An Interaction Force between Allophane Particles in Disperse System

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1. INTRODUCTION

Soil behaviour has much connected with the chemical and physical properties of particles. The water adsorption, creep and thixotropy are mostly affected by its colloidal parts. The fundamental energetic aspect of soil water system has been developed since 1960.[1,2] From mechanical view point, the important thing is not merely in the water energy, but also repulsion and attraction forces acting on the surface of soil particles.

This paper treats the repulsive force between allophane particles in disperse system controlled with pH and urea. The structure of allophane is amorphous, very different from that of other crystallized minerals like montmorillonite or kaolinite. Allophane is of high adsorption of phosphate, a high water holding capacity, thixotropic, and of irreversible physical properties by air drying. The cation exchange-capacity is very unstable. It depends on the pH of the colloidal system. C. E. C. covers 20-40 me/100g in the range of pH less than 6.5. Isoelectric point is about pH 6.5. These properties are giving many interesting phenomena to soil physics and soil mechanics.

2. EXPERIMENT

2.1 PREPARATION OF ALLOPHANE MINERAL

The material used was taken from volcanic ash soil, Kanto Loam (JAPAN), consisting mainly of allophane. It is said in some cases it contains more than 80% of allophane. Though there are several methods of dispersion suitable to the mechanical analysis of soil, a few method of colloidal dispersion for this mineral has been discussed. A method as follows has been tried to get well dispersed colloidal particles.

A suspension of allophane soil was deflocculated with HCl and 1 ml of 30% of hydrogen peroxide was added per 100g of clay to remove organic matter. Then 1m NaCl was added to prepare the clay in the homo-ionic sodium form. One group of specimens was added with 5M urea, the other group is not added. Both groups are set in ultra-sonic bath (37 KHZ, 125 Watts) for 8 hours and added with HCl up to about pH 3. All specimens were dialysed against HCl solution of several pH's, and these dialyses were repeated with fresh HCl solution for one month.

2.2 ARRANGEMENT OF COLLOIDAL PARTICLES FROM THE MATERIAL

A suspension treated in 2.1 was set in the ultra-sonic bath for few minutes followed by high speed centrifugation at about 26,000G for 1 hour. Supernatant was taken out and replaced by controlled pH solution of the same volume withdrawn, and then condensed by overhanging in cellulose tube (23Å mesh) in the air. The volume of supernatant suspension become, when it is condensed, jelly (about 160 in water content).

Notation for the specimens used for the compression test is as follows.

A(o)X: Particle size is about 100 nm. Sample substituted by 1N Na^+, then dispersed in ultra-sonic bath for 8 hours and dialysed against pH X HCl solution (X: 3.0, 5.1 etc.).

A(u)X: do. Sample substituted by Na^+, then 5M/l urea was added and in ultra-sonic bath for 8 hours and dialysed against pH X HCl solution.

2.3   SOME IDENTIFICATION TESTS FOR THE MATERIAL

D. T. A. test: Untreated material is set in a thermal difference analyser to get DTA curve as in Fig. 1. This shows a peak at about 130°C. The peak means typical one due to evaporation of crystallized water. The recess at 292°C is supposed to contain a small amount of gibbsite, a hill at 300 − 400°C is mineral rearrangement of structure. This curve is very same to the typical one of allophane.

X rays diffraction and analysis of electron microprobe: The diffraction by Cu Target emission shows no marked crystallized structure even in treatment with K^+ and Mg^{++}. The analysis of electron microprobe is giving a molecular ratio of Si/Al = 0.9 and the ingredients of the specimens would be $(Si Al_{1.11} Fe_{0.67})$. It may be safely said the sample could be mainly allophane minerals with gibbsite and iron (Table 1).

