Kinetics of interlayer potassium release from micaceous minerals

Robert Carl Sorensen
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Physical Chemistry Commons

Recommended Citation
Sorensen, Robert Carl, "Kinetics of interlayer potassium release from micaceous minerals " (1964). Retrospective Theses and Dissertations. 3888.
https://lib.dr.iastate.edu/rtd/3888

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
This dissertation has been microfilmed exactly as received

SORENSEN, Robert Carl, 1933—
KINETICS OF INTERLAYER POTASSIUM RELEASE FROM MICACEOUS MINERALS.

Iowa State University of Science and Technology, Ph.D., 1964
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan
KINETICS OF INTERLAYER POTASSIUM RELEASE
FROM MICACEOUS MINERALS

by

Robert Carl Sorensen

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Soil Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1964
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>LITERATURE REVIEW</strong></td>
<td>3</td>
</tr>
<tr>
<td><strong>MATERIALS AND METHODS</strong></td>
<td>11</td>
</tr>
<tr>
<td><strong>RESULTS AND DISCUSSION</strong></td>
<td>13b</td>
</tr>
<tr>
<td>K Release from Various Minerals</td>
<td>13b</td>
</tr>
<tr>
<td>Variable Effective Radius of Particles</td>
<td>25</td>
</tr>
<tr>
<td>Diffusion Without Moving Boundary Restrictions</td>
<td>40</td>
</tr>
<tr>
<td>Variable Diffusion Coefficient</td>
<td>47</td>
</tr>
<tr>
<td>Radius Dependence of Moving Boundary Diffusion Equation</td>
<td>62</td>
</tr>
<tr>
<td>Fixed K in Vermiculite</td>
<td>67</td>
</tr>
<tr>
<td>Effect of NaCl Concentration</td>
<td>72</td>
</tr>
<tr>
<td>Effect of Different Extraction Solutions on Illite</td>
<td>77</td>
</tr>
<tr>
<td>Behavior</td>
<td></td>
</tr>
<tr>
<td><strong>SUMMARY</strong></td>
<td>81</td>
</tr>
<tr>
<td><strong>LITERATURE CITED</strong></td>
<td>88</td>
</tr>
<tr>
<td><strong>ACKNOWLEDGMENTS</strong></td>
<td>90</td>
</tr>
</tbody>
</table>
INTRODUCTION

The weathering of micaceous minerals generally involves a loss of K from between the layers of the mineral lattice. The general concepts of this release of interlayer K are well understood, but a mathematical interpretation of the quantitative aspects of the process is still lacking.

The interlayer K in micaceous minerals is extremely difficult to remove by simple exchange with other cations because a very low K concentration in the solution surrounding the mineral particles is required. In the natural weathering of micas, percolating water and plants combine to keep the K in solution very low. In the laboratory, other methods are more satisfactory. Two of these methods are (1) leaching with NaCl solutions and (2) the use of a K precipitant. Although the leaching procedure may simulate the natural conditions of K removal in soils more accurately, the precipitation procedure allows the conditions of experimentation to be more accurately described, and it provides a system that lends itself more completely to a mathematical treatment of K release. Also, with a precipitant, the K in solution can be reduced to a level that will allow a release of K that would not otherwise occur.

The ultimate agronomic objective of these studies is the accurate description of K release in soils. An equation has been derived by Reed and Scott (22) which accurately describes the release of K from biotite and muscovite samples that have a very narrow range of particle size. However, the major portion of the K released in soils is not from mineral samples of this type. Therefore, to mathematically describe K release
in soils, this equation must be generalized to have wider application in regard to mineral type and particle size. This study constitutes a step in this direction. Specifically, various mineral samples have been degraded with sodium tetraphenylboron (NaTPB) solutions and a mathematical interpretation of the K release data has been made.
LITERATURE REVIEW

Interlayer K is an important natural structural feature in many minerals. Some of these minerals have the capacity to incorporate K into their structure when brought into contact with large amounts of K. In many respects K originally present in the mineral (native K) behaves in much the same manner as K which has been added to a mineral (fixed K), yet in other respects these two sources of potassium act very differently. Different types of minerals, and even the same mineral from different sources, may release potassium at different rates.

A number of investigators have attempted to show the relationships between these minerals that are associated with the fixation and release of K. For instance, the relation between vermiculite and biotite was studied by Barshad (5) using base exchange reactions, x-ray analysis, and differential thermal curves. Vermiculite was shown to "fix" K, NH₄, Rb, and Cs ions. Large flakes of vermiculite underwent base exchange almost as readily as very fine particles. When vermiculite was saturated with potassium ions, its properties resembled those of biotite. Ordinary biotite was converted into vermiculite by prolonged leaching with a MgCl₂ solution. As a result of these and other observations, Barshad suggested that vermiculite is simply a Mg-mica with Mg occupying the positions occupied by K in the true micas.

DeMumbrum (7) used NaTPB and sodium cobaltinitrite treatments to remove K from biotite. Data obtained by x-ray diffraction analysis showed that the biotite was partially converted to vermiculite. Treatment of phlogopite with NaTPB followed by Mg saturation also produced a partial
conversion to vermiculite. Muscovite was partially converted to vermiculite with NaTPB and LiNO₃ treatments. This investigator removed the Mg in vermiculite with sodium versenate to show the similarity between this reaction and those occurring when K is removed from muscovite, biotite, and phlogopite.

Arnold (2) discussed the weathering of a number of minerals found in the soil. On the basis of a number of previous observations he suggested weathering sequences for biotite and muscovite. It was proposed that feldspars have a stability to weathering that is intermediate between those of muscovite and biotite, based mainly on the work of Jackson et al. (12).

Other comparisons between minerals were made by Scott and Reed (24) who found that vermiculite, although structurally similar to biotite, released K at a considerably faster rate than biotite. In the same series of papers, Scott and Reed (25) showed that the K in illite was not as easily removed as that in biotite.

In a study of the factors affecting K release, Barshad (4), using several micaceous minerals, showed that the replaceability of interlayer NH₄ or K is affected by (1) the magnitude of the interlayer crystal lattice charge, (2) particle size, (3) presence of difficultly replaceable H, (4) nature of replacing cation, and (5) nature of K. It was also determined that the magnitude of the interlayer charge rather than the origin of the charge determines the amount of cation fixation. Fixed K was more easily replaced than native K.

Mortland (17) studied the effects of a number of conditions on the
release of K from biotite using NaCl solutions. The rate of release of K was constant over a long period of time after which the logarithm of the rate of release decreased linearly with time. The rate of release was linearly related to the temperature and to the square root of the NaCl concentration. An equation was derived in which the three factors, leaching rate, temperature, and NaCl concentration, were taken into account. A linear relation is shown between K release rate and the product of leaching rate, temperature, and the square root of the NaCl concentration.

Reed (20) studied the effects of NaCl-NaTPB extracting solutions on the removal of K from biotite. He showed that a decrease in the K concentration in the extracting solution yields an increase in the rate of removal of K. Reed also showed that there was a critical K concentration in the extracting solution, above which all the K in biotite could not be removed under any circumstances. This level was 7.5 ppm K. The charge density of biotite was shown to be unaffected by the NaCl-NaTPB treatment except at relatively long extraction times. There was no stoichiometric relationship between the decrease in charge and the amount of iron oxidized. In experiments in which the pH of the extracting solution was controlled, Reed showed that H was taken up by the mineral during the degradation process, and, during removal of approximately the last 50% of the K, the amount of H taken up was directly related to the amount of K removed.

Several authors have evaluated the significance of particle size in K release from minerals. The relation of particle size to the rate of release of K from biotite has been studied by Mortland and Lawton (19).
In the initial stages of K-depletion, the finer particles lost more K than the larger particles. However, the K content of all size fractions was about the same after approximately 50% of the K present had been removed.

Scott and Reed (24), on the other hand, noted that smaller biotite particles released K much faster than larger particles when the K was removed with NaCl-NaTPB solutions. These investigators also found that mixing two different size fractions of biotite did not alter the rate of release of K from each fraction indicating no effect of one particle size on another.

Barshad (4) also found particle size to be an important factor in K release in his study of the replaceability of interlayer K and NH$_4^+$.

Jonas and Roberson (13) investigated the influence of particle size on the tendency for three-layer clay minerals to expand. The degree of solvation with a number of solvents was used as a measure of resistance to expansion. X-ray diffraction analysis with two minerals showed that the resistance of the minerals to expansion was decreased by gentle grinding, particularly after treatment with a KCl solution.

The movement of K from one mineral to another in a mixture has been demonstrated by Mortland (16), who mixed a number of soil clays with equal weights of biotite and suspended them in water for 21 days. It was shown that the transfer of K from the biotite to the soil clays was dependent on the amount of "reactive" K in the minerals relative to the K concentration in the bulk solution indicating that K fixation and release are diffusion controlled. Also, he concluded that these processes
can occur simultaneously. The rate of transfer of $K$ from the biotite to the soil clays was inversely proportional to the initial $K$ content of the soil clays.

The role of diffusion was investigated further by Ellis and Mortland (8) who compared the rates with which fixed and native $K$ are released. A marked difference was found between the $K$ release rates in the two cases when the samples were leached with NaCl solutions. Differences between fixed and native $K$ release have also been observed by Reed (20) using NaCl-NaTPB solutions to effect release and by Barshad (4). Ellis and Mortland observed that the rate of release of native $K$ in biotite was nearly constant during the time necessary to remove about 50% of the $K$. For the fixed $K$, the rate of release decreased with time. Furthermore, a linear relationship was observed between the logarithm of the rate of release and the time. The slopes of these curves depended on the extent to which weathering had proceeded before addition of the fixed $K$.

