

## KINETICS OF POTASSIUM EXCHANGE IN HETEROGENEOUS SYSTEMS

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### ABSTRACT

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A plant's nutritional requirement for potassium (K) is usually satisfied by release of  $K^+$  from the phases of soil K. The rates of the reactions between the forms of K in a heterogeneous system are primarily dependent upon the types and amounts of clay minerals present. An overview of the kinetics of K exchange in clay and soil systems will be presented. Discussion will include: rates of K exchange on kaolins, smectites, vermiculites, and soils; models and methods to describe these reactions; and, the rate determining steps involved. A knowledge of the reaction kinetics between the phases of K is paramount in modeling the fate of applied K in soils.

### INTRODUCTION

Thermodynamic data can predict only the final state of a system from an initial nonequilibrium mode. However, to rationalize chemical reaction rates, a knowledge of the kinetics is required. Kinetic studies provide valuable insights into the reaction pathways and into the mechanisms of chemical reactions. Unfortunately, due to theoretical and experimental difficulties, it is often arduous to apply pure chemical kinetics to even homogeneous solutions (Frost and Pearson, 1961). When kinetic theories are applied to heterogeneous soil systems, the problems are magnified.

Kinetic investigations with K in heterogeneous systems are often more valuable than thermodynamic studies. Agricultural soils are nearly always in a state of disequilibrium with regard to K transformation. Soils that have been intensively cropped and fertilized with optimum K rates for many years belong in this group, because equilibrium is often precluded by periodic addition of K fertilizers.

Equilibrium reactions existing between solution, exchangeable, non-exchangeable, and mineral phases of K profoundly influence K chemistry (Fig. 1). The rate and direction of these reactions determine whether applied

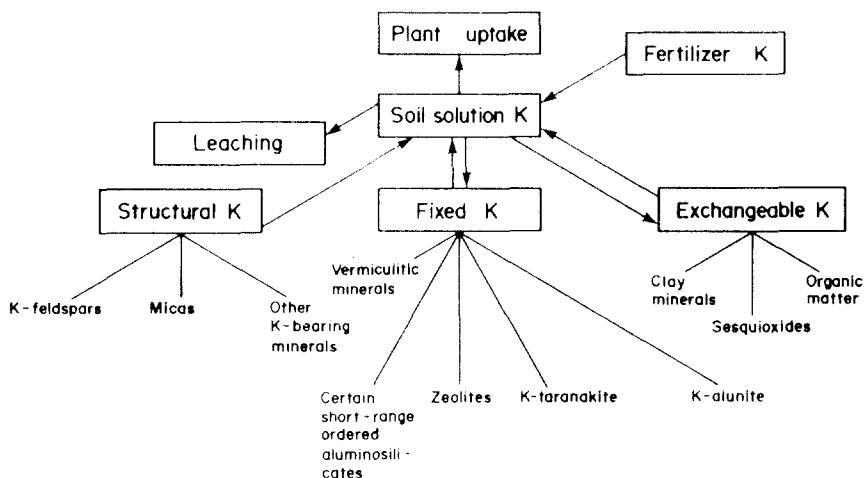
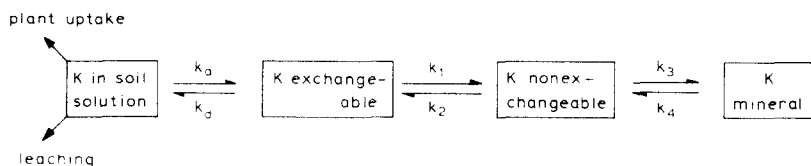


Fig. 1. An overview of the phases of soil potassium.

K will be leached into lower horizons, taken up by plants, converted into unavailable forms, or released into available forms. A voluminous amount of research has been performed on various aspects of ionic exchange with K, but a meager amount has appeared in the literature on kinetics of K reactions in heterogeneous systems. While some research has been performed on the kinetics of reactions on clay minerals, little has been conducted on soil systems where complex mixtures of clay minerals, noncrystalline components, oxides, hydroxides, and organic matter are present (Thomas, 1977). A knowledge of rates of reactions between the phases of soil K is necessary to predict the fate of added K fertilizers in soils, and to make proper K fertilizer recommendations.

