

COLLOIDAL BEHAVIOR OF CLAY IN WHITEWARE SUSPENSIONS

BY

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TABLE OF CONTENTS

	<i>Page</i>
Acknowledgements	iii
List of Tables	vii
List of Figures	viii
Abstract	xi
1. INTRODUCTION	1
2. LITERATURE SURVEY	4
CLAY MINERALOGY	4
Classification	4
Kaolinitic Clay Structure	8
Clay Morphology, Charge, and Cation Exchange Capacity	9
COAGULATION AND DISPERSANT STUDIES	12
Terminology	12
Dispersion Mechanisms and Materials	14
Coagulation Mechanisms and Materials	17
Measurement Techniques: Equipment and Interpretation	21
ZETA POTENTIAL AND SUSPENSION BEHAVIOR	23
Definition	23
Zeta Potential a Measure of Stability	23
Zeta Potential Measurement Techniques	24
PLASTICITY STUDIES	25
Definition	25
Measurement Techniques	26
REFERENCES	28
3. A CRITICAL EVALUATION OF DISPERSANTS	34
INTRODUCTION	34
EXPERIMENT PROCEDURE	37
Suspension Composition	37
Dispersion Composition	40
Suspension Preparation	40
Measurement Methods (rheology and pH)	42
RESULTS AND DISCUSSION	44
Effect of Dispersant Additions on Suspension pH	44
Effects of Dispersant Additions on Rheology	47
Correlation with Surface Area	51

Effects of 1:1 Dispersant Addition	53
Normalized to Na ⁺ Concentration	56
SUMMARY AND CONCLUSIONS	57
REFERENCES	59
4. EFFECTS OF IONIC CONCENTRATION	62
ON RHEOLOGY	
INTRODUCTION	62
EXPERIMENT PROCEDURE	64
Suspension Composition	64
Chemistry of Salt Solutions and Dispersants	65
Batching and Mixing	66
Rheology and pH Measurement	67
RESULTS AND DISCUSSION	68
Effect of Salt Additions on Suspension pH	68
Effects of Salt Additions on Suspension Rheology	74
Effects of Dispersant Additions	83
Double Layer Thickness	84
Affinity of Salt Species	87
SUMMARY AND CONCLUSIONS	88
REFERENCES	90
5. ZETA POTENTIAL MEASUREMENTS ON	92
DISPERSED AND COAGULATED SUSPENSIONS	
INTRODUCTION	92
EXPERIMENT PROCEDURE	95
Suspension Composition, Chemistry and Preparation	95
Measurement Method (/electrophoretic Mobility)	96
RESULTS AND DISCUSSION	98
Effect of pH on the Suspension ζ -potential	98
Effects of Three Dispersants to the Suspension ζ -potential	100
Effects of Salt Addition to the Suspension ζ -potential	104
SUMMARY AND CONCLUSIONS	107
REFERENCES	108
6. EFFECT OF CATION CONCENTRATION	110
ON PLASTICITY	
INTRODUCTION	110
EXPERIMENT PROCEDURE	112
Plastic Body Composition	112
Plastic Body Chemistry	112
Plastic Body Preparation: <i>Body A</i>	114
Plastic Body Preparation: <i>Body B</i>	114
Plastic Measurement Method	115
RESULTS AND DISCUSSION	117

Effect of Cation Concentration on <i>Body A</i> Plasticity	117
Effects of Aging and Non-Aging on <i>Body B</i> Plasticity	119
Effects of Dispersed and Coagulation <i>Body B</i> on Plasticity	120
SUMMARY AND CONCLUSIONS	122
REFERENCES	123
7. CONCLUSIONS	124
REFERENCES	127

List of Tables

<i>Table</i>		<i>Page</i>
I.	Testing variations between dispersant studies in the literature	36
II.	<i>Kaolin</i> and <i>batch</i> composition of the typical whiteware suspensions	38
III.	Evaluated dispersants with chemical formulas and abbreviations	39
IV.	<i>Batch</i> suspension apparent viscosity and pH as a function of the dispersants concentration	45
V.	Salt solubility and ICP concentration analysis	66
VI.	Cation contributions for distilled water and raw materials	67
VII.	Apparent viscosity and pH values as a function of cation concentration for all salts and dispersion levels	70
VIII.	Six salts critical coagulation concentration at three dispersion levels	77
IX.	Calculated double layer thickness for symmetrical electrolytes	87
X.	<i>Body A</i> composition of standard triaxial porcelain plastic body	113
XI.	<i>Body B</i> composition of industrial triaxial porcelain plastic body	113

List of Figures

<i>Figure</i>		<i>Page</i>
2-1.	The tetrahedral layer (a) and octahedral layer (b) present in kaolinite	5
2-2.	The gibbsite structure and brucite structure	6
2-3.	Schematic of kaolinite, mica, and montmorillonite	7
2-4.	Schematic of kaolinite aspect ratio	12
3-1.	<i>Batch</i> suspension pH as a function of the dispersant concentration	47
3-2.	<i>Batch</i> suspension apparent viscosity as a function of dispersant concentration (a) PAA and PMAA and (b) Na-silicate, SHMP, soda ash, and <i>aged 1:1</i>	48
3-3.	<i>Kaolin</i> suspension apparent viscosity as a function of dispersant concentration (PAA and soda ash)	49
3-4.	<i>Batch</i> suspension apparent viscosity curves minima, as a function of Na^+ concentration, for Na-silicate, soda ash, and PAA	50
3-5.	<i>Batch</i> suspension rheology with soda ash and Na-silicate mixtures	54
4-1.	Suspension pH with 0.02 mg/m^2 dispersant	69
4-2.	Suspension apparent viscosity as a function of cation concentration at three levels of dispersant $0.00, 0.02,$ and 0.05 mg/m^2	75
4-3.	Three distinct regions in the apparent viscosity versus cation concentration	76
4-4.	Onset of the CCC for monovalent and divalent cations with chloride salts	78
4-5.	A clear distinction between the onset of the CCC for the monovalent and divalent cations is shown with the sulfate salts	79
4-6.	Suspension apparent viscosity with NaCl and Na_2SO_4 normalized to cation concentration	79
4-7.	Suspension apparent viscosity with MgCl_2 and MgSO_4 normalized to	80

	cation concentration	
4-8.	Suspension apparent viscosity with CaCl_2 and CaSO_4 normalized to cation concentration	80
4-9.	Suspension apparent viscosity with NaCl , MgCl_2 , and CaCl_2 normalized to anion concentration.	81
4-10.	Suspension apparent viscosity with Na_2SO_4 , MgSO_4 , and CaSO_4 normalized to anion concentration	81
4-11.	Suspension apparent viscosity normalized to cation concentration over dispersant concentration range	84
4-12.	Calculated double layer thickness as a function of the ionic concentration for symmetrical electrolytes.	86
4-13.	Suspension apparent viscosity as a function of double layer thickness for NaCl , MgSO_4 , and CaSO_4	86
5-1.	Kaolin suspension ζ -potential as a function of pH, with and without Na-silicate	99
5-2.	Suspension ζ -potential as a function of dispersant addition for PAA, Na-silicate, and soda ash	101
5-3.	Suspension apparent viscosity as a function of Na^+ concentration and dispersant concentration for Na-silicate, soda ash, and PAA	102
5-4.	Suspension ζ -potential as a function of pH for PAA, Na-silicate, and soda ash	102
5-5.	Suspension ζ -potential and apparent viscosity as a function of CaCl_2 concentration	105
5-6.	Kaolin suspension ζ -potential as a function of pH for PAA additions and CaCl_2 additions, with 0.20 mg/m^2 PAA	106
6-1.	Applied pressure dependence and cohesion stress as a function of water content for plastic body (ball clay and water)	111
6-2.	Data generated from the HPASC at shear rate (0.5 rpm)	116
6-3.	Plasticity as a function of cation concentration for a generic triaxial body.	117

6-4.	Plasticity and suspension apparent viscosity as a function of cation concentration	118
6-5.	Ca ⁺² concentration as a function of apparent solids loading during industrial processing	119
6-6.	Cohesion stress as a function of water content for aged and non-aged plastic bodies	120
6-7.	Cohesion stress as a function of applied pressure dependence for two plastic bodies, dispersed and coagulated	121

Abstract

This research investigated the colloidal behavior of kaolinitic clay in aqueous suspensions. The foundation of most current clay suspension behavior is based on early studies conducted prior to the application of colloidal concepts in ceramic systems and also when many of the colloidal theories were being developed. Technological advances in colloid science and the application of the theories greatly enhance the interpretation of the clay suspension behavior. Kaolinitic clay is the primary component responsible for the colloidal behavior of in traditional ceramics because the clay accounts for over 90% of the total surface area and active charge sites.

The impact of cations and anions on colloidal behavior, specifically the dispersion and coagulation, of a whiteware suspension was examined using rheology and electrophoretic mobility measurements. The results indicate the cations are responsible for coagulating the suspension, including sodium, which has been labeled both a dispersant and a coagulant. The anionic species are responsible for dispersing the clay suspension, but zeta potential is an inaccurate measure of suspension stability.

The influence of chemistry changes via cation and anion additions observed in suspensions are also detected in plastic bodies. The plasticity measured by the cohesion stress decreases with increasing cation concentration. It is suggested that the magnitude of the cohesion stress directly influences the formability and stress gradients established during drying.

1. INTRODUCTION

This research investigated the colloidal behavior of kaolinitic clay in aqueous suspensions. The foundation of most current clay suspension behavior is based on early studies conducted prior to the application of colloidal concepts in ceramic systems, and also when many of the colloidal theories were being developed. Technological advances in colloid science and the application of the available theories greatly enhance the interpretation of the clay suspension behavior.

Five factors directly impact the suspension behavior: particle-particle interaction, solids loading of the system, particle size and distribution, particle morphology, and rheology of the suspension medium. The particle-particle interaction, which is the most influential, is a measure of the attractive and repulsive forces between the particles of a system, specifically in a suspension. This interaction is linked directly to the other factors. These forces are influenced by the charge on the particles within the suspension medium. The charge contribution of each particle is a function of the size, more specifically the surface area and available charge sites. As the solids concentration increases above a very dilute suspension, the interaction and flow of particles is also affected by the morphology of the particles along with particle size and distribution. Understanding and controlling these parameters is vital to process improvement.

The particle-particle interaction is linked to the charge distribution on the clay particles in a whiteware suspension because the clay particles comprise the majority of the suspension surface area and therefore active charge sites. The mineralogy of kaolinitic

clay involves a 1:1 sheet silicate with one silica-like layer and one gibbsite-like layer. This suggests that the suspension behavior combines the colloidal aspects of both the silica-like and gibbsite-like surfaces. The effect of dispersion and coagulation on the particle-particle interaction was assessed using rheology and electrophoresis measurements on suspensions and plastic bodies.

To evaluate the effects of dispersants on a clay suspension, five dispersants that are used in the whiteware industry were evaluated using kaolin and a typical porcelain composition suspension. The apparent viscosity, measured using steady-state shear conditions, determined the effectiveness of each dispersant. The investigated dispersants included Na-polyacrylic acid, Na-polymethacrylic acid, Na-silicate, Na-hexametaphosphate, and Na-carbonate. Additions were normalized to the surface area of the powders and the suspension pH was monitored. The rheological results demonstrated all dispersants, except Na-carbonate, were equally highly effective including blended ratios of Na-carbonate and Na-silicate, which had an interactive effect. These results are indicative of specific adsorption of the anionic species causing dispersion in clay suspensions.

In order to understand the influence of anions (Cl^{-1} or SO_4^{-2}) and cations (Na^{+1} , Ca^{+2} , or Mg^{+2}) on coagulation of a clay suspension, the rheology of a typical whiteware batch composition suspension was evaluated as a function of concentration and dispersion level. The effect of salt additions (NaCl , CaCl_2 , MgCl_2 , Na_2SO_4 , CaSO_4 , and MgSO_4) was analyzed by measuring the suspension apparent viscosity under steady-state shearing conditions. The rheology of sodium polyacrylic acid dispersed and non-dispersed batch suspensions as well as pH was also assessed. The results indicate rheological behavior of

the suspension is dependent on the cation concentration, and is essentially independent of the anion concentration.

To provide additional support, electrophoretic mobility measurements were used to evaluate the influence of the anions and cations on the dispersion and coagulation of a clay suspension. Clay suspensions were dispersed with sodium polyacrylic acid, sodium silicate, and sodium carbonate, and coagulated with CaCl_2 . Zeta potential (ζ -potential) values were calculated using the electrophoretic mobility measurements of the clay particles in suspension. Dispersion of the clay suspensions is due to specific adsorption of the anion species, and coagulation is due to cation species. Results suggest compression of the double layer over that of specific adsorption. ζ -potential values are not an effective measure of suspension stability.

Finally, the impact of coagulation and dispersion on the plasticity of two whiteware bodies, a standard triaxial porcelain and an industrial porcelain composition, were quantitatively assessed as a function of cation concentration. In the standard triaxial body, cation levels of individual batches were adjusted with CaCl_2 ; in the industrial body, cation levels were varied by CaCl_2 and by aging. The results demonstrate that increasing the cation concentration via deliberate batching, flocculating, or aging, reduces the plastic body cohesion stress, which is analogous to a plastic yield stress. It is proposed that the magnitude of the cohesion stress impacts the formability of a plastic body, and reduces stress gradient during drying.

It is clear from this work that the following conclusions can be drawn: Na^+ ions are not responsible for dispersing of a clay suspensions, the cation is responsible for coagulating a clay suspensions, and the cation concentration impacts the plasticity of the clay body.

2. LITERATURE SURVEY

CLAY MINERALOGY

Classification

In order to evaluate the behavior of a kaolinitic clay suspension, it is necessary to understand the mineralogy and the features of a clay particle as perceived in the literature. Clay minerals are silicates and belong to the subclass phyllosilicates, that are indicative of $[\text{SiO}_4]^{-4}$ tetrahedra joined together by sharing three of the four oxygens to form a sheet structure that is referred to as the tetrahedral layer.¹ The tetrahedral layer present in kaolinite is shown in Figure 2-1.² Within this subclass, the type of layer to which the tetrahedra is linked further defines the mineral structures. These layers have an octahedral coordination with the cations filling $\frac{2}{3}$ or $\frac{3}{3}$ of the octahedral sites, which are shown in Figure 2-2,³ forming a gibbsite-type or brucite-type layer, respectively. The gibbsite-type layer, which has a dioctrahedral layer organization, indicating there are two cations for every six OH^- anions, has a six-fold coordination of oxygen and hydroxyl anions around an aluminum cation. Minerals that contain this type of layer include kaolinite, halloysite, pyrophyllite, montmorillonite, and muscovite (mica). The gibbsite-type layer found in kaolinite is shown in Figure 2-1. The brucite-type layer, which has a trioctrahedral layer organization indicating there are three cations for every six OH^- anions, has a six-coordination of oxygen and hydroxyl anions except they surround a magnesium cation. Minerals that contain this type of layer include antigorite, chrysotile, talc, vermiculite, and chlorite.¹

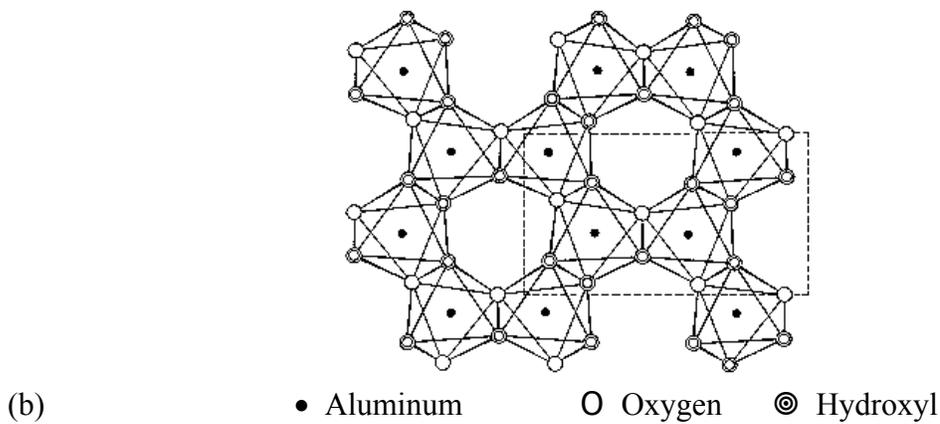
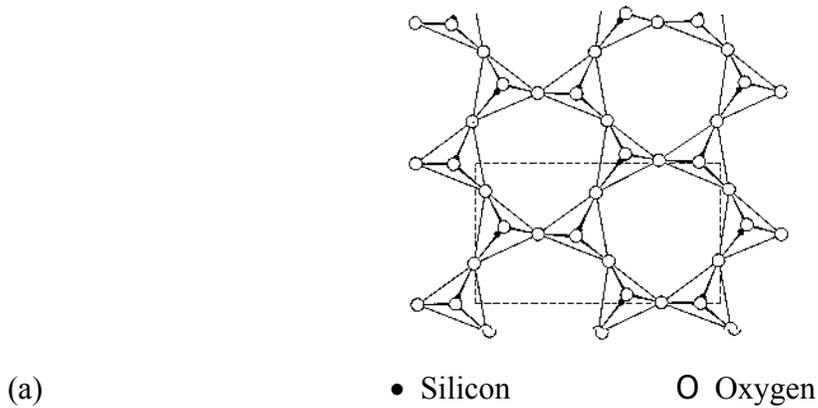


