SOME CHEMICAL BEHAVIORS OF HYDROGEN CLAY MINERALS OF NONTRONITE TYPE FROM A CALCAREOUS PADDY SOIL

SOME CHEMICAL BEHAVIORS OF HYDROGEN CLAY MINERALS OF NONTRONITE TYPE FROM A CALCAREOUS PADDY SOIL

By

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Clays and clay minerals are essentially considered to be electrochemical or polar systems having dominant acidic character, which is fully developed in the so-called H-clays.

On the characters of curves obtained by potentiometric titration of H-clay minerals some light has been thrown by several workers. These works, however, concerned mainly principal types of clays such as bentonite, montmorillonite, kaolinite, halloysite and illite. There have been but few works on special kinds of clays other than above-mentioned or clays such as nontronite or clays in paddy soils that seldom occur.

The acidic character, in other words, the action to combine with or adsorb cations is usually considered, in cases of clays, as due to electro-negative charges originating from electrostatical unbalance in a structure of crystal lattice of clay minerals. In the present work we attempted to investigate electrochemical behaviors of H-nontronite separated from a calcareous paddy soil by titration curves and cation exchange capacities.

Descriptions of Clay Minerals used

The soil from which the clay minerals used were separated is a paddy soil at Shiroishi-city, Miyagi prefecture. The soil has developed on an alluvium derived from weathered materials of calcareuos sedimentary rocks. The soil is more or less impermeable and has a ground water level at about 50 cm depth. The reaction of the plowed layer is pH 7.0 and that of subsurface soil is pH 8.2. Many soft concretions of Ca-salts are observed in the layer of ground water level.

Clays finer than $0.2\,\mu$ are separated through centrifuge method from a plowed surface layer (0-10 cm) and from a subsurface layer (30–40 cm) containing no Ca-concretions.

About one half portion of clays separated from both layers is treated with H_2O_2
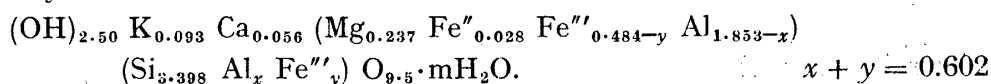
and then by H_2S gas bubble method after Drosdoff[1]. After being freed from Fe-hydroxide, it was treated with 2% Na_2CO_2 solution for 30 min. at boiling temperature to remove any possible Si- and Al-gels which may be left behind unsolved by H_2S-method or that may have been produced as the results of destruction of some minerals owing to a drastic H_2S-digestion. A half of the remainder was treated simply with 2% Na_2CO_3 solution to remove Si- and Al-gels. These two clay portions were leached with a sufficient amount of N/20 HCl solution until they were brought to complete unsaturated state of H-clay and Fe-H-clay. After leaching they were washed with alcohol until they were free from Cl ions and then dried at room temperature and pulverized. The chemical constituents of the sample thus prepared are as follows.

Table 1. Results of chemical analysis of clays ($< 0.2\mu$) from
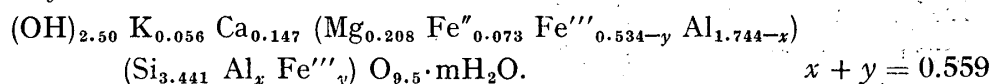a calcareous paddy soil.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	MnO	K_2O	Na_2O	P_2O_5	$+H_2O$	Linked Fe_2O_3 hydrous oxide	Total
H-Clay from surface Soil	% 51.16	% 22.68	% 10.48	% 0.49	% 2.39	% 0.39	% trace	% 1.08	% —	% —	% 12.07	—	% 100.74
H-Clay from subsurface Soil	50.87	22.17	10.35	1.27	2.00	1.00	trace	0.64	—	—	12.10	—	100.38
H-Fe-Clay from subsurface Soil	49.60	21.62	10.09	1.24	1.95	0.98	trace	0.62	—	—	11.80	2.50	100.40

From these results of chemicl analysis we can construct the structural formula of crystal of clay minerals as the following 2 : 1 type H-nontronite.

H-clay in surface soil :

$(OH)_{2.50}$ $K_{0.093}$ $Ca_{0.056}$ $(Mg_{0.237}$ $Fe''_{0.028}$ $Fe'''_{0.484-y}$ $Al_{1.853-x})$

$(Si_{3.398}$ Al_x $Fe'''_y)$ $O_{9.5}\cdot mH_2O.$ $x + y = 0.602$

H-clay in subsurface soil :

$(OH)_{2.50}$ $K_{0.056}$ $Ca_{0.147}$ $(Mg_{0.208}$ $Fe''_{0.073}$ $Fe'''_{0.534-y}$ $Al_{1.744-x})$

$(Si_{3.441}$ Al_x $Fe'''_y)$ $O_{9.5}\cdot mH_2O.$ $x + y = 0.559$

These clays were examined by means of dehydration, differential thermal analysis, X-ray powder diffraction, and electron micrographs. In the differential thermal curves, as shown in Fig. 1, all of them show two endothermic peaks at 150°C and 530–535°C, and an exothermic peak at 850°C. X-ray powder diffraction patterns are quite similar to that of Fe-montmorillonite already reported elsewhere. In electron micrographs, they show angular thin

flakes like those in beidellite or Fe-montmorillonite. Dehydration curves show somewhat a tendency of some parallelism to those of beidellite or illite.

