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II. DEHYDRATION AND REHYDRATION EXPERIMENT

By

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Introduction

We have reported in the preceeding paper of this article on clay minerals separated from a glei-horizon of an alluvial soil. The clays are mainly composed of montmorillonitic 2:1 layer type clays and their mixed-layer minerals with gibbsite-like layers and/or hydrated halloysite although some hydrated halloysites are present in the form of tublar crystals or rather in a form like rolled thin plates. It was noticed by the preceeding experiments of Part I that the content of H_2O^+ was very high. Its amount was 10.64 per cent when expressed as per cent of the weight of the clays after heating at 260°C. Further, the clays contained a very large amount of H_2O^- as high as 12.02 per cent on the same basis. From considerations of the investigations reported in the previous paper it was considered somewhat peculiar that both of hygroscopic water and lattice OH type water are so high. Hydrated halloysite, sepiolite, and palygorskite can obtain 20 or more per cent of water, however, hydrated halloysite must have lost their C.E.C. to the degree of 10 or so me. per 100 g when heated at 100°C, while the present clays showed 36.49 me. per 100 g after heating at 150°C. These clays cantain only a small amout of MgO, therefore, they can not be such clays as sepiolite, palygorskite or other minerals having large amounts of Mg ions. According to Mackenzie, artificial pseudochlorites contain about 26 per cent of water and when they are heated at 300°C they loss 14 per cent of water. He interpreted that this must correspond to the loss of water from the interlayer spaces being incompletely filled with Mg-hydroxide, in addition to the dehydration of very poorly crystallized hydroxide precipitated outside the micells. At about 400°C the second weight loss occurs which may be attributable to the dehydration of the brucite layer, and this dehydration continues more slowly up to 525°C, at which temperature the montmorillonitic layer decomposes. To clarify the reason of the large amount of the weight loss of the colloidal clays we attempted dehydration and rehydration experiments.

Clay Sample used and Experimental Procedures

The colloidal clays ($<0.3\,\mu$) from glei-soil used in the experiments are the same samples on which some discussions were reported in the preceeding article of this series. As already indicated in Part I, the chemical composition

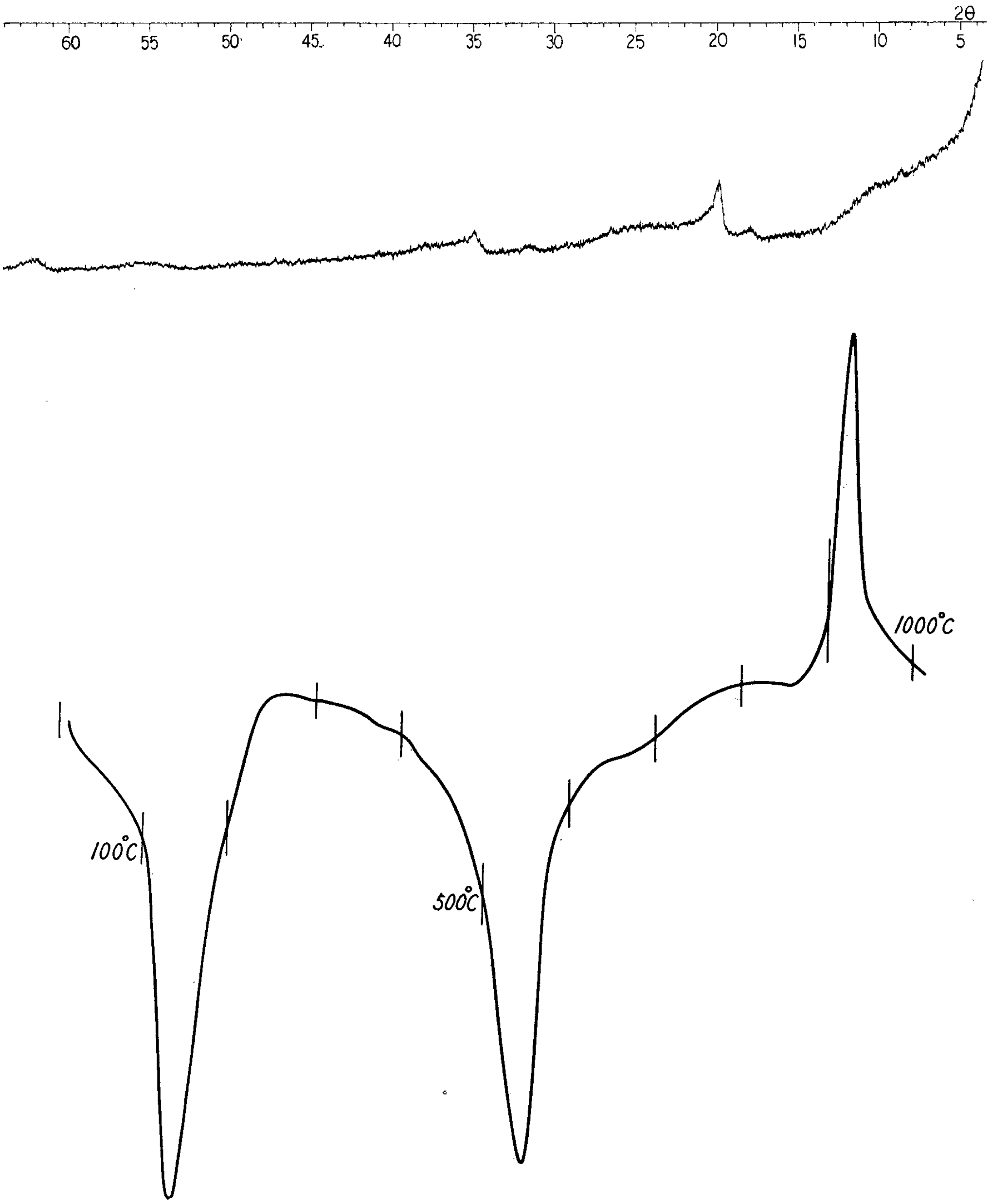

Fig. 1. X-ray diffraction and D.T.A. of the Ca-saturated colloidal clay separated from a glei-soil.

of the H-saturated clays expressed on the basis of the weight when heated at 260°C for 30 minutes are as follows;

SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O^+	H_2O^-
52.02	31.38	3.50	0.57	0.80	0.16	0.09	tr.	11.24	11.65%

The D.T.A. curve of the Ca-saturated clays is shown in Fig. 1. As can be seen from Fig. 1, such a large amount of weight loss as high as about 22.9 per cent is considered to occur at two positions one of which by heating at the temperature below 260°C and the other by heating at the temperature above nearly 350°C to 600°C. There was almost no distinctly strong reaction in the range of the temperature between 260° and 350°C although only a minute depression of the curve seemed to occur.

The C. E. C. of this colloidal clays when determined immediately after fresh preparation of the sample was 48.1 me. per 100 g clays. The clay samples for examinations were prepared in September, 1957, and they were saturated with Ca ion by $CaCl_2$ solution, dried to nearly an equilibrium state against 90–100 per cent R.H. vapor at room temperature, then placed and stored in a desicator of 50 per cent R.H. until June 1958. The experiments of dehydration and rehydration were carried out by using the above samples stored for 8 months in a vapor of 50 per cent R.H.

