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WATER RETENTION BY COLLOIDAL ALLOPHANE AND IMOGOLITE WITH DIFFERENT CHARGES

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Abstract—Water retention curves of colloidal allophane and imogolite with different charges and different pretreatments were measured using a tension plate and a pressure plate apparatus. An irreversible effect of air-drying was found for the water retention of colloidal allophane even for particles of less than 50 nm in Stokes' diameter collected from air-dried soil. This was attributed to the irreversible submicroscopic aggregation of allophane. Fresh allophane colloids with a low absolute net charge retained more water above -100 J Kg^{-1} than did highly charged ones due to the formation of a microporous structure. Allophane did not swell under ordinary conditions, but the relatively highly charged allophane recovered water retention above -100 J kg^{-1} during the wetting process. Imogolite retained 1.5 times more water than Na-montmorillonite at about -650 J kg^{-1} due to micropores formed by intertwining fibrous particles.

Key Words—Allophane, Imogolite, Net Charge, pH, Pressure Potential, Water Retention.

INTRODUCTION

The characteristic physical properties of volcanic ash soils (Andisols) such as high hydraulic conductivity, air permeability and high water retention are attributable to the highly porous soil structure produced by the properties of the colloidal constituents. Allophane and imogolite are the characteristic clay minerals strongly related to these properties, but their water retention curves have not been measured because of the difficulty in preparing enough pure clay minerals to measure these curves.

The water retention of allophanic soils decreases markedly on air-drying (Maeda et al. 1977), the cause of which is regarded to be the irreversible aggregation of allophane (Kubota 1972). One of our purposes was to examine whether the colloidal particles of allophane separated from air-dried soil retain the effects of air-drying.

The surface charges of allophane and imogolite can be controlled by changing the pH conditions because they are typical variable-charge clays (Wada 1980). This phenomenon should be useful for investigating the relationship between the surface charge and water retention of a clay. This is another reason why we used allophane and imogolite to examine the effect of the net charge on water retention. The effects of prior iron oxide removal on water retention were also examined, and a comparison of water retention by allophane, imogolite and montmorillonite was made.

MATERIALS AND METHODS

Allophane Sample

The sample was prepared from fresh soil taken from the allophane-rich lower part of the Kanumatsuchi weathered pumice bed at Kanuma City, Tochigi Prefecture, Japan. It was purified by the following procedure.

FRESH DEFERRATED SAMPLE. A gel-like substance was washed out of the soil with water before the soil was treated with H_2O_2. The aggregates were squashed, and the coarse particles removed using a 0.5-mm sieve. The fine portion was treated with H_2O_2, then deferrated by treatment with $Na_2S_2O_4$-$NaHCO_3$-Na citrate (Mehra and Jackson 1960), followed by 2% Na_2CO_3 at 90 °C for 15 min (Jackson 1956; modified by Wada and Greenland 1970). The particles were dispersed at pH 9–9.5 with NaOH. Particles with a Stokes' diameter smaller than 50 nm were collected by centrifugation. About 100 mL of saturated NaCl solution was added to each liter of allophane colloid to be coagulated; then the sediment was dialyzed against deionized water until the electric conductivity of the external solution was less than 1 mS/m. An electron micrograph of this sample is shown in Figure 1a.

FRESH NON-DEFERRATED SAMPLE. This sample was prepared in the same way as the fresh deferrated sample, except that there was no iron oxide removal or 2% Na_2CO_3 treatment.

AIR-DRIED SAMPLE. The soil was first air-dried, the rest of the procedure being the same as for the fresh samples. The air-dried sample used consisted of allophane colloid with a Stokes' diameter smaller than 50 nm, as in the fresh sample. Deferrated (Figure 1b) and non-deferrated samples were prepared.

Imogolite Sample

This sample was prepared from fresh soil obtained from the imogolite-rich upper part of the weathered Kanumatsuchi pumice bed. After the gel-like substance had been collected by washing the soil with water, it was subjected to H_2O_2 treatment, iron oxide removal and 2% Na_2CO_3 treatment. Purification was performed as follows: The pH of the dilute suspension

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was adjusted to 8–9 with NaOH, and the suspension was subjected to ultrasonic waves for about 10 min. After being allowed to settle for several hours, the dispersed substance (allophane) was removed. This procedure was repeated about 20 times to remove the allophane from the sample. The imogolite next was dispersed by adjusting the pH to 4–5, and colloidal particles with a Stokes' diameter smaller than 50 nm were collected by centrifugation. The pH of the sample was adjusted to 6–7, and about 100 mL of saturated NaCl solution was added to each liter of the sample, then the sediment dialyzed. Although the particles prepared by this procedure still contained about 5–10% allophane (Figure 1c; Karube et al. 1992), we designated it the imogolite sample.