From the results of these investigations the authors conclude that the clays may be expanding 2 : 1 lattice clays of nontronite type containing a rather minor content of Fe.
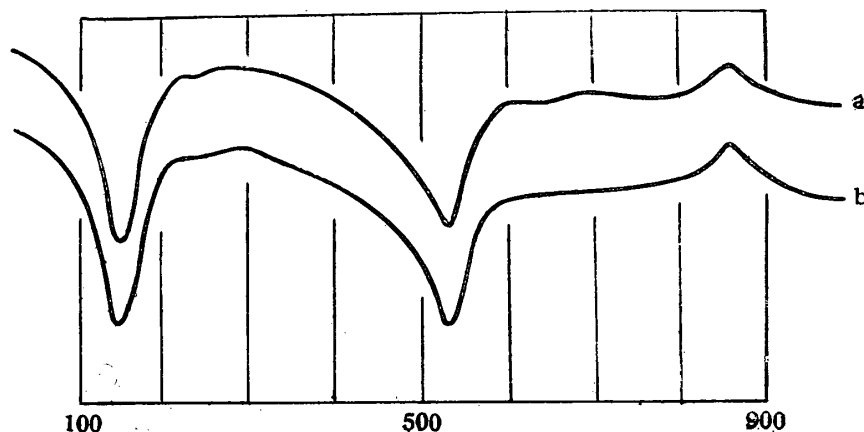

Fig. 1· Differential thermal analyses curves of clays from surface layer (a) and from subsoil (b) of a calcareous paddy soil.
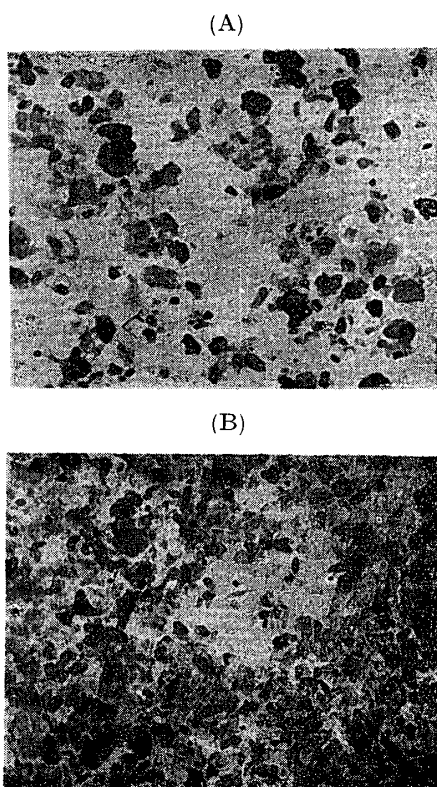
(A)

(B)

Fig. 2. Electron micrographs of fine clays ($<0.2\mu$) in a calcareous paddy soil.   ×10,000
(A) Surface soil clay.
(B) Subsoil clay.

Table 2. X-ray diffraction powder patterns of clay minerals in a paddy soil.

Surface Soil		Subsoil	
I	d	I	d
v.st.	15.40	v.st.	15.19
st.	4.45	st.	4.49
v.st.	3.95	st.	3.95
		v.w.	2.83
m	2.58	m	2.60
		v.w.	1.70
w	1.63	w	1.63
w	1.49	w	1.49
w	1.37	w	1.36
w	1.28	w	1.28

Experiments on Titration

To each of the two series of 0.5 % suspensions of H-clay and H−Fe−clay from surface layer and subsurface layer were added varying amounts of N/50 HaOH or N/50 NH_4OH solutions in increasing order. After being um-stoppered and left stand for 72 hrs. hydrogen ion concentrations were measured potentiometrically through glass-electrode method. The results of pH determinations are shown graphically in Fig. 3 and Fig. 4.

We can observe two or three inflection points on all curves. Titrations of H-nontronite have not been so much studied. However, recently Mitra and Mathur[2] presented some data on this point, which clarified that H-nontronite show three inflection points on their titration curves, the third being a pronounced one. According to Mitra and Rajagopalam[3], even hydrogen muscovite when titrated with NaOH or KOH show three inflection points, the first occurring between pH 6.15 and 7.3, the second at pH 9.0, and the third at pH 10.5. In the present case of H-nontronite, the first inflection point occurs at pH between 5.2 and 5.5, the second at 6.25, the third at 8.1 or 8.2 when titrated with NaOH. This would indicate that there exist three stages of neutralizations of negative charges on clay surfaces, and then we can imagine three different strength of electric fields produced by different kinds of negative charges, consequently, three kinds of H ions in different strength of ionization or dissociation may be present. The nature of these potentiometric titration curves with bases is very characteristic and, as pointed out by Roy and Das[4], this may be used for differentiation of clays provided complete characters of all species of independent clays have been studied to the final detail.

But these differences between such inflection points are not to be clarified theoretically without a complete knowledge of the subject. Although the deferrated H-clay of surface soil shows three inflections, on both of H-Fe-clay curves by Ba ions and NH_4 ions the first inflection point disappears while the distinctly broadened second inflection and the third remain. However, in the clays of subsurface soil, both H-Fe-clays and H-clays show three inflections, especially the first and the third are very pronounced. Furthermore, it is noticed that the second inflection points when Fe-hydrous oxide are linking shift to right hand direction, in other words, to the direction of high base requiring. Considering on the basis of the above-mentioned points, the existence of hydrous Fe_2O_3 linked with clays seems to influence and alter the shapes of titration curves, and also a certain part of negative charges on clay surfaces appears to be thereby weakened or strengthened.