Six portions of the clay sample of about 0.5 g were weighted in each weighing glass bottle and heated at the required temperature for 30 minutes by using an electric funnel of D.T.A. apparutus. The heating temperature applied were the following six points of 70°, 100°, 150°, 200°, 260°, and 310°C. From the results of D. T. A., already reported in Part I of this series, it has become evident that the first endothermic reaction was practically completed when the heating temperature reached about 260°C and the second endothermic reaction emerged after the temperature exceeded about 320°C though a distinct drop started at 350°C. After the samples were heated for each required time the bottles were stoppered and weighed. The difference of weight between that of the fresh sample which had been equilibriumed for 50 per cent R.H. and that of clays after pre-heated gave the loss of weight by heating for each temperature treatment. Next, the weighing bottles containing the above heated clays were placed in a desicator of 50 per cent R.H. for sufficient time, in this experiments 16 days, for equilibrium with 50 per cent R.H. After 16 days equilibrium, which was considered to be sufficient for complete readsorption of the clays, the increased weights were measured, in addition, C. E. C. of the clays after preheated at each temperature were determined using ammonium chloride solution. Other heat experiments were also practiced to investigate more fully the dehydration relationships applying a much longer heating time. The heating temperatures used were 70°, 100°, 157°, and 210°C and heating time applied was selected at eight hours. To clarify the variation of cation exchange capacities when heated at various temperature, the contents of Fe^{++} were determined on the clays after heating at 100°C and 310°C.

Results and Discussion

(I) Variation of various weights

The characteristic features of the dehydration phenomenon of the present clays are that the loss weights were relatively large compared with each heating temperature and that the variation of weights seemed to progress nearly in a linear-like relation on the contrary of rather curvilinear increase in weights in cases of usual soil clays. To discuss variations of weights when clays were heated it is considered to be convenient to express the weights on the same weight basis. In the present case we selected the modified weight of the clays after pre-heating at 310°C for 30 minutes as the common standard to apply all the cases at other heat temperatures. When we calculate the loss weights at each heating temperature by applying the above standard weight the obtained weight losses at 150°, 200° and 260°C situate on a straight line in Fig. 2 but that at 310°C diverges slightly from this line. This will mean that the loss rate when heated at the temperature between 150° and 260°C should be quite the same, however, when the clays are heated at a temperature higher than 260°C or more probably at the temperature in the neighbourhood of 300°C, there should happened another additional type of weight loss. Accordingly, we tried to extend the straight line which connects three points of 150°, 200° and at 260°C towards 310°C on the graph. The point of this line at 310°C showed 12.62 per cent, therefore, we selected 12.62 per cent as the standard weight of the clays which do not contain any additional loss of weight when heated at a temperature higher than 260°C, and another reason for the selection of 12.62 per cent as a standard weight is that the C.E.C. after pre-heating at 310°C was nearly equal to that at 260°C, and the increased weight by readsorption after pre-heated at 310°C was just the same as that at 260°C. These fact may be proof that the clays had received no actual alteration or destruction even after heating at 310°C compared with that at 260°C. According to these considerations, we calculated the following four kinds of weight values and indicated them in Table 1 and Fig. 2. The four are (a) the total loss of weight when heated, (b) the increased weight when equilibriumed with 50 per cent R.H. after pre-heated at various temperatures, this will indicates the amounts of readsorption or rehydration, (c) the amount of water which remained after heating, and (d) the weight which had been lost by heating but could not be recovered by readsorption.

As can be seen from Fig. 2, all of the values of (a), (b), (c) and (d) are shown on two straight lines on both sides below and above 121°C excepting

Table 1. Weight loss, readsorbed water, remaining water, and water lost but not recovered by readsorption when the colloidal clays from glei-soil were heated for 30 minutes at various temperatures.

Heating Temperature °C	70	100	150	200	260	310
(a) Weight loss by heating %	8.27	9.44	10.68	11.28	12.02	12.62
(b) Readsorbed water after pre-heating %	6.88	7.50	8.06	7.84	7.53	7.53
(c) Water remained after pre-heating %	4.34	3.18	1.94	1.34	0.60	0.0
(d) Water lost but not recovered by readsorption %	1.40	1.94	2.62	3.44	4.49	5.09
C.E.C. after pre-heating me.	40.33	—	36.50	34.25	32.89	32.46

those at 310°C. We can recognize several facts which seemed somewhat unusual as such that, 1) the weight loss is very large, 2) the amount increased by rehydration is more or less high when compared with their C. E. C. 3) the weights which were lost by pre-heating but not recovered by readsorption are high, and 4) there remained some water which could not be driven off by heating till up to 260°C. If we examine the curve c in Fig. 2, we are convinced that there would exist two or more different types of water in the clays one of which can be forced out by heating at a relatively low temperature and another type of water may be lost at a higher temperature such as above 138°C. When the four lines of a_1, b_1, c_1 and d_1 are extended toward an ordinate the intersecting points may be considered to be the representing values in a particular condition which is assumed as an idealized state of the clays such as at 0°C or that of the original sample. The intersections of c_1 and c'_2 can be considered to represent the values of the one type of water and that of the other, respectively. The value of the former is 7.10 and that of

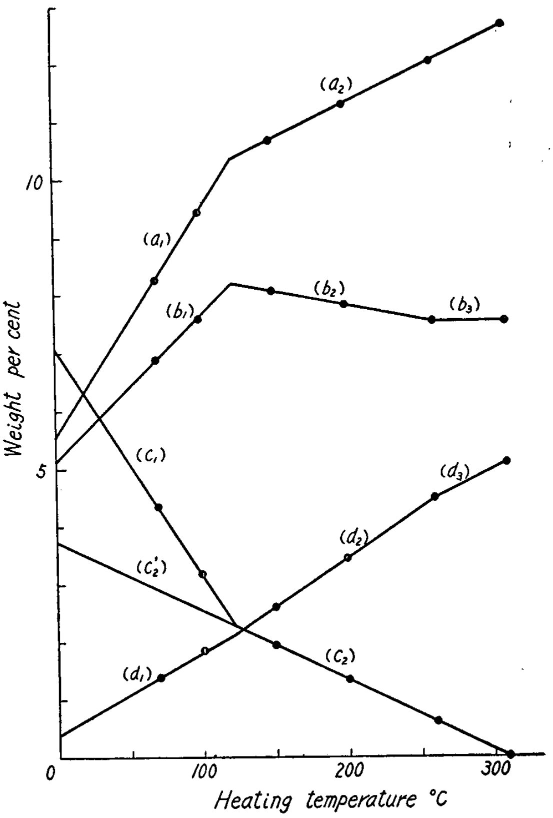

Fig. 2. Variation of weight by heating at various temperatures for 30 minutes.

the later is 3.75 per cent. Therefore the amount of the former type may be the difference of these two, that is 3.35 per cent and the later of 3.75 per cent, can be considered as the water of c_2 type which is contained in the clays at 0°C. The intersect of d_1 at 0°C, 0.40 per cent, indicates the amount of water which had already been lost but could not be recovered by readsorption, then, on the idialized condition at 0°C this must be considered to belong to either type of water of c_1 or c_2. In this concern we will explain later. Following to the above mentioned meaning of *a*, *b*, *c*, and *d*, naturally the following several equations should be satisfied.

$$a=b+d, \text{ then } a-b=d$$
$$a+c=12.62$$
$$b+c+d=12.62$$

However, one point opened to criticism may be whether the relationship expressed by the above equations can practically show a correct one because in the heat experiments the heating time was 30 minutes, accordingly, it was insufficient for a complete equilibrium.

