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Contents:

Structure and Weathering of Potassium Containing Minerals

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1. Introduction

The soil as an ingredient of the pedosphere is a part of the ecosphere which envelops the Earth and in which the life of plants, animals and man is based. This ecosphere is an open and dynamic system in which gains and losses of energy and materials are in dynamic equilibrium. Potassium in the plant root/soil system can be looked at in a similar way; it is also part of an open and dynamic system in which gains and losses are involved in transformation and translocation processes *(Schroeder [1974, 1978])*.

I shall discuss here the structure and weathering of the K containing minerals, especially the 'primary' pyrogenic minerals which constitute the source of all other potassium, whether it be found in high concentration in the potash deposits, in the water of the sea, rivers, soil or rainfall, in living plants or decaying vegetable matter or adsorbed on the mineral and organic colloids of the soil.

Potassium, comprising 2.6% of the lithosphere – the Earth's crust – is the seventh most abundant element and, after iron, calcium and sodium is the fourth most abundant mineral plant nutrient (Figure 1). Through weathering, potassium is set free to the soil which has a K content varying between <0.1 and $>3\%$ K, most frequently about 1%. These orders of K content result in total K contents in the soil ranging between <3000 and $>100\,000$ kg K/ha in the upper 20 cm of soils *(Schroeder [1976])*. Out of this total K content, more than 98% is bound up in the minerals while less than two per cent is found in organically bound or adsorbed form or in the soil solution.

Though plants can take up potassium only in the 'available' form, *i.e.* solution and adsorbed potassium, the mineral potassium constitutes a very large reserve and, even though this can be mobilised only to a variable extent, it is of the greatest importance.

Thanks to the great progress which has been made in the field of mineral analysis (X-ray analysis, electron microscopy, microprobe, infra-red spectroscopy and thermal

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analysis) we are today well informed about the structure and chemistry of the K-containing-minerals.

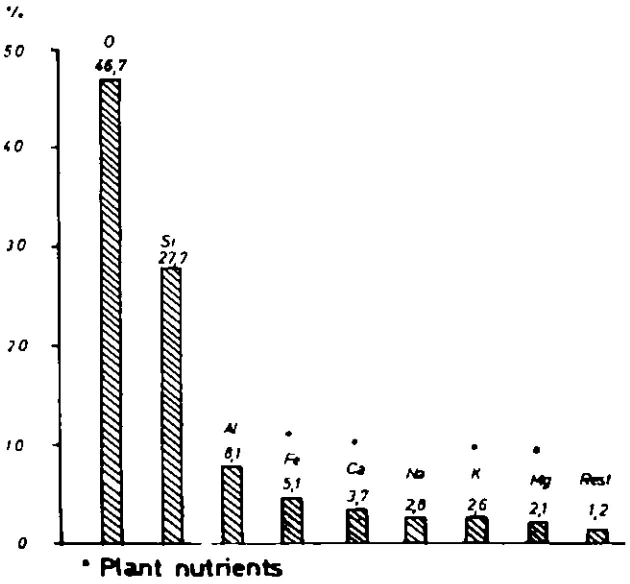

Fig. 1. Average chemical composition of the lithosphere (weight %).

2. Survey of K-containing minerals, mineral structure and bonding strength

2.1 K-containing minerals

Potassium combined in minerals is found predominantly in 'primary' and 'secondary' crystalline silicates and only to a small extent in non-crystalline (amorphous) or para-crystalline compounds (*v.* Section 5).

The K-feldspars, at about 16%, compared with the K-micas at about 5.2%, predominate *(Ahrens [1965])*. Among the micas, biotite (at 3.8%) is more abundant than muscovite (1.4%). However, in sediments formed by weathering, transport and deposition, which cover 75% of the world's dry land and of which the majority of soils consist, this situation is usually reversed because biotite is less stable to weathering *(v.* Section 4.4). Secondary K-containing minerals, typified by illite and the transitional clay minerals, are found in such variable proportions that no quantitative generalisation can be made. This holds also for the K-containing minerals in the soil. Their contents vary greatly depending upon parent rock and the conditions under which the soils have been formed, for example, podsols formed on glacial sands contain only a small percentage of feldspar, mica and illite; chernozems formed on young pleistocene loess contain 15% feldspars, 10% micas and 6% illites and transitional minerals *(Bronger, Kalk* and *Schroeder [1976])*.

2.2 Mineral structure

The structural units of the crystalline silicates are predominantly SiO_4^{4-} tetrahedra (Figure 2 left) and, in lesser quantity $Al(OH)_6^{3-}$ octahedra (Figure 2 right). In these tetrahedra and octahedra the small central Si^{4+} ions (diameter 0.78 Å)* and Al^{3+} ions (diameter 1.14 Å) are surrounded by large O^{2-} ions** (2.64 Å) and OH^- ions (2.77 Å) so the centres of the O and OH ions form the points of the tetrahedron or octahedron as the case may be (Figure 2). Thus, in the silicon tetrahedra, we have 4-coordination and, in the Al octahedra, 6-coordination. Si^{4+} in the tetrahedra can be substituted by Al^{3+}, and Al^{4+} in the octahedra by Mg^{2+} and Fe^{2+}, resulting in stronger negative charges on the tetrahedra and octahedra (Sections 3.1, 4.1 and 4.3).

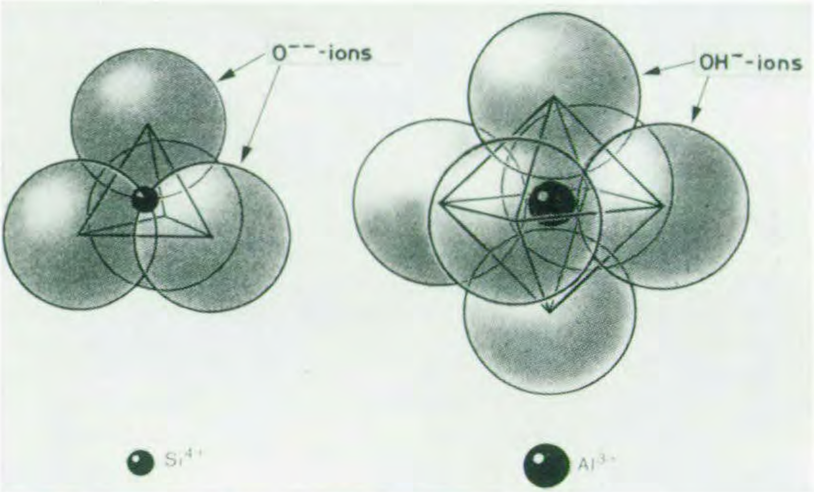

Fig. 2. Si-O-tetrahedra (left), Al-OH-octahedra (right).

According to the kind of bonding between tetrahedra among themselves and with octahedra, various crystalline structures can be formed and, among these, the only ones of interest to us are the framework structure of the feldspars (tectosilicates) and the layer structure of micas, illites and transitional clay minerals (phyllosilicates). Figure 3 illustrates the arrangement of Si-O-tetrahedra in the ideal framework structure of quartz. Owing to the mutual cross linkage of SiO_4^{4+} tetrahedra through O-bridges in three dimensions, each Si^{4+} unit is associated with 4 half O^{2-} units and the resulting crystalline lattice is electrically neutral; the general formula is $(SiO_2)_x$. From this basic structure, the structure of feldspar can be derived *(v.* 3.1).

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* $1\ \text{Å} = 10^{-4}\ \mu m = 10^{-7}$ mm.

** The designation 'ion' is not quite correct since the oxygen is in a state intermediate between atom and ion *(v.* 2.3).

Fig. 3. Simplified tetrahedral arrangement in the framework structure of quartz *(Mackenzie [1975])*.

Figure 4 shows diagramatically the layer structure of mica, here still without K ions. Each layer consists of two sheets of tetrahedra enveloping an octahedral sheet. The sheets are bonded via O bridges. The tetrahedra of each sheet are joined at their apices and form a hexagonal or ditrigonal arrangement of O ions on the outer surfaces, above and below, into which K ions can be installed, and adjoining layers are linked together through these *(v.* 4.1 and Figures 8 and 12). The octahedra are not linked through the apices but at the edges and are in close packing.

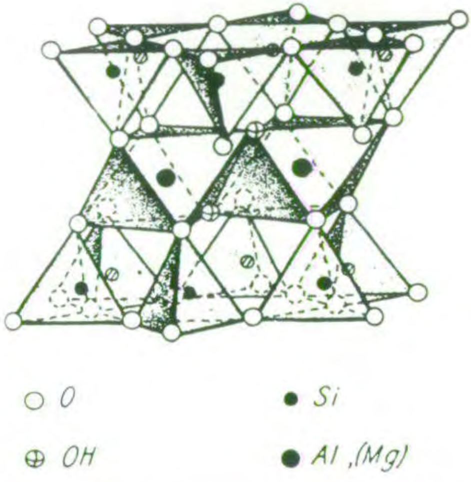


Fig. 4. Model arrangement of tetrahedra and octahedra in a mica layer *(Jasmund [1976])*.

As well as the crystalline silicates there are non- or paracrystalline silicates in which the units are arranged with little or no order *(e.g.* allophane, *v. 5.1*).

2.3 Bonding strength

The bonding within the tetrahedra and octahedra and between them is of a type intermediate between heteropolar and covalent. For instance, in the Si-O-tetrahedra the bonds are 50% ionic and 50% covalent *(Bach [1972])*. When Si in the tetrahedra is replaced by Al the bonds are 63% ionic *(Correns [1968])*. As the size of the central ion increases and charge decreases, bonding strength is reduced, whether in tetrahedra by replacement of Si^{4+} by Al^{3+} or in octahedra by replacement of Al^{3+} by Mg^{2+} or Fe^{2+} (Si–O > Al–O > Mg–O). It is also influenced by other substituents remaining in the framework or layer structure.
The monovalent K ion has a large diameter (2.66 Å), the largest of the mineral nutrients. It is therefore less strongly bound than smaller ions and those of higher charge. Because of its size, the K ion can be enveloped by 7–12 O^{2-} ions in the various minerals (*v.* 3.1 and 4.1), so that the strength of each K–O bond is correspondingly weak *(Rich [1968])*.

3. Potassium in feldspars

3.1 Chemistry and structure

The feldspars are potassium aluminosilicates, their general formula being $KAlSi_3O_8$, according to which the theoretical K content is 14%. However, in naturally occurring feldspars the Si : Al ratio is never exactly 3 : 1 and part of the potassium can be replaced by sodium (and to a lesser degree by calcium) so that the actual K content is always below 14%. The central Si^{4+} ion is replaced by Al^{3+} in one of every four tetrahedra in the lattice: $AlSi_3O_8^-$ compared with $Si_4O_8^o$ in quartz. One K^+ ion is incorporated into the crystal lattice to compensate for the resulting excess negative charge. Thus the tetrahedra form 4-jointed rings forming zig-zag chains and these in turn are joined through O-bridges and as a result a framework structure is preserved. This configuration results in large interstices, which are occupied by K ions in 8-coordination with O-ions. For a survey of the literature of the chemistry and structure of feldspars see *Huang [1977]*, *Radoslovich [1975]*. *Ribbe [1975]*, *Rasmussen [1972]*, among others.

The following polymorphs can be distinguished among feldspars of varying detailed structure and origin:

Orthoclase:	monoclinic-prismatic, in plutonic rocks, normal arrangement of tetrahedra
Sanidine:	monoclinic, less ordered high temperature modification, mainly in volcanic rocks
Microcline	triclinic, well ordered low temperature modification, consisting of magmatite-pegmatite

Adularia: similar to orthoclase, mainly found in lodes and fissures.

All the above four polymorphs have the general formula $KAlSi_3O_8$. The following Na-containing form is also found:

Anorthoclase: (K, Na)$AlSi_3O_8$ and furthermore the so-called 'substituted feldspars'
Leucite: $KAlSi_2O_6$ cubic, with lower Si and higher K content (up to 18%)
Nepheline: (Na, K)$AlSiO_4$ hexagonal-pyramidal, containing more Na than K.

Plagioclases: (Ca, Na-feldspars) may also contain small amounts of potassium.

Feldspars of the formula $KAlSi_3O_8$ have a hardness of 6 on the MOHS scale and the substituted feldspars a hardness of 5½ to 6.

3.2 Weathering

Chemical weathering of feldspars by which K ions are released is of dominant importance but physical weathering is an important prerequisite as it is through this that the feldspars are freed from the parent rock and, with decreasing grain size, their specific surface increases so that chemical weathering can intensify.

Temperature and frost are especially important in physical weathering. Cryoclastic breakdown, due to ice formation, can produce feldspar particles of fine silt (6.3–2 μm) or coarse clay (2–0.6 μm) size.

The small particle size, with high specific surface, favours hydrolysis – chemical reaction with H^+ and OH^- ions of water – and protolysis (or acidolysis) – attack by H^+ ions (or protons) of various acids – *(Pedro [1973], Scheffer* and *Schachtschabel [1976])*. The acids concerned are mainly H_2CO_3 and several organic acids formed in the decomposition of organic matter, and also strong inorganic acids like H_2SO_4 and HNO_3 (as a result of the oxidation of reduced S- and N-compounds).

Weathering of feldspars is incongruent (*v. Engelhardt [1976]*) that is, not all parts of the mineral are dissolved simultaneously *(cf.* NaCl or $CaCO_3$) but weathering operates first on the weakly-bound K ions at surface sites and only later attacks the more stable Al- and Si-tetrahedra.

Figures 5 and 6 clearly illustrate this phenomenon. An aqueous solution of pH 3 was percolated through finely-ground feldspar and Figure 5 shows the total amounts

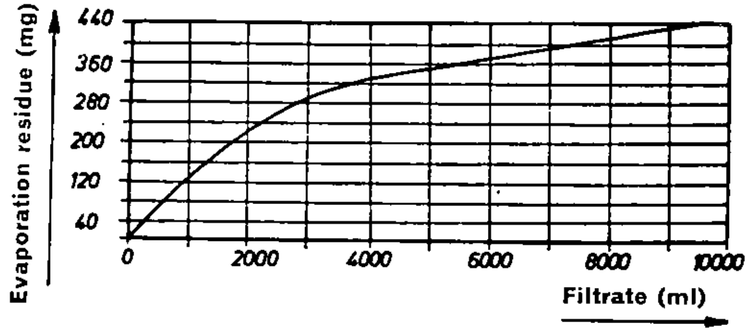


Fig. 5. Dissolution of K feldspar in aqueous solution, pH 3 *(von Engelhardt [1976])*.

dissolved. Dissolution is rapid initially and then approaches equilibrium. Figure 6 shows the composition of the dissolved material; in the early stages predominantly potassium is dissolved and, as percolation proceeds, aluminium and silicon follow. The substances are liberated in the ionic form for they can pass a collodion membrane. The unweathered portion of the particles becomes enveloped in a shell rich in silicon and low in K and Al which hinders futher weathering.

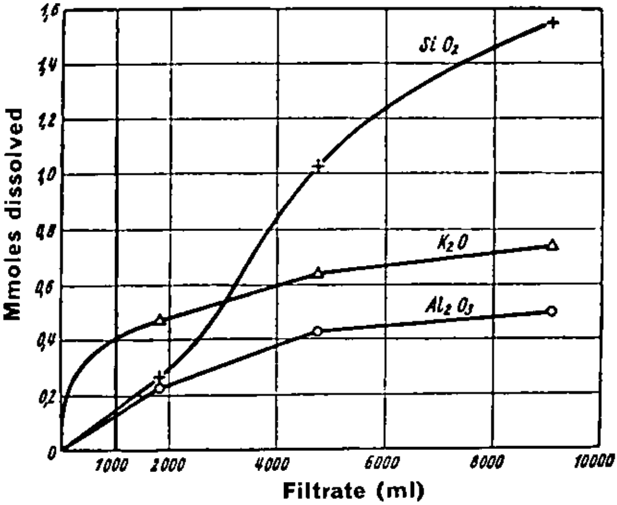


Fig.6. Behaviour of potassium, aluminium and silicon in the dissolution of K feldspar in aqueous solution at pH 3 *(von Engelhardt [ibid.])*.

The hydrolysis (without excess H^+ ions) can be represented in simplified form as follows:

$KAlSi_3O_8 + HOH = HAlSi_3O_8 + K^+ + OH^-$ (rapid first step)
$HAlSi_3O_8 + 4HOH = Al(OH)_3 + 3H_2SiO_3$ (second very slow reaction)

The addition of free H^+ ions leads to increased liberation of K ions and to the rupture of Al-O bonds so that the liberated Al is then found as $AlOH_2$ groups in 4-co-ordination:

$$\equiv\text{Si-}\underset{\substack{|\\ \text{K}}}{\text{O}}\text{-Al}\equiv + H_2O + H^+ \rightarrow \equiv\text{Si-}\underset{\substack{|\\ \text{H}}}{\text{O}} + \equiv\text{Al-OH}_2 + K^+$$

The breaking of the strong Si-O-Si bond probably results from the attachment of OH^- ions to Si as Si-OH groups. In this way the covalent double bond is broken *(Bach [1972], Scheffer* and *Schachtschabel [1976])*.

Another possible way in which Si-O and Al-O linkages might be broken is the chelation (formation of soluble complexes) of Al and Si by phenols, ketones and aliphatic and aromatic acids formed in the humification of plant material or excreted by plant roots *(Bach [1972], Huang [1977])*.