The reason for this may be attributable, partly to an isoelectric nature of Fe hydrous oxide itself and, partly to an action of Fe atoms which possesses
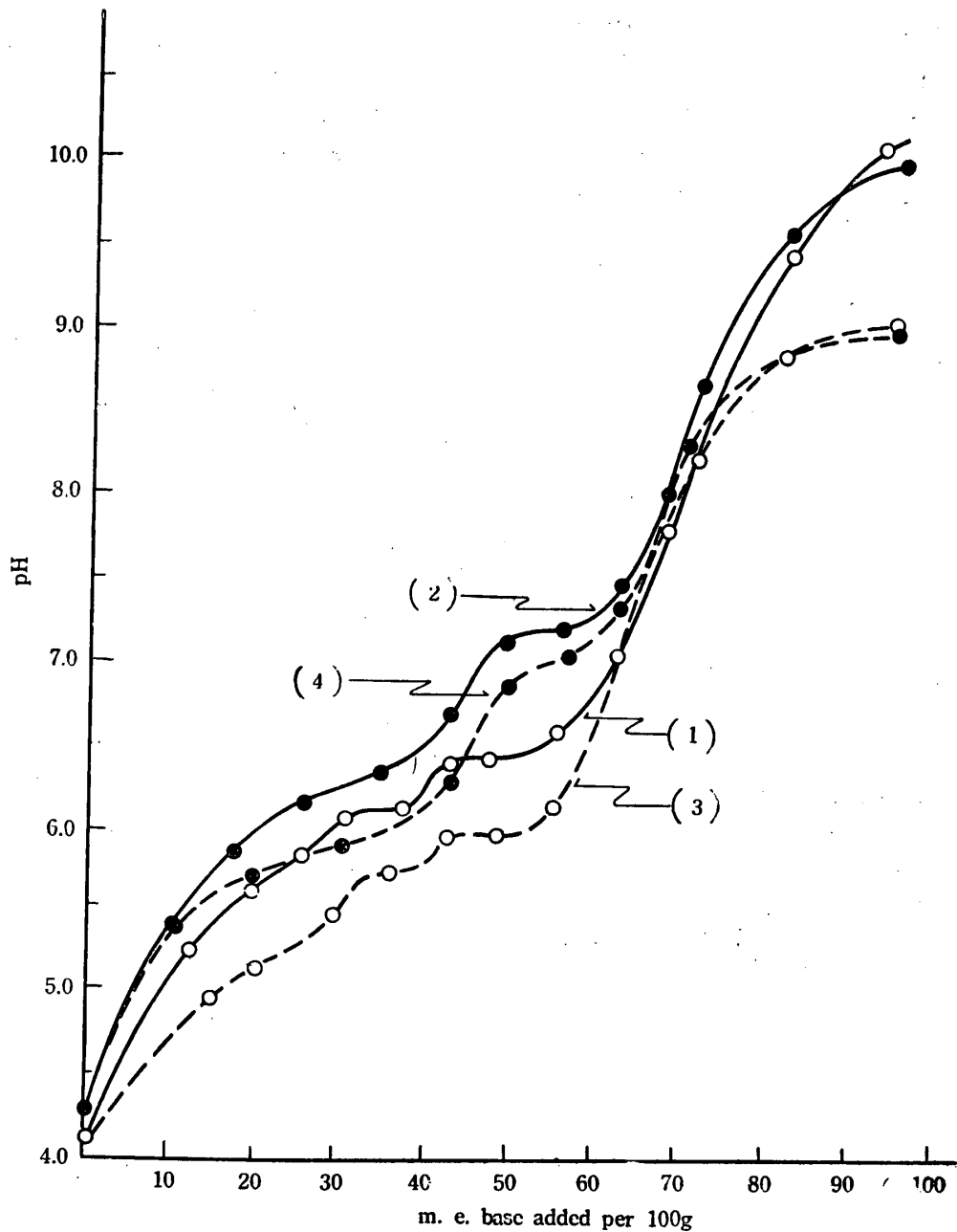
Fig. 3. Titration curves of clays from a surface horizon.
(1) H-clay with NaOH   (2) H-Fe-clay with NaOH
(3) H-clay with NH_4OH (4) H-Fe-clay with NH_4OH

