

Effect of Dilute Salt Solutions on Chernozem Soil Estimated Through the Hydration Properties of the Colloids

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Alkali soils containing illite with high exchangeable K are reported to be less susceptible than those containing montmorillonite to the adverse effect of sodium on their physical properties. Besides, that the adsorption complex of the former attains comparatively lower Na saturation than the latter, the other probable reason for this discrepancy seems to be the inherent difference in the degree of hydration of Na ions owing to differences in the bonding force available on the mineral surfaces. This aspect which is of practical value in understanding salt affected soils where these two minerals are dominant, was studied.

Samples of chernozem soil (containing initially illite and montmorillonite) enriched with three levels of pure illite and bentonite were leached for a number of times in columns with single salt solutions of Na_2CO_3 , NaCl and MgCl_2 , and their clay fractions were studied by differential thermal and X-ray methods. Illite treated samples adsorbed less moisture at maximum hygroscopicity than montmorillonite treated ones, and the energy needed to drive off the moisture from the illite treated samples, as indicated by differential thermal analysis, was also relatively higher than for montmorillonite samples.

Basing on the location and force of sodium bonding on the surfaces of illite and montmorillonite, it was concluded that sodium ions had a tendency towards less hydration on illite than on montmorillonite.

An ESP value of 15 has been tentatively established as the limit above which the adverse effect of Na becomes evident though structural deterioration at ESP as low as 8–10 has been reported by Gardner³ with a similar low salt concentration. According to McNeal and Coleman¹⁰ soil mineralogy provides a qualitative insight into this discrepancy. It is indicated (Velasco-Molina¹⁵) that soil containing a higher percentage of montmorillonite appears to be relatively more adversely affected than that containing illite in physical properties under identical low salt and high Na conditions, because unlike the former, mica like clays show less tendency to swell and disperse under the influence of Na ions¹⁴. Moreover, micaceous clays are reported to contain relatively little Na despite high SAR values in irrigation water (Longnecker and Lyerly⁶) as compared with that adsorbed by an equivalent quantity of montmorillonite (Datta and Szabolcs¹) under similar conditions.

Since clay minerals of arid and semi arid zones, where salt affected soils mostly occur, are illite and montmorillonite, a knowledge of the clay minerals together with the adverse effect of Na on them, is of practical importance when dealing with soil reclamation or irrigation involving either the application of sodic and other salts or their leaching, resulting in

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changes in colloidal behaviour with respect to hydration, dispersion and swelling. Differences in the magnitude of adversity in physical properties shown by illite and montmorillonite as referred to above may be due to the differential hydration behaviour of Na ions on illite and montmorillonite surfaces. This constitutes the purpose of the investigation.

EXPERIMENTAL

Columns of chernozem soil containing initially illite and poorly crystallized montmorillonite, raised in its mineral content by the addition of 5% (on whole soil basis) of each of pure illite and bentonite and leached a number of times separately with Na_2CO_3 , NaCl and MgCl_2 (Datta and Szabolcs, *loc. cit.*) were used in this study.

The material of the columns after leachings were over, was dismantled and shaken with distilled water. The 12-hrs. fraction was siphoned off, centrifuged and washed with distilled water to get it free of any soluble salt. Use of peptizing and deflocculating agent was avoided to leave the clays approximately in their original ionic forms. The clays were subjected to X-ray (CuK_α , Ni filter) in a Mikrometa diffractometer with a chart recorder using oriented flat layer specimens.

Two sets of air dried samples of these clays were equilibrated over 10% H_2SO_4 in a vacuum desiccator for maximum hygroscopicity determination¹¹. From one set the maximum hygroscopicity was determined and from the other detail differential thermal analysis was run in a Derivatograph². Heating rate was 10°C/min. Diluted samples (sample size 200 mgm) using Al_2O_3 as internal diluent were used.

RESULTS

Maximum hygroscopicity : Hygroscopic water adsorbed by the soil particles is composed of H_2O molecules bonded to the surface as a monolayer (firmly bound) and of a varying number of H_2O molecules bonded to the cations, the kind of cations determining the number. Data (Table 1) show that under a high relative humidity corresponding to maximum hygroscopicity, bentonite treated samples sorbed the larger quantity of moisture vapour. This is obviously due to more surface area of bentonite available per molecule of water vapour and its capacity for interlayer swelling. The value was far larger in bentonite treated samples leached with Na_2CO_3 than in those leached with NaCl. This is explained on the basis of a higher degree of sodium adsorption attained by the former¹, which under high relative humidity, adsorbed in addition to the maximum quantity of firmly bound moisture, a good quantity of loosely bound moisture associated with the greater amount of adsorbed sodium.

Differential thermal study : Since organic matter and CaCO_3 contents were negligible, d.t.g. curves showing loss in weight peaks were due mainly to the evolution of water. A comparison of differential thermal curves with d.t.g. curves for the same material confirmed that endothermic peaks observable in the former were due to decomposition reactions owing to the loss of water only.

