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Kinetics of release of non-exchangeable potassium by cation-saturated resins from Red (Alfisols), Black (Vertisols) and Alluvial (Inceptisols) soils of India

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ABSTRACT

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Release of K from seven benchmark soils of India representing Red (Alfisols), Black (Vertisols) and Alluvial (Inceptisols) soil groups was investigated using cation exchange resins saturated with H^+, Ca^{2+}, Na^+ and NH_4^+. Over cumulative reaction periods ranging from 0.25 to 2467 h, efficiency of different cation-saturated resins to replace non-exchangeable K from soils was in the order: $H^+ > Ca^{2+} > Na^+ > NH_4^+$. Alluvial and Red soils released, respectively, the highest and the lowest amounts of K to H^+-resin. All other resins were more effective in desorbing K from smectitic Black soils than from Alluvial soils, having restrictive interlayer space, or Red soils, containing most of K in the feldspars. From the plots of cumulative K release versus square root of time, values of surface K and internal K were calculated. Proton- and Ca^{2+}-saturated resins desorbed more internal K from Black soils, whereas Na^+ and NH_4^+-resins were more efficient in desorbing internal K from illitic Alluvial soils. Potassium release data could be described by first-order and parabolic rate equations. Correlation coefficient and standard error of estimates obtained from least square regression analysis showed that the parabolic diffusion equation could explain better the kinetics of K release, indicating that exchange of K was diffusion-controlled. Potassium release data also conformed to the radial diffusion equation. Diffusion coefficients were calculated for three parts of the reaction, corresponding to (1) 0.25–37, (2) 37–331 and (3) 331–2467 h, representing K release at a fast, intermediate and slow rate, respectively. Diffusion coefficients with different resins were in the same sequence as observed for cumulative amounts of K released.

INTRODUCTION

When levels of soil solution and exchangeable K are decreased by plant uptake or leaching, non-exchangeable K is released to the exchangeable form. In a study conducted by Schmitz and Pratt (1953), 88% of the variation in maize yield was ascribed to the quantity of non-exchangeable and exchange-

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able K. Very few attempts have, however, been made to study the kinetics of non-exchangeable K release from soils (Martin and Sparks, 1983).

Cation exchange resin saturated with protons has been extensively used to study the kinetics of K release in soils (Pratt, 1951; Schmitz and Pratt, 1953; Martin and Sparks, 1983). Although the amount of K extracted with H^+-resin is comparable with that dissolved by acid treatment, there is less danger of disintegration of mineral lattice by using resin than with mineral acid solution (Arvieu and Chaussidon, 1964). Single equilibrium extractions with Ca^{2+}- or Na^+-saturated resins were, however, found to be unsatisfactory for determining non-exchangeable K or soil K reserves accessible to plant roots (Arnold, 1958; Haagsma and Miller, 1963). Talibudeen and Rajendran (1969) proposed a new technique, called the batch equilibration technique, and it has been successfully used by a number of workers (Sharma, 1981; Martin and Sparks, 1983; Bhangu, 1986) to study the nature of non-exchangeable K.

The rate of release of non-exchangeable K from micas (Reed and Scott, 1962; Feigenbaum et al., 1981) and from vermiculite (Mortland and Ellis, 1959) is diffusion-controlled. Mortland (1958) found that the release rate of K from biotite was of the first order using a batch technique, and zero order with a miscible displacement method. Talibudeen et al. (1978) observed that the rate of release of soil K was linearly proportional to the square root of time. It was assumed that K in spherical particles was uniformly distributed and a planar diffusion model was developed for K release from the surface and from the peripheral layers.

In the present investigation kinetics of release of non-exchangeable K from seven surface samples representative of Red, Black and Alluvial soils of India have been investigated by using the batch equilibration technique with resins saturated with H^+, Ca^{2+}, Na^+ and NH_4^+ ions. All seven soil samples were sequentially extracted twenty times (for different time intervals) with each of the four cation-saturated resins. First-order and parabolic kinetic equations have been employed to describe the release of non-exchangeable K from the three soils groups which represent more than 75% of the total land area of India. Since Dhillon et al. (1989) have already reported the kinetics of K release from these soils during sequential extraction with 0.01 *M* chloride solution of Ba^{2+}, Ca^{2+}, NH_4^+ and Na^+, the objective of this paper is to compare the K release pattern observed with resins and electrolytes.

EXPERIMENTAL

Soils

Surface samples of seven benchmark series representing the Red (Alfisols), Black (Vertisols) and Alluvial (Inceptisols) soils of India were collected.