Mortland and Ellis (18) studied the role of diffusion in the release of fixed $K$ from vermiculite. Film diffusion, particle diffusion, and chemical exchange of Na for K at the exchange sites were considered as possible limiting steps. Particle diffusion was eliminated by testing an approximation of the equation for diffusion from a slab with $K$ release data. The chemical exchange of Na for K was discarded as a rate limiting step on the basis of the dependence of rate of $K$ release on particle size and rate of leaching, although the chemical exchange equation applied to the $K$ release data. Film diffusion was considered to be the rate limiting process. However, it can be shown that the equation used by these
investigators to describe particle diffusion does not conform to the boundary and initial conditions necessary for particle diffusion. Furthermore, if the necessary conditions are imposed on the equation employed, it will be found that particle diffusion cannot be eliminated as the rate limiting process.

Using a slightly different approach, Schouwenburg and Schuffelen (23) studied the K exchange behavior of an illite. They found that the Gapon exchange equation accurately describes this behavior if one accepts the existence of three types of exchange sites, each having its own exchange constant. These types of sites were considered to be planar (outer surface sites), edge sites, and interlattice sites. The exchange constant for the interlayer sites was exceedingly large reflecting the difficulty encountered in replacing K ions on these sites.

Some estimates of the values of the diffusion coefficient in vermiculite were obtained by Keay and Wild (15). Using particles of a narrow size range they showed that diffusion within the particles must be the rate limiting step. Rates of exchange were determined for a number of ion-pairs. Diffusion coefficients for Ba in several different vermiculites were determined by self diffusion employing the equation of Barrer (3). The diffusion coefficients ranged from $1.3 \times 10^{-7}$ cm.$^2$/sec. to $4.5 \times 10^{-7}$ cm.$^2$/sec. Energies of activation were calculated according to the Arrhenius equation and ranged from 7.3 Kcal./mole to 19.4 Kcal./mole which are of the same order as those observed by Walker (26) for Mg-Sr exchange. The diffusion coefficients were unrelated to the cation exchange capacity. The energies of activation for the forward and reverse exchanges were unequal. This was attributed to differences in the entropy
The existence of a moving boundary between the weathered and unweathered portions of a mineral particle has been indicated by Mortland (17) who shows by photomicrographs that, of the particles being weathered, the larger particles had a band of weathered material around their outside edges, while the smaller, completely degraded particles did not show this band.

Another incidence of the presence of a moving boundary in a mineral particle through which ions are diffusing was noted by Walker (26) who studied the diffusion of exchangeable cations in vermiculite using optical methods. Large vermiculite particles one to two millimeters on a side and one-tenth millimeter thick were placed in a $2\ M$ SrCl$_2$ solution. The progress of the boundary between the Mg-lattice and the Sr-lattice was followed by direct measurement and x-ray diffraction analysis. As the boundary moved toward the center of the particle, the 14.4 Å peak was reduced while the 15.0 Å peak was enhanced. Similarly, the presence of a moving boundary is indicated by the gradual decrease in the 10 Å peak height and an increase of the 15 Å peak in biotite or the 14 Å peak for illite which Scott and Reed (24, 25) have associated with the amount of K that has been removed.

The presence of the moving boundary in weathering mica particles has been taken into account in an equation derived by Reed and Scott (22) to describe the release of K from biotite and muscovite. The model for the development is a diffusion controlled process taking place in flat circular particles in which the inner boundary of the diffusion area is
moving toward the center of the particle as K is removed. Fick's Law with a constant diffusion coefficient was used as the basic differential equation. After incorporation of factors for converting from a particle basis to a weight basis, the differential equation for K release was

$$\ln \frac{Q}{Q_0} \frac{dQ}{dt} = \frac{-4\pi D (C_a - C_b) t}{\rho \delta r_b^2}$$

where Q is the amount of K remaining in the mineral at time t, Q_0 is the total amount of K in the mineral, \( \tau \) is the interlayer spacing, D is the diffusion coefficient, \( C_a \) and \( C_b \) are the concentrations of K at the weathering front and the edge of the particle, respectively, \( \rho \) is the density of the mica, \( \delta \) is the basal spacing of the mineral and \( r_b \) is the radius of the particle. Upon integration, the equation obtained was

$$\frac{Q}{Q_0} (1 - \ln \frac{Q}{Q_0}) = 1 - \frac{4\pi D (C_a - C_b) t}{Q_0 \rho \delta r_b^2}$$

When \( \frac{Q}{Q_0} (1 - \ln \frac{Q}{Q_0}) \) was plotted against time, three particle sizes of biotite gave the required straight line during the removal of a large amount of K. However, when \( \frac{Q}{Q_0} (1 - \ln \frac{Q}{Q_0}) \) was plotted against \( t/r_b^2 \), three different lines were obtained indicating the radius dependence was incorrect. Replacing \( r_b^2 \) with \( r_b \) allowed the equation to accurately describe the release of K in three sizes of biotite and two sizes of muscovite during the removal of a considerable amount of K.
MATERIALS AND METHODS

The muscovite and biotite samples used in this study were obtained from Ward Natural Science Establishment. The vermiculite was a South Carolina ore obtained from the Zonolite Company. The illite (Goose Lake Grundite) was secured from the Illinois Clay Products Company.

With the exception of illite, all samples were ground in a Cristy and Norris laboratory hammer mill. The < 50 µ fraction of muscovite, biotite, and vermiculite were obtained by dry sieving this ground material. The 50-60 µ vermiculite and muscovite samples were prepared by grinding samples with larger particle sizes and wet sieving. This procedure of grinding and wet sieving was repeated several times to obtain an adequate sample. The 10-20 µ vermiculite and muscovite samples were separated from the ground material that was obtained in conjunction with the 50-60 µ sample preparation, by sedimentation. A 250-300 µ vermiculite sample was also separated from the ground material by wet sieving during the preparation of the 50-60 µ samples.

In the case of illite, a < 50 µ sample was prepared by wet sieving a portion of the material supplied by the Illinois Clay Products Company. This < 50 µ illite was then suspended without chemical treatment and samples of < 2 µ and 10-20 µ illite were separated by sedimentation.

All mineral samples were air-dried and those with < 250 µ particles were crushed to pass a 60 mesh screen before they were used.

The standard method of extracting K from the mineral samples consisted of mixing 0.500-g. samples (110°C. oven-dry basis) with 0.684 g. NaTPB and
10 ml. of 1 N NaCl-.01 M disodium dihydrogen EDTA and allowing the suspensions to stand for varying lengths of time. The suspensions were stored in a constant temperature room at 25°C. when the extraction period was greater than one hour. For periods shorter than one hour, no temperature control was used unless specified in the description of the individual experiment. At the end of the extraction period, the sample was transferred to approximately 115 ml. of 2 N NH₄Cl. Two hundred ml. of water and 20 ml. of 0.2 M HgCl₂ were added and the mixture was boiled for 20 minutes. In some cases 230 ml. of 2 N NH₄Cl and 400 ml. of water were employed. The suspensions were allowed to cool overnight and then filtered under vacuum. The K in the filtrate was determined with a flame photometer. Several aspects of this type of procedure have been discussed by Reed and Scott (21).

The extraction method for illite differed from this standard method in that the extracting solution consisted of 1.7 N NaCl-0.3 N NaTPB-0.01 M disodium dihydrogen EDTA. In this case 30 ml. of HgCl₂ were used instead of 20 ml. The extraction solution for < 50 μ muscovite also differed from the standard solution in that 2 N NaCl was used. The < 50 μ biotite data reported in this manuscript were obtained by Reed (20) with a slightly different method which he has described. Other variations in procedure will be described where data are presented.

Total K in the minerals was determined by HF-HClO₄ digestion according to the method of Jackson (11). Exchangeable K values were obtained by leaching 0.5000-g. samples (110°C. oven-dry basis) with 100 ml. neutral 1 N NH₄OAc.
Particle size analysis of < 50 μ fractions of vermiculite and muscovite was performed with a hydrometer by the ASTM tentative method for grain-size analysis of soils (1) except that a 10-gram sample was used.

K was fixed in 250-300 μ vermiculite by placing 8 grams of the mineral in approximately 50 ml. of 1 N KCl for a week. The KCl solution was decanted and replaced with fresh solution daily. At the end of the contact period the KCl was removed by filtration and the mineral was leached with 70% methanol until the filtrate was chloride free (AgNO₃ test). After removing the methanol with a small amount of water, the mineral was air dried.
RESULTS AND DISCUSSION

K Release from Various Minerals

K is known to be situated in the interlayer area of many micaceous minerals. Most of this K is inaccessible to chemical exchange by other cations. However, this inaccessible K can be removed by extracting solutions containing various compounds without disrupting the lattice of the mineral. A necessary characteristic of these extracting solutions is that the K concentration can be kept low. In this study NaCl-NaTPB extracting solutions, which have this property, were used exclusively.

Different minerals have been shown to be quite different in respect to the release of K. It is, therefore, informative to first examine the available data on the release of K by the minerals used in this study.

Figures 1, 2, and 3 show the amount of K removed from four minerals by extraction with NaCl-NaTPB solutions. One point of similarity between these four minerals is the decrease in the rate of K release with time as indicated by the slopes of the curves. This decrease in K release rate is significant because Mortland (17) has shown that when K was removed from biotite by leaching with NaCl solutions, a period of constant release rate was observed. This difference can be explained by the relatively higher K concentrations in the NaCl extracting solutions. Reed (20) has shown that when the K concentration is as high as 3.5 ppm.
a period of constant release rate from biotite can also be observed with a NaCl-NaTPB extracting solution. However, the concentration of K in the NaCl-NaTPB solutions used to obtain the data in Figures 1, 2, and 3 was considerably lower. Under these conditions no period of constant release rate occurred.

Differences between minerals in regard to the rate of K removal in the early stages of weathering are apparent in these figures. The rate of removal of K from vermiculite is faster than that from illite even though the release is occurring from larger particles. The K release from these two minerals is faster than that from biotite which is in turn faster than that from muscovite. Although Figures 1, 2, and 3 supply general information about K release in these minerals, they do not provide a simple basis for a quantitative characterization of K release.