Kinetic reactions between the four forms of soil K can be depicted as (Sparks, 1985):



where:  $k_a$  = adsorption rate coefficient in  $h^{-1}$ ;  $k_d$  = desorption rate coefficient in  $h^{-1}$ ;  $k_1$  = nonexchangeable fixation rate coefficient in  $h^{-1}$ ;  $k_2$  = nonexchangeable release rate coefficient in  $h^{-1}$ ;  $k_3$  = immobilization rate coefficient in  $h^{-1}$ ; and  $k_4$  = mineralization rate coefficient in  $h^{-1}$ .

#### MODELS TO DESCRIBE K KINETICS IN CLAY MINERALS AND IN SOILS

A number of equations have been used to describe K kinetics in clay minerals and in soils (Key and Wild, 1961; Burns and Barber, 1961; Huang

et al., 1968; Quirk and Chute, 1968; Malcom and Kennedy, 1969; Sparks et al., 1980a,b; Feigenbaum et al., 1981; Sparks and Jardine, 1981; Martin and Sparks, 1983; Jardine and Sparks, 1984; Sparks and Jardine, 1984; Sparks, 1985; Sparks and Huang, 1985). These equations have included the zero-order, first-order, Elovich, and parabolic diffusion equations. The final form of each equation is given in Table I; complete derivations for all of the equations can be found in Sparks and Jardine (1984) and in Sparks (1985). In our research, we have found that the first-order and parabolic diffusion equations best describe K exchange in heterogeneous systems (Sparks and Jardine, 1984).

For a batch technique, if the rate of adsorption of K onto a colloidal surface is proportional to the quantity of K remaining in the solution, the integrated first-order kinetic equation would be expressed as:

$$\ln C_t = \ln C_0 - k_a t \quad (1)$$

where  $C_t$  = concentration of K in solution at time  $t$ ;  $C_0$  = initial concentration of K added at time zero;  $k_a$  = adsorption rate constant;  $t$  = time.

Thus, plotting  $\ln C_t$  versus  $t$  will yield a straight line of slope  $-k_a$  and an intercept of  $\ln C_0$  if the data conform to first-order kinetics.

For a miscible displacement or flow technique, if the rate of K adsorption onto the colloidal surface follows first-order kinetics then:

$$\log (1 - C_t/C_\infty) = k'_a t \quad (2)$$

TABLE I

Equations used to describe kinetics of potassium reactions in heterogeneous systems

*First-order adsorption*<sup>\*1</sup>

Batch technique:

$$\ln C_t = \ln C_0 - k_a t \quad (1)^{*2}$$

Flow technique:

$$\log \left( 1 - \frac{C_t}{C_\infty} \right) = k'_a t \quad (2)$$

*First-order desorption*

Batch technique:

$$\ln (C_\infty - C_t) = \ln C_\infty - k_d t \quad (3)$$

Flow technique:

$$\log (C_t/C_0) = k_d' t \quad (4)$$

*Elovich*

$$(C_\infty - C_t) = (1/\beta) \ln (1 + \alpha \beta t) \quad (6)$$

*Parabolic diffusion*

$$(C_t/C_\infty) = Rt^{1/2} + \text{constant} \quad (7)$$

\*1 The terms in the equations are defined in the text of the paper.

\*2 Refers to equation number in the paper.

where  $C_t$  = amount of K on the colloid at time  $t$ ;  $C_\infty$  = amount of K on the colloid at equilibrium;  $k'_a$  = apparent adsorption rate coefficient.

If the rate of K release from a colloidal surface follows first-order kinetics, then for a batch technique, the integrated equation is:

$$\ln (C_\infty - C_t) = \ln C_\infty - k_d t \quad (3)$$

where  $C_\infty$  = total amount of K that could be released at equilibrium;  $C_t$  = amount of K released at time  $t$ ;  $k_d$  = desorption rate constant.