positive charges in a low pH medium. The magnitude of the abrupt rise of pH at the vicinity of the second inflection point on titration curves becomes almost twice greater when linking with Fe hydrous oxide than the deferrated H-clays. This would indicate that either Fe hydrous oxide may act as bases having some effective OH ions at the interval between pH 5.5 and 7.0, or Fe may weaken
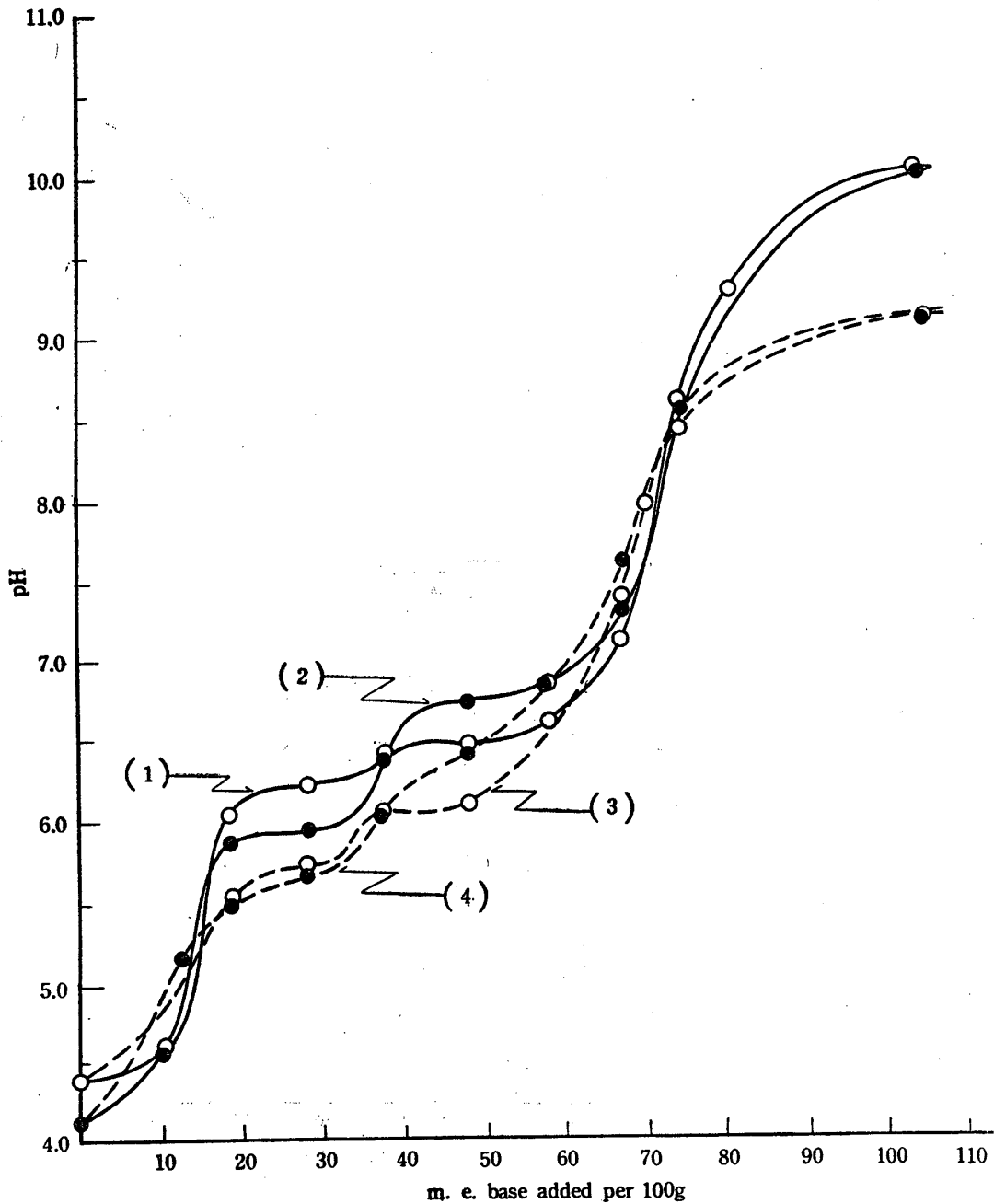
Fig. 4. Titration curves of clays from a subsoil
(1) H-clay with NaOH   (2) H-Fe-clay with NaOH
(3) H-clay with NH_4OH (4) H-Fe-clay with NH_4OH

the linkage of H ions attracted to clay surfaces to a state of more ionizable H ions below pH 5.5. Consequently, we can assume that Fe hydrous oxide in soils or linking with soil clays may have an isoelectric point at or near pH 5.5.

Although it is usually believed that Fe hydroxide gels have isoelectric point at pH 7.1, that may be the case only when Fe hydroxide precipitates are

produced from $FeCl_3$ and alkaline solution in a laboratory. In the case of soils or soil clays conditions may differ. It can be reasonably supported by the work of Schuylenborgh et al.[5] that α-FeOOH or γ-FeOOH having an isoelectric point of pH 5.4 are possible to be formed in natural conditions from high dilution and very slow formation. According to their opinion, the isoelectric point (pH) decreases as the moist precipitates are dried and as the solution from which Fe are precipitated becomes more dilute. Such a condition would exactly fit with the natural condition in a soil of more or less impermeable paddy field. Therefore, it may be true that Fe hydrous oxides in the present clays have isoelectric point of pH 5.4 or 5.5 and the aforesaid appearance is the result of the influence of such Fe hydrous oxides.

It is very interesting that in the case of subsoil clays pH of a completely unsaturated H-Fe-clay is lower than that of deferrated H-clay, and furthermore, pH of H-Fe-clay to which bases of 30 m.e. or slightly more added are also lower than that of H-clays.

Schofield[6] discussed the influence of Fe hydroxide combined with clays upon cation exchange capacities and negative charges of clays.

If Fe_2O_3 linked with clay minerals balance negative charges of clays, as Schofield suggested, the pH of unsaturated H-Fe-clays should be higher than that of H-clays through a course of titration below pH 7.0, provided the same amount of bases are added. But this is not the case in the present experiments.

A lower pH of H-Fe-clay would means that some portions of H ions attached to clays especially those used to neutralizing the bases at an early stage of base addition should be more hydrolizable in the presence of Fe hydrous oxides. It may be reasonably assumed that H ions may be attached more tightly or more closely to clay surfaces in the absence of Fe hydrous oxide, consequently, the ionization of H ions would go on in a lesser degree, but when Fe hydrous oxides are present H ions would be attracted more weakly by balancing of their positive character or owing to much more distance apart from charge spots on clay surfaces through the presence of Fe hydrous oxides at the intermediate position between H ions and charge spots.