Marshall [1977] proposed a joint reaction of H_2O and H^+ ions in the breakdown of orthoclase according to:

$$3\ KAlSi_3O_8 + 12\ H_2O + 2\ H^+ = KAlSi_3O_6 \cdot Al_2O_4(OH)_2 + 2\ K^+ + 6\ H_4SiO_4$$

Pedro [1973] proposes the following scheme for the weathering of orthoclase to kaolinite:

$$2\ KAlSi_3O_8 \xrightarrow{H_2O} Al_2Si_2O_5(OH) + 2\ K^+ + 2\ OH^- + 4\ H_4SiO_4$$

The final weathering products of feldspar (aluminium hydroxide, silicic acid, allophane, kaolinite, beidellite and mica-type minerals) are not of immediate concern within the present terms of reference. The important point is that first of all the K at exterior sites is rapidly liberated, further potassium will only be released from internal sites after breaking of the stable Al–O and Si–O bonds which involves destruction of the Si rich protective shell *(v.supra)*. This is only about 3.10^{-5} mm thick but is most effective in protecting the feldspar crystal from further weathering *(Correns [1968])*.

3.3 Factors concerned in weathering and its consequences

The many factors that influence the weathering of feldspars can be divided into two groups, internal and external. The following are among the internal factors:

a) *Regularity* of the crystal lattice. Microcline is more stable to weathering than sanidine and orthoclase,
b) *Na content* of crystals: Anorthoclase weathers more easily than orthoclase,
c) *Si content:* Substituted feldspars are less stable than feldspars,
d) *Particle size:* The smaller the particles the greater is the surface exposed to hydrolysis and acidolysis.

The following are some of the external factors:

a) *Temperature:* Weathering processes proceed more rapidly at higher temperature,
b) *Solution volume:* Wet conditions favour weathering,
c) *Migration of weathering products*, so that disequilibrium is preserved; weathering is hindered if these products accumulate,
d) *The formation of difficulty soluble products of hydrolysis* which are precipitated and shift the equilibrium to the right,
e) *pH value:* The higher the H^+ ion concentration the more intensive protolysis (and neutralisation of the freed OH ions),
f) *The presence of chelating agents* and the formation of soluble complexes which migrate,
g) Intensive *K uptake* by higher plants, reducing the K concentration of the soil solution so that K release is favoured.

One more important factor should be mentioned: *time*. The longer conditions remain favourable to weathering the greater will be the breakdown and dissolution of feldspar. The various factors will be met with in all kinds of combinations so that it is easy to understand the variation in findings quoted in the literature, any given results are only strictly applicable to the prevailing natural or experimental conditions.

As a generalisation it can be said that appreciable amounts of K will be liberated from feldspar only when weathering is very intensive, notably in the humid tropics *(Pedro [1973])*. But under such conditions the feldspars are also substantially destroyed (*e.g.* in latosols) and are then no more able to serve as a source of reserve K. Figure 7 illustrates strong weathering of a microcline particle.

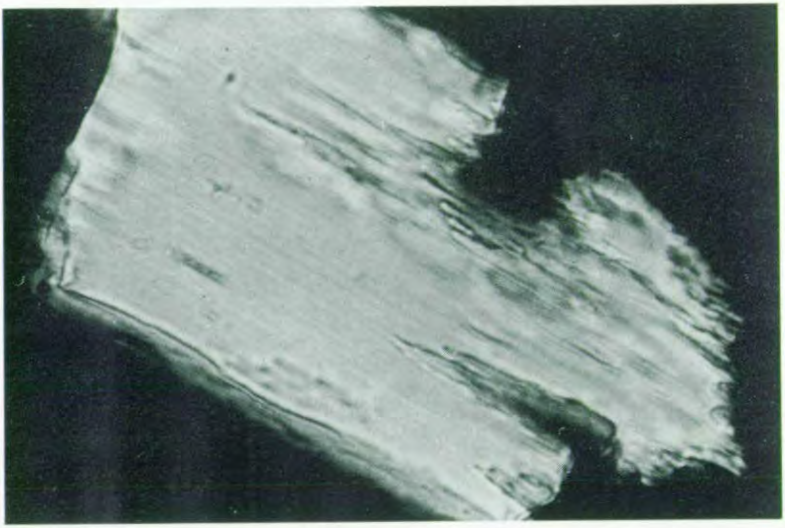


Fig. 7. Microcline particle (about 100 µm) showing evidence of strong dissolution. Nigerian Latosol. Photo *Kalk*.

Little weathering of feldspar occurs in temperate climates. For example, in young soils formed from young pleistocene loess containing 15–20% feldspars, the feldspar content of the top soil is at the most only 5% below that of the parent material. In a brown earth from middle pleistocene loess the loss of K feldspar was up to 8% *(Bronger et al. [1974], Bronger* and *Kalk [1976])*. In coarse-grained glacial sands the breakdown can be greater; however, even here, K feldspars – particularly microcline – can withstand relatively intense weathering. *Jensen* and *De Coninck [1977]* identified feldspars in the clay fraction of a podsol over 1000 years old.

With *Rasmussen [1972]* we can conclude that in the temperate zone the feldspars constitute a very large but rather inaccessible potassium reserve.

4. Potassium in micas, illites and transitional clay minerals

4.1 Chemistry and structure of K micas

The potassium containing micas are, like feldspars, potassium aluminosilicates, but their composition is more complex. They are phyllosilicates and contain along with the Si tetrahedra Al octahedra with varying substitution of the central ions (2.2 and Figure 4). In the ideal case, in the tetrahedra each 4th Si^{4+} is replaced by Al^{3+} and, as in the feldspars, the resulting excess negative charge is neutralised by the entry of K^+ ions (1 K^+ to 4 tetrahedra). These K ions are enclosed in an interlayer position (Figures 8 and 12) so that each K^+ ion is surrounded by 12 O^{2-} ions (*v.* 2.3) in the 6-rings of the adjoining tetrahedra (6 on each side) (see also Figure 14).

In the octahedral sheet two of the three octahedra are filled with Al^{3+} ions (dioctahedral mica, with one 'empty' octahedron) or the three octahedra are filled with three Mg^{2+} or Fe^{2+} ions (trioctahedral mica, all octahedral positions filled). According to chemical composition, colour and origin, the following micas can be distinguished:

Muscovite:	$KAl_2(AlSi_3)O_{10}\ (OH)_2$, dioctahedral, plates, bright coloured, derived from magmatites and pegmatites
Sericite:	Like muscovite but finer grain, mainly of metamorphic origin
Biotite:	$K(Mg,\ Fe^{2+})_3(AlSi_3)O_{10}(OH)_2$, trioctahedral, plates, dark in colour; derived from magmatites, pegmatites and metamorphites
Phlogopite:	$KMg_3(AlSi_3)O_{10}(OH)_2$, trioctahedral, transparent plates of pneumatolytic origin, furthermore
Lepidolite	and
Zinnwaldite:	with additional lithium in the octahedra.

The formulae represent in the 1st position the interlayer-K, in the 2nd octahedral central ions, in the 3rd tetrahedral central ions and in the 4th and 5th the O- and OH-ions of the tetrahedra and octahedra. The K content of muscovite should theoretically be 9.8% and that of biotite 8.7%. However, such contents are practically never found in natural micas because the centres of the tetrahedra and octahedra are variously occupied and the average negative charge per unit never reaches one unit (= 1 K^+) and, also, K in the interlayer positions can be substituted by Na or Ca. Conversely, the Na mica *paragonite* and the Ca mica *margarite* may also contain some K.

The micas are easily fissible and have a relatively low hardness of 2–3 on the MOHS scale.

4.2 Weathering of micas

Physical weathering is an important first step as it is with the weathering of feldspars. The succeeding chemical weathering is even more incongruent than it is in feldspars. Chemical weathering starts with the exchange of K in interlayer positions which is relatively weakly held by H^+ and H_3O^+ (oxonium) ions *(cf.* 2.3 and 4.1). The process starts from the edge of the crystal as shown schematically in Figure 8.

The dissolution of K^+ ions does not proceed on the whole surface, as in feldspar, but zonally at exchange-fronts which penetrate further into the particle as weathering proceeds *(von Reichenbach [1972, 1976])*. This is well seen in Figures 9 and 10. Figure 9 illustrates a biotite particle from which interlayer potassium has been removed experimentally by ion exchange with Ba. Several interlayer positions are already freed of potassium and expanded; the waves to the right of the biotite platelet show how far the exchange of potassium has proceeded in the upper layers. Figure 10 shows the breakdown of a biotite particle by natural weathering showing separation into several 'books' of layers.

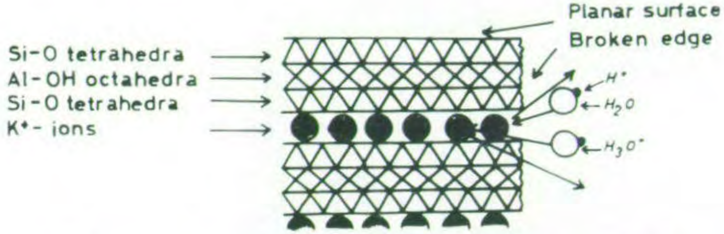
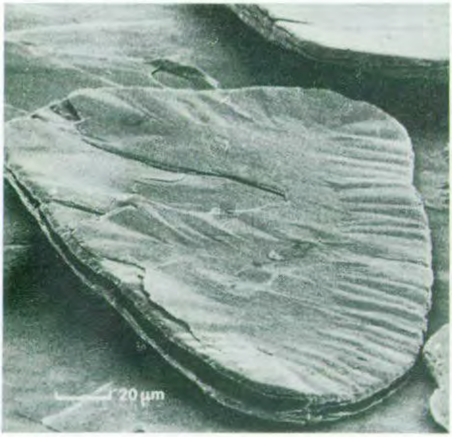


Fig.8. Release of K^+ ions by H_3O^+ ions from muscovite crystal lattice.



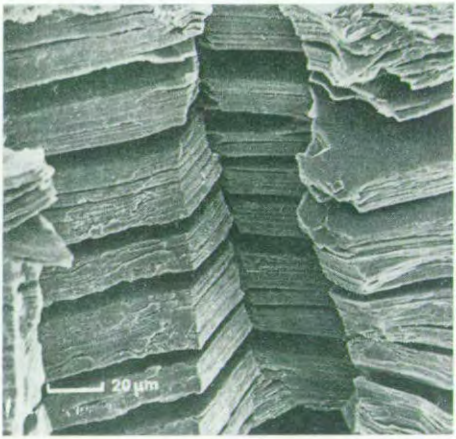


Fig.9. Scanning electron micro-photograph of a biotite particle after experimental extraction of interlayer potassium *(von Reichenbach [1976]).*
Fig.10. Scanning electron micro-photograph of the edge of naturally weathered biotite *(von Reichenbach [1976]).*

The expansion caused by removal of potassium (wavy area in Figure 9) promotes physical weathering (by fracturing) leading to the production of smaller particles. In this manner, by physical and chemical weathering, illite clay minerals develop from the micas via the intermediate stage of hydrous mica – if the mean particle size is less than 2 µm – and further reduction in particle size (about 0.2 µm, *Tributh [1976]* and withdrawal of K leads to the so-called transitional clay minerals and further to the K free minerals montmorillonite (smectite) and vermiculite. Figure 11 represents the process of transformation of micas to clay minerals with the setting free of potassium in a schematic fashion.

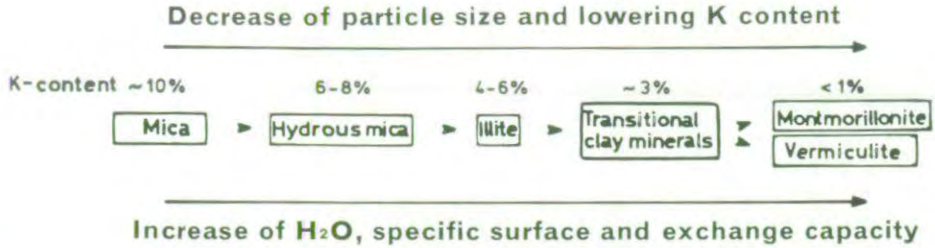


Fig. 11. The transformation of mica to clay minerals with corresponding release of K.

In addition to the most important weathering processes so far described in which K is released from the interlayer positions, destruction of the octahedra and tetrahedra by protolysis is also possible; as a result Mg-, Fe and Al-ions are freed from the crystal lattice and this can bring about intensified K release *(Feigenbaum* and *Shainberg [1975])*.

4.3 Chemistry and structure of illite and transitional clay minerals

The name illite will be used here in *Grim*'s original sense to mean micaceous minerals found in the clay fraction. The meaning of 'transitional clay minerals' is taken to include all clay minerals intermediate between the illites and the montmorillonites and vermiculites. For discussion of the nomenclature, origin and properties of this miscellaneous class of minerals, see *Fanning* and *Keramidas [1977]* and *von Reichenbach* and *Rich [1975])*.

Examples of the chemical composition of illite are given in the following formulae *(cf. Fanning* and *Keramidas [1977] Scheffer* and *Schachtschabel [1976])*.
Dioctahedral illite (derived from muscovite)

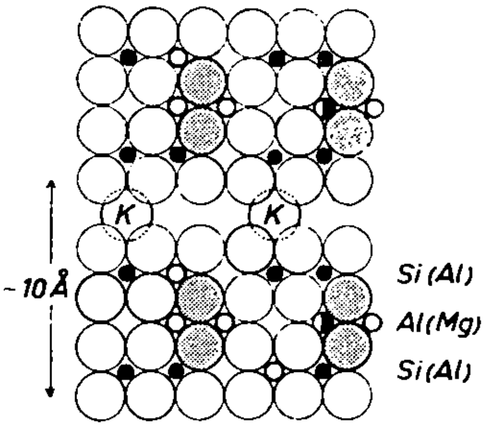
$C = +0.75 \qquad -0.25 \qquad\qquad -0.50$

$(K_{0.58}X_{0.17})\,(Al_{1.55}Fe^{3+}_{0.20}Mg_{0.25})\,(Al_{0.50}Si_{3.50})O_{10}(OH)_2\ .\ n\ H_2O$

X denotes cations which, following the removal of potassium from interlayer positions, are bound at edge sites in exchangeable form to preserve electrical neutrality.
The general structure of illite is similar to that of muscovite (Figure 12 *cf.* Figures 4 and 8); but substitution in the tetrahedra (Al for Si) is less and, instead of containing only Al, the octahedra also contain Fe^{3+} and Mg^{2+}. There thus arises a negative excess charge (C) of −0.75 per formula unit *(cf.* the formula for muscovite in 4.1) so, in order to restore neutrality, cations equivalent to the charge +0.75 *(i.e.* potassium and exchangeable ions) are bound and adsorbed in the interlayer sites. In the example given, these comprise 0.58 parts potassium not yet removed by weathering plus 0.17 exchangeable ions.
Trioctahedral illite (derived from biotite):

$C = +0.66 \qquad +0.39 \qquad\qquad -1.05$

$K_{0.45}X_{0.21}\,(Mg_{2.61}Fe^{3+}_{0.10}Al_{0.29})\,(Al_{1.05}Si_{2.95})O_{10}\,(OH)_2 \cdot n\ H_2O$



Illite

Fig. 12. Schematic illustration of the structure of illite with two layers and interlayer-K (*Scheffer* and *Schachtschabel [1976]*).

Tetrahedral substitution is somewhat higher than in biotite (*cf.* biotite formula in 4.1); thus the octahedra here contain 0.39 parts Fe^{3+} and Al^{3+} in place of divalent ions, resulting in excess positive charge which leads to a total negative charge on the tetrahedra and octahedra of -0.66 which is neutralised by 0.45 parts interlayer potassium (coming from the biotite) plus 0.21 parts exchangeable cations.

Dioctahedral *glauconite*, of very variable composition, is also a mica-like clay mineral but should not be regarded as a mica derivative as it originates from marine sediments and is distinguished from dioctahedral illite in that it has a high Fe^{3+} content in the octahedra and besides K^+ also, Na^+ and Ca^{2+} ions in the interlayer positions.

As can be seen from Figure 11, transitional clay minerals can be derived from illite by further weathering and these are variously structured (Figure 13). The transitional minerals comprise: edge-expanded illite, expanded illite and interstratified minerals made up in regular or irregular manner by mixed layers of illite, montmorillonite or vermiculite. The lower their K content and the higher the substitution of the central ions of the tetrahedra the less useful are they as potassium sources, but they are, on the other hand, capable of *fixing* potassium from the soil solution in their interlayer spaces (*v. van Diest*'s paper in this volume).

4.4 Factors influencing weathering and their consequences

As with the feldspars, internal and external influences should be distinguished. The internal factors are peculiarities of structure (dioctahedral and trioctahedral structure and particle size) while the most important external factors are the same as in the case of feldspar (*cf. van Diest*, in this volume) and in addition the kind and concentrations of ions in the soil solution and the redox potential (see Section 4.4.3).