Figure 2-1. The tetrahedral layer (a) and octahedral layer (b) present in kaolinite.²

The number of tetrahedral layers that sandwich the octahedral layer further defines the classification of clay minerals. The two-layer structure or 1:1 structure contains one tetrahedral layer and one octahedral layer, while the three-layer structure or 2:1 structure contains one octahedral layer between two tetrahedral layers. Kaolinite is an example of a 1:1 dioctahedral phyllosilicate with a gibbsite-type layer. Kaolinite, whose name is derived from the Chinese word Kao-ling meaning “high ridge”, has an empirical chemical formula that may be written as either $\text{Si}_2\text{O}_5 \cdot \text{Al}_2(\text{OH})_4$ or $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.^{1, 4-7}

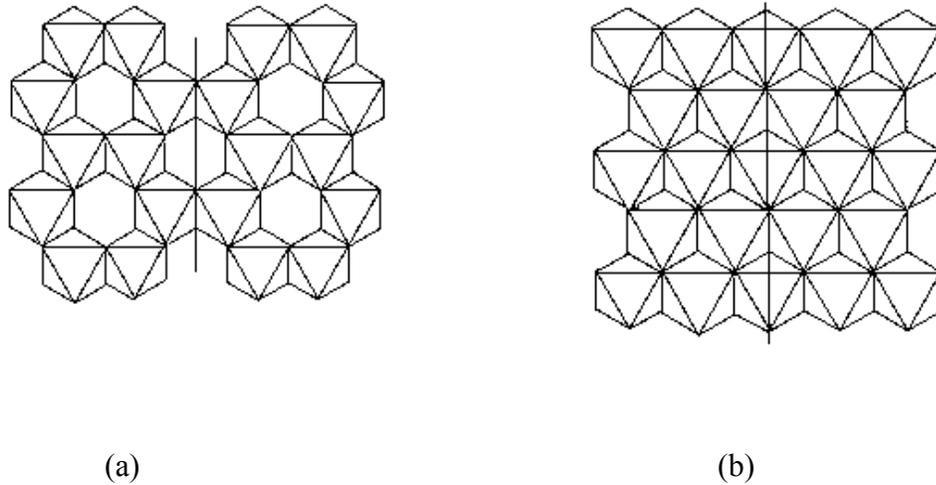


Figure 2-2. The gibbsite structure (a) illustrating that $\frac{2}{3}$ of the octahedral sites are occupied. The brucite structure (b) showing that all ($\frac{3}{3}$) the octahedral sites are occupied.³

Montmorillonite and muscovite (mica) are examples of dioctahedral phyllosilicates, with a 2:1 structure and a gibbsite-type layer. Montmorillonite, which is named after Montmorillon, France, where it was discovered, has a chemical formula of $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$.⁴ It is necessary to define further montmorillonite as a smectite, or as a swelling clay, indicating that water layers exist between the 2:1 sheets. The name Muscovite, which is in the mica mineral group, was derived from its use in muscovy glass and has a chemical formula of $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH,F})_2$. In addition, the muscovite, which is an illite, contains an interlayer, i.e., K, Na, or Ca, rather than water between the 2:1 layers.^{1, 4, 5} Figure 2-3 illustrates the difference between the three clay minerals, kaolinite, montmorillonite, and muscovite.²

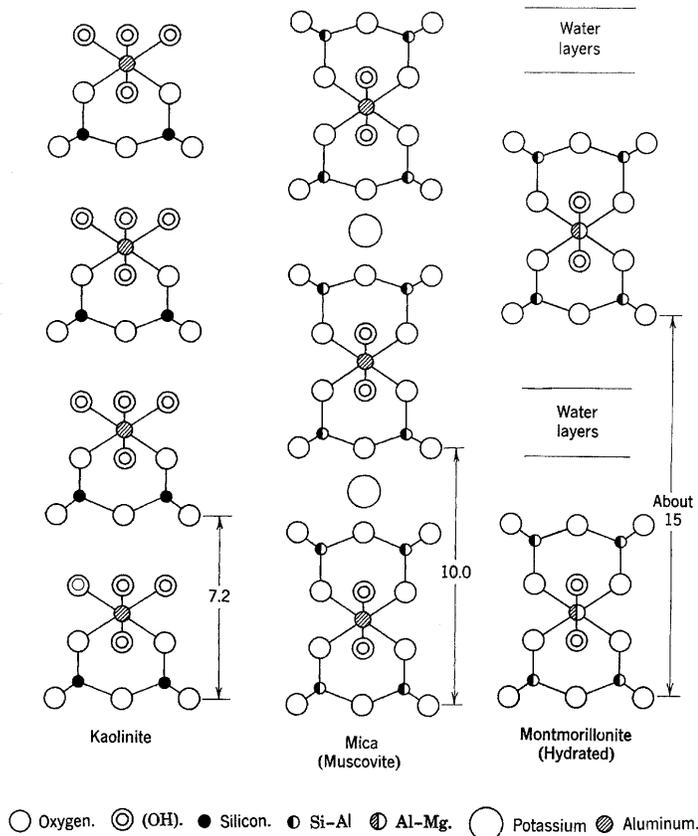


Figure 2-3. A schematic illustration of the layer structures of kaolinite, mica, and montmorillonite, showing the relative spacings between the layers (in Å). The kaolinite crystal is a 1:1 sheet silicate, while mica and montmorillonite are 2:1 sheet silicates.²

Because the octahedral layer is sandwiched between two tetrahedral layers in the 2:1 minerals, smectites and illites, the tetrahedral layer dominates the material behavior. The octahedral layer is only exposed on the edges, which accounts for less than 10% of the total surface area of the particle, (depending on the aspect ratio). In contrast, the gibbsite-type layer on the kaolinite particle is exposed on one basal plane and at the edge, the same as the silica-like layer.⁸⁻¹⁰

Kaolinitic Clay Structure

Kaolinite is the principle component of kaolin clay.⁸ The kaolinite 1:1 sheet has one tetrahedral layer (T) and one octahedral (O), with a thickness between the sheets of 0.72 nm, 7.2 Å.² The average thickness of kaolinite particles is 103 nm (± 30 nm)⁸ indicating the kaolinite particle contains approximately 143 sheets, which are referred to as a book, that stack in a T-O-T-O... sequence.^{1, 5, 11, 12} This insures that one side of the kaolinite particle is a silica-like layer and the other side is a gibbsite-like layer. It has recently been proposed that kaolinite stacks also exist with a pyrophyllite-like, or illite, terminal layer T-O-(T-O-T) and with a smectite terminal layer T-O-(T-O-T)-water-(T-O-T).¹³ The frequency of these non-traditional stacking patterns is difficult to determine because of the instability of kaolinite under the electron beam of the transmission electron microscope (TEM). During this study, 3000 micrographs were obtained providing approximately 100 interpretable images.¹³

The degree of crystallization apparently determines the type of non-traditional sequence is observed. Individual kaolinite sheets are hexagonal in shape, and are either well crystallized, which have highly defined corners, or poorly crystallized, which are smaller and have rounded corners.^{8, 12} The illite terminal layer is observed with well crystallized kaolinite samples, while the smectite terminal layer is observed with the poorly crystallized kaolinite samples. These non-traditional stacking sequences were observed in all of the kaolinite samples studied. These deviations from the traditional stacking sequence may explain some variability in the cation exchange capacity (CEC) of various kaolin clays. The presence of these non-traditional terminal layers may increase the CEC

because the CEC of illite and smectite clays are higher than kaolinite. These stacking features may also impact the isoelectric point (IEP) of kaolinite.

Clay Morphology, Charge, and Cation Exchange Capacity

The CEC of clay, which is expressed in terms of milliequivalents per 100 g of clay, is a measure of the exchangeable cations on the layer of the surface that may be exchanged with cations that are in the water.¹⁴⁻¹⁶ The cations exchanged are counter-ions that are attracted to the negative surface of the clay particle. The exchange capacity is a function of the surface area and the charge on the surface. This charge on the clay particle, in an aqueous medium, has been attributed to various mechanisms. The overall charge in a neutral pH environment is fairly well agreed to be net negative. Although the entire surface is not necessarily negative, both positive and negative zones are said to exist.¹⁷ The basal planes are usually considered to be negatively charged and the edge is considered to be positively charged. The mechanisms said to be responsible for the charge on the basal surface of a kaolinite particle may include: isomorphous substitution of Al^{+3} or Fe^{+3} ions for Si^{+4} ions in the tetrahedral layer and Mg^{+2} or Fe^{+2} ions for Al^{+3} ions in the octahedral layer, which is considered the primary source of the surface charge; broken bonds due to dissociable ions on the surface of the particle; and exchange of cation with the hydrogen from exposed hydroxyl groups.^{2, 5, 12, 16, 18-21} Recently, calculations have shown that the charge contribution due to isomorphous substitution of Al^{+3} for Si^{+4} is insignificant. It is suggested that the negative charge on the edges and the exposed hydroxyl groups on the octahedral layer contribute to the negative charge, and are pH sensitive. Specifically, at high pH, the negative charge increases as well as the

CEC.¹¹ The contribution of negative sites from the silica-like basal plane is reduced to an insignificant contribution as compared with the gibbsite-like basal plane and the edge, which ignores the mineralogical nature of both basal surfaces.

The charge on the edges is due to the protonation/deprotonation of the surface hydroxyl groups, which are sensitive to the suspension pH.¹⁸ The edge charge may be viewed as two fractured surfaces. One surface is gibbsite-like with a positive charge at a neutral pH (gibbsite isoelectric point = 9.8)²² and the other surface is silica-like with a negative charge at a neutral pH (point of zero charge = 2.4),²³ but in the presence of a small concentration of aluminum ions may become positive.¹⁶ Electron micrographs by Thiessen, a commonly referenced study, show kaolin particles with a negative gold sol attached primarily to the edges. This supports most of the literature that indicates the basal planes are negatively charged, and the edges are positively charged at a neutral pH.²⁴ However, Thiessen's study was conducted to show proof of higher adsorption activity at the crystal edge, not to show that the edges were positive, according to van Olphen.¹⁶ It was van Olphen who proposed from Thiessen's results that the edges were positively charged and the faces were negatively charged. This view omits the mineralogy difference between a 1:1 clay (kaolinite) and a 2:1 clay (montmorillonite) that clearly indicates the outer surfaces on kaolinite are not the same and should not be expected to have the same surface charge at a neutral pH. This also raises a question regarding the suspension pH environment and the sample preparation technique used by Thiessen. The pH could alter charge of the silica-like and alumina-like surface. Above the IEP, the surface will be negatively charge and below the IEP, the surface will be positively charged. The preparation of the kaolinite-gold sol samples could influence the

behavior of the gold particles; evaporation of water would impart capillary forces on the gold particles drawing them to the edges. The current use of cryogenic quick-freezing eliminates this problem and captures what is believed to be a more reliable picture of the suspension behavior.²⁵

The approximate aspect ratio of kaolinite is 10:1, face:edge, respectively, as shown in Figure 2-4.⁸ The face length may range from 0.1 to 10 μm .^{6, 9, 21} The surface area contribution from the edges has been calculated to be 16.7%¹⁰ and 18%⁸, and 11.8% was measured using nitrogen adsorption and shadowed micrographs.⁹ Therefore, the majority of the surface is accounted by the basal planes. For a smectite or illite, the basal planes are identical, tetrahedral silica-like layers, and would account for approximately 80% of the surface and active sites for cation exchange. Since on kaolinite, the basal planes are not identical, the silica-like layer and gibbsite-like layer each account for approximately 40% of the entire surface area.⁸ The diminished CEC is observed in kaolinite as compared to a smectite (montmorillonite), 7-20 and 75-100 milliequivalents per 100 g clay, respectively, indicating a reduction in the exchangeable cations with kaolinite.²

Based on the mineralogy of kaolinite, the IEP of kaolinite should be between that of silica (2.0-3.5) and alumina (8.5-10.4).^{8, 11} Published values reported by Ma and Eggleton show the point of zero charge (PZC) of kaolinite to be in the range of 3-5, which is they believe is indicative of the non-traditional stacking sequence of the kaolinite, therefore having a surface more similar to the silica.¹³ The measuring technique and the

morphology of the clay particle may also impact the measured charge on the kaolinite surface, which is addressed in a later section.

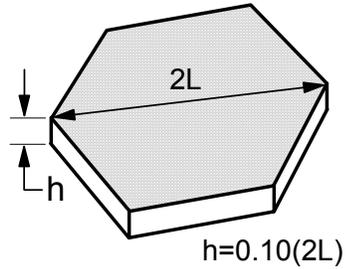


Figure 2-4. Schematic illustrates the aspect ratios of a kaolinite particle. The drawing shows an average particle using a value similar to that obtained from the SEM images.⁸

COAGULATION AND DISPERSANT STUDIES

Terminology

In the literature, the terms dispersion and deflocculation are frequently used interchangeably to describe the existence of sufficient repulsive forces between particles to prevent agglomeration and the formation of flocs in suspension. Dispersion is said to describe the “...*splitting of face-to-face associated aggregates into thinner flakes...*” or the delamination of the particle layers, while deflocculation describes separation of linked particles.¹⁶ The criterion for deflocculation has been described to be the minimum viscosity.²⁶ Dispersed systems are also considered to be stable indicating theoretically that the potential energy (V_T) of the system, which is the sum of the potential energy of electrostatic repulsion (V_R) and the van der Waals attraction (V_A), is substantially higher than $10kT$, with respect to the separation distance of two particles, according to DLVO theory.²⁷⁻²⁹ In this context, dispersion is considered to be induced by deliberate

alteration, chemically or mechanically, the particle–particle interaction such that the particles repel each other.

The definition of dispersion/stability is also a function of the industrial application. In traditional ceramic industries, a stable clay-based suspension contains sufficient dispersant to reduce the suspension viscosity while simultaneously preventing particle segregation. In advanced ceramic applications, stability is achieved with the lowest possible suspension viscosity.

Similarly, the terms coagulation and flocculation are often used interchangeably to describe the existence of sufficient attractive forces between particles in a suspension that promotes agglomeration. There is little distinction made between agglomeration due to existing attractive forces between particles (flocculation) and deliberate chemical alteration to induce particle agglomeration (coagulation). These terms are also used to describe a system that is unstable, or the onset of instability. Theoretically, these two terms indicate the potential energy (V_T) of the system and the derivative $\left(\frac{\partial V_T}{\partial h}\right)$ with respect to the separation distance between two particles, h , is equal to zero.²⁷⁻²⁹

Dispersion Mechanisms and Materials

The foundation for clay-water system behavior was examined in a series of articles written between 1941 to 1954.^{26, 30-41} The dispersion study by Johnson and Norton provided an overview of the work and theories to date, and presented rheological results from the addition of various materials to a clay suspension: bases (CsOH, LiOH, KOH, NaOH, Sr(OH)₂, Ba(OH)₂), basic salts (Na₂CO₃, Na₂SiO₃, (NH₄)₂C₂O₄), neutral salts (NaCl and Na₂SO₄), acids (HCl and H₂C₂O₄), and acid salts (NH₄Cl).²⁶ From the results, it was concluded that “...*(a) the charge on the kaolinite particle controls the degree of deflocculation and is governed by the type of cation and (b) the stability of the system is controlled by the anion of the medium and is governed by the type of anion preferentially adsorbed.*”²⁶ The charge on the particle was responsible for dispersing the suspensions and the results favor preferential adsorption of the anion. The charge on the particle frequently reflects to the degree of deflocculation, but it has also been observed that the mechanism of dispersion impacts the correlation between charge and degree of deflocculation. Deflocculation is influenced by cation type, monovalent, divalent, or trivalent, due to compression of the double layer. Higher charged cations require higher dispersant concentration to overcome the attractive forces with the compressed double layer.

