AN ABSTRACT OF THE THESIS OF

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Title: Dispersion of Some Amorphous and Crystalline Clays

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The critical coagulation concentrations (CCC) of several inorganic electrolytes at varying pH and temperatures were measured on a smectite, hydrated halloysite and amorphous (allophane-imogolite) clay. The CCC was operationally defined as the concentration of electrolyte necessary to give a 50% transmittance reading at 546 nm after 24 hours of settling. Each clay was saturated with the same electrolyte used to determine the CCC.

The critical coagulation concentrations were determined on the clay size fraction (<2μ) for each sample. A preliminary investigation was undertaken to find a chemical dispersant to separate a significant amount of clay from the bulk soil sample without inducing changes in the morphology of the colloid as revealed by transmission electron microscopy. Several particle size determinations for each sample using various chemical dispersants were used to estimate the effectiveness of each dispersant. The smectite sample was effectively dispersed in distilled water, while 0.05% Na₂CO₃ and pH 4.5 HCl were effective in separation of the hydrated halloysite and the imogolite-allophane clay, respectively. The three clays prepared in this manner were further characterized by X-ray diffraction, differential thermal analysis, ion
exchange capacity and percent organic carbon in addition to their behavior in solutions of electrolytes.

The critical coagulation concentrations were expected to be elucidated by the Shulze-Hardy rule and the lyotrophic series for cations and anions. The negatively charged smectite and hydrated halloysite were sensitive to the valence and hydrated size of the cation. The CCC's of smectite were greater than those of the hydrated halloysite clay. Certain ion saturated hydrated halloysite samples, \((\text{NH}_4\text{Cl, (NH}_4\text{)}_2\text{SO}_4, \text{and MgCl}_2)\), resulted in coagulation of the clay without the addition of any electrolyte. The coagulation of the allophane-imogolite clay was sensitive to the valence of the anion and the hydrated size of the cation. This phenomenon is due to the high percentage of positive charge on this clay at the prevailing pH of western Oregon soils.

The pH of the coagulating medium was varied by adding 0.15 meq of \(\text{H}^+\) or \(\text{OH}^-\) per gram of clay to the clay suspension. Decreasing the pH of the medium, decreased the concentration for coagulation for smectite. The addition of acid to the hydrated halloysite suspension resulted in a mutual coagulation of the clay without the addition of any excess electrolyte. The effect of pH on behavior of the allophane-imogolite clay was opposite to the smectite and hydrated halloysite; the CCC decreased with increasing pH and mutual coagulation occurred above pH 6.0. Coagulation of the allophane-imogolite clay at the higher pH is complicated by the unusual electrophoretic characteristics of imogolite at these pH's.

The effect of temperature on the magnitude of the CCC was determined by lowering the temperature of the clay suspensions from 20°C to 4°C. As the temperature was decreased, lower concentrations of electrolyte
were required for coagulation of hydrated halloysite, higher concentra-
tions were required for the allophane-imogolite clay and there was no
difference for the smectite sample.
THE DISPERSION OF SOME AMORPHOUS
AND CRYSTALLINE CLAYS

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Typed by Margi Wolski for John S. Hickman
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THE DISPERSION OF SOME AMORPHOUS
AND CRYSTALLINE CLAYS

I. INTRODUCTION

A significant increase in turbidity in Hills Creek Reservoir in the Willamette basin of western Oregon was noted following a large winter flood in 1964. Unlike some other reservoirs in the area, the turbidity has persisted since 1964. In 1970, a study was initiated to determine the cause, nature and source of turbidity in the reservoir waters (Youngberg et al., 1975). Reservoir and watershed streams were sampled, especially during major storm events. The profiles of major soils in the area were also sampled. High stream turbidites were observed during storm events, particularly in streams draining unstable areas prevalent in pyroclastic materials. Smectite, zeolite and amorphous materials were identified in most of these stream samples. Analyses of reservoir samples after formation of the thermocline indicated the prominence of poorly organized and amorphous components in surface samples while X-ray diffraction peaks for smectite were sharper and more intense with depth. (This suggests that amorphous components tend to remain in suspension longer than the smectite minerals.) The soils developed in pyroclastic parent materials also contained smectite and amorphous clay minerals. Comparison of data on the ease of dispersion of profile samples in distilled water indicated samples high in montmorillonite were not as high in dispersibility as the amorphous components.

Taskey (1978) characterized a large number of sites in the western Cascades of western Oregon to find the relationships of various clay minerals to mass movements. Amorphous gels and hydrated halloysite formed
in weathered basaltic colluvium and volcanic ash were related to flowage
type failures. These materials were saturated or nearly saturated by a
water table perched on an underlying smectite clay layer developed from
pyroclastic tuffs and breccias. The amorphous clays and hydrated halloysite
maintained a saturated condition due to their high water holding
capacity. Disturbing these amorphous gels and hydrated halloysite would
release stored water enabling the particles to rearrange themselves into
a configuration of lower strength, thus promoting landscape instability.
Relatively stable sites contained amorphous materials, dehydrated halloysite
and chloritic intergrades.

The previous work indicates that 1) amorphous material, hydrated
halloysite and smectite are delivered to streams and reservoirs by mass
action, and 2) these components behave differently with respect to
flocculation-dispersion in the waters. Information was needed on how the
flocculation of these components respond to varying electrolyte concen-
trations.

The critical coagulation concentrations (CCC) of several electrolytes
on a smectite, allophane imogolite mixture and hydrated halloysite clay
were experimentally determined. The CCC's are expected to be elucidated
by the Schulze-Hardy rule and the lyotropic series for cations and
anions. Electrolytes used to test the above hypothesis were chosen to be
indifferent, i.e. do not engage in any specific reaction with the sol.
The electrolytes chosen were NaCl, KCl, NH₄Cl, CaCl₂, MgCl₂, NaNO₃,
Na₂SO₄, K₂SO₄, (NH₄)₂SO₄, CaSO₄ and MgSO₄.
II. OVERVIEW OF SURFACE PROPERTIES

General Clay Colloid Theory

Clay suspensions are classified as hydrophobic colloids for which the properties depend on the extensive interface between the particle and the liquid (van Olphen, 1977). The stability of the system can be described by the interaction of particle association (London-van der Waals attraction) and various repulsive forces. When a high concentration of salt is added to the system, the repulsive forces cannot counteract the particle attraction and the system coagulates. The minimum concentration of electrolyte which coagulates a suspension in a given time is the critical coagulation concentration (CCC).

A suspended clay particle may obtain its charge from preferential adsorption of positive or negative ions on the particle surface or from interior defects of the crystals (van Olphen, 1977). Imperfections in the crystal structure of the clay mineral result in an imbalance of charge on the particle. Frequently, substitution of cations of lower valence for those of higher valence in tetrahedral or octahedral coordination result in a net negative charge on 2:1 type clay minerals. This charge is compensated by equivalent amounts of ions of opposite sign sorbed on the clay surface. The electric double layer in this case is defined as the layer of counter ions and the negative charge on the particle surface.

When a continuous phase of liquid surrounds the particle, the counter ions tend to diffuse into the medium creating a diffuse electric double layer or Gouy layer. The extension of the Gouy layer decreases with
increasing electrolyte concentration (Figure 1) and increasing valence of the counter ion (van Olphen, 1977). The Gouy model does not take into account dimensions of the ions or the specific interactions between the surface with the counter ions and the medium (Voyutsky, 1975; van Olphen, 1977).