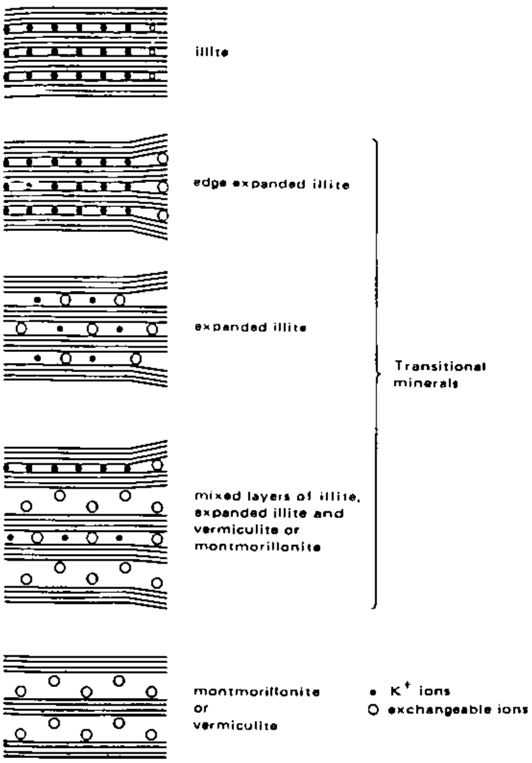


Fig. 13. Schematic illustration of the transitional minerals between illite and montmorillonite or vermiculite.

4.4.1 Dioctahedral and trioctahedral structure

Given equal particle size, the di- or trioctahedral structure of micas and illites determine the ease with which they weather.

The ideal hexagonal arrangement of tetrahedra is not possible for steric reasons (Figure 14 left, *cf.* Figure 4) because the tetrahedra cannot exactly match the octahedra (*v.* ion sizes in 2.2 and Figure 2). In order to form a layer structure with the octahedra, the tetrahedra must rotate to some extent and thus form a ditrigonal arrangement (Figure 14 right). Due to this, the 12 coordination of the O^{2-} ions around the K^+ ions (*v.* 4.1) changes to 2 × 6 coordination through which positions 2, 4 and 6 in Figure 14 (right) cause stronger bonding (because of the shorter K–O distance) than positions 1, 3 and 5. As, in trioctahedral biotite and illite, all the centres of the octahedra are occupied by divalent ions, and in dioctahedral muscovite and illite only two out of three centres with trivalent ions (with one empty octahedron), the configuration of O ions in the tetrahedra of dioctahedral minerals is shifted increasingly towards a ditrigonal arrangement on account of the increased asymmetry of the charges in the octahedra (more rotation of the tetrahedra) and this results in K

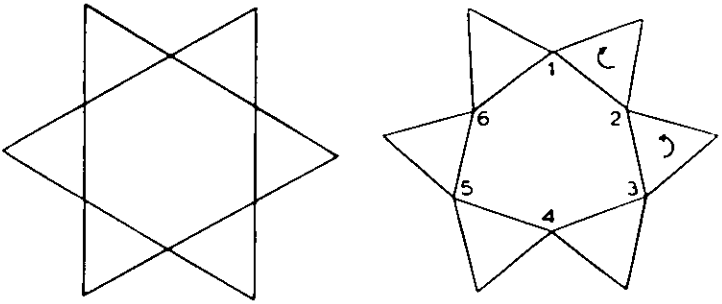


Fig. 14. Ideal hexagonal (left) and actual ditrigonal arrangement (right) of tetrahedra in micas and illites *(Rich [1972])*.

being more strongly held in the interlayer positions. Thus, muscovite and the dioctahedral clay minerals are more stable to weathering than biotite and its derivatives. The different structure of di- or trioctahedral minerals also affects the influence of the octahedral OH ions on the intensity with which K is held between the layers. Because they are strongly dipolar, the OH ions in trioctahedral minerals (with equal charge in the surrounding centres) are perpendicular to the basal plane (Figure 15 top left); in the dioctahedral minerals they are, on the other hand, markedly inclined

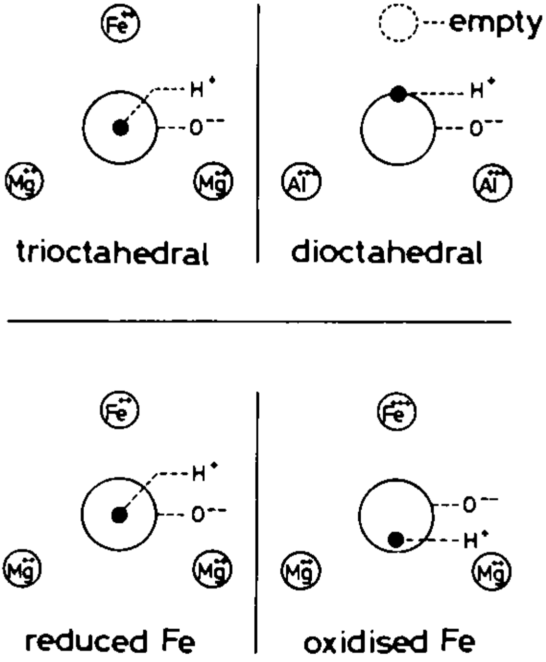


Fig. 15. Effect of composition of octahedral sheet of micas on OH dipole moment; dioctahedral vs. trioctahedral (above) and oxidation of Fe^{2+} to Fe^{3+} (below) *(Rich [1972])*.

to the basal plane as a result of charge asymmetry (Figure 15 top right). Thus the repulsion of the K^+ ions in the interlayer by the positive poles of the OH dipoles is weakened so that the K^+ ions in dioctahedral micas are more strongly held than in trioctahedral minerals. Muscovite and its derivatives are for these reasons also more stable to weathering than biotite and its derivatives.

The difference in stability is well illustrated in Figure 16 which gives the results of extraction by tetraphenylborate of muscovite and biotite of equal particle size.

Orientation of the OH dipole can also be influenced in trioctahedral minerals by the oxidation of Fe^{2+} ions (Figure 15 bottom). When Fe^{2+} is oxidised to Fe^{3+} the OH dipole is inclined to the basal plane as a result of unequal charge distribution thus the repelling effect on the interlayer K is less *(v. supra)*.

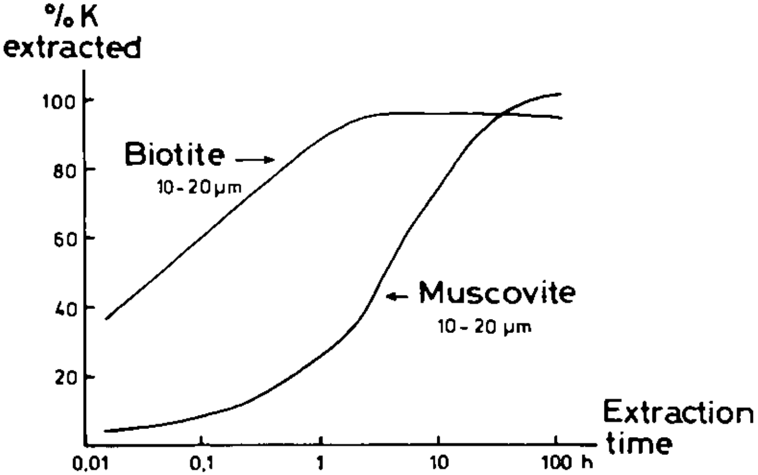


Fig. 16. K extraction by tetraphenylborate from muscovite and biotite of equal particle size *(Scott [1973])*.

An increase in positive charge due to oxidation (with consequent reduction in negative charge and weaker K bonding) could operate counter to this effect. However, it has several times been confirmed that there is no lowering of the negative charge through Fe^{2+} oxidation.

A possible explanation is found in electron transfer from Fe^{2+} to OH^- with loss of hydrogen through which there is no alteration in charge though K bonding is strengthened due to elimination of K repulsion. A more likely explanation is the loss of protons (H^+ ions) from the OH^- ions of the octahedra which would also result in K being more strongly held without any change in charge *(Ross* and *Rich [1974], Veith* and *Jackson [1974])*.

The influence of oxidation of octahedral Fe^{2+} ions has not yet been fully clarified. It has been established that spontaneous oxidation of Fe^{2+} follows experimental

K liberation and that the ratio of adsorbed Fe^{2+} and Fe^{3+} ions influences the oxidation of lattice Fe^{2+} *(Beyme* and *von Reichenbach [1977].*

The influence of the site of negative charges is also unclear. It would be expected that, in all micas and their derivatives, increased substitution of central ions in the tetrahedra would result in K being more strongly held between the layers. However, this has not been widely confirmed. On the other hand, charge site has an influence on the fixation of added potassium *(van Diest,* in this volume). There is no doubt of the connection between total negative charge and the intensity with which interlayer K is held.

The first two structural aspects (ditrigonal arrangement of tetrahedra and orientation of OH dipoles) are the main causes of differences in stability to weathering of muscovite and biotite.

4.4.2 Particle size

Dependance of K liberation on particle size is not as clear in the phyllosilicates as with feldspars. True enough K liberation by weathering is generally greater the smaller the particle size but several workers *(Fanning* and *Keramidas [1977], von Reichenbach* and *Rich [1975])* have contradicted this general view. It has been established that interlayer K is initially released rapidly from large mica crystals due to the preferential liberation of K from the interlayers between adjoining bundles of layers *(cf.* Figure 10). On the other hand, smaller illite particles initially give up interlayer K quite readily, though as liberation proceeds the remaining K is held more strongly and the K in specific interlayer sites is relatively strongly bound. Several explanations are offered for this behaviour. Very probably, expansion and curvature of the layers at the edges – by the entry of larger exchangeable ions – (Figure 9 and expanded illite in Figure 13) with corresponding entrapment of K ions further in is responsible. It is also possible that protons of the OH dipoles in the expanded zones are directed towards free sites so that the K ions in the adjoining interlayer are held more strongly *(Norrish [1973]* see also 4.4.1).

4.4.3 External factors

In general external factors have effects on weathering of phyllosilicates similar to those on feldspars but, because the mica-type minerals function as ion exchangers and some contain Fe^{2+}, the following factors are also important:

a) *Ionic composition of the soil solution:*
A low K content and high content of other easily adsorbed ions (mainly Al^{3+} under acid conditions and Ca^{2+} under near neutral to slightly acid conditions) favour K release *(Laudelout,* in this volume). If a critical threshold K concentration is exceeded and the ratio of K^+ to other cations is high, not only will K release be constrained but K may become fixed *(van Diest,* in this volume). The critical K concentration is higher for the trioctahedral illites and transitional minerals than for the dioctahedral clay minerals *(Fanning* and *Keramidas [1977]).*

b) *Redox potential:*
At high redox potentials more Fe^{2+} in the trioctahedral minerals can be oxidised; this results, among other things, in the biotites and their derivatives being more stable at high than at low redox potential (see 4.4.1).

4.4.4 *Consequences*

Resulting from the differing stability to weathering of di- and trioctahedral phyllosilicates, biotite and its derivatives weather more rapidly than muscovite and its derivatives. Though there is great variation according to location, the content of dioctahedral phyllosilicates is usually higher in soils than that of the trioctahedral. Above all, because of the instability of trioctahedral phyllosilicates, the total phyllosilicate content of soils is usually below that of feldspars, though higher mica content is found in some parent material. In loess soils of the temperate region many investigations *(Bronger et al. [1976])* have shown that the phyllosilicates ($>2\mu m$) decay 1.2–1.8 times as fast as the feldspars (comparing the original loess with surface soil). In strongly weathered tropical soils only the more stable muscovite – if phyllosilicates are present at all – can, after feldspars, play any part as K sources *(Pedro [1973])*.

Figure 17 gives an example of the decline in phyllosilicate ($>2\mu m$) and feldspar content in the formation of a recent chernozem from the parent loess. Although the course of decline in absolute content is parallel, the relative decline in phyllosilicate content is greater. This tendency was expressed more strongly in some other soils but interpretation was more difficult because the loess was not vertically homogenous. *Von Reichenbach* and *Rich [1975]* give a comprehensive review of phyllosilicate content and distribution in various sediments and soils under different climatic conditions.

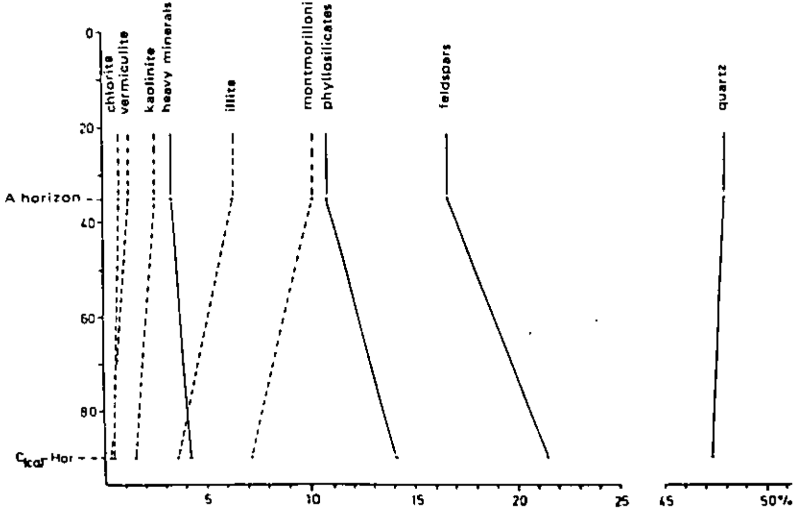


Fig. 17. Mineral distribution in a recent chernozem (Stillfried) developed from young pleistocene loess *(Bronger et al. [1974])*.

5. Allophanes

5.1 Chemistry and structure

Non-crystalline (amorphous) or para-crystalline mineral substances, which arise predominantly from the weathering of volcanic ash, tuffs, pumice and glasses but also by the weathering of primary and secondary silicates, are, here, designated as *allophanes.* They can also be encountered as stages in the formation of new clay minerals from the end products of silicate weathering. Because, in the sense of the present discussion, they are not strictly K-containing minerals (like feldspars, micas, illites and transitional minerals) but are mainly of interest for the part they play in the adsorption of potassium and other ions, they will only be treated briefly. The K content of allophane is very low, only around 0.1% in various representative allophanes *(Sticher [1972]).*

Summaries of the chemistry and structure are given by *Fieldes* and *Claridge [1975]* and *Wada [1977].* Allophanes are hydrous aluminosilicates of varying composition. They contain discrete Si tetrahedra and Al octahedra with Al–O–Si bonds, but without any regular arrangement. Their molar ratio SiO_2/Al_2O_3 lies between 1 and 2. Allophanes are found as weathering products of porous volcanic rocks *(v. supra)* mainly in the fine clay fraction of andosols.

The *imogolites* are often classified with allophane, though they have more defined chain and tube-like paracrystalline structure and a closer SiO_2/AlO_3 ratio (but no significant K content). The *zeolites* have a more framework-type structure (but very irregular and with large cavities containing water). Among the zeolites found in soils derived from volcanic material only *phillipsite* contains some potassium as well as sodium.

Amorphous substances can also occur as end products of silicate weathering and the destruction of clay *(Tributh [1976])* and these can give rise to crystalline clay minerals, *(e.g.* kaolinite and halloysite) by rearrangement of the structural units. *Gebhardt [1976]* found in temperate climates these amorphous substances covering surfaces of clay minerals.

5.2 Potassium relationships

Because the non- or paracrystalline substances mentioned above contain almost no potassium, they are not of prime importance to the present discussion. However, they are important in K adsorption since the allophanes have a high cation exchange capacity (40–100 meq/100 g) and they show high selectivity for potassium ions (as the succeeding paper will show).

6. Summary

This survey of the K-containing minerals has dealt with their chemistry and structure and their transformation by weathering.

The widely occurring K *feldspars* ($KAlSi_3O_8$) are framework-structured tectosilicates; they are generally relatively stable to weathering. In the early stages they easily and rapidly release edge situated K but are then very resistant to further weathering. Under intensive weathering (in the humid tropics) they are much more rapidly broken down and constitute a good K source. In the temperate zone they make up a large but difficultly available K reserve.

The micas are phyllosilicates with layer structure; they are less stable to weathering. The trioctahedral *biotite* – $K(Mg, Fe^{2+})_3AlSi_3O_{10}(OH)_2$ – weathers much more rapidly than the dioctahedral *muscovite* – $KAl_2AlSi_3O_{10}(OH)_2$ –. The same holds for the di- and trioctahedral *illites* and *transitional clay minerals* formed in the weathering of mica, which lead to the K-free clay minerals montmorillonite (smectite) and vermiculite. The trioctahedral minerals are very rapidly broken down under intensive weathering (in the humid tropics) and then only the dioctahedral muscovite approaches feldspar as a K source. In the temperate zone the biotites and their derivatives are the more readily accessible K sources. Because of the difference in stability, the ratio muscovite to biotite in the soil is the reverse of that in the parent material.

The non-crystalline or paracrystalline *allophanes* (including imogolite and zeolite) which mainly arise from porous volcanic material contain little or no potassium. They are significant not as K sources but because of their significance in K adsorption.

Significant advances in the identification and description of the K-containing minerals have been made possible by improvements in research methods (X-ray analysis, electron microscopy, electron microprobe, infra-red spectroscopy and thermal analysis).

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The Physical Chemistry of Equilibria Involving the Potassium Ion in Soils

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Various theories have been proposed during the past fifty or sixty years to give a quantitative description of the ionic exchange reactions in which potassium takes part. There is a simple reason for the attention given to these reactions: the exchange of potassium between the surface of the soil colloids and the soil solution controls concentration in the latter, while the reverse exchange is a preliminary to the incorporation of potassium in the crystalline lattice (retrogradation or fixation) and contributes to the prevention of loss by leaching. The theories have had both empirical and fundamental bases. The more fundamental are those founded directly upon chemical thermodynamics.