Specific surface: The measurement of specific surface was done by BET. The value of specific surface for allophane does not have a constant value. It depends on methods. Generally the value by vapour method is reported as from about 250 m^2/g to 380 m^2/g. The value by N_2 gas is about 211.4, and the values for the specimen are given as 275.0 − 325.8 m^2/g by H_2O vapour method.
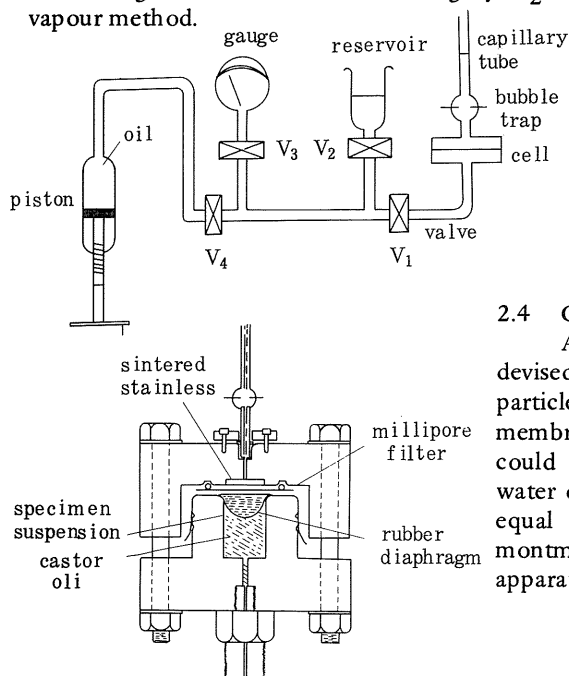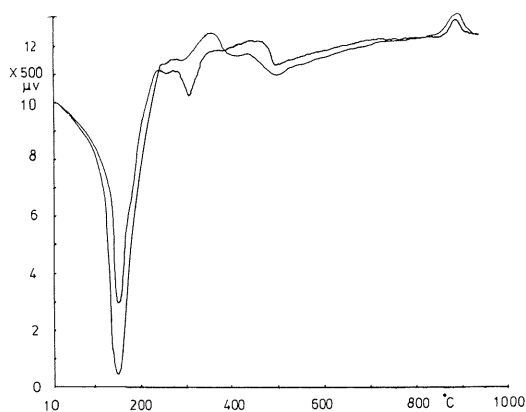

Fig. 1   DTA curves of Specimen

Table 1   Electron Microprobe Analysis of Allophane mineral
Elements detected: Al, Si, Fe.
Counting time 400 secs

	Element	Counts + background	− background
Test-1	Al	8977	2953
	Si	7976	2991
	Fe	6837	2050
$(Si Al_{0.99} Fe_{0.69})$			
Test-2	Al	9678	4174
	Si	8191	3416
	Fe	6003	2171
$(Si Al_{1.22} Fe_{0.64})$			
Mean			
$(Si Al_{1.11} Fe_{0.67})$		(by Dr. Thompson)	

Fig. 2   Cross sectional diagram of compression tester and cell[2]

2.4   COMPRESSION STUDIES

An apparatus for compression test was designed and devised to measure the force between particles. [3] The clay particles were confined between a rubber membrane and a membrane permeable to the water. The repulsion force could be balanced to the force applied by squeezing the water out of disperse system. This balanced force applied is equal to repulsion force between two particles like montmorillonite (face to face type). The operation of this apparatus is all followed after the Barcley's method. [4]

3. RESULTS

3.1 DISPERSION OBSERVED BY ELECTRON-MICROSCOPE

The small particle (100 nm) obtained from specimen A(o) by centrifuging looks like agglomerated grains in Photo 1.
The same sample added by urea A(u) is shown in Photo 2.

Particle size distribution curves obtained by optical counting machine illustrated in Fig. 3. The specimen of urea added A(u) has two peaks. This specimen might be mixed with two groups of particle size distribution. A(u) has more dispersed distribution curve than A(o).

The state of dispersion in suspension was observed by a photon corelation spectrum analyser. The mean vlues of kinetic unit in suspension were calculated under the condition of 50, 100, 200, 400 and 800 m sec scattering time. The diameter of a particle in the suspension (A(u)3) was 100 − 120 nm.

Same observation was done on the suspension not treated by urea (A(o)3). In this case, the average diameter of a single particle was 100 times larger than that of A(u)3. The specimen treated with urea is more dispersive than without urea.