TABLE I

Physical and chemical characteristics of soils

Series	Sub-group	pH[*1]	Electrical conductivity[*1] (dS m^{-1})	Calcium carbonate (%)	Cation exchange capacity (cmol kg^{-1})	Particle size distribution (%)		Textural class	1 *M* ammonium acetate extractable[*2] K (cmol kg^{-1})	1 *M* HNO_3 extractable[*3] K (cmol kg^{-1})
						silt	clay			
Red soils										
Tyamagondalu	Oxic Paleustalf	5.9	0.14	–	3.9	6.8	5.2	Sand	0.15	0.77
Patancheru	Udic Rhodustalf	6.3	0.24	–	10.9	14.9	13.2	Sandy loam	0.29	1.03
Black soils										
Teligi	Typic Pellustert	8.4	0.44	4.4	47.0	30.9	46.7	Clay	0.74	1.79
Kasireddipalli	Typic Pellustert	8.0	0.44	1.1	47.0	40.1	39.7	Silty clay loam	0.82	2.18
Alluvial soils										
Nabha	Typic Ustochrept	7.3	0.25	0.6	12.7	44.3	16.8	Loam	0.28	4.87
Kanjli	Typic Ustochrept	8.2	0.28	0.2	10.1	41.4	16.8	Loam	0.29	4.87
Tulewal	Udic Ustochrept	8.2	0.17	0.2	6.3	10.1	6.0	Loamy sand	0.13	2.31

[*1] 1:2 soil:water.
[*2] Hanway and Heidel (1952).
[*3] Pratt (1965).

These were air-dried and passed through a 2-mm sieve. Descriptions of the soils along with some physico-chemical characteristics are given in Table I. Kaolinite, smectite and illite were the dominant clay minerals present in the Red, Black and Alluvial soils, respectively.

Preparation of cation saturated resins

A cation exchange resin (Dowex 50 WX 8 size > 500 μm) with exchange capacity 5 meq. g^{-1} (on dry weight basis) was used in this study. The resin was immersed in 1 *M* HCl (resin:solution ratio 1:5) for 48 h and washed successfully with 0.1 *M* HCl and deionized water until it was chloride-free. Proton saturated resin was kept immersed in deionized water before use. To prepare Ca^{2+}-, Na^+- or NH_4^+-saturated resins, the H^+ saturated resin was successively washed with 1 *M* and 0.1 *M* solutions of chloride of the respective cations. Finally, the resin saturated with Ca^{2+}, Na^+ or NH_4^+ was washed with deionized water to remove the Cl^- ions. Cation-saturated resins were kept immersed in deionized water. The wet resin was spread on a filter paper sheet placed in a sieve. After the excess water was drained, 2 g of resin was placed in a centrifuge tube.

Extraction of K with cation-saturated resins

Release of soil K by H^+-, Ca^{2+}-, Na^+- and NH_4^+-saturated resins was studied by following the batch equilibration technique described by Talibudeen et al. (1978). One gram of sieved (<250 μm) air-dry soil was placed in a plastic centrifuge tube and wetted overnight with 0.5 ml of deionized water. Resin saturated with H^+, Ca^{2+}, Na^+ or NH_4^+ (2 g) along with 10 ml of deionized water was also added to the centrifuge tube. The soil–resin–water mixture was gently and continuously agitated for intervals ranging from 0.25 to 720 h (0.25, 0.5, 1.0, 1.5, 2.75, 6, 10, 15, 24, 30, 48, 72, 120, 144, 192, 240, 360, 480 and 720 h). Each soil sample was thus run for a total period ranging from 0.25 to 2467 h. The reaction took place at 25°C.

At the end of each reaction period, a fine spray of 25 ml deionized water was used to rapidly (<5 min) separate the resin from the soil on a 500 μm sieve. The resulting soil suspension was centrifuged at 15000 rpm for 10 min. The supernatant solution was separated and its K concentration was estimated by flame photometry. Another 2-g portion of the fresh cation-saturated resin was then added to the centrifuged soil and the mixture resuspended in deionized water as described above to initiate the next reaction period. The separated resin was leached at the rate of 8–10 ml h^{-1} with 80 ml of 1 *M* NH_4Cl. A control portion of each cation-saturated resin was weighed out (in duplicate) at the start of each reaction period and leached in the same way to determine the K content. These were used to correct the estimated K content of the resin.

RESULTS AND DISCUSSION

Relative efficiency of cation-saturated resins

Cumulative K released by different cation-saturated resins was in the order: H^+-resin > Ca^{2+}-resin > Na^+-resin > NH_4^+-resin (Table II). Proton-saturated resin released significantly higher amounts of K from the Alluvial and Black soils than from the Red soils. Calcium-saturated resin was more effective in releasing K from the Black and Red soils as compared with the Alluvial soils. Sodium-resin released relatively less amounts of K from the Red soils than from the Black and Alluvial soils, whereas the amounts of K released by NH_4^+-saturated resin from different soils was in the sequence: Black > Alluvial > Red.

