

# Kinetics of Potassium Desorption in Soil using Miscible Displacement<sup>1</sup>

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## ABSTRACT

Kinetics of K desorption were conducted on samples from the Ap, A2, B2lt, and B22t horizons of two Dothan (Plinthic Paleudults) soils. Aluminum- and calcium- saturated samples were equilibrated with K for 96 hours and then continuously leached with 0.01M CaCl<sub>2</sub> until K was not detected in the leachate. The rate of K desorption from all samples increased rapidly initially and levelled off with time. Desorption was nearly complete in approximately 3 to 4 hours for the Ap, A2, and B2lt horizons, and in 8 to 9 hours for the B22t horizons. Approximately 95–98% of the adsorbed K was subsequently desorbed suggesting K adsorption-desorption in the Dothan soils was reversible. A linear relationship between time<sup>1/2</sup> and percent K desorption indicated that diffusion was the predominant mechanism of K desorption in these soils. Diffusion-controlled exchange would be expected due to the vermiculitic clay minerals present in the soils.

Potassium desorption conformed to first-order kinetics. Apparent desorption rate coefficients ( $k'_d$ ) ranged from 0.3 to 1.3 hour<sup>-1</sup>. The magnitude of the  $k'_d$  values decreased as clay content increased in the soils. This was ascribed to increased intraparticle transport and to increased diffusion in the more clayey samples. The  $k'_d$  values were generally higher in the Al than in the Ca- saturated samples. The effect of flow velocity on rate of K desorption was investigated using velocities of 0.5, 1.0, and 1.5 ml min<sup>-1</sup>. The rate of K desorption increased only slightly with flow velocity.

**Additional Index Words:** first-order reaction, K exchange.

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**E**XCHANGABLE REACTIONS existing between solution and exchangeable phases of soil K profoundly influence K chemistry. The rate and direction of these reactions determine whether applied K will be leached into lower soil horizons, absorbed by plants, converted into unavailable forms or released into available forms. Little has appeared in the literature concerning the kinetics of K desorption in soil systems. A knowledge of the reaction rates between solution and exchangeable phases of soil K is necessary in order to predict the fate of added K fertilizer in soils and to properly make K fertilizer recommendations.

Feigenbaum and Levy (1977) studied K release in 0.01M CaCl<sub>2</sub> and deionized H<sub>2</sub>O extracts from two soils with relatively high K contents. The amount of release was greater from the soil having a high portion of total K in the silt fraction. Talibudeen et al. (1978) observed that the rate of release of soil K was linearly proportional to time<sup>1/2</sup>. They assumed uniform distribution of K in spherical particles and developed planar

diffusion models for K release from the surface and from peripheral layers in these calculations. Surface K ceased to contribute to K release after 24 hours and peripheral K after 840 hours (Talibudeen and Dey, 1968). Arnold (1959) used saturated resins containing either Ca or Na concentrations in excess of exchangeable soil K to investigate desorption of K. Equilibrium of K exchange between the soil and the resin was attained in about 96 hours. Selim et al. (1976) proposed that a kinetic type reaction existed between soil solution and exchangeable K with a first-order desorption rate coefficient ( $k_d$ ).

In a previous study, Sparks et al. (1980) studied the kinetics of K adsorption from solution to exchangeable phases for two Dothan soils. Equilibrium of K exchange was reached in 2 hours with the 5 and 25 µg/ml K solution and in about 24 hours with the 100 µg/ml K solution. This slow rate of K exchange was attributed to diffusion-controlled exchange in these soils with vermiculitic mineralogy. The adsorption rate coefficients ranged from about 0.7 to 22.0 hour<sup>-1</sup> and generally decreased at higher initial concentration of solution K.

This investigation was conducted to determine the rate of K desorption between exchangeable and solution phases in samples previously examined for K adsorption characteristics (Sparks et al., 1980). The magnitude and rate of K desorption were determined using a miscible displacement technique. Apparent K desorption rate coefficients ( $k'_d$ ) and the reaction order were determined. In addition, the effect of flow velocity on the rate of K desorption was investigated.

## MATERIALS AND METHODS

### Soils Studied

Studies were performed on two Dothan soils (fine-loamy siliceous, thermic Plinthic Paleudults) located in Greenville and Nottoway Counties, Virginia. The Greenville County soil had been cultivated for over a century, whereas the Nottoway County soil was forested for 3 decades prior to this study. Bulk samples were selected from the Ap, A2, B2lt, and B22t horizons at these two locations. The samples were air-dried and crushed to pass a 2-mm sieve in preparation for laboratory analyses.