In cases of general soil clays all of hygrocopically adsorbed water can not be completely driven out by heating for 30 minutes but it required a far longer time such as four or much hours, especially, in an extreme case 16 hours. For precise interpretation of the reason, we have practiced other dehydration experiments by heating four eight hours at the temperatures of 70°, 100°, 157° and 210°C. The results of these experiments are also expressed on the same basis of the first experiments and are shown in Table 2 and Fig. 3. As can be seen in Fig. 3, inspite of the different heating temperatures and different heating time, the value of c_1 on the ordinate is 7.50 per cent and that of c'_2 is 3.75 per cent, therefore, the difference between these two becomes 3.75 per cent. This is equal to the sum of the two of c_1 and d_1 in Fig. 2 and the value of c'_2 in Fig. 3 is the same as that of c'_2 in Fig. 2. Consequently, the values *a*, *b*, *c*, and *d* of the second experiment are considered to show the same values of that of *a*, *b*, *c*, and *d* in the different experiment in Fig. 2. It is interesting that these two different experiments can indicate quite the some

Table 2. Weight loss and remaining water when the colloidal clays were heated for eight hours at various temperatures

Heating Temperature°C	70	100	157	210
(a) Weight loss by heating%	8.78	10.31	11.20	12.00
(c) Water remained after heating %	3.84	2.31	1.42	0.62

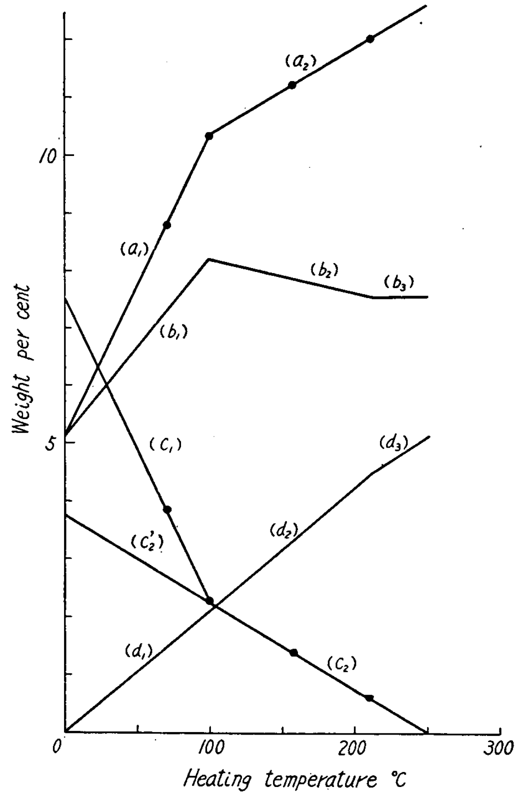

Fig. 3. Variation of weight by heating at various temperatures for eight hours.

idealized values of water contents of the clays. The relationships show by such expressions in Fig. 3 must be prefered to the best one rather than that of Fig. 2, because the heating time was more complete in the former than in the later. However, we can here consider that the relationships observed when the clays are heated for 30 minutes can be translated directly on the relationships in Fig. 3 where the clays are heated for eight hours. For example, the amount of the water remaining after pre-heating or the water lost when heated at a certain temperature may be plotted on the point of the same values of the corresponding lines of *a*, *b*, *c*, or *d* and by this method the required temperatures in the case of eight hours heating can be obtained on the abscissa. If the assumption above mentioned is valid, two or more different types of water contained in clays can be measured when two or three appropriate heating temperatures are selected in favorable regions. In the present case, two points below 100℃ and two points above 150℃ when heated for eight hours gave satisfactory results. The water which were lost when heated at the temperatures between 100℃ and up to 250℃ must be considered to indicate that they were held by the clays with stronger forces than the water which were lost along the c_1 line. Further, we consider that the water lost at the temperature above 100℃ when heated for eight hours should not be these which were adsorbed through exchangeable cations on the clays, with regard to this points we will discuss later, and also the water seemed to be different from those of interlayer water of hydrated halloysite because the required temperature for driving it out was very high. A correct interpretation for the second type of water can not be given through our present knowledge but we are inclined to believe that they may be an interlayer water which are linked between gibbsite-like layers and crystal of 2:1 lattice type clays.

Another interesting fact is that the breaking points of the lines of *a*, *b*, *c* and *d* situated at the same heating temperature of 100℃ and *b* and *c* at 211℃

in Fig. 3, however, in Fig. 2 the breaking points of the lines of *a*, *b*, *c* and *d* came on the temperature of 121°C. This seemed to indicate that the types of loss of water or the forms of the water may differ on the ranges of the above or below that temperature and the loss of water may be correlated with the condition represented by *c* line and more over with variation of readsorption of water influenced by the loss of water or by variation of C.E.C., however,the water lost but could not be recovered not may be correlated directly with *a*, *b*, and *c*. Further, it can be said that the second type water may be completely driven out by heating at 250°C for eight hours or at 310°C for 30 minutes. Unless it becomes evident that the splitting off of the second type water from 3.75 per cent to 2.31 per cent is easier or on the contrary it is far difficult than the loseing of the first type of water when heated at 70°C we can not give it a precise interpretation.

About the unknown loss of weight when the clays are heated at 365°C compared with that at 12.62 per cent at 310°C we can consider a possibility that the exchangeable $Al(OH)_2^+$ corresponding to 48.1 me. per 100 g clays should give off their water. If $Al(OH)_2^+$ losses one mole of water to convert into AlO^+, the decrease of weight must be 18 g per one mol of $Al(OH)_2^+$. If this is the case, the weight loss must be 0.87 g per 100 g clays. $0.0481 \times 18 = 0.866$. The difference between 13.49 per cent at 365°C and 12.62 per cent is 0.87 per cent. We prefer to presume this as a plausible reason for the small decrease of the weight when the clays were heated at the temperature region between 300°C and 365°C.

(II) Calculation of gibbsite-like layers

If gibbsite in the form of single crystal were present in the examined clays the X-ray diffractions corresponding to gibbsite should be observed and also the indications of gibbsite on D.T.A. curve should be recognized. However, as have been clarified in the preceeding report none of them were detected. On behaviors of gibbsite-layers when they exist as a component of mixed layer minerals with 2:1 lattice clays almost nothing has been clarified. In general, when gibbsite is analyzed by D.T.A. strong endothermic peaks must appear between 320° and 330°C and two subsidiary small peaks at about 215°-300°C and 525°C, although the entire absence of these two peaks may be possible in an exceptional case. But we can consider that the condition may be somewhat different when gibbsite-layer are present as an inter-layer sheet between 2:1 lattice clays having considerably strong negative charges. As evident on D.T. A. curve in Fig. 1 there occurred no distinct dropping in the region between 260° and 360°C except for only a slight decline. This may be an indication that there was no marked loss of weight in this region. The weight loss after heating at 365°C was 13.49 per cent, therefore, there was only 0.87 per cent of weight decrease from 310° to 365°C. After the heating temperature exceeded 365°C a distinct dropping of the D.T.A. curve emerges and over 400°C there occurred a strongly sharp endothermic dropping. Thus, in the case of the present clays, it may be reasonable to consider that there would exist some interlayer water between gibbsite-like layer and 2:1 lattice clays. In such case, if splitting off of interlayer water by heating is continued dehydroxilation from gibbsite-layer should not happen. As we explain later the loss of interlayer water can be considered to be continued until the temperature reaches 260° or near 300°C, and only a small loss of weight or faint drop of D.T.A. occurred till 360°C, consequently, the destruction of gibbsite-layer would happened after the clays are heated at a temperature higher than 360°C.

The chemical constituents of the colloidal clays determined and expressed on the basis of the sample heated at 260°C for 30 minutes are shown in the column (A) in Table 3. For the convenience of comparison, the values of (A) were converted into the values of per cent of the weight of which weight loss is 12.62 per cent when heated at 310°C. These are shown in column (B). At first we must consider the existence of gibbsite in soils, especially as a component of mixed layer minerals. However, a large amount of Al_2O_3 in clays suggest a doubt whether 1:1 type clays such kaolinite or halloysite are

Table 3. Chemical constituents of the colloidal clays.