Allophane-Imogolite Sample

This sample was prepared from the same soil as the allophane sample. After air-drying and H_2O_2 treatment, without deferration treatment, colloidal particles less than 50 nm in size were separated by dispersing at about pH 4 with HCl. Because both allophane and imogolite disperse at that pH, they existed together in the sample. The other procedures were the same as those used for the allophane sample. The relative contents of allophane and imogolite were estimated to be about 7:3 from an electron micrograph (Figure 1d).

Montmorillonite Sample

Upton montmorillonite with a Stokes' diameter smaller than 2 μm, 90 $cmol_c\ kg^{-1}$ of cation exchange capacity (CEC), saturated with sodium (Low 1980), was used.

Experiment

The water retention curves of allophane and imogolite were measured over the range of −1.4 to −800 J kg^{-1}. A tension plate apparatus with a membrane filter and sample holder, 2 cm inner diameter and 3 cm high, were used for the range of −1.4 to −50 J kg^{-1}, and a pressure plate apparatus with the same filter and sample holder were used for −50 to −800 J kg^{-1}. Both apparatuses were used for the drying and wetting process.

For the drying process, samples were left more than 2 d for equilibration before measurement after the pH had been adjusted with HCl or NaOH. The initial concentration of the allophane sample after preparation was about 10 g kg^{-1}, and that of imogolite about 1 g kg^{-1}. Three to 7 mL of each sample was pipetted into the sample holder, and suction for the tension plate, pressure for pressure plate were applied. The water content was measured by the oven-dry weighing method when the sample reached equilibrium with the pressure potential after 1–2 d for suction, or after 2–4 d for high pressure.

The first half of the wetting process was the same as that of drying process. After the sample was equilibrated with a certain pressure potential, the potential was raised. The water content was measured when the sample reached a new equilibrium after additional 2–4 d. Some samples for the wetting process were placed into screw-capped glass tubes with water and sonicated for different periods. The dispersed samples were measured in the latter half of the wetting process.

Measurements were performed in triplicate. The coefficients of variation for the mean were estimated to be less than 0.02 for allophane and montmorillonite, and less than 0.03 for imogolite.

The charge characteristics of allophane and imogolite are based on the experimental data of Karube et al. (1990) determined for different pHs following the procedure of Wada and Okamura (1977) using 20 mol m^{-3} NaCl as the saturating salt, and 1×10^3 mol m^{-3} KNO_3 as the displacing agent.

RESULTS AND DISCUSSION

Change in the Water Retention Curve Due to Air-drying

Water retention curves of the air-dried and fresh allophane, both non-deferrated, are shown in Figure 2a. The water content of the air-dried allophane at each pressure potential was lower than that of the fresh one by 23–29% and did not recover even when the sample was treated with ultrasonic waves.

In this experiment, colloidal allophane with Stokes' diameters smaller than 50 nm constituted both the fresh and air-dried samples, and no difference was found between these samples by transmission electron microscopy (Figure 1a, 1b). However, when the colloids were dried to a thickness of 1–2 mm, the air-dried allophane did not become transparent, whereas the fresh allophane did. According to the law of light scattering phenomena, turbidity increases with colloidal particle size (Hiemenz 1986), which indicates that air-dried allophane forms somewhat larger aggregates. Although the Stokes' diameter of the aggregates was not larger than 10 times that of the unit particles, aggregation must be the cause of the irreversible change in the water retention curves.

This irreversibility could not have been caused by free aluminum or iron hydrous oxide because at each pressure potential the water content of the deferrated, air-dried allophane was also lower than that of the fresh sample by 20–23% (Figure 2b). Nor would surface charges have been the cause, because there was no difference in the electric mobilities of the air-dried and fresh allophane. Therefore, the irreversible changes in the water retention curves of allophane due to air-drying must have been caused by the irreversible aggregation of allophane, as has been reported by Kubota (1972). It is reasonable that in nature an allo-