Resin saturated with H^+ ions released more cumulative K than even boiling 1 *N* HNO_3-extractable K (Table I). Possibly it was due to the hydrogen bond transfer through water. The final step of substitution may be the exchange of H_3^+O for K^+. Additionally, H^+ ions also dissolve K minerals and it seems to be a dominant mechanism for release of K from soils by H^+-resin (Feigenbaum and Shainberg, 1975). In the presence of H^+-resin, the pH of the system decreases. It leads to dissolution of octahedral sheets, thereby releasing K, and leaves behind silica relics (Fanning and Keramidas, 1977).

TABLE II

Cumulative amounts of K released (cmol kg^{-1}) in different cation-saturated resins from Red, Black and Alluvial soils

Soil	H^+-resin	Ca^{2+}-resin	Na^+-resin	NH_4^+-resin	C_m
Red soils					
Tymagondalu (s)	4.70	2.99	1.88	1.83	6.75
Patancheru (sl)	5.58	2.73	2.31	1.92	8.00
Mean ± *SE*	5.14 ± 0.44	2.86 ± 0.13	2.10 ± 0.22	1.88 ± 0.05	
Black soils					
Teligi (c)	7.43	3.08	2.35	2.23	13.00
Kasireddipalli (sicl)	7.98	2.89	2.60	2.25	13.50
Mean ± *SE*	7.71 ± 0.28	2.99 ± 0.10	2.48 ± 0.13	2.24 ± 0.01	–
Alluvial soils					
Nabha (l)	9.35	2.40	2.44	1.97	11.10
Kanjli (l)	9.76	2.42	2.71	2.14	11.70
Tulewal (ls)	4.84	2.46	2.09	2.06	7.20
Mean ± *SE*	7.98 ± 1.58	2.43 ± 0.02	2.41 ± 0.18	2.06 ± 0.05	–

The proton-saturated resin released greater amounts of K from Alluvial and Black soils than from Red soils. Alluvial soils having a total K in the range of 39.7–47.7 cmol kg^{-1} and illite as a dominant clay mineral, released K with H^+-resin through exchange and/or dissolution of mineral K. In Black soils, due to the swelling nature of smectites, displacing cations easily penetrated into the interlayer space and released K. Red soils, however, had the highest amount of total K (av. 64 cmol kg^{-1}); the major portion of it was due to K feldspars which, compared with micas, are resistant to dissolution through the H^+-resin. Also, the dominant mineral in these soils was kaolinite which has a low K content. The low pH of the Red soils also did not favour the K^+–H^+/H_3^+O exchange as much as in soils with high pH.

Resins saturated with Ca^{2+}, Na^+ and NH_4^+ release K through the exchange process only. Ammonium-saturated resin released greater amounts of exchangeable K in the initial stages of reaction. But cumulative amounts of K released by NH_4^+-resin were smaller than those released by all other resins. During NH_4^+–K^+ exchange, the lattice would collapse after the NH_4^+ entered the interlayer space, releasing a relatively lesser amount of K (Scott and Smith, 1966). Cumulative K released by the NH_4^+-resin was in the sequence: Black > Alluvial > Red soils. Due to higher polarizability of NH_4^+ than K^+, NH_4^+ is preferred by the exchange surface (Sparks and Huang, 1985). Ammonium, being similar in size, can replace K which is held specifically at edges or wedge zones. These specific sites are greater in Black and Alluvial soils containing 2:1 type clay minerals, than in Red soils, having kaolinite as the dominant clay mineral.

Cumulatively, the Ca^{2+}-resin released larger amounts of K from Black and Red soils as compared with Alluvial soils (Table II). For Ca^{2+}, due to its size and hydration energy (Rich, 1964), it is difficult to exchange with K^+, but in Black soils, due to the swelling nature of smectite, no such hindrance should be observed. Thus, the highest amount of K was released from Black soils. Red soils, having low pH and kaolinite as the dominant clay mineral, had a preference for Ca^{2+} and, thus, released a significantly greater amount of K than Alluvial soils. Due to the larger size, hydration energy and valence of the Ca^{2+} ion, it was difficult for the Ca^{2+}-resin to release interlayer K from tightly held sheets of micas, present in Alluvial soils. Further, due to the common ion effect the Ca^{2+}-resin was less effective in releasing K from Alluvial soils which were calcareous in nature. Sodium resin released higher amounts of K from Black and Alluvial soils than from Red soils (Table II). It may again be ascribed to the swelling-type nature of Black soils and to their high cation exchange capacity. In Alluvial soils the major portion of K is due to micaceous minerals and this interlayer K would be more accessible to replacement by Na^+ (Scott and Smith, 1966).

A comparison of the cumulative amounts of K released in various cation-saturated resins (at 211 h) with those released in electrolytes with similar cations at 240 h (Dhillon et al., 1989) revealed that the efficiency of various resins over respective electrolytes varied from 138 to 564, 57 to 310 and 166 to 991% in case of Ca^{2+}, NH_4^+ and Na^+, respectively. Efficiency of all the resins was high in coarse-textured soils of the Tyamagondalu and Tulewal series, and it may be attributed to the high content of micas in the sand and silt fractions of these soils.

