0038-075X/92/1564-0233$03.00/0
SOIL SCIENCE
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October 1992
Vol. 156, No. 4
Printed in U.S.A.

ADSORPTION AND DESORPTION KINETICS OF CESIUM IN AN ORGANIC MATTER-RICH SOIL SATURATED WITH DIFFERENT CATIONS

CHAIM AHARONI,[1] NANAK S. PASRICHA,[2] AND DONALD L. SPARKS[3]

Samples of soils made homoionic with K, Na, or Ca were reacted with solutions containing Cs ions, and the quantities of Cs sorbed and the rates of exchange were measured. The samples were then reacted with solutions containing K, Na, or Ca, and the quantities of Cs desorbed and the rates of exchange were again measured. Samples made homoionic with Na had a greater ion exchange capacity than samples made homoionic with K, and, in both cases, the ion exchange capacity increased with the organic matter content of the soil. For samples pretreated with Ca, the ion exchange capacity is not related in a simple way to the organic matter content. The kinetics were assessed by plotting the rate of exchange vs. the time and vs. the quantity exchanged. A first-order equation was obeyed during most of the run in Cs desorption experiments and during a limited part of the run in Cs adsorption experiments. An increase in the rate of Cs exchange was observed at the beginning of the experiments especially for Cs adsorption. This increase is presumably due to an increase of the ionic strength of the liquid phase during the exchange process.

The fallout from the nuclear weapon tests conducted on Bikini Atoll Island in 1954 resulted in contamination of the soil with ^{137}Cs and, to a lesser degree, ^{90}Sr. This contamination forced Bikinians to leave the island since food grown on the soils was not safe to eat. Several methods for decontamination of the soil on Bikini Atoll have been studied: removal of the topsoil where the majority of the contaminants are located, treatment of the soil with K salts, and irrigation of the soil with sea water. The latter two methods are cheaper and pose fewer ecological problems than soil excavation. Field studies on Bikini Atoll showed that additions of K reduced ^{137}Cs uptake by vegetables and coconuts, particularly when K was broadcast close to the plant rows (Bikini Atoll Rehabilitation Committee Report 1987).

To develop effective regimes for decontaminating the Bikini Atoll soil, one must understand the exchange of Cs for K, Na, and other cations on the soil. Not only is it important to study the equilibrium aspects of these reactions, but also the kinetics of the exchange reactions must be investigated since Cs appears to be mobile in the soils.

Few studies on the dynamics of Cs in soils have appeared in the literature. Sawhney (1966) studied Cs exchange kinetics on clay minerals. However the soils on Bikini Atoll are almost devoid of any clay minerals. They are limestone or gravelly limestones formed from a variety of organisms in addition to coral (Stone 1987, unpublished data). Organic matter contents are quite high, particularly in surface horizons (Table 1).

The kinetics of chemical processes in soils and clay minerals have been described by various equations. First-order equations have been used to describe the kinetics of K adsorption (Sparks et al. 1980 a and b; Sparks and Jardine 1984; Sivasubramaniam and Talibudeen 1972; Ogwada and Sparks 1986), and N (Stanford et al. 1975; Kohl et al. 1976; Carski and Sparks 1987), P (Griffin and Jurinak 1974; Vig et al. 1979), B (Griffin and Burau 1974; Carski and Sparks 1985; Sharma et al. 1989), S (Hodges and Johnson 1987), and Cl reactions (Thomas 1963; Pasricha et al. 1987).

The Elovich equation has been applied to the adsorption of P (Chien and Clayton 1980; Chien et al. 1980; Sharpley 1983), K (Sparks et al. 1980 a and b; Havlin and Westfall 1985), B (Peryea et al. 1985), S (Hodges and Johnson 1987), and As (Elkhatib et al. 1984) on soils and soils components. The parabolic equation and other fractional power functions have also been applied to sorption of various ions (Havlin and Westfall 1985; Havlin et al. 1985; Sparks 1988).

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[1] Dept. of Chemical Engineering, Technion—Israel Inst. of Technology, Haifa, Israel, 32000.

[2] Dept. of Soil Science, Punjab Agricultural Univ., Ludihana, India.

[3] Dept. of Plant and Soil Sciences, Univ. of Delaware, Newark, DE 19717-1303.

Received Sept. 30, 1992; accepted March 3, 1993.

