J. Indian Chem. Soc.,
Vol. L, November 1973, pp. 715-720

Exchange Behaviour of Trace Element Cations viz. Co^{2+}, Ni^{2+} and Mn^{2+} in Mixed (heteroionic) Clays in Presence of Different Major Cations

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Manuscript received 10 *February* 1972; *accepted* 10 *September* 1973

Exchange behaviour of the trace element cations were studied in alkaline to acidic clays where clays had different degrees of saturation in respect to trace cations. The release of Co^{2+}, Ni^{2+}, and Mn^{2+} ions by H^+ ion was studied by using varying concentrations of H_2SO_4 and H-resin.

The release of M_1^{2+} (where M_1^{2+} is either Co^{2+} or Ni^{2+} or Mn^{2+}) was found to increase with increase in the proportion of M_1^{2+} in clays and is also a function of H^+ concentration. The order of release of the metal ions is $Mn^{2+} > Ni^{2+} \gg Co^{2+}$ in case of exchange by H^+ of H_2SO_4 and is $Ni^{2+} \approx Co^{2+} > Mn^{2+}$ in case of exchange by H^+ of H-resin. The effect of complementary cations, viz., Mg^{2+}, Ca^{2+} and H^+, with the exception of Na^+, was found to be very small and may be stated as $H^+ \gg Mg^{2+} \gg Ca^{2+} > Na^+$ and the effect of Na is considered to be probably due to the high pH of the clay.

SOIL *p*H is one of the factors on which the exchangeability of trace element cations depends. When other parameters are constant, availability generally increases with decrease in *p*H. When the exchangeable metallic cations are replaced by H^+ ions due to cropping conditions or to acids formed by biological agencies or by otherwise, the soil becomes unsaturated (acid). Acid soils are usually deficient in Ca^{2+} from the stand point of crop growth. For this reason, specially in humid climates, the base unsaturated soils respond to the application of $CaCO_3$. The strongly alkaline soils contain exchangeable Na^+ as the predominant cation. Moderately alkaline soils are high in exchangeable Mg^{2+} and Ca^{2+}, exchangeable Na^+ is relatively less. The object of the present investigation is to study the effect of such major cations in the exchange characteristics of trace element cations in clays.

Experimental

The hydrogen clay was prepared by electrodialysing the clay fraction ($< 2\mu$) isolated from a sample of Bihar bentonite. The predominant clay mineral is montmorillonite as determinated by X-ray analysis. Its b.e.c. is 71.2 m.e./100 g. The 3.51% colloidal suspension used in this investigation has a *p*H value of 3.6. The Mn-, Co- and Ni- clays were prepared, by treating with 0.5*N* solutions of the respective sulphates, keeping *p*H at 4.0. Ca-clay was prepared by leaching H-clay with 0.5*N* solution of a mixture (1 : 1) of $CaCl_2$ and $Ca(NO_3)_2$. The leached clays were washed free from metal ions, with smallest amount of acidulated water (*p*H-4). Three to four instalments of 200 ml each of acidulated water were required for clay salts prepared from 200 ml of H-clay. This precaution necessiates to prevent hydrolysis. These were suspended in double distilled water. Mg-saturated clay was prepared from H-clay by adding MgO in amount slight excess of equivalent to b.e.c. and allowing to stand nearly two weeks with occasional shaking. The clay was separated from solid MgO aggregates, if any, and total Mg (exchangeable and soluble) was estimated. The calculated amount of H-clay was added to react with free soluble Mg so that finally the exchangeable Mg^{2+} becomes practically equal to the b.e.c. of the clay. Na-clay was prepared from H-clay by adding the requisite amount of standard NaOH solution.

In order to determine the content of exchangeable cations in the respective clay salts, 20 ml portions of the clay-salt were leached by N/30 H_2SO_4, (at 60° to 70°) for about 30 min in five or six instalments (total volume of the leachate—200 ml for 20 ml clay salt). The content of the particular cation in the leachate was determined. Not all the absorbed trace metal ion could be exchanged and the presence of fixed ions was shown by decomposing the residual clays left after acid leaching as was reported earlier (Mukherjee *et al.*). Though the maximum amount of exchangeable metal ion obtained from M_1-clay is lower than the b.e.c. of the H-clay (Table 1), because of the competitive influence of H^+ ions always present in the leaching solution M_1-clays prepared in such manner are considered saturated for the purpose of the exchange study.