Surface and internal K

Plots of cumulative K released versus square root of time (Fig. 1) were curvilinear throughout the period of extraction, indicating that equilibrium

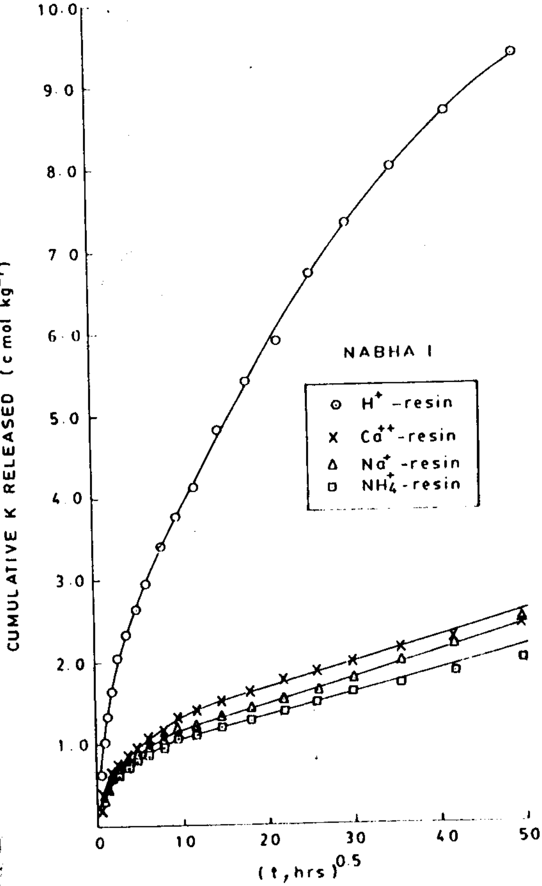

Fig. 1. Cumulative amounts of K released with time in different cation-saturated resins.

TABLE III

Surface and internal K (cmol kg^{-1}) in Red, Black and Alluvial soils

Soils	Surface K				Internal K			
	H^+-resin	Ca^{2+}-resin	Na^+-resin	NH_4^+-resin	H^+-resin	Ca^{2+}-resin	Na^+-resin	NH_4^+-resin
Red soils								
Tyamagondalu (s)	2.28	1.20	0.90	0.90	2.42	1.79	0.98	0.93
Patancheru (sl)	2.12	1.25	1.00	1.10	3.46	1.48	1.31	0.82
Mean ± *SE*	2.20 ± 0.08	1.23 ± 0.03	0.95 ± 0.05	1.00 ± 0.01	2.94 ± 0.52	1.64 ± 0.16	1.15 ± 0.17	0.88 ± 0.06
Black soils								
Teligi (c)	2.07	1.60	1.40	1.38	5.36	1.48	0.95	0.85
Kasireddipalli (sicl)	2.20	1.52	1.55	1.32	5.78	1.37	1.05	0.93
Mean ± *SE*	2.14 ± 0.07	1.56 ± 0.04	1.48 ± 0.08	1.35 ± 0.03	5.57 ± 0.21	1.43 ± 0.06	1.00 ± 0.05	0.89 ± 0.04
Alluvial soils								
Nabha (l)	2.57	1.05	0.85	0.77	6.78	1.35	1.59	1.20
Kanjli (l)	2.32	0.90	0.92	0.95	7.44	1.52	1.79	1.19
Tulewal (ls)	2.37	0.85	0.78	0.78	2.47	1.61	1.31	1.28
Mean ± *SE*	2.42 ± 0.08	0.93 ± 0.06	0.85 ± 0.04	0.83 ± 0.06	5.56 ± 1.56	1.49 ± 0.08	1.56 ± 0.14	1.22 ± 0.03

was not established even after 2467 h. In contrast, Martin and Sparks (1983) obtained an equilibrium after 960 h with H^+-resin. The soils used in this study, however, continued to release K throughout the reaction period, although at relatively slower rates. Fig. 1 shows plots of cumulative K released by different cation saturated resins versus $t^{0.5}$ for Nabha loam (an Alluvial soil). Plots for all other soils were similar in shape and consisted of two parts. The first non-linear part indicated rapid K release from the surface sites. The second linear part represented K release from interlayer sites. When the linear part of the plot was extrapolated to the ordinate, it gave the amount of surface exchangeable K (Talibudeen and Weir, 1972). The difference between cumulative K released and surface K was used to calculate the internal K (Table III).