### Soil Characterization Analyses

Particle size analysis, soil pH, organic matter content, CEC, exchangeable bases, and clay mineralogy of the four horizons of the two soils are reported elsewhere (Sparks et al., 1980).

### Sample Preparation

Prior to initiation of the kinetic desorption studies, subsamples of the Ap, A2, B2lt, and B22t horizons from each of the two Dothan soils were both Al- and Ca- saturated using either 1N AlCl<sub>3</sub> or 1N CaCl<sub>2</sub>. The soil was subsequently washed with deionized water followed by a 1:1 acetone-H<sub>2</sub>O mixture until a negative test for Cl<sup>-</sup> was obtained with AgNO<sub>3</sub>. The soils were saturated with Al or Ca as in most mineral soils these are the two predominate cations. Also, by first saturating with these cations, most native exchangeable K was removed from the soils. The samples were then air-dried and crushed to pass a 2-mm sieve for laboratory analyses and for K desorption studies. Sample pH and CEC after saturation were reported previously (Sparks et al., 1980).

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### Kinetics of Desorption Studies

Desorption studies were carried out using triplicate 1-gram Al- and Ca- saturated samples which were placed in 80-ml polypropylene centrifuge tubes with 50 ml of a 50  $\mu\text{g/ml}$  K solution. The suspension was shaken for 96 hours at 25°C on a reciprocating shaker. At the end of the equilibration period, the 50-ml suspension was injected with a syringe into a 47-mm Nucleopore Filter. The filter was attached to a Fractometre Alpha 200 fraction collector and the sample was leached with 0.01M  $\text{CaCl}_2$ . The  $\text{CaCl}_2$  was passed through the soil at flow velocities of 0.5, 1.0, and 1.5  $\text{ml min}^{-1}$ . Ten-milliliter aliquots were collected until K was not detected in the leachate. Potassium in the leachate was determined by atomic absorption spectrophotometry.

Cumulative desorption values ( $\mu\text{g K/g soil}$ ) for each soil treatment were plotted against reaction time (minutes) on a semilogarithmic scale. Desorption varied with flow rate and since by definition the desorption rate coefficient ( $k_d$ ) is constant a new term, apparent desorption rate coefficient ( $k'_d$ ), was defined for each flow rate in the system. The  $k'_d$  and the reaction order were determined using the following equation (Sivasubramanian and Talibudeen, 1972)

$$\ln \left( \frac{K_t}{K_0} \right) = -k'_d t \quad [1]$$

which can also be written as

$$K_t = K_0 \exp (-k'_d t) \quad [2]$$

where

$K_t$  = quantity of K on soil exchange sites at time  $t$  of desorption,

$K_0$  = quantity of K on exchange sites at zero time of desorption,

$t$  = time in hours, and

$k'_d$  = apparent desorption rate coefficient in  $\text{hours}^{-1}$ .

This equation is valid if K adsorption is assumed to be negligible. The  $\log (K_t/K_0)$  vs.  $t'$  relationship is linear if the rate of release of K follows first-order kinetics. The  $k'_d$  value for zero flow velocity was obtained by a graphical extrapolation of the  $k'_d$  for 0.5, 1.0, and 1.5  $\text{ml min}^{-1}$  flow velocity to 0.0  $\text{ml min}^{-1}$  velocity.

### RESULTS AND DISCUSSION

Potassium desorption in the Dothan soils conformed to first-order kinetics (Fig. 1). The first-order rate equation described K desorption for an average of 165 and 173 min for the Al- and Ca- saturated samples, respectively, in the Ap, A2, and B21t horizons, and for an average of 439 and 505 min for the Al- and Ca- saturated samples, respectively, in the B22t horizon (Table 1). These represent times when K desorption was virtually complete in the respective soil horizons. The first-order rate equation described K desorption well with  $r$  values ranging from  $-0.993$  to  $-0.998$  (Fig. 1). The finding that the kinetics of K desorption is first-order supports the proposal by Selim et al. (1976).

The  $k'_d$  values at a flow velocity of 1.0  $\text{ml min}^{-1}$  decreased from the Ap to the B22t horizons in the Greenville and Nottoway soils as clay content increased (Table 1). Desorption would be expected to be slower where higher contents of clay are present due to increased intraparticle transport and to diffusion. There tended to be a higher  $k'_d$  in the Al- than in the Ca- saturated systems (Table 1). The range in the  $k'_d$  values in the four horizons was small which was also observed for the adsorption rate coefficients (Sparks et al., 1980). The small range in the  $k'_d$  values suggests that similar desorption reactions were occurring throughout the soil profile at this flow velocity (Evans and Jurinak, 1976).