3.2 COMPRESSION TEST

The test has been done by the apparatus with temperature control accurate to within 0.5℃. The pressure applied was from 3
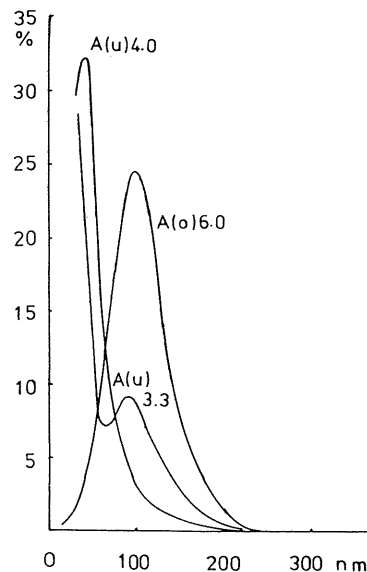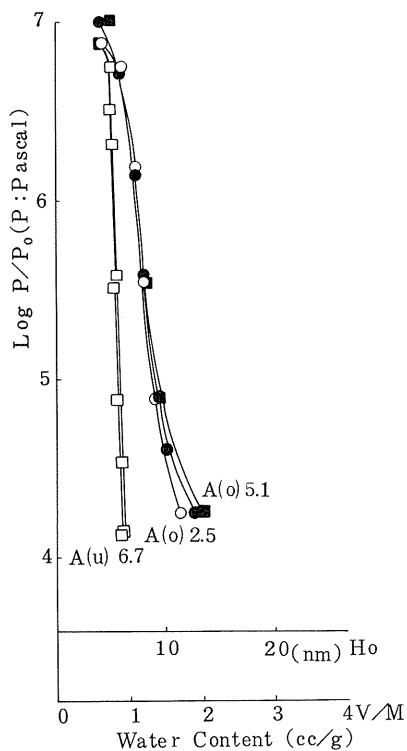

Fig. 3 Distribution curves of particle size

Fig. 4-1 Compression curves (after 2nd) for different pH and treatment
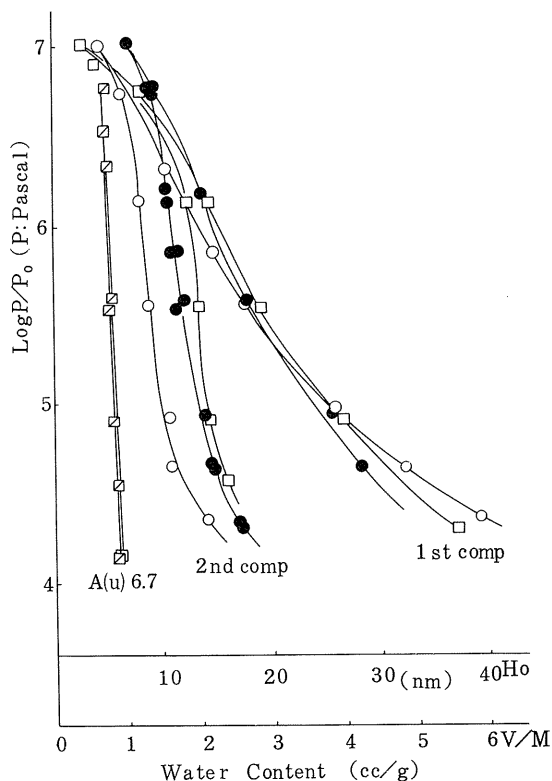

Fig. 4-2 Hysteresis of compression curves for different pH and treatment
○: A(u)6.5, ●: A(u)4.2, □: A(u)2.6

psi (about 2,000 Pascals) to about 1,400 psi (about 10^7 Pascals). Time to balance to the applied pressure was much longer at low pressure than high. But it would be complate enough within 24 hours as far as the suspension confined in the cell was small quantities of $10 - 20$ cc.

Hysteresis can be seen in the 1st and 2nd compression curves. There are no marked hysteresis after the 2nd. In Fig. 4-2 the 1st and 2nd compression curves at different pH are shown in terms of pressure and particle distance H_o or water content. Fig. 4-1 gives the difference between specimen of no urea and specimen with urea. A curve for urea treatment $A(u)$ which gives hysteresis and shifts to the left for curves without urea $A(o)$.

3.3   VAPOUR PRESSURE CURVE

The vapour pressure of the specimen against moisture content are measured by desication method. One of the values was alternatively replaced by centrifugal method because no suitable desication agent (Fig. 5).

The effect of temperature on the results of vapour pressure curves was corrected in the terms of room temperature 25°C.

The colloidal suspension confined in the cellulose tube of 23Å mesh was centrifuged for about one hour. Centrifugal force was calculated from the force acting per one gram, that was Rw^2.

R: radius of centrifuging,   w: angular velosity.

Fig. 5   A comparison of the values of H_2O vapour pressure and centrifuging pressure by the compression test for the specimen $A(u)$ 6.7.