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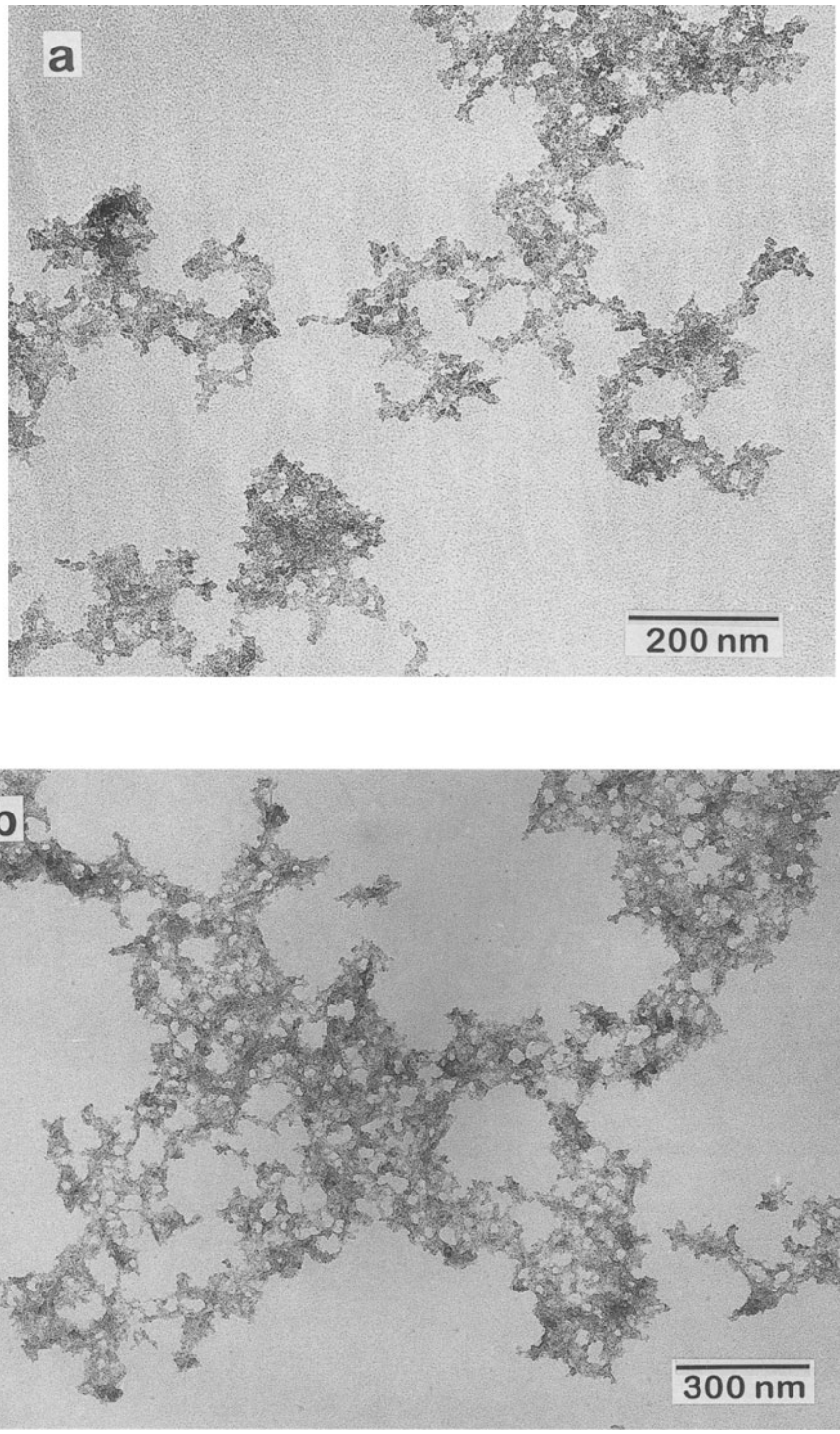
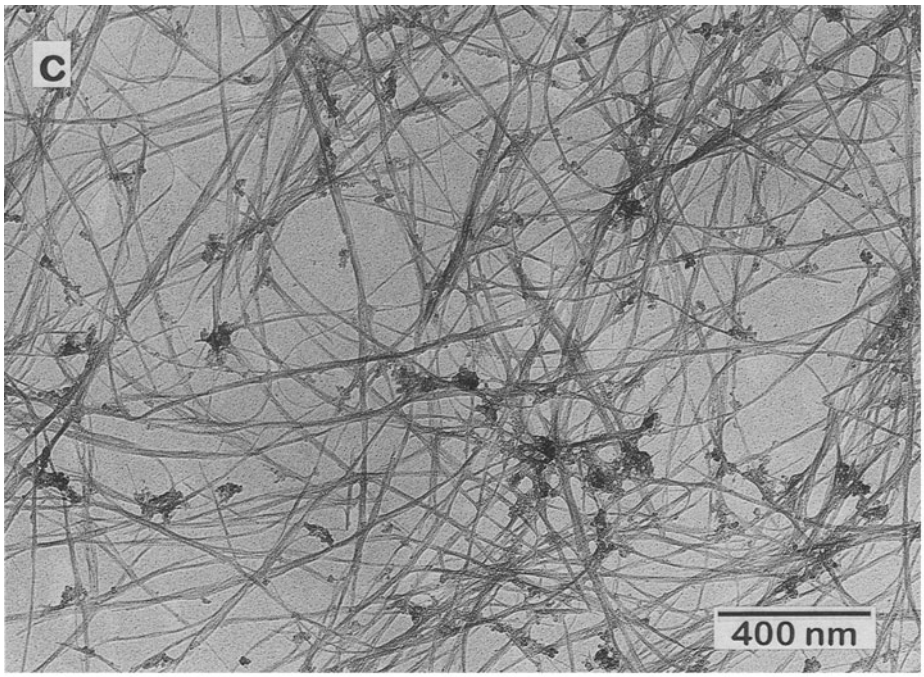