TABLE 1

Chemical properties of the soils studied

Depth	0–25 cm	25–40 cm	40–60 cm
Organic Matter content (g kg^{-1})	55	18	9
Al oxide content, (NH_4 oxalate extractable, mg kg^{-1})	0.01	0.01	0.01
Fe oxide content, (NH_4 oxalate extractable, mg kg^{-1})	0.00	0.00	0.00
pH (1:2 soil:water)	8.3	8.6	8.9

The applicabilities of some of the most frequently used equations are compared in various studies. Sparks and Jardine (1984) compared a number of equations for describing K exchange. Sharma et al. (1989) compared the applicability of various equations to the kinetics of B release. In recent theoretical treatments on the kinetics of soil chemical processes (Aharoni and Sparks 1991; Aharoni et al. 1991), it was shown that the S-shape rule, which was derived for the kinetics of adsorption on various adsorbents (Aharoni 1984), is generally applicable for describing the kinetics of ion adsorption and desorption on soils. This rule states that in solid-liquid processes, the plot of the reciprocal of the rate, Z, against the time t, is S-shaped: it is convex at small t and concave at large t. The region around the inflection point, corresponds to a range of time at which an Elovichian equation is applicable, the initial convex part to a range at which a fractional power equation is applicable, and the final part at which the plot is concave to a range at which an equation similar in form to the first-order equation is applicable.

The objective of this study was to investigate the kinetics of Cs-K, Cs-Na, and Cs-Ca exchange on three soil horizons from a Bikini Atoll soil. The samples of soil were made homoionic with K^+, Na^+, and Ca^{2+}, and the rates of exchange of these ions by Cs^+ was determined; these "Cs adsorption runs" were followed by "Cs desorption runs" in which Cs^+ was subsequently exchanged by the ion it had previously replaced.

MATERIALS AND METHODS

Bulk soil samples were obtained from surface (0–25 cm) and subsoil (25–40 cm and 40–60 cm) horizons at the Bikini Atoll. The air-dried samples were ground to pass through a 2-mm sieve in preparation for laboratory analysis. Basic chemical properties of the soil horizons are given in Table 1.

Prior to kinetic measurements, the soil samples were made homoionic with Na^+, K^+, and Ca^{2+} by treating them with 1N Cl^- solutions of the cations. Excess electrolyte was removed using deionized water until a negative test for Cl^- was obtained with $AgNO_3$.

Kinetic measurements

The kinetic studies were conducted using the stirred flow reaction technique developed by Carski and Sparks (1985).

In the Cs adsorption runs, 1 g of homoionic soil was placed in the chamber. A 0.02 N solution of $CsClO_4$ was passed through the chamber at a rate of 1 ml·min^{-1} using a peristaltic pump, while the suspension was continuously mixed with a magnetic stirrer. $CsClO_4$ was used rather than CsCl in order to avoid formation of undesired complexes (Sadusky and Sparks, 1991). Aliquots were taken every 2 min during the first 20 min, every 4 min during the next 20 min, and every 6 min during the next 30 min. A fraction collector was used for collecting the aliquots at the desired times. A blank run without soil was also performed.

Each Cs adsorption run was followed by a Cs desorption run, in which Cs^+ was exchanged by the same cation it had previously replaced, using 0.02 N solutions of $KClO_4$, $NaClO_4$, and $Ca(ClO_4)_2$. Cesium was analyzed using atomic absorption spectrophotometry. The quantities of adsorbed and desorbed ions were determined using the approach of Sadusky and Sparks (1991).

RESULTS AND DISCUSSION

The rates of the exchange processes in the three soil horizons are depicted in Figs. 1-3 as plots of: (a) Cs^+ adsorbed by soil samples pretreated with one of the cations: K^+, Na^+, Ca^{2+} and (b) Cs^+ desorbed from the same samples when the same cations, K^+, Na^+, Ca^{2+}, are readsorbed, vs. time.