O: Vapour pressure balanced with water content of the specimen.
◉:   Pressure applied to the specimen with centrifuging squeezing out the water
□:   Compression test
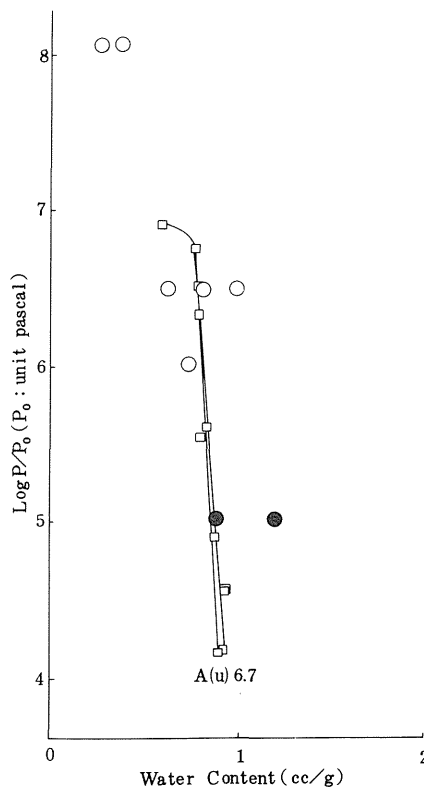
4. DISCUSSION

4.1   DISPERSION OF ALLOPHANE

The diameter of unit particle is assumed to be 50Å $-$ 100Å by calculation from surface area and density of particle.[5]

To get the unit particle as well as uniform dispersion is very difficult with usual dispersion method. Davies (1933)[6] discussed the difficulties of dispersion in allophane and suggested very dilute HCl as a suitable dispersing agent. By this method, the number of small particle less than 2μm in diameter will increase rapidly when concentration of H^+ increases, because of getting higher the potential of cation in surface. Birrel and Fieldes (1952)[7] argued that iron sesquioxides which helped cementing soil aggregates were set free to exert them flocculation action when HCl was used and they suggested alkaline medium appears to be effective.[8]

As far as grains concerned, by urea and HCl treatment allophane gives a good dispersion of small grains of 100 nm in the scope of E. M. as in Photo 2,3.

The average distance between particles H_o can be calculated on an assumption that the distance is very short, and particles are not so irregular in shape and size, $H_o = 2V/mA$. Where V is volume of

water, m is dry weight of specimen, A is specific surface (300 m^2/g). On this assumption, the distance H_O is about 4 nm at the top pressure of 10^7 pascals.

Allophane colloid keeps a well suspended liquid up to 1% concentration of suspension, but above which concentration, the suspension changes into jelly. Particle shows the strong thixotropic behaviour even in concentration less than 1%. It depends on pH values.

4.2 SURFACE STRUCTURE OF ALLOPHANE

An addition of hydrogen chloride is helpful to make allophane dispersive. It improves cation charge of the surface high and may disolve the cementing material. The surface of minerals are generally of asperities in sense of crystallized surface. The atom on this surface give rise easily to reaction with additives to produce functional groups on the site. There are several kinds of functional groups, silanol, one of them is H-bonded. On the surface of mineral, OH functions as the active site. The higher the degree of crystallization is, the lower the density of OH is, while the less crystallized, the higher the density.

A single kaolinite (1:1) can be considered as two dimentional. The macromolecules are cross linked by hydrogen bond Al-OH—O-Si to the three dimentional lattices. Weiss, A (1961)[9] investigated on the dispersion of kaolinite suspension. Each monolayer of kaolinite crystals in bond builds 3 dimensional layer structure. The bonding between macromolecular can be disconnected by certain low moleculars like urea and alcohol penetrating into lattices and making loose expansion of the distance between layers. They behave as structure breaker.

A part of structure of allophane has a similarity to that of kaolinite. Much as they may be not crystallized, allophane could have the higher density of active OH like kaolinite. In this experiment, the silica-almina ratio of allophane is about 1, and the two crystals Si, tetrahedral and Al octahedral chains are thought to exist to give -SiO and -AlOH. The structure unit having these functional groups is hydrogenbonded.[10,11] It can be supposed that the surface, on which oxigen is exposed from SiO-surface, reacts to make bonds easily with Al(OH).

4.3 ADDITIVE EFFECT OF UREA AND HCl ON DISPERSION

Allophane is amphoteric and has a negative charge at pH 7. The iso-electric point is reported about pH 6.5. The more pH decreases, the more positive charge increases. The addition of urea to A(o) makes the suspension coagulative, because urea solution is basic and the addition of urea makes pH of the suspension increased up to 6.5 − 7.0, and electrical repulsion by particle surface will be suppressed. By this treatment, small particles settled down from the suspension would behave very viscous. The stable suspension can be got after the addition of HCl to decrease pH up to 3.