Both clays of a surface soil and subsurface soil have quite similar amounts of chemical constituents, however, the shapes of titration curves are different to some extent. The reason for such a difference and the reason why the pH of H-Fe-clay is lower at an early stage of neutralization may be due to the essential structural form of crystal lattice produced by substitution in Si-tetrahedral layer.

The amounts of m.e. bases added which correspond to the first, the second, and the third inflection point of the deferrated H-clay of surface soil are 28.0, 40.0, and 69.0 m.e., respectively, and in the case of the deferrated H-clay of

subsurface soil they are respectively 15.0, 5.0, and 71.5 m.e. per 100 gr. The values at the third inflection points are quite equal to the m.e. of cation exchange capacities measured by NH_4OAc or NH_4Cl at pH 5.5. The pH which correspond to the first, the second, and the third inflection point of the deferrated H-clay from surface soil are respectively 5.95, 6.25 and 8.20 when titrated with NaOH and that of H-clay from subsurface soil are 5.38, 6.30 and 8.20 respectively.

From these results of titration experiments, we may consider that the strength of acid properties of H-nontronite used may be of the same order of beidellite and that the clays possess acidic character resembling that of tribasic acids.

Experiments on Cation Exchange Capacities

We can find extremely numerous studies on cation exchange capacity and numerous methods have been proposed for determining cation exchange capacity of soils and soil clays. However, we can not as yet find a precise method or procedure by which an accurate value of cation exchange capacity of clays, can be evaluated especially, that of clay having cation attracting forces of various strengths in it. In general, cations used for determination of cation exchange capacity are Na, Ca, Ba, or NH_4 ions and, recently NH_4 ions or Ba ions of chloride or acetate seems to be used as a usual method. However, in many cases, it is still difficult to obtain a constant value. The reason may be due to several disturbances originating from soil itself or from salt solution used and techinque applied. When treating a soil with alkalies cation exchange capacities are not necessarily constant but vary (a) with the time of reaction, (b) with temperature, and (c) with the amount of samples used in regard to the amount of alkali. Furthermore, when solutions of acetates are used more cation is adsorbed, as the cation hydroxide of these acetates is more insoluble in water. These results have been obtained by several workers. In addition, it was also found that more cation is adsorbed in case the soil contains more amorphous sesquihydroxide or sesquihydroxide-silcic acid gels.

Our present clay samples are purely free from such gels as sesquihydroxide or sesquihydroxide-silic acid because they have been treated with 2% Na_2CO_3 solution to remove any gels contained after the removal of Fe hydrous oxide gels linked with clays by H_2S method. Consequently, in the present experiments we need not bother about any disturbances caused by such contaminating gels and there is no cations adsorbed on clays before determination because the samples have been converted into pure hydrogen clays, then there is no reason to give high value due to a formation of insoluble cation hydroxide produced by expelled cations from clays. Accordingly, the phenomena are merely a replacement of H ions which differ in easiness of replacement by cations in a salt solution.

We can find but few reports on the relationships between cation exchange capacities and the types of soil clays. Mehlich[7] clarified the matter by his extensive works. According to him, with clays of hydrous micas or 2 : 1 lattice type cation adsorption capacities determined by NH_4OAc and $BaOAc$ are virtually the same provided the pH of mediums are below 7.0, but Ba ions are adsorbed from $BaOAc$ solution in greater amounts than NH_4 ions from NH_4OAc when medium pH is higher than 7.0 or in presence of $CaCO_3$. Finally, he concluded that a method employing a divalent cation buffered at about pH 8.0 is best adapted for the evaluation of the cation exchange status of soils with a variety of types of colloidal materials. Other workers also found the same.

We have attempted in this work to test the adaptability of Ba ions and NH_4 ions for determinations of cation exchange capacity in the case of clays with some complex structure of crystal lattice such as nontronite and, if possible, to clarify the details of a precise condition of medium pH and to consider the relationships between cation exchange capacity and the complexity of crystal structure of nontronite through characteristic behaviors of Ba ions and NH_4 ions.

To 0.5 gr. of the same clay samples of H-Fe- clay and deferrated H-clay used in the previous titration experiments 250 ml. of N/2 solution of Ba salts or NH_4-salts are added. The salts used are chlorides below pH 4.3 or 4.4 the reactions of which are adjusted by dil. HCl to a required pH, in the range of pH between 4.3 or 4.4 and 7.0 acetates are used by adjusting their pH by HCl, and on alkaline side, chlorides are used, although $BaCl_2$ solutions are buffered with triethanolamine after Mehlich's method and the pH of NH_4Cl solutions are raised by addition of NH_4OH solution. After the addition of a salt solution and standing for 24 hrs. clays are filtered and washed with alcohol to remove Cl ions. When acetate solutions are used clays are leached once with solutions of N/2 $BaCl_2$ or NH_4Cl after the finishing of filtration of the original salt solution and then washed with alcohol to free from Cl ions. The clays thus washed are leached with N/5 HCl solution up to 250 ml. followed by another washing with distilled water till Cl ions are removed. All of the leachate and the washed water are combined and evaporated to an appropriate volume. Ba ions replaced from clays by H ions are determined as $BaSO_4$ gravimetrically and NH_4 ions are determined by a distillation method. The results are shown graphically in Fig. 5 and Fig. 6 and numerically in Table 3 as follows.