	(A) %	(A)/99.03 (B) %	(B)/69.802 (C) %	(D) mols
SiO_2	52.02	52.5295	57.3300	0.95455
Al_2O_3	31.38	31.6874	26.6717	0.26164
Fe_2O_3	3.50	3.5343	5.0633	0.03171
FeO	0.57	0.5756	0.8246	0.01148
MgO	0.80	0.8078	1.1573	0.02870
CaO	0.16	0.1616	0.2315	0.00413
K_2O	0.09	0.0909	0.1302	0.00138
Na_2O	tr.	tr.	tr.	tr.
H_2O^+	11.24	10.3706	8.2442	0.45801
H_2O^-	11.65	12.62	—	—

Remark ;

1) (A) Per cent on the basis of the weight after heated at 260°C for 30 min.
2) (B) Per cent on the basis of the weight after heated at 310°C for 30 min.
3) (C) Per cent on the basis where the contents of hydrated halloysite and that of exchangeable Al ions have been substracted from (B).
4) (D) The amounts of mols of elements in (C).
5) $99.03=100-0.97$, $12.62-11.65=0.97$, $11.24-0.97=10.27$, $10.3706=10.27/99.03\times 100$
   $69.802=100-(\text{halloysite}+\text{exch.-Al}+H_2O)$
6) Amount of hydrated halloysite
   $3.75/12.242\times 100=30.63\%$

present. As we clarified in Part I of this articles, X-ray diffraction investigations proved no marked peaks at 7.15~7.40 Å. The second doubt is a possibility of the co-existence of 1 : 1 type clays and 2 : 1 type clays as a mixture where two kinds of montmorillonitic and beidellite series may be possible, however, the SiO_2/R_2O_3 ratio of the elements in the column (B) is 2.52. If we use this ratio, the former case is impossible because the Al_2O_3 content which corresponds to montmorillonitic clays becomes negative, in the later case the SiO_2/R_2O_3 ratio becomes 9.63. The case is also impossible because there exists no quartz in the clays according to the X-ray diffraction test. Consequently, on the basis of considerations already mentioned in the preceeding papagraph, the contents of SiO_2, Al_2O_3, and H_2O^+ correspond to the halloysite present were substracted from the amounts in the column (B), and the remainder was transformed into 100 per cent. The results are shown in the column (C). The amount of Al_2O_3 in the (C) is also fairly high and the SiO_2/R_2O_3 ratio becomes 2.95. The ratio nearly resenbles that of beidellite clays, however, in the present case, the content of H_2O^+ is too high. According to Ross and Hendricks(1), hydrated Al-silicates having montmorillonite structure are considered to be an end member of beidellite series and they have a large amount of Al-substitution in Si-tetrahedral layer such as $(Al_{0.83}Si_{3.17})$ and $Al(OH)_2^+$ attaches on their exchange spots. Such a case is impossible because the C.E.C. of the present clays is too low for the above case. Roy and Osborn (2) suggested the existence of the following structure

$$[Al(OH)_2]_{0.33}Al_2(Si_{3.67}Al_{0.33}O_{10})(OH)_2$$

In the above case, the ratio of $SiO_2/Al_2O_3=2.75$ and $H_2O : Al_2O_3=1 : 1$, and exchange capacity is 59 me. per 100 g. However, in the case of the present clays, the ratio of H_2O^+ to R_2O_3 is 1.49, their exchange capacity is 47.5 me. per 100 g, and $SiO_2/R_2O_3=2.95$. Therefore, the present clays have smaller amount of Al_2O_3 and a less Al-substitution but a far larger amount of H_2O^+. This may not be the case of which Roy and Osborn had reported. Here, we came to the consideration of the existence of mixed-layer minerals composing of gibbsite-layer and montmorillonitic clays. Especially, according to Sudo and Hayashi (3), there are many mixed-layer minerals having gibbsite-layer in Japanese soils. In this case, if Al atoms which are constructing a gibbsite-layer are surrounded by only anions of (OH), the mols of H_2O^+ should be equal to the sum of mols of Al, Fe^{3+}, Fe^{2+} and Mg. There are far excess of H_2O^+ than the sum of the above cations, even when the amount of H_2O^+ corresponds to the exchangeable cations of $Al(OH)_2^+$ of the clays was calculated. Then, there would be another type of H_2O^+ in the crystal lattice which can not be lost even when heated at 260°C. According to Russell (4), in soils there exist a gibbsite-layer which is presumed by him as follows; $[Al(OH)_x$

$(H_2O)_{3-x}]^{+(3-x)}$, where x may vary according to the medium pH. When $x=1$, Al atoms of gibbsite-layer should possess 2.5 mols of water, however, when $x=2$ water molecules must be 2 molecules. By interstratifying with such a gibbsite-layer, 2 : 1 lattice clay form dioctahedral vermiculite or diocta-chlorites. Under natural conditions of the soil such as glei-soil it is reasonable that x may be 2. If this is the case, naturally, water molecules of gibbsite-layers in mixed-layer minerals should be two molecules per Al atom or four molecules per Al_2O_3. Therefore, when the difference between the sum of mols of Al_2O_3, Fe_2O_3, and one-half of the mols of FeO and MgO and the mols of H_2O^+ estimated, it will give the values of three times of the mols of Al_2O_3 which are forming the gibbsite-layers. However, before we perform this calculation we need some other calculations because the values in column (A) in Table 2 are considered to contain the excess Al_2O_3 corresponding to the C.E.C. of the clays because the chemical analysis were carried out on the H-saturated samples. The clays contain 30.63 per cent of hydrated halloysite as will explained later. To realize the chemical composition of 2 : 1 lattice type clays we must eliminate the amounts of elements which correspond to that of hydrated halloysite and those of exchangeable cations of the clays other than hydrated halloysite.

The values in the column (B) are those that hydrated halloysite of 30.63 per cent and exchangeable Al ions correspond to 48.1 me. per 100 g are included. The amount of hydrated halloysite of 30.63 per cent can be obtained by the calculation, 3.75/0.12242×100, because the amount of 3.75=7.50−3.75 in Fig. 3 was lost by heating at 70°C and furthermore we recognized about 15–20 per cent of rolled thin film-like crystals on the electron micrograph. To obtain the contents elements of the clays where only 2 : 1 lattice clays are present without hydrated halloysite and exchangeable Al ions we calculate the column (C). The amounts of elements correspond to hydrated halloysite and that of exchangeable $Al(OH)_2^+$ may be as follows.

hydrated halloysite	SiO_2	12.512
	Al_2O_3	10.618
	H_2O	3.750
exchangeable $Al(OH)_2^+$	Al_2O_3	2.452
	H_2O	0.866

Therefore, the sum of the above two becomes 30.198.

Here, we will calculate the amount of the gibbsite-layer tn the clays by using the values in column (C). When the assumption of Russell can be used for this case, the excess amount of water which belongs to $[Al(OH)_2(H_2O)]^+$ can be obtained as the excess amount over that corresponding to the amounts of Al_2O_3, Fe_2O_3, FeO and MgO on the basis that all of these elements are existing the components in 2 : 1 type crystal structure. Fortunately, there is almost no trioctahedral 2 : 1 lattice clays. Then, if the excess of the mols of H_2O^+ above the sum of mols of Al_2O_3, Fe_2O_3 and one-half of FeO and MgO is divided by 3, the quotient gives the number of the gibbsite Al_2O_3. If we apply the values in the column (D) where all of hydrated halloysite and exchangeable Al ions were omitted, the calculations may be as follows.

Al_2O_3	0.26164	H_2O^+	0.45801
Fe_2O_3	0.03171		0.31344
$\frac{1}{2}FeO$	0.00574		0.14457
$\frac{1}{2}MgO$	0.01435		
	0.31344		0.14457/3=0.04819

The amount of Al_2O_3 which belong to gibbsite-like layers become 0.04819 mols per 100 g of the clays in the column (D). Accordingly, the mols of Al_2O_3 to be considered as the constituents of 2 : 1 lattice clays should be 0.21345. And the mols of water molecules which are constructing a crystal structure of gibbsite-layers must be 0.19276.