Adsorption at Equilibrium

The results depicted in Figs. 1–3 show that all the exchange processes were carried out until equilibrium was approached. In the stirred flow procedure that was used in the present study, a

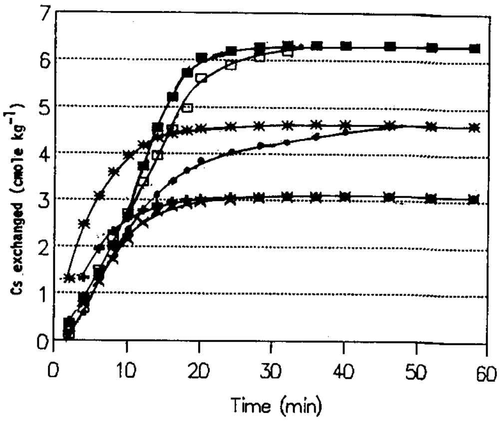

FIG. 1. Quantity of Cs exchanged vs. time in the 0–25-cm horizon of the Bikini soil. ● = K pretreatment, adsorption of Cs; * = K pretreatment, desorption of Cs; □ = Na pretreatment, adsorption of Cs; ■ = Na pretreatment, desorption of Cs; × = Ca pretreatment, adsorption of Cs; † = Ca pretreatment, desorption of Cs.

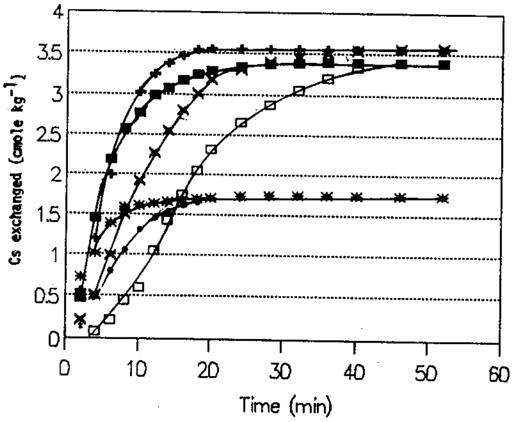

FIG. 2. Quantity of Cs exchanged vs. time in the 25–40-cm horizon of the Bikini soil. ● = K pretreatment, adsorption of Cs; * = K pretreatment, desorption of Cs; □ = Na pretreatment, adsorption of Cs; ■ = Na pretreatment, desorption of Cs; × = Ca pretreatment, adsorption of Cs; + = Ca pretreatment, desorption of Cs.

solution containing a constant concentration of the replacing ion is continuously supplied to the soil sample, and the solution resulting from the exchange and containing the replaced ion is continuously removed. Therefore, unlike in batch methods, the exchange is total, whether the replacing ion is more strongly or more weakly adsorbed than the replaced ion. We assume, therefore, that the number of equivalents of Cs adsorbed at equilibrium represents the total capacity of the soil sample for exchangeable cations, q_{inf}. This number of equivalents should also be equal to the number of equivalents released at the desorption run that followed the adsorption run. Almost all the results in Figs. 1–3 are consistent with this postulate.

The results (see Table 2) also show that the attempts to produce "homoionic" samples by pretreating the soil with 1N Cl solutions of either K^+, Na^+, or Ca^{2+} produced samples with unequal capacities for ion exchange. In the three horizons tested, the capacity was larger when the sample was pretreated with Na^+ than when it was pretreated with K^+. One also notes that for both the K^+ and Na^+ pretreatments, the ion exchange capacity decreased with the depth from which the soil samples were taken, and there is a clear correlation between the exchange capacity and the organic matter content (Tables 1 and 2); however, for samples treated with Ca^{2+}, the ion exchange capacity is not correlated in a

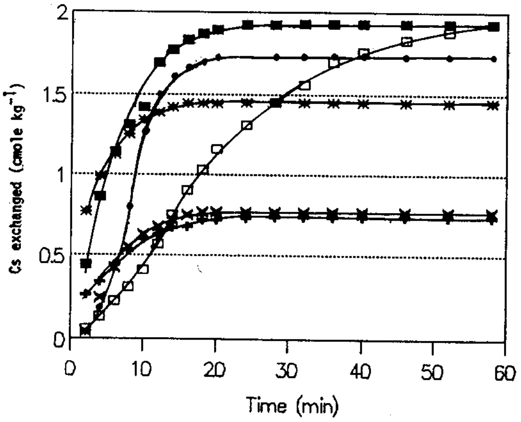

FIG. 3. Quantity of Cs exchanged vs. time in the 40–60-cm horizon of the Bikini soil: ● K pretreatment, adsorption of Cs; * = K pretreatment, desorption of Cs; □ = Na pretreatment, adsorption of Cs; ■ = Na pretreatment, desorption of Cs; × = Ca pretreatment, adsorption of Cs; + = Ca pretreatment, desorption of Cs.