In 1924, Stern elaborated the theory of the electric double layer by assuming the counter ions have certain finite dimensions and specific, non-electrical interactions with the surface. In the Stern model, the first layer or several layers of counter ions is attracted to the surface by electrostatic and adsorption forces. This layer, for which the electric potential falls off sharply with distance, is termed the "Stern layer" (Voyutsky, 1975). Beyond the Stern layer, the remainder of the counter ions are distributed in a manner similar to the Gouy layer (Figure 2). The addition of electrolytes compresses the diffuse part of the double layer by increasing the number of counter ions in the Stern layer, resulting in a decrease in the Stern potential, \( \phi_0 \) (van Olphen, 1977). Increasing the valence of the counter ions or decreasing the hydrated radius compresses the electric double layer and this also gives rise to a lower Stern potential (Overbeek, 1952; Voyutsky, 1975).

Interactions between charged colloidal particles are the result of a balance between the repulsive forces and London-van der Waals attractive forces. London-van der Waals attraction forces between atoms are a result of interactions of dipole moments and the polarizing action of a dipole in one molecule on that of another molecule (Overbeek, 1952a). The attractive force between a pair of atoms is small and decays rapidly with the distance between atoms. Since London-van der Waals forces are
Figure 1. Gouy model for electric potential distribution at two electrolyte concentrations for constant and pH dependent charged surfaces (from van Olphen, 1977).
Figure 2. Stern model for electric potential distribution.
additive between atom pairs, the total attraction between clay particles is the sum of attractive forces for all atoms of both particles. This summation results in a force comparable to particle repulsion and an attractive energy inversely proportional to the square of the distance of separation (van Olphen, 1977).

Repulsive forces are a combination of short range repulsion and electric double layer repulsion. The short range forces include Born repulsion and specific adsorption forces. Born repulsive forces are a result of protruding structural points which can come into contact during coagulation. Specific adsorption forces are the result of molecular adsorption on the surface, particularly water adsorbed on the surface or in the hydration shell (Gast, 1976).

Electric double layer repulsion results when the diffuse layers of approaching particles overlap (Overbeek, 1952a). The work required to overcome the increase in free energy associated with the overlapping of the diffuse layers is the electric double layer repulsion (Gast, 1976). This repulsive energy is a function of the counter ion valence, counter ion hydration and electrolyte concentration as described by the Gouy and Stern models of the double layer.

A method of surveying the interaction between clay particles at various electrolyte concentrations can be obtained by adding the attractive and repulsive potential at each particle distance (Figure 3). The net particle interaction is primarily due to London-van der Waals attraction and electric double layer repulsion except at very small values of particle separation where short range repulsion results in a steep rise of the potential curve (see Figure 3). Since London-van der
Figure 3. Net interaction energy as a function of particle separation for three electrolyte concentrations (from van Olphen, 1977).
Waals attractive forces are similar within a certain type of clay mineral, the electric double layer repulsion largely determines whether clays are coagulated or dispersed (Gast, 1976). At high electrolyte concentrations, the net potential curve only shows repulsion at very small particle separations. Therefore, coagulation occurs at a maximum rate. At intermediate and low electrolyte concentrations, the coagulation process is slowed by a net long range repulsion, an energy barrier (Figure 3). The magnitude of this repulsive barrier is regulated by the range and magnitude of the electric double layer repulsion. Since compression of the double layer is ruled by counter ion hydration, concentration and valence, this simple stability theory expounds the Schulze-Hardy rule of indifferent electrolytes and the lyotrophic series for the coagulating power of cations and anions (van Olphen, 1977).

Hardy formulated the Schulze-Hardy rule in 1900 as follows (in van Olphen, 1977);

"The coagulation power of a salt is determined by the valence of one of its ions. This prepotent ion is either the negative or positive ion, according to whether the colloidal particles moves down or up the potential gradient. The coagulating ion is always the opposite electrical sign to the particle."

The lyotrophic series for the flocculation power of ions on clays decreases slightly in the order Cs>Rb>NH$_4$>K>Na>Li for monovalent cations and F1>Cl>Br>NO$_3$>I>CNS for anions (van Olphen, 1977). The lyotrophic series for cations also corresponds to decreasing ionic radius and increasing hydrated radius.
Coagulation Studies and Measurement of Coagulation Value

Historically, most of the studies on the coagulation of clay suspensions have dealt with crystalline layer type clay minerals. Determination of the coagulating mechanism of montmorillonite has received considerable attention. Slabaugh and Culbertson (1951) investigated the mechanism by which various inorganic salts affect the dispersion, viscosity and electrical properties of a hydrogen bentonite using a rotational viscometer. The effect of the coagulation of sodium montmorillonite on particle size, concentration of montmorillonite and ion exchange was studied by Kahn (1958). Coagulation with NaCl, CaCl$_2$, AlCl$_3$ and La(NO$_3$)$_3$ was measured by viscosimetry and optical transmission. Coagulation characteristics of montmorillonite have also been measured by the amount of HCl needed to reach a maximum flow time in a viscometer (Mitra and Sandelya, 1969) and measurements of Rayleigh ratios by light scattering techniques (Swartzen-Allen and Matejevic, 1976).

Schofield and Samson (1954) studied the mechanism of coagulation of kaolinite using a viscometer. Hsi and Clifton (1962) compared the coagulation behavior of three samples; metahalloysite, well crystallized kaolinite and a mixture of metahalloysite and poorly crystallized kaolinite. Coagulation by several chloride and sodium salts was measured as the settling time needed for a sharp boundary to appear between the settled floc and the liquid. This study was undertaken to determine if coagulation behavior would assist in characterizing clay samples in a way related to the origin and history of the clays. Coagulation rates for kaolinite, illite, montmorillonite and selected estuary sediments were
determined in solutions of various ionic strengths by Edzwald (1972) to describe the coagulation of clay minerals in estuaries. Relationships between the coagulation of montmorillonite, kaolinite, halloysite and illite and their exchangeable cations contents were examined by the changes in settling time using a soil hydrometer for Na, K, Mg and Ca cations by Krickenberger (1977). The influence of mineralogical composition, saturating ions and electrolyte concentration on the coagulation of selected crystalline clays were investigated to explain the reductions in hydraulic conductivity of many sodic soils (Arora and Coleman, 1979). Critical salt concentrations were optically determined at 530 nm after 24 hours of settling.

Recently, the coagulation of poorly and non-crystalline colloids have received more attention. Aomine and Egashira (1968) visually determined the coagulation value of several electrolytes on some allophanic and crystalline clays to determine if coagulation behavior is an aid for characterizing allophanic clays. Also the effects of pH and clay concentration were preliminarily examined. Horikawa and Hirose (1975) investigated spectrophotometrically the coagulation rate of montmorillonite, hydrated halloysite, allophane and imogolite with several inorganic and organic electrolytes. Horikawa in a series of papers (1975a, 1975b, 1976) compared the electrokinetic behavior of allophane and imogolite and binary mixtures of imogolite with montmorillonite, kaolinite, hydrated halloysite and allophane using a micro-electrophoresis technique. The mode of particle association of binary mixtures of imogolite and other clay minerals was examined by electron microscopy using a freeze-etching technique (Horikawa et al., 1976).
Results of coagulation studies reported in this section are integrated into the Results and Discussion section.
III. PRELIMINARY INVESTIGATION: SEPARATION OF CLAY FROM SOIL MATERIAL

When the true nature of a colloid is investigated, it is important to disperse the clay fraction in such a manner not to induce changes in the nature and properties of the colloid. Dispersion pretreatments often used with amorphous and poorly crystalline clays can influence the true nature of the clay (Dingus, 1973). The objective of this preliminary investigation was to find a procedure to separate a significant amount of clay from bulk soil samples without altering the morphology of the clay colloid. Transmission electron microscopy (TEM) was used to examine particle morphology.

