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RECENT STUDIES IN POTASSIUM FIXATION

Work since 1939 on K fixation has been concerned mainly with the following aspects: fixation and soil-moisture content, the role of clay minerals, fixation and the exchange complex, fixation as an equilibrium process and, to a lesser extent, fixation as affected by humus and soil reaction. "Fixed K" is commonly taken to mean that which is only moderately rapidly available to plants, as distinguished from (a) the readily available fraction, including exchangeable K, water-soluble K salts and K in inorganic matter and (b) that which becomes available only very slowly, including the K of feldspar and muscovite. Attoe and Truog⁽¹⁾ for example record that the non-exchangeable K extracted with 0.5 n. HCl at room temperature—amounting to quantities up to 90% of those extracted in the exchangeable form—was moderately available to plants, while in some soils the benefits of fixation may largely counterbalance the disadvantages of slower availability⁽²⁾.

Soil moisture. Drying of soil

Raney and Hoover⁽³⁾ showed that 23 per cent of the 2160 p.p.m. of K applied to a montmorillonitic soil became fixed during 1 month of moist storage, and that 57 per cent became fixed on subsequent air-drying. With a kaolinitic soil, moist fixation was much smaller, while air-drying appeared to release some of the fixed K to the exchangeable form. In light soils responsive to applied K, air-drying distinctly increased the fixation of applied K, but had little effect on the native soil K. Subsequent wetting caused a slow release into solution or into the exchangeable form⁽⁴⁾, while saturation with moisture of Mississippi-delta soils, high in K, markedly increased the exchangeable-K content⁽⁵⁾. Walsh and Cullinan⁽⁶⁾ also showed that fixation by alternate wetting and drying was not permanent: it was, however, large enough to cause severe K-deficiency symptoms in a first crop of mustard in pots, while the growth of a second crop indicated a release of K from the fixed state.

Attoe⁽⁷⁾ concluded that fixation is of two kinds: (a) that which proceeds in moist soil, increases with pH and fixes K in a form fairly soluble in 0.5 n. HCl, and (b) that which proceeds on drying, is independent of pH and fixes K in a form fairly resistant to extraction with 0.5 n. HCl. In some soils, unfertilized with K, drying caused an increase in exchangeable-K content. Attoe and Truog⁽¹⁾ suggest that the drying fixation of applied exchangeable K follows a definite law expressed in the equation $\log Y = k \log X + c$, in which X is the rate of application, Y the amount remaining exchangeable of that applied, and k and c are constants determined by the extent of fixation.

Ayres^(8,9), using K salts at concentrations between 0.1 n. and 0.001 n. on acid soils, showed that the concentration of the percolating K solution is an important factor in fixation, and concluded that for any given soil there is a concentration, of K applied in solution, below which sorption does not occur; thus the use of small amounts of K fertilizers in irrigation water may result in loss of the nutrient by leaching. Hauser⁽¹⁰⁾ obtained evidence of a critical moisture content of the soil below which K could not enter the lattice of the clay crystals. Martin *et al.*⁽¹¹⁾, while noting that the greatest fixation occurred on drying at high temperature, believe that the results do not suggest that a dehydration is directly involved: the effect noted on drying may be due to an increased concentration of salts in the soil. Wood and DeTurk⁽²⁾ recorded that, in a mature Illinois soil, heavy K applications became fixed in an acid-insoluble form, while in a younger soil the acid-soluble form became greatly increased.

Clay minerals

Volk⁽¹²⁾ recorded that a powdered pure kaolinite fixed 440 p.p.m. of K, muscovites from 0-1700 and a bentonite 8850 p.p.m. Jacob⁽¹³⁾ ascribed the very strong fixation in tropical soils to montmorillonite, and Hauser⁽¹⁰⁾ reported of a variety of Dutch

soils that mica minerals were the most strongly fixing. Seatz and Winters⁽¹⁴⁾ also confirmed the great fixing power of mica and montmorillonite types. Stanford⁽²⁷⁾ reported that micaceous minerals are responsible for rapid moist fixation in calcareous soils, owing to the fact that Ca, Mg and Na are quite readily replaced by K. The fixation is an exchange reaction. Acid illite under moist conditions, however, fixes only fairly small quantities unless NaOH, Ca(OH)₂, phosphate, fluoride, etc., are used to remove (by an exchange reaction) H, Fe and Al ions from the intramicellar spaces. With the exception of fluoride, these treatments reduced the drying fixation in bentonite, probably through a blocking of exchange positions of interplanar surfaces. Martin *et al.*⁽¹¹⁾ suggested the possibility that fixation occurs at a limited number of attraction spots having special properties due either to their position in the lattice or to the nature of the soil minerals with which they are associated. Page and Baver⁽¹⁵⁾, in attempting to reconcile different theories, suggested that drying fixation is related to the ionic size of K and the contraction of the montmorillonite lattice: K ions of ionic diameter 2.66Å would be strongly held in the spaces, of diameter 2.8Å, between the hexagonally arranged oxygen ions. When large ions, such as diethylamine, were used to prevent sheet contraction on drying, K fixation was reduced to one tenth. Univalent and divalent cations of ionic size close to the size of certain free spaces within the lattice were susceptible to fixation. Martin *et al.*⁽¹¹⁾ emphasize that X-ray diffraction data do not support Page and Baver's lattice-shrinkage theory as a general explanation of the fixation of K in non-replaceable form.