If the rate of K release follows first-order kinetics, then for a miscible displacement or flow technique, and for the solid phase, the integrated equation is:

$$\log (C_t/C_0) = k'_d t \quad (4)$$

where  $C_0$  = amount of K on the exchange sites of the colloid at zero time;  $k'_d$  = apparent desorption rate coefficient.

One should realize that the absolute velocity constants for the K adsorption and desorption processes ( $k_a$  and  $k_d$ , respectively) are comprised of numerous diffusional and chemical rate constants (Jardine and Sparks, 1984). It is appropriate to suggest that for the adsorption process, the rate of K adsorption  $r_a$  is:

$$r_a \propto k_1 + k_2 + k_3 \quad (5)$$

where  $k_1$  = rate constant associated with film diffusion processes;  $k_2$  = rate constant associated with interparticle diffusion, or, independently, the rate constant associated with surface diffusion;  $k_3$  = chemical rate constant.

Depending on the type of system which is being studied, one or more of the rate constants (viz.,  $k_1$ ,  $k_2$ ,  $k_3$ ) may be negligible or absent. Of the processes which contribute to the overall rate, the rate constant which is lowest will be the rate-limiting kinetic parameter and will have the greatest impact on the observed velocity constant,  $k_a$ . Analogous expressions can be obtained for the desorption process.

The first-order equation has been utilized by many soil chemists and mineralogists to describe K kinetic reactions in clay minerals and in soils (Mortland and Ellis, 1959; Mortland, 1961; Reed and Scott, 1962; Huang et al., 1968; Scott, 1968; Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980a,b; Feigenbaum et al., 1981; Sparks and Jardine, 1981; Martin and Sparks, 1983; Jardine and Sparks, 1984; Sparks and Jardine, 1984). Sparks and Jardine (1984) studied the kinetics of K adsorption on kaolinite, montmorillonite, and vermiculite. The first-order equation described K adsorption on the clays extremely well which conformed to findings of others (Keay and Wild, 1961; Klobe and Gast, 1967). The first-order equation also seems to describe K reactions between solution and exchangeable phases in soil systems (Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980a,b; Sparks and Jardine, 1981; Sparks and Rechcigl, 1982; Jardine and Sparks, 1984; Sparks and Jardine, 1984).

The modified Elovich equation to describe K sorption in clays and soils after integration would read (Sparks, 1985):

$$(C_{\infty} - C_t) = (1/\beta) \ln (1 + \alpha\beta t) \quad (6)$$

where  $(C_{\infty} - C_t)$  represents the net amount of K sorbed by the soil at time  $t$ , and  $\alpha$  and  $\beta$  are constants during any one experiment.

The Elovich equation has been successfully used to describe P adsorption and release in soils and clays (Chien and Clayton, 1980; Chien et al., 1980) but has limited utility for describing K reactions in clays and soils (Martin and Sparks, 1983; Sparks, 1985; Sparks and Jardine, 1984).

The parabolic diffusion equation for K reactions in soils and clays can be expressed as:

$$(C_t/C_{\infty}) = Rt^{1/2} + \text{constant} \quad (7)$$

where  $C_t$  = quantity of K adsorbed or desorbed at time  $t$ ;  $C_{\infty}$  = amount of K adsorbed at equilibrium;  $R$  = an overall diffusion coefficient.

Numerous researchers have used the parabolic diffusion law to describe kinetic reactions involving K in clay minerals and soils (Barshad, 1951, Keay and Wild, 1961; Reed and Scott, 1962; Rausell-Colom et al., 1965; Quirk and Chute, 1968; Ismail and Scott, 1972; Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980a,b; Feigenbaum et al., 1981; Martin and Sparks, 1983; Jardine and Sparks, 1984; and Sparks and Jardine, 1984). The parabolic diffusion law has been used successfully in describing non-exchangeable and mineral release of K from clays (Barshad, 1954; Chute and Quirk, 1967; Feigenbaum et al., 1981), but it does not always adequately describe kinetics of exchange between solution and exchangeable forms of K (Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980b; Jardine and Sparks, 1984). One of the problems in using the parabolic equation for soil systems may be ascribed to the nebulous interpretation of the slope parameter. Sivasubramaniam and Talibudeen (1972) obtained parabolic plots for Al-K exchange on British soils which gave two distinct slopes; the authors theorized this could be ascribed to two simultaneous diffusion-controlled reactions. The authors speculated that the rate-controlling step in the adsorption of  $\text{Al}^{3+}$  and  $\text{K}^+$  was the diffusion of the ions into the subsurface layers of the solid.