Losses in weight in three successive stages were calculated from thermogravimetric curves and are presented in Table 1. Three hundred degrees centigrade was chosen as the first stage because it is the standard single value (Ross and Hendricks¹²), denoting the loss

of adsorbed and interlayer water and the beginning of the loss of OH lattice water. However, all the samples, as seen from the completion of the first dehydroxylation reactions (Table 2) and from the slope of the t.g. curves, lost most of the adsorbed moisture within 200°. The 300°–700° stage was chosen to record the loss of the OH lattice water.

TABLE 1
Dehydration characteristics

Leaching agent	Sample*	Exchangeable cation % attained on leaching	Loss on 105° %	Moisture loss (%) based on thermo-gravimetric curves				Maximum hygroscopicity %
				0–300°C	300–700°C	700–1000°C	Total	
Na ₂ CO ₃	Chz.	17.20	3.98	8.43	5.5	1.51	15.44	7.13
	Chz. + 5% IL	17.10	2.93	8.38	4.3	1.79	14.47	4.58
	Chz. + 5% BT	20.80	8.10	12.65	5.2	2.10	19.95	11.35
MgCl ₂	Chz.	24.99	3.90	9.20	5.4	1.03	15.63	5.30
	Chz. + 5% IL	28.53	2.23	8.13	5.7	—	13.83	4.12
	Chz. + 5% BT	31.40	3.98	8.95	5.6	1.02	15.57	5.61
NaCl	Chz.	12.00	2.58	8.85	5.9	1.02	15.77	3.95
	Chz. + 5% IL	12.36	2.58	6.93	6.2	1.53	14.66	3.33
	Chz. + 5% BT	13.87	2.85	9.95	5.9	0.08	15.93	5.00
H ₂ O	Chz.	—	2.08	7.60	5.4	—	13.00	3.28
	Chz. + 5% IL	—	3.73	8.00	5.9	1.29	15.19	4.46
	Chz. + 5% BT	—	3.50	8.60	5.6	1.02	15.22	4.85
	Experimental Illite	—	3.83	7.43	4.7	1.57	13.70	5.36
	Experimental Bentonite	—	9.03	20.18	4.3	1.61	26.09	11.28

* Chz. = chernozem; IL = illite; BT = benonite.

Since all of the samples were equilibrated over 10% H₂SO₄ at maximum hygroscopicity, it is interesting to compare the water loss specially at the first dehydration reaction temperature with that adsorbed at maximum hygroscopicity. The amount of water desorbed and its order as the data in Table 1 show, were consistent with those adsorbed at maximum hygroscopicity. The relative difference was again marked between NaCl and Na₂CO₃ treatments, MgCl₂ treated samples being intermediates.

There was no effect either of mineral addition or of adsorbed ions on OH-lattice water. There was an almost uniform release of moisture in the 300°–700° range with all of the samples. Differences between total moisture release (0°–1000°C) were apparently due to differences in the 0°–300° range of moisture desorption.

Both the maximum hygroscopicity data and moisture desorption characteristics in the 0°–300° range also point out that the illite treated chernozem irrespective of the ion adsorbed on it, gave lesser adsorption of moisture vapour at maximum hygroscopicity than

the chernozem colloid without any mineral treatment. It suggests that addition of pure illite to the chernozem decreased the magnitude of sorption forces available on the chernozem colloidal surfaces.

TABLE 2
Differential thermal analysis data

Treat- ment	Sample	First endotherm		Peak temp. of second endotherm °C
		Temp. at commence- ment and end of the reaction °C	Peak temp. °C	
Na ₂ CO ₃	Chz.	40-190	160	570
	Chz. + 5% IL	30-180	170	575
	Chz. + 5% BT	40-160	160	560
MgCl ₂	Chz.	40-180	160	560
	Chz. + 5% IL	50-205	180	580
	Chz. + 5% BT	50-180	160	575
NaCl	Chz.	20-200	142	575
	Chz. + 5% IL	60-300	258	660
	Chz. + 5% BT	70-180	140	560
H ₂ O	Chz.	50-180	150	565
	Chz. + 5% IL	80-	178	570
	Chz. + 5% BT	80-200	150	560
	Experimental Illite	40-	140	720
	Experimental Bentonite	40-280	215	725