The exchange complex

Joffe and Levine in a series of papers^(16, 17, 18, 19, 20) present evidence that K, in order to become fixed, must take on the exchange state, and Martin *et al.*⁽¹¹⁾ found strong evidence that certain cations, when present in the exchange complex of some soils, can pass from a loosely held to a very strongly held state, and concluded that K fixation involves an exchange adsorption followed by a fixation resulting in a reduction of the total exchangeable cations of the soil, the transformation possessing many of the

characteristics of a chemical reaction: the degree to which it occurs depends on the concentration of the potassium ion in the soil solution and on its amount in the exchange complex, equilibrium is reached rapidly, but the reaction is only very slowly reversible. Wood and DeTurk⁽²⁾ noted that additions of K₂HPO₄ gave twice the replaceable-K content given by additions of KCl, and concluded that new exchange positions were formed independently by the PO₄ linkage without disturbing the native exchange valencies. Seatz and Winters⁽¹⁴⁾, studying the relationship between fixation, exchange capacity and the complementary ion, suggested that the exchangeable K is in equilibrium with the K-bearing soil minerals and that when the degree of K saturation of the colloids is altered by fertilizing or cropping, K tends to be respectively fixed or released. 7 soils, for example, appeared to have an equilibrium level near the 400-lb. rate of application (220 p.p.m.). In 2 soils of the same colloid content and exchange capacity, fixation was greater in the one with a higher proportion of mica and montmorillonite. In 14 Mississippi-delta soils, an increase in base saturation was associated with an increase in fixation until complete saturation was reached, after which a decrease in fixation ensued⁽⁵⁾.

Equilibrium and release

Wood and DeTurk^(2, 21) established that on some Illinois soils K applied in heavy dressings became fixed in a fairly insoluble form, but became exchangeable again as the soils were depleted of exchangeable K. The replaceable, acid-soluble and acid-insoluble forms were in a slowly shifting equilibrium, shifts obeying the law of mass action. In experiments in Iowa⁽²²⁾ the existence of an equilibrium was indicated by the close correlation between (a) the K released to the exchangeable form after this form had been removed by leaching and (b) the original replaceable-K content of the soil. Release was greatest from heavy alluvial soils, and greater from soils under grass than under forest.

A montmorillonitic soil showed⁽³⁾ a temporary equilibrium between exchangeable and non-exchangeable K within a week after leaching with neutral ammonium acetate,

with a second level of equilibrium in a month, whereas in a kaolinitic soil only one level of equilibrium occurred, within 1 and 2 weeks after leaching. Recent studies of the release of fixed K to an exchangeable or a non-exchangeable but plant-available form are those of Chandler *et al.*⁽²³⁾ who noted, in 11 soils continuously cropped with clover, an initially rapid and then slow decrease of the exchangeable-K content to an equilibrium determined by the rate of release from the fixed form, this rate being high in 4 and low in 3 soils; and of Ayres *et al.*⁽²⁴⁾ who noted in Hawaiian soils under Napier grass a release of 3400-4200 lb. of K₂O per acre in 4½ years from non-exchangeable sources, with little corresponding decrease in the level of exchangeable K.

The rate of release from Ca-saturated soils was only one half of the rate in H-saturated soils, which, it is suggested, may explain the occurrence of K deficiency in high-lime areas⁽²²⁾. Ayres^(8, 9) noted that an increasing degree of Ca saturation in acid soils increased the desirable sorption of and prevented the loss of K from solutions of low concentration. Joffe and Levine⁽¹⁸⁾ referred the increased fixation which generally follows liming not to the Ca, but to the higher pH and consequent effect on the relative base saturation of the exchange complex. Raney and Hoover⁽⁹⁾ reported that Ca-saturated soils containing small, medium and large quantities of

artificially fixed K released respectively greater, similar or smaller quantities of K into the exchangeable form than the same soils when H-saturated.

Organic matter

Hauser⁽¹⁰⁾ reported that humus soils without clay colloids did not fix K, but that when the humus of mineral soils was oxidized their K-fixing capacities were greatly reduced. Pchelkin⁽²⁵⁾ found that the oxidation by H₂O₂ of the organic-matter content of chernozems reduced the fixing power of these soils. Martin *et al.*⁽¹¹⁾, working with arid soils, could not attribute fixation to the presence of organic matter, and Joffe and Levine⁽¹⁸⁾ found that the addition of organic matter depressed fixation. In the Mississippi-delta soils, of pH 5-8, the addition of organic matter markedly increased the leachable and the available K⁽⁵⁾, while on fine sandy loams, very responsive to K, added organic matter prevented the fixation of applied K and changed more than 70 p.p.m. of native K from the non-exchangeable to the exchangeable form⁽⁴⁾. A biological fixation in unleachable form of up to 200 lb./acre of K is reported by Hurwitz and Batchelor⁽²⁶⁾ on adding plant material to a neutral silt loam. Biological activity may thus be of importance in the fixation occurring during moist storage.

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