Methods to disperse well-crystallized clays are somewhat standardized while the methods to separate poorly crystalline clays vary among researchers. Aomine and Egashira (1968) separated the clay fraction from allophanic and crystalline clay soils (including montmorillonite) by treating with 6% \( \text{H}_2\text{O}_2 \) on a hot plate and dispersing with slight amounts of HCl or NaOH after sonic vibration. Horikawa and Hirose (1975) removed iron oxides from crystalline clay samples (montmorillonite, hydrated halloysite and kaolinite) before mechanically dispersing in water. Hsi and Clifton (1962) dispersed halloysite and kaolinite samples (<10μ) in distilled water with a malted milk mixer. Dingus (1973) investigated the effect of peroxide and DCB pretreatments, along with several dispersion methods, on the induced changes in morphology and composition of amorphous clays from weathered tephra. (Halloysite was also observed in some samples.) Results of his study are summarized as follows:

A. Not all of the dispersion methods were successful in dispersing
B. Slightly acid distilled water was the most effective dispersant for ando soils;

C. The peroxide pretreatment for samples high in imogolite caused an increase in iron oxide particles to be oriented along imogolite strands;

D. Samples receiving both $\text{H}_2\text{O}_2$ and DCB pretreatments form abundant amounts of gel material not present before pretreatments.

It was the intention during present studies to use the clay mineral as formed in situ. Therefore, special precautions were taken to keep the soil moist and not to remove organic matter and iron coatings. Soil samples (described in the following section on MATERIALS AND METHODS) were mechanically agitated by air jetting for 3 minutes at 25 psi in 250 ml of various dispersants. Samples were then brought to volume in a Bouyoucos cylinder with distilled water and the particle size of the $<2 \text{ mm}$ fraction determined by a modified pipette method (Kilmer and Alexander, 1949; Chu and Davidson, 1953). The effectiveness of each dispersant was determined by comparison of similar samples dispersed in sodium pyrophosphate, a standard dispersing agent (Yaalon, 1976). The morphology of the clay was examined by TEM. A Phillips EM 300 operated at 80 or 100 KV and 15-20 $\mu\text{A}$ beam current was used to observe dilute suspensions of clay material applied by drop method to Formvar (Gard, 1971) carbon-coated copper grids.

The smectite sample (D-3-S) was effectively dispersed in distilled water (Table 1). An electron micrograph (Plate 1) displays the thin plate morphology common for smectites.
Table 1. Equivalent spherical diameter (% by weight) of smectite (D-3-S), hydrated halloysite (D-2-H) and imogolite-allophane (D-2-A) soil samples determined with different dispersants.

<table>
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<th>Dispersant</th>
<th>Equivalent Spherical Diameter</th>
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<tr>
<td></td>
<td>&gt;53μ</td>
<td>53-20μ</td>
<td>20-5μ</td>
<td>5-2μ</td>
<td>&lt;2μ</td>
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<td>Smectite (D-3-S)</td>
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<tr>
<td>Na-pyrophosphate</td>
<td>28.5%</td>
<td>21.4%</td>
<td>13.9%</td>
<td>7.0%</td>
<td>29.2%</td>
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<td>Distilled water</td>
<td>27.9</td>
<td>19.7</td>
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<td>Imogolite-allophane (D-2-A)</td>
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<td>Na-pyrophosphate</td>
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<td>25.2</td>
<td>14.6</td>
<td>6.0</td>
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<td>2% Na₂CO₃</td>
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<td>43.8</td>
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<td>0.2% Na₂CO₃</td>
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<td>25.2</td>
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<td>0.1% Na₂CO₃</td>
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<td>0.05% Na₂CO₃</td>
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<td>32.9</td>
<td>9.9</td>
<td>4.6</td>
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<tr>
<td>Na-pyrophosphate</td>
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<td>18.6</td>
<td>25.2</td>
<td>9.6</td>
<td>13.3</td>
</tr>
<tr>
<td>2% Na₂CO₃</td>
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<td>37.4</td>
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<tr>
<td>0.2% Na₂CO₃</td>
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<td>19.6</td>
<td>22.0</td>
<td>9.5</td>
<td>13.7</td>
</tr>
<tr>
<td>0.1% Na₂CO₃</td>
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<td>22.7</td>
<td>9.3</td>
<td>13.1</td>
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<tr>
<td>0.05% Na₂CO₃</td>
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<td>14.8</td>
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<tr>
<td>pH 5.0 HCl</td>
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<td>5.7</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>pH 3.5 HCl</td>
<td>31.7</td>
<td>63.8</td>
<td>3.8</td>
<td>0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Plate 1. Electron micrograph of sample D-3-S (smectite) dispersed in distilled water.
Hydrated halloysite (D-2-H) dispersed in $\text{Na}_2\text{CO}_3$, but not in acidified distilled water (Table 1). A 0.05% $\text{Na}_2\text{CO}_3$ solution was the most effective dispersant. Both tubular and spheroidal halloysite were observed in transmission electron microscopy (Plate 2). These morphologies are typical of hydrated halloysite found in western Oregon volcanics (Dingus, 1973; Harris, 1973; Taskey, 1978).

The poorly crystalline material (allophane-imogolite D-2-H) dispersed well in weak solutions of $\text{Na}_2\text{CO}_3$ and $\text{HCl}$ (Table 1). The sample dispersed in slightly acid distilled water contains imogolite (strand like material) and probably allophane (Plate 3) existing in the larger aggregates of various sizes and shapes (Hemni and Wada, 1976). Dispersing the same sample in 0.2% $\text{Na}_2\text{CO}_3$ destroys the "strand-like" morphology of imogolite by forming a gel-like material (Plate 4) not present in the slightly acid dispersed sample. Therefore, slightly acid distilled water (pH 4.5 $\text{HCl}$) was chosen as the dispersant for sample D-2-A. No attempt was made to separate allophane from imogolite in this sample.
Plate 2. Electron micrograph of sample D-2-H (hydrated halloysite) dispersed in 0.05% Na$_2$CO$_3$. 

0.5μ
Plate 3. Electron micrograph of imogolite and allophane from sample D-2-A dispersed in slightly acid distilled water (pH 4.5 HCl).
Plate 4. Formation of gel material in sample D-2-A (imogolite-allophane) after dispersion in 0.2% Na$_2$CO$_3$. 
IV. MATERIALS AND METHODS

Source of Samples

Soil samples were collected from an unstable landscape on the Dome Creek drainage in the watersheds of the Middle Fork Willamette River and Hills Creek Reservoir (Figure 4). The site is located in eastern Lane County, Oregon (NW¼, NW¼, Sec 31, T.24S., R.4E.). Youngberg et al. (1971) and Taskey (1977) have described the soils, geology, vegetation and landscape of the sampling area. The location of the three soil samples and the sampling sites used in other studies at Dome Creek are given in Figure 5. The sample of hydrated halloysite (D-2-H) was taken at the same location as hydrated halloysite (MFW-D-1-C) found by Taskey (1977).