Various studies that followed indicated that the Na⁺ ion was responsible for dispersing the clay-water systems.²⁶ Some specifically indicate that this applied only at low pH.^{6, 12, 42, 43} The initial addition of NaCl is said to reduce the effects of edge-to-face attraction by compressing the double layer thereby promoting dispersion, and further addition will reverse the behavior causing coagulation.^{43, 44} The dispersion of the clay systems may

also occur if the pH is increased causing the edges to become negatively charged, electrostatic stabilization. The overall negative surface of clay particles dictates, through colloidal behavior, that the counter-ions will compress the double layer, reducing the repulsion between particles and increasing the effective attraction between particles. Another study indicated that the potential of the particle is controlled by the cation species, which in turn controls dispersion, and the maximum potential develops when the only cations present are monovalent, and the cation concentration is very low.⁴⁵ In addition, various organic and inorganic compounds (i.e., sodium oxalate or citrate, sodium polyphosphates, sodium ligno sulfonate, and sodium carboxymethyl cellulose) were shown to disperse the clay-water system. It is suggested that dispersion occurs by these materials adsorbing to the edge of the kaolinite particles or possibly onto the hydroxyl faces; the mechanism of dispersion is either steric or electrosteric stabilization.^{46, 47} The cation directly governs coagulation by compressing the double layer, and indirectly influences dispersion by requiring sufficient anionic species concentration to overcome the attractive forces between particles. The adsorption of anions occurs on positive sites, mostly on the gibbsite-like surface. The use of sodium polyphosphates as a dispersant have been investigated as a function silicate structure, i.e., tripolyphosphate, tetraphosphate, and orthophosphate, and the variation of the ratio of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$.^{21, 48} It was suggested that the dispersion mechanisms of polyphosphates included replacing polyvalent cations with monovalent cations in the double layer, eliminating positive charge on the edge sites, adsorbing anions on the particle faces, or adsorbing anions on the edges. By using the various sodium polyphosphates, it was determined that the “...polyphosphates are adsorbed by kaolinite

and that exchangeable calcium and/or magnesium on the clay is partially replaced by sodium....” In very concentrated suspensions, the dispersion increases with the following ratios P_2O_5/Na_2O : 0.6, 0.5, and 1.0; the dispersion mechanism indicated for these inorganic dispersant was electrostatic. These results support the adsorption of the anion being responsible for dispersion, and suggest that substitution of sodium ions for either calcium ions or magnesium ions will reduce the degree of compression in the double layer, therefore reducing the effective attractive forces between particles.

Another common dispersant used for clay suspension is sodium silicate, which is also referred to as waster glass, containing various ratios in $Na_2O:SiO_2$. An early study of sodium silicate indicated the ratios depended on the company that manufactured the material. The effectiveness of sodium silicate on dispersing a clay system with various ratios was examined.⁴⁹ The results showed the most effective sodium silicate occurs when the ratio of $Na_2O:SiO_2$ is between 1:3.33 and 1:4 due to “... *the presence of colloidal silica which adsorbs the Na^+ ions thus disturbing their equilibrium with the OH^- ions and allowing the latter to become more active in forming hydroxyl ion complexes with the positive charged particles and ions on the clay particles and allowing the clay particles to reach maximum charge for that particular solution.*” This suggests that the dispersion is due to the adsorption of Na^+ ions by the colloidal silica, an increase in the double layer thickness, and a shift in pH, electrostatic stabilization. The sodium silicate in solution is in the form of polyions that retain the Na^+ ions on the edge of these layered cubic structures.^{50, 51} These polyions are adsorbed onto clay particles imparting dispersion by electrosteric stabilization.

Two common organic dispersants that are used with clay-water systems are sodium polyacrylate (PAA) and sodium polymethacrylate (PMAA). It is suggested by Celik, et.al. that PAA addition reverses the charge on the edge of the kaolinite particle and thereby lowers the edge isoelectric point and causes the dispersion.⁴³ Also, recoagulation occurs with PAA (and sodium metasilicate) when the Na^+ concentration exceeds 0.1 mol dm^{-3} . Various molecular weights of PMAA were evaluated as to their effectiveness to disperse a clay-water system. The results indicated that lower molecular weights were able to both electrosterically stabilize the suspensions and sequester the cations from flocculating.⁵² These organic polymers have also been examined in an alumina system, which correlates with the gibbsite layer of the kaolinite.⁴⁷ The study investigated the adsorption of the polymers, PAA and PMAA, as a function of the suspension pH, and the results indicated that the configuration of the polymer changes with pH. At low pH, the polymer functional groups are nondissociated, which reduces the number of negative charge sites, and the polymer forms small coils. This reduces the effectiveness of the polymer for dispersion by electrosteric stabilization. At high pH, the fraction of dissociated functional groups increases, which increases the number of negative charge sites. The polymer forms large chains, due to repulsion between negative functional groups, and are able to effectively cover more particle surface area imparting electrosteric stabilization.

Coagulation Mechanisms and Materials

During the dispersion investigation of the clay-water system by Johnson and Norton, it was shown for a hydrogen kaolinite that the basis of flocculation was the absence of charge on the particle.²⁶ With the addition of large quantities of electrolytes to the

suspension, the charge on the particle is reduced thus allowing the suspension to coagulate. The electrolyte concentration drives the sodium ions into the solvated water hull, which surrounds the particle, and neutralizes the adsorbed ions. The “swelling” of the water hull or layer of water that envelops the particle is reduced, and therefore the repulsive force between the particles is diminished. The reduced thickness of the surrounding layer allows the van der Waals attractive force to dominate the behavior of the particle system, whose results are comparable to the diffuse double layer described by the DLVO theory.

The diffuse double layer theory is the most generally accepted explanation for coagulation.²⁸ The attractive forces (coagulation) are controlled by the thickness of the diffuse double layer and repulsive forces (dispersion) are determined the particle-particle interaction. The thickness of the double layer is reduced or compressed by increasing the concentration of counter ions in solution, via electrolyte addition, causing coagulation.^{6,}

15, 19, 28, 43, 44 The effectiveness of coagulation is a function of the electrolyte counter-ion charge and concentration. Overbeek reviewed the work by Schulze and Hardy that indicated the ratio of mono-, di-, and tri-valent ions concentrations necessary to coagulate

are the inverse of the charge (z) to the sixth power $\left(\frac{1}{z}\right)^6$, i.e., $\left(\frac{1}{1}\right)^6$, $\left(\frac{1}{2}\right)^6$, and $\left(\frac{1}{3}\right)^6$,

respectively.²⁸ These ratios were derived from the theoretical definition of coagulation in which the potential energy of the system and its derivative, with respect to the separation distance of the particles, are both equal to zero. Certain contributing factor will reduce these ratios including greater adsorption of electrolytes with higher valency and low initial ζ -potential “...in the most extreme case, when the approximation of Debye and

Hückel holds well even to $\left(\frac{I}{1}\right)^2 : \left(\frac{I}{2}\right)^2 : \left(\frac{I}{3}\right)^2$."²⁸ The flocculation types and

measurement techniques also impact these ratios. Rapid and slow coagulation have been used to define and to applied to measuring the effects of electrolyte additions. Rapid coagulation is defined on the basis that every particle-particle encounter results in permanent agglomeration, while during slow coagulation only a fraction of the particle-particle encounters successfully create permanent agglomerates.⁵³ With this definition, time becomes an important parameter to assess the degree of coagulation within some time period. For comparative purposes, it is necessary that all testing use the exact same time allowance to determine coagulation, but this is impractical.

Different coagulation/flocculation structures have been proposed to describe the influence of chemical alteration, electrolyte concentrations and pH levels on the clay particle behavior. These clay structures include the 'house of cards', or edge-to-face, and the 'pack of cards', or face-to-face.^{2, 16, 19, 44, 45} The 'house of cards' structure forms agglomerates with the particle edges adhering to the basal planes creating a high volume structure. This structure is generated at low suspension pH values that promote positive edge sites to attach to the negative face of the particle.^{44, 45} The structure is said to exist in a relatively salt-free environment with monovalent cations, has higher apparent viscosity compared with the 'pack of cards' structure, and flocculates rapidly with large sedimentation volume.²

The 'pack of cards' structure occurs in highly concentrated salt environment with polyvalent cations, has a lower apparent viscosity compared with the 'pack of cards' structure, and coagulates less rapidly with a smaller sedimentation volume.² At low

solids content, these “...*roughly primary spherical particles...*” frequent reduce the suspension apparent viscosity.⁴⁵

Because the clay particle is viewed with two negatively charge basal planes, despite the mineralogical inconsistency with kaolinite, this ‘pack of cards, structure would be predicted less frequently than that of the ‘house of card’. In a recent investigation discussed by Güven, using electron microscopy with a fast cryofixation technique to lock the suspension structure, the structure of coagulated smectites showed only ‘pack of cards’ structure.²⁵ No ‘house of cards’ structures were observed with the smectite, which has two negatively charged basal surfaces. These results suggest that the ‘pack of cards’ structure would also be predominant with kaolinite, and that the ‘house of cards’ structure may not exist with the kaolinite. The viscosity differences previously supporting the different structures may be due to compression of the double layer by the cation with some affinity of the anionic species to the clay surface.

Various electrolytes have been used to coagulate the clay-water system including NaCl, which has also been associated with dispersion previously discussed.^{29, 43, 44} At low salt concentration levels, it is proposed that NaCl additions compresses the double layer of both positively and negatively charged regions thus reducing ‘house of cards’ attraction.^{16, 44}

Measurement Techniques: Equipment and Interpretation

Numerous approaches have been used to evaluate changes in a clay-water system due to dispersion or coagulation. Early studies evaluated the effectiveness of a dispersant by its rate of flow through a tube.⁴⁹ Coagulation studies were frequently evaluated by a series of tubes with varying levels of coagulant.^{16, 53} In order to investigate the rate of coagulation, rapid versus slow coagulation, microscope particle counting, light scattering, light adsorption, and turbidity techniques were utilized.^{28, 53} The rate of filtration and rate of fall has also been used to evaluate coagulation of a clay system.⁵⁴

Rheological equipment has advanced into a range of viscometers^{19, 43, 48, 52, 55} or viscosimeters,^{26, 55} rheometers^{56, 57}, and rheogoniometer.⁵⁸ The viscometers or viscosimeters defined as: "...instrument for the measurement of viscosity",^{59, 60} "...measurement of fluids under high rate of shear.",⁶¹ and "...the material is undergoing shear...." Rheometers are defined generically as "an instrument for measuring rheological properties."^{59, 60} The rheogoniometers are used to study normal stresses⁶² and are defined as "a rheometer designed for the measurement of normal as well as shear components of the stress tensor",^{59, 60} "the ability to measure normal forces and to determine their distribution as a function of radial distance and tangential shear stress." and "...a rotary rheometer...."⁶³ Geometry variability (i.e., cone and plate, parallel plate, and coaxial cylinders) and testing conditions (i.e., stress controlled, strain controlled, steady state, and dynamic testing) have advanced, too.

The interpretation of the rheological results generated from this equipment is usually divided into two groups. The first group extrapolates a yield stress, often referred to as the Bingham Yield Stress, to a shear rate of zero, from the generated viscosity versus its

shear rate data.^{19, 43, 58} The second group uses either an apparent viscosity (shear stress/shear rate ratio at a given shear rate for non-Newtonian fluids)²⁵ or a minimum viscosity to assess the changes in the suspension behavior.^{26, 48, 52, 56-58} The yield stress values give a measure of the force necessary to initiate flow of the suspension, but the behavior of the material in motion is not characterized. The apparent viscosity value can characterize the suspension in motion at a given shear rate. The chosen shear rate may correspond to the at conditions which the material is subjected during processing, making the apparent viscosity values more applicable.

ZETA POTENTIAL AND SUSPENSION BEHAVIOR

Definition

In the clay-water system, the clay particle has a negative charge in a neutral environment. From the surface of the particle to some distance into the bulk water solution, there exists charge decay, which is described by various theories including: diffuse double layer, Gouy-Chapman, Stern, Helmholtz and Debye-Hückel.^{14, 15, 64, 65} Within this region, or diffuse layer, there exist, according to some of the theories, a Helmholtz layer, a Stern layer or plane, and a surface of shear or shear plane. Zeta potential (ζ -potential) is a measure of the potential within the diffuse double layer, specifically the potential at the shear surface which is defined as “...the envelope where shear appears in the fluid adjacent to a rigid body when fluid and solid are in relative motion.”,⁶⁵ “...the potential at the surface of shear between the charged surface and the electrolyte solution.”,¹⁵ “...the average potential in the surface of shear.”,⁶⁴ or “...the electrostatic potential at, or very near to, the beginning of the diffuse double layer.”⁶⁶

Zeta Potential a Measure of Stability

The ζ -potential is often used to refer to the stability of a suspension, the term ‘critical ζ -potential’ was used to describe the minimum level required for a stable suspension, below which the system would flocculate. It was determined that the ‘critical ζ -potential’ was about 25-30 mV.²⁸ The ζ -potential is considered the determining factor as to whether particles will attract or repel each other. Specifically, aggregation behavior and flow is an important parameter while investigating stability.^{6, 14, 29} The increase of particle

electrokinetic potential, or surface charge, is considered to be responsible for dispersing a flocculated suspension.²⁹

Zeta Potential Measurement Techniques

The ζ -potential is measured using one of four methods: electrophoresis, electro-osmosis, streaming potential, or sedimentation potential.^{15, 64, 67} Electrophoresis induces the suspended particles to move under an applied electric field. The velocity of the particles under a known electrical field provides information regarding the surface potential of the particles. Electro-osmosis induces the liquid, rather than the particles, to move under an applied electric field. The measure of the liquid velocity or the volume of liquid moved provides the surface potential information. Streaming potential moves the liquid but instead of an applied electric field, a pressure gradient is applied to move the liquid. The pressure and the measured potential, which is established across the particle network or plug, provide the charge information of the system. Sedimentation potential is generated by charged colloidal particles settling in a liquid. Gravity or centrifugal force promotes the settling, and the potential of the system can be determined.

The electrophoresis method is the most commonly used, and has been the most successful owing to the practical application of this electrokinetic phenomenon.¹⁵ The ζ -potential is calculated by measuring the mobility of the particle and applying Smoluchowski's equation (1), where U_E is the electrophoresis mobility, ϵ is the permittivity, ζ is the zeta potential, and η is the velocity of the medium:

$$U_E = -\frac{\varepsilon\zeta}{\eta}. \quad (1)$$

Techniques include particle microscope, moving boundary, and zone electrophoresis. The most common of these is the particle microscope electrophoresis where the velocity is determined by measuring the velocity of a particle over a given distance. Multiple measurements are collected and averaged.

Electroacoustics is a recently developed technique to measure electrophoretic mobility by applying an electric field to a colloidal system and measuring the resulting sound wave.¹⁴ This effect is called the electrokinetic sonic amplitude or ESA. This technique allows concentrated suspensions to be measured as well as determining particle size.⁶⁸

PLASTICITY STUDIES

Definition

The definition of plasticity has evolved from the early description of the feel of the clay mass, or plastic body, between thumb and finger or ‘good’ versus ‘bad’ plasticity into a variety of more technical interpretations.^{69, 70} A review of plasticity by Bloor included definitions from a variety of sources including:⁷⁰

- *“That property which many bodies possess on changing from under pressure without rupturing, which form they retain when the pressure is ceases”* (Reis)
- *“That property which enables a material to be deformed continuously and permanently without rupture during the application of a force that exceeds the yield value of the material.”* (Wilson)

- *“That property of a body by virtue of which it tends to retain its deformation after the reduction of the deforming stress to its yield stress.” (A.S.T.M., 1949)*

Additional plasticity definitions include *“...in clay materials is essentially a matter of the bonding force between the clay mineral particles and the lubricating action of water between these same particles”¹²* and *“...the property which allows the material to be deformed (or shaped) without cracking or breaking, under the influence of an applied force, and to retain its new shape...describes the property without defining and units in which it might be measured.”⁶* With these definitions and the lack of definitive parameters, the term is difficult to completely comprehend. Some literature clearly states that it is a theoretical term⁶⁹ or that it is not possible to define.^{41, 71}

A recent view of plasticity that is less ambiguous was stated to be *“The extent and character of shear behavior in a body under pressure, within the elastic or reversible compaction pressure range.”⁷²*

Measurement Techniques

The definitions are sufficiently vague and open to interpretation such that wide ranges of plasticity measurement techniques have been proposed. The techniques include the parameters that are encompassed into most of the definitions: 1) yield value, 2) deformation without breaking, and 3) retention of form after removing stress. Bloor’s review of plasticity measurement techniques can be divided into eight categories, concentric-cylinder viscometer, tensile tests, compression tests, torsion tests, shear test, hybrid apparatus, and indenter tests. These methods combine rheology techniques used

with suspensions and techniques used with soils or metals.⁷³⁻⁷⁶ Each test establishes a relation between stressing force and strain produced, or between the shearing stress and rate of shear, by which the plasticity of a material is then quantified.