TABLE 2

Ion exchange capacities of soils saturated with different ions (cmole·kg^{-1})

Depth	0–25 cm	25–40 cm	40–60 cm
K pretreatment	4.69	1.75	1.72
Na pretreatment	6.33	3.40	1.93
Ca pretreatment	3.10	3.59	0.77

simple way to the organic matter content. These results indicate that the organic matter is the soil component mainly responsible for the ion exchange capacity, as expected in soils almost devoid of clay minerals and rich in organic matter. The apparent inconsistency associated with treatment with Ca^{2+} is possibly due to the fact that this ion is capable of forming complexes with some of the components of the organic matter, and the concentrations of these components in the organic matter are likely to differ in the three horizons examined.

Kinetics of exchange

Figures 1–3 show that all the exchange processes tested are fairly rapid, and equilibrium is practically attained at ranges of time between 15 and 50 mins. They also show that at any time t during the exchange process, the quantity exchanged, q, is larger in a desorption run (Cs exchanged by K, Na, or Ca) than in the corresponding adsorption run (K, Na, or Ca exchanged by Cs).

In order to assess the kinetics, the rates dq/dt were estimated from the data depicted in Figs. 1–3 and plotted vs. the time t and vs. the quantity exchanged, q, (some of the plots are given in Figs. 4-9). In most desorption runs, the rate decreases with the time and with the quantity exchanged during all the run, whereas in most adsorption runs, a region at which the rate increases with t precedes the region at which the rate decreases.

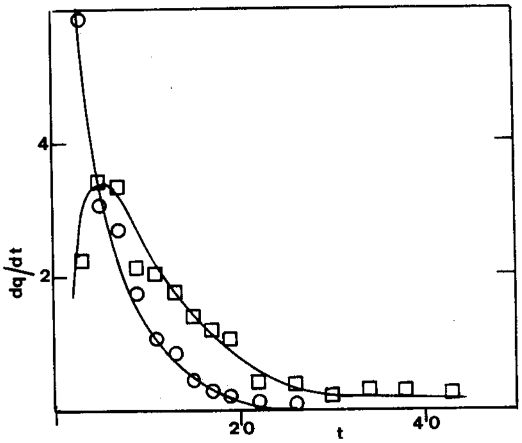

FIG. 4. Rate of Cs exchange (μEq Cs·g^{-1} soil·min^{-1}) vs. time (min): 0–25 cm horizon, K pretreatment. □ adsorption of Cs, ○ desorption of Cs.

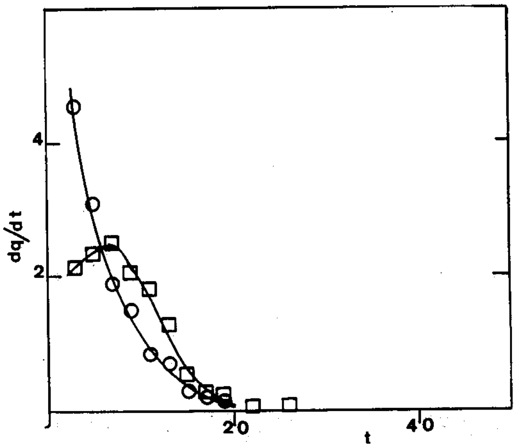

FIG. 5. Rate of Cs exchange (μEq Cs·g^{-1} soil·min^{-1}) vs. time (min): 0–25 cm horizon, Ca pretreatment. □ adsorption of Cs, ○ desorption of Cs.

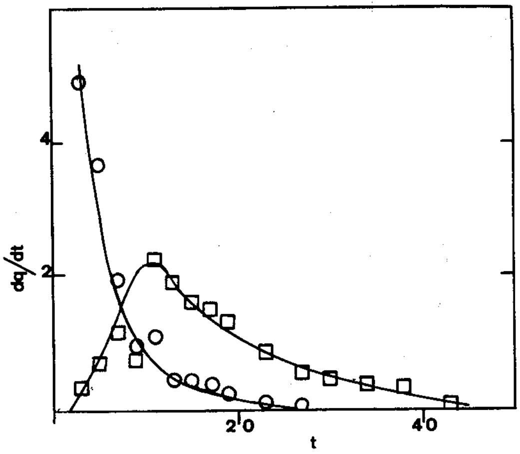

FIG. 6. Rate of Cs exchange (μEq Cs·g^{-1} soil·min^{-1}) vs. time (min): 25–40 cm horizon, Na pretreatment. □ adsorption of Cs, ○ desorption of Cs.