Chute and Quirk (1967) and Sparks et al. (1980b) noted nonlinearity with the parabolic diffusion equation for the initial minutes of K desorption in clays and soils, respectively. They attributed this deviation to film diffusion-controlled exchange in the early minutes of K exchange.

Only a few researchers have successfully applied the zero-order equation to describe K kinetic reactions in clays and soils (Mortland, 1958; Burns and Barber, 1961). Burns and Barber (1961), investigating the effect of temperature and moisture on exchangeable K in some silt loam soils, found that the rate of release of K over an extensive period of time conformed initially to first-order kinetics while subsequent release followed zero-order

kinetics. Mortland (1958) found that the initial rate of K release from biotite was zero-order which indicated that some factor was obviously restricting the rate or release of K independently of the amount left in the mineral.

#### REACTION RATE BETWEEN SOLUTION AND EXCHANGEABLE PHASES OF K

The reaction rate between soil solution and exchangeable phases of K is strongly dependent on the type of clay minerals present (Barshad, 1951; Sivasubramaniam and Talibudeen, 1972; Sparks, 1980; Sparks et al., 1980a,b; Sparks and Jardine, 1981; Sparks and Rechcigl, 1982; Jardine and Sparks, 1984; Sparks and Jardine, 1984; Sparks, 1985), and on the method employed to measure kinetics of K exchange (Sparks and Rechcigl, 1982). Vermiculite, smectite, kaolinite, and hydrous mica vary drastically in their ionic preferences, in ion binding affinities, and in types of ion exchange reactions. Such fundamental differences in these clay minerals account for the varying kinetics of exchange.

Kinetics of K exchange on kaolinite and smectite are usually quite rapid (Malcom and Kennedy, 1969; Sparks, 1985; Sparks and Huang, 1985; Sparks and Jardine, 1984). An illustration of this is shown in Fig. 2. In the case of kaolin clays, the tetrahedral sheets of adjacent clay sheets are held tightly by hydrogen bonds; thus, only planar external surface (edge) sites are available for ionic exchange. With smectite, the inner peripheral space is not held together by hydrogen bonds, but instead it is able to swell with adequate hydration and thus allow for rapid passage of ions into the interlayer. Malcom and Kennedy (1969) found that the rate of Ba-K exchange on kaolinite and smectite was rapid with 75% of the total exchange occurring in three seconds. Sparks and Jardine (1984) found that the rate of K exchange

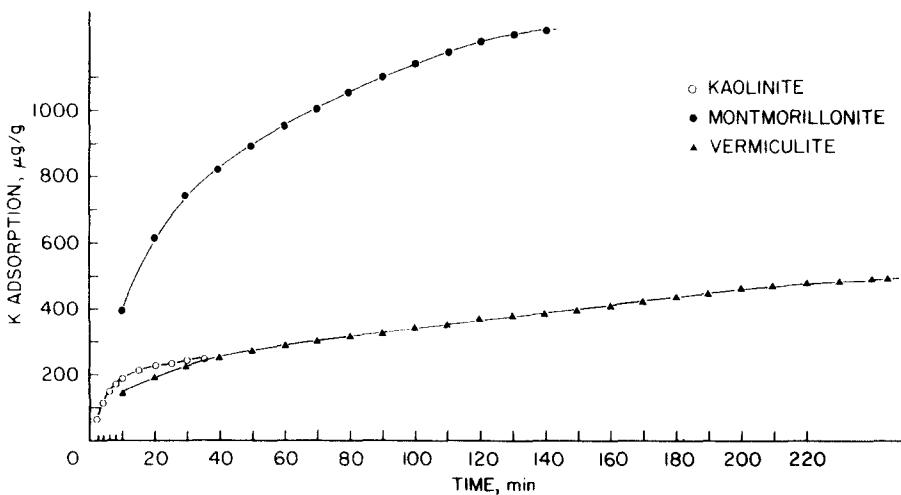


Fig. 2. Adsorption of K by kaolinite, smectite and vermiculite vs. time.

