

CATION EXCHANGE CAPACITY OF SOME EAST PAKISTANI CLAYS

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Bejaipur clay occurs abundantly in a particular locality of the District of Mymensingh, and Mirpur clays (Red and Black) and Dacca river silt are also abundantly available in the District of Dacca, East Pakistan. Dacca river silt and Mirpur clays are locally used in the manufacture of bricks, tiles, etc., and Bejaipur clay is used for the manufacture of ceramic bodies by some ceramic industries of East Pakistan. Cation exchange capacity (c.e.c.) of these clays has been determined which also throw some light to the mineralogical composition of these clays.

A clay consists of a number of clay minerals. The chemical composition of these minerals is normally hydrated aluminium silicates resulting from weathering of igneous rocks. In water medium a clay particle behaves as a negatively charged particle and it is a polyvalent in nature. The electrical neutrality is maintained of these charged particles by a swarm of positively charged ions like Na^+ , K^+ , Ca^{2+} , Mg^{2+} , etc., cations are held by only feeble electrical forces and are easily replaceable by others. J.T. Way first reported his finding to the Royal Agricultural Society that soils were able to remove ammonia from aqueous solution. Maclean¹ and Kerr² reported that soil acidity and ion exchange properties of soils were due to clay content. The absorption of cations by a clay mineral does not involve any structural change³ in the mineral. In the process one cation is taken up from the solution and another is released in the solution. Exchange is taken place between two types of cations, so the process is known as cation exchange process. Total amount of cation exchange taken place in 100 g of clay is known as cation exchange capacity (c.e.c.) of the clay. It is very usual for a neutral clay to absorb several cations, common ones are H^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Al^{3+} . It is customary to distinguish between clays in which one cation is predominantly or exclusively absorbed. Thus a sodium clay is one in which the absorbed cation is sodium and it may be represented as (clay) Na and the exchange reaction between two cations may be expressed as (clay) Na + $\text{NH}_4(\text{OH}) = (\text{clay}) \text{NH}_4 + \text{NaOH}$. C.e.c. is an important physical property and it has got relation with various important physical characteristics of the clay, e.g., plasticity, shrinkage, drying property, viscosity of a clay slip, etc., particularly when the clay is in the water medium. So c.e.c. value provides useful information to the ceramist as to the nature of the minerals in a clay.

With a view to get adequate knowledge of working properties of some East Pakistani clays, c.e.c.

of Bejaipur clay, Mirpur clays (Red and Black) and Dacca river silt were determined.

Experimental

Clay was beneficiated by the method described by M. Khuda *et al.*^{4,5} and dried at 100°C and powdered to 200 mesh. The direct method⁶ was used. Ammonium clay was prepared by treating clay with ammonium salt solution. Mattson⁷ used ammonium chloride solution for leaching soils, the washed soil being used for determination of the total cation exchange capacity. Pierre and Scarseth⁸ also used ammonium chloride for the same purpose. Ten g of beneficiated clay was taken in a 500 ml conical flask and to this 300 ml. 1.0N ammonium chloride solution was added. The contents was shaken for nearly five hours in a shaking machine and then was allowed sufficient time to settle clay particles. The solid phase was separated by decantation and clay was treated again with 200 ml ammonium chloride solution. Four times such treatments were carried out with ammonium chloride solution to ensure complete replacement of exchangeable ions of clay. After the last treatment contents was allowed to remain undisturbed overnight. The supernatant liquid was siphoned off and filtered through a Buchner funnel through a No. 542 filter paper. The clay was then washed with methyl alcohol several times, until the washing no longer produced a yellow colour with Nessler's solution. The clay sample was then transferred to a long necked Kjeldhal flask, sodium hydroxide solution was added to distill off ammonia which was collected in a known volume of standard N/10 sulphuric acid. The liberated ammonia was estimated by a back titration with a standard solution of alkali. The experimental procedure using ammonium acetate for making ammonium clay is the same as the one described.

In the second set of experiments hydrogen clay was made by treating the sample with N/10 hydrochloric acid. The contents was shaken for five

hours nearly in a shaking machine, it was then diluted with distilled water and was centrifuged. Similar treatments were carried out four times to ensure complete replacement of exchangeable ions of a clay. Clay was washed with methyl alcohol till it was free from acid. It was then transferred to a conical flask and suspended it on sufficient quantity of water, 50 ml of normal potassium chloride or sodium chloride solution was added and the suspension was vigorously shaken. The liberated acid was titrated against standard sodium hydroxide solution.

In the third set of experiments clay was converted to sodium clay by leaching clay with sodium chloride solution. It was then washed till the washing gave negative test of chloride. Clay was then transferred to a conical flask and hydrogen form cation exchange resin was added to it. Sufficient quantity of water was added to keep them in suspension. Contents was shaken for 10 hr in a shaking machine and then resin was separated and transferred to a column and then resin was eluted with normal acid. Sodium was estimated in the washing.

Results

Results of cation exchange experiments of the clay samples under study are given in Tables 1, 2, 3, and 3(a) and the results of the chemical analysis are given in Tables 4(a) and 4(b).

TABLE 1.—AMMONIUM CHLORIDE AS THE LEACHING AGENT.