Nature of Clay Fraction

Methods

Each clay sample was characterized using X-ray diffraction (XRD), differential thermal analysis (DTA), ion exchange capacity at pH 7.0 and percent organic carbon. Samples were stored in sealed plastic bags at 4°C to prevent drying. The clays were separated from the bulk soil using the chemical dispersants discussed in the previous section. Portions of each sample were prepared for XRD analysis (Taskey, 1977) and oriented on glass slides using the paste method (Theisen and Harward, 1962). XRD patterns were obtained using Cu Kα radiation at 35 KV and 25 mA on a Phillips Norelco X-ray diffractometer with a focusing monochromator and scintillation counter.
Figure 4. Location of Dome Creek sampling site.
Figure 5. Location of samples D-3-S (smectite), D-2-A (imogolite-allophane), D-2-H (hydrated halloysite) and sampling sites used in other studies at Dome Creek.
Differential thermal analyses were obtained with a Dupont model 900 Differential Thermal Analyzer equipped with a high temperature cell (1200°C) and micro-cup sample holders with matched platinum-platinum 13% rhodium thermocouples. Samples analyzed were Mg saturated using MgCl$_2$ wash solutions followed by several water rinses and allowed to equilibrate over saturated Mg(NO$_3$)$_2$·6H$_2$O (54% relative humidity). Al$_2$O$_3$ was used as a thermal reference and nitrogen gas as an inert atmosphere.

The ion exchange capacity at pH 7.0 was measured essentially according to the procedure of Chichester et al. (1970). Chloride analyses used in the determination of anion exchange capacity were determined potentiometrically with a chloride ion electrode (La Croix et al., 1970; and Cantliffe et al., 1970). Organic carbon contents were determined with a Leco carbon analyzer (model WR-12).

Results of Characterization

Smectite (D-3-S). The clay sample, D-3-S, is principally composed of smectite as depicted in the XRD and DTA patterns (Figures 6 and 7, respectively). Expansion to the two layer complex upon solvation with ethylene glycol and glycerol and rehydration of the heated potassium saturated XRD sample are characteristic of montmorillonite (Harward et al., 1968). The DTA curve (Figure 7) shows a large low temperature water loss, a dehydroxylation endotherm at about 670°C and an S-shaped endothermic-exothermic peak system at about 900°C which is also characteristic of montmorillonite (Mackenzie, 1970). Some zeolite and possibly beidellite are also present in the sample. The consistent 9Å spacing on the XRD pattern is indicative of zeolite (American Society
Figure 6. X-ray diffraction pattern of sample D-3-S (smectite).
Figure 7. Differential thermal analysis patterns of smectite (D-3-S), imogolite-allophane (D-2-A), and hydrated halloysite (D-2-H).
for Testing Materials, 1957), while the presence of beidellite is suggested by the small shoulder at 14.7Å on the Mg-glycerol XRD pattern (Harward et al., 1968) and the endotherm at 516°C on the DTA pattern (Mackenzie, 1970).

Amorphous/Poorly Crystalline Material (D-2-A). Sample D-2-A gives an XRD pattern (Figure 8) characteristic of allophane and other non-crystalline materials (Wada, 1977). Characteristic imogolite morphology was observed in transmission electron microscopy (Plate 3), but the broad reflections typical of imogolite (Yoskinaga and Aomine, 1962) did not appear in the XRD pattern. This may result from a low amount of imogolite in the sample (no attempt was made to determine the percentage of imogolite in the sample) and the lack of any "pretreatment cleanups" in dispersing the clay fraction (Wada and Tokashiki, 1972; and Inoue and Wada, 1971). A large exotherm present on the DTA pattern (Figure 7) at 250-430°C obscures any chance of a small endothermic peak characteristic of imogolite at 390-420°C (Yoshmaga and Aomine, 1962) or the lack of an intermediate temperature endotherm characteristic of allophane (Wada, 1977). Since an inert atmosphere (N₂) was used in the DTA, the exotherm should not result from organic matter. This exotherm may be due to plant opal (Welding and Drees, 1976; and Taskey, 1977).

Imogolite and allophane are considered to be the major materials present in sample D-2-A. Imogolite was positively identified in TEM and allophane was strongly suggested by results from TEM and XRD. Allophane is also often associated with imogolite in Ando soils (Wada, 1977).

Hydrated Halloysite (D-2-H). The XRD patterns and DTA curves indicate the presence of hydrated halloysite in sample D-2-H (Figures 9 and 7).
Figure 8. X-ray diffraction pattern sample D-2-A (imogolite-allophane).
Figure 9. X-ray diffraction pattern of sample D-2-H (hydrated halloysite).
XRD patterns exhibit the irreversible dehydration characteristics of hydrated halloysite; a 10-11Å spacing when fully hydrated, collapsing to 7.5Å upon heating to 105°C and remaining in the dehydrated state (7.6Å) when equilibrated at 54% relative humidity. In the glycerol solvated Mg saturated sample (heated to 105°C), partial collapse was observed (7-10Å spacing) which is expected for hydrated halloysite (Askenasy et al., 1973). The 02,11 peak intensity (4.46Å) was at least half that of the 7-11Å peak, which indicates spheroidal halloysite (Brindley, 1961; Dixon and McKee, 1974). Spheroidal halloysite was also observed in TEM (Plate 2). The DTA pattern of sample D-2-H contains a large low temperature endotherm and an asymmetric dehydroxylation endotherm, both associated with hydrated halloysite (Mackenzie, 1970).

The ion exchange capacity at pH 7.0 and percent organic carbon for the three clay samples are given in Table 2.

**Procedure to Measure Critical Coagulation Concentration**

Each dispersed clay was washed three times in the respective electrolyte and then rinsed three or four times in deionized water using a high speed centrifuge. After 3 or 4 rinses, no chloride was detected in the supernatant solution using a AgNO₃ test. The saturated clay was diluted to 0.2 percent suspension with deionized water. A series of 6 ml test tubes containing 2 ml of the clay suspension was added to 2 ml of various concentrations of the same electrolyte used to saturate the clay.

The clay suspensions were thoroughly mixed and initial percent transmittance was measured for each sample at 546 nm with a Coleman Jr.
Table 2. Ion exchange capacity (meq/100 g.) at pH 7.0 and percent organic carbon of samples D-2-A (imogolite-allophane), D-2-H (hydrated halloysite) and D-3-S (smectite).

<table>
<thead>
<tr>
<th></th>
<th>D-2-A</th>
<th>D-2-H</th>
<th>D-3-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEC</td>
<td>22 meq/100 g</td>
<td>33 meq/100 g</td>
<td>73 meq/100 g</td>
</tr>
<tr>
<td>AEC</td>
<td>6</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>% C</td>
<td>1.55%</td>
<td>0.90%</td>
<td>0.83%</td>
</tr>
</tbody>
</table>
spectrophotometer. The initial transmittance was subtracted from the percent transmittance after 24 hrs. of settling, converted to a scale of 0 to 100 and plotted against molar concentration. This procedure was repeated using different concentrations to obtain a plot enabling the determination of the CCC (Figure 10). The CCC was taken as the concentration of electrolyte necessary to give a 50% transmittance reading. The pH of the supernatant solution of the clay suspension was measured at or near the CCC with a Beckman Model 4500 pH meter and a Fisher Bioprobe Combination electrode.