The proton-saturated resin released significantly greater amounts of surface K from all the soils as compared with other resins. As discussed earlier, this was possibly due to release through dissolution of K minerals. With the Ca^{2+}-, NH_4^+-and Na^+-saturated resins, Black soils containing relatively larger amounts of ammonium acetate extractable K (Table I), released a greater amount of surface K compared with the Red and Alluvial soils. From smectitic Black soils, compared with Na^+ and NH_4^+ saturated resins, H^+- and Ca^{2+}-saturated resins released significantly greater amounts of internal K. The proton-saturated resin was more effective in releasing internal K from Black and Alluvial soils than from Red soils. This could be due to the dominant presence of K in feldspars in Red soils, which are resistant to acid dissolution. Sodium- and NH_4^+-saturated resins released significantly greater amounts of internal K from illitic Alluvial soils as compared with Red and Black soils. Possibly, Na^+ was able to release K from partially closed sheets of micas present more in Alluvial soils (Scott and Smith, 1966). The higher efficiency of Na^+ to release interlayer K from Alluvial soils than from other soil groups was also observed during extraction of soil K with 0.3 *M* NaTPB (Dhillon et al., unpubl. data).

First-order kinetics

Data pertaining to release of K by different resins by the batch equilibration technique were fitted to a first-order kinetic equation (Sparks and Carski, 1985) as given below:

$$\ln (C_\infty - C_t) = \ln C_\infty - K_d t \qquad (1)$$

where C_∞ is the total amount of K that could be released at equilibrium and was calculated from the intercept of the plot of C_t vs. $1/t$; C_t is amount of K released at time t and K_d is desorption rate constant. Plots of ln $(C_\infty - C_t)$ vs. t were nonlinear during the initial 22 h. However, later on, the relationship became linear giving two separate lines with different slopes: (1) from 22 to

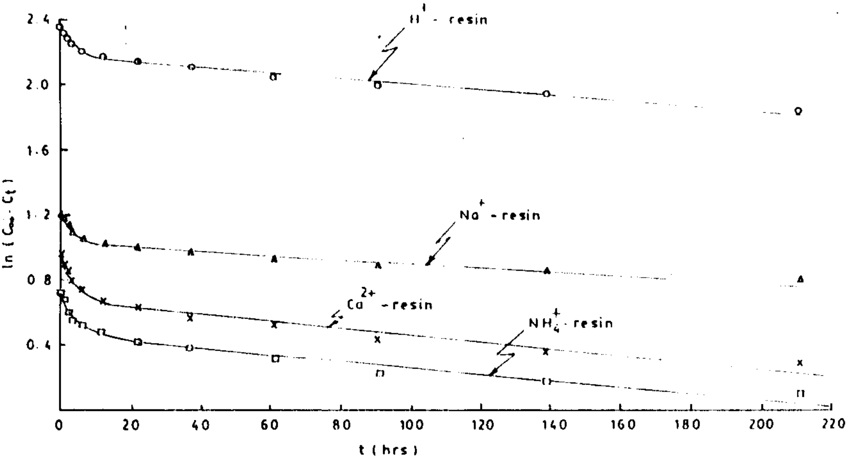

Fig. 2. First-order kinetics of K desorption from Nabha loam in different cation-saturated resins (22–211 h).

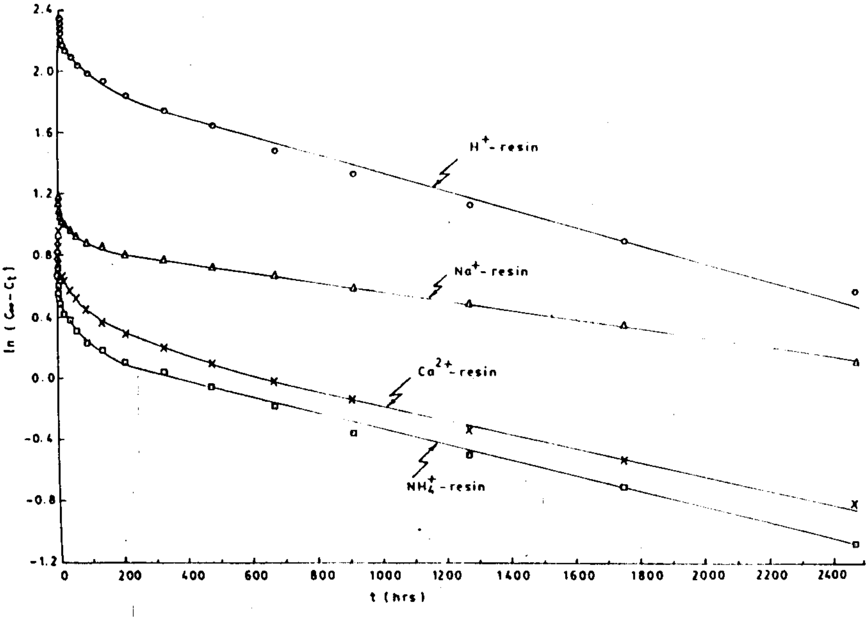

Fig. 3. First-order kinetics of K desorption from Nabha loam in different cation-saturated resins (211–2467 h).