Consider the following example of ionic exchange (a very common one in soils) written in the form of a chemical reaction:

$$\text{Soil K} + \text{Ca}^{2+} \rightleftarrows \text{Soil Ca} + 2\text{K}^{+} \qquad \text{(i)}$$

The symbols K^+ and Ca^{2+} have the same meaning as in any ordinary electrochemical reaction, soil K and soil Ca representing amounts of soil providing two equivalents of exchange capacity whose negative charges are balanced by the ions K^+ or Ca^{2+}. The expression describes the conservation of electrical charge in the system and the conservation of matter present before and after the exchange reaction. As the anions of the salts whose cations are exchanged take no part in the exchange reaction there is no need to include them in the model even though the systems represented to left or right of the expression cannot actually exist. Finally the reversibility symbol $\rightleftarrows$ is important, signifying as it does that the distribution of K^+ in the presence of Ca^{2+} between the soil solution and the soil colloid surface is the same whether the exchange reaction proceeds from left to right or *vice versa*. If this is really so then the methods of chemical thermodynamics may be rigourously applied. In the case of potassium, the effect of reactions commonly known as 'fixation' is that true reversibility will not be observed experimentally. Such behaviour is not confined to the exchange of potassium in soils: the variation in the accessibility of exchange sites according to the direction of the reaction can cause irreversibility but this is easily eliminated, the reaction of H^+ ions with the crystalline lattice of clays does not rule out the thermodynamic treatment of exchange reactions in which hydronium ions take part. It is

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the same for potassium. Since the empirical descriptions of ionic exchange reactions can be related to the thermodynamic treatment, it is with the latter that we shall begin.

The thermodynamics of ionic exchange

The thermodynamic study of chemical reactions in general and of ionic exchange is in point of fact very straightforward. The difficulties and abstractions involved are only apparent. If it is accepted that, according to the second law of thermodynamics, it is impossible starting with a system in equilibrium to obtain net work, it is useful to define a function of the condition of the system (defined by pressure, temperature and its chemical composition) such that its change is equal to the net work done in any transformation. Clearly, if the system is in equilibrium such change must be zero. Perhaps the application of this concept to an extremely simple system will make this clearer. Imagine a mass m resting on a plane surface. Assuming that the state of this system can be completely defined by its height h above the plane surface, we can define a function $f = mgh$ the change of which δf is equivalent to the net work done. If for a given displacement δh the corresponding $\delta f = 0$, that is if there is no change in height above the plane, the mass is in equilibrium. If f is negative, the mass has fallen and the reverse is the case if f is positive. These excessively simple considerations may allow us to understand that when it is the composition which defines the state of the system one can use a function which has the same characteristics as f in exactly the same way: it can only be defined in relation to a given reference level and its sign and magnitude show whether the system is at equilibrium or approaching or receding from equilibrium. Such a function is the chemical potential, μ, and this is defined more simply and less explicity that the function f above. The meaning of the chemical potential of the Ca^{2+} ion in the earlier example (i) is the increase of the capacity of the system to furnish work when one Ca^{2+} ion is added. This extremely simple definition, and inexact if taken literally, is sufficient to meet the needs of this discussion. Returning to equation (i) describing ionic exchange between Ca^{2+} and K^+, if a potassium ion passes from the soil solution to the colloid surface, the net energy change of the system involved in this process is $2\mu'_K - 2\mu''_{K^+}$ where μ' refers to the chemical potential in the solution and μ'' to the surface phase, similarly in the case of calcium the change will be $\mu''_{Ca^{2+}} - \mu'_{Ca^{2+}}$. From this viewpoint, therefore, the balance of the exchange (ΔG) is:

$$\Delta G = 2\mu'_{K^+} - \mu'_{Ca^{2+}} + \mu''_{Ca^{2+}} - 2\mu''_{K^+} \qquad \text{(ii)}$$

The chemical potential is only defined in comparison with a given reference level. Put in another way, it is only differences in chemical potential that matter. In just the same way, in topography, heights are only measurable as differences and their numerical values can be compared when related to a known reference level. Such a reference level will be constant within a country, but neighbouring countries may not use the same reference. Similarly for the two phases (soil solution and colloid surface) in which potassium may exist it is possible to choose different reference levels for the expression of its chemical potential.

As the choice of reference level is arbitrary it can be dictated by convenience only, one may use for instance the same reference for the two phases: colloid surface and solution, whatever it is.

It is useful at this stage to bring in the definition of a new function, that of 'activity' which is derived from the chemical potential. If the index $^{(o)}$ is assigned to the chemical potential corresponding to the state of the system chosen as reference the activity is defined thus:

$$\mu_{K^+} = \overset{(o)}{\mu}_{K^+} + RT \ln a_{K^+}$$

where R is the gas constant and T the absolute temperature. The reason for choosing this relation to define this new function is that it replaces a difference in values of a function by a ratio as a result of its logarithmic nature. By introducing the concept of activity into the expression of ΔG above (ii) it becomes:

$$\Delta G = 2\overset{(o)}{\mu'}_{K^+} - 2\overset{(o)}{\mu''}_{K^+} + \overset{(o)}{\mu''}_{Ca^{2+}} - \overset{(o)}{\mu'}_{Ca^{2+}} + RT\ln \frac{a'^{2}_{K^+} \cdot a''_{Ca^{2+}}}{a''^{2}_{K^+} \cdot a'_{Ca^{2+}}} \qquad \text{(iii)}$$

The first four terms can be grouped as one expression $\Delta G^{(o)}$. Then, at equilibrium we shall have:

$$\Delta G = 0$$

and consequently

$$\Delta G^{(o)} = -RT\ln \frac{a'^{2}_{K^+} \cdot a''_{Ca^{2+}}}{a''^{2}_{K^+} \cdot a'_{Ca^{2+}}} \qquad \text{(iv)}$$

If identical reference levels have been chosen to describe the chemical potentials in the soil solution and at the colloid surface we would have:

$$\overset{(o)}{\mu'}_{K^+} = \overset{(o)}{\mu''}_{K^+} \quad \text{and} \quad \overset{(o)}{\mu'}_{Ca^{2+}} = \overset{(o)}{\mu''}_{Ca^{2+}}$$

and consequently:

$$\Delta G_o = 0$$

and $a'^{2}_{K^+} \cdot a''_{Ca^{2+}} = a''^{2}_{K^+} \cdot a'_{Ca^{2+}}$

Here we must introduce a third definition, that of the activity coefficient which is such that:

$$f_{K^+} \cdot C_{K^+} = a_{K^+}$$

where C_K is the concentration of potassium whose numerical value will depend upon the units in which the concentration is expressed. The choice of unit is quite arbitrary.

Now, taking the symbol γ for activity coefficient in solution and f for activity coefficient in the adsorbed state:

$$\gamma_K^2 \, C'^2_{K^+} \cdot f_{Ca} \, C''_{Ca^{2+}} = f_K^2 \, C''^2_{K^+} \, \gamma C'_{Ca^{2+}} \qquad \text{(v)}$$

The choice of the standard state which defines the level to which change in chemical potential is related or with reference to which the activities are measured can be made so that in dilute solution we have:

$$\gamma_{K^+} = \gamma_{Ca^{2+}} = 1$$

Then, we have:

$$\frac{a''_{K^+}}{\sqrt{a''_{Ca^{2+}}}} = \frac{C'_{K^+}}{\sqrt{C'_{Ca^{2+}}}}$$

which is the so-called 'ratio law'.
If the soil solution is assumed to contain only salts of the cations Ca^{2+} and K^+ and concentrations are expressed in milli-equivalents per litre, if C_o is the value for this concentration, we shall then have:

$$C'_{Ca^{2+}} = \frac{C_o}{2}(1-\alpha)$$

$$C'_{K^+} = C_o \, \alpha$$

where α is the proportion of the K^+ ion in the soil solution. Similarly, if β is the proportion of the K^+ ion adsorbed on the surface of the colloids which have an adsorption capacity of B mE per g.

$$C''_{Ca^{2+}} = \frac{B}{2}(1-\beta) \text{ and } C'_{K^+} = \beta \cdot B$$

Then the equilibrium condition becomes:

$$\frac{C_o}{B} \, \frac{\alpha^2}{1-\alpha} \cdot \frac{1-\beta}{\beta^2} = \frac{f^2_K}{f_{Ca}} \qquad \text{(vi)}$$

Conclusions can be drawn from this relationship about variation of the proportion of K^+ in the soil solution with its total salinity or with the cation exchange capacity. The relationship has important practical consequences for plant nutrition. Unfortunately they are not quantitative for reasons which are all too evident: they only indicate that the activity coefficient ratios of the adsorbed cations are effectively constant. The treatment of results on the basis which has just been described is usually presented as a consequence of the Donnan equilibrium but we have seen that it is just a consequence of the thermodynamic treatment of ionic exchange choosing identical references for the chemical potentials of adsorbed and solution ions, the consequence of this choice being that the value of ΔGo is always zero whatever may be the ionic exchange under consideration.
However, it is of use in accounting for some well known experimental facts such as,

for example, that the Mg^{2+} ion displaces reaction (i) less towards the right than does Ca^{2+} or, in other words, that Ca^{2+} has a higher affinity for the soil colloids.

The quantitative expression of this selectivity is quite possible in the Donnan equilibrium because the ratios f_{Ca}/f^2_K and f_{Mg}/f^2_K are not identical. It is, however, more convenient to dispose of a scale in the measurement of the substitution capacities of the cations, one pair in relation to the others, just as in the study of oxidation-reduction reactions the redox couples are classed in such a way that it is possible to predict in which direction the reaction will go when two redox systems interact. It suffices to choose different reference levels for the surface and the soil solution such that the balance, $\Delta G(o)$ is not always zero. We shall then have for the exchange under consideration a characteristic value as, for example, for the following exchange reaction:

$\text{Clay} - K + Ca^{2+} \rightleftarrows \text{Clay Ca} + 2K^+$
$\Delta G^{(o)} = 1$ kcal per equivalent

This arrangement permits the use of an inherent property of thermodynamic functions of the type $\Delta G^{(o)}$ which has just been defined: the change involved in the passage from state A to state B is dependent of the path by which it proceeds.

Suppose we are faced with the problem of the experimental determination of $\Delta G^{(o)}$ for the exchange between Mg^{2+} and K^+ and that for one reason or another this measurement is difficult or impossible. The alternative is to proceed in two stages: first the replacement of K in the soil by the Ca^{2+} ion, then the replacement of Ca^{2+} by the Mg^{2+} ion. The net result of both operations being the exchange of K^+ by Mg^{2+} as shown in the following equations:

$\text{Soil K} + Ca^{2+} \rightleftarrows \text{Soil Ca} + 2K^+$ (1)
$\text{Soil Ca} + Mg^{2+} \rightleftarrows \text{Soil Mg} + Ca^{2+}$ (2)
$\text{Soil K} + Mg^{2+} \rightleftarrows \text{Soil Mg} + 2K^+$ (3)

If $\Delta G^{(o)}$ is known for reactions (1) and (2) it can be calculated for reaction (3).

It would be the same if we had measurements of the heats of exchange for reactions (1) and (2); this would suffice to obtain that for reaction (3). This demonstrates the predictive value of the thermodynamic method and of a simple method for checking experimental findings. Clearly, if the heats of exchange are measured for all three reactions, the values observed should be such that the sum of the first two is equal to the third.

We have not yet considered how to obtain the value of $\Delta G^{(o)}$ when it has been decided not to choose the same reference levels for adsorbed and solution ions. It is a condition of the thermodynamic equilibrium that the chemical potentials of the cations must be the same in solution and in the adsorbed states, but, if they are measured in relation to different reference levels, the activities are no longer identical. The condition of the equilibrium

$$\Delta G^{(o)} = -RT \ln \frac{a'^2_{K^+} \cdot a''_{Ca^{2+}}}{a''^2_{K^+} \cdot a'_{Ca^{2+}}}$$

can be written:

$$\Delta G^{(o)} = RT\ln K_c - RT\ln \frac{\gamma^2_{K^+}\ f_{Ca^{2+}}}{\gamma_{Ca^{2+}}\ f^2_{K^+}}$$

where K_c is a selectivity coefficient defined by

$$K_c = \frac{C'^2_{K^+}\ C'_{Ca^{2+}}}{C''^2_{K^+}\ C'_{Ca^{2+}}}$$

and γ and f are the activity coefficients in the solution and adsorbed phases respectively. There is nothing in the above treatment to dictate the units in which the concentrations should be expressed; the only guide is experimental convenience. The selectivity coefficient is an experimental value and if, at a given value of the ratio $C'^2_{K^+} / C'_{Ca^{2+}}$ in the solution with which the soil is in equilibrium, the value of the ratio $C'^2_{K^+}/C''_{Ca^{2+}}$ for the adsorbed cations is measured, it is possible to calculate the selectivity coefficient.

When we have a range of values for the selectivity coefficient covering the possible composition of the exchange complex, we can calculate $\Delta G^{(o)}$. An argument that we shall not reproduce here shows that $\Delta G^{(o)}$ is substantially equal to the mean value of the selectivity coefficient for all possible values for composition of the exchange complex.

Some might raise the objection that, if the result of applying the principles discussed is to summarize a number of experimental values in a single parameter, too much condensation of information is involved.

In fact, it is interesting to have a method of calculating how potassium will be distributed between the solution and the colloid surface. This distribution depends upon the nature of the cations present, their relative concentrations, the concentrations and types of salts and the electrical properties of the surface of the soil colloids.

Without any doubt the thermodynamic treatment of experimental results is of practical value but it has not been widely used by the majority of authors who have been concerned with the study of ionic exchange of potassium during recent years. Such research has resulted in the formulation of a selectivity coefficient which is sufficiently constant to make possible the calculation of the proportion of potassium adsorbed. One of these is very well known and is much used though it dates from nearly half a century ago. In place of the selectivity coefficient described above, the following expression can be used:

$$K^2_G = K_c \times C''_{Ca^{2+}}$$

If the concentrations are expressed in milliequivalents per litre this takes the name 'Gapon constant' whose value is independent of the units chosen to express the quantities of adsorbed ions. It is directly related to the thermodynamic constant since it can be shown that its logarithm over the whole range of possible values for the proportion of potassium adsorbed is equal to half the value of the logarithm of the thermodynamic exchange constant.

Actually, it is impossible that K_G should be constant, its usefulness lies in that it scarcely varies over a relatively large range of composition of adsorbed cations. A'tempts have been made to use deviations of the Gapon constant to characterise exchange sites in the soil which fix potassium with varying strength. Other researches on 'constants' have used the selectivity coefficient as expressed in the equation above. Whatever units are chosen to express the concentrations of the two cations involved in the exchange reaction, the equilibrium condition remains the same though the numerical values of concentrations, of activity coefficients and expressions derived therefrom will alter. Such 'constants' are those of Vanselow or Kerr and they are now of historical interest only.

The search for more or less empirical constants for calculating the degree of adsorption of potassium has gone on for a long time because of the difficulty of taking into consideration at the same time all the factors which determine this degree. In parallel with this type of research has been the elaboration of a model of ionic exchange and its adaptation to the study of problems in soil science; this is the diffuse double layer theory. The bases of this theory have been known since the beginning of the century, the theory has been developed and much used in the last forty years and still has its supporters

In fact, it presents a very much simplified picture of ionic exchange between Ca^{2+} and K^+: the colloid surface carries a uniformly distributed electrostatic charge and is surrounded by an array of cations arranged in accordance with the spatial charge distribution. The monovalent and divalent cations are distributed in this array in a manner depending upon their proportions in the solution and the electrical properties of the colloid surface. In the main these are the factors listed above but with considerable simplification: the only property of the cations which is taken into consideration is their charge, and the distribution of mono- and divalent cations follows the basic electrostatic laws and the distribution law of Maxwell-Boltzmann. Obviously, this description is oversimplified and one would not expect that the double layer theory would give meaningful results as far as concerns equilibria between K^+ and the divalent cations. In fact the theory is not confirmed directly by experimental results on ionic exchange.

The logic of these conclusions has been confirmed experimentally. If we calculate the value of the thermodynamic equilibrium constant predicted by this theory for mono- and divalent cations, the value obtained will be applicable to point charges and not to cations of finite dimensions which are affected by other than electrostatic forces. One can attain this value experimentally by extrapolating the values of exchange constants for real cations to a zero value for their respective volumes. Agreement between the limiting experimental value and theory is as good as might be expected. It can be said that the diffuse double layer theory has very limited application in the case of our problem. This observation is only an apparent contradiction with the successful application of this theory in other fields of soil science as, for example, the negative adsorption of anions: evidently in the latter case, the restriction imposed on the theory by assuming point charges loses much of its weight.

This review of the different approaches used in the study of ionic exchange equilibria would not be complete without mention of the technique of modelling equilibrium reactions and the kinetic processes in which the potassium ion in soils may be involved. It must be pointed out that it is difficult to take into account all the reactions implicating the cations which take part in an exchange reaction with potassium even in the simplest system, let alone the clay–water–electrolyte system. This is especially the case when ion pairs of the type $CaCl^+$ or $CaSO_4{}^+$ are formed and of which account should be taken in calculating exchange equilibria and correcting activities. The position in the soil is obviously even more complex. Allowance must be made for precipitation of calcium in the form of carbonate and sulphate as, once it is precipitated it takes no more part in the exchange with potassium. Again, ionic equilibria between cations of different valency are much influenced by the concentration and composition of the soil solution. Finally, equilibria are modified by movements of the soil solution and they are not established strictly instantaneously. Certainly, these are not all unknowns but they can only be taken into account individually.

It is now possible to calculate ionic concentrations in the soil solution which satisfy many of the equilibrium conditions, and their parameters can be measured. The next ten years will be marked by further progress in research in this field.