It is observed from these results that the values with Ba ions are always higher than that by NH_4 ions, especially in a range of a strong acid medium such as below pH 3.5. Furthermore, there are several portions having a nearly constant value of cation exchange capacity on the curves. The lowest one lie at a strong acidic range, below pH 3.2, the second is observed at the pH range
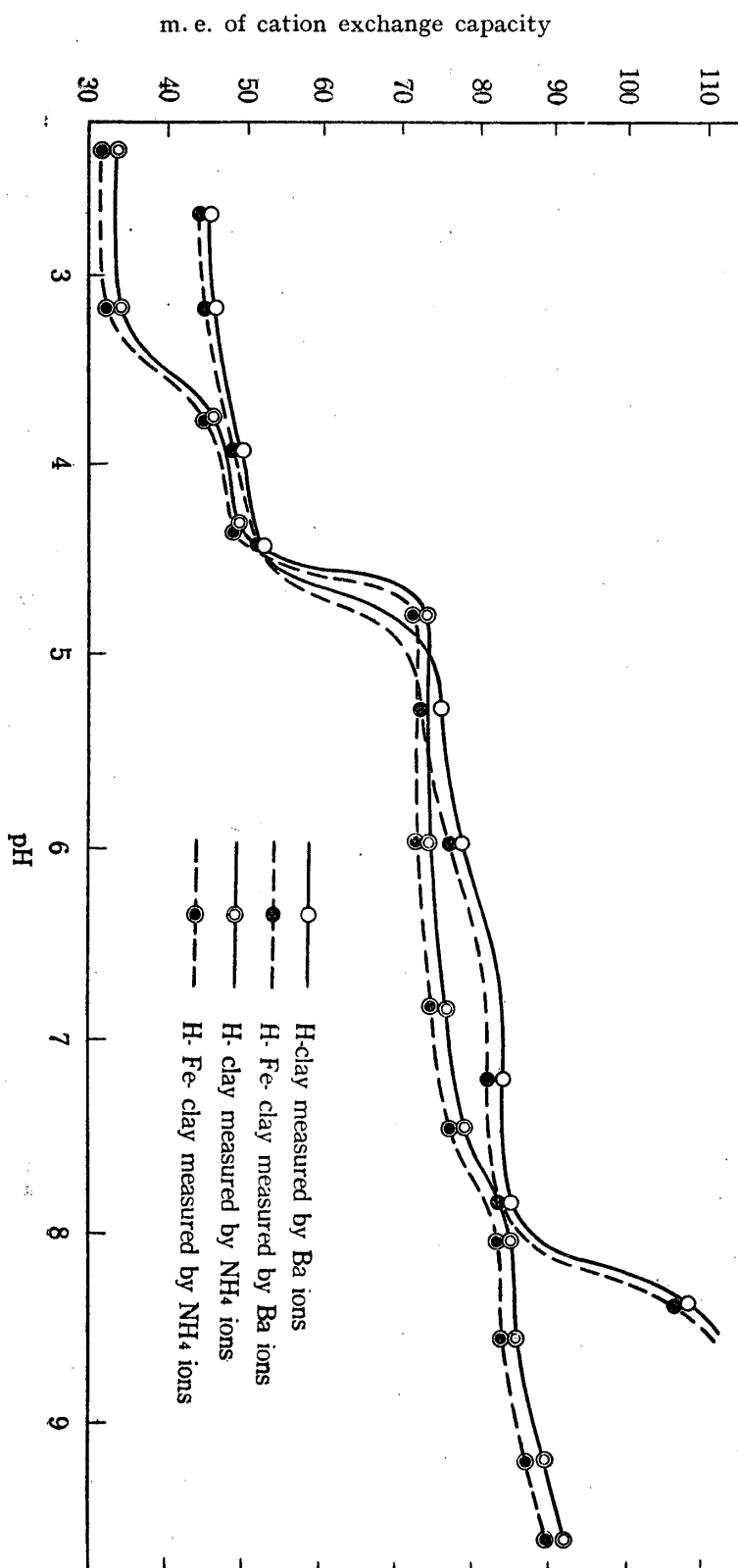
m. e. of cation exchange capacity