The relation between the adsorptive groups and their adsorption properties are explained by two kinds of adsorption, that is, inside negative charge and outside negative charge.[11] The former is of negative charge existing inside of the structure which is apt to absorb low molecular cation NH$^+$ and specific ions. The latter has adsorbent group existing on the surface of structure.

The structure of allophane in which the hydrogen bond is attacked by urea expands to reform a new structure which provides a new surface of adsorption to H$^+$. These principles could be identified by compression curve showing a difference between pH 2.5 − 5.1 if not treated by urea. As is shown in Fig. 4, comparing two groups, the particles in A(u) treated by urea are compressed more tight than A(o). Another group of specimens, A(o) 2.5, A(o) 5.1 do not show a big difference each other. These facts could tell that the decreasing of pH does not always have a much influence on the surface charge any more when surface is saturated with cation.

The exchange of surface charges increased by penetration of H$^+$ into the loose structure as well as a new surface given by urea. These additional effects of urea and HCl would make the allophane particle with cation dispersive. The positive charges would prepare the surface potential with morerepulsive force.

4.4 VAPOUR PRESSURE AND COMPRESSION FORCE

The repulsion force by compression and vapour pressure may be different in sense of mechanical force. But the concept of potential energy between face to face may be valid to interpret these phenomena energy of water attracted by particles. The force between particles may have a connection with the state of water adsorption on surface.

4.5 STRUCTURE OF AGGREGATE COMPRESSED

As shown in Photo 3, a part of dispersed particles after compression is just like spherical ball sticking together. Massive units of allophane are supposed as very small particles which diameter can be guessed as less than 100 nm. Water penetrates into aggregates, whcih shows the specific surface about 300 m^2/g, while the value for N_2 gas is about 211 m^2/g. These difference would come out of the structure of aggregate with large porosity.[13] Under the high pressure at 10^7 pascals (100 atm), the aggregates deform flat and water is squeezed out. Each particle is packed together by compression until from 40 nm to 5 nm. This means the structure of the dispersion system is put under a large deformation, if strain applied is attained to some extent,and structure will be broken to make irreversibly more stable state.

The porosity n is $n = \dfrac{1}{1 + (M/V\rho)}$ where M: mass of particles dried, V: water volume and density of particles. A porosity obtained from Fig. 4 at 10^7 pascals is about 0.614, which is in the state of close packing, provided the particles are equal and spherical.

From these studies, the force between particles must be divided into two parts, one is a force inside the aggregate, and the other outside the unit particles. The adding of urea is effective to degrate the inside-force and exerts the aggregate deplation. Some reports have been done on the thixotropic properties of allophane particles.[14] Thixotropy could be discussed as the change of the structure. The stronger the repulsive force is, the more.thixotropic the suspension is. While the smaller repulsion force is, the smaller hysteresis between the 1st and 2nd compression curves. It is supposed that thixotropy of allophane could be expected much more in a suspension treated by urea and in high concentration of H ion than not treated ones.

5. SUMMARY

1)   Allophane particles in suspension behave as smaller particles by adding of urea. The water in colloidal system is squeezed out easily in favour of consolidation. From these, urea would be a structure breaker to the particles bonded like allophane.

2)   Raising up of H ion makes the particles dispersive in use of urea. The structure of particles developes in low pH rather than high pH. As can be observed from the compression curves, the lower the pH, the more thixotropic the suspension is.

3)   Forces acting on the surface of allophane particle would have a relationship with its vapour pressure curve representing an index of water energy level.