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Factors Affecting the Availability of Potassium in Soils

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1. Introduction

1.1 Early history

There have been important changes in the first twenty-five years of the existence of the *Scientific Board of the International Potash Institute* in ideas on the mechanisms of nutrient uptake from the soil.

Interest in these mechanisms developed about a century ago. The earliest workers thought that the total quantity of a nutrient in the soil was all important but, during the last two decades of the nineteenth century, the thought gained ground that a part of the nutrient which was easily extractable would better indicate true availability to the plant. The extracting agent used was intended to simulate the extracting power of an absorbing root.

It was known that roots excrete carbon dioxide, thus the idea developed that carbonic acid would solubilise that part of the soil minerals most exposed to its action. This concept, published by *Czapek* in 1896, must now be looked upon as an important breakthrough in agronomic thinking. It led to the use of CO_2-enriched water as an extractant of plant-available nutrients. At the same time, *Dyer [1894]* advanced the thought that the acidity of root sap was responsible for dissolving certain fractions of nutrients in the soil and he introduced the 1% citric acid reagent that has been much used in soil testing, even up to the present day.

The usefulness of these weak-acid extracting agents was largely responsible for the firm establishment of the idea that plant roots acidify their soil environment. In retrospect, it is remarkable that soil scientists remained unaware of the fact that, in nutrient solution culture, many plants cause the pH of the medium to rise, but it must be admitted that the pH-raising effect is most easily discernible when dilute nutrient solutions are used and that early workers with nutrient cultures often used rather concentrated solutions. Also, during the first half of the 20th century, soil

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scientists did not seem to pay much attention to the work of plant physiologists, while the latter showed little inclination to delve deeply into processes taking place outside the root.

In 1939, *Jenny and Overstreet* published a paper that gave additional support to the thought that plant roots acidify the soil. They advanced the concept of contact exchange which had been suggested earlier by *Devaux [1916]* and by *Comber [1922]*. These authors stated that H^+ ions on the root surface could be directly exchanged for nutrient cations on the negatively charged clay surfaces. They saw no need for the involvement of the soil solution as an intermediary between plant roots and soil colloidal material.

Although some contemporaries disagreed with the views advanced by *Jenny and Overstreet*, there was still a general consensus of opinion that root action was responsible for solubilising nutrients in the immediate root environment, thus making them available for uptake. As yet, little thought was given to the influence that the mobility of a nutrient in the soil might have on its availability to plants.

1.2 Mobility

In 1954, *Bray* published a thought-provoking article, in which he stated that 'the mobility of nutrients in soils is one of the most important single factors in soil fertility relationships'. *Bray* recognised that 'regardless of whether the root and clay surfaces are so close that contact exchange, as postulated by *Jenny and Overstreet*, can take place, the amount obtained from the immediate contact would be small and insufficient to make the root functional. The significant source of nutrients to the root surface comes from movement of diffusion into the film of water between the root surface and the soil surface'.

Bray realised that the primary functioning of an active root is not to be sought in any solubilising action but in the fact that, by absorbing nutrients, the root lowers the nutrient concentration in its immediate environment to such an extent that a concentration gradient is created in the soil solution surrounding the root, causing nutrients to diffuse towards the root. Such diffusion, in turn, will lead to the solubilisation of soil minerals. *Bray* felt that when, as in the case of phosphate, such soil minerals were sparsely soluble, the main factor limiting availability would be their rate of dissolution rather than the rate of movement of phosphate ions through the soil solution. However, *Fried and Shapiro [1956]* published data on phosphate patterns in various soils from which it could be calculated that the quantities of phosphate that can be removed from soils by frequent periodic leaching with water are many times larger than the quantities of phosphate actually removed by plants. Thus it became evident that, in general, physical and chemical factors inhibiting rapid movement of a sparsely soluble nutrient to an absorbing root must be held responsible for limiting supply rather than the potential of a soil to supply the nutrient.

1.3 Interaction with other ions

Most of the work on nutrient availability done during the first half of the twentieth century concerned single nutrients only or, in a few cases, just nutrient cations or nutrient anions. Little attention was paid to possible interaction between cations and anions which could affect the availability of nutrients to plants. A review article by *Walker [1960]* drew attention to the fact that many plants do not absorb equivalent quantities of nutrient cations and anions. He pointed out that, generally, when plants are grown on a medium containing available N mainly as NO_3^-, they absorb more nutrient anions than cations. To prevent the development of a difference of potential between the root and the soil, the plant is likely to make adjustments, possibly by excreting HCO_3^- or OH^- ions, or by taking up H^+ ions. *Walker* emphasised that, as long as cation uptake does not exceed anion uptake, there is little need to postulate a theory of contact exchange for cation uptake.

1.4 Mass flow and diffusion

In 1962, *Barber* proposed an important amendment of *Bray*'s concept by advancing the thought that two processes are concerned in the movement of ions through the soil, namely mass flow of the soil solution to the root induced by transpiration, and diffusion of ions along a concentration gradient due to lowering of their concentrations as a result of uptake at the root surface.

Mass flow is caused by water moving through the soil to the root in response to the plant's demand for water. This soil water is a more or less dilute solution containing a number of chemical elements, some essential to the growth of plants and others not, present either in ionic or non-ionic form, as, for instance, soluble organic compounds. The quantity of such a solute arriving at the root surface depends on its concentration in the soil solution and on the volume of water withdrawn by the root. Both entities, *viz.* concentration of a nutrient in the soil solution and total volume of water absorbed by a plant from its root medium can be measured.

It is also possible to determine the total quantity of a nutrient which is taken up by a plant during its growth period, so it is possible to calculate whether or not the quantity of nutrient arriving at the root by mass flow matches nutrient uptake. When the solution moving to the root contains a relatively high concentration of an ion, mass flow may bring more of that ion to the root surface than the root absorbs. Consequently, the ion will accumulate in the soil near the root surface. The increased concentration of the ion sets up a concentration gradient along which the ion will diffuse in a direction counter to that of mass flow. If the concentration of the ion in the soil solution is low, the quantity arriving at the root by mass flow may well be insufficient to meet the plant's needs. Uptake by the root will then lower its concentration in the soil solution so that a concentration gradient is established along which the ion will diffuse *towards* the root so that the latter obtains nutrient both through mass flow and diffusion.

Barber listed the factors which together determine the extent of the concentration gradient of an ion in the soil solution. These factors are:

a) Initial concentration of the ion in the soil solution.
b) Rate of uptake of the ion per unit root surface.
c) Rate of diffusion of the ion to the root surface.
d) Rate of movement of the ion to the root by mass flow.
e) Rate of diffusion of the ion along the surface of soil particles.

f) Rate of replenishment of the ion from solid constituents of the soil containing the nutrient under consideration.
g) The capacity of the soil to replenish.

1.5 Capacity and intensity

The concepts of 'capacity' and 'intensity' are implicit in *Barber*'s thinking. Capacity measures the ability of a soil to maintain a steady supply of a particular nutrient from the solid to the liquid phase of the soil. It is also called 'buffering capacity'. The total quantity of a nutrient that can be drawn from the solid phase into the soil solution when this is continually depleted is called the 'labile pool' of that nutrient. The capacity factor is more or less identical to *Barber*'s factor (g), which is one of the factors determining the extent of the concentration gradient of an ion in the soil solution. The size of this 'capacity factor' or 'buffering capacity' is an important determinant of nutrient availability. A fuller description of nutrient availability demands knowledge of the concentration of the nutrient in the soil solution which is in equilibrium with the solid phase of the soil. The concentration of the nutrient in the equilibrium soil solution or the quantity that can be drawn into solution by extraction with water or with a dilute solution of a neutral salt represents the so-called 'intensity factor', which can be identified with factor (a) in *Barber*'s list.

Knowledge of both 'capacity' and 'intensity' provides a foundation for defining nutrient availability in soil. Both can be determined easily in the laboratory, even on a routine basis. Nevertheless, it must be kept in mind that the factors (b) to (f) listed by *Barber* will supply additional information on rates of movement of nutrients in soils towards the root surface and, thus, on availability. These factors are not as easily determined in the laboratory as are capacity and intensity, but knowledge of them is needed for a complete description of availability.

In the following, we shall be concerned with the influence of some soil constituents and some soil characteristics which determine the availability to plants of soil potassium and the fate of potassium applied as fertiliser will be included in the discussion as appropriate.

2. Soil minerals

The behaviour of potassium in soil can be simply described in summary fashion by the following scheme:

K non-exchangeable $\rightleftarrows$ K exchangeable $\rightleftarrows$ K in soil solution $\rightarrow$ K in plant. (1)

The scheme indicates that the reactions between the solution and solid phases are reversible, suggesting that the soil minerals can function as both sources of and sinks for K. This simple model is not concerned with the nature of the minerals which can retain K in exchangeable or non-exchangeable positions. The discussion which follows will make it clear that the conditions obtaining in a soil at any time will determine whether either primary or secondary minerals will release or entrap K, thus regulating the availability of soil- or fertiliser-K to plants.

The capacity of a soil to supply potassium to crops over an extended period of time is fundamentally dependent upon:

a) The K content of the primary minerals.
b) The rate of release of K by the primary minerals.
c) The quantity of clay (secondary) minerals present.
d) The type of clay minerals.

The preceding paper *(Schroeder [1979])* discusses fully the structure of primary and clay minerals and the chemistry of weathering.

2.1 Primary minerals

Most of the potassium contained in primary minerals is found in feldspars and micas. Orthoclase and microcline usually dominate among the feldspars and the most important micas are biotite and muscovite. Temperate soils usually contain both types but the micas are the main source of K supply to plants as shown in Table 1 giving the results of an early experiment by *Plummer [1918]*. He ground each mineral to a fine powder screened through the finest grade of bolting cloth. The K in freshly ground micaceous material was comparatively readily available to plants. CO_2-enriched water was much more effective than plain water in releasing K from primary minerals and in predicting its availability.

Table 1. The availability of K in freshly ground K-bearing minerals

Source of K	K removed by oats, mg per pot	mg K removed by 5 extractions*	
		with H_2O	with CO_2-enriched H_2O
K_2SO_4	253	—	—
Biotite	202	4.37	43.4
Muscovite	177	4.02	28.1
Orthoclase	62	3.39	15.6
Microcline	13	3.00	10.2

* 30 g of material in 200 ml total extractant, shaken for 96 hours *(J.K.Plummer [1918])*

It should not be inferred from *Plummer*'s results that K is only released when the minerals are finely ground. In fact release rates are often slower from finely ground than from coarsely ground materials, as *von Reichenbach and Rich [1969]* found. The amount of K removed from muscovite by Ba^{2+} exchange was larger for the 20–5 μ fraction than for the finer particles. *Mortland and Lawton [1961]* found the same in NaCl extraction of biotite. The bending of mica layers is thought to promote the release of K and bending appears to be more pronounced in coarser particles.

Besides feldspars and micas, there are many other primary minerals that contain sizeable quantities of K which becomes available on weathering. In many parts of the world the so-called greensand soils, containing glauconite, are well known for their ability to supply K to plants, but there are also some minerals which are known for their ability to fix K added to the soil, making it unavailable to plants. Allophane and zeolite are examples of such minerals.

Allophane contains very little K but has a definite affinity for K, which can cause fertiliser K to become fixed and unavailable. From their work with synthetic aluminosilica gels, comparable to natural allophanes, *van Reeuwijk* and *de Villiers [1968]* concluded that these materials could fix considerable quantities of K in a way similar to illitic clay minerals and that no specific chemical reaction was involved. However, *Sticher [1972]* pointed out that the properties of the aluminosilicates used may have been characteristic of freshly prepared gels and not representative of natural allophanes.

The formation of zeolites is favoured by high pH of the lake water in which the volcanic ash from which they are formed has settled. They are also formed in dry conditions by the presence of alkalis. The Na/K ratio of zeolite in sedimentary rock is considerably lower than that in the surrounding lake- and soil-water, indicating that they have a strong affinity for K, and this has led to the suggestion that soils containing zeolites have the capacity to fix K. *Schuffelen* and *van der Marel [1955]* included an artificial zeolite in the series of soils and minerals which they tested for K fixation capacity and found that it fixed more K than most of the other materials examined. They found that allophanes fixed large amounts of K and that K could also be fixed by feldspars.

These results show that, in addition to the secondary minerals, some primary minerals and minerals like allophane and zeolite, which form a transitional group between the primary and secondary minerals, have the capacity fo fix K. Thus the K-bearing soil minerals should not always be looked on as constituting a source of K; they can also function as a sink for K originating from other soil components of from fertiliser.

2.2 Clay minerals

When a primary mineral like biotite acts as a source of K, releasing it to the soil solution, it undergoes structural change and gradually loses its identity. *Mortland et. al. [1956]* grew four successive crops of wheat on a mixture of quartz sand and finely ground biotite and found (Table 2) that as K was depleted, the cation exchange capacity of the biotite increased. The removal of K by the growing plants allowed cations other than K to enter the mineral along with water, causing the layers of the mineral to expand. X-ray analysis showed that during cropping the original diffraction pattern of biotite largely disappeared, to be replaced by that of vermiculite.

Table 2. Effect of four crops of wheat on some properties of biotite added in various quantities as a K source to the growth medium

Biotite added per culture, g	Properties of biotite residue at the completion of the experiment*	
	K content, %	CEC, me/100 g
25	2,4	54
50	3,6	38
100	4,5	30

* original biotite: K content, 5,8%; CEC 14 me/100 g *(M.M.Mortland et al. [1956])*

Thus, removal of K causes a primary mineral to lose its original characteristics and to take on the properties (cation exchange capacity and layer expansion) of a clay mineral. If, however, the cations that replace K in the formation of vermiculite from mica are later replaced again by K, the mineral layers may be drawn together so tightly that the regained K is entrapped in non-exchangeable form.

To determine whether a soil contains K-fixing minerals, the soil is suspended for a certain period in water containing a known quantity of K. After the appropriate time, an electrolytic extractant is percolated through the soil to determine how far the K taken up by the soil can be recovered by exchange with another cation. That part of the K not recovered is considered to have become fixed in the crystal lattice. Drying of the soil between contact with the K-containing solution and extraction often increases K fixation, the likely cause being the removal of water molecules from the inter-layer position and subsequent closure of the lattice layers entrapping K^+ ions.

The quantity of K recovered during the percolation is also influenced by the cation used. Because NH_4 has a similar charge and similar ionic size, it can be fixed in the sites which fix K. Thus, if ammonium is used in the percolation treatment, it may give misleading results because NH_4 is likely to replace inter-layer K at the edges of the particles, but it also causes the layers to collapse at the edges, entrapping K at sites in the inner inter-layer positions and this will be erroneously included in the non-exchangeable fraction.

It is generally difficult to extrapolate from laboratory measurements of fixation to predict field behaviour. The amount of native soil-K or added fertiliser-K which can be released to a crop is governed largely by the intensity of cropping, as exemplified in results reported by *Hemingway [1963]*. He grew a grass-legume mixture for three years in field plots under various fertiliser treatments. All herbage was removed and both non-exchangeable and exchangeable K were measured before and after the 3-year period (Table 3).

Under severe K stress (N fertiliser without K), non-exchangeable K made a sizeable contribution to the K supply of the crop. This suggests that the K concentration in the soil solution was kept so low that equilibrium in equation 1 (above) was shifted to the right. Conversely, when K was given without N, growth was impeded by N starvation and there was an increase in the non-exchangeable fraction during the course of the experiment. Thus the laboratory technique used would indicate that K

Table 3. Loss of exchangeable and non-exchangeable potassium from soil during a three-year period of growth of a legume-grass mixture

Form of fertiliser added	Loss of K from soil, kg per ha*	
	exchangeable	nonexchangeable
None	179	36
Nitrogen	202	64
Potassium	11	–31
Potassium + nitrogen	191	1

* K added as fertiliser was counted to become a part of the exchangeable fraction
(R.G. Hemingway [1963])

had occupied positions in which it was fixed, though a more vigorously growing crop would have been able to extract K from these positions. Such findings indicate that the laboratory measurements have only limited application to field conditions. Cropping intensity largely determines whether or not the designations 'exchangeable' and 'non-exchangeable' are synonymous with 'available' and 'non-available' and whether or not K designated as 'fixed' by laboratory standards is really useless in terms of plant nutrition.

The name illite is given to a variety of secondary minerals belonging to the mica group. Although they show some similarity to primary micaceous minerals, it is doubtful whether illites are formed as degradation products of the weathering of micas. They have a high K content (usually around 6%) and are thus thought to make a large contribution to the K nutrition of plants. However, much of the K in illites is an intimate part of the clay-mineral structure and is not readily released. Because they contain native K, the cation exchange capacity of illites is lower than that of smectites, even though the former have a higher charge density. The information given in Figure 1 shows that illite can supply comparatively large quantities of K to a rapidly growing crop.