Four critical coagulation concentrations were determined for each different ion saturated clay:

control - sample at 20°C with no addition of acid or base;
4°C - sample at 4°C with no addition of acid or base;
acid - sample at 20°C with addition of one drop of HCl adding 0.15 meq (H⁺) per gram of clay;
base - sample at 20°C with addition of one drop of NaOH adding 0.15 meq (OH⁻) per gram of clay.

The plots of percent transmittance vs. molar concentration were not replicated and therefore do not lend themselves to statistical analyses.
Figure 10. An example plot of molar concentration vs. percent transmittance (%T) used to determine the critical coagulation concentration (CCC).
V. RESULTS AND DISCUSSION

**Smectite**

**Structural Model of Smectite**

The smectite model is often used in the description or application of electric double layer theory. Montmorillonite and some beidellite have been identified as the smectites composing sample D-3-S. These smectites are composed of an octahedral sheet of aluminum surrounded by two tetrahedral sheets of silica in which the oxygens are shared. Montmorillonite is characterized by a substitution of Mg for Al in the octahedral layer, while in beidellite, the substitution is Al for Si in the tetrahedral layer.

The isomorphic substitution is the principal source of negative charge on smectite clays and is compensated by the adsorption of cations on the surface of the clay. The octahedral substitution in montmorillonite results in a lower ionic attraction than the tetrahedral substitution in beidellite. The negative charge in both montmorillonite and beidellite is low enough to allow separation of the clay layers, although the amount of separation may differ with different compounds (Harward and Brindley, 1965; Sayegh et al., 1965; Harward et al., 1968).

Idealized half unit cell formulas for these smectites are given below (Borchardt, 1977):

- Montmorillonite: \((\text{Si}_4)(\text{Al}_{1.5}\text{Mg}_{0.5})_0\text{O}_{10}(\text{OH})_2\)
- Beidellite: \((\text{Si}_{3.5}\text{Al}_{0.5})(\text{Al}_2)_0\text{O}_{10}(\text{OH})_2\)

Values lower than the substitution of 0.5 Mg or 0.5 Al result from impurities found in most soils and/or the substitution of Fe\(^{3+}\) for Al\(^{3+}\).
in the octahedral sheet.

**Coagulation of Smectite**

The coagulation of the smectite clay (D-3-S) was more sensitive to the valence of the cation than the valence of the anion (Table 2). The CCC's for monovalent cations were greater than the CCC's for divalent cations and a decrease in hydration number resulted in a decrease in the CCC. Lowering the temperature from 20°C to 4°C did not influence the CCC of the suspension.

Since smectite is primarily negatively charged (MacEwan, 1961; Borchardt, 1977; van Olphen, 1977), it is not surprising that the properties of the cation exert a considerable influence on the CCC. The Schulze-Hardy rule and the lyotrophic series of coagulating power of cations predict that an increase in cation valence and decrease in hydrated radius will increase the coagulating power of the cation. These factors lead to a decrease in electric double layer repulsion and an increase in the rate of coagulation (van Olphen, 1977). Therefore, a lower concentration of electrolyte is needed to reach the CCC for cations of higher valence and/or smaller hydrated radius.

The CCC's of the control smectite decreased in the order of 

\[ \text{NaCl} > \text{NaNO}_3 > \text{KCl} > \text{Na}_2\text{SO}_4 > \text{K}_2\text{SO}_4 > \text{NH}_4\text{Cl} > (\text{NH}_4)_2\text{SO}_4 > \text{CaCl}_2 > \text{MgSO}_4 > \text{MgCl}_2 > \text{CaSO}_4. \]

Amine and Egashira (1968) found that the coagulation value of bentonite primarily depended on the valence and hydration number of the cation. The CCC (meq/l) decreased in the order of 

\[ \text{Na} > \text{K} > \text{NH}_4 > \text{Ca} > \text{Ba} > \text{Mg} > \text{Al} \]

for chloride electrolytes. Mitra and Sandilza (1969) reported similar
Table 3. Critical coagulation concentrations (meq/liter) for sample D-3-S (smectite). pH in parenthesis.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Control (20°C)</th>
<th>4°C</th>
<th>Acid (20°C)</th>
<th>Base (20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>10.0 (5.3)</td>
<td>10.0</td>
<td>4.0 (4.2)</td>
<td>16.0 (7.5)</td>
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<tr>
<td>KCl</td>
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<td>4.3</td>
<td>2.6 (4.5)</td>
<td>11.0 (7.3)</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>2.3 (5.0)</td>
<td>2.3</td>
<td>1.2 (4.4)</td>
<td>2.3 (6.4)</td>
</tr>
<tr>
<td>CaCl₂</td>
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<td>1.1</td>
<td>0.75 (4.6)</td>
<td>1.5 (7.1)</td>
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<td>MgCl₂</td>
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<tr>
<td>NaNO₃</td>
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<td>7.0</td>
<td>3.0 (4.5)</td>
<td>12.0 (6.6)</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>3.4 (5.5)</td>
<td>3.6</td>
<td>2.2 (4.5)</td>
<td>4.8 (6.5)</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>2.7 (5.7)</td>
<td>2.7</td>
<td>1.5 (4.2)</td>
<td>8.0 (6.8)</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>2.1 (5.3)</td>
<td>2.3</td>
<td>1.5 (4.3)</td>
<td>4.4 (6.8)</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0.36 (5.9)</td>
<td>0.35</td>
<td>0.11 (4.6)</td>
<td>1.3 (7.1)</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>0.90 (5.8)</td>
<td>0.90</td>
<td>0.31 (4.4)</td>
<td>1.4 (6.9)</td>
</tr>
</tbody>
</table>
results in the coagulation of a Tinpahari bentonite. Coagulation value decreased and swelling volume at the coagulation point decreased in the order of NaCl > KCl > NH₄Cl > MgCl₂ > CaCl₂ = Al(NO₃)₃ > Th(NO₃)₄. Arora and Coleman (1979) also found that Mg and Ca saturated smectite required a lower critical salt concentration than the Na saturated clay.

Mitra and Sandilya (1969) report that MgCl₂ has a lower coagulating power than CaCl₂. Since the ionic radius of Mg is smaller (hydrated radius larger) than Ca, the electric double layer theory would also predict MgCl₂ to have a larger CCC than CaCl₂. The results for smectite in Table 3 and that of Aomine and Egashira (1968) indicate the reverse.

This anomaly may result because Mg can be involved in hydroxy interlayer formation (Borchardt, 1977) as well as in reducing the double layer repulsion. Therefore, more MgCl₂ will be needed to coagulate the smectite. With the sulfate anion, the order of CCC is Na > K > NH₄ > Mg > Ca.

In the above situations, the same electrolyte was used to saturate as well as coagulate the clay. Most often the CCC or coagulating power of various electrolytes is reported for a specific saturated clay mineral. Commonly, Na montmorillonite or Na bentonite is used in which other ions are added as electrolytes. This coagulation process is more complicated because an ion exchange reaction of the counter ion for the ion on the clay surface occurs besides the build-up of the diffuse layer. (It is recognized, however, that all clay suspensions in water can age and the exchange of the added cations with aluminum plays an important role in coagulation (Swartzen-Allen and Matyevic, 1976).) When using Na montmorillonite as the specific saturated clay, the flocculating power of the counter ions still depends on the valence and hydrated radius of the
counter ion (Kahn, 1958; Edzwald, 1972; Mitra et al., 1972; Horikawa and Hirsoe, 1975; Swartzen-Allen and Matejevic, 1975; Swartzen-Allen and Matejevic, 1976).