The plots of dq/dt vs. q are linear in desorption and tend to become linear at large t in adsorption. This suggests that the kinetics of Cs exchange essentially obey a first-order equation and that another process, which causes increase of the rate with increasing time, interferes with these kinetics at the beginning of the adsorption runs (see below). At the range at which the first-order equation is valid the kinetics are given by

$$dq/dt = k\ (q_{\mathrm{inf}} - q) \qquad (1)$$

where q_{inf} is the ion exchange capacity and k is a kinetic constant. The values of k are calculated

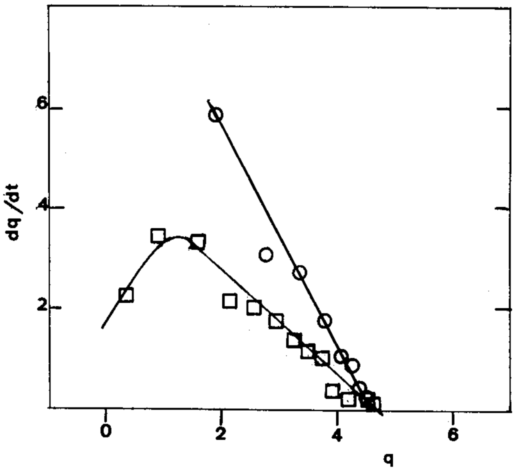

FIG. 7. Rate of Cs exchange (μEq Cs$\cdot$g^{-1} soil$\cdot$min^{-1}) vs. quantity exchanged (μEq Cs$\cdot$g^{-1} soil), 0–25 cm horizon, K pretreatment. □ adsorption of Cs, ○ desorption of Cs.

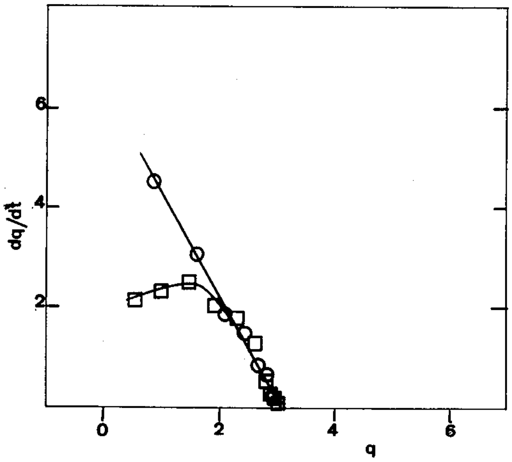

FIG. 8. Rate of Cs exchange (μEq Cs$\cdot$g^{-1} soil$\cdot$min^{-1}) vs. quantity exchanged (μEq Cs$\cdot$g^{-1} soil), 0–25 cm horizon, Ca pretreatment. □ adsorption of Cs, ○ desorption of Cs.

from the plots for the desorption runs (Figs. 7–9); k is between 0.19 to 0.21 min^{-1}, and it does not vary significantly with the nature of the exchanged ion or with the soil horizon. For the adsorption runs, k can be estimated only from the slope of the plots at the end of the runs, and the values found are as expected lower between 0.1 and 0.2 min^{-1}. The fact that the kinetics of Cs exchange obey a first-order equation is consistent with the kinetics of other soil chemical processes (see literature survey above); however, it is not possible to verify the applicability of the above mentioned S-shape rule, because the kinetics at small t are masked by the effects of another phenomenon.