Figure 4 shows the K removal from these minerals with the extraction time plotted on a logarithmic scale. This allows the K removal characteristics in the early stages to be easily observed and at the same time permits their representation over a long time period. The curves for vermiculite and illite in Figure 4 differ from those for muscovite and biotite in that they consist of a series of straight line segments. However, this type of plot has no theoretical significance, thus, no conclusions regarding the nature of the release process can be drawn from these observations.

Both Figure 1 and Figure 4 indicate that a significant portion of the K in < 2 µm illite is not extractable by these methods whereas essentially all of the K in vermiculite and biotite is removed. It is
Figure 1. K removed from biotite, illite, and vermiculite in different extraction periods with NaCl-NaTPB solutions.
Figure 2. K removed from biotite and muscovite in different extraction periods with NaCl-NaTPB solutions.
Figure 3. K removed from muscovite in different extraction periods with NaCl-NaTPB solutions
Figure 4. Comparison of four minerals in regard to the amount of K removed and the logarithm of the extraction periods.
thought that essentially all of the K in < 50 μm muscovite is extractable; however, the long extraction period required for its removal makes this fact somewhat difficult to ascertain. Since only a portion of the total K in illite is extractable, attention will be given to characterizing the release of only the extractable portion.

An equation has been derived by Reed and Scott (22) which is designed to describe K release from mineral particles. They assumed these particles to be flat circular plates from which K ions moved by diffusion from the "weathering front" to the exterior solution. The position of the weathering front was assumed to be dependent on the amount of K which had been removed from the particle. Diffusion within the particle was considered to be the limiting step in K removal.

The equation of Reed and Scott is

\[ \frac{Q}{Q_0} (1 - \ln \frac{Q}{Q_0}) = 1 - \frac{4\tau D (C_a - C_b)}{\rho \delta r_b Q_0} t \]  

where Q is the amount of K remaining in the mineral at time t, Q₀ is the total K in the mineral, \( \tau \) is the width of the interlayer space, D is the diffusion coefficient, \( C_a \) and \( C_b \) are the K concentrations at the weathering front and at the edge of the particle, respectively, \( \rho \) is the density of the mineral, \( \delta \) is the basal spacing for the mineral, and \( r_b \) is the particle radius. Letting \( u = \frac{Q}{Q_0} \) and \( K' = \frac{4\tau D (C_a - C_b)}{\rho \delta r_b Q_0} \) for simplification the equation becomes

\[ u (1 - \ln u) = 1 - K't. \]
If this equation fits the experimental data a plot of $u (1 - \ln u)$ against $t$ should yield a straight line. A more rigorous test of the application of this equation can be made by plotting $\log [u (1 - \ln u)]$ against $\log t$, bearing in mind that a straight line having slope one is required for correct application of the equation.

Figures 5, 6, 7, and 8 show this type of plot for samples of biotite, muscovite, vermiculite, and illite. Curves for samples with narrow particle size range and samples with wide particle size range are presented for each mineral. The 10-20 $\mu$ vermiculite and both illite curves refer to the extractable K in the mineral instead of the total K. From Figures 1 and 4 it is evident that only 65% or 81.5 me. K per 100 g. can be extracted from $< 2 \mu$ illite by the NaCl-NaTPB solution employed. Thus, the $< 2 \mu$ illite data plotted in Figure 8 was calculated on the basis of a $Q_o$ value of 81.5 me. per 100 g. rather than the total K value of 125 me. per 100 g. Similarly, it has been found that only a portion of the K in 10-20 $\mu$ vermiculite and 10-20 $\mu$ illite is extractable. Thus, the amount of extractable K in these samples was determined, and these values were used for $Q_o$ in the calculation of the data for Figures 7 and 8.

These figures show the applicability of the equation of Reed and Scott. K removal from narrow particle size fractions of muscovite and biotite is described very well by this equation. Also, K removal from $< 50 \mu$ muscovite and biotite is accurately described during the release of a large part of the K, but departures are noted in the latter stages of weathering. The equation does not apply to either the narrow or wide particle size range samples of illite or vermiculite.
Figure 5. The relationship between log \(1-u(1-ln u)\) and the logarithm of the extraction period with two fractions of biotite.
Figure 6. The relationship between \( \log \left[ 1-u(1-\ln u) \right] \) and the logarithm of the extraction period with three fractions of muscovite.
Figure 7. The relationship between log [1-u(1-ln u)] and the logarithm of the extraction period with two fractions of vermiculite
Figure 8. The relationship between log \([1-u(1-ln u)]\) and the logarithm of the extraction period with two fractions of illite.
Modifications in the equation of Reed and Scott are therefore necessary for the accurate description of K removal from < 50 \mu m muscovite and biotite samples and from both the narrow and wide particle size range samples of vermiculite and illite. In samples such as illite, in which only a portion of the K is extractable, only the removal of this extractable portion will be considered.

Variable Effective Radius of Particles

It has been observed by Jonas and Roberson (13), Mortland and Lawton (19), and Scott and Reed (24) that the radius of mineral particles affects their K release properties. The moving boundary diffusion equation derived by Reed and Scott (22) takes into account the effect of particle size on K removal. However, in their model the mineral sample contains particles of a simple constant radius whereas, in practice, the particles in most mineral samples will vary in particle size. Also, the equation and experimental evidence of Reed and Scott show that the smaller particles should lose all their extractable K first; therefore, as the weathering of the mineral proceeds, the average radius of the particles participating in the release of K should increase. This effect should be relatively unimportant for mineral samples with a narrow size range of particles, but should be significant for a sample with a wide range of particle size. The K release characteristics of mineral samples with a wide range of particle size would, therefore, be expected to deviate from the behavior predicted by the equation of Reed and Scott. However, it should be possible to generalize the equation of Reed and Scott to take this effect into account. The basic feature of such an equation must be some func-
tional relationship between the effective particle radius at a given
time and the degree of weathering. The relationship chosen here was that
\( r_c \), the effective radius, varied linearly with \( u \), the fraction of K left
in the mineral. Furthermore, it was assumed that \( r_c \) increased from \( \bar{r} \)
(the average of the maximum and minimum radius) at time zero to \( r_m \) (the
maximum radius) when weathering was complete. A mathematical description
of this assumption is

\[ r_c = (\bar{r} - r_m) u + r_m. \]  

(3)

The differential equation derived by Reed and Scott is

\[ \ln \frac{Q}{Q_0} \, dQ = -\frac{K}{r_b^2} \, dt \]  

(4)

where \( K = \frac{4\pi D(C_a - C_b)}{\rho \delta Q_0} \).

However, their subsequent investigation of the radius dependence of K
removal from biotite and muscovite showed that in order for their equation
to accurately describe this removal, \( r_b \) had to be replaced by \( r_L \). Making
this change in Equation 4 and replacing \( Q/Q_0 \) by \( u \) gives

\[ \ln u \, du = -\frac{Kdt}{r_b}. \]  

(5)

Substituting \( r_c \) (Equation 3) for \( r_b \) in Equation 5 gives

\[ \ln u \, du = -\frac{Kdt}{(\bar{r} - r_m)u + r_m}. \]  

(6)

Integration of Equation 6 yields
For any mineral sample in which the particle size range can be described as less than some value of radius (for example, < 50 \( \mu \) and < 2 \( \mu \) samples), the value of the term \( \frac{r_m - \bar{r}}{r_m} \) will be one-half. In this instance Equation 7 reduces to

\[
\frac{2}{7} u^2 \left( \ln u - \frac{1}{2} \right) + \frac{8}{7} u \left( 1 - \ln u \right) = 1 - \frac{8Kt}{7r_m}.
\]  

The left side of this equation will be referred to as "Term A". If the K removal from a mineral is described by this equation, Term A should be linearly related to time. Equation 8 was applied to the K release data obtained with < 50 \( \mu \) muscovite, < 50 \( \mu \) biotite, < 50 \( \mu \) vermiculite, and < 2 \( \mu \) illite. The results are shown in Figures 9, 10, 11, and 12. In no case was a straight line obtained. It must be concluded, therefore, that this concept of a variable radius effect was not adequate to explain the K release behavior of these four mineral samples. However, these results do not eliminate other functional relationships between \( r_c \) and \( u \) from consideration.

To obtain a more realistic functional relationship and more appropriate boundary values, a determination of the particle size distribution in < 50 \( \mu \) muscovite was performed. The results are shown in Figure 13. The value of 12.5 for \( \bar{r} \) (the average of the maximum and minimum radii) appears to have been a good estimate of the effective particle radius at the beginning of the degradation since approximately
Figure 9. The relationship between Term A (left side of Equation 8) and the extraction period with muscovite.
Figure 10. The relationship between Term A (left side of Equation 8) and the extraction period with biotite.
Figure 11. The relationship between Term A (left side of Equation 8) and the extraction period with vermiculite
Figure 12. The relationship between Term A (left side of Equation 8) and the extraction period with illite.
Figure 13. Particle size distribution in < 50 μ muscovite
50% of the particles have radii greater than 12.5 μ. On the other hand, the number of particles of a given size is more closely related to the logarithm of the radius than to the radius itself as was assumed in Equation 3.