The pitfalls of numerous plasticity techniques were reviewed. Specifically, the sample testing was either unconstrained or too restrictive.⁷² The unconstrained testing limits the pressure that can be applied to the sample, which is part of the definition of plasticity. The sample must be constrained in order to apply necessary pressure to compact the material, and to be able to measure the shear behavior under pressure. Using principles from a soil mechanics technique called direct shear testing,⁷⁷ the High Pressure Annular Shear Cell (HPASC) was constructed to measure plasticity. The HPASC has been used effectively to measure variations in alumina and clay plastic bodies.^{72, 78, 79}

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3. A CRITICAL EVALUATION OF DISPERSANTS

INTRODUCTION

In the whiteware industries, the forming process usually begins with the preparation of a suspension. Depending on the product, a suspension can either be used without modification (such as a slip casting operation in the sanitaryware industry), de-watered in a filter press to create a plastic body (used by dinnerware and electrical insulator manufacturers), or spray dried to form granulate (for dry pressing of dinnerware and tile). Uniformity in the suspension preparation stage is essential for controlling subsequent processing steps.

The degree of dispersion, or how fluid a system becomes, plays an important role in the mixing, transportation, and filtration of the whiteware suspensions and ultimately the forming process. Even more important is the consistency of the suspension from batch to batch while maintaining all constituents in suspension -- that is, preventing the larger particles from segregating due to sedimentation. The suspension uniformity impacts all later steps of the production process.

The objective of this work was to explore the role of five dispersants on clay suspensions. We define clay suspensions as those having greater than 85% of the surface area accounted for by clay, of which a large fraction is kaolinite. The addition of dispersants to a clay suspension causes a reduction in viscosity by increasing the repulsive forces between the particles in the suspension. The three mechanisms which may be responsible for dispersion include: electrostatic, steric, and electrosteric; in this work, electrosteric stabilization is considered to be the dominant mechanism.¹⁻³ In the context of this work,

the terms dispersed and flocculated (or coagulated) are preferred over the terms stable and unstable because the definition of stability varies within the industry, and usually denotes the relative tendency of particles to remain in suspension. In the porcelain industry, a stable suspension is one in which the tendency for particle segregation is avoided by preparing the suspension at a dispersant concentration below that necessary to obtain the minimum viscosity. From an advanced ceramic processing perspective, a stable suspension is at the lowest possible viscosity. Also, we define flocculation to be due to the attractive (van der Waals) forces between particles in suspension and coagulation to be due to the deliberate alteration of surface charge by reducing repulsive forces between particles in suspension.

Comparing the results of previous dispersant studies is hindered by the different research conditions that were used, e.g., suspension compositions, chemical additives, processing procedures, or evaluation techniques. Some examples of these variations are illustrated in Table I.⁴⁻⁸

Failing to normalize the quantity of dispersant to the suspension surface area is the major underlying problem with existing dispersant studies that correlate the amount of dispersant to a weight percent or mass of material being dispersed. Clays have a large variation in surface area. The measured surface area of various kaolins has ranged from 13.5 to 26.9 m²/g (Kingsley, Kentucky-Tennessee Clay Co., Mayfield, KY and Edgar Plastic Kaolin, EPK, Zemex Minerals, Inc., Edgar, FL, respectively). Dispersion mechanisms are driven by the adsorption of the dispersing species onto available surface sites making surface area the critical parameter to explain the interaction between suspension behavior and dispersant. Therefore, it is essential to correlate the material

surface area with the amount of dispersant necessary to achieve a dispersed suspension, thereby permitting the comparison of various dispersants with a given material, as well as materials of different compositions or different sources.

Table I. Testing variations between dispersant studies in literature⁴⁻⁸

Suspension Composition	Chemistry Additives	Evaluation Technique	Ref.
Na-kaolinite and China clay (pH and dispersant concentration)	Na-metasilicate and Na-polyacrylate (g/100g clay)	Viscometer, with couette and cone and plate geometry, using Bingham yield stress	4
China clay (solids concentration)	Na-polyacrylate (2.1% by weight)	Rheogoniometer, steady state and oscillatory shear, with cone and plate geometry, using dynamic rigidity and steady shear on steady couple	5
Kaolin (pH and stability ratio)	Polyethylenimine (mg/g clay)	Spectrophotometer, using % light transmittance	6
Italian clay used for ceramic tile (dispersant molecular weight)	Na-polymethacrylate (weight %)	Viscometer, with cylindrical coaxial geometry, using apparent viscosity @ 27.9 s ⁻¹	7
China clay (pH and dispersant concentration)	Na-silicate and Na-metasilicate (g/100g clay)	Bingham yield stress	8

This work evaluated the efficiency of five sodium-based dispersants in two clay suspensions: Na-polyacrylic acid (PAA), Na-polymethacrylic acid (PMAA), Na-silicate, Na-carbonate, a 1:1 mixture of Na-carbonate and Na-silicate, and Na-hexametaphosphate. Additional ratios of Na-carbonate and Na-silicate (1:2 and 2:1) were examined in the kaolin suspension. The efficiency of the dispersant was measured by the change in apparent viscosity as a function of dispersant concentration. The suspension pH was also measured as a function of the dispersant and concentration.

EXPERIMENTAL PROCEDURE

Suspension Compositions

The first suspension was composed of only kaolin (referred to hereafter as *kaolin*) and the second suspension was composed of the components of a typical whiteware batch (referred to hereafter as *batch*). The typical *batch* composition is listed in Table II; the two clays (a kaolin and a ball clay) were calculated to contribute 93.8% of the total *batch* surface area, which was determined using the B.E.T multi-point method (Gemini III 2375 Surface Area Analyzer, Micromeritics, Norcross, GA). Due to the higher viscosity of the *kaolin* suspensions as compared to the *batch* suspensions (attributed to differences in particle packing and morphology), the *kaolin* suspensions were prepared at a lower solids loading (30 v/o) than that used for the *batch* suspensions (40 v/o). (The abbreviation v/o represents volume percent.)

Table II. *Kaolin and Batch* composition of the typical whiteware suspensions*

Raw Material	Supplier	Wt. % (d.w.b.)	Specific Surface Area (m²/g)	% of Batch Surface Area
Kaolin	Edgar Plastic Kaolin (EPK)	29.0	26.9	76.1
	Zemex Miniearls, Inc., Edgar, FL			
Ball Clay	Todd Light	7.0	25.9	17.7
	Kentucky-Tennessee Clay Co., Mayfield, KY			
Alumina	A10 Alcoa, Leetscale, PA	12.5	1.0	2.7
Quartz	Ogledbay Norton Industrial Sands, Inc. Glenford, OH	29.5	0.9	1.2
Nepheline Syenite	A200, Unimin Canada Ltd. Nephton/BlueMountain, Ontario	22.0	1.1	2.3

*Materials are listed on a dry weight basis (d.w.b.). The kaolin listed was also used in the *kaolin* suspension

Table III. Evaluated dispersants with chemical formulas and abbreviations used throughout this paper

Dispersant	Supplier	Chemical Formula	Abbreviation
Na-Polyacrylic Acid	Darvan 811, R. T. Vanderbilt Co., Norwalk, CT	$H-(NaC_3O_2H_3)_n-H$	PAA
Na-Polymethacrylic Acid	Darvan 7, R. T. Vanderbilt Co., Norwalk, CT	$H-(NaC_4O_2H_5)_n-H$	PMAA
Na-Hexametaphosphate		$(NaPO_3)_6$	SHMP
Na-Silicate (x=0.22) [□]	Sodium Silicate Solution, Technical Grade, Fisher Scientific, Pittsburgh, PA	$xNa_2O \cdot (1-x)SiO_2$	Na-silicate
Na-Carbonate		$Na_2CO_3 \cdot 10H_2O$	Soda ash
Soda Ash:Na-silicate Blend (1:1)		as noted above	1:1

[□]Ratio determined by ICP of the Na-Silicate solution, Acme Analytical Laboratories Ltd., Vancouver, British Columbia, Canada

Dispersant Composition

Table III lists the six dispersants, their nominal chemical formulas, and the abbreviations commonly used, which are also referred to in the text. The amount of dispersant added to the suspensions was based on the surface area of the suspension. The dispersant concentration range used for both the *kaolin* and the *batch* suspensions was 0.0 to 1.0 mg/m². All dispersants were added as aqueous solutions.

Suspension Preparation

Suspensions were prepared with distilled water using the typical industrial batching and mixing approach (i.e., clay slurried with water followed by the addition of the non-plastics). To ensure homogeneity between individual batches, *kaolin* and *batch* compositions were initially prepared as 13 liter suspensions at 35 v/o and 45 v/o solids, respectively, and mixed using a high intensity mixer (Model D-38-H, SHAR, Inc., Fort Wayne, Indiana; 500 rpm, 0.15 m impeller, tip speed: 4.0 m/s) without any dispersant. *Kaolin* suspension samples were taken from the 13 liter batch and diluted to 30 v/o (specific gravity = 1.5) using distilled water with incremental dispersant additions to create the dispersant demand curve.

For the *batch* suspensions, the dispersant concentration range was achieved by dividing the 13 liter batch into two separate suspensions. Both were reduced to 40 v/o (specific gravity = 1.7); one suspension had only distilled water added to create the 0.0 mg/m² endpoint, and the other had sufficient dispersant added to create the 1.0 mg/m² endpoint.

By blending these two endpoint suspensions in the appropriate ratios, the desired concentration range was achieved. For example, 10 ml of the suspension containing 1.0 mg/m² was blended with 90 ml of the 0.0 mg/m² suspension, to produce a suspension with a dispersant level of 0.10 mg/m².

All *kaolin* and *batch* suspension samples were stored in sealed polypropylene bottles for two weeks prior to testing to eliminate aging as a variable.⁹⁻¹¹

Two different methods were used to prepare the 1:1 (soda ash:Na-silicate) suspensions. The first set was prepared by mixing the soda ash and Na-silicate suspensions created by the endpoint ratio blending technique, which were stored and aged independently (referred in the text as *aged 1:1*). Mixing equal amounts of soda ash suspension and Na-silicate suspension at each dispersant level produced the *aged 1:1* suspensions that spanned the 0.0 – 1.0 mg/m² concentration range. After mixing, the properties of these suspensions were measured.

To further evaluate the dispersion character of the blended soda ash and Na-silicate, a second set consisted of three groups of 1:1 suspensions prepared by mixing the 1:1 dispersant mixture with the *batch* suspensions, which were then stored and aged prior to testing:

Group 1. Soda ash and Na-silicate solutions were measured and blended with each other. This “premix” 1:1 solution was then added to the non-dispersed suspension and mixed for two minutes.

Group 2. The soda ash and Na-silicate solutions were measured individually. The soda ash solution was added to the non-dispersed suspension and mixed for

two minutes. The Na-silicate solution was then added to the suspension and mixed for an additional two minutes.

Group 3. The order of addition was reversed from *Group 2*. The Na-silicate solution was added first to the suspension followed by the soda ash solution, with a similar mixing procedure.

The effects of blending different ratios of soda ash and Na-silicate were also investigated in the *batch* suspension. Soda ash:Na-silicate ratios of 1:2, 1:1, and 2:1 were prepared using the mixing procedure outlined above for *Group 1*.

Measurement Methods (rheology and pH)

Under controlled temperature conditions (25°C), the apparent viscosity was extrapolated to a shear rate of 1.0 s^{-1} under steady-state conditions. Shear-thinning non-Newtonian behavior was exhibited. The high shear rate (η_{∞}) and low shear rate (η_0) Newtonian-like regions were outside the measured region so the power-law model could be used to describe the suspension rheology, following the form:¹²

$$\eta = K \dot{\gamma}^{n-1} \quad (1)$$

which can be re-written as:

$$\log \eta = \log \eta_{1.0} + (n - 1) \log \dot{\gamma} \quad (2)$$

where K is defined as the apparent viscosity at a shear rate of 1.0 s^{-1} , $\eta_{1.0}$.

The steady-state shear behavior of each suspension was measured using a stress-controlled rheometer (SR-200 Dynamic Stress Rheometer, Rheometrics Scientific, Piscataway, NJ) with 25 mm parallel plate geometry. The parallel plate geometry was chosen over the truncated cone and plate geometry because of the potential for fixture damage due to the possibility of particles larger than the recommended 50 μm cone and plate gap. With the parallel plate geometry, the viscosity is calculated using equation (3), where M is the torque, G_c is the gravitational constant, and R is the plate radius.

$$\text{Parallel Plate Viscosity: } \eta = \frac{2M(G_c)}{\pi \left(\frac{R}{10}\right)^3} \quad (3)$$

$$\text{Shear Stress: } \tau = \frac{M}{2\pi R^3} \left[3 + \frac{d \ln M}{d \ln \dot{\gamma}} \right] \quad (4)$$

Equation (3) may be derived from equation (4) where τ is the shear stress and it is assumed that $\frac{d \ln M}{d \ln \dot{\gamma}}$ goes to 1.0, or less, and generates a 3% or lower error, in the calculation of the shear stress.¹³ Viscosity was measured by a steady-state stress-sweep test from high to low stress, and the data were used to produce apparent viscosity versus shear rate curves. The apparent viscosity at a shear rate of 1.0 s^{-1} was calculated from the regression of the linear region of the log apparent viscosity versus log shear rate data.

The pH of the suspensions was measured for each dispersant concentration (Accumet 15, Fisher Scientific, Pittsburgh, PA). Buffer solutions 7.0 and 10.0 were used to calibrate the combination electrode. After the samples were aged for two weeks, the suspension pH was again measured.

RESULTS AND DISCUSSION

Effect of Dispersant Additions on Suspension pH

At the minimum in the viscosity curve, the addition of these six dispersants generated two distinct trends in the pH measurements and these are illustrated in Figure 3-1 for the *batch* suspensions and are listed in Table IV. (Similar behavior was observed in the *kaolin* suspensions.) The pH value of the *batch* suspension without dispersant was 7.4. PAA, PMAA, and SHMP additions resulted in little change in the suspension pH value (7.2-7.6). Na-silicate, soda ash, and 1:1 showed a dramatic change in the suspension pH value (9.3-10.2). The change in the pH of the 1:1 suspensions were indifferent to the addition sequence; all 1:1 suspensions, *aged 1:1* and Groups 1-3 showed a similar increase in pH as a function of dispersant concentration. The two trends were observed for the entire dispersant range evaluated.

The apparent viscosity curves of the *batch* suspension shown in Figure 3-2 clearly illustrate that the Na-silicate and the PAA both disperse equally well, and are independent of the change in the suspension pH. Conversely, the suspension pH at the minimum apparent viscosity for both soda ash and Na-silicate similarly increased with dispersant addition, but the same minimum in the apparent viscosity curve was not obtained. Therefore, despite these two distinctly different pH responses, it is proposed that for these experiments, over the pH range investigated, pH is not a governing factor.

Table IV. *Batch* suspension apparent viscosity, η , (Pa·s at 1.0 s^{-1}) and pH as a function of the dispersants concentration with the minimum viscosity and corresponding pH in bold.