The CCC of smectite was altered when the pH of the supernatant was changed using HCl or NaOH. As the pH of the smectite suspension increases, the CCC also increases (Table 3). Swartzen-Allen and Matejevic (1976) report an increase in the CCC with increasing pH and a spontaneous coagulation below pH 3.5 for various electrolytes on a Na saturated montmorillonite. They report that in the acidic pH range, the pH dependent charges located on the edge of the smectite are positively charged resulting in the edge to face association and partial coagulation before the addition of electrolyte. At neutral or basic pH's, the edge charges are neutral or negative, thus decreasing the edge to face association and subsequently increasing the CCC.

The ion exchange capacity at pH 7.0 of sample D-3-S consist entirely of cation exchange capacity (Table 2). Consequently, the edge charges are neutral or negative and a higher CCC is found for the base than the acidic or control smectite suspensions (Table 3). The sign of the edge charges are also illustrated by the negative electrophoretic mobility of a Na-bentonite clay (Figure 11) reported by Horikawa (1976). The negative electrophoretic mobility increases only slightly above pH 7.0 indicating the presence of a constant negative charge.

**Allophane and Imogolite**

**Structural Models of Allophane and Imogolite**

Several attempts have been made to deduce structural models for
Figure 11. Negative electrophoretic mobility of a Na-bentonite clay (Horikawa, 1976).
allophane and imogolite. Allophane is composed of fine hollow spheres or polyhedra 35 to 50Å in diameter. These particles can form aggregates of various sizes and shapes (Henmi and Wada, 1976). Imogolite consists of bundles 100-300Å in diameter (Yoshinaga and Aomine, 1962) made of finer filiform units. These finer units are tubes which have inside and outside diameters of 10 and 20Å respectively (Wada et al., 1970), which are separated by 18-22Å (Yoshinaga et al., 1968). Wada and Yoshinaga (1969) reported that the SiO₂/Al₂O₃ ratio of allophane ranged from 1.3-2.0, while the ratio of imogolite was 1.05-1.15.

Wada (1967) suggested a chain like structure made of silica tetrahedra and aluminum octahedra for allophane. Udagawa et al. (1969) proposed a kaolin like sheet structural model for allophane and suggested that the SiO₂/Al₂O₃ ratio and the chemical environment of formation of allophane are the controlling factors that determine the structure. Brindley and Fancher (1970) further elaborated the kaolin like sheet model by proposing a kaolin defect structure with vacant tetrahedral positions which account for the chemical composition commonly found for allophane. Okada et al. (1975) report that part of the aluminum in allophane is in four fold coordination and that the sheet structure rather than the chain structure exist.

Proposed models of allophane at SiO₂/Al₂O₃ ratios of 1.0 and 2.0 are given in Figure 12 (Okada et al., 1975). The aluminum in four fold coordination substitutes for Si in the tetrahedral layer at a rate of 30% as Al₂O₃/(SiO₂+Al₂O₃). A 30% substitution would give a lower SiO₂/Al₂O₃ ratio than the 1.3-2.0 SiO₂/Al₂O₃ ratio found for allophanes by Wada and Yoshinaga (1969). To allow the proposed model of allophane to
Figure 12. Structural models for allophane at SiO$_2$/Al$_2$O$_3$ ratios of 2.0 (a) and 1.0 (b) (Okada et al., 1975).
account for the variable SiO$_2$/Al$_2$O$_3$ ratio, Okada et al. (1975) proposed that vacant cation sites may exist in either the tetrahedral or octahedral layer. The amount and location of vacant sites depends on whether the SiO$_2$ content increases or decreases beyond the critical composition.

Imogolite was first described by Yoshinaga and Aomine (1962). Russel et al. (1969) indicated the structure of imogolite may consist of a gibbsite chain structure in which every third aluminum atom is missing. Si$_2$O$_7$ groups then fill the gap left by the missing aluminum atoms and link against AlOH chains. Wada and Yoshinaga (1969) also reported a similar structural model for imogolite. Their model consists of chains of octahedral aluminum linked by trigonal SiO$_2$ chains. Neither the Russel et al. (1969) or Wada and Yoshinaga (1969) structural models account for the tubular morphology of imogolite.

Cradwick et al. (1972) found evidence for an orthosilicate group in imogolite by converting silicate anions to ethers and identifying with gas chromatography. In this model, the orthosilicate anion could replace hydrogen from three hydroxyl groups surrounding a vacant octahedral site in the gibbsite sheet. The fourth SiO bond is neutralized by a proton and points away from the sheet. This structural model (Figure 13) requires a shortening of the O-O distance around the vacant octahedral site, thus accounting for curling of the gibbsite sheet. The postulated cylinder consists of 10, 11 or 12 unit cells of gibbsite which results in an outside diameter of 18.3-20.2Å, consistent with the morphology found by Wada et al. (1970).
Figure 13. Structural model of imogolite (Cradwick et al., 1972).
Coagulation of Allophane and Imogolite

The coagulation of allophane and imogolite is more sensitive to the valence of the anion than to the valence of the cation (Table 4). The CCC of the allophane-imogolite mixture decreases with increasing valence of the anion and increasing hydration number of the cation.

The CCC of divalent anion electrolytes was less than that of monovalent anions for allophane and imogolite. The valence of the cation did not alter the CCC. The Schulze-Hardy rule predicts that the electrical sign of the particle is opposite that of the coagulating ion. Therefore, since the valence of the anion greatly influences the CCC, the electrical sign of the allophane-imogolite particles should be positive at the prevailing pH.

The electrical sign of the allophane-imogolite mixtures have also been determined using microelectrophoresis and proton release and uptake data. Horikawa (1975a, 1975b, 1976) studied the electrophoretic behavior of allophane, imogolite and binary mixtures of allophane and imogolite (Figure 14). Imogolite is shown to have a positive electrophoretic mobility at lower pH's and zero electrophoretic mobility beyond pH 9-10. This is contradictory with the data from buffering curves of imogolite given below (Inoue and Wada, 1971).