Preparation of heteroionic (mixed) clays :

Heteroionic clays having the desired ratios of cations may be prepared from H-clay in two ways : (i) by adding calculated amounts of bases or (ii) by leaching with mixture of salt solutions of known ratio of the cations. For the binary clays obtained by the former method, it has been shown that the cation which has been added first is more difficult to exchange than the other added next (Vanselow[2], Renold[3], Mukherjee[4]). Mukherjee[5] and Ganguli & Mukherjee[6] showed that the difference in exchangeability of a cation from two binary clays, having same proportion of cations but prepared by reversed manner of addition of bases, become evident only when a 'critical ratio' of the two ions concerned was exceeded. When saturating an exchanger by the latter method i.e., by leaching with mixed ions, the ions are not adsorbed in the same proportion as these were present in the leaching solution (Pochhali[7], McLean *et al.*[8]). To avoid these effects, in the present investigation heteroionic clays were prepared by mixing the base saturated clays prepared separately. Sufficient time was allowed (two weeks or more) before using the mixed clays for exchange studies. In exchange reactions the equilibrium is a dynamic one and one finds in tagged experiments like

$$\text{Co-clay} + \text{Co}^*\text{-salt} \quad \text{Co-}^*\text{clay} + \text{Co-salt}$$

radioactive species of the same cation from a salt solution exchanges with the ordinary species in the clay exchanger (Hodgson[9]). It is natural therefore that cations from one clay exchanged with the cation of the other and after equilibrium was attained, separately saturated clay salts lost their entity as mutual exchange of sites of cation occurred and the clay mixture behaved as a single heteroionic clay

$$M_1\text{-clay}_1 + M_2\text{-clay}_2 \rightleftharpoons M_2\text{-clay}_1 + M_1\text{-clay}_2.$$

For the preparation of heteroionic (mixed) clays, a definite amount of M_1-clay was mixed with calculated quantities of M_2-clay and the mixtures were allowed to stand for two weeks or more with occasional shaking for attainment of equilibrium. M_1 is either Co^{2+}, Ni^{2+} or Mn^{2+} and M_2 is either H^+, Ca^{2+}, Mg^{2+} or Na^+. For each type of heteroionic clay four sets were prepared. The amounts mixed were such that the ratio of exchangeable M_1 and M_2 ions were 25 : 75, 15 : 85, 10 : 90 and 5 : 95. These were termed M_1–M_2-clays. The exchangeable trace element cations determined from these mixed clays when divided by the equivalent fraction of the trace element cation as added were found to be practically the same as that of the original saturated M_1-clay.

Exchange study :

The exchange studies with heteroionic clays were made with acid as also with H-resin. The amount of H^+ (H_2SO_4 or H-resin) was added at four levels viz., corresponding to 0.5, 1.0, 2.0 and 3.0 times the symmetry concentrations calculated with respect to the b.e.c. of the original H-clay from which the mixed clay salts were prepared. Exchange of trace cations in lower concentrations of acid from M_1-Na-clays being very small, these clays were studied in further details in the lower level of acid concentrations. In case of M_1-Ca-clays, also, exchange studes were made with lower levels of acid concentration viz., S/4, S/8 and S/16. Exchange studies were done by the methods reported earlier (Mukherjee *et al.*[1,10]). Details of studies undertaken are given below :

Clay system	Sets	Levels
	(25 : 75, 15 : 85, 10 : 90 & 5 : 95)	(S/2, S, 2S, 3S where S=Sym. Concentration)
i) *Exchange with H-resin*		
M_1-Mg-clay	all sets	all levels
Others	25 : 75	all levels
-do-	all sets	'S' only
ii) *Exchange with H_2SO_4*		
M_1-Mg-clay	25 : 75	all levels
Others	all sets	all levels

The amount of the cation exchanged for hydrogen ion was determined by analysing the leachate by methods reported earlier (Mukherjee *et al.*[1,10]).

Results and Discussions

Table 1 shows the *p*H, clay content and exchangeable cation content of clay-sols. The exchange (release) data for H_2SO_4 of M_1-Ca-clays are presented in Table 2, of M_1-H-clays in Table 3 and of M_1-Na-clays in Table 4, where M_1^{2+} is either Co^{2+} or Ni^{2+} or Mn^{2+}. The release data of M_1^{2+} from the mixed M_1-Mg-clays by H-resin are presented in Table 5. Table 6 shows the ratio :

$$\frac{\text{release by H-resin}}{\text{release by } H_2SO_4}$$

TABLE 1—EXCHANGEABLE CATION IN DIFFERENT CLAY-SALTS

Clay-Salt	Clay Content %	*p*H	Exchangeable metal ion m.e./100 g.
Co-bentonite	3.4	4.8	60.0
Ni-bentonite	2.6	4.9	61.0
Mn-bentonite	3.1	4.8	57.3
Mg-bentonite	3.3	7.7	71.8
Ca-bentonite	2.2	6.3	64.0
Na-bentonite	2.8	9.3	71.2
			(taken as equal to the b.e.c. of H-clay)