Concentration (mg/m ²)	PAA		PMAA		Na-silicate		Soda ash		SHMP	
	η	pH								
0.00	1.74E+02	7.39	1.74E+02	7.39	1.74E+02	7.39	1.74E+02	7.39		
0.05	1.42E+01	7.54	2.09E+01	7.43	1.60E+01	7.90	1.01E+02	8.12	5.64E+00	7.46
0.10	3.45E-01	7.50	1.94E+00	7.45	4.57E-01	8.21	6.13E+01	8.44	2.11E-01	7.39
0.15	1.10E-01	7.62	1.00E-01	7.65	1.33E-01	8.57	3.16E+01	8.66	9.20E-02	7.32
0.20	6.90E-02	7.63	7.00E-02	7.62	8.90E-02	8.93	1.75E+01	8.98	9.20E-02	7.28
0.30	1.15E-01	7.67	1.29E-01	7.65	6.30E-02	9.45	1.11E+01	9.49	9.40E-02	7.24
0.40	1.82E-01	7.68	1.65E-01	7.68	1.03E-01	9.86	1.19E+01	9.81	9.00E-02	7.20
0.50	2.11E-01	7.69	2.56E-01	7.71	1.40E-01	10.15	1.30E+01	10.02	9.20E-02	7.21
0.70	5.80E-01	7.73	6.36E-01	7.74	1.07E-01	10.57	1.99E+01	10.21	1.29E-01	7.21
0.90	9.62E-01	7.73	1.32E+00	7.76	1.90E-01	10.83	2.84E+01	10.31	1.36E-01	7.24
1.00	1.69E+00	7.79	1.51E+00	7.83	1.86E-01	10.86	3.30E+01	10.24	1.71E-01	7.26

Table IV. (continued)

Concentration (mg/m ²)	<i>Aged 1:1</i>		<i>1:1 Group 1</i>		<i>1:1 Group 2</i>		<i>1:1 Group 3</i>	
	η	pH	η	pH	η	pH	η	pH
0.00	1.74E+02	7.39	1.74E+02	7.39	1.74E+02	7.39	1.74E+02	7.39
0.05	8.72E+01	7.95	1.55E+01	8.26	5.00E+00	8.22	1.21E+01	8.22
0.10	4.51E+01	8.37	2.09E+00	8.49	1.51E+00	8.62	1.23E+00	8.62
0.15	1.73E+01	8.63	1.51E-01	8.86	1.32E-01	8.86	9.70E-02	8.86
0.20	4.14E+00	8.83	4.80E-02	9.27	5.00E-02	8.93	4.60E-02	8.93
0.30	1.21E-01	9.25	4.90E-02	9.54	5.40E-02	9.52	3.70E-02	9.52
0.40	1.01E-01	9.60	5.20E-02	9.93	4.20E-02	9.87	6.10E-02	9.87
0.50	8.60E-02	9.93	7.00E-02	10.02	3.80E-02	10.17	5.70E-02	10.17
0.70	1.18E-01	10.27	1.40E-01	10.44	7.60E-02	10.66	6.90E-02	10.66
0.90	1.53E-01	10.46	4.18E-01	10.70	1.45E-01	10.80	8.50E-02	10.80
1.00	1.79E-01	10.52	9.12E-01	10.69	2.02E-01	10.92	1.03E-01	10.92

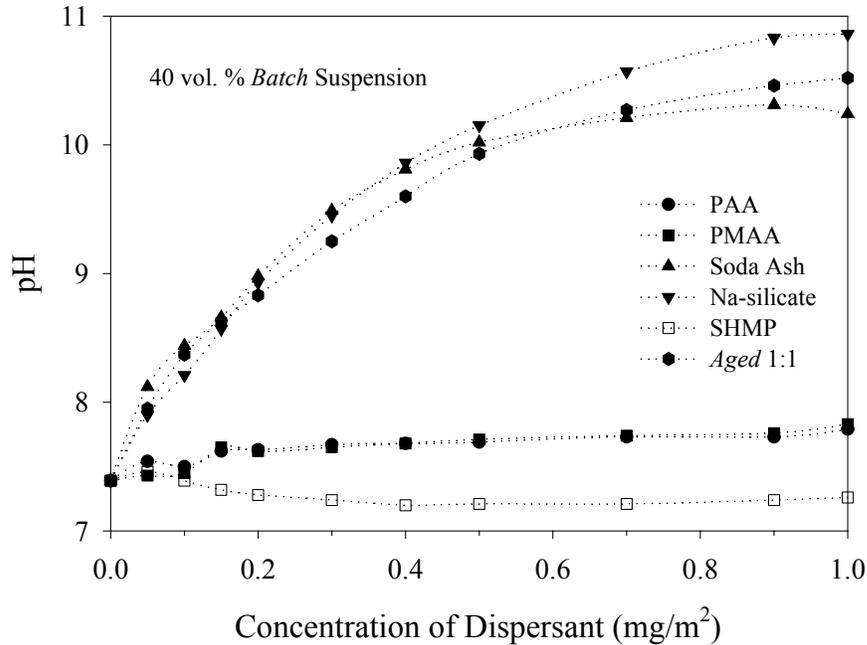


Figure 3-1. The suspension pH as a function of the dispersant concentration, for all six dispersants in the *batch* suspension.

Effects of Dispersant Additions on Rheology

The effects of the five dispersants on the apparent viscosity of the *batch* suspensions are shown in Figure 3-2 and listed in Table IV. Similar rheology measurements were observed in the *kaolin* suspensions with these dispersants as presented in Figure 3-3. The behavior of the five dispersants can be divided into two categories, based on the rheological measurements.

The first category contains soda ash that was an ineffective dispersant producing a gradual change in the apparent viscosity of only a factor of 10 over the entire dispersant concentration range. The change was a more gradual change than that observed in the second category, highly effective. The minimum in the apparent viscosity curve occurred between 0.20-0.30 mg/m². The apparent viscosity of this dispersant increased slightly,

similar to the PAA and PMAA, as the dispersant concentration exceeded the minimum in the apparent viscosity curve, suggesting that the cation contribution is compressing the double layer. This subject is further addressed elsewhere.¹⁴

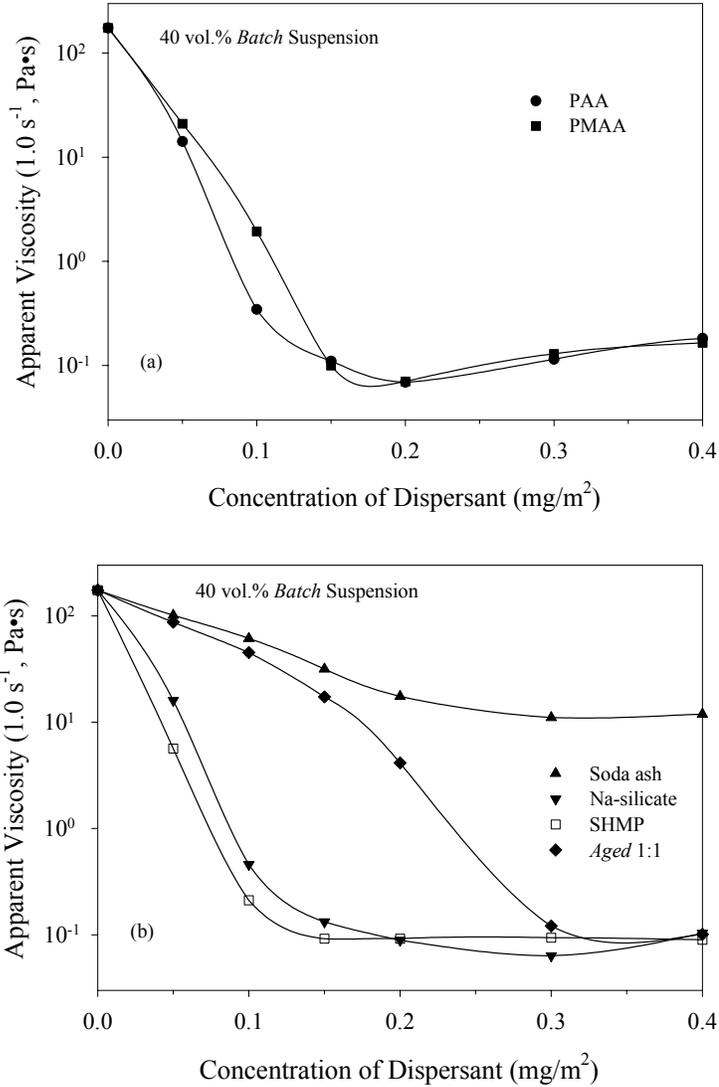


Figure 3-2. The apparent viscosity at 1.0 s^{-1} of the *batch* suspensions as a function of dispersant concentration (a) PAA and PMAA and (b) Na-silicate, SHMP, soda ash, and *aged 1:1*, in the *batch* suspension.

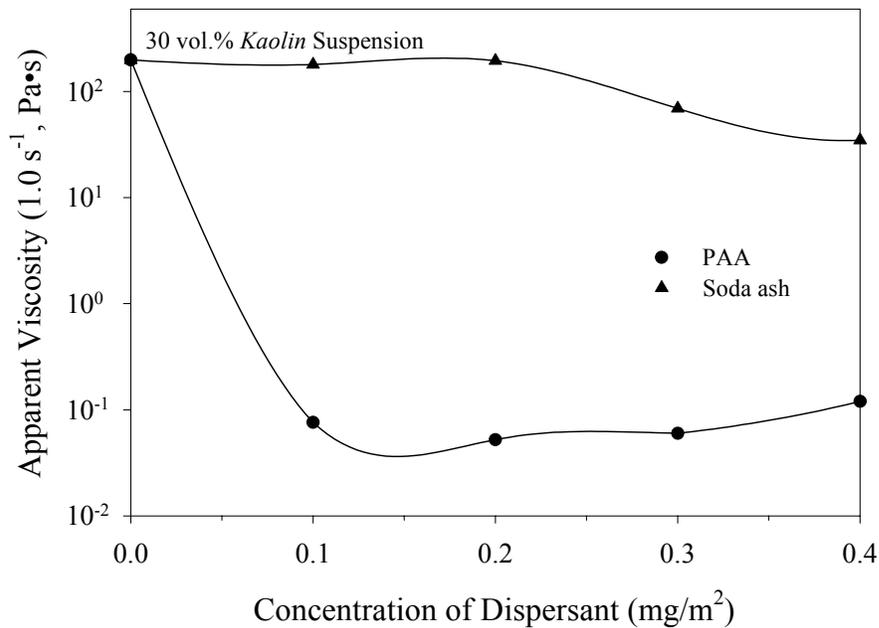


Figure 3-3. The effectiveness of the sodium-based dispersants, metered by apparent viscosity at 1.0 s^{-1} , as a function of dispersant concentration PAA and soda ash, in the *kaolin* suspension.

The second dispersant category can be considered highly effective, which includes PAA, PMAA, Na-silicate, and SHMP. The apparent viscosity values for these suspensions were reduced by a factor of approximately 1000 from the initial apparent viscosity of $1.74 \times 10^2 \text{ Pa}\cdot\text{s}$ for the suspension without dispersant addition.

The minima in the apparent viscosity curves for all four of these dispersants occurred at a concentration of approximately 0.20 mg/m^2 indicating the surface coverage necessary to create electrosteric stabilization between the particles in suspension. Although the gradual increase in viscosity of the PAA and PMAA suspensions at dispersant concentrations $> 0.20 \text{ mg/m}^2$ (Figure 3-2) has been attributed to bridging flocculation, charge neutralization, or depletion coagulation, the increase in viscosity is consistent with

compression of the double layer due to excess Na^+ .¹⁵ Figure 3-4 illustrates the increased viscosity as a function of Na^+ concentration.¹⁴

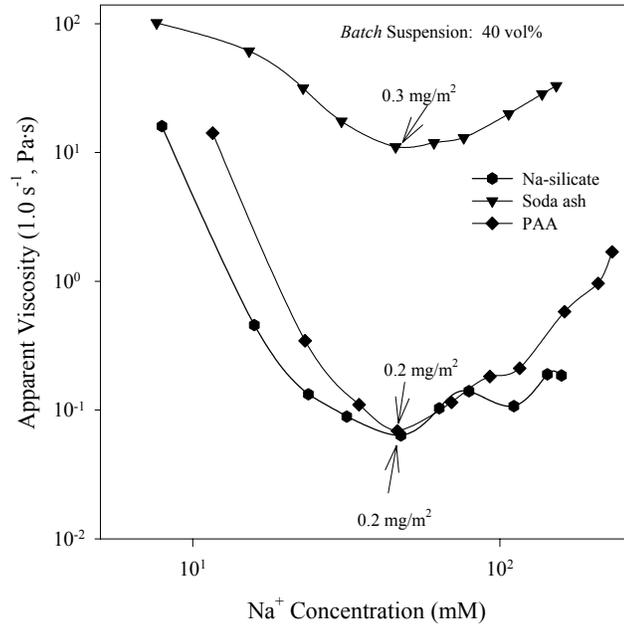


Figure 3-4. In the *batch* suspension, the apparent viscosity as a function of Na^+ concentration for Na-silicate, Soda Ash, and PAA. The minimum of soda ash differs from Na-silicate by two orders of magnitude despite similar pH values.

Up to 0.20 mg/m^2 , the rheological behavior of the Na-silicate and SHMP is similar to the PAA and the PMAA, suggesting polymer-like behavior by the Na-silicate and SHMP. Several studies have also indicated that these two dispersants can have polymer-like behavior. One suggests that chains of SHMP contain 5-6 $(\text{NaPO}_3)_x$.¹⁶ Two conformations have been suggested for the Na-silicate that would explain the polymer-like behavior. The first suggests chains containing 4-5 $(\text{Na}_2\text{SiO}_3)_x$ members, similar to the SHMP.¹⁶ This model assumes a 1:1 ratio of $\text{Na}_2:\text{SiO}_2$ but earlier work showed the ratio varies by brand as well as by application.^{17, 18} Chemical analysis of the Na-silicate

used showed the ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ to be approximately 1:4 (0.22:0.78). Therefore, a more probable structure, proposed by Iler,¹⁸ and supported by NMR spectroscopy,¹⁹ is a small three-dimensional, internally condensed silicate polyion or charged “particle”. These polyions contain as few as eight Si atoms with the Si atoms at the corners of a cube and each having one SiOH group which may ionize giving $(\text{Si}_8\text{O}_{20})^{-8}$.¹⁸ This structure requires a ratio of 1:2 of $\text{Na}_2\text{O}:\text{SiO}_2$ to form. As the ratio of SiO_2 increases condensation of silica monomers, $\text{Si}(\text{OH})_4$ surround the core polyion indicating the 1:4 solution would have 8 silica monomers attached. These highly (negatively) charged polyions adsorbed on the clay surface account for the efficient particle dispersion.