Clay	Ion exchange capacity (me/100 g)	Average (me/100g)
Bejaipur	3.86	3.93
	3.93	
	4.01	
Mirpur (Red)	10.31	10.58
	10.61	
	10.83	
Mirpur (Black)	14.32	14.63
	14.68	
	14.91	
River silt (Dacca)	19.61	19.35
	19.42	
	19.01	

TABLE 2.—AMMONIUM ACETATE AS THE LEACHING AGENT.

Clay	Ionexchange capacity (me/100g)	Average (me/100g)
Bejaipur	3.75	3.83
	3.85	
	3.92	
Mirpur (Red)	10.52	10.76
	10.81	
	10.86	
Mirpur (Black)	14.92	14.86
	14.97	
	14.70	
River silt (Dacca)	19.21	19.13
	19.11	
	19.08	

TABLE 3.—N/10 HYDROCHLORIC ACID AS THE LEACHING AGENT.

Clay	Acid liberated with 1N KCl (me/100g)	Average (mg/100g)	Acid liberated with 1N NaCl (me/100g)	Average (me/100g)
Bejaipur	4.31	4.18	4.02	4.07
	4.01		4.09	
	4.21		4.11	
Mirpur (Red)	10.88	10.84	10.71	10.68
	10.92		10.63	
	10.72		10.69	
Mirpur (Black)	14.54	14.41	14.01	14.59
	14.31		14.81	
	14.38		14.94	
River silt (Dacca)	19.32	19.34	19.31	19.21
	19.30		19.11	
	19.40		19.22	

TABLE 3(a).—HYDROGEN FORMED CATION EXCHANGE RESIN AS THE LEACHING AGENT.

Clay	Ion exchange capacity (me/100g)	Average (me/100g)
Bejaipur	3.21	3.21
	3.28	
	3.15	
Mirpur (Red)	10.12	10.07
	10.08	
	10.02	
Mirpur (Black)	14.21	14.15
	14.13	
	14.10	
River silt (Dacca)	19.01	19.09
	19.17	
	19.09	

TABLE 4(a).—RESULTS OF CHEMICAL ANALYSIS.

Constituents %	Bejaipur clay (Elutriated)	River silt (Dacca) (Elutriated)
SiO ₂	57.09	50.08
Al ₂ O ₃	30.04	23.37
Fe ₂ O ₃	0.32	3.91
CaO	0.04	1.18
Na ₂ O	0.21	0.08
K ₂ O	0.11	0.05
TiO ₂	trace	trace
Ignition loss	11.99	21.01

TABLE 4(b).—RESULTS OF CHEMICAL ANALYSIS.

Constituents %	Mirpur (Red) Clay (Elutriated)	Mirpur (Black) clay (Elutriated)
SiO ₂	55.96	48.79
Al ₂ O ₃	23.07	26.46
Fe ₂ O ₃	9.57	2.50
CaO	0.10	0.21
Na ₂ O	0.23	0.08
K ₂ O	0.12	0.04
TiO ₂	trace	trace
Ignition loss	10.21	21.50

Discussion

Exchangeable ions in a clay are mostly due to the presence of clay minerals and its cation exchange capacity depends on the type or types of clay minerals associated with it. In case of pure clay minerals c.e.c. is known. When a clay is a mixture of several clay minerals c.e.c. is the sum contributed by each component. Though it is not possible to identify each clay mineral from c.e.c. yet its c.e.c. value gives indication about the major fraction of clay minerals present in the mixture. C.e.c. were found to be 3.93, 10.58, 14.63, and 19.35 for Bejaipur clay, Mirpur clays (Red and Black), and river silt (Dacca) respectively using ammonium chloride as the leaching agent. As a leaching agent ammonium acetate is always preferable to ammonium chloride, because acidity may be developed by ammonium chloride which may cause some decomposition of the clay.⁹ From the above results it is observed that none of them being affected by ammonium chloride. Even it is observed that clays are unaffected by decinormal acid solution. C.e.c. value in Table 3 and 3(a) confirmed this. Acid liberated from hydrogen formed clays by NaCl or KCl solution was titrated by standard alkali. Hydrogen formed cation exchange resin as the leaching agent was also found suitable. To achieve quantitative exchange of ions it requires longer period of shaking of the mixture of the clay sample and the hydrogen formed cation exchange resin in presence of water. Lower values of c.e.c. of all clays in Table 3(a) are due to the incomplete exchange of cations between the clay and the hydrogen formed cation

exchange resin. C.e.c. of Bejaipur clay in any way would not be more than 4 and this value is lower than that of pure kaolinite.³ This is due to the presence of impurities, mostly very fine particles of sand, quartz¹⁰, which has little or no contribution in c.e.c. Infrared absorption spectra of Bejaipur clay is also similar to those of kaolinite.¹¹ It shows that Bejaipur clay is an impure kaolinite clay mineral. C.e.c. of Mirpur clay (Black) is higher than that of Mirpur clay (Red). This is due to some organic matter associated with Mirpur clay (Black)⁵, chemical analyses, infrared absorption spectra^{11,12,13} and c.e.c. indicate that Mirpur clays (Red and Black) contain varying proportions of impurities. C.e.c. of River silt (Dacca) is the highest among c.e.c. values of other clay samples. It contains appreciable amount of organic matter and probably this is one of the main reasons for higher value of c.e.c. of River silt.

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