Figure 1. Transmission electron micrographs. a) Fresh (before observation) deferrated allophane. b) Air-dried deferrated allophane. c) Fresh deferrated imogolite. d) Air-dried non-deferrated allophane–imogolite.

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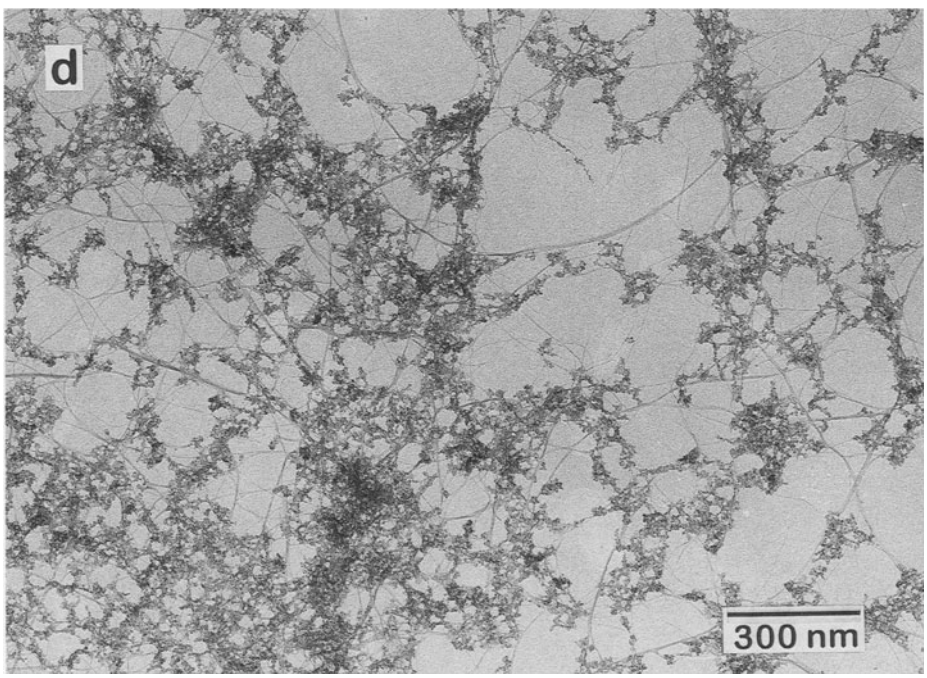


Figure 1. Continued.

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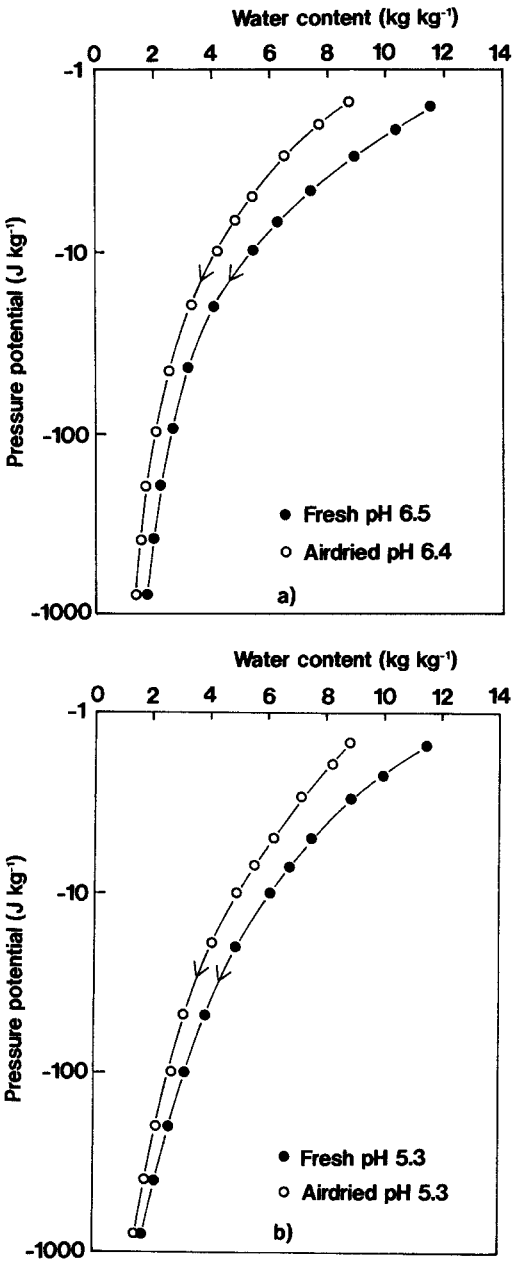