Correlation with Surface Area

With the dispersant results and the importance of surface area in dispersion studies, the dual nature of the surfaces of a kaolin particle can be clearly demonstrated. All of the clays used in these suspensions were kaolinitic.^{11, 20-22} Kaolinite, the major component of kaolin clays, is generally considered to consist of one silica-like surface and one alumina-like layer, which have been described as a quartz layer or siloxane surface (tetrahedral layer) and a gibbsite layer or hydroxide surface (octahedral layer), respectively.^{21, 23-27} It is usually considered to possess negatively charged basal planes and positively charged edges.^{8, 11, 24, 28-31} This model, however is inconsistent with the mineralogy. As a 1:1 sheet silicate, kaolinite is composed of a tetrahedral layer $[\text{Si}_2\text{O}_5]^{-2}$ and an octahedral layer $[\text{Al}_2(\text{OH})_4]^{+2}$, and based on the colloidal behavior of silica (isoelectric point 2.3-3.5) and hydrated alumina (isoelectric point 8.5-9.5) in the pH range between 3.5 and 8.5 the

silica-like surface must be negative while the aluminum hydroxide-like surface is positive.³²⁻³⁴

Despite the dissimilar nature of these two surfaces, the colloidal view of a clay particle is typically divided into two categories, edge and basal planes, and the dissimilar nature of the basal planes is overlooked. A typical aspect ratio of a clay particle is 1:10, edge to face, which calculates the edge accounting for only 18% of the total surface area, indicating that the basal planes have the greatest influence and contribution to the surface area and available adsorption sites.^{34, 35}

Because PAA and PMAA have a limited affinity for silica surfaces similar to the silica-like basal planes and because the silica-like basal plane carries a net negative charge at the pH level investigated, it is only necessary for the polymers to adsorb onto the alumina-like basal plane surface to create a completely dispersed suspension.³² The *batch* suspensions require approximately 0.20 mg/m² PAA and PMAA to reach the minimum in the apparent viscosity curve. Under similar experimental conditions, pH and dispersant normalized to the powder surface area, the affinity of PMAA to the surface of alumina powders extrapolated to a pH of 7.5, required 0.45 mg/m² PMAA to coat the surface of the alumina.¹ These results coupled with the results of the *batch* suspension (and *kaolin* suspension) indicate that only 40% of the clay surface is covered with the PMAA in the *batch* suspension. Because the edge surface area of a clay particle is approximately 18% of the available surface area, for a clay particle with an aspect ratio of 1:10, the edge cannot account for the 40% PMAA adsorbed. PMAA has little affinity to the silica-like surface, and therefore, adsorption of PMAA onto the aluminum hydroxide-like surface, which accounts for 41% of the calculated surface area of a 1:10 clay particle,

corresponds well with the amount of PMAA necessary to achieve the minimum suspension viscosity.³⁴ Similar results from another study were obtained for kaolinite indicating that the surface area of only the edges was insufficient to account for the amount of PMAA adsorbed onto the surface. Therefore, adsorption occurs on the basal planes but suggested that this adsorption on the basal planes was due to favorable and nonfavorable sites, rather than on adsorption to the aluminum hydroxide-like basal plane surfaces.³⁶

Effects of 1:1 Dispersant Additions

The initial rheology results suggested an intermediate dispersant effectiveness category showing a combined effectiveness of the first and the second categories, with the *aged 1:1* dispersant. The apparent viscosity behavior of this suspension begins by following the path of the ineffective dispersant, soda ash. But as the *aged 1:1* concentration increases, the suspension approached that of the highly effective dispersants. The rheology of the soda ash and the Na-silicate suspensions is illustrated in Figure 3-5 along with the results for the *aged 1:1* suspension. The behavior of the *aged 1:1* curve is similar to the soda ash curve but at 0.3 mg/m² follows the behavior of the Na-silicate curve. Recalculating the *aged 1:1* to account for only the presence of Na-silicate now behaves similar to the Na-silicate curve. Groups 1-3 suspensions illustrates that the dispersant addition sequence to be unimportant. The behavior of the 1:2 and 2:1 (soda ash:Na-silicate) suspensions corresponds most closely to the Na-silicate suspension.

The apparent viscosity of the soda ash suspension showed a very gradual change, a factor of 10, over the dispersant concentration range from 0.0 to 1.0 mg/m^2 . The minimum in the apparent viscosity curve occurs at 0.30 mg/m^2 for the soda ash indicating that maximum dispersion has occurred. The lack of efficiency, as measured by the change in the apparent viscosity, suggests that the suspension was incapable of further dispersion. In the Na-silicate suspension, a dramatic drop in the apparent viscosity, a factor of 1000, occurred with a concentration of 0.20 mg/m^2 .

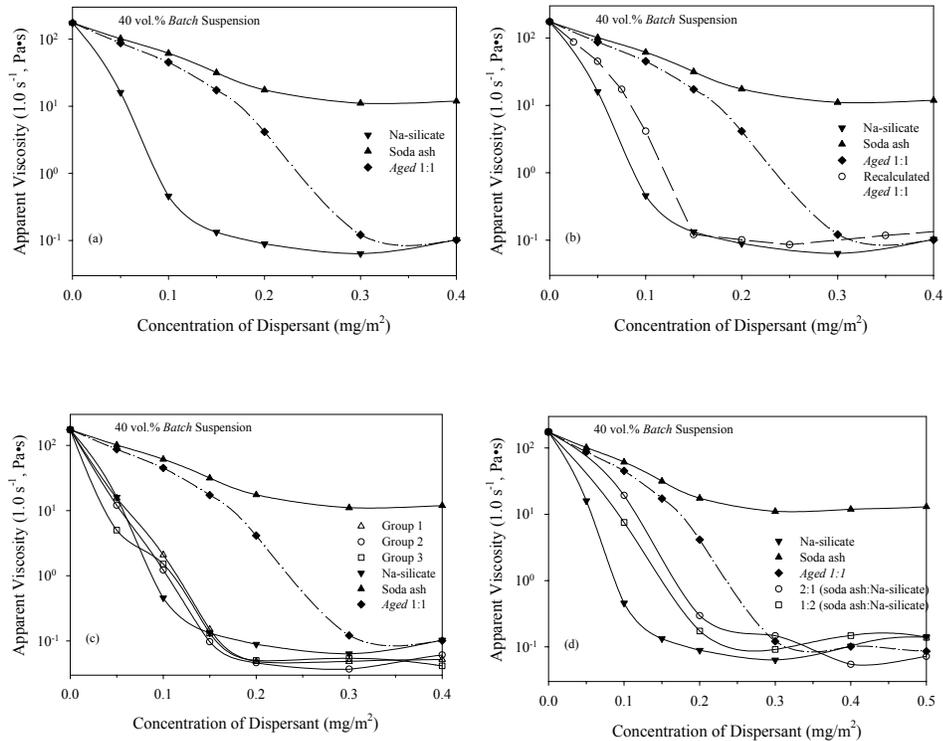


Figure 3-5. The apparent viscosity as a function of dispersant concentration of the *batch* suspensions containing mixtures of soda ash and Na-silicate.

The *aged 1:1* suspension behavior showed little change up to a concentration of 0.15 mg/m^2 ; the apparent viscosity values were similar for the soda ash and the *aged 1:1*, 31.6 and 17.3 $\text{Pa}\cdot\text{s}$, respectively. Above this dispersant concentration level, the *aged 1:1*

rheological behavior deviated from the soda ash suspension, and responded similarly to the Na-silicate suspension. At a dispersant level of 0.40 mg/m^2 , the apparent viscosity values were similar for the Na-silicate and the *aged 1:1*, 0.103 and 0.101 Pa·s, respectively.

The *aged 1:1* suspension with 0.1 mg/m^2 responded as if it contained only 0.05 mg/m^2 of Na-silicate. Figure 3-5 shows the *aged 1:1*, soda ash, and Na-silicate apparent viscosity curves with the revised dispersant concentration calculations (re-calculated 1:1) with only Na-silicate is present demonstrating the 're-calculated 1:1' curve closely follow the behavior of the Na-silicate curve. The apparent viscosity of the *aged 1:1* exhibits only the effects of the Na-silicate and not the soda ash.

The three 1:1 suspension dispersant curves, Groups 1-3, were compared to that of the *aged 1:1* suspension prepared which was prepared by the blending technique, to assess the effects on the rheology due to the addition sequence. All 1:1 dispersant curves are shown in Figure 3-5. The rheological behaviors of the three new 1:1 suspensions, Groups 1-3, were identical, and similar to the Na-silicate suspensions. The apparent viscosity values of the new 1:1 suspensions are independent of the sequence of dispersant addition, indicating that there is a preferential adsorption of the silicate anion over the carbonate anion. These results indicate that the initial data was impacted by the preparation technique, which blended aged soda ash and aged Na-silicate suspensions, *aged 1:1*. Once silicate anions were introduced, the carbonate anions were displaced by the silicate ions. The apparent viscosity of the Na-silicate and the 1:1 suspensions prepared in groups 1-3 are similar, despite the fact that the 1:1 suspensions contain half as much Na-silicate.

These results indicate interaction between the soda ash and Na-silicate. The rheological behavior of the 1:2 and 2:1 soda ash:Na-silicate suspensions also indicate an interactive effect between the dispersants. The apparent viscosity curves shown in Figure 3-5 are more similar to the Na-silicate curve than either the soda ash or the *aged 1:1*. Potential mechanisms include: 1) improved packing efficiency of the two dispersants on the particle surface, 2) the carbonate anion may complex with Ca^{+2} thus increasing the double layer thickness by reducing the divalent cation concentration, or 3) the soda ash may increase the concentration of negative sites on the Na-silicate polyions.¹⁸ Further work is necessary to decipher which mechanism is responsible for the increased efficiency.

Normalized to Na^+ Concentration

Normalizing the suspensions' apparent viscosity results to the active portion of the dispersants, and the suspension surface area has shown the effectiveness of the five dispersants and dispersant blends. By examining these results as a function of the Na^+ concentration in suspension, the impact of Na^+ ions on the dispersion can be isolated further as illustrated in Figure 3-4 with soda ash, Na-silicate, and PAA. The degree of dispersion is not the same as indicated by the minimum of soda ash requiring a higher concentration of Na^+ ions compared with the PAA and Na-silicate. At the viscosity minima for soda ash and Na-silicate, the apparent viscosity values differ by a factor of 176 (1.11×10^1 and 6.30×10^{-2} Pa·s, respectively), despite having identical pH values of 9.5. These results further demonstrate the apparent viscosity values are independent of Na^+ ion concentration and suspension pH. In addition, despite the degree of dispersion

similarity between Na-silicate and PAA at the same Na^+ concentration, the pH values differ greatly, 9.5 and 7.6, respectively. These results indicate that the apparent viscosity values are independent of Na^+ ion concentration and suspension pH within this pH range. The impact of the cation level on the rheology is observed beyond the dispersion minimum, where coagulation begins due to the presence of Na^+ ions as counter-ions compressing the double layer.¹⁴

Because all dispersants were sodium based, these variations in apparent viscosity must be due to the anionic species in the dispersants, which is in agreement with part of Johnson and Norton's statement, that... "*(a) the charge on the kaolinite particle controls the degree of deflocculation and is governed by the type of cation and (b) the stability of the system is controlled by the anion of the medium and is governed by the type of anion preferentially adsorbed*".²⁴ However, they also argue that the cation controls the dispersion and the presence of monovalent cations (Na^+) insures the most dispersed suspension over the presence of polyvalent cations. Above the minimum in the dispersion curve, as a function of dispersant concentration, the presence of the cation increases the apparent viscosity by compressing the double layer. It has also been shown that the same concentration of Na^+ ions does not create the most dispersed system indicating the anion is dictating the degree of dispersion.

SUMMARY AND CONCLUSIONS

The effectiveness of these dispersants, as measured by the apparent viscosity, can be categorized into two groups: highly effective (PAA, PMAA, SHMP, Na-silicate, and 1:1) and ineffective (soda ash). All of these dispersants are Na-based and therefore, the

monovalent cation (Na^+) is not responsible for the dispersion but rather the anionic species. The 1:1 dispersant was initially considered a combination of the highly effective and the ineffective dispersants. However, subsequent investigations demonstrated that the intermediate results were an artifact of the suspension preparation technique. The blending ratios of soda ash and Na-silicate produce an interactive effect provoking a well dispersed suspension with less Na-silicate than anticipated. All dispersants, except soda ash, create approximately the same degree of dispersion in these clay suspensions. In this study, suspension pH does not correlate with apparent viscosity and dispersant effectiveness.

The dispersant results using PAA and PMAA in conjunction with alumina studied by Cesarano, et.al.¹ clearly support the mineralogical point of view of one silica-like layer that is negative and one alumina-like layer that is positive.

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4. EFFECTS OF IONIC CONCENTRATION ON RHEOLOGY

INTRODUCTION

The coagulation of a clay suspension by electrolyte (salt) addition is a commonly accepted phenomenon, but disagreement persists regarding which ionic species is accountable, cation or anion.¹⁻⁶ In this context, coagulation is defined as the deliberate alteration of interaction potential in order to achieve agglomeration in a suspension. Flocculation herein is defined as agglomeration due to attractive forces between suspension particles without intentionally altering the surface potential. Coagulation indicates agglomeration due to compression of the diffuse double layer around the particle or by specific adsorption of ions onto the particle surface.^{2, 7}

That the concentration and charge of the counter- and co-ions in the bulk solution influences the diffuse double layer thickness is well established.^{2, 5, 7} Increasing either the concentration or charge of the counter-ion will compress the double layer thickness. The double layer thickness (L) is calculated as the inverse of the Debye-Hückel parameter (κ)⁷:

$$\text{Double Layer Thickness: } L = \frac{1}{\kappa} = \left[\frac{\epsilon kT}{e^2 \sum_i n_i z_i^2} \right]^{1/2} . \quad (1)$$

This calculation of the double layer thickness assumes symmetrical electrolytes, i.e., 1:1 or 2:2 such as NaCl or MgSO₄, and does not apply to asymmetrical electrolytes, i.e., 1:2 or 2:1 such as Na₂SO₄ or CaCl₂.^{1, 2}

At 25°C, the calculation reduces to:
$$L = \frac{\sqrt{I}}{3.288} \cdot \quad (2)$$

The reduced calculation requires only the ionic concentration (I) data, which includes solution concentration (n_i) and charge, (z_i). The original calculation also requires the Boltzmann constant (k), temperature, and the charge on an electron.

Specific adsorption requires near surface interaction between the ions from the bulk solution and the atoms on the surface of the particle.² Two effects may indicate specific adsorption “ (1) ...shift in the point of zero charge (p.z.c.) as the ion concentration is increased, and (2) specifically adsorbed ions are able to alter the sign of the zeta potential (ζ -potential) if they are present at high enough concentrations...”⁷

These two coagulation mechanisms, double layer compression and specific adsorption, are dependent on the particle surface potential, ionic concentration, and the relative affinity of the co-ions and counter-ions to the suspension particles. In the whiteware suspension that was examined, the clay particles dominate the suspension behavior, as it is the primary contributor of surface area in the suspension. Kaolintic clay, which was used in the batch composition, is primarily comprised of the mineral kaolinite, a 1:1 sheet silicate composed of a silica-like basal plane and an alumina-like basal plane with a net negative charge at a neutral pH.^{2, 8-10} This indicates that cations are responsible for compressing the double layer.^{3, 11-14} Previous studies evaluating clay properties frequently ‘prepare’ the clay prior to testing.¹⁴⁻¹⁷ These preparation techniques usually involve washing the clay with some of the following: acidic solutions,^{14, 16, 17} basic solutions,¹⁴⁻¹⁶ an electrolytic solution with a desired cation,^{14, 17} electro dialysis,^{15, 16} and finally multiple rinsing cycles with distilled or de-ionized water.¹⁴⁻¹⁷ These procedures

are undertaken to purify the clay and usually to produce a single “cationic clay”, i.e. Na-kaolinite, Ca-kaolinite, or Al-kaolinite. But, by creating these cleaned homoionic clays, the nature of the original clay and its properties have been altered thereby generating results that may be an artifact of the clay preparation technique and not necessarily of the clay.¹⁸

Using rheological measurements, the onset of coagulation of a suspension can be evaluated as a function of the ionic concentration adjusted with electrolyte solutions. Evaluating the rheological behavior of (1) monovalent cations with monovalent and divalent anions, and (2) divalent cations with monovalent and divalent anions can isolate the dominating species, cations or anions, controlling clay suspension coagulation. Additionally, the changes determined by the rheological measurements can be linked to the calculated thickness of the diffuse double layer, assuming the electrolyte solutions are indifferent to the clay surface.

EXPERIMENTAL PROCEDURE

Suspension Composition

The effects of ionic concentration and dispersion level on the suspension rheology were evaluated using a typical whiteware composition, as listed on a dry weight basis (d.w.b.) in Table II. The percentage of clay listed includes both kaolin and ball clay that combined to account for 93.8% of the batch surface area that was determined using N₂-adsorption B.E.T. multi-point method, (Gemini III 2375 Surface Area Analyzer, Micromeritics, Norcross, GA).

Chemistry of Salt Solutions and Dispersants

All salts were added to the suspensions via saturated salt solutions that were diluted to the appropriate level. This processing route was chosen to help insure reliable and consistent salt concentration. Directly adding crystalline salts to the suspensions would introduce some potential error sources. First, because some salts are hygroscopic, the hydration tendencies of the salt can lead to weighing errors. Secondly, the addition of salts directly into the suspension creates localized salt-particle clusters. Furthermore, the time required for salt dissolution becomes a factor for both of these error sources. The concentration of the six saturated salt solutions was initially determined by the solubility limit of each salt listed in Table V, but the actual cation concentrations were determined by Inductively Coupled Plasma (ICP) Spectroscopy (ACME Analytical Laboratories Ltd., Vancouver, British Columbia, Canada). Due to the low solubility limit, the maximum concentration of the CaSO₄ saturated solution was limited relative to the other salts tested.

Sodium Polyacrylic Acid, PAA, (Dispex®, Ciba Specialty Chemicals, Basel, Switzerland, formerly Allied Colloids) was used to disperse the batches at two levels, 0.02 and 0.05 mg/m². The dispersant was added to the water prior to the addition of the powders.