A new equation for r_c was derived on the basis of a logarithmic relation between r_c and u. Again the effective radius was considered to vary from r to r_m. Under these conditions

\[ r_c = r_m \left( \frac{r}{r_m} \right)^u \]  \hspace{1cm} (9)

Substituting r_c (Equation 9) for r_b in Equation 5 yields

\[ \left( \frac{r}{r_m} \right)^u \ln u \, du = \frac{K}{r_m} \, dt. \]  \hspace{1cm} (10)

Integrating the left side of this equation from 1 to u for the variable u and the right side from 0 to t for the variable t gives

\[ \frac{\ln u}{a} \left( e^u - 1 \right) - \sum_{n=1}^{\infty} \frac{a^{n-1} u^n}{n \cdot n!} = - \sum_{n=1}^{\infty} \frac{a^{n-1} u^n}{n \cdot n!} + \frac{K t}{r_m} \]  \hspace{1cm} (11)

where \( a = \ln \frac{r}{r_m} \). Since the left side of the equation cannot be represented in closed form, a non-exact solution must be used. As the K release data are only correct to three significant figures, the values of the left side of Equation 11 can not have more than three significant figures. Since \( u \leq 1, \frac{a^{n-1} u^n}{n \cdot n!} \leq \frac{a^{n-1}}{n \cdot n!} \) for all integer values of \( n > 0 \). Therefore, if the error of the series on the right is less than one part per thousand, the error of the series on the left will also be less than this value if any finite number of terms of the series are taken. The
value of the fifth term in the series on the right is 0.0005. Since this is an alternating series, the total error involved in truncating this series after the fourth term is less than 0.0005. As a result, four terms in the series were accepted for these calculations. The equation as used was then

\[
\ln \frac{u}{a} \left( e - 1 \right) - \left( u + \frac{au^2}{4} + \frac{2au^3}{18} + \frac{3au^4}{96} \right) = -0.851 + \frac{Kt}{r_m}
\]

(12)

where \( a = \ln 0.5 \). If this expression describes the K release from a mineral, a linear relationship will exist between the left side of Equation 12, henceforth referred to as "Term B", and time. This relationship for \(< 50 \mu m\) muscovite is depicted in Figure 14. This figure shows that Equation 12 does not describe the K removal from \(< 50 \mu m\) muscovite. Also, a comparison of Figure 13 with Figure 14 shows the introduction of a logarithmic increase in effective radius yields little or no improvement over the linear increase.

Since a more accurate functional relationship between \( r_c \) and \( u \) did not result in an accurate description of K removal from \(< 50 \mu m\) muscovite, attention was given to the value chosen for \( \bar{r} \), the effective radius at the beginning of the degradation. The value of \( \bar{r} \) that would allow Equation 7 to describe the K release from \(< 50 \mu m\) muscovite was, therefore, determined with three selected data points. The calculated value for \( \bar{r} \) was 2 \( \mu m \) which corresponds closely to the radius of the smallest particles in the sample shown by the particle size distribution in Figure 13. Substituting this value for \( \bar{r} \) in Equation 7 gives
Figure 14. The relationship between Term B (left side of Equation 12) and the extraction period with muscovite.
Figure 15 shows the relationship between the left side of Equation 13, hereafter referred to as "Term B", and time for the case of < 50 µ muscovite. The use of the minimum radius rather than the average radius resulted in a linear relationship as was expected.

The effect of a logarithmic increase in effective radius as shown in Equation 9 was also determined with \( r = 2 \). Equation 11 with \( a = \ln 0.08 \) must be used. In this case, it was also necessary to include the fifth and sixth terms of the series in Equation 11 to obtain the desired accuracy. In this case the applicable equation was

\[
\frac{\ln u}{a} (e - 1) - \frac{6}{n=1} \frac{a^{n-1} u^n}{n \cdot n!} = - \frac{6}{n=1} \frac{a^{n-1}}{n \cdot n!} + \frac{Kt}{r_m} .
\] (14)

If Equation 14 describes the K release data, the left side of Equation 14, hereafter referred to as "Term C", should be linearly related to the time. Figure 16 shows that this equation does describe the K release observed with < 50 µ muscovite.

The hypothesis that the radius of the smallest particle present was the correct quantity for \( r \) was tested further with < 50 µ vermiculite. A determination of the particle size distribution in < 50 µ vermiculite showed that the smallest particles present in the sample were also approximately 2 µ in radius. Since little difference had been observed whether a logarithmic or linear increase in effective radius was used with muscovite, the latter was chosen for this test with vermiculite. Therefore, Equation 13 was used. Figure 17 shows that the left side of Equation
Figure 15. The relationship between Term D (left side of Equation 13) and the extraction period with muscovite.
Figure 16. The relationship between Term C (left side of Equation 14) and the extraction period for muscovite
Figure 17. The relationship between Term D (left side of Equation 13) and the extraction period with vermiculite.
Term D) is not linearly related to time. Therefore, for < 50 µ
vermiculite, the substitution of the minimum radius for \( \bar{r} \) did not allow
Equation 13 to describe the K release behavior.

The results obtained with < 50 µ muscovite indicate that Equation
13, in which \( \bar{r} = 2 \), describes K removal from that mineral. However,
this selection of \( \bar{r} \) is incompatible with the model. Also, the results
obtained with vermiculite show that this selection did not provide a
basis for the description of K removal from that mineral. Therefore,
it is conceivable that the success with these equations for muscovite is
associated with the incorporation of a \( \frac{K}{r_b} \) term in the equation of Reed
and Scott which is not constant but \( u \) dependent. This could be due not
to a variable radius but to a change in some quantity in the term K
which varies with particle radius.

Diffusion Without Moving Boundary Restrictions

A distinct boundary between the K-depleted portion and the un-
weathered portion of micaceous mineral particles has been shown to exist
by Mortland (17). This boundary moves when K is released. Nevertheless,
Mortland and Ellis (18) have had some success in explaining K release
from these minerals without taking this moving boundary into account.
Thus, the applicability of this concept of K release without moving
boundary restrictions was applied to particles with the same geometry as
that described by Reed and Scott. To obtain this equation the well-known
differential equation for diffusion from an infinitely long cylinder
\[ \frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \]  \hspace{1cm} (15)

must be solved. The initial condition is \( C(r, 0) = C_o \) and the boundary condition is \( C(r_b, t) = C_b \) where \( C(r, t) \) is the concentration of K at time, \( t \), and distance from the center of the particle, \( r \). \( C_o \) and \( C_b \) are the K concentrations in the interlayer space and at the periphery of the particle, respectively, \( r_b \) is the radius of the particle, and \( D \) is the diffusion coefficient. The solution of this equation with these boundary conditions is

\[ \frac{C-C_b}{C_o-C_b} = \sum_{m=0}^{\infty} \frac{J_0(\lambda_m r) e^{-D\lambda_m^2 t}}{\lambda_m J_1(\lambda_m r_b)} \]  \hspace{1cm} (16)

where \( J_0(\lambda_m r) \) and \( J_1(\lambda_m r_b) \) are Bessel Functions and \( \lambda_m \) is the eigenvalue of these functions. Similar solutions are given by Churchill (6) and Ingersoll, Zobel, and Ingersoll (10).

Fick's First Law can be stated in the following manner:

\[ \frac{dQ}{dt} = D \left( \frac{\partial C}{\partial r} \right)_{r_b} \]  \hspace{1cm} (17)

where \( Q \) is the amount of K remaining in the mineral at time \( t \), \( D \) is the diffusion coefficient, \( A_b \) is the area through which diffusion can occur, and \( \left( \frac{\partial C}{\partial r} \right)_{r_b} \) is the concentration gradient at the point where \( A_b \) is measured, in this case at the periphery of a particle of radius \( r_b \). The concentration gradient can be obtained by differentiating Equation 16 partially with respect to \( r \), using Formula 6 on page 268 of Wylie (27).
to differentiate the Bessel Function. The result is

$$\frac{\partial C}{\partial r}(r,t) = -\frac{2}{r_b}(C_o - C_b) \sum_{m=1}^{\infty} \frac{J_1(\lambda_m r)}{J_1(\lambda_m r_b)} D \lambda_m^2 t.$$  (18)

Evaluating Equation 18 at $r = r_b$,

$$\frac{\partial C}{\partial r}(r_b,t) = -\frac{2}{r_b}(C_o - C_b) \sum_{m=1}^{\infty} e^{-D \lambda_m^2 t}.  \tag{19}$$

Substituting Equation 19 into Equation 17 and using the same diffusion area as Reed and Scott (22), the following expression is obtained:

$$\frac{dQ}{2} = -\frac{4\pi D}{r_b^2}(C_o - C_b) \sum_{m=1}^{\infty} e^{-D \lambda_m^2 t} dt.  \tag{20}$$

Integration of the left side of this equation between the limits of $Q_o$ and $Q$ for the variable $Q$ and the right side between the limits of 0 and $t$ for the variable $t$ gives

$$Q - Q_o = \frac{4\pi D}{r_b} \left( \sum_{m=1}^{\infty} \frac{1}{2} \frac{e^{-D \lambda_m^2 t}}{\lambda_m} - \sum_{m=1}^{\infty} \frac{1}{\lambda_m} \right).  \tag{21}$$

Dividing by $Q_o$, the total amount of K in the mineral,

$$\frac{Q}{Q_o} - 1 = \frac{4\pi D}{r_b^2 Q_o} \left( \sum_{m=1}^{\infty} \frac{1}{2} \frac{e^{-D \lambda_m^2 t}}{\lambda_m} - \sum_{m=1}^{\infty} \frac{1}{\lambda_m} \right).  \tag{22}$$

When $t = 0$, hence when $Q = Q_o$, both sides of this equation must vanish. This is seen to be true. As $t \to \infty$, $Q \to 0$; therefore, both sides of the equation must approach -1. This can only be true if
Incorporating this restriction into Equation 22 gives

\[
\frac{Q}{Q_o} - 1 = -1 + \frac{4\pi (C_o - C_b)}{r_b^2 Q_o} \sum_{m=1}^{\infty} \frac{1}{\lambda_m^2} e^{-D\lambda_m^2 t}. \quad (24)
\]

Setting \( \frac{Q}{Q_o} = u \) and \( \frac{4\pi (C_o - C_b)}{r_b^2 Q_o} = R \) gives

\[
u = R \sum_{m=1}^{\infty} \frac{1}{\lambda_m^2} e^{-D\lambda_m^2 t}. \quad (25)
\]

Since the magnitude of \( D \) is not known, it is impossible to test the applicability of this equation as it stands. Therefore, a simplifying assumption must be made. For this purpose all terms in the sum except the first can be assumed to be negligible. The size of the error incorporated by this assumption is difficult to estimate because a correct value for \( D \) is lacking. However, with the \( \lambda_m^2 \) term in the denominator, the series should converge rapidly, particularly at longer times. With this assumption Equation 25 reduces to

\[
u = \frac{R}{\lambda_1} e^{-D\lambda_1^2 t}. \quad (26)
\]

or

\[
\ln u = \ln \frac{R}{\lambda_1} - D\lambda_1^2 t. \quad (27)
\]

Since \( u < 1 \), it is more convenient to use the negative of Equation 27,
\[-\ln u = -\ln \frac{R}{\lambda_1^2} + D\lambda_1^2 t, \quad (28)\]

to test the applicability of this theory. In this equation, \( R \) must equal \( \lambda_1^2 \) to satisfy the initial condition that \( u(0) = 1 \). If \( K \) release from a mineral is accurately described by this equation, \(-\ln u\) should be linearly related to time. Figures 18 and 19 show the relationship between \(-\ln u\) and time for two fractions of muscovite and two fractions of biotite, respectively. In no case is the relation linear.