211 h (Fig. 2), and (2) from 211 to 2467 h of reaction period (Fig. 3). The first-order plots shown in Figs. 2 and 3 are for Nabha loam. Plots for all other soils were similar in shape. The nonlinear relationship in the early stages of the reaction may be attributed to fast K release from easily accessible sites on the external planar surfaces. The first linear relationship (22–211 h) was obtained due to release of K at an intermediate rate from peripheral edge sites. Release of K from the interlayer exchange sites (Bolt et al., 1963) was responsible for the second linear relationship.

The desorption rate constants were calculated from the slopes of two linear portions according to the method of Jardine and Sparks (1984). These are listed in Table IV. The rate constants obtained in the present study are consistent with those reported by Argyriadis et al. (1978) and Martin and Sparks (1983). With H^+-, Ca^{2+}- and Na^+-resins, for the first part of the reaction Tyamagondalu sand had a higher first-order rate constant than Patancheru sandy loam (Table IV). Within the Black soils, Teligi clay had higher rate constants than Kasireddipalli silty clay loam for the H^+-, Ca^{2+}- and NH_4^+-resins. Possibly the free calcium carbonate in the Teligi clay contained occluded K which was released by these cation-saturated resins. In general, average rate constants for K release by the H^+-resin were higher for Alluvial soils followed by Red and Black soils. This may be attributed to the dominance of illite in the clay fraction of the Alluvial soils. Sparks et al. (1980) reported that desorption rate coefficients decreased as clay content increased in the soils. First-order rate constants for desorption of K from some Alluvial soils by the H^+-resin were higher in coarse-textured than in fine-textured soils (Bhangu, 1986). Sharma (1981) attributed the higher rate constants in

TABLE IV

First order rate constants ($\times 10^{-3}$) for desorption of K from Red, Black and Alluvial soils by different resins

Soils	H^+-resin		Ca^{2+}-resin		Na^+-resin		NH_4^+-resin	
	(i)[*1]	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
Red soils								
Tyamagondalu (s)	0.99	0.26	1.23	0.48	1.15	0.36	1.05	0.33
Patancheru (sl)	0.90	0.30	1.14	0.46	1.07	0.39	1.21	0.36
Black soils								
Teligi (c)	0.47	0.23	1.18	0.46	0.92	0.24	1.41	0.30
Kasireddipalli (sicl)	0.36	0.25	1.07	0.37	1.11	0.36	1.07	0.38
Alluvial soils								
Nabha (l)	0.95	0.57	1.27	0.49	0.69	0.31	1.12	0.52
Kanjli (l)	1.09	0.54	0.96	0.51	0.75	0.43	0.92	0.30
Tulewal (ls)	1.04	0.24	0.98	0.44	0.97	0.40	1.01	0.40

[*1] (i)=22–211 h; (ii)=211–2467 h.

coarse-textured Alluvial soils to the presence of the readily weatherable K-bearing biotite mineral. In the present investigation, though both the soil groups (Alluvial and Black) contained large amounts of fine fractions (silt+clay), the magnitude of the rate constants was defined by the mineralogical make-up of the soils. With Ca^{2+}- and Na^{+}-saturated resins, first-order desorption rate constants for different soils were in the sequence: Red > Black > Alluvial. Smectitic Black soils having a large number of wedge zones, released K faster to the NH_4^+-resin during the first part of the reaction (Table IV). Sparks and Carski (1985) have already reported that the kinetics of K exchange on kaolinite and smectite are usually quite rapid. For the second part (211–2467 h) of the reaction, Black soils exhibited the lowest magnitudes of desorption rate constants for all the resins, since in the initial 211 h these swelling-type soils had lost a substantial portion (68 to 74% of total cumulative K released) of K as compared with Red and Alluvial soils (54 to 66%).

Parabolic rate law

Data pertaining to K release by different cation-saturated resins was also fitted to the parabolic rate equation as given by Sparks and Carski (1985):

$$C_t/C_\infty = Rt^{0.5} + \text{constant} \qquad (2)$$

where C_∞ is the amount of K that could be released at equilibrium; C_t is amount of K released at time t and R is an overall diffusion constant. Plots of C_t/C_∞ vs. square root of time (Fig. 4) gave a nonlinear relationship upto approximately 91 h of the reaction period. For the later period (upto 2467 h) a linear relationship was obtained. The initial curvilinear relationship due to release of K from the external planer surface sites, suggested that film diffusion was the rate-controlling process (Helfferich, 1962). Jardine and Sparks (1984) attributed the nonlinear relationship for the desorption of K to the strong preference of Ca^{2+} for readily accessible exchange sites on the planar surface. The later linear part of the parabolic plot was attributed to K release from difficultly accessible sites which were intraparticle-diffusion-controlled.