on a Washington County, Texas kaolinite was rapid with an apparent equilibrium reached in 40 min while equilibrium of K exchange in a Gonzales County, Texas montmorillonite was attained in  $\sim 140$  min (Fig. 2). The rate of K exchange on vermiculite (Fig. 2) and mica is low. Both clay minerals are 2:1 lattice clays with peripheral spaces which impede many ion exchange reactions. Micaceous minerals typically have a more restrictive interlayer space than vermiculite since the area between layer silicates of the former is selective for certain cations (viz.,  $K^+$ ,  $Cs^+$ , and others). In 1963, Bolt et al. theorized the existence of three types of binding sites for K exchange on a "hydrous mica". The authors hypothesized that slow kinetics were due to interlattice exchange sites, rapid kinetics to external planar sites, and intermediate kinetics to interlayer lattice edge sites.

Only a few researchers have investigated the kinetics between solution and exchangeable forms of K in mixed soil systems (Talibudeen and Dey, 1968; Talibudeen and Sivasubramaniam, 1976; Goulding and Talibudeen, 1979; Goulding, 1980; Sparks et al., 1980a,b; Goulding, 1981; Sparks and Jardine, 1981; Sparks and Rechcigl, 1982; Jardine and Sparks, 1984; Sparks and Jardine, 1984).

Sparks et al. (1980a) studied the kinetics of K adsorption in two Dothan soils from Virginia. A low rate of K exchange in these soils was ascribed to interparticle transport and to diffusion processes which reflected the relatively large quantities of vermiculitic material present in the soils. The adsorption rate coefficients ( $k_a$ ) ranged from about 1 to  $20\text{ h}^{-1}$ , which suggested low rates of reaction as compared with values of 81 to  $216\text{ h}^{-1}$  calculated for Florida soils (Selim et al., 1976). This could be explained on the basis of the predominance of kaolinite in the Florida soils as compared with vermiculitic minerals in the Virginia soils.

Sparks and Jardine (1981) investigated the kinetics of K adsorption and desorption in a Matapeake soil from Delaware. A diffusive process was noted and found to be slower for K desorption than for K adsorption. This would be expected due to the difficulty in desorbing K from partially collapsed interlayer positions of the vermiculitic clay minerals. Once K is adsorbed into this peripheral space, the Coulombic attraction between  $K^+$  and the silicate layers would be greater than the hydration forces between the individual  $K^+$  (Kittrick, 1966; Sawhney, 1966). Thus, a partial layer collapse would occur. The observation of slower desorption than adsorption suggests that K kinetics are nonsingular and that hysteresis could be occurring (Ardakani and McLaren, 1977; Rao and Davidson, 1978; Sparks et al., 1980b). Lower rates for K desorption have also been noted by others (Talibudeen and Dey, 1968; Feigenbaum and Levy, 1977).

Jardine and Sparks (1984) found that the kinetics of K adsorption and desorption in an Evesboro soil were explained by two simultaneous first-order reactions at temperatures of 283 and 298 K which were ascribed to sites of varying K activity. Reaction 1 was ascribed to external surface sites of the organic and inorganic phases of the soil which are readily accessible for

cation exchange, while reaction 2 was attributable to interlayer sites of the 2:1 clay minerals which predominated in the  $< 2 \mu\text{m}$  clay fraction.