On the basis of these observations, it is evident that an approximate equation for diffusion without moving boundary restrictions offers no advantages over the equation and model of Reed and Scott. Instead, it is not as useful as the moving boundary equation for characterizing the release of \( K \) from micaceous minerals in NaCl-NaTPB solutions. Under these conditions, the equation of Reed and Scott characterizes the release of \( K \) from 10-20 \( \mu \) samples of muscovite and biotite and to a certain extent the release from < 50 \( \mu \) samples of these minerals, whereas Equation 28, which was developed without moving boundary restrictions, does not (Figure 18). Therefore, attention was again turned to the equation of Reed and Scott.

It must be remembered that although the simplified equation did not describe the release of \( K \) from micaceous minerals in NaCl-NaTPB solutions, the complete equation (Equation 25) has not been tested. Therefore, since the error from truncating the series is quite large at short times, the value of this equation cannot be entirely eliminated until it can be tested more completely. Also, it should be emphasized that the merits
Figure 18. The relationship between $-\ln u$ and the extraction period with two fractions of muscovite
Figure 19. The relationship between $-\ln u$ and the extraction period with two fractions of vermiculite.
of excluding the restriction imposed by a moving boundary have been evaluated with K release data that was obtained with mineral samples in NaCl-NaTPB solutions. This theory may be more applicable to the release of K that occurs under other extraction conditions.

Variable Diffusion Coefficient

In the theoretical equation describing K release from micaceous minerals derived by Reed and Scott (22), the diffusion coefficient, D, was assumed to be constant. In a mineral sample having a wide range of particle size, however, it is possible that different values of D exist in particles of different sizes. This view is supported by the relatively large effect of particle size on K release. Therefore, the effect of generalizing the equation of Reed and Scott to take this possibility into account was considered.

It has been observed that the rate of K release by mineral samples decreases as the amount of K removed increases (Figures 1, 2, and 3). A decrease in D that is associated with a decrease in $r_a$, the radius of the weathering front, for each particle could be involved in this change. However, the applicability of Equation 2 with a constant D to the data obtained with 10-20 μ samples of muscovite and biotite (Figures 5 and 6) rules out this possibility. Therefore, it can be assumed that if a variable D is involved in this decrease in release rate, the various particles must have different D values. Furthermore, since the small particles are completely weathered first and the rate of release increases with time it can be assumed that D is inversely related to the size of the particle. Consequently, D for a sample with a wide range of
particle size would increase with the degradation period because the effect of the smaller particles would disappear.

Each particle in a mineral sample releases K at a characteristic rate that is related to the size of the particle even though other particles of different sizes are also present (24). Thus to characterize the K release behavior of a mixture of particles of different sizes a complex summation procedure would be needed. A simple approximation can be made, however, by characterizing the sample in terms of one "effective" particle size which reflects the behavior of all the particles. Furthermore, this hypothetical particle would have to reflect any effects that arise from a continued removal of the smaller particles from participation in the release of K. In other words, the "effective" $r_a$ of this hypothetical particle will account for the range in particle size and the net effect of the degradation on the particle sizes still participating. A variable diffusion coefficient for the whole sample that is related to particle size must then be accounted for by a differential equation relating the change in diffusion coefficient with the change in this "effective" $r_a$. Also, the diffusion coefficient for the hypothetical particle will be the "apparent" diffusion coefficient for the whole sample.

The change in apparent diffusion coefficient would be directly related to the coefficient itself. Also, to introduce the assumption that D varies inversely with particle size it must be assumed that particles manifest different values of D because they differ in resistance to expansion. This tendency for each particle to expand will be inversely related to the length of the weathering front. Therefore D would be inversely proportional to $2\pi r_a$. 
The change in $D$ with respect to $r_a$ can be written mathematically as

$$\frac{dD}{dr_a} = \frac{kD}{2\pi r_a}$$  \hspace{1cm} (29)$$

remembering that $D$ and $r_a$ are "apparent" diffusion coefficient and "effective" $r_a$ in the hypothetical particle, respectively. The proportionality constant $k$ is a property of a particular mineral. The boundary condition selected for this equation will be

$$D(r_b) = \frac{2\pi b r_b}{k}$$  \hspace{1cm} (30)$$

that is, at the instant weathering begins, the diffusion coefficient will be directly proportional to the particle radius. This is in accord with the size of the force resisting weathering at time zero. Upon integration of Equation 29 and application of the boundary condition, Equation 30, the result is

$$\ln D = \ln \frac{r_a}{r_b} + \ln \frac{k}{2\pi b r_b}.$$  \hspace{1cm} (31)$$

In order to put this equation in terms of $u$, the fraction of the total $K$ remaining, use must be made of a relation employed by Reed and Scott (22)

$$\frac{r_a^2}{r_b^2} = \frac{Q}{Q_0} = u.$$  \hspace{1cm} (32)$$

At this point the "effective" $r_a$, a property of the hypothetical particle, is replaced by $u$, a measurable parameter of the sample. Substituting Equation 32 into Equation 31 results in the expression
\[
\ln D = \frac{k}{4\pi} \ln u + \ln 2\pi br_b \quad (33)
\]

or
\[
D = 2\pi br_b u \frac{k}{4\pi} \quad . \quad (34)
\]

To evaluate the effect of a variable diffusion coefficient, Equation 34 must be substituted into Equation 5 to obtain
\[
\ln u \ du = - \frac{8\pi b u}{r_b \rho S Q_o} (C_a - C_b) \ dt \quad . \quad (35)
\]

Integration of this expression gives
\[
u^m (1 - m \ln u) = 1 - \frac{K'}{K''} t \quad (36)
\]

where \( m = 1 - \frac{k}{4\pi} \) and \( K' = \frac{8\pi b (C_a - C_b)}{r_b \rho S Q_o} \).

Equation 36 differs from that of Reed and Scott (Equation 2) by the parameter \( m \) which is characteristic of the mineral being studied. The value of \( m \) is dependent only on the proportionality constant in Equation 29. This equation is only a generalization of the equation of Reed and Scott since the substitution of \( m = 1 \) reduces this expression to their equation. In this case Equation 34 becomes
\[
D = 2\pi br_b u^o = 2\pi br_b \quad (37)
\]

which shows that for \( m = 1 \), \( D \) is constant. The value of \( m \) is in no way restricted except that Equation 36 cannot be used if \( m = 0 \). However, the substitution of \( m = 0 \) or \( \frac{k}{4\pi} = 1 \) into Equation 35 yields an equation which can be integrated. The equation thus obtained can then be used in place
The value of $m$ that is appropriate for a given mineral cannot be computed directly but must be obtained by graphical solution or other approximate methods. To evaluate the applicability of this equation to K release behavior of minerals, two integer values of $m$ were used. These values were $m = -1$ and $m = 0$. The equation corresponding to $m = -1$ can be obtained directly from Equation 36 and is given by

$$\frac{1 + \ln u}{u} = 1 - K't$$  \hspace{1cm} (38)

which corresponds to $D = 2\pi b_r u^2$. For the case where $m = 0$ Equation 36 fails, thus, Equation 35 with $\frac{k}{4\pi} = 1$ must be integrated. This gives the relatively simple solution

$$\ln^2 u = 2K't.$$  \hspace{1cm} (39)

A plot of the left side of either Equation 38 or Equation 39 against time should give a straight line if the respective equation applies. However, more information can be obtained if $\log \left(1 - \frac{1 + \ln u}{u}\right)$ or $\log (\ln^2 u)$ is plotted against $\log t$. With this type of plot greater emphasis is given to that part of the extraction period when a major portion of the K is released. The curves obtained by these plots should have a slope of unity if the equation is applicable.

Equation 38 failed to describe the release of K from <50 $\mu$ muscovite and <50 $\mu$ biotite, whereas Equation 39 failed to describe the K release from <50 $\mu$ vermiculite and <2 $\mu$ illite. On the other hand, the applicability of Equation 39 to the K release behavior of the muscovite
and biotite samples is evident in Figures 20 and 21. Figures 22 and 23 show the applicability of Equation 38 to the release of K from < 50 \( \mu \) vermiculite and < 2 \( \mu \) illite, respectively. In each case, experimental values of \( \log 1 - \frac{1+1n u}{u} \) or \( \log (1n u)^2 \) are linearly related to \( \log t \) and the slopes of the curves expressing these relationships are approximately one.

Figures 20, 21, 22, and 23 attest to the high degree of success attained in the description of the K release behavior of mineral samples with wide particle size ranges by two equations embodying the concept of a variable diffusion coefficient. Therefore, the K release behavior of mineral samples with a wide range of particle size is similar to that of a hypothetical sample that has one effective particle size and a variable diffusion coefficient.