The values of parabolic rate constants obtained in the present study (Table V) are in line with those reported by Martin and Sparks (1983). For all the cation-saturated resins, except Na^{+}-resin, parabolic rate constants were in the order: Alluvial > Red > Black. Lowest magnitude of parabolic rate constants in Black soils may be attributed to higher clay content. The smaller particles generally release K^{+} through cation exchange reactions at a slower rate than coarser particles (Von Reichenbach and Rich, 1969; Rich, 1972). Within Alluvial soils, except for the coarse-textured Tulewal loamy sand soil, parabolic rate constants were highest with the H^{+}-resin. In Red and Black soils, parabolic rate constants were higher with the Ca^{2+}-resin. In the swelling-type Black soils where size of cation was not of much consideration, and

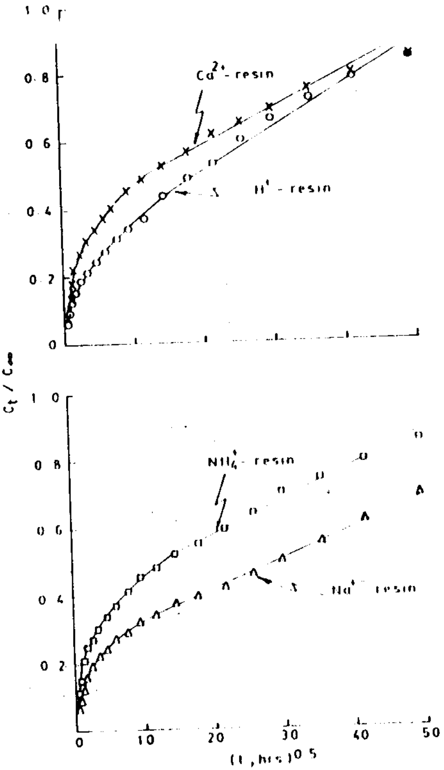

Fig. 4. Parabolic plots for K desorption from Nabha loam in different cation-saturated resins.

in low-pH kaolinitic Red soils divalent Ca^{2+} was preferred more by the exchange surface compared with other monovalent cations. Though the cumulative amounts of K released from Black soils to all the resins were considerably high (Table II), the relatively lower values of first-order rate constants and parabolic rate constants reveal that substantial amounts of K from Black soils were released during the first 22 h of the reaction, represented by a non-linear portion of the plots. Chute and Quirk (1967) ascribed this fast release of K to mass action exchange.

To determine whether the first-order or the parabolic rate equation described better the release of K, a least square regression analysis was carried out. The correlation coefficient (r) and the standard error of the estimate (SE) were calculated for each equation. In almost all the soils, the parabolic equation described the kinetics of K release better than the first-order kinetic equation, indicating the diffusion-controlled exchange. However, the para-

TABLE V

Parabolic rate constants ($\times 10^{-3}$) for desorption of K from Red, Black and Alluvial soils by different resins

Soils	H^+-resin		Ca^{2+}-resin		Na^+-resin		NH_4^+-resin	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
Red soils								
Tyamagondalu (s)	15.8	7.1	19.2	9.3	17.2	8.1	16.5	7.7
Patancheru (sl)	16.0	8.3	17.3	8.9	17.3	8.8	17.0	7.4
Black soils								
Teligi (c)	10.9	8.4	16.2	8.1	12.2	5.7	16.2	5.8
Kasireddipalli (sicl)	9.8	9.1	14.6	7.3	13.7	6.5	13.2	6.7
Alluvial soils								
Nabha (l)	19.6	11.9	19.5	9.1	13.6	9.0	18.4	9.7
Kanjli (l)	21.3	11.4	17.0	10.2	15.0	10.2	15.3	7.9
Tulewal (ls)	16.7	7.1	17.5	10.0	17.5	9.5	18.2	10.0

For legend see Table IV.

bolic rate equation allows to compute only an overall diffusion constant (R). To calculate diffusion coefficients, K release data were fitted to a model as described by Chute and Quirk (1967). This model is based on radial diffusion in a cylinder in which the concentration of potassium on the cylindrical surface is constant and the concentration of potassium throughout the cylinder is initially uniform. It is assumed that the diffusion of potassium through the upper and lower faces of the cylinder (corresponding to external cleavage faces) is negligible. Radial diffusion equation as simplified by Chute and Quirk (1967) is:

$$(M_t/M_\infty)(1/t)=(4/\pi^{0.5})(D/a^2)^{0.5}t^{-0.5}-(D/a^2) \tag{3}$$

where M_t is the quantity of K which had left the cylinder in time t; M_∞ is the corresponding quantity of K after an infinite time; D is the diffusion coefficient and a is the radius of the cylinder. A plot of (M_t/M_∞) $(1/t)$ vs. $t^{-0.5}$ should give a straight line with a slope $(4/\pi^{0.5})$ $(D/a^2)^{0.5}$ from which the diffusion coefficient D can be calculated. In the present study, C_∞ values for different soils for the H^+-resin only (Table II) have been taken as M_∞. This M_∞, as per cent of total K, was 11–13, 48–87 and 18–25 in Red, Black and Alluvial soils, respectively. The radius of the cylinder, a, was calculated from the weighted mean diameter of 0–2 μm and 2–20 μm size particles only, assuming that the "diameter: thickness" ratio of the particle was 10:1 (Sharma, 1981).