#### KINETICS OF NONEXCHANGEABLE AND MINERAL K RELEASE

The release of nonexchangeable K is thought not to be the result of dissolution of primary K bearing minerals but is actually an exchange reaction. This exchange is too slow to be measured with normal methods of determining exchangeable K. When this slow exchange occurs in the interlayers of clay minerals such as mica, the replacing ion must first enter the unexpanded interlayer without its hydration shell. Then or simultaneously the interlayer will expand upon hydration of these ions allowing fixed or trapped  $\text{K}^+$  to hydrate and slowly diffuse to exchange sites on outer parts of the clay particle (Barshad, 1954; Rausell-Colom et al., 1965). Evidence also exists for very slow solid state diffusion of unhydrated nonexchangeable  $\text{K}^+$  out of these interlayers and inward diffusion of exchanging cations. This diffusion occurs in 1.0 nm areas of interlayers that are near expanded 1.4 nm areas (Rausell-Colom et al., 1965).

The more easily released forms of nonexchangeable K versus the more slowly released forms as described by Haylock (1956), MacLean (1961), Moss and Coulter (1964), Beckett (1970), and Addiscott and Johnston (1975) are thought to be released by two different mechanisms. Unfortunately, the exact nature of these two mechanisms is not well understood. Some information about the release of K from interlayers has been gained by observing cation replacement weathering fronts in large flakes of mica (Rausell-Colom et al., 1965; Scott, 1968; Wells and Norrish, 1968).

Much work has been performed on the release of interlayer K from trioctahedral micas (Walker, 1950; Mortland et al., 1956; Arnold, 1958; Mortland, 1958; Bassett, 1960; Reed and Scott, 1962; Scott and Reed, 1962; Quirk and Chute, 1968; Wells and Norrish, 1968; Malquori et al., 1975; Feigenbaum et al., 1981). It is convenient to work with trioctahedral micas since their interlayer K is more easily removed than the interlayer K in dioctahedral micas (Reed and Scott, 1962). The trioctahedral micas are also much more subject to acid dissolution than their dioctahedral counterparts (Wells and Norrish, 1968). The more unstable trioctahedral mica-ferruginous biotite can be completely broken down by H-saturated resin in about 10 days releasing all of its K (Arnold, 1958). This explains the much higher rate coefficient for K release from these micas than has been observed for dioctahedral micas. Because of their instability, trioctahedral micas generally occur only in soils where little weathering has taken place and thus such soils contain large quantities of nonexchangeable K (Milford and Jackson, 1960).

There is a paucity of classical kinetic analysis of nonexchangeable and mineral K release in the literature (Mortland, 1958; Mortland and Ellis, 1959; Huang et al., 1968; Feigenbaum et al., 1981; Martin and Sparks, 1983). Feigenbaum et al. (1981) investigated the rate of release of K and structural

cations from biotite, phlogopite, and muscovite in two particle size ranges in dilute electrolyte solutions (0.001 M) and at pH 3.0 and 7.0. The rate of K release from phlogopite and biotite was similar to the rate of release of other structural cations under acidic conditions and significantly higher under neutral conditions. The authors felt these findings indicated that structural decomposition of phlogopite and biotite was dominant in acidic conditions, and the rate of interdiffusion increased in neutral conditions. The rate of K release from muscovite was about 5 and 15% slower than from biotite and phlogopite, respectively. The rate of K release from muscovite was higher than the rate of Al release. Feigenbaum et al. (1981) concluded that muscovite was the most stable of the three micas and that the decomposition mechanism for K release in muscovite was less important.

Few studies have been conducted on nonexchangeable K release from whole soils. Ion exchange resins are the most practical techniques for this purpose since time and K concentration in solution can be carefully controlled. Martin and Sparks (1983) investigated the kinetics of nonexchangeable K release from two Coastal Plain soils from Delaware using a H-resin. The level of solution K markedly affects the release of nonexchangeable K from clays. The K concentration in the solution phase must be kept very low, or K release will be inhibited (Reed and Scott, 1962; Rausell-Colom et al., 1965; Fanning and Keramidas, 1977; Feigenbaum et al., 1981). The concentration of soluble K in the soil resin suspension used by Martin and Sparks (1983) ranged from 1.00 to  $1.50 \cdot 10^{-3} \text{ mmol l}^{-1}$ . Rausell-Colom et al. (1965), using a leaching technique, found that concentrations of solution K up to  $1.0 \text{ mmol l}^{-1}$  did not retard K release from trioctahedral mica whereas concentrations above  $0.10 \text{ mmol l}^{-1}$  inhibited K release from dioctahedral mica.

