Potash Review

Monthly communications by the International Potash Institute, Berne (Switzerland)

Subject 1

Agricultural Chemistry **February 1956**
30th suite

The energies of replacement of calcium by potassium in soils*

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Primary interest in the chemistry of soils revolves about them as media for the nutrition of plants. Early studies emphasized the composition of the soil solution. Later studies stressed the cationic composition and the capacity of the exchange complex. The capacity factor in the cationic nutrition of plants certainly deserves the consideration it has received in terms of the continuous nutrition of the plant throughout its growing period. The rates of delivery of cations from the exchange complex of the soil to the growing plant are a factor in plant nutrition; and the transportation of the cations is associated with the supply of anions in the soil solution. Undoubtedly the rate of transfer of the cations between the exchange complex and the plant root is adequate in any soil containing a normal complement of nitrates, sulfates, phosphates and bicarbonates. However, the removal of a metallic cation from the exchange complex of the soil involves a cationic exchange reaction. But exchange reactions are governed by changes in free energy.

Energies of exchange not only determine whether or not reactions will occur; they also determine the nutritional balance of the suite of cations which will be exchanged from the soil. Hydrogen from the plant root exchanges for metallic cations from the clay. The free energy of the hydrogen exchange governs the flow of cations, in general, from the exchange complex to the plant root. But, the nutritional balance of the metallic cations that will be delivered by the hydrogen exchange is governed in turn by the energy of exchange for the replacement of one metallic cation by another. The investigation reported herewith deals only with the nutritional balance of potassium and calcium as reflected by the free energy of the reaction for the replacement of calcium by potassium in the soil.

*Energies of replacement, preferably of exchange, as used in this paper, are based on thermodynamic considerations which guided the thinking throughout this investigation. This method of approaching cationic exchange differs from the conventional one, but its results expressed as cationic ratios agree in the end with those deduced through the principles of *Donnan*. The uncertainties surrounding the soluble anions in the clay system, of necessity considered in the *Donnan* concept, are avoided and the cation exchange is treated by strict thermodynamic principles. This justifies the use of energies rather than ratios for expressing the results. Such treatment reduces cationic exchange to a simpler reasoning more readily comprehended.

Energies of exchange for cation exchange

Energy of exchange represents the intensity factor in plant nutrition. The intensity factor is expressed most conveniently as energy of exchange per chemical equivalent of cations. Cationic exchange implies automatically that two kinds of cations are exchanging between two systems of anions. In order to evaluate the energetics of cation exchange for a soil, it is convenient to choose a true solution as the reference system for the cationic exchange. Conventional usage by chemists has established the standard state as a hypothetical solution in which the activity of each of the reacting cations is one molar. The standard state provides a suitable point of reference for evaluating the energetics of cationic exchange. The standard state will be the point of reference if the concentrations of the cations used in the energy equation are expressed in moles per liter.

Evaluation of energies of exchange may be accomplished through the medium of a dilute electrolyte which has been equilibrated with the soil. Equilibration establishes the free energy of exchange for the cations in the eletrolyte at the same value that exists for them in the soil. The electrolyte may be separated from the soil and analyzed by conventional methods. The results may be used then to compute the energy of exchange for the electrolyte with the standard state as a point of reference.

The activities of the metallic cations in a very dilute electrolyte are equal, for practical purposes, to the concentrations. The energy of exchange, Δ F in calories per chemical equivalent at 25° C may be computed from the relation:

$$\Delta F = 1364 \log \frac{a_K}{\sqrt{a_{Ca}}}$$

where a_K and a_{Ca} express the activities in moles per liter of potassium and calcium, respectively, in the dilute electrolyte (6). Any other choice for expressing the concentrations would refer the reaction to some state other than the standard state. Because of the equilibration, the energy change computed from the above equation is the total for the transfer of one chemical equivalent of potassium from the standard state to the soil in return for one chemical equivalent of calcium moving from the soil to the standard state under reversible conditions. Negative values imply that the reaction between the soil and the standard state would proceed spontaneously. Positive values imply that the reaction would proceed in the reverse direction. As a consequence of the relationships between a soil, a dilute electrolyte and the standard state, a dilute electrolyte may be viewed as an excellent instrument with which to evaluate the energetics of cationic exchange for soils.

A dilute electrolyte used as an instrument with which to evaluate cationic exchange preferably should be so dilute that the activities of the cations approach their concentrations, and so dilute that the electrolyte does not penetrate the ionic atmosphere of the charged colloidal particles to an appreciable extent. Ordinarily the fortuitous concentrations of anions in the displaced or extracted soil solution will suffice for evaluation of the energy of exchange for any pair of cations.