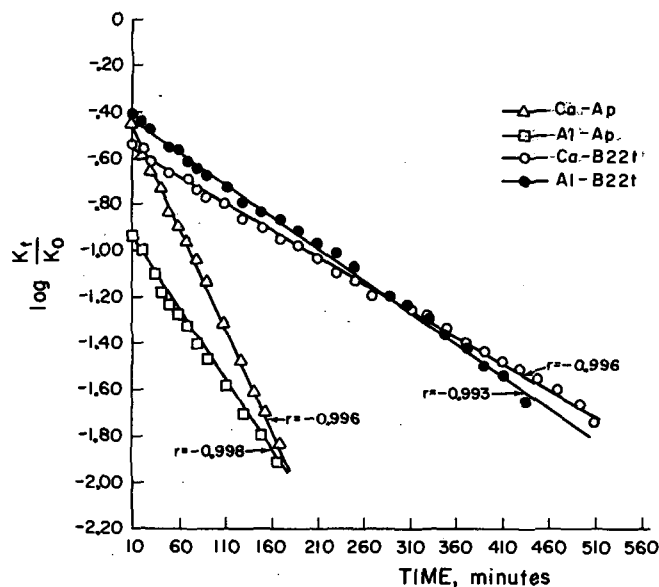


Fig. 1— $\log(K_t/K_0)$  vs. time of leaching with 0.01M  $\text{CaCl}_2$  from Ap and B22t horizons of Nottoway County soil where  $K_t$  represents the quantity of K on soil exchange sites at time  $t$  of desorption.

Kinetics of K desorption in the two Dothan soils was 2 to 8 hours slower (Fig. 2-3) than the kinetics of K adsorption (Sparks et al., 1980). This would be expected due to the difficulty in desorbing K from partially collapsed interlayer positions (Sawhney, 1966). Once K is adsorbed into the interlayer positions the coulombic attraction between K ions and the clay layers would be greater than the hydration forces of the ion, resulting in partial layer collapse (Sawhney, 1966). The observation of slower desorption than adsorption conforms with findings of others (Kuo and Lotse, 1973) and suggests that the K kinetic reactions in the Dothan soils were nonsingular or that hysteresis could be occurring (Ardakani and McLaren, 1977; Rao and Davidson, 1978).

Potassium desorption as plotted by the Elovich equation (Chien and Clayton, 1980) in the original Al- and Ca- saturated systems was rapid at first and levelled off with time in the Ap horizon (Fig. 2) and in the B22t horizon (Fig. 3) of the Nottoway soil suggesting ease in desorption initially followed by more difficult desorption reactions. This trend was also observed for the kinetics of K adsorption in these soils (Sparks et al., 1980). The % K desorbed at 10 min in the Al- and Ca- saturated Ap horizon was approxi-

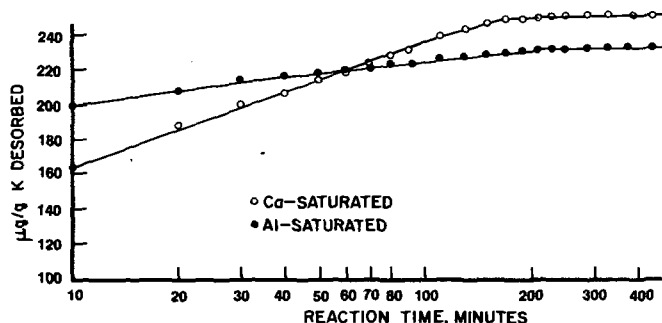


Fig. 2—Potassium desorption at 25°C using 0.01M  $\text{CaCl}_2$  from Nottoway County Ap soil horizon (Al- and Ca- saturated) as a function of time plotted on a semi-logarithmic scale and at a flow velocity of 1.0  $\text{ml min}^{-1}$ .

**Table 1**—Apparent desorption rate coefficients ( $k'_d$ ) calculated at 1.0 ml min<sup>-1</sup> flow velocity, values of  $K_e$ , and the amount of time the first-order rate equation described K desorption for Dothan Soil from Greenville and Nottoway Counties.