Figures 7 and 8 show that the K release behavior of 10-20 \( \mu \) vermiculite and illite samples is not described by Equation 2. Apparently, these minerals differ from muscovite and biotite in that samples with a narrow range of particle size do not release K with a constant \( D \). Instead, the behavior of the 10-20 \( \mu \) samples of vermiculite and illite is more comparable to that observed with < 50 \( \mu \) vermiculite and < 2 \( \mu \) illite, respectively. Therefore, a need for testing the applicability of Equations 38 and 39 to the release of K from the narrow particle size fractions of illite and vermiculite was indicated. Figure 24 shows that K release behavior of two narrow size fractions of vermiculite is accurately described by Equation 38. However, Figures 25 and 26 show that the release of K from 10-20 \( \mu \) illite is not described by either Equation 38 or
Figure 20. The relationship between log (ln²u) and the logarithm of the extraction period with < 50 \( \mu \) muscovite
Figure 21. The relationship between $\log (\ln^2 u)$ and the logarithm of the extraction period with $< 50 \mu$ biotite
Figure 22. The relationship between $\log \left[1 - \frac{1 + \ln u}{u}\right]$ and the logarithm of the extraction period with $< 50 \mu$ vermiculite.
Figure 23. The relationship between $\log \left[ 1 - \frac{1+\ln u}{u} \right]$ and the logarithm of the extraction period with $< 2 \mu$ illite.
Figure 24. The relationship between $\log \left[1 - \frac{1 + \ln u}{u}\right]$ and the logarithm of the extraction period with two fractions of vermiculite.
Figure 25. The relationship between $\ln^2 u$ and the logarithm of the extraction period with 10-20 $\mu$ illite
Figure 26. The relationship between log $[1 - (1 + \ln u)/u]$ and the logarithm of the extraction period with 10-20 $\mu$ illite.
Equation 39.

All of the K in the 50-60 μ and 250-300 μ vermiculite samples were not extracted by the NaCl-NaTPB solution. Thus, only the extractable K has been considered in each test involving their K release behavior. On the other hand, all of the K in < 50 μ vermiculite was extractable and included in the test. This selection of the Q₀ value for each sample can be justified on the practical basis that only the release of extractable K can be characterized. However, in the present test of the applicability of the equation based on a variable D, it should be noted that an inaccurate estimate of the total extractable K would affect the value of u and thus the slope of the curve plotted in Figure 24. In other words, the slope of the curve could differ from 1 because Q₀ was inaccurate.

The applicability of Equation 38 to all of the vermiculite samples (Figures 22 and 24) would indicate, however, that this problem was not involved in this study.

The concept of a variable diffusion coefficient applies to vermiculite samples that have wide or narrow ranges of particle size. On the other hand, biotite samples with a narrow range of particle size have a constant D (Figure 6). This difference in the K release behavior of vermiculite and biotite samples must be associated with the mineralogical character of the individual particles. The South Carolina Vermiculite that has been used in this study is primarily an interstratified mineral. Thus, the variable diffusion coefficient exhibited by vermiculite is probably associated with the existence of different diffusion coefficients in the various layers of individual particles. In this event, the
apparent D for the sample would change with the period of extraction (and thus u) because the layers with a large D would be K depleted first. The fact that Equation 38 characterizes the K release behavior of the 50-60 \( \mu \) and the 250-300 \( \mu \) vermiculite samples would indicate that the resulting relationship between D and u is described by Equation 36 when \( m = -1 \).

Since the behavior of < 50 \( \mu \) vermiculite involves the same relationship between D and u, it would appear that there may be a relationship between the size of the particles and the type of layers in the particles. Or, the behavior of the < 50 \( \mu \) and the narrow range vermiculite samples are both governed by a variable D that is associated with the presence of different layers.

Grundite-illite is not well defined minerallogically. However, it is considered to be an interstratified mineral and to some extent a mixture of contracted and expanded micaceous minerals. Figures 25 and 26 show that Equation 36 with \( m = -1 \) or \( m = 0 \) does not describe the K release behavior from 10-20 \( \mu \) illite. However, the complex mineralogical nature of the material may require the use of some other value of m. The greater success attained in describing the release of K from < 2 \( \mu \) illite (Figure 23) can be attributed to the higher degree of mineralogical uniformity expected with micaceous mineral samples that contains only small particles.

The equation incorporating the variable diffusion coefficient (Equation 36) has been shown to be applicable to the K release behavior of several mineral samples. Table 1 indicates the degree of success attained by using this equation for each mineral to which the equation applies. In all cases the release of at least 70% of the extractable K has been explained.
Table 1. Summary of the effectiveness with which Equation 36 describes the K release behavior of several minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$\frac{k^a}{4\pi}$</th>
<th>% extractable K explained</th>
<th>Slope of curve&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 50 μ muscovite</td>
<td>1</td>
<td>75</td>
<td>1.07</td>
</tr>
<tr>
<td>&lt; 50 μ biotite</td>
<td>1</td>
<td>90</td>
<td>1.10</td>
</tr>
<tr>
<td>&lt; 50 μ vermiculite</td>
<td>2</td>
<td>80</td>
<td>1.05</td>
</tr>
<tr>
<td>&lt; 2 μ illite</td>
<td>2</td>
<td>70</td>
<td>0.98</td>
</tr>
<tr>
<td>50-60 μ vermiculite</td>
<td>2</td>
<td>80</td>
<td>1.10</td>
</tr>
<tr>
<td>250-300 μ vermiculite</td>
<td>2</td>
<td>80</td>
<td>1.01</td>
</tr>
</tbody>
</table>

<sup>a</sup> $D = 2\pi br_b u$ (Equation 34).

<sup>b</sup> Theoretical slope is 1.00.

Only two values of $m$ were used in this study. A wider range of applicability may be possible if a relatively simple method of calculating the value of $m$ appropriate to a given mineral could be obtained. Also, the slight departures of the minerals discussed here from the proposed theory may be diminished or removed by a more accurate selection of $m$.

Radius Dependence of Moving Boundary Diffusion Equation

In the theoretical derivation of an equation describing the release of K from micaceous minerals, Reed and Scott (22) found that the term $r_b^2$ (where $r_b$ is the particle radius) was involved. These investigators tested the radius dependence of their equation with K release data obtained with biotite and muscovite samples in NaCl-NaTPB solutions. This test showed that the radius term in their equation should be $r_b$. Scott
and Reed did not account for this discrepancy in their theoretical
treatment, but they suggested that one of the quantities in the term
\( \tau D(C_a - C_b) \) was a function of the radius of the particle.

In the preceding chapter, the equation of Reed and Scott was
generalized by incorporating a variable diffusion coefficient. In doing
so, it was assumed that \( D \) is a linear function of radius. Since this
generalized equation has proven applicable to the K release behavior of
many mineral samples, it is evident that the radius dependent term in
\( \tau D(C_a - C_b) \) is \( D \). Furthermore, when \( D \) is introduced as a linear function
of radius, the resulting equation contains the term \( r_b \) not \( r_b^2 \). Thus,
the conclusions of Reed and Scott concerning the \( r_b \) term have been put on
a theoretical basis.

It may be argued that the equation as applied by Reed and Scott did
not include a variable diffusion coefficient, and that conclusions based
on a consideration of a variable \( D \) are, therefore, not applicable to their
equation. On the contrary, it can be stated that the expression derived
for the diffusion coefficient (Equation 30) is very general, being
undefined only at \( u = 0 \). The equation with a constant diffusion coefficient
(Equation 2) is only a special case of Equation 30 when \( k = 0 \). Therefore,
all of the conditions imposed in the derivation of this equation for the
diffusion coefficient apply whether the \( D \) exhibited by the mineral is
variable or constant.

More experimental evidence for the choice of \( r_b \) rather than \( r_b^2 \) in
the moving boundary diffusion equation was obtained with K extraction data
for two fractions of muscovite. The K extraction behavior of narrow
particle size fractions of muscovite is described by Equation 2, but to test the radius dependence of this equation it must be noted that

\[ K' = \frac{K}{r_b^2}. \]

Therefore, if the curves obtained by plotting \( \log [u(1-\ln u)] \) against \( \log \frac{t}{r_b^2} \) for each muscovite size fraction are coincident, \( r_b \) is the correct radius term for the equation. Figure 27 verifies that this is, indeed, the case with muscovite.

K extraction data for three narrow size fractions of vermiculite were also used in a test of the radius dependence predicted by Reed and Scott. The K release behavior of vermiculite has been described by Equation 32. Therefore, in this case, the curves obtained by plotting \( \log \left[ 1 + \frac{1}{u} \right] \) against \( \log \frac{t}{r_b^2} \) for each fraction should be coincident if \( r_b \) is the correct term. In Figure 28 the K release data for the three vermiculite samples yield the same curve. Thus, \( r_b \) must express the correct radius dependence for this mineral.

The upper end of the vermiculite curve in Figure 28 is curved just as it was in Figure 24 because Equation 32 does not describe the release of the last 20% of the extractable K. However, the K release behavior of all three fractions departed from Equation 32 in essentially the same manner. Consequently, \( r_b^2 \) has been shown to be the correct radius term for Equation 32 even where the equation does not accurately describe K release.

It must be concluded from these results and those of Reed and Scott that the correct radius term in the moving boundary diffusion equations is \( r_b \) rather than \( r_b^2 \).
Figure 27. The relationship between $\log [1-u(1-ln u)]$ and $\log \frac{t}{r_b}$ with two fractions of muscovite
Figure 28. The relationship between \( \log \left[ 1 - \left(1 + \ln u\right)/u \right] \) and \( \log \frac{t}{r_b} \) with three fractions of vermiculite
Fixed K in Vermiculite

Barshad (5), Ellis and Mortland (8), and Reed (20) have observed that K which has been fixed in a mineral is much more easily removed than native K. The kinetics of the extraction of fixed K from vermiculite by leaching with NaCl solutions have been studied by Mortland and Ellis (18). However, the kinetics of the extraction of fixed K by NaCl-NaTPB solutions have not been studied. Therefore, K was added to a sample of 250-300 μ vermiculite which had 70 me. native K per 100 g. The total K of the K-treated vermiculite was 160 me. per 100 g., and the exchangeable K was 4 me. per 100 g. Therefore, if it is assumed that all of the original 70 me. native K per 100 g. is still present, there was 86 me. fixed K per 100 g. in the treated sample. The K in this treated vermiculite was extracted with NaCl-NaTPB solutions and the same methods as were used with other vermiculite samples.