(III) Variation of C.E.C. and oxidation of Fe^{++} ions.

The C.E.C. of the present colloidal clays when determined immediately after preparation of the fresh sample in October 1957, was 48.1 me. per 100 g. However, when the same sample which was stored for eight months in a desicator of 50 per cent R.H. was measured in June 1958 their C. E. C. was 41.62 me. per 100 g. For all the experiments of hydration, rehydration, and C.E.C. after pre-heated the clays stored for eight months were used. The values of C.E.C. after pre-heated at various temperatures are indicated in Table 1 and Fig. 4. From Fig. 4 we can recognize two different types of variation of C. E.C. when the present clays are heated. One of which is observed in a linear-like variation when heated below 70°C and the other as a curvilinear decrease when heated at temperatures higher than 100°C. The former is presumed to be due to the alteration of hydrated halloysite into a dehydrated form and the later may be attributable to oxidation of Fe^{++} ions in crystal lattice of the clays. Concerning these points we

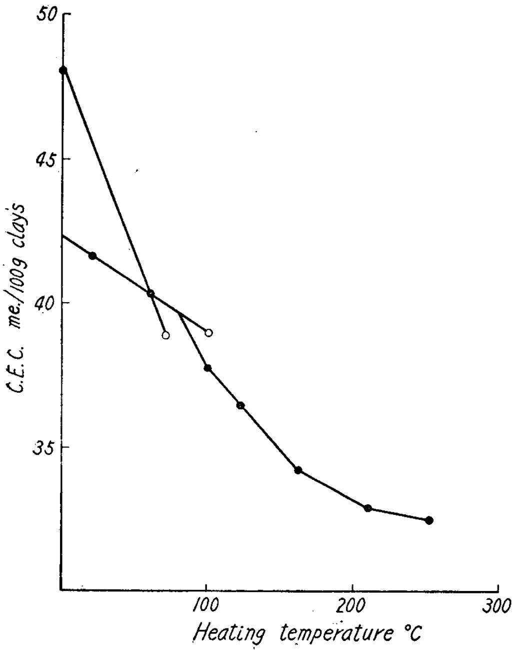

Fig. 4. Variation of C. E. C. of the colloidal clays when heated at various temperatures.

will explain in the following.

According to the calculation in the preceeding paragraph, the amount of Al_2O_3 which can be assumed to be that of 2:1 lattice clays may be 0.21345 per 100 g of the clays in column (C). If we presume that all of the elements in the columns (C) or (D) excepting that which correspond to gibbsite-like layers are constructing crystals of dioctahedral 2:1 lattice clays of montmorillonite type, the total sum of the number of cation atoms of the above Al_2O_3 and those of Fe_2O_3, FeO and MgO may be composing of lattice structure together with one-half of the atoms of SiO_2. Based on this assumption we can calculate the amount of Al atoms which are substituting for Si atoms in the tetrahedral layer. The amount of Al-substitution must be two-thirds of the amount of the difference between the total sum of Al, Fe^{3+}, Fe^{2+} and Mg^{2+} and that of one-half of Si atoms. Accordingly, unless we can know at what temperature all of the hydrated halloysite are converted into a dehydrated form we may be unable to calculate the C. E. C. of other clays, however, it may be reasonable to consider that when the clays are heated at 100°C all of the hydrated halloysite should have been dehydrated. However, since the 2:1 lattice clays which may be unstable to some extent owing to their conditions of occurrence, there remained a doubt that when the clays are heated at 100°C a certain alteration which would bring about a decrease in their C.E.C. would have happened. Concerning these points we will explain later.

At first, we will calculate the C.E.C. of the clays correspond to those in the column (C). By using the mols number in (D), and the amount of Al_2O_3 in the 2:1 lattice clays which have been calculated above,

$$\begin{array}{lr} \text{Al-atoms} & 0.42690 \\ \text{Fe}^{+++} & 0.06341 \\ \text{Fe}^{++} & 0.01148 \\ \text{Mg}^{++} & +0.02870 \\ \hline & 0.53049 \end{array} \qquad \begin{array}{lr} & 0.53049 \\ \frac{1}{2}\text{SiO}_2 & 0.47728 \\ \hline & 0.05321 \\ & \\ \multicolumn{2}{r}{0.05321\times 2/3=0.03548} \end{array}$$

Then, the amount of Al-substitution in Si-tetra-layer is 0.03548. The total negative charge and the net negative charge are as follows.

$$\begin{array}{lr} \text{Al} & 0.03548 \\ \text{Fe}^{++} & 0.01148 \\ \text{Mg} & 0.02870 \\ \hline & 0.07566 \end{array} \qquad \begin{array}{lr} & 0.07566 \\ \text{Ca}+\text{K}\cdots & -0.01102 \\ \hline & 0.06464 \end{array}$$

The net negative charge of the clays in the column (C) must be 0.06464 per 100 g, that is 64.64 me. Klages and White (5) pointed out that when the 0.2 ~0.5 μ fraction of Crosby A_2 horizon was treated with citric acid their C.E.C. increased 96.98 per cent from 58.03 to 87.16 me. per 100 g. They interpreted it as such that the clays are interlayered with gibbsite-like layer and then can be considered to be dioctohedral vermiculite or dioctahedral chlorite type minerals. According to their conclusion, C.E.C. of 2 : 1 lattice clays having gibbsite-layers must be inactivated through gibbsite-layers and when gibbsite-layers are removed their C.E.C. return into an active form. However, the charges of the 2 : 1 lattice clays which are interstratified with gibbsite-layers must be sealed in and be rendered inactive. The portion thus inactivated must be as follows;

$$0.04819\Big/\left(\frac{0.95455+0.03548}{2}\right)\times 100=9.735$$

In addition, as can be understood from Fig. 3, the value of the line (c_1) at 70°C is 3.84 per cent, and that of the line (c_2') is 2.72 per cent. The difference between these two may be assumed to be the interlayer water of hydrated halloysite portion which is interstratified with 2 : 1 lattice clays. If this is valid, the C.E.C. owing these hydrated halloysite can be active to the temperature at 100°C but the C.E.C. of 2 : 1 lattice clays which are linked with these halloysite must be inactivated as in the case of gibbsite-layers. The amount of 2 : 1 lattice clays thus inactivated may be calculated.

$$3.84-2.72=1.12\ \%$$

This interlayer water corresponds to 9.149 per cent of the dehydrated halloysite. These dehydrated halloysite contain 0.031716 mols of Al_2O_3 per 100 g of the original clays and it corresponds to 0.04544 mols of Al_2O_3 of the column (C) clays, consequently, it also corresponds to 9.179 per cent of the 2 : 1 lattice clays in the column (C). Then, the total of the inactivated portion of the 2 : 1 lattice clays becoomes as follows,

$$9.735+9.179=18.91\ \%$$

Consequently, the active portion may be 81.09 per cent. Therefore, the negative charge of the 2 : 1 lattice clays in the fresh original clays must be as follows,

$$64.64\times 0.8109\times 0.6980=36.588\ \text{me./100 g}$$

where all of Fe^{2+} ions are in an active form. Consequently, the C.E.C. of the original clays in the column (B) must be obtained as the sum of the above value and the C.E.C. of hydrated or dehydrated halloysite.