Figure 2. Water retention curves of allophane with a Stokes' diameter <50 nm. a) Non-deferrated allophane. b) Deferrated allophane. (The unit of pressure potential "J kg^{-1}" is convertible to "kPa" providing the density of water is 1 Mg m^{-3}.)

phanic soil, once air-dried, would show a marked irreversible decrease in water retention because larger aggregates would have been formed irreversibly by air-drying (Kubota 1976; Maeda et al. 1977).

Change in the Water Retention Curve by Deferration Treatment

The water retention curves of the non-deferrated fresh allophane at pH 6.5 (−4.5 $cmol_c$ kg^{-1} of net charge) (Figure 2a) and of the deferrated one at pH 5.3 (−5 $cmol_c$ kg^{-1} of net charge) (Figure 2b) were very similar, though the deferrated allophane had slightly higher water retention at about −10 to −100 J kg^{-1}. This relation did not change when the pH values were adjusted to be equal. Therefore, the effect of deferration treatment on the water retention curve of allophane was small.

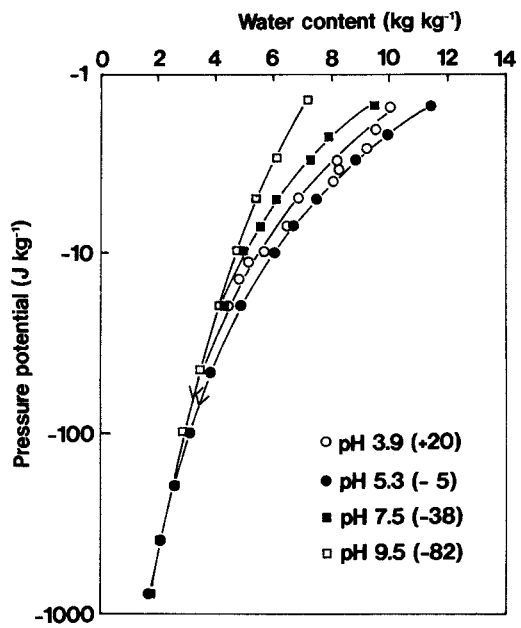


Figure 3. Water retention curves of deferrated fresh allophane with different charges. Values in parentheses indicate net charge in $cmol_c$ kg^{-1}.

Water Retention Curves of Allophane with Different Net Charges

Figure 3 shows water retention curves of deferrated allophane with different net charges controlled by pH. The effects of the net charges appear on the curves above the −100 J kg^{-1} pressure potential. The higher the absolute value of the net charge, the lower the water retention, and vice versa.

In suspension, allophane with a low absolute net charge coagulates, producing low bulk density, resulting in higher water retention than that for allophane with a high absolute net charge. These features are consistent with those of allophanic soils which, in nature, have a low absolute net charge, low bulk density and high water retention. Moreover, because allophane forms a primary floccule (domain) even when apparently well dispersed (Karube et al. 1996), the water retention of dispersed allophane also is ascribable to the microscopic pores of these domains.