Equation 38 described the release of native K from 250-300 μ vermiculite. Therefore, its applicability to the release of K from the K-treated vermiculite was evaluated. Figure 29 shows that the relation between log \[ 1 - \frac{1+\ln u}{u} \] and log t for this material is linear. Also, the slope of the curve is 1.02. Thus, the applicability of Equation 38 to the release of K from the vermiculite sample has been established.

A curve for the release of native K from the original (untreated) 250-300 μ vermiculite sample is shown in Figure 29 for comparison. This curve is based on the extractable portion of the native K. On the other hand, the data for the treated vermiculite curve were calculated on the
Figure 29. The relationship between \( \log \left[ \frac{1- (1+ \ln u)}{u} \right] \) and the logarithm of the extraction period with fixed and native K in vermiculite.
basis of the total K; thus, this curve includes the release of both fixed and native K. The similarity of the two curves in regard to their relation to Equation 38 and the absence of breaks in the treated vermiculite curve indicates that the release behavior of fixed K is not significantly different from that of native K when the K is extracted with NaCl-NaTPB solutions.

In Figure 29, the treated vermiculite curve differs from the original vermiculite curve in the latter stages of degradation. Whereas the release of native K from the original sample is described by Equation 38 over the removal of 80% of the extractable K, the release of native and fixed K from the treated sample is described over the removal of nearly 100% of the K. Furthermore, it should be noted that 20% of the total K (native) in the original sample was nonextractable. Therefore, the release of only 64% of the total K in the original sample has been described by Equation 38. On the other hand, Equation 38 applies to the release of essentially all of the native K in this sample after it is K-treated. Apparently, the KCl treatment affected the release characteristics of the native K. The explanation for this change in behavior is not known.

Equation 38 may be applicable to the release of fixed and native K in vermiculite samples for the same reasons. It has been suggested that different diffusion coefficients in the various layers of a given particle may be a major factor in these samples. On the other hand, other aspects regarding fixed K must be considered. When vermiculite is placed in KCl, the K concentration at the periphery of the particle would increase
to the point where the lattice would contract even though the interior of the particle is still saturated with Mg or Ca. The fact that the lattice of high charge density minerals like vermiculite can contract and trap interlayer cations has been verified with various micaceous minerals that have been Na saturated and then treated with KCl. As a result, a non-uniform distribution of fixed K in the particle can be expected. That is, the concentration of fixed K in the interlayer space would decrease with the distance from the periphery of the particle. This K distribution should affect the rate of K release observed at different stages of K-depletion. At the beginning of the degradation period there would be a faster release of K because there is a higher concentration of fixed K at the periphery. Thus, the net effect of this nonuniform K distribution in the layers would be similar to that expected with a uniform K distribution but different diffusion coefficients in different layers. The results of the present experiments do not provide a means for determining which situation exists in this sample.

Ellis and Mortland (8) showed that there was a linear relationship between the logarithm of the rate of fixed K release from vermiculite and time when the K was removed by leaching the vermiculite with NaCl solutions. To determine if the same relationship exists for the extraction of fixed K from vermiculite by NaCl-NaTPB solutions, the rate of release of K from the K-treated vermiculite was computed. Figure 30 shows that the logarithm of this rate of release is not linearly related to the time. Thus, it is evident that different types of K release must be involved in the two methods of extraction.

This difference can be attributed to a difference in the K concentra-
Figure 30. The relationship between the logarithm of the rate of fixed K release and the extraction period with 250-300 μ vermiculite
tions of the two extracting solutions. The K concentration in NaCl-NaTPB solutions is controlled by the solubility product of KTPB whereas in the leaching procedure it is controlled by the purity of the NaCl and extent of contact between the NaCl solution and the mineral. Thus, the concentration of K is held at a low level in NaCl-NaTPB solutions whereas it may increase to relatively high values in the NaCl solution.

Effect of NaCl Concentration

Addition of NaCl to NaTPB extraction solutions increases the number of Na ions available for the replacement of K ions in the mineral. However, the NaCl addition may also reduce the solubility of NaTPB. A reduction in the concentration of TPB in the solution will result in an increase in the concentration of K in the extracting solution. Consequently, the rate of K release can also be affected.

The effect of different NaCl concentrations in NaCl-NaTPB extracting solutions was determined with < 50 µ vermiculite samples. As usual, 0.5000 g. vermiculite was placed in 10 ml. of 0.2 N NaTPB-0.01 M EDTA solution. In this experiment however, the NaCl concentrations of the extracting solution was adjusted to 0, 0.3, 0.7, 1.0 and 1.7 N. Also, the temperature of the extracting solution was maintained at 25° C. by means of a water bath.

Three reactions involving Na or K which are important in the extraction of K from a mineral in a NaCl-NaTPB solution can be expressed as follows:
where TPB is the tetraphenylboron ion. The chemical exchange of Na for K on the exchange sites of a mineral is thought to occur instantaneously provided Na ions are present in excess. Therefore, it can be assumed that chemical exchange of Na for K does not control the K level in the extracting solution. Thus, the Na-K concentration interdependency may be determined from the following system of equations provided solid NaTPB and KTPB are present:

\[
[\text{Na}][\text{TPB}] = K_1 \tag{40}
\]

\[
[\text{K}][\text{TPB}] = K_2 \tag{41}
\]

where the brackets denote concentrations of the ions and \(K_1\) and \(K_2\) indicate the solubility product constant for NaTPB and KTPB, respectively. A relation between the Na and K concentrations in the extracting solution in contact with a mineral can be obtained by combining Equations 40 and 41 because the term \([\text{TPB}]\) is common to both. This relation is

\[
[\text{K}] = h [\text{Na}] \tag{42}
\]

where \(h = \frac{K_2}{K_1}\).

Equation 42 shows that an increase in the Na concentration in a NaCl-NaTPB extracting solution will cause an increase in the K concentration.

To determine the quantitative effect of different NaCl concentrations it is necessary to introduce a relationship that describes the K
release behavior of a mineral sample in NaCl-NaTPB solutions. In the case of < 50 μ vermiculite Equation 38 has been found to be applicable (Figure 22). Therefore the Na concentration dependence of the K release behavior may be obtained by substituting h[Na] from Equation 42 for C_b (which is the same as [K]) in Equation 38. This gives

\[
\frac{1+\ln u}{u} = 1 - c (C_a - h [Na])t
\]

(43)

where \( c = \frac{8πbr}{Q_o b_o r_b} \).

Equation 43 can also be expressed by

\[
\log [1- \frac{1+\ln u}{u}] = \log [c (C_a - h [Na])] + \log t
\]

(44)

Therefore, \( \log [1- \frac{1+\ln u}{u}] \) should be linearly related to \( \log t \) for the release of K under any conditions where K release behavior is described by Equation 38.

Figure 31 shows the relationship between \( \log [1- \frac{1+\ln u}{u}] \) and \( \log t \) for K release experiments in which < 50 μ vermiculite is determined by the different Na concentrations (as described by Equation 45). It is evident in Figure 32 that for \( t = 5 \) and \( t = 1 \) a linear relationship does exist.

The values of \( (1- \frac{1+\ln u}{u}) \) for a Na concentration of 1.2 N depart slightly from the straight lines. This can be explained by the fact that these values were obtained in a separate experiment from the rest. It has been observed in many cases that small differences in results will occur if the same experiment is repeated on different days. These
Figure 31. The relationship between log \( \frac{1 - (1 + \ln u)}{u} \) and the logarithm of the extraction period with < 50 \( \mu \) vermiculite and four extracting solutions.
Figure 32. The relationship between \( \log \left[ 1 - \frac{(1 + \ln u)}{u} \right] \) and the Na concentration with < 50 \( \mu \) vermiculite and two extraction periods.
differences are attributed to environmental effects.

The release of K from < 50 µ vermiculite samples in four solutions that differed in NaCl concentration was described by Equation 38. This means that the kinetics of K release by vermiculite was not changed by the NaCl concentration. Instead, different rates of release were achieved by varying the NaCl concentration. Since this effect of NaCl concentration is described by Equation 45 it can be explained on the basis of the solubility products of NaTPB and KTPB. These conclusions are valid, however, only if solid NaTPB and KTPB are present.

Effect of Different Extraction Solutions on Illite Behavior

It has been pointed out that Grundite-illite is not well defined mineralogically. Therefore, a complex K release behavior for this material can be anticipated. This has been the case in this investigation. None of the illite samples released all of their K. Also, none of the equations that have been applicable to the K release of other minerals have completely characterized the release of the extractable K in illite. Therefore, a few exploratory experiments on the effect of different extraction conditions on the K release behavior of illite were carried out to obtain more information about this mineral.

As usual, 0.5000 g. samples of < 2 µ illite were placed in extracting solutions that were 0.01 M in respect to EDTA. However, to vary the intensity of the extraction conditions the following three extracting solutions were used: A. 10 ml. 1.7 N NaCl-0.3 N NaTPB; B. 15 ml. 1 N NaCl-0.067 N NaTPB; C. 10 ml. 0.2 N NaTPB.
The results of this experiment are presented in Figure 33. In this figure the amount of K removed has been related to the logarithm of the extraction period. This was done to give more emphasis to the initial extraction period when most of the K was extracted. Also, linear relationships with this plot have been observed earlier with illite. No significance is attached to the linearity of these curves but the changes induced by the extraction conditions should be more evident with them.