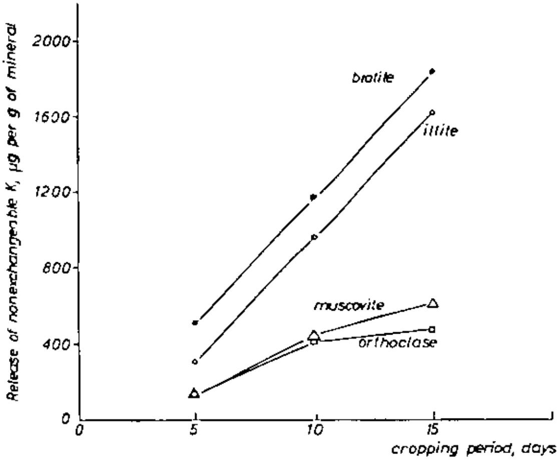

Fig. 1. Release of K from different minerals during intensive cropping of mixtures of the minerals with quartz sand. Particles of biotite, muscovite, and orthoclase <50 μ, those of illite <20 μ. All minerals were added in quantities to supply the same total amount of K per culture. *(G.P. Verma:* Ph.D. thesis, Iowa State Univ. *[1963])*

Due to the pivotal function performed by K in illites, they have a relatively large percentage of exchange sites showing marked preference for K. Thus, when K saturation is low, K is held with a high binding energy in the interlayer positions, mainly at the so-called K-specific sorption sites. K will only be found on non-specific sites when K saturation is increased. Consequently, a given K concentration in the soil solution will be at equilibrium with a larger amount of exchangeable K in a soil containing illitic minerals than in a soil of lower clay content. Thus, less K fertiliser is needed to achieve a certain K intensity in a light-textured soil than in a heavy soil. However, the K capacity of the light soil is generally too low to sustain an adequate K intensity once plants start to draw K from the soil solution, while the higher K capacity of a heavier soil can maintain the K intensity for much longer. *Grimme et al. [1971]* have contrasted the relationships between K intensity and K capacity in two soils containing widely different quantities of illitic minerals (Figure 2).

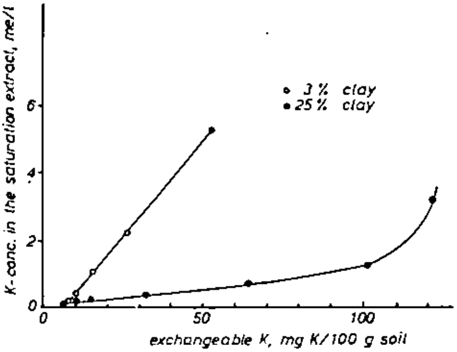

Fig. 2. The relationship between exchangeable K and K concentration in the soil solution for two soils differing in clay content. *(H. Grimme et al.:* Landw. Forsch. *26*, 1, Sonderheft, 165–176 *[1971])*

Clay minerals of the smectite group and those of the kaolinitic and halloysite types have few K-specific sorption sites. The K-fixation capacities of soils containing these minerals are low and the clay minerals easily release their K to the soil solution as it is depleted of K by plant uptake.

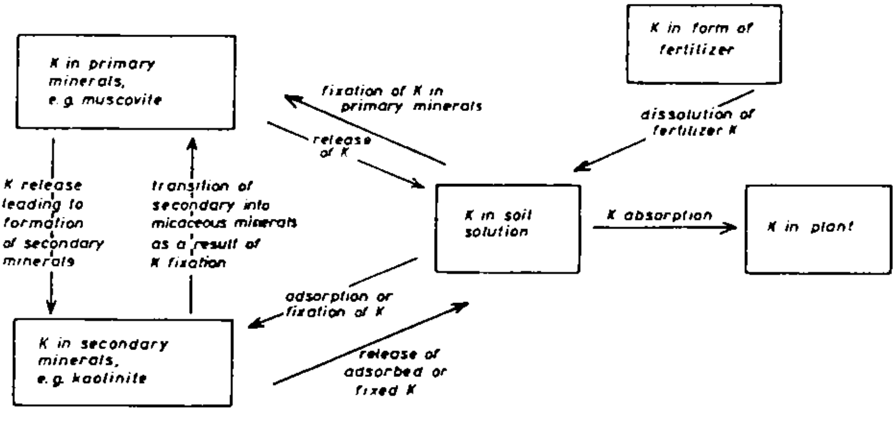

Fig. 3. Locations and pathways of potassium in soil.

It was said above (2.1) that primary minerals can serve as both sinks for and sources of K. When such minerals lose K from the lattice structure, they lose their identity and are converted to secondary clay minerals. *Hutchings [1890]* long ago suggested that the reverse process could occur, i.e. the conversion of clay minerals like kaolinite into micaceous minerals. *Volk [1934]* showed that K added to soil as fertiliser increased the mica content. This process is regarded as a reversal of the weathering process in which K is entrapped in expanding 2:1 layer silicates. Thus the reaction sequence presented at the beginning of this section can be extended as in Figure 3.

3. Soil organic matter

The ways in which soil organic matter may influence the availability of K depend upon its characteristics. Because K is not a constituent of any quantitatively important organic plant component, the amount of K contained in undecomposed or partially decomposed plant material in soil is bound to be small.

Humification of plant residues and soil organisms can produce a type of organic matter with high cation exchange capacity. It is possible that organic matter is important in holding soil K in exchangeable form. However, humus retains divalent cations (Mg, Ca) more strongly than the monovalent (K, Na). Whether this promotes or hampers the availability of K to plants depends on the conditions. Weaker retention of K relative to Ca and Mg may increase K availability but, at the same time, it renders the K more liable to leaching.

In tropical soils, in which kaolinitic clay minerals having low CEC predominates organic matter can make a sizeable contribution to the retention capacity, as i, shown in Table 4 *(van Raij [1969])*.

Table 4. Some characteristics of topsoils in Sao Paulo, Brazil

Soil No.	% clay	% O.M.	CEC, me/100 g soil		% of CEC in O.M.
			in clay	in O.M.	
	Soils with an argillic B horizon				
1	5	0.8	1.0	2.2	69
2	6	0.6	1.2	2.1	64
3	12	2.5	1.8	8.2	82
4	19	2.4	1.4	6.0	81
5	38	2.3	2.0	4.3	68
6	18	3.2	1.2	7.9	87
7	64	4.5	9.4	15.0	62
	Soils with a latosolic B horizon				
1	59	4.5	12.8	16.1	56
2	52	2.7	3.1	6.4	67
3	24	1.2	1.0	2.9	74
4	25	2.0	2.2	4.0	65
5	56	6.5	1.4	14.9	91

(B. van Raij [1969])

These findings emphasise the importance of organic matter in tropical soils for the maintenance of soil fertility, not just for nutrients like N, P and S, which may be structural constituents of the organic material from which it is formed, but also for nutrient cations, including K, whose availability may largely depend on the contribution of soil organic matter to cation exchange capacity.

Organic matter has well known indirect effects on the availability of soil K, in that it promotes aggregate formation and stability and thus water-holding capacity and aeration which favour root extension. These latter two subjects will be dealt with in later sections.

4. pH

pH has a complex influence on the availability of soil nutrients. In the case of nutrients, such as nitrogen, whose availability depends largely on the activity of soil microbes, any change in pH may affect their availability in that such a change affects the type, size and activity of the micropopulation. For nutrients whose availability is a function of solubility of chemical compounds, *e.g.* phosphate, a change in pH may affect their solubility and thus their availability.

Both microbiological and chemical factors can influence the availability of soil K as well, but more remotely so. In many soils of temperate regions, soil microbes are an important factor in creating and maintaining soil aggregate stability which, in turn, governs soil moisture and soil air characteristics. The effects of these two soil-physical factors on K availability will be discussed in sections 5 and 6. In the present section, attention will be given to the influence of pH on some soil-chemical factors influencing K availability.

4.1 Influence on K fixation

It is well known that pH affects K fixation, but again here, the influence is indirect in that pH largely determines which cation predominates in the inter-layer positions of clay minerals. It is now generally agreed that in acid soils aluminium can occupy many of the exchange sites. Acidification may lead to accumulation of polymeric hydroxy-aluminium ions in inter-layer positions so that such sites no longer contribute to the total cation-exchange capacity of the clay minerals. However, in vermiculite, aluminium ions also prevent K ions from occupying these sites and may thus be instrumental in lowering the K-fixation capacity of the soil. Hence, the effect of increasing acidity on K fixation will depend on whether or not the soil contains vermiculite-type clay minerals and whether or not increasing acidity releases aluminium ions which block inter-layer K-fixation sites. Conversely, the effect of liming an acid soil on K fixation depends on whether or not the increasing Ca concentration leads to a displacement of aluminium and thus to an exposure of sites with a potential for fixing K.

It is therefore not surprising that the literature contains conflicting information on the influence of pH on K fixation. *York et al. [1953]* give an example where liming an acid soil increases K fixation (Figure 4). This Figure also shows that alternate wetting and drying increased K fixation. However, there was little interaction between

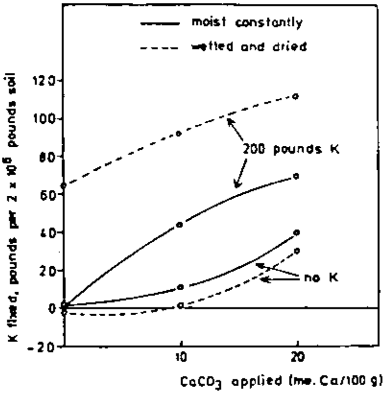

Fig. 4. Effect of drying Mardin silt loam on lime-induced potassium fixation. *(E. T. York et al.:* Soil Sci. *76*, 379–387 *[1953])*

the two effects, as the effect of drying and wetting was about the same at all liming levels.

The effect of liming on K-fixation capacity will also determine whether the soil minerals will release or fix K. In this respect, *Rich [1964]* investigated the behaviour of a soil containing vermiculite. The soil was washed repeatedly with 1N $Ca(OAc)_2$ solution containing a small quantity of K ($K/Ca = 1.35 \times 10^{-4}$) and adjusted to three different pH levels. His results (Figure 5) show that below pH 4.35 the soil acted as a K source, and above it as a sink for K.

It is to be expected that laboratory findings like that shown in Figure 5 can be extrapolated to field conditions. This would imply that liming an acid soil to improve

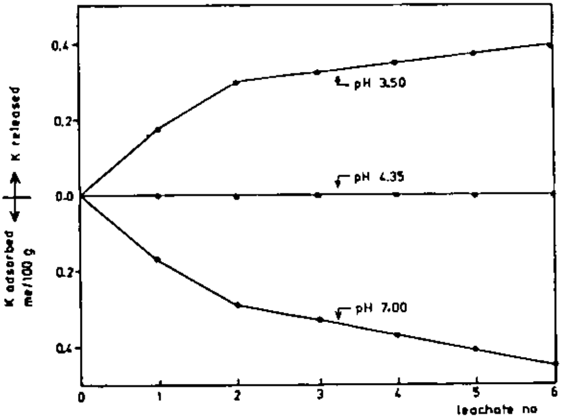

Fig. 5. Release of K to, or removal from, *N* $Ca(OAc)_2$ by Nason soil as affected by pH. *(C. J. Rich:* Soil Sci. *98*, 100–106 *[1964])*

general growth conditions might increase the need for K fertiliser to ensure adequate crop nutrition. An example will be given in the following.

In the Netherlands, estimates of plant-available soil K are obtained by extracting soil with 0.1N HCl. It was found, however, that the quantity of K extractable with 0.1N HCl needed to be valued differently for soils differing in clay content or in pH. The higher the clay content and the higher the pH, the more the numerical value of the K-HCl reading had to be reduced in order to give a true index of the K status of a soil.

The negative effect of clay content on K availability was discussed in Section 2 (see Figure 2). It was shown that a given quantity of exchangeable K per unit weight of a light-textured soil gives a higher K concentration in the soil solution than does the same quantity of exchangeable K in a heavy-textured soil. The negative effect of pH was demonstrated by *York et al. [1953]* and *Rich [1964]* (Section 3).

The use of empirical factors to allow for varying pH and clay content is realised in the calculation of K values, as follows:

$$\text{K value} = \frac{\text{K-HCl value} \times \text{b}}{0.15\ \text{pH(KCl)} - 0.05}$$

'b' varies with the percentage of soil particles $< 16\,\mu$ (the higher the percentage, the lower 'b'). At pH below 7, the K-HCl value will be multiplied by more than 1, indicating that each unit of K extractable with 0.1 N HCl represents a larger quantity of available soil K, the lower the pH value of the soil is *(Henkens [1977])*.

Extension workers saw the need for such corrections long before the scientific background was understood. However, scientific progress in the last 25 years has provided the physico-chemical basis for the findings of practical workers in the field.

The correction factors used were intended only for Dutch conditions. Nevertheless, they have also proved to be useful under conditions very different from those obtaining in the Netherlands. In greenhouse trials, *Muchena [1975]* tested K availability in 11 soil types from various regions of Kenya. The soils were cropped with sorghum and the K content of the above-ground parts of the plants was correlated with the quantities of K extracted from the soils by different extractants. The correction factors used in the Netherlands were employed to transform the values obtained with the *Mehlich* method (extraction with 0.1N HCl and 0.025N H_2SO_4) and the Dutch method (0.1N HCl). Correlation was notably improved by use of the correction factors.

Linear correlation coefficients	
Mehlich	0.905
corrected *Mehlich*	0.956
K-HCl	0.912
K-HCl corrected (*i.e.* K value)	0.961

4.2 Influence on organic matter

pH also influences the quantity of available K in organic matter. However, in contrast to its effect on the availability of K in clay minerals, the effect of increasing pH is likely to improve the K-supplying power of organic matter. The CEC of soil organic matter is much more pH-dependent than that of clay minerals. The difference is shown clearly in Figure 6 after *Helling et al. [1964]*. Soils whose capacity to retain cations in exchangeable positions is located mainly in the organic-matter fraction are in a much better position to function as sources of plant-available K when the pH is kept high. When, as in tropical soils, the clay mineral is largely kaolinite, with very low CEC and K content, organic matter is most important for safeguarding the supply of K to plants. Whether organic matter can serve as a K source for plants in such soils depends much on the soil pH. However, while liming increases the CEC of organic matter, it also increases its rate of mineralisation. Little research appears to have been done in the tropics on the influence of liming on the capacity of organic matter to serve as a source of plant-available K.

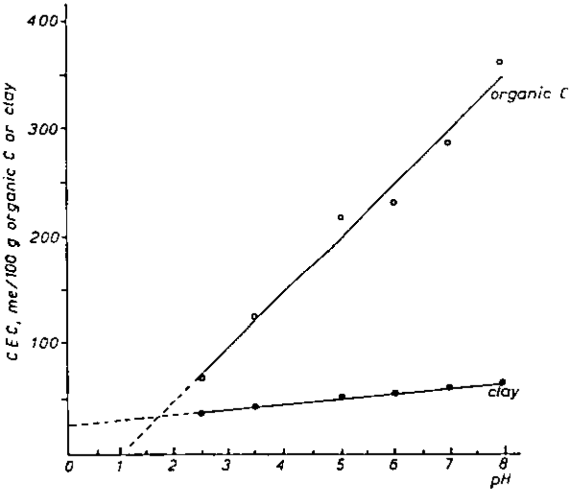

Fig. 6. Effect of pH on the CEC of organic matter and clay in 60 North American soils. *(C.S. Helling et al.:* Soil Sci. Soc. Amer. Proc. *28*, 517–520 *[1964])*

4.3 Influence on other cations

Measures taken to modify soil pH may be the addition of liming materials to a soil considered too acid, or addition of sulphur or other acidifying agents to a soil thought to be too alkaline. The latter is seldom practised so it is usually taken for granted that adjustment of soil pH is more or less synonymous with liming. Liming materials normally contain Ca, sometimes also Mg. It is to be expected that the mere addition of these alkaline-earth cations, apart from their influence on pH, would also directly affect the availability of K to plants, as will be discussed in 7.1. By influencing the activities of Ca, Mg and Al in the soil solution, pH also affects the activity of K and thus its availability.

5. Aeration

Soil organic matter content and pH can both affect soil aeration. Soil organic matter directly or indirectly promotes aggregate stability. It plays a direct part in forming a matrix in which mineral particles may become entangled to form soil aggregates. Between soil aggregates there may be relatively wide pores which are important for the diffusion of gases.

More indirectly, soil organic matter forms a substrate on which soil organisms live. Such organisms may produce substances which act as cementing agents in the formation of aggregates from mineral particles (*Costerton et al. [1978]*).

The role of pH in promoting soil aeration is likewise associated with the action of soil organisms. Earthworms and bacteria are particulary active in producing cementing agents. Both types of organisms prefer alkaline conditions and are practically absent from acid soils. Liming may therefore stimulate the growth of earthworms and bacteria, and the cementing agents produced enhance the formation of aggregates which are important for the establishment of wide pores through which both oxygen and carbon dioxide can diffuse.

Good aeration favours both root extension and the functioning of uptake mechanisms in the root responsible for the selective withdrawal of K from the soil solution. At this point it is appropriate to refer back to *Barber*'s factor 'the rate of uptake of an ion per unit root surface' (1.4). It is obvious that total uptake will be determined not only by the rate of uptake per unit root length but also by the total root length (root extension).

The rate at which K is taken up appears to be particulary dependent on oxygen supply. Table 5 shows that the absorption of K is much more affected by soil compaction and soil aeration than is the absorption of Ca or Mg and that the growth of maize is closely related to the K content of the tops.

K translocation in plants was also found to be influenced by soil aeration. *Shapiro et al. [1956]* observed that K content of maize tops decreased with decreasing aeration, although the K content of the roots increased.