The amount of water retained in the micropores is related to the strength of the gel structure against pressure. Because the gel structure due to flocculation is

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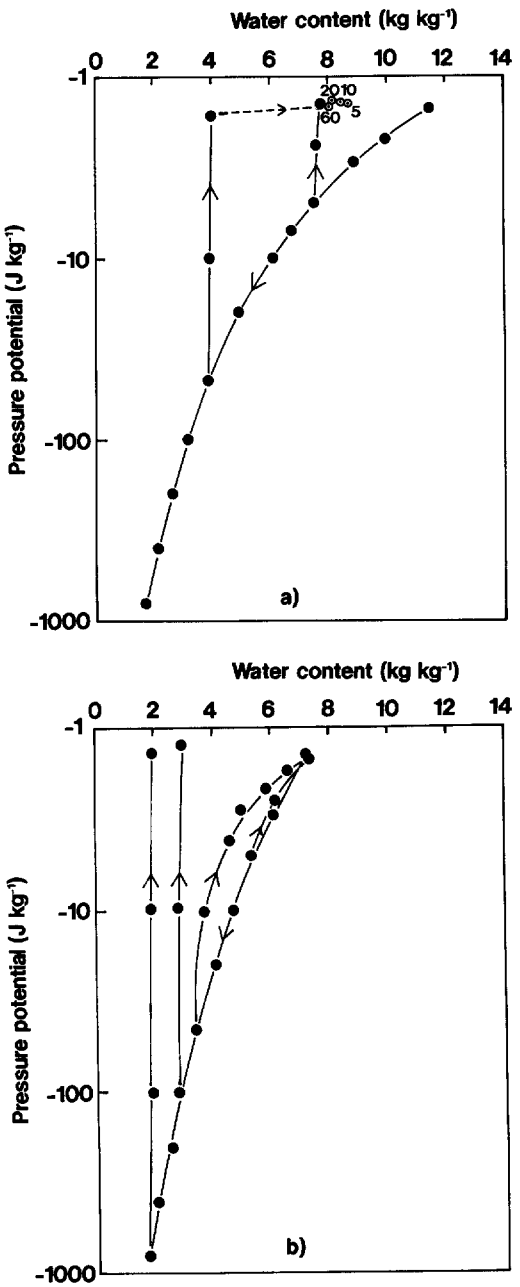


Figure 4. Wetting process for deferrated fresh allophane. a) At pH 5.3 (net charge -5 $cmol_c$ kg^{-1}). Numerals along the broken line indicate the sonicated time (min). b) At pH 9.5 (net charge -82 $cmol_c$ kg^{-1}).

less dense and relatively weak, the water retention of flocculated allophane decreases with pressure potential decrease at a higher rate than for a dispersed one. This difference ceased to be observed below -100 J kg^{-1} when the difference in gel strength became negligible. Allophane has a unique mechanism of high water retention that differs from swelling.

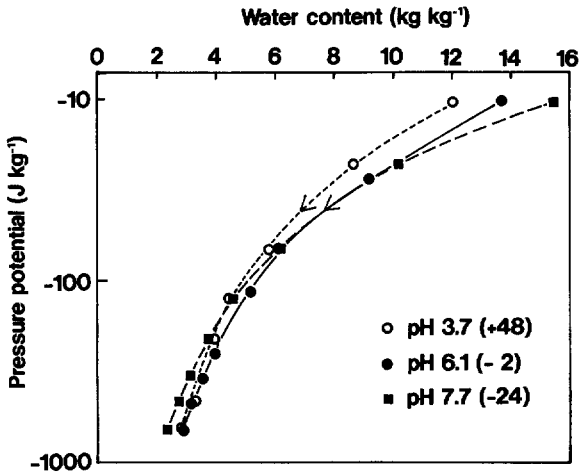


Figure 5. Water retention curves of deferrated fresh imogolite with different charges.

Irreversibility of the Water Retention Curves of Allophane

Water retention curves in the drying and wetting processes for fresh deferrated allophane at pH 5.3 and 9.5 are shown in Figure 4. Allophane at pH 5.3 (-5 $cmol_c$ kg^{-1} (Figure 4a) did not recover the water retention from -5 J kg^{-1} of pressure potential. In contrast, allophane at pH 9.5 (-82 $cmol_c$ kg^{-1}) recovered from -50 J kg^{-1} showing a different curve, but did not recover from -100 J kg^{-1}. Allophane swells only when it has a high charge density and is well dispersed. Because the allophane that swells has low water retention compared to that of coagulated allophane at high pressure potential (low suction), swelling did not produce a very big change in water retention.

Allophane at pH 5.3, when first treated with -50 J kg^{-1} of pressure potential, then sonicated through the glass tube, recovered its water retention to some extent at -1.4 J kg^{-1} (Figure 4a). Ultrasonic treatment apparently had the reverse effect with time because, when the allophane was well dispersed, its water retention decreased. Its final water retention, however, was close to that of the well-dispersed allophane at pH 9.5 (Figure 4b).