Table 2 records the d.t.a. endothermic peaks and the starting and end of the endothermic reactions. The point where the curve departs from the base line is taken to be the commencement of reaction and the end of the endotherm is reckoned by extrapolating the end of the water-loss reaction of d.t.g. curves on d.t.a. curves (Mackenzie⁸). Since the endothermic reactions as stated before were attributable mainly to water-loss decomposition reactions, the temperature range and the peak temperature of the endotherms give an estimate of the energy necessary to drive off water causing the reactions. Close observation of the data shows that the addition of 5% illite to chernozem colloid material increased the temperature range of the endothermic reactions and also the peak temperature of the endothermic peaks. The increase was observed in all the illite treated samples as compared with bentonite treated ones, irrespective of cation saturation. The wide and high range of the first endothermic temperatures and the high value of its peak temperature show that relatively more energy was needed to drive off the adsorbed moisture from illite treated samples than from the others. This together with the observations that illite treated samples had contained less adsorbed moisture (as shown by maximum hygroscopicity) to give out during first dehydration reaction, suggests that adsorbed water molecules on illite surfaces might enter into a difficult and complex reaction alone or being associated with adsorbed

ions. The bentonite enriched chernozem colloid contained higher hygroscopic moisture and at the same time the energy of desorption was relatively lower as may be seen from the first endotherm temperature.

X-ray study : X-ray diffraction with illite and bentonite enriched chernozem colloids, treated with Na_2CO_3 , NaCl and MgCl_2 , were run to study, particularly, the (001) reflections and the behaviour of interplanar hydration. It was observed that bentonite enriched samples gave a considerably diffused pattern in the (001) reflection region on treatment with Na_2CO_3 and to a lesser degree with NaCl . MgCl_2 treatment resulted in relatively well defined (001) reflection. The addition of bentonite (as high as 5%) failed to effect the X-ray pattern by way of increased intensity in its basal reflection, particularly (001). Bentonite in these clay mineral mixtures, might have been partly overlooked because we selected a 12-hrs coarser clay instead of taking a finer clay fraction in which bentonite is more readily detected (Jackson⁵). But the failure to get the increased intensity seems to have been caused by high diffuseness brought about by the interplanar hydration, particularly, with Na_2CO_3 treatment.

Samples enriched with illite, on the other hand, recorded an increase in the original illite reflection resulting in a prominent intensity peak in 10 Å region. The intensity was particularly higher with MgCl_2 treatment. Heating to 500° did not further increase the intensity to any appreciable degree. Whereas, in the case of bentonite rich and Na_2CO_3 (or NaCl) treated samples, heat treatment largely modified the diffuseness of the (001) reflection resulting in a more orderly reflection as did glycerol treatment. This again points out that, unlike illite, there exists in bentonite a great capacity of interplanar hydration, specially when Na constitutes the predominant ion.

DISCUSSION

Differential adsorption of moisture on illite and bentonite surfaces and the energy of its release, is of practical importance specially when Na is the exchangeable ion. A plausible explanation of this differential behaviour between illite and bentonite rich samples is, therefore, attempted.

In a given system, the position of all exchangeable Na with respect to the clay mineral surface is not the same. Some exchangeable Na will be closer to the clay mineral surface than the other. This depends on whether the ions are attached to broken bonds, edges of the flakes or the basal plane, and on this depends the mass of water that will be adsorbed and its molecular configuration. Therefore, the position of ions with reference to the clay surface governs the bonding energy with which it is held by that given clay. For alkali cations, this bonding energy seems to be stronger on illite surface as indicated by Marshall⁹ who has shown that for a constant concentration of alkali cations, the order of ionisation is kaolinite > montmorillonite > illite.

There is evidence of some sort of definite configuration of the water molecules initially adsorbed on the surfaces of clay minerals^{4,13} and cations, present on the mineral surface depending upon the bonding force, influence the perfection of this arrangement and perhaps also the nature of the configuration of water molecules. In illite, in addition to the bulk

of the exchange taking place at broken bond, a part of the exchange occurs between basal flake surfaces firmly held together. The latter is slow and illite needs a longer time than bentonite to complete the same degree of exchange reaction. From this and all the foregoing considerations, it may be said that Na ions that are adsorbed on illite are relatively strongly held and as a consequence water vapour that associates with those ions might enter into a difficult combination due to its structural characteristics. This explains why a higher energy level was needed to release sorbed water from illite enriched samples.

Since the degree of water sorption of Na^+ depends upon the bonding force of the ion⁷ and as the latter is relatively weaker on bentonite surfaces, as discussed earlier, water sorption is greater in Na-bentonite. Consequently, exchangeable Na may be at a greater distance from the bentonite mineral surface and separated from it by water molecules. This explains why at a relatively lower energy level all the sorbed water could be driven from bentonite enriched samples.

What holds good for the differential adsorption of water vapour and its energy of release by Na-illite and-bentonite systems may hold good for their differential hydration behaviour and the whole range of related properties associated with hydration. In view of what has been said, it may be assumed that Na ions will have a tendency towards less hydration on illite surfaces than on bentonite. It may be due to this that alkali soil containing illite and a high amount of exchangeable K^+ is less susceptible to the development of adverse physical properties while montmorillonite soil is more adversely affected.

The present study only indicates a trend. Further elaborate study is considered necessary to obtain a clear insight into this aspect since this has a practical value in the understanding of salt affected soils.

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