Table 5. Effects of soil aeration and soil compaction on the growth and cation composition of maize plants

Treatment	Maize yield, g/pot		Composition of maize tops, me/100 g		
	tops	roots	K	Ca	Mg
At 15% soil moisture					
NP	20.8	12.9	54	16	29
NP, soil compacted	8.7	4.3	21	20	38
NPK	24.5	14.2	80	18	23
NPK, soil compacted	10.7	5.2	73	28	39
At 40% soil moisture					
NP	13.3	5.6	24	18	33
NP, soil aerated	17.3	8.7	33	16	29
NPK	18.1	9.0	53	24	30
NPK, soil aerated	27.7	17.8	84	16	26

(K. Lawton [1945])

6. Soil moisture

Drew and Nye [1969] showed that only about 6% of the total K required by ryegrass would be found in exchangeable form in the soil within the root hair cylinder. So, much K must diffuse to the root from soil outside this zone. K diffuses to the absorbing root over a longer distance than does P but not as far as NO_3. *Kauffmann and Bouldin [1967]* found that the diffusion path in moist soil was about 1 cm long. Later, *Grimme et al. [1976]* showed that the length of the diffusion path depended on soil moisture content (Figure 7). Near the absorbing surface (in this case an ion exchange resin) the exchangeable K content of the soil is lower in the wet than in the dry soil. Also the cylinder around the resin which is depleted of K has a larger diameter in the wet than in the dry soil.

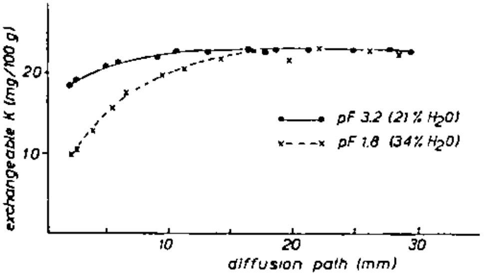

Fig. 7. Decrease in exchangeable soil K caused by diffusion into an ion exchange resin at two soil moisture levels. *(H. Grimme:* Bull. Indian Soc. Soil Sci. *10*, 3–22 *[1976])*

Bearing in mind the importance of aeration for K uptake by the root, it will be clear that there is a limit to the extent to which increasing moisture content will improve the K nutrition of plants and for each species there will be a specific moisture content above which any advantage of accelerated diffusion will be offset by a reduced capacity of the root's K uptake mechanism to translocate K from the ion free space into the symplast. This mechanism has a high oxygen demand.

K diffuses through the soil by way of both water-filled soil pores and water films surrounding soil particles. When the soil is moist and part of the larger pores is filled with water, movement of K^+ ions will be relatively little hampered by the attractive forces exerted by the solid soil particles. Under certain conditions, such forces can considerably retard the movement of K^+ ions, and it will be clear that this retardation will be particularly evident when much of the soil particles consists of negatively charged clay particles which tend to retain K on their absorption sites. In a drier soil only the narrow pores are completely filled with water, water in the larger pores having retracted to form a film around the particles. In these conditions diffusion can take place only in the immediate vicinity of solid particles whose attractive forces will strongly retard the movement of K.

When the larger pores are empty of water, the distance over which ions have to travel is increased by the tortuosity of the path. Equations describing the diffusive flux of ions in a soil include a so-called impedance factor representing the degree of tortuosity of the diffusion pathway.

Lowering the water availability may reduce K uptake by plants through a combination of two factors: 1. reduced root activity caused by water shortage, and 2. reduced diffusive flux due to the longer diffusion pathway and the resistance offered by the solid particles. Experiments in which the roots of test plants were divided between two media were designed to test the influence of the latter factor alone *(Grimme [1976])*. In one medium, half the root system was supplied with all the nutrients except K and with a constant water source. The other medium was a soil in which the moisture and available K contents were varied. The results are shown in Figure 8 and indicate that uptake of K by maize was greatly reduced by lowering the soil moisture content but that the reduction could be partially offset by raising the quantity of available K in the soil.

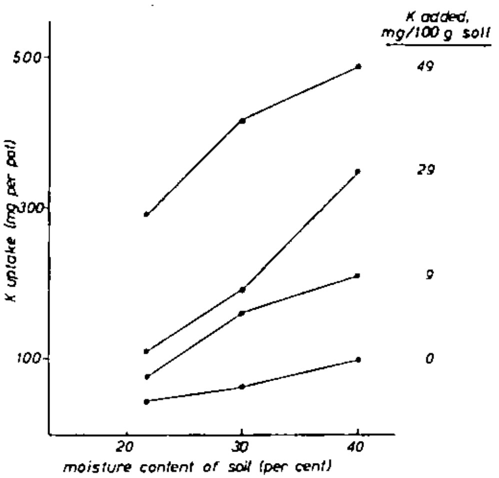

Fig.8. The effect of variations in soil moisture content at 4 soil K levels on the K uptake of maize plants grown in a split-root experiment. *(H.Grimme*, Ind. Soc. Soil Sci. Bull. *10*, 3–22 *[1976])*

7. Other ions in the soil

7.1 Cations

It is well established that metabolic absorption by roots is regulated by enzyme-controlled uptake mechanisms, the so-called carriers *(Osterhout [1935])*. It was shown that there are a number of mechanisms in the root, each of which appears to be specific to one nutrient and, as well as these 'specific carriers, the root also has 'common carriers', possibly one for cations and one for anions. Cations compete for sites on the common cation carrier and, similarly, anions compete with respect to the common anion carrier. Much of our knowledge about carrier-controlled ion uptake stems from work done during the past 25 years *(Epstein [1966 and 1972])*. The ion-uptake characteristics of many plants suggest that K is absorbed in preference to other cations. When, in short-term experiments, normally fed plants are temporarily placed on a series of nutrient solutions each containing only K and one other cation, it is usually found that, on an equivalence basis, the plants take up more K than the complementary cation. This characteristic might have been acquired during evolutionary processes in which sea-borne plants with relatively high K demands were forced to adapt to situations in which the Na supply was many times larger than the K supply. Later, when the plants had invaded the continents, the situation changed, but only insofar as in soil solutions Ca^{++}, Mg^{++}, H^+ or Al^{+++} dominate K^+. The plant can only obtain sufficient K from a soil solution containing much more Ca for example, by selective ion uptake.

Selective ion uptake implies that, while roots absorb K preferentially, they can exclude a large part of the Ca which arrives at the root surface in the flow of moisture. This Ca may accumulate at the root wall or in the ion free space but such an accumulation is limited as it must set up a process by which Ca diffuses back into the soil solution and away from the root. Such a process is, however, retarded by the effect of soil moisture flowing in the opposite direction. We would therefore expect that the Ca : K ratio in the immediate vicinity of the root or in the ion free space would be even higher than it is in the soil solution outside the zone influenced by the root. The value of this ratio in the neighbourhood of the root is a function of both the Ca and K concentrations of the original soil solution and of the absorption characteristics of the plant root and the rate of transpiration.

It sometimes appears as though soil chemists underestimate the influence of the plant itself and the influence of climatic conditions on the Ca : K ratio in the rhizosphere when they emphasise the role played by Ca in affecting the K-supplying capacity of the soil.

The intensity of K supply can be measured either by simply determining the K concentration in the solution in contact with the root or, indirectly, by measuring the K potential or activity ratio $a_K/(a_{Ca+Mg})^{1/2}$. Those who advocate the use of the activity ratio contend that the availability of soil K to plants depends on both the potential of K^+ and the potentials of Ca^{2+} and Mg^{2+} *(Beckett [1964])*. If, for example, two soils differ in their combined Ca + Mg activities, the value in soil 1 being four times higher than in soil 2, the K activity in the solution of soil 2 would have to be twice as high as that in soil 1 for K availability to be equal in the two soils. *Mengel [1963]*, working with solution cultures and *Wild et al. [1969]* with sand cultures, showed, however, that K uptake is a function simply of the K concentration in the soil solution rather than of the activity ratio.

Any benefit to be expected from linking the availability of K to the activities of Ca and Mg in solution- and sand-culture experiments may stem from the assumption that the divalent cations influence the ease with which K is absorbed by plant roots. It is not possible to measure exactly the Ca concentration in the immediate vicinity of an active root, but whether Ca will obstruct or promote the uptake of K depends upon the concentration of Ca in the solution *(Epstein [1962])*. It was further shown *(Rains and Epstein [1967])* that the K concentration determines whether Ca will stimulate or inhibit the uptake of K. Mg has sometimes been found to suppress *(Carolus [1938])* and sometimes to enhance *(Viets [1944])* the uptake of K.

The ways in which *Mengel* and *Wild et al.* tested the validity of the activity ratio concept are open to criticism. They worked with systems in which the growing media contained no material able to retain cations in exchangeable form. Thus their experiments were not fit to test how activity ratios may reflect the ratios of the capacities of K and (Ca + Mg) in natural soils. However, it can be said that activity ratios may be useful in supplying information on relative capacity values but not on absolute capacity values.

The latter disadvantage can be overcome when activity ratios are used to determine the so-called potential buffering capacity (PBC) of a soil. The PBC is expressed as the ratio dQ/dI or the rate of change in K capacity per unit change in K intensity. If experimentally obtained values for K capacity are plotted against the corresponding values for $a_K/(a_{Ca+Mg})^{1/2}$, the slope of the relationship expresses the ability of the soil to maintain K supply (or K availability) as the labile pool of K is depleted. But again we may ask the question whether there is any advantage in using the activity ratio rather than the simple K concentration as a measure of K intensity. In many acid soils, Al is the dominant cation on the exchange sites. Liming often lowers the availability of soil- and fertiliser K (4.2). Ca applied in liming material may raise soil pH to a level at which hydrous Al-oxides are precipitated. The resulting disturbance in the equilibrium between exchangeable and solution Al forces Al out of the lattice to be replaced by Ca. Calcium is not as effective as Al in blocking K-specific sites and hence, as Ca replaces Al, exchangeable K, or the labile pool, will increase. Whether such an increase in the labile pool raises or lowers K availability depends upon the circumstances. If the removal of exchangeable Al means that K has access to inter-layer positions with a high K specificity, the K gained by the clay mineral will become more or less fixed. However, if the Al was blocking the passage of K held on non-specific sites, its removal will increase K availability. On the other hand, should Al block the passage of fertiliser K to K-specific sites, adding K may lead to a considerable rise in K availability. This is evident from Figure 9,

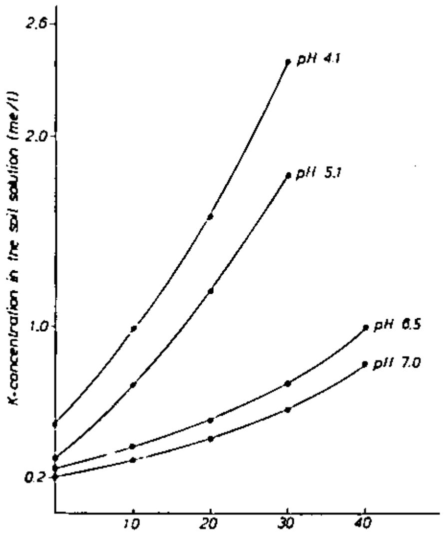

Fig. 9. Relation between amount of K applied and the concentration of K in the solutions of four gray-brown podzolic soils, having similar CEC values and differing in pH. *(K. Neméth:* Plant and Soil *42*, 97–107 *[1975])*

where addition of fertiliser K was most effective in raising K concentration in the solution of the most acid soil.

Obviously, in acid soils, the activity ratio $a_K/(a_{Ca+Mg})^{1/2}$ cannot be an indicator of K intensity. *Tinker [1964]* has proposed using Al^{3+} as reference ion in such soils, but, again, it remains to be shown that activity ratios really reflect the capacity of the soil to supply K to plants. In an early paper, *Beckett [1964]* stated that 'the activity ratio should provide an adequate comparative measure of the potential of labile K and of the availability to plants of K in the soil so long as its uptake is not limited by metabolic factors or antagonisms at the root surface'. It is clear from the discussion above that, even though they may not limit K uptake, metabolic factors certainly affect it. It may be for this reason that simple measurements of K concentration in the soil solution or of exchangeable K are often more useful estimates of K availability than are activity ratios.

If it is wished to have information on both the K intensity and the K capacity of a soil, the electro-ultrafiltration method of *Neméth [1972]* is worth considering. This method is quicker and less laborious than the measurement of PBC and it can be used irrespective of the main cation complementary to K.

7.2 Anions

Anions influence K availability mainly indirectly. There is no strong evidence to show that variations in the quantities of NO_3, H_2PO_4, Cl or SO_4 in the soil will affect the labile pool of soil K. However, the tendency of soil K to pass from the solid soil particles into the solution depends on the difference between the actual and equilibrium K concentration in the soil solution. Anions may be indirectly involved in creating this difference.

It stands to reason that a rapidly growing plant needs more K than a slow growing one. Thus the former is more effective in lowering K concentration in the soil solution and setting up the concentration gradient that is needed to induce K to leave the solid phase. So anything that promotes growth will indirectly promote the release of K. An example was given in Table 3, which showed that applying N made more non-exchangeable K available.

It has been postulated *(Higinbotham et al. [1967])* that plants take up anions actively, i.e. against an electro-chemical potential gradient and that, under a number of circumstances, cations enter the plant more or less passively as counter-ions of the actively absorbed anions. Such evidence is, however, stronger for Ca and Mg than it is for K. There is much evidence that ions are absorbed by a dual transport mechanism *(Epstein et al. [1963])*. Generally, uptake of cations by the low concentration mechanism is indifferent to the nature of the anion, whereas uptake by the high concentration mechanism is much affected by the anion, but the concentration of K at which K uptake starts to be affected by the nature of the anion is higher than the concentrations ordinarily found in soil solutions.

Nitrate uptake followed by nitrate reduction in plants gives rise to the formation of organic anions. Monocotyledonous plants fed with NO_3 usually take up more anions than cations, and malate is the predominant organic anion formed. It is likely that some of the malate is translocated back to the root where it is broken down to bicarbonate and this is believed to be excreted by the roots in quantities equivalent to the difference between nutrient anions and cations absorbed. K is the main cation accompanying malate during transport to the root. Having delivered the malate in the root, the K ions are thought to serve again in accompanying NO_3 taken up in excess of cations, in an upward direction. Thus, nitrate uptake is thought to stimulate K uptake *(Dijkshoorn [1962]; Kirkby [1974])*.

8. Summary

The availability of soil potassium to plants depends on a number of chemical and physical soil characteristics as well as on the effects these characteristics have upon the activity of plant root systems. Many of these characteristics are interrelated. In the past 25 years, our knowledge of the influence of soil minerals, soil organic matter, pH, aeration, soil moisture and other ions in soil on soil K availability has increased greatly. It is to be expected that, in the years ahead, further attention will be given to the interactions between these factors in influencing soil potassium availability.

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The Evaluation of Soil K Status by Means of Soil Testing

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1. Introduction

Fertiliser is used when the nutrient demand of a crop expected to yield at a given level exceeds the amount of nutrient which the soil can supply within a growing season. Chemical soil tests are needed to determine the nutrient supplying ability of the soil and hence the quantity of fertiliser which must be applied to overcome any shortcoming.

There are many soil testing methods and a great deal of work has been expended in the search for the 'best' method. So far, however, no method has been accepted as universally applicable. There are many reasons for this. Some of the relevant ones will be discussed in this paper.

When a method of analysis is assessed by measuring crop response to the nutrient in question it is found that results are not consistent between different locations and from one season to another. Usually soil analysis does not account for more than 50% of the variance in crop response, frequently for much less than 50% *(Cooke [1972])*. Against the background of all the effort that has gone into devising and calibrating soil tests it seems disappointing that the correlation between soil analysis and crop response is so poor, but it also seems that the low level of correlation cannot be surpassed.

2. A brief historical review

The idea that the soil solution is the medium from which plants draw their nutrients, is not new. *(Woodward [1699], de Saussure [1804], Schloesing [1866], Whitney* and *Cameron [1907]), Daubeny [1846])* introduced the idea of the buffering of the soil solution at an early date. This led to the discovery of the 'base' exchange properties of soils by *Way [1850]* and it was soon generally realized that the quantities of nutrients

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dissolved in the soil solution were not sufficient to meet the plants' requirements and that nutrients combined with the solid components of the soil were also involved in the nutrient supply to plant roots. *Dyer [1894], [1891]* tried to simulate the dissolving action of plant roots by using 1% citric acid as an extractant for the available nutrient fraction and was probably the first to use field experiments for calibrating a soil testing method. In the wake of *Dyer*'s work many extractants were tried among which concentrated mineral acids were found to be the least suitable *(Opitz [1907])*. However, in the years to follow several lanes of approach were still being pursued. *V. Wrangel and co-workers ([1926], [1930])* investigated soil solutions and their usefulness as indicators of nutrient availability. *Mattson [1926]* and *Wilson [1928]* introduced electro-dialysis and *Köttgen* and *Diehl [1929]* electro-ultrafiltration. Electro-ultrafiltration (EUF) was taken up again and modified by *Németh [1971a, b]*.

But the main trend was for rapid methods, and the search went on for extractants which would dissolve the plant available fraction with the least possible expenditure of time and labour. *(Lunt et al. [1950]; Egnér et al. [1960], Ahmad et al. [1973]). Devaux [1916]* introduced the theory of contact exchange and this was later elaborated by *Jenny* and *Overstreet [1939]* lending support to those who considered that fraction of nutrients which was bound to the surfaces of the soil particles to be the most important. Later this theory of contact exchange was refuted by *Lagerwerff [1960]* and *Olsen* and *Peech [1960]* who were able to demonstrate that nutrient uptake took place via the soil solution.

A completely new development was initiated by *Bray [1954]* with a paper on the importance of nutrient mobility as a factor of nutrient supply to plant roots. These ideas were taken up by *Barber [1960]*, *Barber and associates [1962]* and by *Nye and his group* (see *Nye* and *Tinker [1977])*. This approach proved to be more fruitful than the 'nutrient potential' approach of *Woodruff [1955]* and *Schofield [1955]*, on whose work *Beckett [1964]* based his Q/I concept.