Differences in Water Retention between Allophane, Imogolite and Montmorillonite

The water retention curves of deferrated imogolite are shown in Figure 5. The water content of imogolite is more than twice that of allophane (Figure 3) at -10 J kg^{-1}, and about 1.4-fold at -800 J kg^{-1}. The relation between the net charge and water retention was similar to that of allophane, except for imogolite at pH 7.7, for which the water retention differed below about -250 J kg^{-1}. Under flocculation, imogolite formed a relatively dense structure at low pressure potentials. Because this mechanism is different from that for al-

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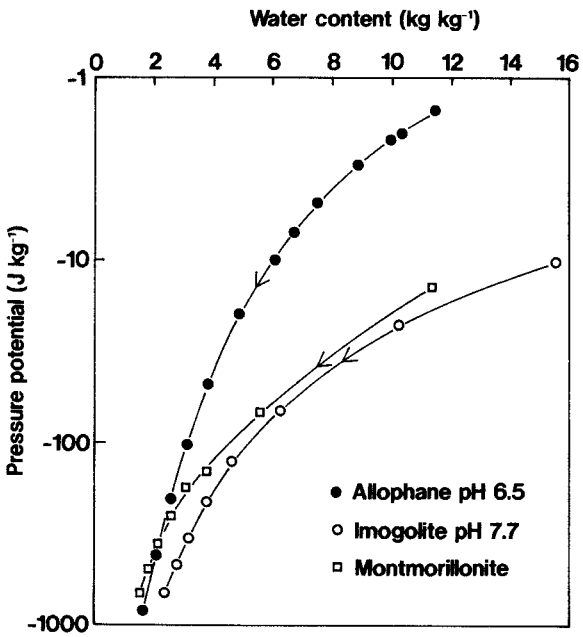


Figure 6. Water retention curves of deferrated fresh allophane, imogolite and Na-montmorillonite.

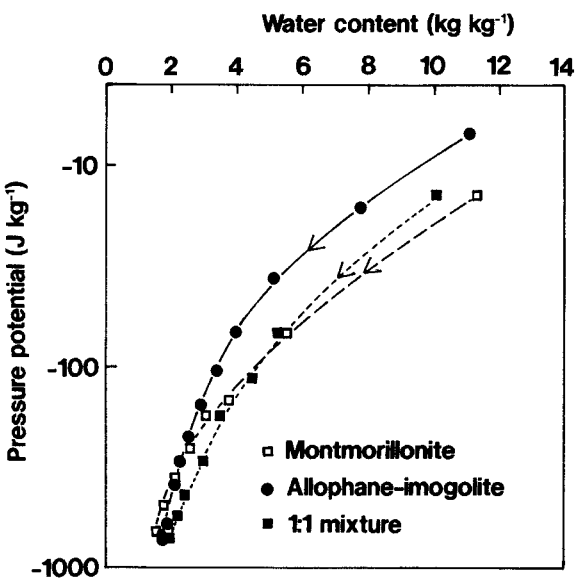


Figure 7. Water retention curves of non-deferrated air-dried allophane–imogolite, Na-montmorillonite and a mixture of them.

lophane, the flocculation of imogolite is ascribable to a thick, bundled arrangement of its fibrous particles.

The water retention curves of allophane, imogolite and Na-montmorillonite are shown in Figure 6. The water retention of imogolite was 1.5 times as high as that of montmorillonite at about -650 J kg^{-1}. Montmorillonite retained more water than allophane above -400 J kg^{-1}, but the relation was reversed below that pressure potential.

In Figure 7, allophane–imogolite was mixed with montmorillonite in the mass ratio of 1:1. This mixture had a higher water retention than both allophane–imogolite and montmorillonite in the range of -100 to -800 J kg^{-1}. This means that the number of 3–0.4 μm microscopic pores increased in the mixture due to the association of the allophane–imogolite with the montmorillonite.

Relation between the Water Retention Curve and Specific Surface Area

Low (1980), who found a relationship between the water retention curves and specific surface areas of clays, proposed the following empirical formula based on 34 Na-smectites;

$$\ln (\pi + 1) = \alpha(m_s/m_w) + \beta \qquad [1]$$

where π is the swelling pressure (atm; related to the pressure potential by the equation 1 atm = -101.3 J kg^{-1}); m_s and m_w are the masses of the solids and water; α, β constants; and α is the parameter of the specific surface area S, with the relationship $\alpha = kS$, in which k is a constant. This relationship was applied to each clay (Figure 8) to obtain the α values.