However, we must be aware of the fact that when these clays are dehydrated or heated the C.E.C. of halloysite and also that of 2 : 1 lattice clays containing Fe^{2+} ions should be altered. To clarify this point we determined both of C.E.C. and the Fe^{2+} contents of the clays. When the clays were heated at 100°C for eight hours their C.E.C. was 37.77 me. and the content of FeO decreased to 0.457 per cent, therefore, the FeO was oxidized to 19.8

per cent of the amount in the non-heated original clays. The C.E.C. of the clays after heated at 252°C for eight hours was 32.46 me. and the content of FeO decreased to 0.03 per cent. This corresponds to 5.3 per cent of the total FeO in the original clays, then 94.7 per cent of FeO had to be oxidized. When we plot the actually determined C.E.C. at various temperatures heating Fig. 4 may be obtained as shown as black dots, while 48.1 me. of the fresh clays at 0°C and that of 41.62 me. of the stored clays at 21°C when it was determined. As can be seen from Fig. 4, the line connecting two points of 41.62 me. at 21°C and 40.33 me. at 60°C intersect the ordinate at about 42.40 me. at 0°C and on the point of 39.02 me. at 100°C. This line can be considered to show the variation of C.E.C. of the stored clays when heated at temperature up to 100°C. The condition at 60°C may be considered as such that there exist 9.149 per cent of hydrated halloysite linked with 2:1 lattice clays in a form of mixed-layer minerals as has been explain previously and 18.615 per cent of dehydrated halloysite and 72.237 per cent of 2:1 lattice clays which contain 3.136 per cent of the gibbsite-layer in them. Also, the condition at 100°C may be as such that all of hydrated halloysite both of separated form and those of a mixed-layer type have been dehydrated and a part of Fe^{++} ions in 2:1 lattice clays were oxidized. The content of FeO and C.E.C. of the clays after heated at 100°C for eight hours were 0.457 per cent, that corresponds to 80.2 per cent of the fresh original clays, and 37.77 me. per 100 g, respectively. Then, the negative charge of the 2:1 lattice clays after heated at 100°C should becomes as follows.

$$\begin{array}{r} 0.03548 \\ 0.00921 \\ \underline{0.02870} \\ 0.07339 \\ -\ \underline{0.01102} \\ 0.06237 \end{array} \qquad 62.37 \times 0.8109 \times 0.6980 = 35.303$$

Therefore, the C.E.C. of dehydrated halloysite when heated at 100°C must be 9.18 me. per 100 g.

$$\{(37.77 - 35.303)/26.88\} \times 100 = 9.18$$

The content of FeO when the clays had been heated at 252°C was 0.03 per cent and it corresponds to 5.3 per cent of the fresh clays content. In a similar way the C.E.C. of the clays after heated at 252°C can be obtained.

$$53.77 \times 0.8109 \times 0.6980 = 30.434$$

Therefore, the C.E.C. of dehydrated halloysite after heated at 252°C becomes as follows.

$$\{(32.46 - 30.43)/26.88\} \times 100 = 7.55$$

From these results, we can consider that the C.E.C. of dehydrated halloysite may not necessarily be constant but decreases the heating temperature becomes higher and higher from 9.2 me. per 100 g at 100°C to 7.5 me. at 252°C.

Next, we will discuss the C.E.C. at 70°C. As explained later, oxidation of Fe^{++} ions in the clays is presumed to start at 80°C, on this condition at 70°C there would exist all of Fe^{++} ions in a ferrous-iron state, consequently, the C.E.C. corresponding to 2:1 lattice clays must be as follows,

$$64.64 \times 0.8109 \times 0.6892 = 36.126$$

where the C.E.C. of the whole clay can be presumed to be 40.00 me. through the line (*b*) in Fig. 4. Then, the difference between this 40.00 and above obtained 36.126 me. must correspond to the C.E.C. of the sum of the C.E.C. of dehydrated halloysite and that of hydrated halloysite remaining at 70°C heating owing to their presence as a mixed-layer structure. Since the amount of hydrated halloysite remaining after heating at 70°C must be 9.149 per cent as already mentioned, the halloysite dehydrated should be 18.851 per cent. Here, if we assume that the C.E.C. of dehydrated halloysite is 9.50 me. per 100g, because the line (*c*) in Fig. 5 which may show the decreasing of the C.E.C. of dehydrated halloysite comes at 9.50 at 70°C, the following calculation can be practiced.

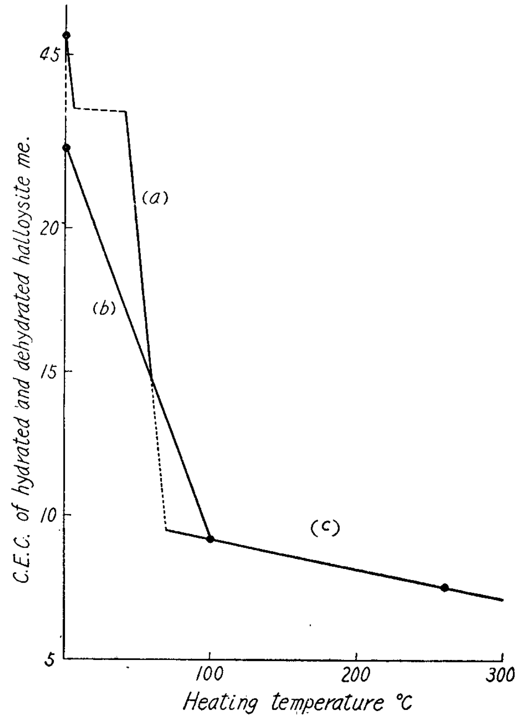

Fig. 5. Variation of C.E.C. of hydrated and dehydrated halloysite when heated at various temperatures.

$$40.00 - 36.126 = 3.874$$
$$9.50 \times 0.18851 = 1.791$$
$$\{(3.874 - 1.791)/9.149\} \times 100 = 22.77$$

The C.E.C. of 39.0 me. at 100°C represents the value of the clays where all of hydrated halloysite have been dehydrated and Fe^{++} ions have not been oxidized, therefore, this value must be adopted to the state at 70°C heating. When we connect the point of 39.0 me. at 70°C and 40.33 me. at 60°C the line (*a*) in Fig. 4 can be obtained, and this line intersects the the ordinate at 48.25 me. This value is slightly higher than that of the actually determined 48.1 me. of the fresh clays. If we apply this 48.25 me. as the idealized value of the C.E.

C. for the fresh clays, the C.E.C. of hydrated halloysite in a fresh state can be calculated.

$$48.25-(64.64\times 0.8109\times 0.6937)=11.889$$
$$11.889-(22.77\times 0.09149)=9.806$$
$$\{9.806/(30.63-9.149)\}\times 100=45.65$$

The C.E.C. of hydrated halloysite can be considered to be 45.65 me. per 100 g in a fresh condition, and this value may be a considerably plausible one when compared with the values cited in Reference Clay Minreals (6).

If the above two values are valid, it is an interesting fact that the C.E.C. of hydrated halloysite will be 22.77 me. when they are interstratified with active 2 : 1 lattice layer clays in a form of mixed-layer type and this value is just one-half of the value of the C.E.C. of free separated crystals of hydrated halloysite. We know of no precise method to detect the value of the C.E.C. of such interstratified hydrated halloysite and unfortunately no work on the point is found to date, thus, a detail study is necessary. The value of 48.1 me. of the actually determined fresh clays is slightly lower than that calculated above, but this difference may be considered to be attributable to an analytical error or a slight decrease of C.E.C. during the preparation of the clays before analysis. When we presume that the C.E.C. of dehydrated halloysite at the temperatures above 100°C should decrease along the line (*c*) in Fig. 5, the rate of oxidation of Fe^{++} ions can be calculated. The rate of oxidation of Fe^{++} ions by heating are as follows.

Temperature (°C)	80	100	122	162	211	252
Per cent of Fe^{++} oxidized	0	19.8	40.0	70.9	89.4	94.7

As can be seen from Fig. 6, oxidation of Fe^{++} ions seemed to start at the heating temperature of about 80°C and almost all of them are considered to be oxidized at the temperature of about 300°C for eight hours heating. About 95 per cent of Fe^{++} ions are very unstable and easily oxidizable but a small portion of about 5 per cent seemed to be very stable because they can not be attacked even when after heated at 300°C.