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The cationic composition of the soil solution

The thermodynamics of the equilibrium between a soil and the soil solution requires that the energy of exchange for any pair of cations in the exchange complex and in the solution will be the same. And each combination of cations in the exchange complex will be characterized by an energy of exchange that is constant irrespective of the moisture content of the soil or of the fortuitous amounts of anions that may be present in the solution. Differences in the concentrations of the anions in the soil solution, whether produced by changes in the moisture content of the soil or by the addition or removal of small amounts of salts, will be associated with differences in the concentrations of the cations in solution, because the anions in solution must be accompanied by chemical equivalents of cations. However, the distribution of the cations in the solution will always be such that they will reflect a constant energy of exchange for a specific combination of cations in the exchange complex.

Differences in cationic concentrations and differences in cationic ratios in the soil solution would appear to be of no fundamental significance, whereas the ratio of the molar concentration of a monovalent cation to the square root of the molar concentration of the divalent cation, which reflects energy of exchange, is the important criterion by which to judge the soil solution.

That the energy of exchange is a constant property of a soil for different concentrations of anions in the soil solution is supported by the results of *Burd* and *Martin* (3) who investigated the composition of the soil solution displaced from soils at different moisture contents. Their results for potassium and calcium were converted to potassium-calcium ratios and to energies of exchange (table 1). Doubling the moisture contents of the soils reduced the concentrations of the cations by about half and increased the ratio of potassium to calcium by about 1.4 times; yet these changes reflect energies of exchange that were a constant within practical limits. Furthermore, the four soils which they studied were similar as regards the energy of exchange for potassium and calcium.

Extensive investigations of the soil solution by the early soil scientists virtually were abandoned with the inception of exchange chemistry. As a consequence, today, we tend to gauge the nutrient balance of soils by the cationic composition of the exchange complex. However, the correlations between plant nutrition and cationic balances in the soil suggest that different cationic balances are necessary in different kinds of soil, so that percentage saturation is not an infallible guide to a balanced nutrient medium. Since the nutritional balance between a specific pair of cations in a plant will be determined primarily by the energy of exchange for the cations in the soil, it is reasonable to suppose that energy of exchange as measured in the soil solution should be universal in scope, applicable to all types of exchange materials as a criterion of the balance of the cations for plant nutrition. Numerous correlations exist between plant growth and cationic composition of the exchange complex for different kinds of soil. However, no such correlations are available with respect to energy of exchange. The purpose of this investigation was

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to establish broad limits or ranges for energies of exchange in relation to the nutritional balance of potassium and calcium in soils.

Table 1

Free energy change, Δ F, accompanying the replacement of calcium by potassium in soils at different moisture contents as calculated from data reported by *Burd* and *Martin**

Soil number	Moisture content	Cations in displaced solution			
		K	Ca	K/Ca	Δ F
	%	ppm	ppm	me/me	calories
5	9.0	125	845	0.076	– 2260
	18.0	85	410	0.106	– 2270
8	7.3	250	1310	0.086	– 1980
	14.8	150	640	0.120	– 2070
9	7.5	130	985	0.068	– 2280
	14.3	85	475	0.092	– 2320
	9.0	165	790	0.107	– 2070
11	13.6	180	560	0.165	– 1920
	16.6	140	420	0.171	– 1980

* Calculations were made in terms of concentrations. Corrections for activity coefficients would change the energy values slightly but the relative differences between results for a single soil would be negligible

Plant nutrition in relation to the energies of replacement of calcium by potassium

The plant, in the final analysis, must be the criterion by which a medium is judged as a suitable substrate for growth. The relationships between plant nutrition and energies of exchange may be ascertained most readily by considering those soils for which an abundance of experimental data is already available. The intensity factor in cation exchange as exemplified by energy of exchange is a fundamental measure, and if those soils for which correlations already exist are evaluated in terms of energies of exchange, the results should provide the necessary guide posts for evaluating the nutritional status of any kind of an exchange medium with respect to the potassium-calcium balance.

The Putnam soils in Missouri have been studied extensively for many years. Understanding of these soils is based upon results from field plots, greenhouse pots, electrodialyzed clay, and soil tests. Briefly summarized, the results have shown that general farm crops are supplied with adequate amounts of potassium on limed land when the potassium level of soil is of the order of 200 lb to 300 lb per acre corresponding to a saturation of the exchange complex of 1.7 to 2.6%, as measured by *Bray*'s test for potassium (2). All crops have been observed to be deficient in potassium on Putnam soils containing 100 lb per acre or less of exchangeable potassium. Corn in seasons with adequate amounts of rainfall is deficient in potassium on Putnam soil with a test level of 120 to 140 lb per acre of potassium, but the deficiencies are not apparent in dry seasons.

Graham (4) in his interpretations of the results of the Missouri soil tests, suggests that soils of the montmorillonitic type function satisfactorily when the cationic distribution in the exchange complex is of the order of 2% potas-

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sium, 10% magnesium, and 65% to 85% calcium. With the preceding considerations as a guide, the relationships between energy of exchange for the replacement of calcium by potassium and the potassium content of the soil were investigated. Both electrodialyzed Putnam clay and soils from field plots were used.