It is evident that each curve in Figure 33 consists of three straight line segments. The third segment of the curves appear to be parallel. The same is true of the first segments, but there are not sufficient data points to warrant definite conclusions regarding these segments. On the other hand, the slopes of the center portion of each curve increased when the intensity of degradation was increased.

These observations suggest that the Grundite-illite used in this study consists of two mineralogically different materials. For one material, the difference in extraction procedures had little effect on the K release behavior of the mineral. This is shown by the fact that the rate of K release was the same for each procedure over the range of time represented by the third segment. On the other hand, the rate of K release from the other material (second segment) increased as the intensity of the extraction was increased.

If two materials having different mineralogical properties are present, characterization of the K release behavior of this mineral will be difficult. It has been shown (Figure 23) that an equation derived on the basis of a variable diffusion coefficient (Equation 38) describes
Figure 33. K removed from < 2 μ illite in different extraction periods with three extracting solutions
the release of K over the range of the second segment of the curve for Extraction A in Figure 33. However, if the release of all of the extractable K is to be characterized, different assumptions may be needed for each material present. This will require more information about the mineralogical composition of <2 μ illite.
SUMMARY

A theoretical equation

\[
\frac{Q}{Q_0} \left(1 - \ln \frac{Q}{Q_0}\right) = 1 - \frac{4\tau D (C_a - C_b) t}{Q_0 \rho \delta r_b}
\]

was derived by Reed and Scott (22) to describe the K release from circular mica particles in solutions containing NaTPB. \(Q\) is the amount of K remaining in the particles at time \(t\), \(Q_0\) is the total amount of K in the mineral, \(\tau\) is the width of the interlayer space, \(D\) is the diffusion coefficient, \((C_a - C_b)\) is the concentration gradient over the weathered part of the particle, \(\rho\) is the density of the mica, \(\delta\) is the basal spacing of the mica, and \(r_b\) is the radius of the particle.

The applicability of this equation to fractions of several minerals has been evaluated. The release of K by narrow size fractions of muscovite and biotite is described by the equation over the removal of a large amount of the K. However, the K release behavior of < 50 \(\mu\) fractions of these minerals is described only over the release of a relatively small amount of the K. For vermiculite and illite, the equation is not applicable to either wide or narrow particle size range samples.

When the K release is plotted against the logarithm of time, the curves for vermiculite and illite are similar in that each consists of a series of straight line segments. On the other hand, the curves for muscovite and biotite are smooth. However, since this type of plot has no theoretical significance, no conclusions can be drawn from this observation.
It has been found that smaller particles are degraded faster than larger particles even though larger particles are present. Therefore, in a mineral sample with a wide range of particle size, the average radius of particles releasing K increases as degradation proceeds. An equation was derived on the basis that this average or "effective" radius varies linearly with the fraction of the K left in the mineral. Also, it was assumed that the "effective" radius increased from the average of the maximum and minimum radii at the beginning of the degradation to the maximum radius when all the particles were degraded. It was shown that this equation does not describe K release from < 50 μ muscovite.

A determination of the particle size distribution of < 50 μ muscovite revealed that the number of particles of a given size was more closely related to the logarithm of the radius than to the radius itself. On this basis, a second modification of the equation of Reed and Scott incorporating a logarithmic change in the "effective" radius was made. Again, the effective radius was assumed to increase from the initial average radius to the maximum radius. The resulting equation was also inapplicable to < 50 μ muscovite.

It was then assumed that the selection of the initial effective radius may have been incorrect. The initial effective radius that would allow the equation with a linear change in "effective" radius to describe K release from < 50 μ muscovite was determined. This value, 2 μ, corresponded closely with the minimum radius of the particles of this sample. When this minimum radius rather than the average radius was used as the effective radius at the beginning of the degradation, the equation
described $K$ release from $<50 \mu$ muscovite whether a linear or logarithmic change in radius was employed. However, the $K$ release behavior of $<50 \mu$ vermiculite was not described by this equation when the minimum particle radius was used. Therefore, it was concluded that the usefulness of the concept of a variable effective radius with $<50 \mu$ muscovite was not due to the radius correction as such but was due to the introduction of a term $K/r^2_b$ in the equation of Reed and Scott that was dependent on the fraction of $K$ removed. Consequently, attention was turned to terms in $K$ that might vary with the amount of $K$ removed.

First, however, in view of the success of Ellis and Mortland (8) and Mortland and Ellis (18) in describing $K$ release from micaceous minerals without the use of moving boundary restrictions, a similar approach was considered here. An equation was derived based on the model of Reed and Scott except that the moving boundary restrictions were not included. Since this equation contained an infinite series an approximate equation was obtained by truncating the series. This approximate equation did not describe the $K$ release from any of the minerals studied. Therefore, it was concluded that this equation did not offer any advantages over the moving boundary equation. Instead, it was less applicable than the moving boundary equation which has been shown to apply to the release of $K$ from a number of mineral fractions.

It has been stated that some quantity other than $r^2_b$ in the $K/r^2_b$ term of the equation of Reed and Scott may be a function of the fraction of the $K$ remaining in a mineral. It was noted that the rate of $K$ release decreased faster than predicted by the equation of Reed and Scott.
this basis it was assumed that particles of different sizes may have different diffusion coefficients, and these diffusion coefficients may be inversely related to the particle radius. Therefore, as degradation progresses, the smaller particles (with the largest D) would be degraded first, and the apparent D for the whole sample would increase. A hypothetical sample was defined which would consist of particles of one radius, but would reflect all the properties of an actual sample with a wide range of particle size. For the hypothetical sample, the diffusion coefficient would be a function of the extent to which the degradation had proceeded. An equation was derived for this relationship between the apparent diffusion coefficient and the degree of K removal. This expression was incorporated for the apparent D into the equation of Reed and Scott, to obtain a new equation which contained one parameter, m, which could be selected in accordance with the nature of the mineral studied.

It was found that setting m = 0 allowed the equation incorporating a variable diffusion coefficient to describe the release of K from < 50 μm muscovite and biotite over the removal of more than 75% of the K. A similar equation where m = -1 described the K release behavior of < 50 μm vermiculite and < 2 μm illite over the removal of a considerable amount of the K. Therefore, it can be concluded that this modification of the equation of Reed and Scott is very effective in describing the release of K from mineral samples with a wide range of particle size.

The equation incorporating a variable diffusion coefficient was also tested with vermiculite samples with a narrow particle size range. This sample did not satisfy the assumption regarding range of particle size
that was made in the derivation of the equation with a variable diffusion coefficient. Nevertheless, the equation accurately described the K release behavior of these materials over the release of 80% of the K. This was explained on the basis that the diffusion coefficient varies from one layer to the next in a single particle as well as from one particle size to the next.

The theoretical equation of Reed and Scott contains a particle radius term $r_b^2$. These investigators found experimentally that the correct term was $r_b$, not $r_b^2$. They suggested that some quantity in the term $\tau D (C_a - C_b)$ was directly proportional to $r_b$. The derivation of the equation for the variable diffusion coefficient just described brought out the fact that the diffusion coefficient was linearly related to $r_b$. Therefore, the replacement of $r_b^2$ with $r_b$ in the theoretical equation derived by Reed and Scott has been put on a theoretical basis. To corroborate that $r_b$ is the correct term, two narrow size fractions of muscovite and three narrow size fractions of vermiculite were used to test the radius dependence of the moving boundary diffusion equation. It was found that $r_b$ was the correct term for both minerals.

The moving boundary diffusion equation involving the variable diffusion coefficient described the release of nearly all the fixed and native K in 250-300 μ vermiculite. On the other hand, only 64% of the native K in the untreated sample was described by this equation. Thus, the K treatment must have affected the release character of the mineral in regard to the native K.

The release of fixed and native K from the treated vermiculite was
described by the same equation. Thus, the variability in the diffusion coefficient for the two forms of K was comparable. In the case of native K this variability was associated with different diffusion coefficients in the various layers. The same explanation may apply to the fixed K. On the other hand, a nonuniform distribution of fixed K would be anticipated since trapping of other cations in the interior of the particles occurs when vermiculite is treated with KCl. The relative importance of this nonuniform distribution and a variable diffusion coefficient has not been determined.

Mortland and Ellis (18) showed that the release of fixed K in vermiculite by leaching with NaCl solutions could be expressed by a linear relation between the logarithm of K release rate and time. This relation was not observed for fixed K release from vermiculite in NaCl-NaTPB solutions. This can be explained by the difference in the concentration of K in the two extracting solutions.

The effect of the NaCl concentration in NaCl-NaTPB extracting solutions on K release was studied with five extracting solutions differing only in NaCl concentration. The moving boundary diffusion equation with a variable diffusion coefficient described the K release observed with all extracting solutions. However, the amount of K released in a specified period decreased when the NaCl concentration was increased. This decrease has been attributed to the effect of Na on the K concentration in the extracting solution and explained in terms of the solubility product constants for NaTPB and KTPB when solid NaTPB and KTPB are present in the solution.
When the K release from < 2 μ Grundite-illite was plotted against the logarithm of the extraction period for three extracting solutions, a curve composed of three straight line segments was obtained in each case. The last segments of the three curves were parallel, whereas the slope of the second segment increased when a solution that extracted K with a greater intensity was used. This suggests the presence of two materials in this sample. The rate of release of K from one of these materials increased with the intensity of the extraction whereas that from the other material is unaffected. A complete description of this complex K release behavior of Grundite-illite will require more information concerning the mineralogical nature of this material.

In conclusion, it can be stated that a very applicable moving boundary diffusion equation with a variable diffusion coefficient has been developed. By proper selection of the functional relationship between the diffusion coefficient and the degree of degradation, the release of over 75% of the K from muscovite, biotite, and vermiculite samples with a narrow or wide range of particle size can be accurately described. Although the release of over 70% of the extractable K in < 2 μ illite has been described by this equation, little success has been achieved with 10-20 μ illite.
LITERATURE CITED


ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. A. D. Scott for his advice and assistance during the course of these studies and in the preparation of this manuscript.