Cation exchange as influenced by the type of cations in different clay minerals

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Introduction

Physical and chemical properties of most soils are influenced by their ion-exchange characteristics, including the amount and balance of individual ions present (Rayment and Lyons, 2011). Cation Exchange Capacity (CEC) is a general indicator of soil/clay storage capacity for available positively-charged plant nutrients such as calcium, magnesium, potassium and sodium. According to Jackson (2005), the range and mean values of CEC for natural clays differ when different cations (particularly Ca or K) are used in the exchange reactions.

The literature is abundant with reports on cation exchange phenomena in clays resulting from clay-cation interactions (Bergaya et al., 2006). Many empirical results have been presented without clear description of the fundamental forces that govern cation selectivity or fixation. Several authors (Bergaya et al., 2006) have developed models to compute selectivity coefficients from the contributions of electrostatic versus specific energies of adsorption as a function of cation valence and hydrated radius. The importance of clay layer charge in cation exchange selectivity has also been reported (Teppen and Miller, 2005). Recent models also define cation exchange selectivity in terms of polarizability-based electrostatic and covalent interactions (Sposito, 2008; Marchuk and Rengasamy, 2011).

Recently Marchuk and Rengasamy (2011) developed the ionicity indices for various cations involved in clay-cation bonds. The degree of ionicity of these bonds will dictate the ease of cation exchange and hence, the cation exchange capacity of the clays. We started the present experiment with an aim to understand the involvement of bonding mechanism in exchange reactions. We report here the results of our preliminary experiments.

Materials and Methods

The clays examined in this study were obtained from variety of sources and are described in detail in Table 1. The clays were used without any pre-treatment. Firstly, 5 g of each of raw clay sample was dispersed in 200ml of DI water and shaken in an end-over-end shaker for 16 hours. Then clay suspensions were transferred into 500ml measuring cylinders, shaken for 1 minute and left for 8 hours to settle. The observed dispersion for kaolinite and halloysite were low and hence a few drops of 0.1M NaOH were added to each clay sample to increase dispersion.

Table 1. Clays used in this study and their source.

Sample no.	Clay	Source
Clay 1	Kaolinite KGa-1b	Washington county, Georgia, USA
Clay 2	Halloysite	Matauri Bay, Northland, New Zealand
Clay 3	Illite-smectite ML* ISCz-1	Czechoslovakia
Clay 4	MMT** STx-1b	Texas, USA
Clay 5	MMT** SCa-3	Otay, San Diego County, California, USA
Clay 6	Stop 12 Vermiculite	Carl Moss Ranch, Llano County, Texas

* - Mixed layer clay; ** - Montmorillonite.

For determinations of exchange capacities for K, Na, Ca and Mg clay samples were prepared by treating a portion of the clay suspension with ≈ 220mL of a 1.0 M solution of the monovalent (K and Na) and 0.5 M solution of the divalent (Ca and Mg) chlorides. The suspensions were shaken over night, centrifuged to remove excess salts. The clay samples were then washed several times with 250mL of 70 vol. % ethanol/water solution to remove soluble cations.

The extraction of the exchangeable cations was carried out by shaking clays with ≈ 250mL of 1 M NH_4Cl solution in a centrifuge bottle overnight, followed by centrifugation and collection of supernatant solution. The procedure was repeated three times. These extractions were combined and the cations (K, Na, Ca and Mg) displaced by NH_4Cl were measured by inductively coupled plasma atomic emission spectrometry (ICPAES). Sum of exchangeable cations is considered as CEC in this report.

Particle size measurements were performed using a NICOMP 370 Particle Sizer with a fixed 90° scattering and external (optical fibre) angle, and a 632.8-nm wavelength helium-neon laser. The instrument operates in two analysis modes: unimodal (Gaussian) and multi-modal (Nicomp) distributions. The multi-modal analysis we found to be most suitable for the wide distribution of particles found in clay suspensions.

Prior to measurement, samples were shaken and left for 20 hours to settle. All samples were placed in the machine for 5 minutes prior to starting measurements to eliminate temperature differences between the sample and an instrument. For each sample particle size was recorded after 5, 10, 15, 30 and 60 minutes. The instrument parameters were set as follows: automatic choice of channel width; solid particle mode; the autocorrelator was set to clear after each sample. The following values were recorded: mean particle diameter, standard deviation, chi-squared (χ^2), baseline adjustment, fit error and residual. Results presented here acquired using intensity-weighted distribution with the Nicomp analysis mode recorded after 60 min.

Results and Discussion

The exchangeable K, Na, Ca, Mg and CEC for each sample are presented in Table 2. Data represent an average of duplicates for all determinations. Values of CEC tend to be high, compared to the reported data in the literature because of the high pH induced by the addition of NaOH during sample preparation.

Table 2. Experimental cation-exchange capacities for standard clays.