Energies of exchange for electrodialyzed Putnam clay

Electrodialyzed Putnam clay was treated with different amounts of exchangeable potassium and calcium, and equilibrated with a 0.00035 molar solution of chloride containing the same proportions of potassium and calcium that were present in the clay (6). The system containing 2% of potassium and 80% of calcium exhibited an energy of exchange of –3007 calories establishing a value of about –3000 calories as typical of a soil in which the balance between potassium and calcium was satisfactory.

Changing the potassium saturation of the clay by 1% changed the energy of exchange by 300 calories. Changing the calcium saturation of the clay by 1% changed the energy of exchange by 5.5 calories. Increasing the amounts of potassium decreased the numerical value for energy of exchange while increasing the amounts of calcium increased the numerical value for energy of exchange. The relatively small effect of different degrees of calcium saturation on the energy of exchange focuses attention on the potassium saturation of the clay as the dominant factor in the delivery of potassium by the soil. Consequently in the following investigation of field soils, all of which had been limited, only the potassium level of the soil was treated as a variable.

Energies of exchange for Putnam soils containing different amounts of exchangeable potassium

Samples of soil were collected from plots on the experiment station field for which the past performances with respect to potassium were known. These were air-dried and tested by the conventional soil testing procedures (4). Samples of the same soils were placed in Buchner funnels in quantities sufficient to fill the funnels, and were saturated with distilled water. After 1 hour the funnels were placed under suction for 15 minutes. The equilibrated extracted soil solutions were analyzed for potassium and calcium. The energy of exchange was computed from the equation

$$\Delta F = 1364 \log \frac{a_K}{\sqrt{a_{Ca}}}$$

The results are presented in figure 1.

All of the samples which contained less than 100 lb per acre of potassium, as measured by the soil tests, were from plots on which the crops have exhibited potassium deficiency symptoms persistently over a period of years. The energies of exchange for these soils ranged from –3600 calories to –4080 calories per chemical equivalent. A test level of 120 lb per acre of potassium for which deficiencies occurred in normal seasons corresponded to an energy of exchange of –3500 calories. Test levels for potassium of 200 lb per acre corresponded to an energy of exchange of –3000 calories. The energy level

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of −3000 calories corresponds to that obtained for the electrodialyzed Putnam clay with 2% of potassium and 80% of calcium in the exchange complex. The test level of 200 lb per acre has been found to be reasonably adequate for most farm crops.

The correlations between plant growth and potassium level in the soil, as reported by *Bray* (2), suggested that maximum yields were not attained until the level of potassium in the soil amounted to 300 lb per acre. Such a level corresponded to an energy of exchange of about −2600 calories in the Putnam soil (fig. 1).

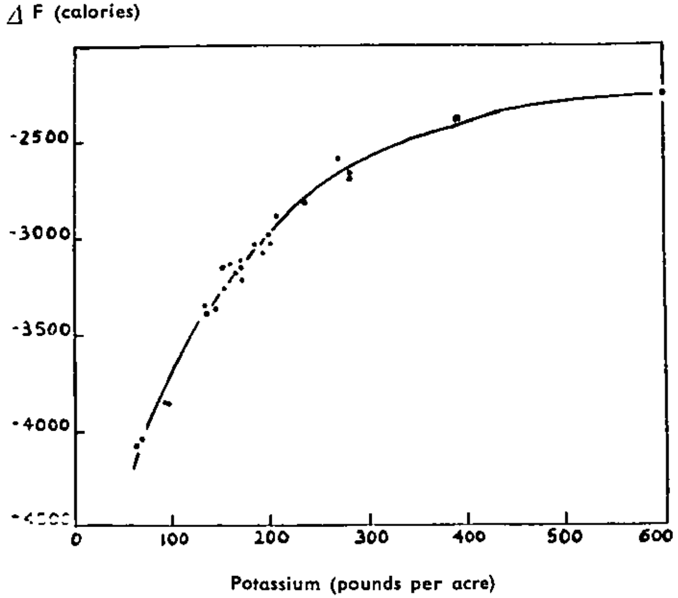

Figure 1 Changes in the equivalent free energy for the replacement of calcium by potassium in Putnam soils in relation to the exchangeable potassium content of the soils

Potassium levels from 300 to 600 lb per acre were produced by heavy applications of potash fertilizer. They were associated with energies of exchange ranging from −2600 calories to −2250 calories. Excessive amounts of potassium in the soil have been known to result in the "luxury" consumption of potassium. Energies of exchange of the order of −2000 calories result when the exchange complex of the soil contains either excessive amounts of potassium or deficient amounts of calcium. If energy of exchange rather than the absolute amounts of cations in solution governs the nutritional balance of cations in a plant, it is conceivable that excessive amounts of potassium would lead to calcium deficiencies in plants. Calcium deficiencies were not apparent in the corn grown on the Putnam soil with an energy of exchange of −2250 calories for the replacement of calcium with potassium. Hence one may conclude that for calcium deficiencies to occur the energies of exchange must be of the order of −2000 calories or less.