The cause of the rate increase that takes place at small t is not completely clear. At small t, ion exchange is rapid and other factors can become rate-determining. In the stirred-flow procedure used in the present work, the kinetics can possibly be determined by the rate at which the solution containing the exchangeable ions is introduced into the adsorption cell or by the diffusivity of these ions in the liquid phase surrounding the soil particles. However, there are indications that the rate increases observed in the present work are unlikely to have been caused by these factors. These indications are: (i) the rate at which the ions were introduced into the adsorption chamber, 20 μEq/min, was significantly larger than the rates of ion exchange at their maximum value (see Figs. 4–6), and (ii) at the ranges of time at which the rate of adsorption increases with t, a rate decrease in the corresponding desorption run was often observed. It is unlikely that the supply and diffusion of the exchangeable ions in the solution are rate-determining in an adsorption run and not in the corresponding desorption run performed at similar conditions.

It is likely that the difference in the shapes of the kinetics curves for adsorption and desorption is related to the following experimental fact.

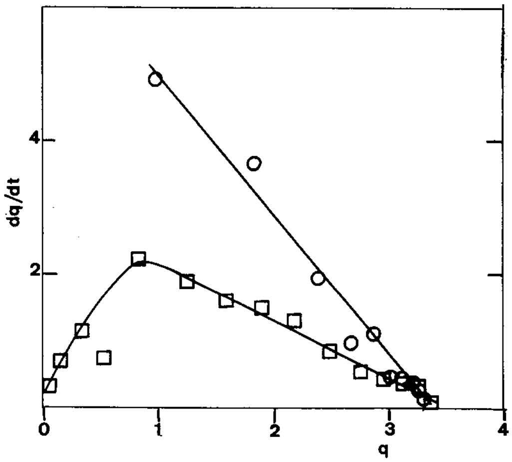

FIG. 9. Rate of Cs exchange (μEq Cs$\cdot$g^{-1} soil$\cdot$min^{-1}) vs. quantity exchanged (μEq Cs. g^{-1} soil), 25–40 cm horizon, Na pretreatment. □ adsorption of Cs, ○ desorption of Cs.

In the adsorption runs, the sample of soil was initially dispersed in pure water, and the water was subsequently replaced by an electrolytic solution (the Cs salt solution), whereas in the desorption runs the sample was initially dispersed in an electrolytic solution (Cs salt solution), which was subsequently replaced by another electrolytic solution (K, Na or Ca solution). In the latter case, the solution had a large ionic strength from the beginning of the run, and this strength did not vary significantly with the time, whereas in the former case the ionic strength was small at the beginning of the run and increased subsequently. The fact that an amount of ions adsorbed by variable charge soils increases with increase in the ionic strength of the liquid phase is well known. The present work illustrates a situation in which a significant increase of the ionic strength occurs during the exchange process, and the rate increase it induces interferes with the effect because of the decrease of the concentration of the exchangeable ions.

REFERENCES

Aharoni, C. 1984. Kinetics of adsorption: the S-shaped Z(t) plot. Sorpt. Sci. Technol. 1:1–29.

Aharoni, C., and D. L. Sparks. 1991. Kinetics of soil chemical reactions—A theoretical treatment. *In* Rates of soil chemical processes. D. L. Sparks, and D. L. Suarez (eds.). SSSA Spec. Publ. 27, SSSA, Madison, WI.

Aharoni, C., D. L. Sparks, S. Levinson, and I. Ravina. 1991. Kinetics of soil chemical reactions: Relationships between empirical equations and diffusional models. Soil Sci. Soc. Am. J. 55:1307–1312.

Birnholtz, H. 1981. Effect of surface diffusion on the kinetics of chemisorption on heterogeneous surfaces. Thesis, Department of Chemical Engineering, Technion, Haifa, Israel.

Birnholtz, H., A. Nir, N. Lotan, and C. Aharoni. 1984. Surface diffusion as a rate determining step in activated chemisorption. Can. J. Chem. Eng. 62:233–240.

Carski, T. H., and D. L. Sparks. 1985. A modified miscible displacement technique for investigating adsorption - desorption kinetics in soils. Soil Sci. Soc. Am. J. 49:1114–1116.

Carski, T. H., and D. L. Sparks. 1987. Differentiation of soil nitrogen fractions using a kinetic approach. Soil Sci. Soc. Am. J. 51:314–317.

Chien, S. H., and W. R. Clayton. 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. Soil Sci. Soc. Am. J. 44:265–268.

Chien, S. H., W. R. Clayton, and G. H. McClellan. 1980. Kinetics of dissolution of phosphate rocks in soils. Soil Sci. Soc. Am. J. 44:260–264.

