04, which is easily detectable.

The majority of the stop-flow run in the Ca to Mg (run V) direction is shown in Fig. 4. Flow was stopped

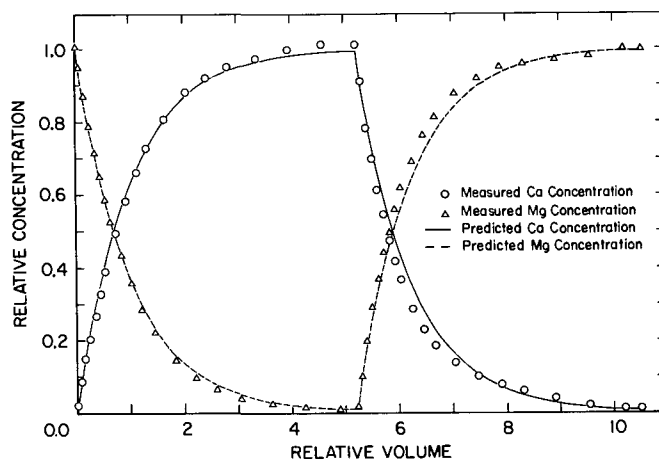


Fig. 3. Calcium and Mg relative effluent concentrations for run III. Initial equilibrium was with Mg.

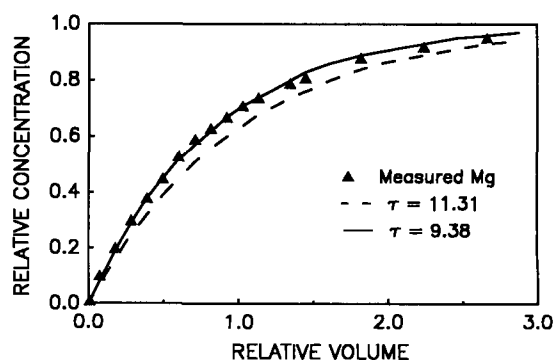


Fig. 4. Stop-flow test starting in equilibrium with Ca solution. Flow was stopped at a relative concentration of 0.6.

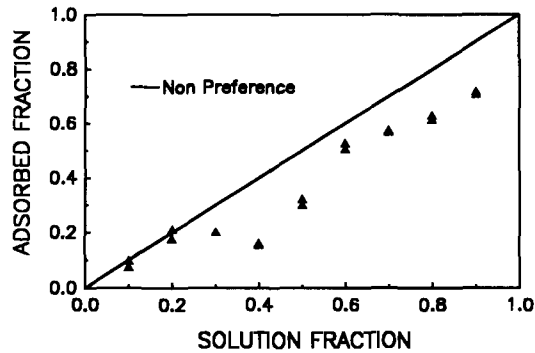


Fig. 5. Equilibrium fraction of Mg adsorbed vs. Mg in solution.

after seven data points had been collected so that the maximum effect should be observed on the 8th, 9th, and 10th data points. Also indicated are the best fit curve and the curve predicted using $\tau = 11.31$. The best fit curve indicates that Eq. [11] describes the data very well. The τ value used for that curve was not significantly different from the other values obtained for reactions in that direction. There is no appreciable discontinuity in the effluent curve that might suggest the chamber solution and adsorbed phases were not in equilibrium. A similar run (run VI) performed in the other direction also agreed with previous results.

Exchange Isotherms

The Ca/Mg exchange isotherm is shown in Fig. 5. The solution fraction on the horizontal axis is the molar proportion of Mg in the influent solution with which the soil was allowed to come to equilibrium. The adsorbed fraction on the vertical axis is the proportion of the exchange complex occupied by Mg. It was calculated as the difference between the total amount of ion displaced by the BaCl_2 solution and the initial amount of the ion in solution in the chamber. The amount displaced was the total measured in the effluent, and the initial amount of solute in the chamber was calculated as the chamber volume multiplied by the solution concentration. The diagonal line in Fig. 5 is the nonpreference isotherm.

The isotherm presented in Fig. 5 indicates a preference for Ca over Mg for this soil. The isotherm is not as smooth as other data reported because effluent measurements included ions from both the solution and adsorbed phases. Under the experimental conditions described, solution phase ions exceed adsorbed phase ions by a factor of about three so that small measurement errors have a significant effect on calculated adsorbed quantities. This condition could be improved with either greater total adsorption capacity or a reduced solution concentration. However, neither of these proved practical for this experiment.

The preference for Ca over Mg is consistent with the results from the kinetics experiments. The area under the desorption curves represents the total ion desorbed and displaced from the chamber solution. On this basis the amount of Mg displaced by Ca is greater than the amount of Ca displaced by Mg.

The isotherm results agree with a considerable amount of research that indicates that Ca is generally preferred over Mg (e.g., Udo, 1978; Robbins and Carter, 1983; Selim et al., 1987) on most soils, partic-

ularly those with smectitic clays. Sposito et al. (1983), however, working with Wyoming bentonite, showed that the apparent preference of Ca over Mg shown by a number of researchers was due to formation of monovalent complexes with Cl^- such as CaCl^+ . Thus, ternary and not binary phenomena were being studied.

No preference was expected in this experiment because ClO_4^- was used as the counter ion. However, both the kinetics experiments and the exchange isotherm indicate that there was preference for Ca over Mg on the soil used.

SUMMARY

The basic assumption that the chamber in the stirred-flow method is well mixed was tested and found to hold for flow rates up to 2.20 mL min^{-1} . We determined that the fastest reaction measurable with the method had $t_{1/2}$ values between 0.3 and 3 min. Calcium-Mg exchange was found to be effectively instantaneous (i.e., too fast to measure) so that local equilibrium could be assumed. Exchange isotherms and kinetic experiments indicated a preference for Ca over Mg on the soil studied.

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