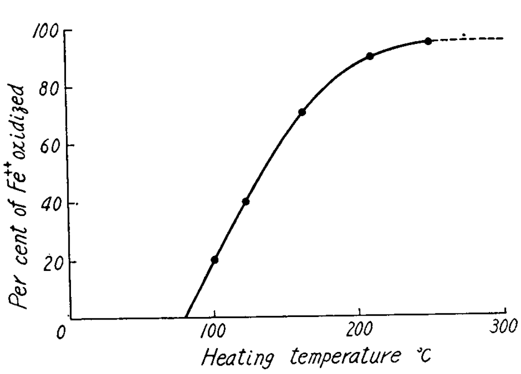

Fig. 6. Rate of oxidation of Fe^{++} ions in the colloidal clays when heated.

(IV) Readsorption of water

Clays can adsorb water molecules on their planar surfaces of crystals through both van der Waal's force and the force operating by exchangeable cations. The amounts of water adsorbed may be varied according to not only surface area of clays and kinds and amounts of exchangeable cations or magnitudes of the negative charges of clays but also to the degree of humidity of air where they occur. It has already been known that there is a certain relationship between the humidity of air and the amount of water adsorbed by clays. Kelley, Jenny and Brown (7) said that water adsorbed by clays can be split off at 150°C and when clays are saturated with Ca-ions, the amounts of water molecules adsorbed by clays are always from seven to nine times of the C.E.C. of clays or 17～18 per exchangeable Ca-ions. According to them, soil colloids or clay minerals such as montmorillonite or beidellite possess Si-O-Si plane and their crystal surfaces are of O^{--} or OH^- plane, therefore, this may be the main reason for the high amount of adsorbed water. They showed a graph which indicates the relation between C.E.C. of clays and the amount of water lost at 150°C. In soil clays, water is lost in the proportion of 0.144 g per me. of C.E.C. Hendricks, Nelson, and Alexander (8) studied on adsorption and dehydration of water by montmorillonite in relation with various exchangeable cations and also with different humidity. Their result showed that the loss of adsorbed water occurs in three stages of at the ranges 150°～170°C, 180°～200°C and 230°～250°C; and the water lost at higher temperature can be absorbed at more lower relative humidity, for instance, the water lost at 240°C will be adsorbed at 5～10 per cent R.H. but the water lost at 200°C can be adsorbed at about 25 per cent R.H.

When the assumption is permissible that readsorption of water by clays after pre-heating can proceed until the same amount of water as that presented before dehydration is adsorbed, there must be a certain constant relationship betweeen the amounts of water readsorbed and the magnitudes of C.E.C. of the clays. However, we must recall to mind that such a relation may be possible when all of the clay surface are exposure freely to water vapour and no alteration had occurred on the surface area and C.E.C. If there exist an interlayer water in clays clay surfaces which are linked with these water layer must be impossible to absorb water molecules unless the interlayer water had been driven out. Hofmann and Endel (9) found that Ca-saturated smectites can be heated up to 300°C～390°C without loseing their capacity to re-expand with moisture after heating. Thus, we can consider that the water readsorbing capacity of the present Ca-clays would be altered to any extent by heating at the temperature up to 310°C as in this experiment. A comparison between the readsorbed water and C.E.C. of the clays when heated at various temperatures are indicated in the following.

Heating Temp. (°C)		Readsorbed Water		C.E.C. after heated	(b)/(c)
for 30 min.	for 8 hrs.	g/100g clay (a)	m.mols/100g (b)	(c)	
70	60	6.90	383.3	40.33 me.	9.50
100	83	7.50	416.7	—	—
150	122	8.06	447.8	36.50	12.27
200	162	7.84	435.5	34.25	12.72
260	211	7.53	418.3	32.89	12.72
310	250	7.53	418.3	32.46	12.76

As can be seen in the above figures, the values of (*b*)/(*c*) when the clays are heated at 70°C is much lower than those when heated at higher temperatures. The values of (*b*)/(*c*) when the clays were heated at temperatures higher than 150°C for 30 minutes are almost equal, especially in the three cases of the temperatures above 200°C. This may be an evidence that there had occurred no alteration in the surface area or clay structures. For the reason of the lower values of (*b*)/(*c*) when the clays were heated at the temperature of 70°C for 30 minutes we can not give a precise interpretation.

According to our calculation presented in the preceeding paragraph, in the case of C.E.C. of 40.33 me. when heated at 70°C for 30 minutes almost all of hydrated halloysite are considered to be converted into a dehydrated form, therefore, the reason of the lower value of (*b*)/(*c*) must be sought in some other reason. However, if a part of hydrated halloysite remained in the clays in the form of mixed-layer minerals with 2:1 lattice clays even when heated at a temperature above 70°C up to 100°C, the reason may be attributed to a presence of hydrated halloysite. We feel this may be the main reason but we can not obtain strong evidence on the point. It is noticeable that in all cases the values of (*b*)/(*c*) are considerably higher than seven or nine times of C.E.C. given by Kelley, Jenny and Brown. From this we can assume that the ratio of surfaces area to C.E.C. is much larger than the usual clays or otherwise the distribution of the charge spots on these clay surfaces should be very sparse. There is one point to be explained that hygroscopic water which is adsorbd by van der Waals' force and also that adsorbed by exchangeable cations on the present examined clay surfaces seemed to be easily dehydrated. In usual clays, especially, in the case of Ca-saturated smectites, all of hygroscopically adsorbed water can be lost when clay are heated, at least, at 240°C∼250°C.

We must here explain a fact concerning dehydration of adsorbed water which are attracted by exchangeable cations on clay surfaces. In cases of usual clays, especially, in the case of Ca-saturated smectites, hygroscopic water adsorbed by exchangeable Ca-ions can not be driven off completely unless the clays are heated at 240°∼250°C. In the present clays 2.31 per cent of the water remained when heated at 100°C but it was lost completely when heated at 250°C, then it seemed as if this remaining water were those adsorbed by Ca ions on clays. However, this may not be valid in the present clays because when the remaining water is those adsorbed by Ca ions the water readsorbed after pre-heating must be less than the amount of that remaining. In spite of remaining water presented 2.31 per cent the readsorbed water at that time was 0.69 per cent more than that after heating at 211°C and 250°C. Therefore, we are forced to consider that in the present clays hygroscopically adsorbed water can be split off very easily even when heated at as a low temperature as 100°C and the same amount which had been lost can be readsorbed when the clays are exposured to humid vapour.

(V) Water dehydrated but not recovered readsorption

As has already been explained, the colloidal clays separated from a glei-soil seemed to contained a relatively high amount of water which can be easily driven off through heating at relatively low temperatures. These waters can be considered to be composed of a form of hygroscopically adsorbed water and or those of interlayer water. A certain part of them lost when heated at 122°C for 30 minutes or at 100°C for eight hours, however, the remaining part was more or less difficult to be split off. In general, almost all of water lost by heating can be recovered by readsorption when pre-heated clays are placed in a vapour of humidity when if the humidity were quite the same as that where the clays had been equilibriumed before their pre-heating. Therefore, if there exist considerable amounts of water which was lost but not recovered by readsorption, these waters can not be such a type of water as hygroscopically adorbed or those adsorbed by hydration capacities of exchangeable cations. We are inclined to the opinion that these waters would have been present as an interlayer water, and, in the present case, they must be in the form of interlayer water of hydrated halloysite of separated crystals and also those in hydrated halloysite which are components of mixed-layer minerals with 2:1 lattice type clays and another type of interlayer belonging to gibbsite-like layer in a mixed-layer minerals.