Elkhatib, E. A., O. L. Bennett, and R. J. Wright. 1984. Kinetics of arsenite sorption in soils. Soil Sci. Soc. Am. J. 48:758–762.

Griffin, R. A., and J. J. Jurinak. 1974. Kinetics of the phosphate interaction with calcite. Soil Sci. Soc. Am. Proc. 38:75–79.

Griffin, R. A., and R. G. Burau. 1974. Kinetics and equilibrium studies of boron desorption from soil. Soil Sci. Soc. Am. Proc. 38:892–897.

Havlin, J. L., and D. G. Westfall. 1985. Potassium release kinetics and plant response in calcareous soils. Soil Sci. Soc. Am. J. 49:366–370.

Havlin, J. L., D. G. Westfall, and S. R. Olsen. 1985. Mathematical models for potassium release kinetics in calcareous soils. Soil Sci. Soc. Am. J. 49:371–376.

Helfferich, F. 1962a. Ion Exchange. Ch. 6, section 6.3. McGraw-Hill, New York.

Helfferich, F. 1962b. Ion exchange. Ch. 6, section 6.8. McGraw-Hill, New York.

Hodges, S. C., and C. Johnson. 1987. Kinetics of sulfate adsorption and desorption by cecil soil using miscible displacement. Soil Sci. Soc. Am. J. 51:323–331.

Kohl, D. H., F. Vithayathil, R. Whitlow, G. Shearer, and S. H. Chien. 1976. Denitrification kinetics in soil systems. The significance of good fits of data to mathematical forms. Soil Sci. Soc. Am. J. 40:249–253.

Ogwada, R., and D. L. Sparks. 1986. Kinetics of ion exchange on clay minerals and soils. I. Evaluation of methods. Soil Sci. Soc. Am. J. 50:1158–1162.

Pasricha, N. S., D. L. Sparks, and C. V. Toner. 1987. Competitive anion adsorption kinetics on soils of variable charge. Agronomy Abst. p. 172.

Peryea, F. J., F. T. Bingham, and J. D. Rhoades, 1985. Kinetics of post-reclamation boron dissolution. Soil Sci. Soc. Am. J. 49:836–839.

Saduski, M. C., and D. L. Sparks. 1991. Anionic effects on potassium reactions in variable-charge Atlantic Coastal Plain soils. Soil Sci. Soc. Am. J. 55:371–375.

Sawhney, B. L. 1966. Kinetics of cesium sorption by clay minerals. Soil Sci. Soc. Am. Proc. 30:565–569.

Sharma, H. S., N. S. Pasricha, and M. S. Bajwa. 1989. Comparison of mathematical models to describe boron desorption from salt affected soils. Soil Sci. 147:79–84.

Sharpley, A. N. 1983. Effect of soil properties on the kinetics of phosphorus desorption. Soil Sci. Soc. Am. J. 47:462–467.

Sivasubramaniam, S., and O. Talibudeen. 1972. Potassium - aluminum exchange in acid soils. I. Kinetics. J. Soil Sci. 23:163–173.

Sparks, D. L. 1989. Kinetics of soil chemical processes. Academic Press, New York, pp. 4–38.

Sparks, D. L., and P. M. Jardine. 1984. Comparison of kinetic equations to describe K-Ca exchange in pure and in mixed systems. Soil Sci. 138:115–122.

Sparks, D. L., L. W. Zelazny, and D. C. Martens. 1980a. Kinetics of potassium exchange in a Paleudult from the Coastal Plain of Virginia. Soil Sci. Soc. Am. J. 44:37–40.

Sparks, D. L., L. W. Zelazny, and D. C. Martens. 1980b. Kinetics of potassium desorption in soils using miscible displacement. Soil Sci. Soc. Am. J. 44:1205–1208.

Stanford, G., R. A. Vanderpol, and S. A. Dzienia. 1975. Denitrification rates in relation to total and extractable soil carbon. Soil Sci. Soc. Am. Proc. 39:284–289.

Thomas, G. W. 1963. Kinetics of chloride desorption from soils. J. Agric. Food Chem. 110:201–203.

Vig, A. C., C. R. Biswas, and M. K. Sinha. 1979. Kinetics of phosphorus desorption and diffusion in differential P - fertilized soil. Bull. Indian Soc. Soil Sci. 12:279.