for different M_1-M_2-clays, where the ratio of exchangeable M_1 and -M_2 is only 25 : 75. The release of trace element cations from all the clays by H-resin added at the symmetry concentration together with the corresponding ratio

$$\frac{\text{release by H-resin}}{\text{release by } H_2SO_4}$$

are presented in Table 7. For exchange study four sets of different ratios of exchangeable M_1 and M_2 were generally used.

TABLE 2—RELEASE OF M_1^{+2} FROM M_1-Ca-CLAY BY H_2SO_4

Ratio of exchangeable cations in the mixed clay (M_1^{2+} : Ca^{2+})	H_2SO_4 added in terms of S	Release of Co^{2+} in terms of % of total exchangeable Co^{2+} Clay content—1.7% Clay taken—0.17 g Total vol.—20 ml.	Release of Ni^{2+} in terms of % of total exchangeable Ni^{2+} Clay content—1.7% Clay taken—0.17 g Total vol.—20 ml.	Release of Mn^{2+} in terms of % of total exchangeable Mn^{2+} Clay content—1.7% Clay taken—0.34 g Total vol.—40 ml.
		*p*H—5.7	*p*H—5.6	*p*H—5.6
25 : 75	0.062	—	8.0	—
	0.125	12.0	11.6	13.6
	0.25	—	—	19.2
	0.5	36.4	34.8	—
	1.0	54.0	53.2	55.2
	2.0	66.0	70.0	74.8
	3.0	76.4	79.2	82.0
			*p*H—5.7	*p*H—5.8
15 : 85	0.125	—	8.6	—
	0.5	—	36.0	39.3
	1.0	—	52.0	52.6
	2.0	—	71.3	—
	3.0	—	81.3	—
		*p*H—6.0	*p*H—6.0	*p*H—5.9
10 : 90	0.062	7.4	—	—
	0.125	—	7.9	10.0
	0.5	34.0	37.0	37.0
	1.0	48.0	51.0	56.0
	2.0	70.0	72.0	74.0
	3.0	76.0	78.0	80.0
		*p*H—6.1	*p*H—6.0	*p*H—6.0
5 : 95	0.062	—	6.8	—
	0.125	7.0	—	40.0
	0.5	30.0	36.0	40.0
	1.0	48.0	52.0	52.0
	2.0	64.0	70.0	72.0
	3.0	72.0	78.0	78.0

TABLE 3—RELEASE OF M_1^{2+} FROM M_1-H-CLAY BY H_2SO_4

Ratio of exchangeable cations in the mixed clay (M_2^{2+} : H^+)	H_2SO_4 added in terms of S	Release of Co^{2+} in terms of % of total exchangeable Co^{2+} Clay content—1.7% Clay taken—0.17 g Total vol.—20 ml.	Release of Ni^{2+} in terms of % of total exchangeable Ni^{2+} Clay content—1.8% Clay taken—0.18 g Total vol.—20 ml.	Release of Mn^{2+} in terms of % of total exchangeable Mn^{2+} Clay content—1 8% Clay taken—0.36 g Total vol.—40 ml.
25 : 75		*p*H—4.1	*p*H—3.9	*p*H—4.0
	0.5	48.4	48.8	48.8
	1.0	64.0	61.2	68.0
	2.0	74.0	72.4	79.6
	3.0	83.6	77.2	85.6
15 : 85		*p*H—4.1	*p*H—3.8	*p*H—4.0
	0.5	48.0	46.0	49.3
	1.0	61.3	64.6	69.3
	2.0	74.0	72.0	80.0
	3.0	83.3	77.3	86.0
10 : 90		*p*H—3.9	*p*H—3.8	*p*H—3.7
	0.5	45.0	44.0	49.0
	1.0	62.0	62.0	65.0
	2.0	75.0	73.0	76.0
	3.0	84.0	79.0	86.0
5 : 95		*p*H—3.8	*p*H—3.7	*p*H—3.7
	0.5	46.0	44.0	46.0
	1.0	62.0	61.0	68.0
	2.0	72.0	72.0	82.0
	3.0	80.0	76.0	88.0

