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Cation Exchange in Soil as Influenced by Concentration of the Ions in Solution*

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Clay fractions were separated from representative black, red, alluvial and laterite soils. Various cationic clays were prepared and ion exchange experiments were conducted by equilibrating the clay salts with chloride solutions of the cations. After the attainment of equilibrium, the cations remaining in solution ware estimated. The percentage of cation exchanged increased as the concentration of the replacing cation increased upto 2 to 3 symmetry and then there was a definite decrease. This trend, however, varied with soil type, clay salts and electrolytes used. NaCl as the replacing cation showed very poor exchange, whereas maximum exchange was observed with $CaCl_2$.

Cations in solution remain nearly at equilibrium with those in exchangeable form. Therefore, the chemical reaction involving cations in solution involves also the cations in exchangeable form. The exchange of cations in soil is influenced markedly by the nature of the replacing and replaced cations, concentration of replacing cation and nature of colloidal fraction in respect of the clay mineral composition. These properties of are considerable importance to the growth of plants in soils because ions occurring in soils as exchangeable cations form a part of nutrient supply. There is very little experimental work along these lines with reference to soils of South India. Keeping these aspects in view, clay samples from five representative soils were examined in detail with special emphasis on the degree of exchange.

MATERIALS AND METHODS

Soils representing the black, red, alluvial, high level laterite and low level laterite soil groups were collected from Peelamedu, Manvi, Aduthurai, Nanjanad and Pattambi respectively. Selection of soils was made in such a way that they represented the principal four groups of soils which are characterised by the predominance of a particular clay mineral in each group.

1. **Separation of clay:** Clay samples were separated as sodium clay by adopting the procedure for the separation of various mechanical fractions of the soil. The clay separated from the soil was further treated with six per cent hydrogen peroxide for the removal of organic matter.

2. **Preparation of Ca, Mg, K and Na-Clays:** The separated clay

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samples were treated with respective chloride solutions to prepare the cationic clays according to the method of Scheuring and Overstreet (1961).

3. **Exchange experiments:** The exchange experiment was conducted at a room temperature of 28° C and at a concentration of 0.1 normal chloride solution of the cations. The treatments which were indicated by Vanselow (1932) are described below, taking the case of Ca-clay with KCl with or without $CaCl_2$ as example. Exchange experiments with the various treatments were conducted according to the procedure of Krishnamoorthy and Overstreet (1950).

TABLE I. Treatments

Treatments No.	Ca-clay (me/l)	KCl (me/l)	$CaCl_2$ (me/l)	Symmetry concention
1.	20	100	—	5.0
2.	30	100	—	3.3
3.	40	100	—	2.5
4.	50	100	—	2.0
5.	50	80	20	2.0
6.	50	70	30	5.0
7.	50	50	50	2.0
8.	40	40	60	2.5
9.	30	30	70	3.3
10.	20	20	20	5.0

Depending on the quantity of clay available, only limited number of treatments was included under each clay salt of the soil groups. Calcium clay was equilibrated with KCl, $MgCl_2$ and Nacl respectively with or without calcium chloride solution to give a total concentration of 100 me/litre. Other clays which were equilibrated similarly with chlorides of cations other than that carried by the clays are as follows; Mg-clay: $CaCl_2$; KCl and Nacl; K-clay: $CaCl_2$, $MgCl_2$ and Na-Clay : $CaCl_2$, $MgCl_2$ and KCl.

RESULTS AND DISCUSSION

The cation exchange capacity of clays of black, red, alluvial, low level and high level laterite soils included in present study were 79.0, 37.0, 45.0, 27.8 and 33.8 me/100 g clay respectively. The cation exchange as influenced by concentration of the ions in solution is discussed below.

1. Black soil clay

(a) **Symmetry concentration** (Treatments 1 to 4): In the case of Ca and Mg-clays, the percentage of cation exchanged increased as the concentration increased to 2 to 3 symmetry concentrations. Subsequently, a definite decrease in cation exchanged was observed. In the case of K and Na clays similar trends were noticed in which the cation exchange increased up to two symmetry concentration.

(b) **Concentration of replacing cation at various symmetries** (Treatments 4 to 10): The effect of concentration of replacing cations irrespective of symmetry concentration was studied and it was observed that similar trends were obtained for $CaCl_2$ with Mg-clay and K-clay. The trends for $MgCl_2$ with K-clay and Ca-clay, were identical.

2. **Red Soil clay :** In the case of red soils, only limited number of treatments (1, 2, 9 and 10) were inclu-

TABLE. II. Pnrcentage of cation exchanged in Black soil clay

Type of clay salt	Cation exchanged	Treatments 1	2	3	4	5	6	7	8	9	10
Ca—clay	Mg	16	44	35	29	30	25	11	16	5	4
	K	38	59	64	59	49	53	28	27	36	23
	Na	65	43	33	39	6	1	Nil	Nil	Nil	Nil
Mg—clay	Ca	64	70	88	97	71	65	38	39	39	44
	K	90	72	64	59	47	37	33	28	33	30
	Na	9	43	6	17						44
K—clay	Ca	54	83	97	86	66	59	42	40	37	30
	Mg	33	33	37	38	26	23	13	6	Nil	20
	Na	2	6	22	17	6	7	17	8	Nil	1
Na—clay	Ca	88	82	85	97					12	58
	Mg	59	65	64	59					37	32
	K	71	47	55	56					32	36

TABLE III. Percentage of cation exchanged in Red soil clay

Type of clay salt	Cation exchanged	Treatments 1	2	9	10
Ca-clay	Mg	27	30	9	6
	K	58	51	13	4
	Na	3	15	2	3
Mg-clay	Ca	41	46	23	Nil
	K	40	36	18	1
K-Clay	Ca	86	96	25	26
	Mg	29	27	14	7
	Na	10	15	14	9
Na-clay	Ca	56	58	45	52
	K	58	65	40	39

ded in the conduct of exchange experiment.