The total amount of nonexchangeable K released from the 0.45–0.60 m depth of two soils was investigated by Martin and Sparks (1983) using a homoionic H-resin. Equilibrium in K release was attained in about 40 days for the two soils. Nonexchangeable K release rate coefficients ( $k_2$ ) were calculated for all depths of the two soils. They ranged from 1.2 to  $2.2 \cdot 10^{-3} \text{ h}^{-1}$  in the Kalmia soil and from 1.5 to  $2.9 \cdot 10^{-3} \text{ h}^{-1}$  in the Kennansville soil. The magnitude of the  $k_2$  values suggested low rates of nonexchangeable K release from the two soils. The magnitude of the  $k_2$  values differed little between depths in the two soils as would be expected from the similar clay mineral suites and clay contents in the two soils.

#### METHODS TO INVESTIGATE KINETICS OF K REACTIONS IN HETEROGENEOUS SYSTEMS

Most K kinetic studies with soils and clay minerals have employed batch techniques (Sparks, 1985) which usually require centrifugation to obtain a clear supernatant solution for subsequent analysis. The uncertainty in the time required for separation of solid from liquid phases using centrifugation is most critical at short time intervals (Sparks and Recheigl, 1982) and the

reactions may be faster than the separation time. Also, in order to measure the kinetics of a chemical reaction properly, the technique must not change the reactant concentration. Thus, the sample and the suspension must have a similar solid to solution ratio at all times. Unfortunately, this has not been true in most batch studies. Most studies have employed large solution:soil ratios where the concentration in the solution and the amount of adsorption both vary simultaneously. An exception is the work of Van Riemsdijk (1970) and Van Riemsdijk and De Haan (1981) in which the solution concentration was held constant. Barrow (1983) has noted that the relation between adsorption and time should only be treated as a simple, two-dimensional relation if adsorption is constant. Unless the technique of Van Riemsdijk and De Haan (1981) is used, these conditions do not apply to experiments in which a wide solution:soil ratio is used.

Another problem with the batch technique is the process of mixing solution and soil. If mixing is inadequate, the rate of reaction will be limited. Yet vigorous mixing can cause abrasion of the soil particles leading to high rates of reaction. The breakdown of particles with the batch technique could be a serious problem if one is studying K reactions since release of K could occur from K bearing minerals. For these reasons, we believe researchers should avoid batch techniques when studying kinetics of K reactions in heterogeneous systems.

Flow or miscible displacement techniques have been used to a lesser extent to investigate the kinetics of K reactions in clay minerals and soils (Mortland, 1958; Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980b; Sparks and Jardine, 1981; Sparks and Rechcigl, 1982; Jardine and Sparks, 1984; Sparks and Jardine, 1984). These techniques have several advantages over the batch technique including: (1) possibly simulating ionic reactions in the field; (2) measuring short reaction times; and (3) avoiding separation of liquid from solid by centrifugation (Sparks and Rechcigl, 1982). A number of leaching materials have been used with these techniques. Mortland (1958) investigated the kinetics of K release from biotite using 0.1 M NaCl. Garman (1957) studied the rate of release of K from soils using 0.01 M HCl while Sparks et al. (1980b) used 0.01 M CaCl<sub>2</sub> to investigate the release of K from soils.

## CONCLUSIONS

Voluminous amounts of research have been conducted on the chemistry and mineralogy of K in heterogeneous systems. However, our understanding of the kinetics of the reactions in these systems is limited. A comprehension of the dynamics of K release from all four phases of K is of vital importance for making efficient and profitable K fertilizer recommendations.

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