TABLE 4—RELEASE OF M_1^{2+} FROM M_1-Na-CLAY BY H_2SO_4

Ratio of exchangeable cations in the mixed clay (M_1^{2+} : Na^+)	H_2SO_4 added in terms of S	Release of Co^{2+} in terms of % of total exchangeable Co^{2+} Clay content—1.7% Clay taken—0.17 g Total vol.—20 ml.	Release of Ni^{2+} in terms of % of total exchenagable Ni^{2+} Clay content—1.7% Clay taken—0.17 g Total vol.—20 ml.	Release of Mn^{2+} in terms of % of total exchangeable Mn^{2+} Clay content—1.7% Clay taken—0.34 g Total vol.—40 ml.
25 : 75		pH—7.4	pH—7.4	pH—7.5
	0.5	3.3	4.4	0.5
	0.75	10.8	—	8.8
	1.0	31.2	29.6	33.2
	2.0	60.4	61.6	66.4
	3.0	70.4	72.0	78.4
15 : 85		pH—7.6	pH—7.4	pH—7.7
	0.5	3.3	3.8	0.4
	0.75	6.3	—	6.4
	1.0	28.0	24.6	25.3
	2.0	66.0	65.4	62.0
	3.0	71.3	73.3	77.3
10 : 90		pH—7.7	pH—7.5	pH—7.8
	0.5	2.4	3.2	0.6
	0.75	5.8	—	4.1
	1.0	21.0	19.0	20.0
	2.0	65.0	66.0	65.0
	3.0	72.0	77.0	74.0
5 : 95		pH—7.7	pH—7.8	pH—7.8
	0.5	2.0	3.2	—
	0.75	4.0	—	—
	1.0	12.0	16.4	15.0
	2.0	60.0	66.0	66.0
	3.0	68.0	76.0	74.0

TABLE 5—RELEASE OF M_1^{2+} FROM M_1-Mg-CLAYS BY H-RESIN

Ratio of exchangeable cations in the mixed clay (M_1^{2+} : Mg)	H-resin added in terms of S	Release of Co^{2+} in terms of % of total exchangeable Co^{2+} Clay content—3.1% Clay taken—0.62 g Total vol.—40 ml.	Release of Ni^{2+} in terms of % of total exchangeable Ni^{2+} Clay content—2.7% Clay taken—0.54 g Total vol.—40 ml.	Release of Mn^{2+} in terms of % of total exchangeable Mn^{2+} Clay content—3.2% Clay taken—0.64 g Vol vol.—40 ml.
25 : 75		pH—6.2	pH—6.0	pH—6.1
	0.5	41.2	40.0	31.6
	1.0	51.6	51.2	42.4
	2.0	63.6	65.6	50.4
	3.0	70.8	71.2	63.6
15 : 85		pH—6.3	pH—6.2	pH—6.2
	0.5	38.0	41.3	27.3
	1.0	54.6	50.6	38.6
	2.0	60.6	61.3	52.0
	3.0	67.3	71.3	62.0
10 : 90		pH—6.7	pH—6.7	pH—6.7
	0.5	40.0	44.0	30.0
	1.0	49.0	51.0	38.0
	2.0	65.0	64.0	54.0
	3.0	68.0	73.0	62.0
5 : 95		pH—6.8	pH—6.8	pH—6.8
	0.5	42.0	42.0	30.0
	1.0	48.0	48.0	40.0
	2.0	62.0	62.0	48.0
	3.0	72.0	74.0	62.0

TABLE 6—RELEASE OF TRACE ELEMENT CATIONS FROM M_1-M_2-CLAYS BY ACID/H-RESIN

(Ratio of exchangeable M_1 & M_2 = 25 : 75)

H_2SO_4/H-resin added in terms of S	Ratio— Exchange with H-resin / Exchange with H_2SO_4; Clay content—1.7%; Clay taken—0.34 g; Total vol.—40 ml.	Ratio— Exchange with H-resin / Exchange with H_2SO_4; Clay content—1.8%; Clay taken—0.36 g; Total vol.—40 ml.	Ratio— Exchange with H-resin / Exchange with H_2SO_4; Clay content—1.3%; Clay taken—0.34 g; Total vol.—40 ml.	Ratio— Exchange with H-resin / Exchange with H_2SO_4; Clay content—3.2%; Clay taken 0.32 g; Total vol.—20 ml.
	Mn-Ca-clay	Mn-H-clay	Mn-Na-clay	Mn-Mg-clay
0.5	—	0.614	—	0.752
1.0	0.731	0.617	0.818	0.752
2.0	0.679	0.733	0.632	0.653
3.0	0.751	0.812	0.739	0.757
	Co-Ca-clay	Co-H-clay	Co-Na-clay	Co-Mg-clay
0.5	0.945	0.760	1.8	1.0
1.0	0.851	0.769	0.935	0.992
2.0	0.860	0.853	0.794	0.926
3.0	0.879	0.885	0.886	0.903
	Ni-Ca-clay	Ni-H-clay	Ni-Na-clay	Ni-Mg-clay (Clay content—2.7% Clay taken—0.27 g)
0.5	0.986	0.803	1.2	0.936
1.0	0.887	0.835	1.1	0.962
2.0	0.828	0.867	0.843	0.916
3.0	0.847	0.964	0.894	0.903