Using the specific surface areas of allophane, imogolite and montmorillonite calculated from their structural models and water contents at -650 J kg^{-1}, the average thickness of the water film at that pressure potential was estimated (Table 1). The inside surfaces

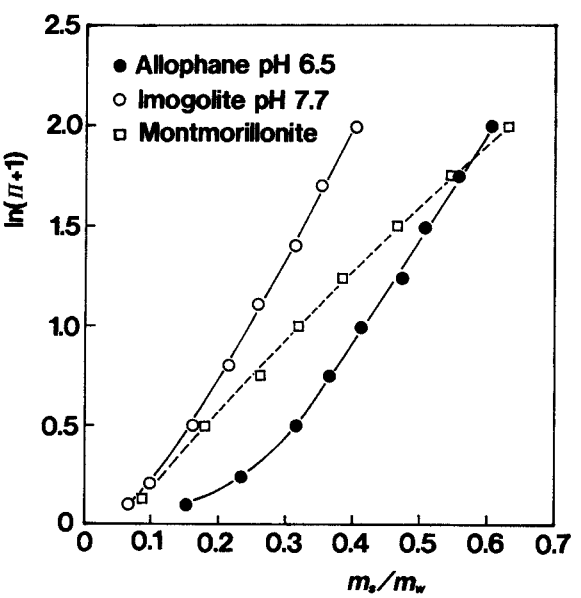


Figure 8. Relationships between ln (π + 1) and m_s/m_w for fresh deferrated allophane, imogolite and Na-montmorillonite. π is the pressure (atm) and m_s and m_w are the masses of the solids and water.

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Table 1. Relationships between the specific surface area S, parameter α and the average water film thickness at -650 J kg^{-1} t_{-650}.

	S† m^2 kg^{-1}	α‡	(m_w/m_s) kg kg^{-1}	m_w'/m_s§ kg kg^{-1}	t_{-650}¶ nm
Allophane	6.2×10^5	5.9	1.67	0.108	2.5
Imogolite	8.6×10^5	6.2	2.50	0.103	2.8
Montmorillonite	8.1×10^5	3.5	1.58	—	2.0

† S of allophane and imogolite was taken as the outside surface area, and calculated from $6\ D_0^2/(\rho_s(D_0^3 - D_i^3))$ for allophane, and $4\ D_0/(\rho_s(D_0^2 - D_i^2))$ for imogolite, where D_0 and D_i respectively are the outer and inner diameters, and ρ_s is the density of solids. Numerically, D_0 = 4.6 nm and D_i = 2.8 nm were used for allophane, D_0 = 2.2 nm and D_i = 1.03 nm for imogolite, and ρ_s = 2.7 Mg m^{-3} for both.

‡ α is the parameter related to the specific surface area (Low 1980).

§ m_w'/m_s is the water content of the pore water inside the unit allophane and imogolite (Wada and Wada 1977).

¶ t_{-650} was calculated from $(m_w - m_w')/(m_s S \rho_w)$, where ρ_w is the density of water.

of the unit particles of allophane and imogolite were neglected because the volume of water in the particle did not change over the range of measurement used. The specific surface areas are not completely different for these 3 clay minerals, the α values being close for allophane and imogolite, evidence that there is structure formation, even during the drying process, that differs from that of montmorillonite. Imogolite had the highest value of average or apparent water film thickness at -650 J kg^{-1}, the lowest comparable pressure potential in this experiment. This high water retention of imogolite, in terms of the specific surface area, is ascribable to the micropores formed by its intertwined fibrous particles.

CONCLUSIONS

The allophane separated from air-dried soil had 23–29% lower water retention than the allophane from fresh soil at a pressure potential of -1.4 to -800 J kg^{-1}. Because the Stokes' diameter in both samples was less than 50 nm, the difference in retention is ascribed to submicroscopic irreversible aggregation caused by air-drying.

The allophane prepared from fresh soil had different water retention curves above -100 J kg^{-1} that depended on the pH, that is, the net charge of allophane. The higher the absolute value of the net charge, the lower the water retention above that pressure potential. This phenomenon differs from swelling and is ascribable to the formation of a microporous structure.

The water retention curves of allophane generally were irreversible. But when allophane had a high absolute net charge, water retention recovered to a certain extent at a pressure potential above -100 J kg^{-1} during the wetting process.

Imogolite had higher water retention 1.5 times that of Na-montmorillonite at about -650 J kg^{-1}, and more than twice that of allophane at -10 J kg^{-1}. Water retention of allophane also was higher than that of montmorillonite below -400 J kg^{-1}. When montmorillonite was mixed with allophane–imogolite, the water retention of the mixture was higher than for either of the clays between -100 and -800 J kg^{-1} because of their association. The high water retention of imogolite is explained not only by its high specific surface area but by the micropores formed by its intertwined fibrous particles.

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