It was observed uniformly that higher percentage of cation exchange occurred with increase in concentration of replacing cation in solution. Considering the interaction between the clay salt and cationic chlorides, it was noticed that NaCl, as the replacing cation showed very poor exchange of cation in all clay salt and it was markedly low in the case of Ca-clay. On the other hand, Ca as the replacing cation in solution has brought about high per cent of cation exchange in all clay salts.

3. **Alluvial soil clay:** In the case of alluvial soil clay all the ten treatments were included in the experiment for Ca and K clay. But, for Mg and Na-clays only five treatments were taken into consideration. In the case

TABLE IV. Percentage of cation exchanged in Alluvial soil clay

Type of clay salt	Cation exchanged	Treatments									
		1	2	3	4	5	6	7	8	9	10
Ca-clay	Mg	25	41	33	29	10	15	17	8	5	47
	K	71	66	64	59	47	43	31	28	23	10
	Na	6	7	12	14	15	2	13	11	25	3
K-clay	Ca	56	85	76	88	66	59	40	37	26	16
	Mg	19	18	25	31	31	30	6	9	Nil	5
	Na	7	6	9	29	12	15	7	20	32	31

Type of clay salt	Cation exchanged	Treatments				
		1	2	3	4	10
Mg-clay	Ca	66	65	87	96	46
	K	53	59	64	62	11
	Na	Nil	2	9	17	11
Na-clay	Ca	71	75	95	94	62
	Mg	49	55	56	61	4
	K	58	75	74	72	27

of Ca and Na-clays, the percentage of exchange increased with the concentration of cation in solution. However, such trend could not be observed in Mg and K-clays. In all clay salts, there was uniform reduction in the percentage of cation exchanged at high concentration such as five symmetry.

The behaviour of various cationic chlorides as modified by the clay salts with which they were allowed to react was examined. Considering $CaCl_2$, it was observed that exchange of cation increased in Na, Mg and clays. NaCl showed very low exchange of cation at all concentrations. But with regard to KCl and $MgCl_2$ it was noticed that at higher concentrations namely at five symmetry the percentage exchange of cation was low. In all cationic chlorides, it was generally observed that high percentage of cation exchange took place at, 2, 2.5 and 3.5 symmetry values.

4. **Laterite soil clays:** As far as laterite soils were concerned, it was more or less an exploratory experiment

in as much as very limited number of treatments alone (1, 2, 3, 4 and 10) were considered. In both the laterite soils, only Ca and K clays were examined.

TABLE V. Percentage of cation exchanged in high level Lateriate Soil clay

Type of clay salt	Cation exchanged	Treatments 1	2	3	4	10
Ca-clay	Mg	9	23	34	31	24
	K	36	36	32	59	7
	Na	11	7	6	16	Nil
K-clay	Ca	86	95	82	75	20
	Mg	9	16	18	20	27
	Na	11	7	6	14	2

Percentage of cation exchanged in low level laterite soil clay

Type of clay salt	Cation exchanged	Treatments 1	2	3	4	10
Ca-clay	Mg	8	32	56	37	2
	K	17	24	27	22	3
	Na	11	7	6	4	36
K-clay	Ca	64	87	72	62	26
	Mg	9	8	11	14	Nil
	Na	11	19	9	8	2

In the case of K-clays of both the laterite soils, there was higher exchange of cation with calcium as the replacing cation in solution and this exceeded many times the percentages of cation exchange with NaCl and Mg Cl_2 as displacing cationic solutions. Both Na and Mg chlorides showed similar trends in K clays and Ca Clays of both the laterite soils. under Ca-clay, the exchange of cation was more with $MgCl_2$. In all cases, the highest percentage of cation exchanged was observed at 2.5 to 3.3 symmetries and exchange was comparatively low at higher concentrations (5 symmetry).

Thus, comparing the various soils in the matter of effect of symmetry concentrations in black soil, the cation exchange increase in symmetry concentrations in Ca, Mg and Na-clays. Similarly in the case of alluvial soil, corresponding increases in cation exchange was noticed in Ca and Mg-clays. Similar observations were made in the case of K-clay in laterite soils. Mukherjee (1951) conducted similar study with Ca, K, Na and NH_4 clays and concluded that there were progressive increases in cation exchanged with increase in symmetry concentrations.

The present study revealed that in majority of the cases, there was an increase in the degree of adsorption with increase in electrolyte concentration, Chinnadurai (1967) noticed similar observations. In the present study also homovalent cations like Ca and Mg were found to behave similarly.

Considering the effect of various displacing cations on Ca-clay of the soils studied, the magnituda of exchange followed a similar descending order namely K, Na, Mg for all the soils in the present study. Though the four different soils had dissimilar composition of various clay minerals, it is a matter of curiosity as to how the above mentioned order of magnitude of cation exchange with reference to Ca-clay was consistently obtained.

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