ACKNOWLEDGEMENT

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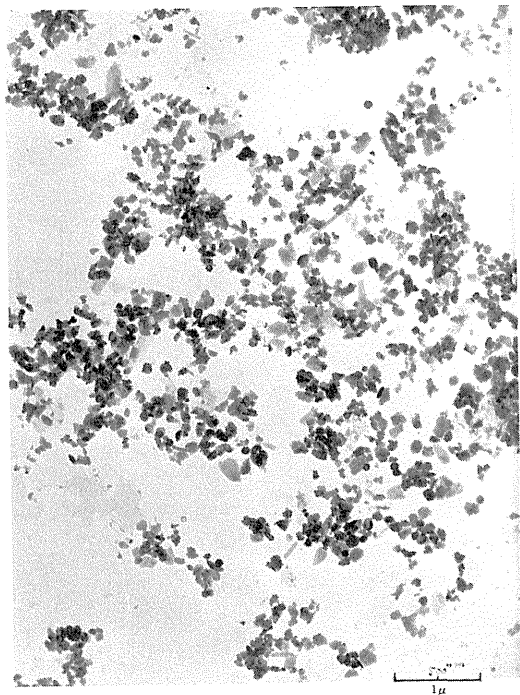photo 1
   Taken by Dr. Thompson.   SAMPLE A(o) 6
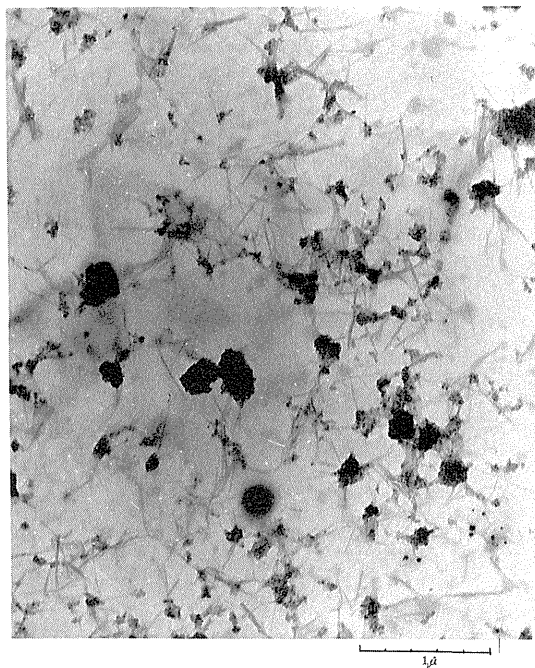

photo 2
Taken by Dr. Thompson   SAMPLE A(u) 3.3
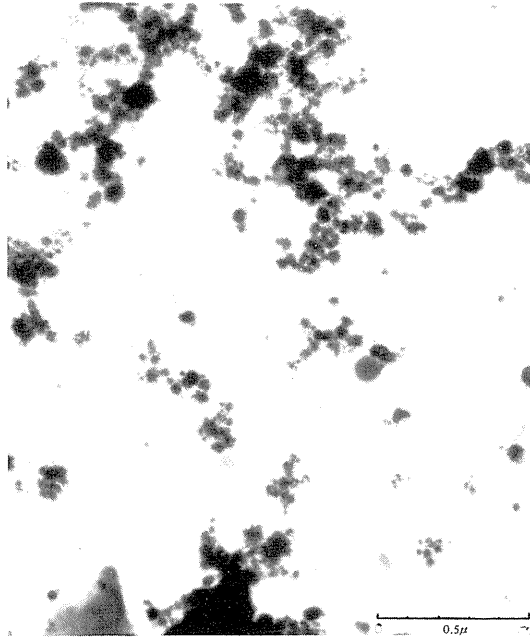   pH 3.3

Photo 3
Taken by Dr. Thompson.　　SAMPLE　A(u) 3.0

アロフェンの分散系における粒子間の相互作用について

安 富 六 郎

　わが国に広く分布する火山灰はアロフェン鉱物を多量に含む。アロフェンは他の一般の土鉱物と異なり非晶質であり，粒子表面の物理化学性にも著しい特徴がある。吸着比表面積は大きく，イオンの特異的吸着を示す。力学的にはチクソトロピーを示し，これらは土壌物理的にも土質工学的にも重要な性質である。

　この研究はアロフェン粒子表面に作用する力をコンプレッション試験器を用いて実測し，粒子の分散・凝集状態と力学的諸性質との関係をしらべた基礎的研究である。

　関東ロームのコロイド粒子間に作用する水素結合力を低下させるために尿素を添加し，コンプレッション試験，光分散解析及び電子顕微鏡写真などから分散状態をしらべた。その結果，次のことがわかった。

　1）　アロフェンコロイドは尿素の添加によって粒子間反発力が弱められ，より小さい分散粒子をつくり，排水圧密的現象を容易に進行させる。

　2）　H^+ の上昇によって粒子は分散的になるが，コロイド系はゲル化し，強いチクソトロピー的性格を示す。これらの傾向はコンプレッション曲線から容易に予想される。

　3）　コンプレッション曲線と蒸気圧曲線はほぼ同一の曲線領域を有する。このことは粒子間に作用している力が水蒸気のエネルギーポテンシャルと密接であることを示す。

　4）　尿素添加によって強い凝集状態を示し，さらにH^+増加によって強い分散性を示すことは尿素がアロフェン粒子間に作用する結合力の一部（水素結合）を破壊するためと予想される。