<table>
<thead>
<tr>
<th>pH</th>
<th>Ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 5.5</td>
<td>$\text{Al-OH} \rightarrow \text{Al-OH}^+ \rightarrow \text{Al-OH}_2^+$</td>
</tr>
<tr>
<td>&gt; 8.0</td>
<td>$\text{Al-OH}_2^+ \rightarrow \text{Al-OH} \rightarrow \text{Si-OH} \rightarrow \text{Si-O}^-$</td>
</tr>
</tbody>
</table>
Table 4. Critical coagulation concentrations (meq/liter) for sample D-2-A (imogolite-allophane). pH in parenthesis.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Control (20°C)</th>
<th>4°C</th>
<th>Acid (20°C)</th>
<th>Base (20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1.4 (5.0)</td>
<td>1.5</td>
<td>4.3 (4.6)</td>
<td>0 (6.9)</td>
</tr>
<tr>
<td>KCl</td>
<td>1.6 (5.9)</td>
<td>1.8</td>
<td>3.8 (4.6)</td>
<td>0 (6.5)</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>3.0 (5.4)</td>
<td>3.8</td>
<td>5.0 (4.6)</td>
<td>0 (6.7)</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.7 (5.4)</td>
<td>1.9</td>
<td>3.6 (4.7)</td>
<td>0 (7.0)</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.94 (5.9)</td>
<td>0.95</td>
<td>2.1 (4.7)</td>
<td>0 (6.7)</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>2.0 (5.6)</td>
<td>2.4</td>
<td>4.5 (4.6)</td>
<td>0 (6.2)</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.05 (5.8)</td>
<td>0.07</td>
<td>0.14 (5.0)</td>
<td>0 (6.4)</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.07 (6.0)</td>
<td>0.08</td>
<td>0.15 (4.9)</td>
<td>0 (6.3)</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0.07 (5.6)</td>
<td>0.08</td>
<td>0.14 (4.4)</td>
<td>0 (6.3)</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0.04 (6.0)</td>
<td>0.05</td>
<td>0.09 (4.9)</td>
<td>0 (6.5)</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>0.12 (6.0)</td>
<td>0.14</td>
<td>0.28 (4.9)</td>
<td>0 (6.6)</td>
</tr>
</tbody>
</table>
Figure 14. Electrophoretic mobilities of allophane, imogolite and a mixture of 80% allophane and 20% imogolite (Horikawa, 1976).
However, in the Cradwick et al. (1972) structural model of imogolite (Figure 13) the SiOH's which create the negative charges at higher pH's are isolated on the inner surface of the imogolite tubes and do not add to the negative electrophoretic mobility of imogolite.

Allophane has both positive and negative electrophoretic mobilities consistent with the state of ionization of allophane as suggested by Wada (1967) as follows:

<table>
<thead>
<tr>
<th>pH</th>
<th>Ionization</th>
<th>Al ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;3</td>
<td>S=Si-OH</td>
<td>Al=(OH+0.5)2</td>
</tr>
<tr>
<td>7</td>
<td>S=Si-OH, O=Si-O-</td>
<td>Al=(OH+0.5)2</td>
</tr>
<tr>
<td>10</td>
<td>S=Si-OH, O=Si-O-</td>
<td>Al=(OH1.5)2</td>
</tr>
<tr>
<td>&gt;12-13</td>
<td>O=Si-O-</td>
<td>Al=(OH-0.5)2</td>
</tr>
</tbody>
</table>

The structural model for allophane allows for both Al and Si on the outside edges (Figure 12). In the pH 5.5-7.0 range, the binary mixture of allophane (80%) and imogolite (20%) gave an electrophoretic mobility curve similar to that of allophane alone. At pH's above pH 8.5, the mobility of allophane was decreased by the addition of imogolite and coagulation was indicated (Harikawa, 1976).

The CCC for the cations increased with decreasing hydration number, the opposite of that found for the montmorillonite sample. This agrees with the coagulation values found for an allophanic clay by Aomine and Egashira (1968). The phenomenon was explained as follows: anions
accompanying cations of larger hydration number have to approach more closely to the positive charged clay particles than those with cations of a lower hydration number. This causes a reduction in the double layer repulsive forces and the consequent increase in the rate of coagulation.

Aomine and Egashira (1968) found that the CCC (meq/1) decreased in the order of NaNO₃ > NH₄Cl > CaCl₂ > KCl > MgCl₂ > NaCl > Na₂SO₄ for an allophane clay sample. Similar results were found for an imogolite and allophane mixture, where NaNO₃ > KCl > CaCl₂ > MgCl₂ > NH₄Cl > NaCl > Na₂SO₄. The results agree well with the CCC's found for sample D-2-A, where the CCC decreased in the order NH₄Cl > NaNO₃ > CaCl₂ > KCl > NaCl > MgCl₂ > MgSO₄ > (NH₄)₂SO₄ = K₂SO₄ > Na₂SO₄ > CaSO₄. In all cases, the anion has the dominant role in the coagulation of allophane and imogolite. The data for NaNO₃ and NaCl also agree with the lyotrophic series for anions where NO₃⁻ is expected to have a lower coagulating power (higher CCC) than Cl⁻ anions (van Olphen, 1977).

Horikawa and Hirose (1975) also found that allophane was sensitive to anions, but the valence effect of anions was not so significant in an imogolite suspension. They reported that the measurement of the coagulation value of imogolite was complicated, however, by fine air bubbles which reduced the variation in optical density used to determine the coagulation value.

Increasing or decreasing the pH of the suspension has a considerable influence on the CCC of the allophane-imogolite mixture (Table 4). Decreasing the pH with a small amount of HCl increased the CCC of all electrolytes. Similar results are also reported by Aomine and Egashira (1968). When some NaOH was added to the allophane-imogolite suspensions (pH 6.0-7.0), the allophane-imogolite suspension coagulated without the
addition of excess electrolyte. According to the Cradwick et al. (1972) structural model of imogolite, at higher pH's the outer surface of the imogolite tubes is uncharged which decreases the absolute value of the surface potential. London-van der Waals attractive forces leads to a rapid coagulation of the imogolite tubes. Horikawa (1975b) hypothesized that the fibrous imogolite strands stick to allophane particles during coagulation resulting in an immobilization of allophane by the network of imogolite particles.

The CCC's found for the allophane imogolite sample were greater at 4°C than 20°C. This may result from the balance between the increase in the viscosity of the electrolyte solution and changes in the electric double layer repulsive force (Gast, 1977) at lower temperatures. The rate of sedimentation of a particle is inversely proportional to the viscosity of the medium (Voyutsky, 1975). Since the rate of sedimentation is decreased, a higher concentration of salt is required to produce a 50% transmittance reading in 24 hrs. The effect of lowering of the temperature on the electric double layer repulsive force was not determined for this sample.

**Hydrated Halloysite**

**Structural Model of Hydrated Halloysite**

Hydrated halloysite is a 1:1 layered alumino-silicate with two interlayers of water between platelets. The morphology of hydrated halloysite is often tubular or rod shaped (Bates et al., 1950). More recently however, platy and spheroidal halloysite have been identified (Sudo and Takakashi, 1956; and Souza Santos et al., 1966). Bates (1950)
proposed that the misfit between tetrahedral and octahedral sheets and the large distance between 1:1 layers may explain the tubular structure of halloysite. Brindley (1961) suggests that halloysite consist of layers similar to those in kaolinite, but the layers have irregular stacking and are randomly displaced parallel to the a and b axis. Both a monoclinic (Chukhrov and Zvayagun, 1966; and Kohyama et al., 1968) and triclinic unit cells (Honjo et al., 1954) have been proposed for halloysite.

Coagulation of Hydrated Halloysite

The coagulation of hydrated halloysite, like smectite, is sensitive to the valence of the cations (Table 5). Certain ion saturated clays however, \((\text{NH}_4\text{Cl}, (\text{NH}_4)_2\text{SO}_4, \text{and MgCl}_2)\) coagulate without the addition of any excess electrolyte (CCC equal zero). These electrolytes are not indifferent electrolytes for this sample. This phenomenon was not noticed in the coagulation of allophane-imogolite or smectite, nor is predicted from electric double layer theory.