Clay	pH	EC, dS/m	Treatment	ζ mV	Exchangeable cations, cmol$_c$/kg				Σ of Exch. Cations
					K	Na	Ca	Mg	
Kaolinite	10.7	0.01	K	-29	5.35	5.51	0.21	1.29	12.36
			Na	-36	1.31	9.66	0.19	1.23	12.40
			Ca	-10	1.02	5.52	4.86	1.23	12.62
			Mg	-20	0.95	5.43	0.18	7.28	13.84
Halloysite	9.3	0.03	K	-50	1.56	6.65	0.37	0.73	9.31
			Na	-58	0.81	6.87	0.27	0.73	8.68
			Ca	-39	0.74	6.70	2.55	0.74	10.73
			Mg	-41	0.57	6.64	0.16	2.33	9.70
Illite-smectite	8.3	0.01	K	-49	45.05	19.82	0.26	1.74	66.88
			Na	-57	5.88	69.35	0.27	1.78	77.27
			Ca	-32	5.34	19.45	45.24	1.74	71.76
			Mg	-34	5.46	19.92	0.27	49.12	74.77
Texas MMT	9.8	0.01	K	-59	98.72	13.20	0.27	1.76	113.96
			Na	-61	1.62	96.49	0.27	1.79	100.18
			Ca	-34	6.10	14.17	94.51	1.81	116.59
			Mg	-36	3.91	14.04	0.27	95.67	113.89
Otay MMT	10.5	0.02	K	-55	122.80	9.27	0.18	1.94	134.19
			Na	-57	2.24	132.26	0.18	2.57	137.25
			Ca	-35	2.39	9.70	131.49	1.78	145.37
			Mg	-37	3.03	9.78	0.18	130.95	143.94
Vermiculite	10.4	0.01	K	-50	85.44	33.04	0.61	24.23	143.33
			Na	-52	8.43	158.54	0.68	18.37	186.03
			Ca	-26	3.32	33.92	138.75	14.97	190.95
			Mg	-31	4.32	35.07	0.65	154.82	194.86

Comparing the CEC of monovalent cationic clays, K-saturated clays have lower CEC’s than Na-saturated clays with the exception of halloysite and Texas MMT. Similarly for the divalent cationic clays, Mg-saturated clays have lower CEC’s than Ca-saturated clays with the exception of kaolinite, illite-smectite and vermiculite. CEC of K-vermiculite is vastly lower than that of Na-vermiculite. This is probably because of the great affinity of the vermiculite interlayer for potassium.

The ionicity indices of clay-cation bonds are in the order Na > K > Mg > Ca (Marchuk and Rengasamy, 2011). The results presented here do not show a similar order for CEC values for homoionic clays. But, when monovalent ions and divalent ions are separately considered, the higher were the ionicity indices, the greater was the CEC. There are exceptions, as mentioned earlier. Differences in the CEC of homoionic clays are attributed to differences in particle size (Fig. 1).

The changes in particle size after ion adsorption are given as the mean particle size measured. The mean particle size increased in all clay samples in the order Na < K < Mg < Ca. The changes in size observed correlate well with zeta potential data.

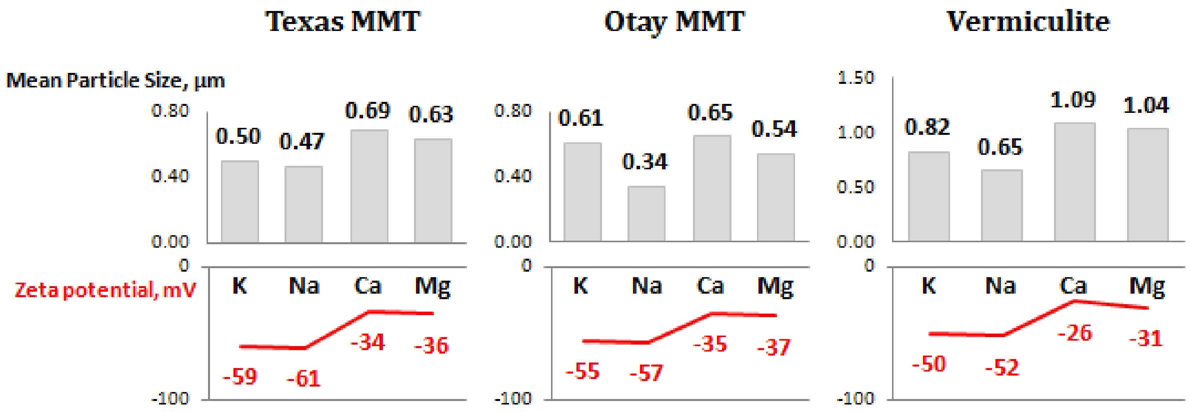

Fig. 1. Mean particle size (Intensity-WT NICOMP Distribution) and Zeta potential of clays.

Conclusion

It appears that ionicity index alone does not determine CEC. Other factors such as cationic charge, charge density on clay particles and other clay structural factors are involved in cation exchange phenomena. Our further studies will address these issues.

References

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