Horizon	Saturation treatment	$K_e$ †		Time of first-order conformity‡		$k'_d$	
		Greenville	Nottoway	Greenville	Nottoway	Greenville	Nottoway
		$\mu\text{g/g soil}$		min		hour <sup>-1</sup>	
Ap	Al	220	225	152	160	0.90	0.87
	Ca	251	259	163	170	1.30	1.23
A2	Al	238	242	161	175	0.96	0.92
	Ca	259	264	166	183	0.81	0.79
B21t	Al	249	251	162	177	0.84	0.80
	Ca	265	273	169	186	0.70	0.64
B22t	Al	310	312	438	440	0.44	0.40
	Ca	351	362	500	510	0.36	0.30

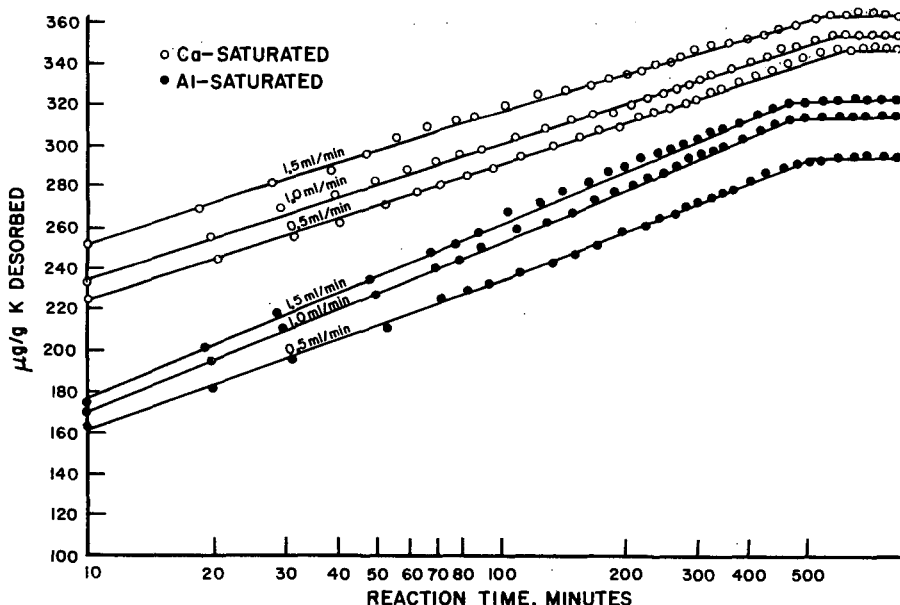
† Represents quantity of K on exchange sites at zero time of K desorption.

‡ Represents time for which the first-order rate equation described K desorption.

mately 84.4 and 62.4%, respectively. In the Al- and Ca- saturated systems of the B22t horizon, 56.0 and 64.0% of the K was desorbed in 10 min, respectively. The rate of K desorption for a given cation saturation was exponentially related to the percent K saturation until almost all K was desorbed, at which point it decreased (Fig. 2 and 3). The reaction was nearly completed in about 3 and 4 hours in the Al- and Ca-saturated systems, respectively, of the Ap horizon (Fig. 2). Desorption was essentially completed by this time as little K was detected in the leachate solutions. Approximately 95–98% of the adsorbed K in these soils was subsequently desorbed. This would suggest that K adsorption-desorption using miscible displacement is a reversible process. However, approximately 2–5% of the adsorbed K could not be desorbed by Ca which could result from adsorption of K on specific sites. The Al-saturated Ap horizon initially desorbed more K than the Ca-saturated soil, but by the end of the desorption reaction the total amount of K desorbed was greater for the Ca-saturated soil. The latter observation parallels the adsorption data obtained earlier (Sparks et al., 1980). This would be expected since the Ca-saturated system initially adsorbed more K (Table 1).

The effect of different flow velocities in the B22t horizon of the Nottoway soil is shown in Fig. 3. At any given time, the amount of K desorbed increase as flow velocity increased. These data agree with findings of Sivasubramaniam and Talibudeen (1972) and are a result of more displacing Ca passing through the column at the faster flow velocity. The apparent equilibrium between K-Ca exchange favored Ca adsorption and K desorption at higher flow velocities. The slower flow velocity would provide a greater contact time between solution desorbed K and the soil. In the Dothan soils, the rate of K desorption increased slightly with flow velocity since the rate is concentration dependent (Fig. 3). However, the  $k'_d$  values increased little with flow velocity (Table 2).

A low rate of K desorption has been noted by others (Talibudeen and Dey, 1968; Feigenbaum and Levy, 1977). The slow K desorption probably indicates diffusion-controlled exchange due to the vermiculitic clays present in the Dothan soils (Barshad, 1954; Reed and Scott, 1962; Chute and Quirk, 1967; Sawhney, 1966; Sparks et al., 1980). Different types of exchange sites in vermiculite have different desorption rates. While the external planar surface sites and the edge sites desorb K readily, the desorption of K from inter-

**Fig. 3**—Potassium desorption at 25°C using 0.01M CaCl<sub>2</sub> from Nottoway County B22t soil horizon (Al- and Ca- saturated) as a function of time plotted on a semi-logarithmic scale and at flow velocities of 0.5, 1.0, and 1.5 ml min<sup>-1</sup>.