Table V. Salt solubility and ICP concentration analysis*

Chemical Formula *	Reported Solubility (g/100c)	Reported Solubility (mM)	Measured Concentration via ICP (mM)	Temperature (°C)
NaCl	35.7	6.16×10^3 [Na ⁺]	6.09×10^3 [Na ⁺]	0
½ Na ₂ SO ₄ •10H ₂ O	5.5	3.41×10^2 [Na ⁺]	2.90×10^3 [Na ⁺]	0
MgCl ₂ •6H ₂ O	167	8.21×10^3 [Mg ⁺]	5.23×10^3 [Mg ⁺]	20 [◇]
MgSO ₄ •7H ₂ O	71.0	2.88×10^3 [Mg ⁺]	2.86×10^3 [Mg ⁺]	20 [◇]
CaCl ₂ •2H ₂ O	97.7	6.71×10^3 [Ca ⁺]	5.88×10^3 [Ca ⁺]	0
CaSO ₄ •2H ₂ O	0.241	1.40×10^1 [Ca ⁺]	1.42×10^1 [Ca ⁺]	20 [◇]

*All chemicals reagent grade from Fisher Scientific, Pittsburgh, Pennsylvania;
[◇]temperature assumed, not specific in literature.

Batching and Mixing

Thirteen-liter batches were mixed using a high intensity mixer (Model D-38-H, SHAR, Inc., Fort Wayne, Indiana; 500 rpm, 0.15 m impeller, tip speed: 4.0 m/s), then apportioned into 200 ml samples. By using this large batching process, the mixing consistency between the individual suspensions was improved. Batches were mixed at dispersion levels of 0.00, 0.02, and 0.05 mg/m², and evaluated in conjunction with the six salts. Each batch was mixed at a calculated solids loading of 35 v/o (1.6 specific gravity or 59 weight %), based on the weight percentage and the specific gravity for each raw material.

The ionic concentration of the individual suspensions was adjusted by adding the distilled water and the saturated salt solutions, then mixed (Model RZR50, Carframo Ltd., Ontario, Canada; 80 rpm, 0.056 m impeller, tip speed: 0.075 m/s). These additions reduced the solids loading of all suspensions to 30 v/o (1.5 specific gravity or 54 weight

%). After the ionic strength of each individual suspension was adjusted, the suspension containers were sealed for a minimum of two weeks prior to testing. By doing this, the intentional changes to the ionic strength were isolated from potential aging effects. Only distilled water was used throughout the batching and salt addition processes, in order to minimize additional ionic species from being introduced into the suspensions. The ionic contribution from the distilled water was minimal compared to the ionic contribution from the raw materials. Table VI shows the cation contribution from the distilled water and the dissolution of the batch components.

Table VI. Cation contribution for distilled water and raw materials

Material	Ca⁺² (mM)	K⁺ (mM)	Mg⁺² (mM)	Na⁺ (mM)
Distilled Water	2.50E-03	2.56E-03	4.11E-03	4.35E-03
Ball Clay	9.01E-01	1.18E-01	7.77E-01	6.61E-01
Kaolin	3.17E-01	2.30E-02	8.23E-02	1.39E-01
Nepheline Syenite	1.50E-02	2.69E-01	4.11E-03	3.59E+00

Rheology and pH Measurements

The steady-state shear behavior was measured using a stress-controlled rheometer (SR-200 Dynamic Stress Rheometer, Rheometrics Scientific, Piscataway, New Jersey) with a cone and plate geometry. Using a steady-state, stress-sweep test, measurements were collected from high stress (high shear rate) to low stress (low shear rate) in order to eliminate thixotropic effects. The apparent viscosity values reported for each suspension were extrapolated to a shear rate of 1.0 s⁻¹ using a power law regression that was applied to the linear region above the zero shear viscosity and below the infinite shear viscosity of the log viscosity versus log shear.^{7, 11, 19}

The pH of the suspensions was measured (Accumet 15, Fisher Scientific, Pittsburgh, PA), including all salt types and all dispersion levels, after the samples were aged for two weeks. Suspensions were not diluted, therefore continuous stirring was implemented during testing with a combination electrode (Corning Combination Electrode, Model #476087, Corning, NY). The pH meter was calibrated with 7.0 and 4.0 buffer solutions prior to measuring the suspension pH values.

RESULTS AND DISCUSSION

Effects of Salt Additions on Suspension pH

The suspension pH involving the chloride salt changed more than those adjusted with sulfate salts. Previous work, however, demonstrated that the suspension behavior is unaffected in this pH range.¹¹ Figure 4-1 illustrates the suspension pH measurements at a dispersion level of 0.02 mg/m² for the six salts over the entire cation concentration range that was investigated. Similar pH trends were measured in the 0.00 and 0.05 mg/m² dispersed suspensions, and all pH data is listed in Table VII.

It has been proposed that a clay suspension pH decreases during cation exchange capacity (CEC) measurements because the following reactions occur at the edge of the clay particle:²⁰



The aspect ratio of a clay particle is approximately 10:1 for face to edge with the calculated edge surface area contributing less than 20% of the clay particle surface area.^{21, 22} Therefore, the number of available edge sites limits the pH reduction, and a significant decrease in the pH is not observed with the salt additions. An increase in the cation (M^+) concentration will shift the reaction to the right causing the suspension pH to decrease. This pH decrease may be masked if the clay has been washed or the surface has been otherwise been chemically altered. In order to achieve a specific homoionic clay, the existing H^+ at the edge sites are replaced with another cation during clay preparation procedure. It is also possible that the pH decrease is enhanced if the homoionic clay prepared is a H-kaolinite.

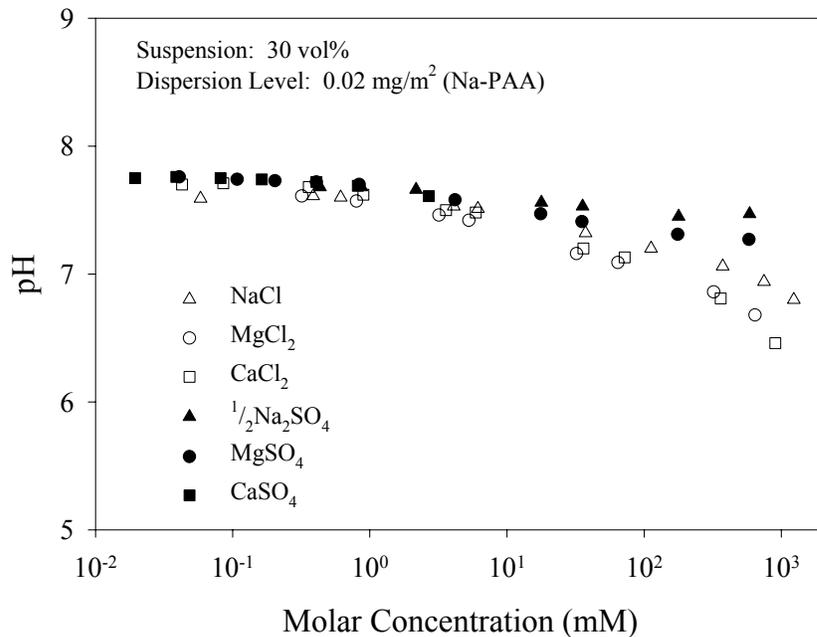


Figure 4-1. Suspension pH as a function of molar concentration for the suspensions dispersed with 0.02 mg/m². Similar pH trend was observed with the 0.00 and 0.05 mg/m² dispersed suspensions.

Table VII. Apparent viscosity and pH values as a function of cation concentration for all salts and dispersion levels

0.00 mg/m²	Cation Concentration (mM)	pH	Apparent Viscosity (1.0 s⁻¹, Pa•s)
NaCl	1.23E+03	6.8	1.53E+01
	7.47E+02	7.0	1.49E+01
	3.73E+02	7.1	1.42E+01
	1.12E+02	7.2	1.11E+01
	3.73E+01	7.4	9.61E+00
	6.13E+00	7.5	8.10E-01
	4.09E+00	7.5	1.13E+00
	6.20E-01	7.6	3.90E-01
	3.80E-01	7.6	
	6.00E-02	7.6	
MgCl ₂	6.42E+02	6.7	1.73E+01
	3.21E+02	6.9	1.89E+01
	6.42E+01	7.1	1.70E+01
	3.21E+01	7.2	1.71E+01
	5.27E+00	7.4	1.27E+01
	3.19E+00	7.5	9.95E+00
	8.00E-01	7.6	2.17E+00
	3.20E-01	7.6	3.30E-01
	8.00E-02	7.6	
4.00E-02	7.6		
CaCl ₂	9.02E+02	6.4	1.61E+01
	3.61E+02	6.7	1.69E+01
	7.22E+01	7.1	1.50E+01
	3.61E+01	7.2	1.64E+01
	5.92E+00	7.5	9.78E+00
	3.59E+00	7.5	1.04E+01
	9.00E-01	7.6	2.03E+00
	3.60E-01	7.6	7.40E-01
Na ₂ SO ₄	5.87E+02	7.4	4.91E+00
	1.78E+02	7.3	5.38E+00
	3.56E+01	7.5	2.83E+00
	1.78E+01	7.5	2.27E+00
	2.17E+00	7.6	5.80E-01
	8.70E-01	7.6	5.30E-01
	4.30E-01	7.7	3.90E-01
MgSO ₄	5.79E+02	7.1	1.31E+01
	1.76E+02	7.2	1.36E+01
	3.51E+01	7.3	1.25E+01
	1.76E+01	7.3	1.32E+01
	4.18E+00	7.5	8.46E+00
	8.40E-01	7.6	1.04E+00
4.10E-01	7.6	6.60E-01	

	2.00E-01	7.7	4.70E-01
	1.10E-01	7.7	5.70E-01
	4.00E-02	7.7	3.50E-01
CaSO ₄	2.69E+00	7.5	6.62E+00
	8.20E-01	7.6	1.70E+00
	4.10E-01	7.7	6.90E-01
	1.60E-01	7.7	4.60E-01
	8.00E-02	7.7	5.00E-01
	4.00E-02	7.7	1.70E-01
	2.00E-02	7.7	1.80E-01

0.02 mg/m²	Cation Concentration (mM)	pH	Apparent Viscosity (1.0 s⁻¹, Pa•s)
NaCl	1.23E+03	6.8	1.51E+01
	7.47E+02	6.9	1.06E+01
	3.73E+02	7.1	8.94E+00
	1.12E+02	7.2	7.46E+00
	3.73E+01	7.3	5.51E+00
	6.13E+00	7.5	8.10E-01
	4.09E+00	7.5	2.70E-01
	6.10E-01	7.6	
	3.90E-01	7.6	
	6.00E-02	7.6	
MgCl ₂	6.42E+02	6.7	1.44E+01
	3.21E+02	6.9	1.50E+01
	6.42E+01	7.1	1.23E+01
	3.21E+01	7.2	1.29E+01
	5.27E+00	7.4	1.28E+01
	3.19E+00	7.5	5.00E+00
	8.00E-01	7.6	4.80E-01
	3.20E-01	7.6	1.70E-01
	8.00E-02	7.6	6.00E-02
	4.00E-02	7.7	
CaCl ₂	9.02E+02	6.5	9.60E+00
	3.61E+02	6.8	1.30E+01
	7.22E+01	7.1	1.56E+01
	3.61E+01	7.2	1.39E+01
	5.92E+00	7.5	1.03E+01
	3.59E+00	7.5	6.45E+00
	9.00E-01	7.6	1.20E-01
	3.60E-01	7.7	9.00E-02
	9.00E-02	7.7	3.00E-02
	4.00E-02	7.7	3.00E-02

Na ₂ SO ₄	5.87E+02	7.5	4.77E+00
	1.78E+02	7.5	2.99E+00
	3.56E+01	7.5	1.24E+00
	1.78E+01	7.6	8.20E-01
	2.17E+00	7.7	3.00E-02
	8.70E-01	7.7	5.00E-02
MgSO ₄	4.30E-01	7.7	5.00E-02
	5.79E+02	7.3	1.23E+01
	1.76E+02	7.3	1.35E+01
	3.51E+01	7.4	1.41E+01
	1.76E+01	7.5	1.40E+01
	4.18E+00	7.6	7.07E+00
	8.40E-01	7.7	2.62E+00
	4.10E-01	7.7	5.80E-01
	2.00E-01	7.7	7.00E-02
	1.10E-01	7.7	4.00E-02
CaSO ₄	4.00E-02	7.8	2.00E-02
	2.69E+00	7.6	4.87E+00
	8.20E-01	7.7	3.30E-01
	4.10E-01	7.7	4.00E-02
	1.60E-01	7.7	3.00E-02
	8.00E-02	7.8	4.00E-02
	4.00E-02	7.8	4.00E-02
	2.00E-02	7.8	2.00E-02

0.05 mg/m²	Cation Concentration (mM)	pH	Apparent Viscosity (1.0 s⁻¹, Pa•s)
NaCl	1.23E+03	6.7	1.10E+01
	7.47E+02	6.9	1.33E+01
	3.73E+02	7.0	9.60E+00
	1.12E+02	7.2	7.28E+00
	3.73E+01	7.4	3.88E+00
	6.13E+00	7.6	1.00E-02
	4.09E+00	7.6	2.00E-02
	6.10E-01	7.6	
	3.80E-01	7.7	
	6.00E-02	7.7	
MgCl ₂	6.42E+02	6.7	1.34E+01
	3.21E+02	6.9	1.32E+01
	6.42E+01	7.2	1.55E+01
	3.21E+01	7.3	1.50E+01
	5.27E+00	7.6	2.53E+00
	3.19E+00	7.6	7.80E-01

	8.00E-01	7.7	2.00E-02
	3.20E-01	7.7	2.00E-02
	8.00E-02	7.7	2.00E-02
	4.00E-02	7.7	3.00E-02
CaCl ₂	9.02E+02	6.5	1.58E+01
	3.61E+02	6.9	2.14E+01
	7.22E+01	7.2	1.82E+01
	3.61E+01	7.3	1.56E+01
	5.92E+00	7.7	4.51E+00
	3.59E+00	7.7	3.19E+00
	9.00E-01	7.7	4.00E-02
	3.60E-01	7.8	2.00E-02
	9.00E-02	7.8	2.00E-02
	4.00E-02	7.8	1.00E-02
Na ₂ SO ₄	5.87E+02	7.4	5.06E+00
	1.78E+02	7.5	2.71E+00
	3.56E+01	7.5	6.20E-01
	1.78E+01	7.6	1.10E-01
	2.17E+00	7.7	2.00E-02
	8.70E-01	7.8	3.00E-02
	4.30E-01	7.8	3.00E-02
MgSO ₄	5.79E+02	7.2	1.41E+01
	1.76E+02	7.3	1.44E+01
	3.51E+01	7.3	1.58E+01
	1.76E+01	7.4	1.43E+01
	4.18E+00	7.5	4.62E+00
	8.40E-01	7.6	1.77E+00
	4.10E-01	7.6	2.00E-02
	2.00E-01	7.7	3.00E-02
	1.10E-01	7.7	2.00E-02
	4.00E-02	7.7	4.00E-02
CaSO ₄	2.69E+00	7.6	2.96E+00
	8.20E-01	7.6	2.00E-02
	4.10E-01	7.7	2.00E-02
	1.60E-01	7.7	1.00E-02
	8.00E-02	7.7	2.00E-02
	4.00E-02	7.8	2.00E-02

Effects of Salt Additions on Suspension Rheology

The suspension rheology as a function of the cation concentration for all six salts, at the three dispersion levels, are shown in Figure 4-2 and the data is listed in Table VII. The rheological behavior, which was similar for all levels of dispersion and salt types, can be divided into three distinct regions illustrated in Figure 4-3, which isolates CaCl_2 at 0.02 mg/m^2 . These three regions in the apparent viscosity curves are indicators of the particle-particle interactions controlling the suspension behavior. Region I occurs at low salt concentrations where the suspension apparent viscosity is most fluid and remains relatively unchanged as a function of cation concentration. A plateau in the apparent viscosity values with respect to the initial salt additions defines this region. The lowest apparent viscosity values indicate that the repulsive forces are sufficient to inhibit agglomeration and interaction between suspension particles despite the salt additions. The concentration of counter-ions (cations) is below the necessary level to compress the double layer of the negatively charged particle, and allows van der Waals forces to dominate particle-particle interactions. Region II shows a dramatic change in the apparent viscosity with only a small increase in CaCl_2 concentration. The critical coagulation concentration (CCC) of the CaCl_2 in the suspension occurs within the region where an abrupt change occurs in the apparent viscosity. Sufficient counter-ions are present to compress the double layer so that the van der Waals attractive forces begin to dominate the suspension. The CCC is defined in this region as the inflection point of the curve fit to the data points. Region III, which involves the highest salt concentration, shows little change above the maximum apparent viscosity achieved in Region II despite increased CaCl_2 concentration. This region is defined as a plateau of apparent viscosity

above the CCC that is unchanged upon further salt additions. The attractive forces between the particles completely dominate the suspension behavior. The coagulated suspension structure measured by the apparent viscosity is similar for all salt types and all levels of dispersion suggesting a similar final structure is formed in all cases. Region III was unattainable with salt solution additions of CaSO_4 due to solubility limitations, and would have required undissolved $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) to be added to the suspension.