When data were plotted according to eq. 3 three separate linear relationships having different slopes were obtained for reaction periods of 0.25–37, 37–331 and 331–2467 h (Fig. 5). Talibudeen et al. (1978) had referred to

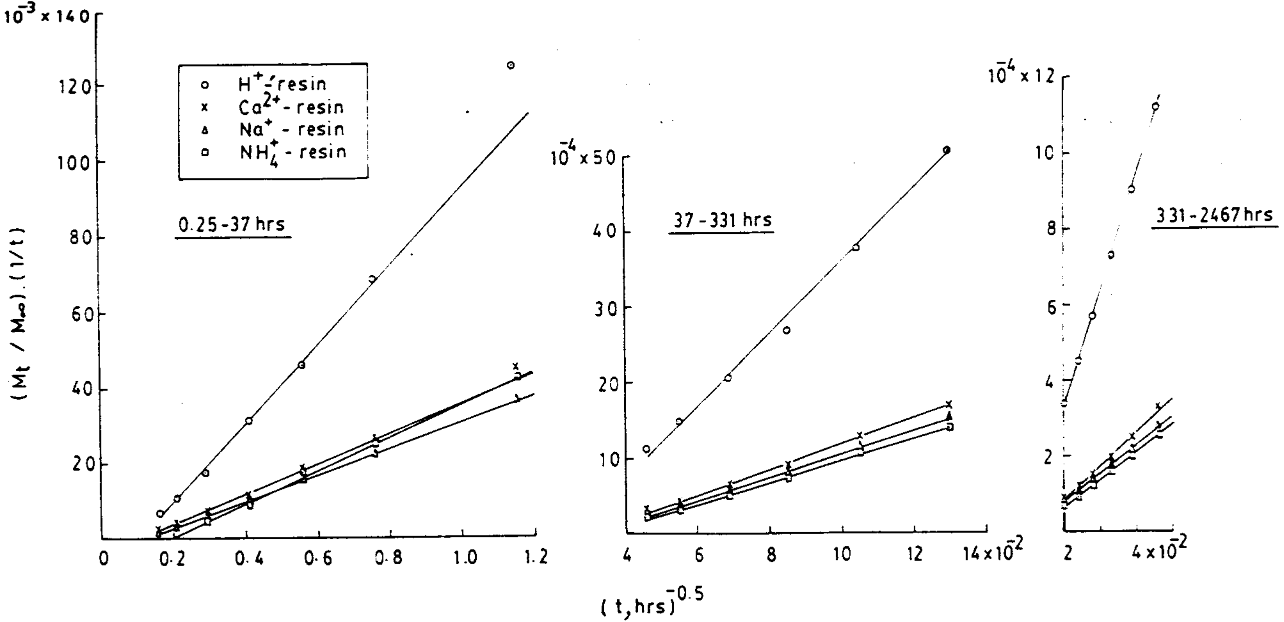

Fig. 5. Plots of (M_t/M_∞) $(1/t)$ vs. $(t)^{-0.5}$ for K desorption from Nabha loam in different cation-saturated resins.

these three linear parts as representing simultaneous rates of K release from the surface of the soil complex (the fastest process), the weathered periphery and the micaceous matrix. These workers further suggested that "surface" K would virtually cease to contribute after 24 h and "peripheral" K after 35 days. From the slopes of these linear parts, the diffusion coefficients *D* were calculated and these varied from 1.58×10^{-20} to 2.65×10^{-18}, 3.11×10^{-21} to 5.42×10^{-19} and 7.75×10^{-22} to 2.26×10^{-19} cm^2/s for the first, second and third phase, respectively. As release of K proceeded, the rate of diffusion was slowed down.

With the H^+-resin, diffusion coefficients were highest for Alluvial soils (except the Tulewal loamy sand) followed by Black and Red soils. Red soils though containing the highest amount of total K, recorded the lowest diffusion coefficients because a major portion of K in these soils was present as K feldspars. Resins saturated with Ca^{2+}, Na^+ and NH_4^+ released K only through the mechanism of exchange. For the first part of the reaction (0.25–37 h), which represented release of K from the external planar surface of the exchange complex, diffusion coefficients were higher for Black soils than for Alluvial and Red soils. Black soils were fine in texture and possessed high cation exchange capacity. For release of K during the second and third parts of the reaction, diffusion coefficients showed in the sequence Alluvial $\geqslant$ Black $>$ Red. The Tulewal soil was, however, an exception due to its coarse texture. In general, diffusion coefficients with different resins as recorded for the test soils showed the sequence: H^+-resin $>$ Ca^{2+}-resin $>$ Na^+-resin $>$ NH_4^+-resin, which is also the order of absolute amounts of K released by these resins.

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