The water dehydrated by heating but not recovered by readsorption of the present clays are shown in Table 1 and as (*d*) line in Fig. 2 and also in Fig. 3. Since this water can be measured by the difference between the loss of weight when heated and that when readsorbed after pre-heating, the apparent amount can be shown as the difference of (*a*) and (*b*) or the values of (*d*) in Fig. 2 and Fig. 3. The most remarkable feature is that water of this type increases nearly linear like as the heating temperature increases up to 260°C for 30 minutes inspite of the quite different types of variations of both of loss weights by heating and amounts readsorbed after pre-heating. The actual amount of the total loss of weight when these clays were heated at 250°C must be 7.20 per cent, nevertheless the water indicated by (*d*) line was only 5.09 per cent. This can be explained easily by Fig. 3. If we select as an example the case of heating at 100°C for eight hours in Fig. 3, the weight loss by heating is 10.31 per cent and the amount recovered by readsorption 7.97 per cent, then, the difference between these two is 2.34 per cent. However, loss weight must be increased from 5.12 per cent to 10.31 per cent, therefore, these differences is 5.19 per cent and the increases of readsorption must be 2.85 per cent because it increased from 5.12 per cent to 7.97 per cent. Consequently, the apparent amount becomes $5.19-2.34=2.85$ per cent. Such an apparent amount may be brought about as a result of the increase of readsorbed water. When interlayer water existed between two crystal surfaces water molecules can not be adsorbed on these clay surfaces but if these interlayer water had been lost the clay surfaces freed from these water layer will become exposure for adsorption of water molecules. Therefore, it may be plausible to consider that the increase of these readsorbed water can be attributable to the loss of interlayer water between halloysite crystals. The increase of the water which can be lost by heating but not recovered by readsorption in the region of heating at the temperatures higher than 100°C is brought about through two origins one of which may be the loss of interlayer water 2.31 per cent of which remained even when heated at 100°C and the other can be induced by the reduction of C.E.C. when heated at relatively high temperatures.

(VI) Water remained after heated

The water remaining after when the clays are heated at various temperatures are indicated in Table 1 and also as (*d*) line in Fig. 2 and Fig. 3. As can be seen from Fig. 3, these water can be completely driven out when the clays are heated at 310°C for 30 minutes or at 255°C for eight hours. As has been explained, these water seemed to be hygroscopically adsorbed water. In the case of hydrated halloysite, interlayer water sheet form between two crystals and the ratio of water molecules against Al-atoms should be 1:1 according to the following formula.

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \cdot 2H_2O$$

Therefore, in the case of mixed-layer minerals composed of gibbsite-like layer and 2:1 clays, when interlayer water sheet is present between these two crystal layers the ratio of water molecules of interlayer sheets to the number of Al-atoms in gibbsite-layer or that of dioctahedral 2:1 lattice clays also should be 1:1. Consequently, in the present case, the ratio of water molecules of the remaining water in the interlayer sheet to Al-atoms of gibbsite layers must be 1:1. The amount of Al_2O_3 which is assumed to be present as gibbsite-like layer was calculated in the preceeding paragraph. The amount of gibbsite-layer was 0.04819 mols per 100 g of the clays indicated in the column (C) in Table 1, accordingly, it corresponds to 0.03364 mols per 100 g of the original whole clays. The number of this Al-atoms becomes 0.06728 mols. If the water molecules present in the same ratio of 1 : 1 as in the case of hydra ted halloysite, the mols number of interlayer water in this case must, of course, be 0.06728 mols. The mols number of the remaining water after heated at 100°C in Fig. 3 is 0.1283 mols. This means that the interlayer water remaining after pre-heating at 100°C should be present in a much higher ratio than that of hydrated halloysite. This value is nearly equal to twice, 1.91 of the above mols of Al-atoms. Therefore, the remaining water at 100°C must be considered to be present in a ratio of two times that of hydrated halloysite, then, it will suggest that the interlayer water may exist on both sides of a gibbsite-layer in a condition of temperature at 100°C and water much more than 2.31 per cent at the lower temperature would exist in the form of more than two layers on one side surface. If this is valid, the water layer more than two layers per one gibbsite-like layer, that is two layer sheet between gibbsite and 2 : 1 lattice crystal, may be relatively easily split off by such a low temperature heating as below 100°C, however, a mono-layer sheet between gibbsite and 2 : 1 lattice clays can be driven out only when heated at a temperature above 100°C.

Summary

The dehydration and rehydration tests were carried out on the colloidal clay fraction separated from glei-horizon of an alluvial clayey soil. The colloidal clays contain a large amount of water lost when heated at the temperature below 300°C.

Water loss appeared to proceed as if progressing in two portions of linear relation. The one happened in the range of heating temperature below 100°C and the other occurs between 100° and 280°C. The former are interpreted by the writers that a interlayer water sheet of hydrated halloysite would be lost below 70°C. Here we have doubt on whether the hydrated halloysite which were presumed to be present can actually exist as a form of separate grain crystals. As we had shown by electron micrographs in the preceeding articles of this series, we could not recognize so much tubular grains as 30 per cent, and also the marked peaks at 7.3–7.4 Å and at 10.0–10.1 Å or near so, by X-ray diffraction patterns. Accordingly, we have inclined to assume the presence of hydrated halloysite either in the form of randomly interstratified mixed-layer type of dehydrated halloysite and hydrated halloysite or more probably in the complex random mixed-layer minerals which may be composing from hydrated halloysite, 2 : 1 lattice minerals and gibbsite-like layers. In spite of D.T.A. results quite resembling that of halloysite, the clays showed very sharp and

two deep endothermic peaks and their X-ray diffraction patterns in the low angle region gave the diffused-like broad band at the position from 7.6 to 17 Å and it weakened markedly by heating at 390°C.

The water lost at the temperature from 70° to 100°C may be explained as the water sheets belonging to mixed-layer type minerals composing gibbsite with montmorillonitic or beidellite type minerals. They are considered to exist on both sides of gibbsite layer and on the fresh non-heated and non-dried state they would be present as a form of multi-layered water sheet. The water excess than two-layers per one layer of gibbsite can be easily given off at a relatively low temperature heating as 70°~100°C. The interlayer water of two sheets per one gibbsite-layer can be more or less difficultly driven off. It seemed necessary to be heated at a temperature above 100°C but all of these waters can be split out at about 250°C for eight hours or about 300°C for 30 minutes.

From the results of the determinations of C.E.C. and the contents of FeO of the clays after heated at various temperatures the rate of oxidation of Fe^{++} ions in the clays can be calculated. It seemed to start at about 80°C and nearly 95 per cent of Fe^{++} ions can be oxidized at about 300°C. By these calculations the writers suggested that the C. E. C. of dehydrated halloysite decrease when the clays are heated at a temperature above 70°C from 9.50 me. to 7.5 me. per 100 g and the C.E.C. of the fresh hydrated halloysite should be 45.65me. per 100 g.

References

1) Ross, C.S. and S.B. Hendricks (1945). U.S.G.S. Prof. Paper, 205-13,23.
2) Roy R. and S.B. Osborn (1954). Amer. Min., **39**, 853.
3) Sudo T. and H. Hayashi (1955). Clays and Clay Minerals, Penn. State Univ., p. 389-412.
4) Russell, E.J. (1950). Soil Condition and Plant Growth, Longmans, p.95-96.
5) Klages, M.G. and J.L. White (1957). Soil Sci. Soc. Amer. Proc., **21**, 16.
6) Reference Clay Minerals A. P. I. Research Project 49 Preliminary Report, No. 7, p. 93-95.
7) Kelley, W.P., H. Jenny and S.M. Brown (1936). Soil Sci., **41**, 259.
8) Hendricks, S. B., R. A. Nelson and L. T. Alexander (1940). J. Amer. Chem. Soc., **62**, 1457.
9) Hofmann, U. and J. Endell. Angew. Chem., **52**, 708.