However, there has been little response to the new ideas that have evolved over the past two decades in practical soil testing and most methods in current use are empirically based.

3. Methods of soil analysis

It is not intended to give a complete account of soil testing methods in present use nor will technical details of individual methods be explained. This review will be restricted to a discussion of the potentialities of the various methods and the information to be gained from the results obtained with them.

The various soil testing methods can be classified according to the fractions of soil K which are covered. The different forms of soil K are discussed in this volume by *Schröder [1979]* and *van Diest [1979]* and their characteristic properties need not be described here.

3.1 K concentration in the soil solution

K concentration in the soil solution is an important index of availability *(Rowell et al. [1967], Nye [1972])* because K diffusive flux towards the roots takes place in the soil solution (see *van Diest [1978])* and the rate of diffusive flux depends on the concentration gradient that develops in the soil adjacent to an actively absorbing root. Under conditions of a given K demand by the plant and the ability of the root to reduce the K concentration at its surface to a certain minimum concentration the concentration gradient is, among other things, a function of the initial concentration in the soil solution.

The K concentration in the soil solution appears to provide a very good common measure of K availability in soils of very different properties *(Németh* and *Harrach [1974], Jankovic* and *Németh [1974], Németh* and *Forster [1976])* (Figure 1). *Beckett*'s *[1964]* activity ratio (AR_o) is a relative measure of K concentration in the soil solution in that K concentration is expressed relative to the square root of standardized Ca + Mg concentrations. A number of criticisms have been levelled against the use of 'K potentials' and AR_o in soil fertility studies *(Mengel [1963], Wild et al. [1969])*. In fact, *Beckett* himself has discussed the limitations of the method *(Beckett [1967])*.

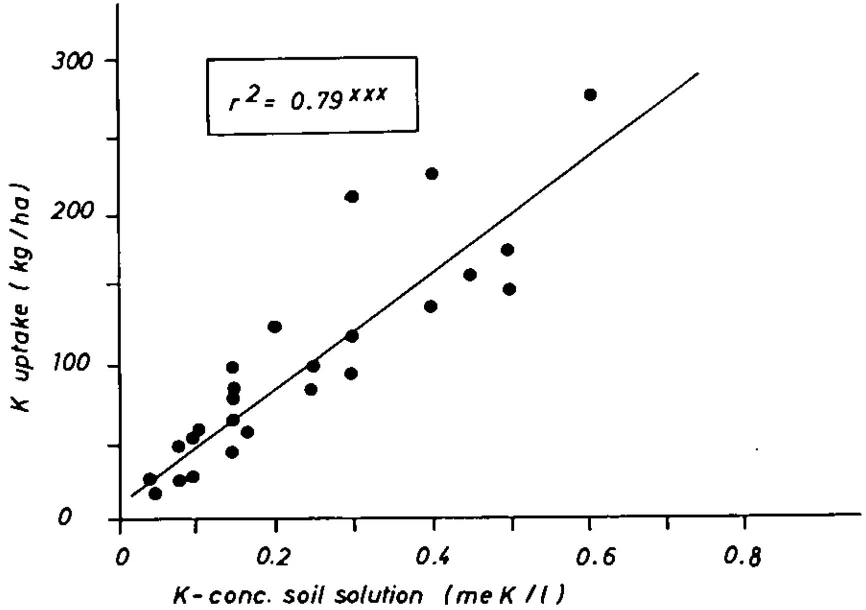

Fig. 1. Relationship between K concentration in the soil solution and K uptake of broad beans (6 soils with 4 K levels on each soil; clay content 14–38 per cent).

The amount of K present in the soil solution represents only a very small proportion of total soil K and is much less than a crop requires in a growing season. A measurement of the K concentration does not reveal whether this concentration is well buffered or not and how much fertilizer would have to be added should the concentration be considered inadequate.

K dissolved in the soil solution is a very labile fraction and may change without K being added because it is sensitive to fluctuations in soil water content and total electrolyte concentration. The plants, however, do respond to changes in K concentrations caused by the above mentioned factors *(Németh* and *Grimme [1974], Grimme* and *Németh [1975])*.

3.2 Easily extractable K

Schachtschabel and *Heinemann [1974]* proposed 0.025 N $CaCl_2$ which was already in use for Mg as an extractant for 'available' potassium, and this was shown by *Grimme* and *Németh [1976a, b]* to be a good indicator of the K status of soils. The quantities of K determined by this method are well correlated with K concentration in the soil solution and with crop response. The proportion of total exchangeable K extracted varies from 40 to 80% and depends on clay content and clay mineralogy thus taking into account the selective bonding effect of soil clays for K.
There is a variety of methods which one would expect to yield results similar to those obtained with the $CaCl_2$-method *(Black [1968], Ahmed et al. [1975])* because only a fraction of total exchangeable K is determined.

3.3 Exchangeable K

The majority of soil testing methods for K employ the extraction of exchangeable K or of quantities that come close to exchangeable K *(Black [1968], Scheffer-Schachtschabel [1976])*. A variety of extracting solutions are in use: neutral unbuffered electrolyte solutions, weak or strong acids, buffer solutions. There is probably

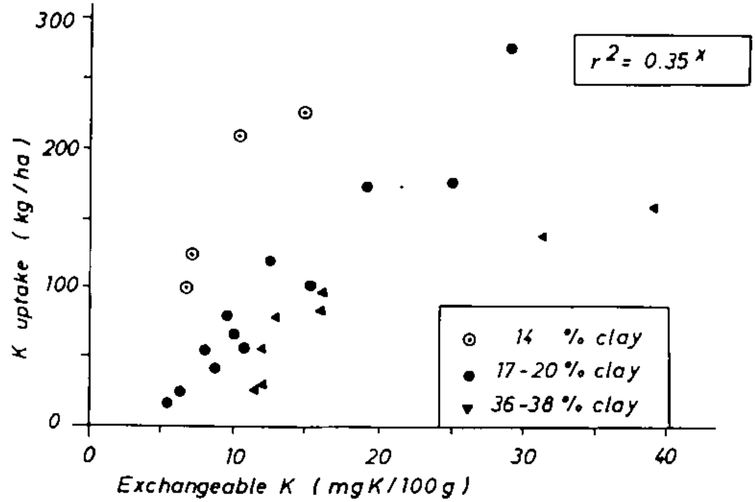

Fig. 2. Relationship between exchangeable K and K uptake of broad beans (same experiment as in Fig. 1).

no feasible variation which has not been tried, but none has been proved to give unambiguous and universally applicable results. Figure 2 demonstrates the poor relationship between exchangeable K and K uptake, if soils of different clay contents are included (14–38%). However, this is to be expected since, while exchangeable K represents that fraction adsorbed on external and accessible internal surfaces, it is not directly related to the K flux towards the roots *(Grimme et al. [1971], Nye [1972])*. It constitutes only a quantity measurement. It is mainly the clay content and the clay mineralogy which modifies the availability of exchangeable K *(Grimme et al. [1971a, b], Grimme [1976], McLean [1978])* so that the relation between exchangeable K and K uptake is very much improved if exchangeable K is expressed as a fraction of C.E.C. In that case a relationship like that in Figure 1 is obtained. Some authors use the total exchange capacity as reference *(Black [1965], McLean [1978]* others merely clay content *(von Braunschweig [1965], Quémener [1976])*. In the Netherlands the so called K-value is employed, which is the 0.1 N HCl-extractable K multiplied by a correction factor taking account of the effects of pH, organic matter and the fraction $< 16\ \mu$ *(van Diest [1978])*.

3.4 Non-exchangeable K

There is no question that plants are able to take up more K from a soil than the exchangeable complement *(Schachtschabel [1937])*. The 'available' non-exchangeable reserves are usually extracted with 1 N strong acids *(De Turk et al. [1943], Schachtschabel [1961], Haylock [1956])* and give a measure of the long-term K supplying power of soils. Electrodialysis, exchange resins and Na-tetraphenylborate have also been used *(Reitemeier et al. [1946], Quémener [1976])*. One has to bear in mind, however, that it is only when growth rates are low – *i.e.* low yields – that non-exchangeable K can be considered a useful K source. In many cases yields are reduced, if a large proportion of the K requirement has to be covered by non-exchangeable K, because the release rate is too low to meet the K demand of a vigorously growing crop *(Grimme [1974])*.

3.5 Electro-ultrafiltration (EUF)

To the knowledge of the authors the EUF method of soil analysisis the only method in practical use which takes dynamic aspects of nutrient supply into account. It allows the determination of intensity, quantity and buffering parameters *(Németh [1976])*. It also allows an assessment of the change of mobile soil K with time (Figure 3).

The EUF procedure makes use of nutrient desorption in an electric field. A soil suspension is subjected to an electric field which causes ions to move out of the suspension. This initiates a desorption process which continues as long as the electric field acts on the soil. The quantities removed are plotted as a function of time. Either constant or variable field strengths are used. Both procedures have their advantages. Variable field strength (Figure 3) is usually employed in routine work and from the results of a large number of field experiments a system of recommendations for extension work has been developed (Table 1) *(Németh [1978])*.

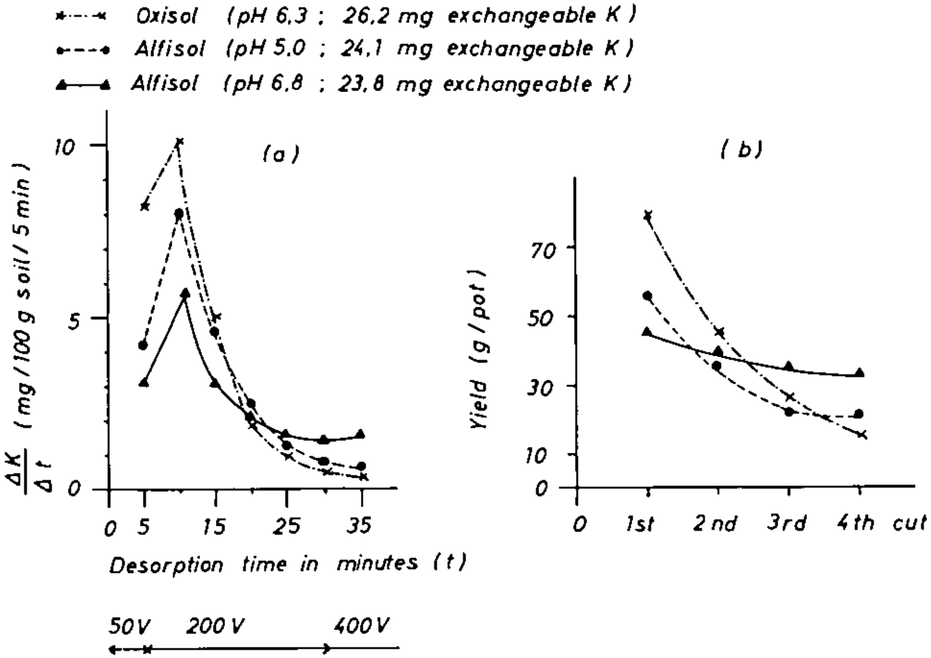

Fig. 3. Comparison of EUF desorption characteristics of 3 different soils (2) and the decrease of rye-grass yield with time (b). The soils contain similar amounts of exchangeable K but differ in K selectivity and buffering power. The yield curves are parallel to the desorption curves.

Table 1. Quantity of K required to raise the K-EUF values to 15 mg/100 g of soil as a function of initial K-EUF value and clay content. In field experiments 15 mg/100 g was found to give optimum K supply for high yielding sugar beet (~ 54 to/ha).

K_{EUF}	K application (kg K/ha)			
	clay content (%)			
(mg/100 g/35 min)	10	10–20	20–30	30–40
1	600	1200	1600	3000
2	560	1050	1300	1800
3	480	900	1100	1400
4	420	800	900	1100
5	370	700	800	900
6	330	600	700	800
7	270	450	550	650
8	240	300	400	500
9	210	250	300	350
10	190	200	250	300
11	150	150	150	200
12	120	120	120	150
13	90	90	90	90
14	60	60	60	60
15	0	0	0	0

3.6 Biological methods

One would expect plants to be efficient in measuring available soil K. In fact, field trials are always needed to calibrate chemical methods, but for the purpose of extension services they are far too cumbersome. Tests with small soil samples such as the *Neubauer* and the *Stanford-de Ment* methods *(Schachtschabel [1937], de Ment et al. [1959], Quémener [1976])* are still very tedious and too time consuming for practical purposes. But the most important drawback is the fact that, because of the high plant density employed, they impose a much higher stress on the soil K reserves than would a normal crop and thus overestimate the supply rate under field conditions.

4. Conclusions

The determination of the K status of soils is usually carried out by extracting the soils with salt solutions, weak or strong acids, or buffers of acids and their salts. Depending on their composition these solutions extract the loosely bound K and a variable proportion of more tightly bound K from external and internal surfaces of the soil matrix and the amount extracted more or less approximates with exchangeable K. Exchangeable K is a measure of the quantity which can be relatively easily mobilised as compared to the non-exchangeable K. But no information is obtained as to the rate at which it is mobilized, thus no true evaluation of availability can be made. There are instances, where exchangeable K may even be misleading *(Grimme [1976])*.

Since the factors affecting availability are known it is possible to select methods to provide the information wanted, and group them according to the parameters they measure. One has to distinguish between intensity, quantity and capacity, which give information on the immediate availability, the mobile reserves and the storage capacity, respectively.

The availability is mainly governed by the rate of transport towards the roots. But diffusion measurements are difficult and time consuming. It is, therefore, expedient to measure a parameter that is closely related to diffusion. This would be the K concentration in the soil solution, or the K saturation of the inorganic CEC, that is, the quantity/capacity ratio. For routine purposes, extraction with 0.025 N $CaCl_2$ appears to be a promising method *(Schachtschabel* and *Heinemann [1974], Grimme* and *Németh [1976])*. This method takes into account the clay content of soils and extracts a decreasing proportion of the exchangeable K with increasing clay content. The results are closely correlated with K concentration and K diffusion. This method is essentially an intensity method.

From a knowledge of K concentration alone, it is not possible to know whether the reserves of exchangeable K are large enough to sustain an adequate concentration for the duration of the growing period. This requires a knowledge of the quantity of exchangeable K and if possible the buffering capacity. The buffering capacity is given by the slope of the adsorption isotherm, and is a useful parameter when adjusting the fertilizer dose. K concentration in the soil solution, or for that matter the degree of K saturation, does not provide the information needed to estimate the fertiliser requirement, since the change of K concentration with increasing K content of the soil depends on the inorganic CEC.

The correct and complete evaluation of the K status of soils and, hence, the correct forecasting of K fertiliser need may seem to be somewhat complicated. However, once the desired level of K in a soil has been achieved, one of the conventional methods is quite adequate for monitoring soil K and thus checking the effects of fertiliser policy since it will certainly indicate whether soil K is declining, increasing or being maintained at a constant level.

Because there is a correlation between K concentration and the degree of K saturation, it is quite acceptable to use exchangeable K values, modified for clay content, when assessing the K status for routine advisory purposes. With these two parameters it is possible to estimate the degree of availability and to estimate the K fertiliser requirement. Yet, we should always remember that the nutrient supply to plants depends upon dynamic processes in the soil and that the routine analytical methods now in use reflect only a static situation and therefore give only a partial and approximate measure of true K availability. Soil testing is essential for efficient fertiliser use. The usefulness of soil testing rests on the correct choice of method.

The term 'availability' describes an obviously complex situation and must not be confused with the term 'available quantity' as is often done. Quite often, the quantity extracted by some extractant is termed available K. In the last analysis, all the potassium in a soil is available, not just the exchangeable K but also the nonexchangeable K. Only the degree of availability differs. For a plant it is not so much the quantity present which counts but the rate at which the required quantity is supplied. It is, therefore, not surprising that often there is no correlation between soil test results and response because the method chosen determined a 'quantity' parameter, without supplying information on the degree of availability. Actually, both parameters are needed, because it is necessary to know both whether the rate at which a nutrient is supplied to the roots is adequate to keep up with the growth rate of the plant and whether the quantity of nutrient present is sufficient to meet the plant's demand. As far as potassium is concerned it is also necessary to know the shape of the buffer curve in order to be able to calculate correctly the quantity of fertiliser needed. This amounts to taking into account clay content and mineralogical composition of the clay fraction. Knowing that a number of factors influence K availability and that plant demand depends on the crop grown and the growing conditions it is evident that there is not one optimum K level. The optimum K level varies with crop, yield level and weather conditions. A high yielding crop having a root system with a low surface area requires a higher supply rate than a low yielding crop with an extensive root system. In a dry soil, a higher K concentration is required to maintain an adequate supply than is needed in a wet soil. There is therefore a choice either to recommend a K dressing sufficiently large to ensure that crop growth will not be limited by K supply even under adverse growing conditions or a more modest rate that will be near optimum for average conditions but below optimum if conditions are adverse. The latter recommendation carries a risk that yield will be sacrified. The soil nutrient level that can be considered adequate will depend on the agricultural system, the overall productivity and the prevailing economic conditions.

5. Summary

Following a brief account of the history of soil testing, various methods are discussed. There is no detailed description of methodology, the discussion centring on the evaluation of information obtained by measuring the different fractions of soil K

(K in the soil solution, easily extractable K, exchangeable K, non exchangeable K EUF-K). The significance of these fractions with respect to plant growth is discussed and a distinction is made between available K and the availability of soil K.

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