TABLE 7—RELEASE OF TRACE METAL CATIONS FROM M_1-M_2- CLAYS BY H-RESIN AT 'S' CONCENTRATION AND RATIO OF EXCHANGE WITH H-RSIIN AND EXCHANGE WITH H_2SO_4.

Ratio–M_1 : M_2	25 : 75		15 : 85		10 : 90		5 : 95	
System	Release % of S	Ratio	Release % of S	Ratio	Release % of S	Ratio	Release % of S	Ratio
Mn-Mg-clay	10.6	0.751	5.8	—	3.8	—	2.0	—
Mn-Ca-clay	10.1	0.731	6.1	0.771	3.9	0.696	1.9	0.731
Mn-H-clay	10.5	0.617	6.1	0.586	4.0	0.615	1.9	0.558
Mn-Na-clay	6.8	0.819	3.9	1.0	2.0	1.0	0.82	1.1
Co-Mg-clay	12.6	0.969	8.2	—	4.9	—	2.4	—
Co-Ca-clay	11.5	0.852	6.8	—	4.5	0.937	2.2	0.916
Co-H-clay	12.3	0.769	6.9	0.751	4.7	0.757	2.3	0.741
Co-Na-clay	7.3	0.933	4.2	1.0	2.0	0.952	0.89	1.5
Ni-Mg-clay	12.8	0.963	7.6	—	5.1	—	2.4	—
Ni-Ca-clay	11.8	0.887	6.8	0.871	4.5	0.883	2.3	0.884
Ni-H-clay	12.8	0.836	7.2	0.742	4.9	0.788	2.2	0.709
Ni-Na-clay	7.8	1.14	4.3	1.14	2.2	1.1	0.86	1.14

The release data for H_2SO_4 for different systems (viz., Mn–Ca–, Mn–Mg, Mn–H–) and different sets (0.5S, 1.0S, 2.0S, 3.0S) may be represented graphically (not shown here) and comparison amongst different systems and sets can be made. Similarly exchange data for H-resin can be presented graphically and comparison of exchange isotherms of a particular cation viz., Mn^{2+}, Ni^{2+}, Co^{2+} in presence of different complementary cations viz., Mg^{2+}, Na^{2+}, H^+, Ca can be made. From such comparison with the help of figures (not shown here) the following observations are made :

i) release of M_1^{++} increases with increase of proportion of M_1^{++} in clays;

ii) for a particular set, the release increases with increase in the amount of acid/H-resin used for exchange;

iii) except with M_1-Na-clay, the percentage release of M_1^{++} when divided by the equivalent fraction of M_1+M_2 present in the clay, i.e., when calculated on the 100% M_1 basis, does not vary with the proportion of M_1 in the clay i.e., the release is almost independent of the ratio. With M_1-Na-clay, except at 3S and in most cases at 2S concentrations of acid/H-resin added, there is a tendency of gradual decrease of the release of M_1^{++} with increase in proportion of Na^+ in clay. This is probably due to *p*H being gradually higher;

iv) ratio of exchange with H-resin to exchange with acid is generally less than one. But in case of S/2 and in some cases at S concentrations with M_1-Na-clays, the ratio is more than one. In these cases the release is also much smaller;

v) the order of release is $Mn^{2+} > Ni^{2+} > Co^{2+}$ for H_2SO_4 and is $Ni^{2+} \approx Co^{2+} > Mn^{2+}$ for H-resin.

The effect of complementary cations viz., Mg^{2+}, Ca^{2+} and H^+, with the exception of Na^+, is very small, if at all, in the exchange of trace element cations. The effect of complementary ions on the case of release may be stated as—

$$Mg^{2+} \gg H^+ \gg Ca^+ > Na^+$$

It may be mentioned that from his experiments on limited exchange with acids (Marshall[11]), reported that Na-treatments produced a well marked complementary ion effect where as K, Mg and Ca treatments did not.

Thanks of the authors are due to Prof. S. K. Mukherjee, Member, National Commission on Agriculture, for his helpful discussion

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