**Table 2—Effect of flow velocity on the magnitude of the  $k'_d$  of the Ap and B22t soil horizons from Nottoway County.**

Horizon	Flow velocity, ml min <sup>-1</sup>	$k'_d$ (hour <sup>-1</sup> )	
		Al-saturated	Ca-saturated
Ap	0.0	0.83†	1.11†
	0.5	0.85	1.18
	1.0	0.87	1.23
	1.5	0.91	1.32
B22t	0.0	0.33†	0.26†
	0.5	0.37	0.28
	1.0	0.41	0.30
	1.5	0.48	0.34

† These  $k'_d$  values were obtained by plotting a regression line of the triplicate  $k'_d$  values vs. flow velocity. The  $r$  values were 0.970 and 0.973 for the Ap and B22t horizons, respectively, which were significant at the 1% level of probability.

layer sites involves a low rate of diffusion (Sawhney, 1966). That diffusion was the predominant mechanism of K desorption in the Dothan soils is illustrated in Fig. 4-5 by the linear relationship between time<sup>1/2</sup> vs. % K desorption in both the Ap and B22t horizons of the Nottoway soil. Barshad (1954) ascribed a linear relationship between time<sup>1/2</sup> vs. % K desorption to diffusion-controlled exchange. There was some deviation in linearity of the diffusion plots during the initial period of K desorption for both horizons (Fig. 4-5). Chute and Quirk (1967) note that diffusion-controlled exchange may not be strictly obeyed during the initial period of K desorption. This could be due to mass action exchange at sites on external surfaces (Chute and Quirk, 1967).

Although not shown, similar K desorption kinetics were observed in the A2 and B21t horizons of the Nottoway soil and in the Ap, A2, and B21t horizons of the Greenville soil. This would be expected due to the similar clay mineral suites and clay contents in these horizons (Sparks et al., 1980).

Both soils desorbed considerably more K in the B22t horizon (331  $\mu\text{g K/g soil}$  which represents the mean of the Al- and Ca-saturated B22t horizons at three flow velocities) than in the other three horizons (mean of 245  $\mu\text{g K/g soil}$ ). The larger quantity of desorbed K in this horizon (Fig. 3) is attributed to the higher clay content present. The higher quantity of clay would offer more exchange sites to adsorb K, and, subsequently, to desorb K. Loss of K was complete in about 8 and 9 hours for the Al- and Ca-saturated systems, respectively.

### ACKNOWLEDGMENT

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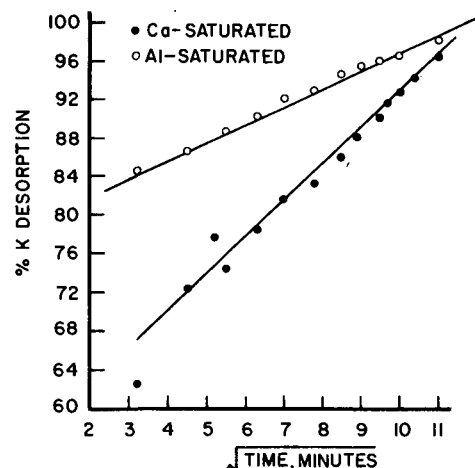


Fig. 4—Percent K desorption vs. time<sup>1/2</sup> for Nottoway County Ap soil horizon (Al- and Ca-saturated).

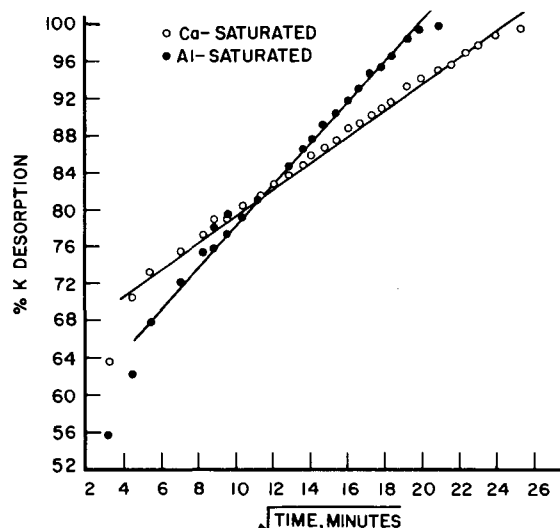


Fig. 5—Percent K desorption vs. time<sup>1/2</sup> for Nottoway County B22t soil horizon (Al- and Ca-saturated).

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