Hydrated halloysite is predominately negatively charged in the pH range studied in this experiment. The electrophoretic mobility as a function of pH demonstrates the negatively charged surface of a hydrated halloysite studied by Horikawa (1976) (Figure 15). The significance of the valence of the cation on the CCC is consistent with the Shulze-Hardy rule for a negatively charged clay (van Olphen, 1977). Hsi and Clifton (1962) report that the higher the valence of the cation, the lower the concentration needed to coagulate samples of hydrated halloysite, well crystallized kaolinite and a mixture of hydrated halloysite and poorly crystallized kaolinite. Horikawa and Hirose (1975) also found that the
Table 5. Critical coagulation concentrations (meq/liter) for sample D-2-H (hydrated halloysite). pH in parenthesis.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Control (20°C)</th>
<th>4°C</th>
<th>Acid (20°C)</th>
<th>Base (20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.52 (5.8)</td>
<td>0.45</td>
<td>0 (4.8)</td>
<td>2.1 (7.0)</td>
</tr>
<tr>
<td>KCl</td>
<td>0.26 (6.2)</td>
<td>0.23</td>
<td>0 (4.6)</td>
<td>2.3 (7.1)</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>0 (5.7)</td>
<td>0</td>
<td>0 (4.4)</td>
<td>0.20 (6.8)</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.10 (6.2)</td>
<td>0.10</td>
<td>0 (5.4)</td>
<td>0.34 (6.9)</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0 (6.2)</td>
<td>0</td>
<td>0 (5.1)</td>
<td>0.10 (6.8)</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.01 (5.9)</td>
<td>0.01</td>
<td>0 (4.4)</td>
<td>1.5 (6.9)</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.30 (6.3)</td>
<td>0.24</td>
<td>0 (4.8)</td>
<td>1.7 (6.9)</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.22 (6.3)</td>
<td>0.14</td>
<td>0 (4.8)</td>
<td>1.4 (6.7)</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0 (4.9)</td>
<td>0</td>
<td>0 (4.1)</td>
<td>0 (6.4)</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0.01 (6.2)</td>
<td>0.01</td>
<td>0 (5.1)</td>
<td>0.80 (7.0)</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>0.04 (6.3)</td>
<td>0.04</td>
<td>0 (5.1)</td>
<td>0.30 (7.2)</td>
</tr>
</tbody>
</table>
Figure 15. Electrophoretic mobility of a hydrated halloysite (Horikawa, 1976).
coagulating power of cations is higher when the valence is higher for a sample of hydrated halloysite. Also, the larger the hydration number of the cation, the greater the CCC. The valence of the anion did not influence the CCC of sample D-2-H. This parallels the coagulation of smectite.

The saturation of D-2-H with NH₄Cl, (NH₄)₂SO₄ and MgCl₂ resulted in a coagulation behavior different than expected. In each case, no excess electrolyte was needed to coagulate the control suspension. KCl, NH₄Cl and (NH₄)₂SO₄ have been found to intercalate within the halloysite structure by replacing interlayer water (Wada, 1958, 1959a, 1959, 1963; Garrett and Walker, 1959; Carr et al., 1978). The CCC of the KCl saturated sample however, behaved as expected. The ammonium salts may result in hydrogen bonding between the hydrogen atom of NH₄ and an oxygen atom of the silicate layer (Wada, 1959a). The intercalation of ammonium salts in halloyosite may cause the peculiar coagulaion behavior, although the intercalation complexes can be destroyed by washing with water (Wada, 1958; and Carr et al., 1978). Krickenberger (1977) attributed changes in settling time of a halloysite to differential loss of water in the sample depending on the cation to which the sample was exposed. MgCl₂ does not form such an interlayer complex (Wada, 1959a), but still causes coagulation of halloysite clay. NaNO₃ saturated hydrated halloysite also coagulated with a very small amount of salt, much less than expected from the presence of the Na cation. The mechanism of coagulation for these electrolytes is not known.

The pH of the suspension exerts a considerable influence on the CCC of sample D-2-H (Table 5). The CCC of hydrated halloysite suspensions
increased as the pH was increased. As the pH decreased, more charges on the edge of the halloysite particle are positive. This is indicated in Figure 15 by the decreasing negative electrophoretic mobility below pH 6.0. Schofield and Samson (1954) found the negative edges are attracted to the positive edges and coagulation occurs without the addition of electrolyte for kaolinite. As the pH is increased above that of the control sample, the edge charge becomes more negative. Coagulation is now due to face-to-face bonding and the rate of coagulation is increased by the addition of electrolytes (Dixon, 1977).

Lowering the temperature from 20°C to 4°C decreased the CCC (Table 5). This is the opposite found for the other clay samples, although the smectite increase in CCC with temperature was very small. Balances between changes in viscosity and the electric double layer repulsive force have been mentioned as possible explanations for changes in the CCC with temperature. A specific relationship to explain the temperature effect on the coagulation of hydrated halloysite was not determined.

Implications to Natural Systems

The clay samples used in this study were obtained from soils on the watershed of Hills Creek Reservoir. The coagulation of different clays has obvious implications to reservoir turbidity. Youngberg et al. (1971) emphasized the prominence of poorly organized or amorphous components in surface suspended sediment samples at the reservoir. Suspended sediment analyses from samples at greater depths showed an increase in smectite materials. This suggests that amorphous components tend to remain in suspension longer than well crystallized smectite
minerals. Exchangeable calcium and magnesium dominated the exchange sites of the reservoir suspended sediment samples. Limited sampling of reservoir waters indicate concentrations of 0.20 meq/liter and 0.13 meq/liter of divalent and monovalent cations, respectively, and a pH of 7.1-7.4.

The coagulation data reported in this study (tables 3, 4, and 5) suggest that smectite would remain in suspension longer than the amorphous clays. This is postulated because the CCC's for the smectite are usually greater than those of the allophane-imogolite clay, particularly in the pH range (7.1-7.4) found in the reservoir waters. Due to the unusual coagulating power of imogolite, however, the allophane-imogolite mixture coagulated without the addition of excess electrolyte. Horikawa (1976) indicated that imogolite can also coagulate montmorillonite and hydrated halloysite clays in a similar fashion. However in this study, imogolite was not present in the smectite (D-3-S) or hydrated halloysite (D-2-H) samples.

Imogolite was not identified in the reservoir water samples, but its presence is strongly suggested from transmission electron microscopy of soil samples located in mass failures within the watershed of the reservoir in this study and by Taskey (1977). Assuming imogolite is present in the reservoir waters, no data is available as to the preferential attraction of imogolite to either smectite or allophane. If imogolite was strongly attracted to smectite over allophane, the imogolite would coagulate the smectite in preference to allophane leaving the amorphous allophane at the surface. This process may explain the results of the Hills Creek Reservoir Turbidity Study (Youngberg et al.,
1971). Although dissolved anion data is not available from the reservoir study, it is believed that electrolyte concentrations in the reservoir waters are too low to coagulate either amorphous or smectite clay without the addition of imogolite. The concentration of electrolyte is high enough, however, to coagulate any hydrated halloysite present in reservoir waters.
VI. SUMMARY

The coagulation of smectite and hydrated halloysite was sensitive to the valence and hydrated size of the cation, while the allophane-imogolite clay was sensitive to the valence of the anion and hydrated size of the cation. Certain electrolyte saturated hydrated halloysite clays, however, coagulated without the addition of any excess electrolyte. These data follow closely the expected coagulation predicted by the Shulze-Hardy rule and the lyotrophic series for cations and anions. As the pH of the coagulating medium was increased, the CCC's increased for hydrated halloysite and smectite and decreased for the allophane-imogolite clay. As the temperature was decreased from 20°C to 4°C, the CCC decreased for hydrated halloysite, increased for allophane-imogolite and remained unchanged for the smectite sample.