pH

H-clay measured by Ba ions

H- Fe- clay measured by Ba ions

H- clay measured by NH4 ions

H- Fe- clay measured by NH4 ions

Fig. 5. Relationships between pH of medium and cation exchange capacity
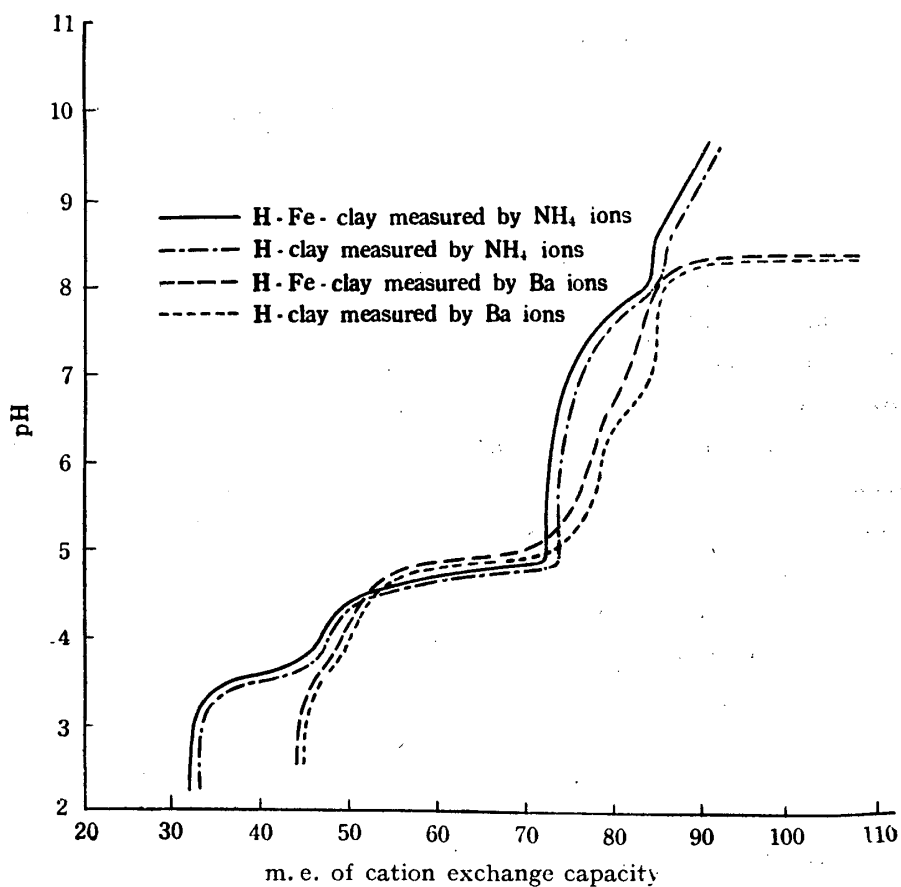
m. e. of cation exchange capacity

Fig. 6.   Relationships pH of medium and cation exchange capacity.

Table 3. Cation exchange capacities of the original H-nontronite and the deferrated H-nontronite from a calcareous paddy soil determined by Ba ions and NH4 ions at various pH. (m.e. per 100 gr. clay)

		Chloride				Acetate			Chloride				
	pH	2.71	3.19	3.94	4.43	5.25	5.96	7.18	7.84	8.37			
Ba ions	H–Fe–Clay (A)	44.4	45.0	49.0	51.2	73.1	76.8	81.5	83.6	107.9			
	H–Fe–Clay (B)	45.4	46.0	50.1	52.4	74.9	78.5	83.4	85.5	110.3			
	H–Clay	45.3	45.8	49.7	51.9	75.9	78.6	84.0	84.3	107.3			

		Chloride				Acetate			Chloride				
	pH	2.37	3.19	3.75	43.1	4.77	5.96	6.81	7.44	8.06	8.54	9.19	9.63
NH₄ ions	H–Fe–Clay (A)	31.3	32.0	45.5	48.6	72.1	72.6	75.0	77.1	83.4	83.9	87.5	90.0
	H–Fe–Clay (B)	32.0	32.1	46.5	49.7	73.8	74.2	76.7	78.9	85.3	85.8	89.5	92.1
	H–Clay	33.4	33.9	46.1	49.4	73.9	74.0	76.1	79.0	85.3	85.9	89.6	91.6

(A). values calculated on the basis of clays with Fe hydrous oxide.
(B). values calculated on the basis of clays free from Fe hydrous oxide.

from 4.8 to 6.0 on NH_4 ions curves, although there is no such portion on Ba ions curves, and the third are observed in a range of pH from 7.0 to 7.8 on Ba ions curve and from 8.0 to about 8.7 on NH_4 ions curves. The lowest constant values of m.e. of C. E. C. determined by Ba ions and NH_4 ions differ considerably, the former being 45.0 m.e. but the latter amounts to only 34.0 ,m.e.. Such differences between both ions become narrower at pH 3.8 and almost negligible at pH 4.4. This would indicate that of the cation exchange capacities which can be measured below pH 4.5 there may be two different kinds of H ions replaced by cations, that is, those which can be replaced by either ions of Ba or NH_4, and those which are replaced merely by Ba ions but not by NH_4 below pH 3.8. We can realize from the curves in Fig. 5 and Fig. 6 that there is no broad range of pH but a point at which cation exchange capacities by Ba ions and NH_4 ions will coincide.

The points on which two curves of Ba ions and NH_4 ions are crossing lie at the points of pH 4.5 and pH 5.0 and the m.e. of cation exchange capacities corresponding to them are 53 m.e. and 74 m.e. respectively in the deferrated H-clay, 52 m.e. and 72 m.e. in the case of H-Fe-clay. The latter values of cation exchange capacities, that is 72 or 74 m.e., are nearly equal to the m.e. bases added which correspond to the third inflection points on the titration curves. The small discrepancy of about 2 m.e. between the values measured by titration curves and that measured by C. E. C. would result from errors induced by using samples prepared at different times. Therefore, if we now assume these values are equal, the amount at this point must be considered to correspond the cation exchange capacity obtained by a replacement of H ions of "isomorphous charges" on clay surfaces but excluding that from OH groups.

Recently, Mitra and Mathur have presented some data on cation exchange of H-attapulgite and H-nontronite. According to them, when Ba ions in $N\text{-}BaCl_2$ solution are used all H ions of H-nontronite are replaced even when the solution of $BaCl_2$ has as low a pH as 5.0. If the conclusion of Mitra and Mathur is true, the latter value of pH, say pH 5.0, should be the point where all H ions including that from OH groups must be replaced and the cation exchange capacity values are considered to be correct. However, if this is so, a question would arise what is the reason for the increase of cation exchange capacity as the pH of medium increase from pH 5.2 upward when measured by Ba ions and from pH 6.0 upward when NH_4 ions are used. The highest constant values can be observed in a relatively broad range of pH at an interval of pH from 7.0 to 7.8 on Ba ions curves and at an interval of pH from 8.0 to 8.7 on NH_4 ion curves. In addition, these two constant values of cation exchange capacity are almost equal amounting to 84.0–85.0 m.e. per 100 gr. H-clay and 83 or 84 m.e. per 100 gr. H-Fe- clay. The increased amounts from 72 or 74 m.e. to 85

or 84 m.e. are considered to be due to a replacement of H ions from OH groups by cations.