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Additional evidence of potassium deficiencies in soils for which the energies of exchange exceeded –3500 calories

The plots of Broadbalk Field at Rothamsted, England, are well supplied with calcium but deficient in potassium. *Voelcker* (5) reported the composition of drainage water from these plots. His data have been converted to energies of exchange with the following results.

Untreated soil –4180 calories
Fertilized soil –3730 calories
Manured soil –3610 calories

In all cases the energies of exchange reflected values which, when based upon the earlier consideration of the Putnam silt loam, would be interpreted as conducive to potassium deficiencies. Manuring and fertilization may have supplied the growing crops with sufficient potassium, but the supply of potassium in the exchange complex of the soil remained too low for desirable plant nutrition without continued use of the treatments.

Bray (1) reported the cationic composition of a number of soils and the concentrations of cations in dilute electrolytes equilibrated with the soils. These results may be interpreted in terms of pounds per acre of potassium, percentage saturation of the exchange complex by potassium and energies of exchange. The results are summarized in table 2.

Table 2

Energy of exchange for the replacement of calcium by potassium in soils for which data were reported by *Bray*

Sample number	Exchange capacity me/100 g	Base saturation %	K lb/acre	K %	Energy of exchange calories
S 6754	11.3	100	125	1.4	– 3540
S 6758	37.9	79	203	0.7	– 3640
S 6760	26.0	100	133	0.7	– 3680
S 6761	24.3	86	125	0.7	– 3760
S 6762	9.9	80	94	1.2	– 3510
S 6763	10.0	24	39	0.5	– 3340
S 6767	19.9	74	156	1.0	– 3590
S 6769	16.1	41	125	1.0	– 2990

All of the samples for which data were reported by *Bray* were low in potassium, according to the consideration that a potassium level of 200 to 300 lb per acre would be adequate, excepting No. S 6758 which contained 203 lb per acre. All of the samples were low in potassium if one considers 2% of the exchange capacity as representing an adequate level. Also, all of the samples were low in potassium, excepting samples S 6763 and S 6769, based upon an energy of exchange of –3500 calories as being excessive. However, these two samples were very low in calcium as reflected by the low degree of saturation of the soil by total bases. In their present state, they would be expected to

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deliver potassium and calcium in a desirable balance for plant growth. But if limed, the resulting energies of exchange would be expected to reflect potassium-deficient conditions.

The results reported by both *Voelcker* and *Bray*, when interpreted in terms of energies of exchange, lend additional support to the conclusion reached earlier that an energy of exchange of –3500 calories or more must be associated with a supply of potassium inadequate to balance the calcium in the soil for good plant nutrition.

Within the limits of the evidence that has been presented, one may conclude that energies of exchange represent fundamental properties of soils with respect to the cationic nutrition of plants; and that energies of exchange for the replacement of calcium by potassium should fall within a range of –2500 to –3000 calories for balanced nutrition of plants. Energies of exchange in excess of 3500 calories were associated with conditions that resulted in potassium deficiencies in the growing crops. Energies of exchange of –2000 calories or less may be expected to be associated with calcium deficiencies created by excessive amounts of potassium, but experimental evidence at this end of the energy scale was not available in the results that were studied.

The concepts of energies of exchange for characterizing the exchange reactions of soils introduce a means of evaluating the intensity factor as contrasted to the capacity factor of cationic relationship in soils. Soil testing procedures based upon the exchange capacity and the percentage saturation of the exchange capacity by cations, when correlated with the results of field experiments, provide a solution to the problem of desirable cationic balances for the particular kinds of soils for which the correlations were made. However, energies of exchange, when correlated with the cationic nutrition of plants through the exchange complex of the soil represent fundamental quantities that should be universal in scope, applicable to all soils in which cationic exchange is the dominant phase in cationic nutrition of plants. They should apply beyond soil boundaries, beyond localities, and beyond the limits of experience of the individual.

This paper sets forth some broad limits pertaining to the potassium-calcium relationships for soils in which calcium was the dominant divalent cation and potassium was the dominant monovalent metallic cation in the exchange complex. It must be recognized that complementary ion effects from other monovalent cations, particularly sodium, and possibly ammonium will also govern the total cationic balance in the plant. And when monovalent cations other than potassium are present in appreciable amounts in the exchange complex of the soil, their contribution to the energetics of cation exchange must be considered. Establishing the limits and ranges for the effects of complementary ions should be a fruitful field of investigations for the future.

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