Hitherto, it has been generally accepted that H ions of OH groups at broken edges of clays can be replaced by cations at pH 6.0 or over. According to the results of this experiment with NH_4 ions this may be true but a complete replacement can be attained at such a high pH as 8.0 or over, while with Ba ions such a replacement begins at pH 5.0 and finishes at pH 7.0. Then, the cation exchange capacity determination including a replacement of H ions from OH groups should be carried out preferably by NH_4 ions at pH 8.2 or 8.5 or by Ba ions at pH interval between 7.2 and 7.7 using an appropriate buffering agent such as triethanolamine.

If we seek the third constant values of m.e. of cation exchange capacity on the titration curves of Fig. 4, they do not coincide with the third inflection point but points of higher pH are obtained such as pH 8.8 on the NH_4 ions curve and pH 9.6 on the Na ions curve. This will show that the third inflection point on a titration curve indicates the neutralization point of merely H ions of isomorphous charges. Therefore, when we desire to obtain a complete neutralization of all H ions including H ions from OH groups we must add more bases till a higher pH than ordinary recognized inflection point is attained.

By the differences between cation exchange capacity of H-Fe-clay and that of H-clay an action of Fe-hydrous oxide which influences the capacities of clays to adsorb cations from salt solutions can be shown. If we compare these values, the differences are greater above pH 4.5 when NH_4 ions used or above pH 5.0 when Ba ions used than below these pH downward to about pH 3.0. In the range below pH 3.0 the differences become slightly larger in the case of NH_4 ions used. The increase of differences above pH 4.5 or 5.0 is considered to be due to a low isoelectric (pH) of Fe hdydrous oxide while the small increase below pH 3.0 would be attributable to an action of positive charges of Fe atoms which will be active in this pH range. The fact that when Ba ions are used there is practically no difference below pH 3.0 would suggest that an action of Ba ion to combine with negative charge spots of clay is so strong that Fe hydrous oxide can exercise no influence but in the case of NH_4 ions an existence of Fe hydrous oxide will have influence toward lowering a cation exchange capacity of clay to some extent. In the present case, 15.7 m.e. of Fe_2O_3 lowered the cation exchange capacity of 1.1 or 1.4 m.e. at pH 2.37 or 3.19, respectively.

Marel[8] has pointed out that determination of cation exchange capacity must be carried out with NH_4Cl solution at pH about 5.5 but not at pH 7.0. As a conclusion from our present experiments, we can propose appropriate determining conditions of cation exchange capacity of soil clays, at least like those of

H-nontronite here used, as follows.   When we need a value of replacement of isomorphous charges of clays by cations it should be operated by solutions of NH_4 ions at pH about 5.5 or at an interval of pH 4.8 and 6.0, however, Ba ions are unfavorable because they do not show no constant value at this region, and when the values including replacemant of H ions from OH groups are needed it should be carried out by Ba ions at about pH 7.4 or at about pH 8.3 or 8.4 by NH_4 ions.

As Roy and Das pointed out recently, for a differentiation of a mineralogical make-up of soil clays or for a characterization of clay minerals a titration method by Ba ions may be useful, but Ba ions are too strong to differentiate charges of clays having complex structure like nontronite.

It may be considered that in the future cation exchange capacity determination with both of Ba ions and NH_4 ions will become a useful key for a characterization or a differentiation of clays provided full studies on the point are pursued.

Summary

H-nontronite from which linked hydrous Fe_2O_3 has been removed and H-nontronite combined with hydrous Fe_2O_3 were separated from a calcareous paddy soil and investigated by electrochemical titration and by cation exchange studies.

The results of experiments have made it clear that H-nontronite show three inflection points on titration curves and also on cation exchange curves, although with Ba ions it was uncertain.

This is attributed by the writers to the existence of three kinds of H ions different in strength on clay surface.   These H ions may become replaceable at varying pH by varying cations.   As to the real causes accounting for such three inflections we fail to interprete theoretically and express their characteristics numericaly, however, it may be supposed that this may be due to the inherent characteristics of crystal structure of nontronite here studied.

From the results of cation exchange capacity determinations it is clarified that for determination of cation exchange capacity which showing the replacement results of H ions of isomorphous charges Ba ions are unfavorable and NH_4 ions must be used at pH interval between 4.8 and 5.8, most safely at about pH 5.5. However, for determination of cation exchange capacity including all H ions replaced from OH groups Ba ions in $BaCl_2$ solution are useable at an interval of pH between 7.1 and 7.7 provided it is buffered with triethanolamine, and also NH_4 ions at pH between 8.0 and 8.6.

An inflection point of titration curves, the final one at the highest pH in our experiments is considered that it does not necessarily represents a complete neutralization point including H ions from OH groups. A complete neutrali-

zation of all H ions including H ions from OH groups should be obtained at a higher pH such as 8.7 when NH_4 ions are used and 9.6 when Na ions used which correspond to the pH of the terminal point of the portion of the third constant value on cation exchange capacity curve.

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