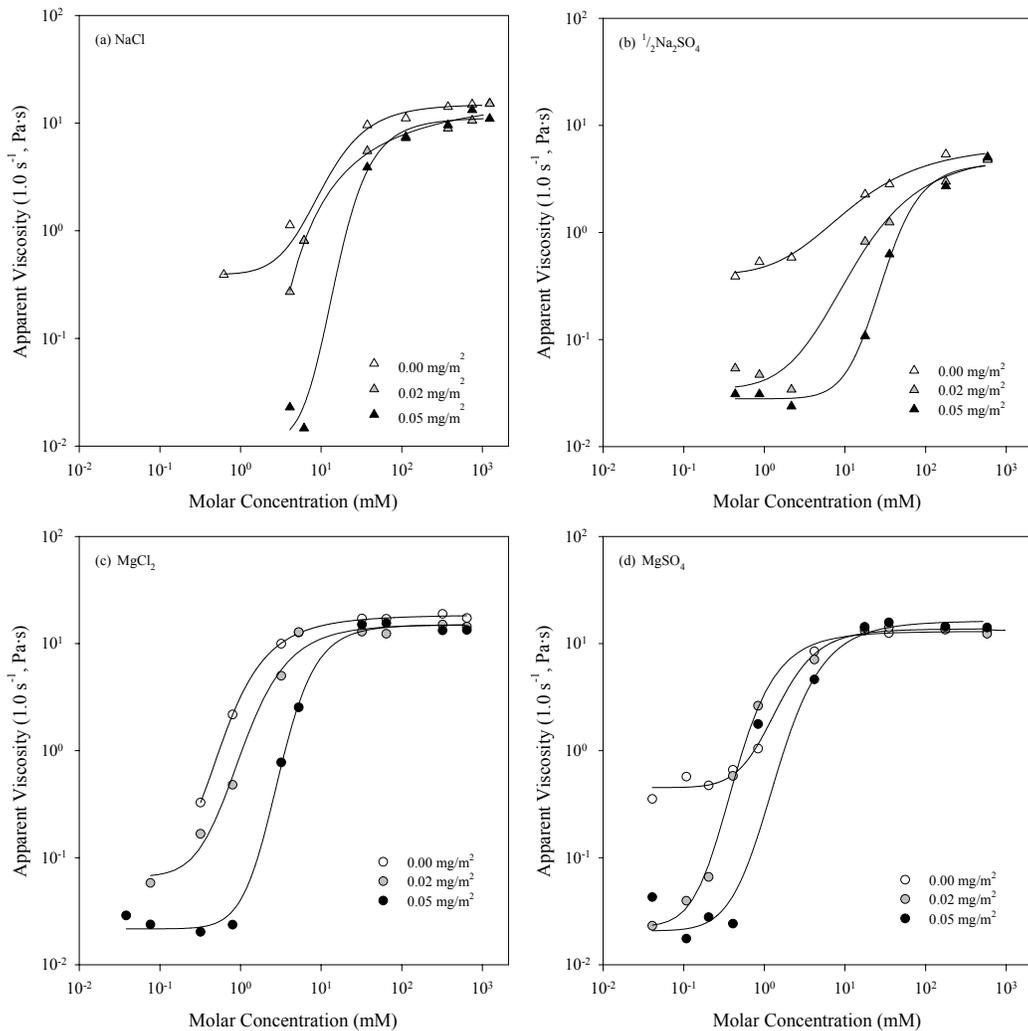


Figure 4-2. The apparent viscosity as a function of cation concentration for the three levels of dispersant $0.00, 0.02,$ and 0.05 mg/m^2 Na-PAA is shown for the six salts (a) NaCl, (b) Na_2SO_4 , (c) MgCl_2 , (d) MgSO_4 , (e) CaCl_2 , and (f) CaSO_4 .

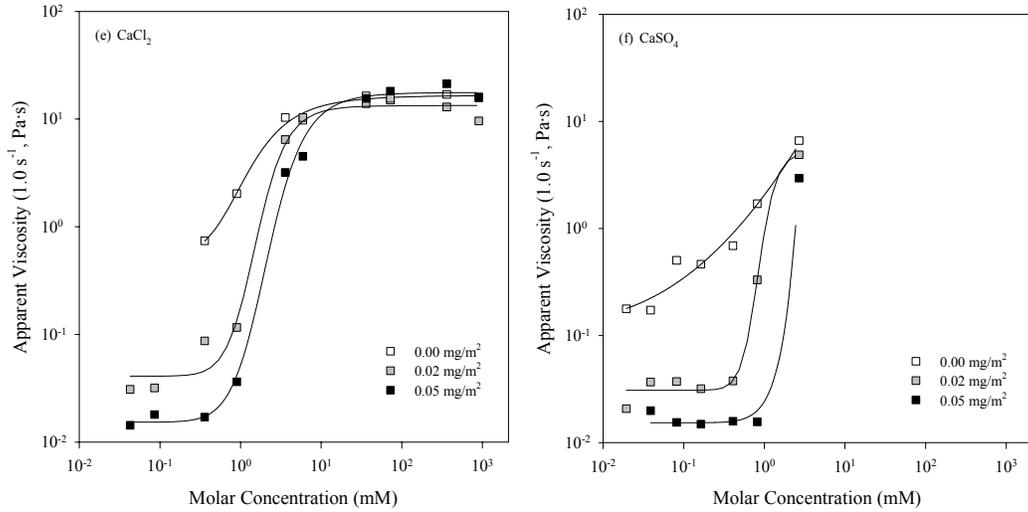


Figure 4-2. (continued)

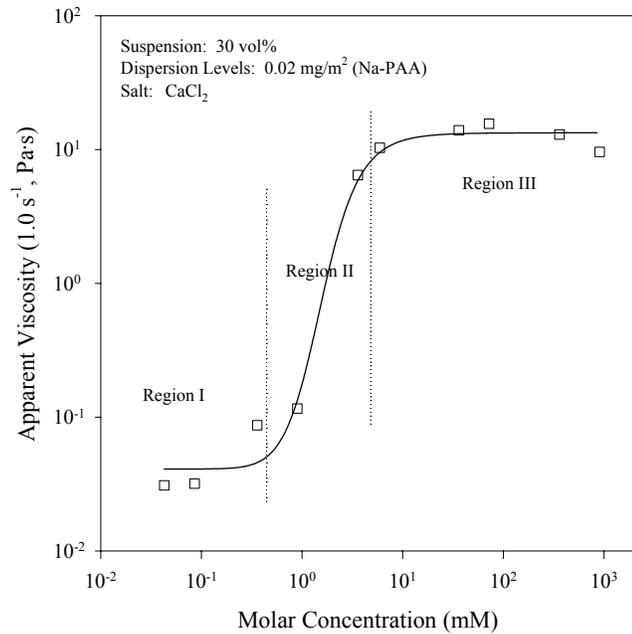


Figure 4-3. The apparent viscosity as a function of molar concentration for CaCl_2 . Three distinct regions in the apparent viscosity behavior were observed: Region I was independent of cation additions (dispersed), Region II showed a dramatic change due to cation addition (coagulation onset), and Region III was again independent of cation additions (coagulated).

The rheological behavior observed in the suspension across these three regions indicates the mechanism responsible for coagulation is compression of the double layer rather than

specific adsorption of the counter-ion. Table VIII lists the CCC for all salts at each dispersion level.

Table VIII. Six salts critical coagulation concentration at three dispersion levels

Electrolyte	0.00 mg/m² CCC (mM)	0.02 mg/m² CCC (mM)	0.05 mg/m² CCC (mM)
NaCl	9.8	6.5	26
½ Na ₂ SO ₄	2.2	11	43
MgCl ₂	1.0	1.5	4.8
MgSO ₄	1.6	0.65	2.6
CaCl ₂	0.80	2.1	4.2
CaSO ₄	1.9	0.97	2.5

The effects of chloride salt additions, CaCl₂, MgCl₂, and NaCl, on the apparent viscosity are shown in Figure 4-4 as a function of cation concentration. These curves clearly illustrate a distinction between the CCC of the divalent cations (Ca⁺² and Mg⁺²) and the monovalent cation (Na⁺) in suspension. The monovalent CCC is 6.5 mM compared to a divalent CCC of 2.1 and 1.5 mM for CaCl₂ and MgCl₂, respectively. In Region III, the suspension apparent viscosity plateau for the three chloride salts is similar. Likewise, these features exist in the sulfate salt suspensions shown in Figure 4-5.

A comparison of the sulfate and chloride anions, normalized to the cation concentration from the salt additions, are illustrated for the three cations, Na⁺, Ca⁺², and Mg⁺², in Figures 4-6, 4-7, and 4-8, respectively. The apparent viscosity behavior for both anions (Cl⁻ and SO₄⁻²) is similar for the Ca⁺² cations. Slight deviations were noted with the Na⁺ and Mg⁺² ions. The CCC of MgSO₄ occurs at a lower concentration than that of MgCl₂ with 0.02 and 0.05 mg/m² dispersant and the two curves, MgCl₂ and MgSO₄, are similar without dispersant; the CCC of NaCl occurs at a lower concentration than that of Na₂SO₄

with 0.02 mg/m^2 and the two curves, NaCl and Na_2SO_4 , are similar with 0.00 and 0.05 mg/m^2 .

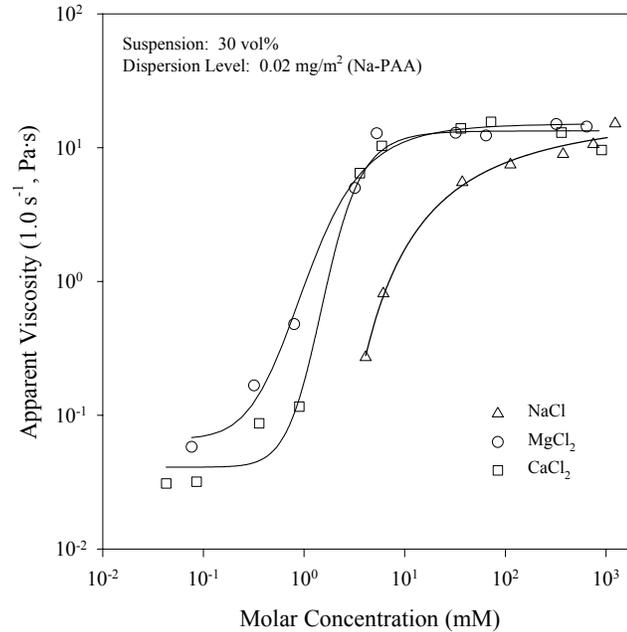


Figure 4-4. The apparent viscosity as a function of molar concentration for three chloride electrolytes. A clear distinction between the onset of the CCC for the monovalent and divalent cations is shown with the chloride salts.

The results in Figure 4-2 presented the concentration as a function of the cation species. Figures 4-9 and 4-10 show the suspension ionic concentration of the chloride and sulfate salts, respectively, in terms of the anion species, rather than the cation species, Figures 4-4 and 4-5. After normalizing the ionic concentration to the anion species, at the same anion concentration the apparent viscosity values of the salts with monovalent and divalent cation species do not coincide, indicating the anion species is not responsible for the suspension rheological behavior.

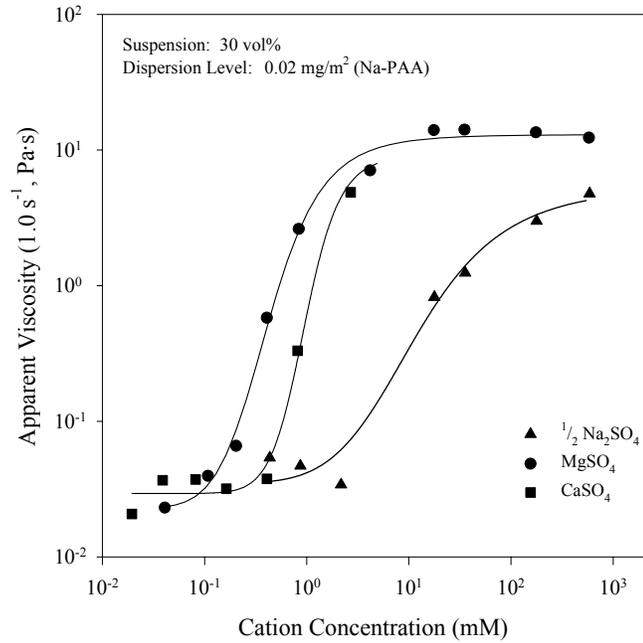


Figure 4-5. The apparent viscosity as a function of molar concentration for three sulfate electrolytes. The onset of the CCC for the monovalent and divalent cations.

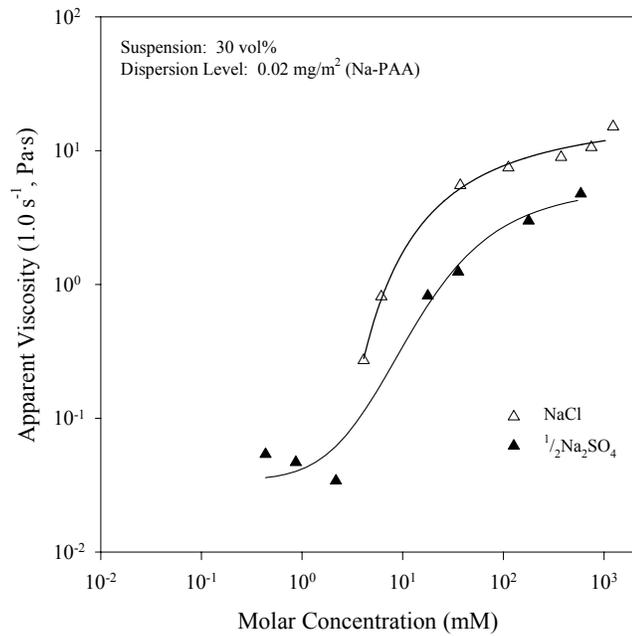


Figure 4-6. The apparent viscosity of the suspension with NaCl and Na₂SO₄ which are shown normalized to the cation concentration.

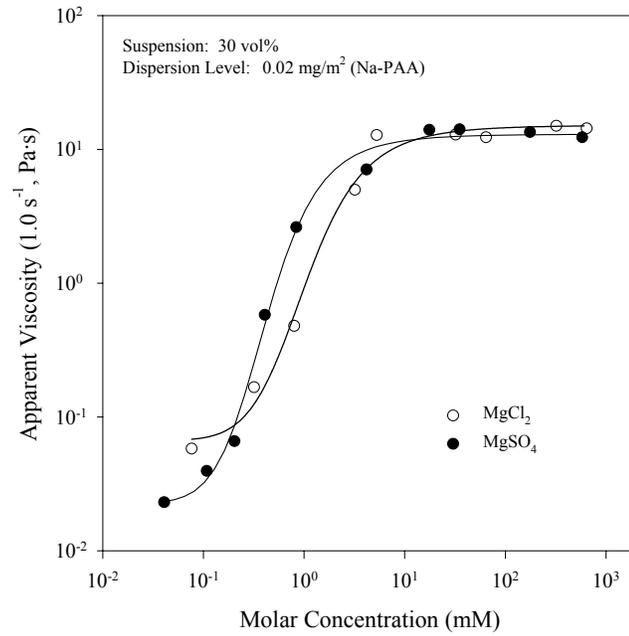


Figure 4-7. The apparent viscosity of the suspension with MgCl₂ and MgSO₄ which are normalized to the cation concentration.

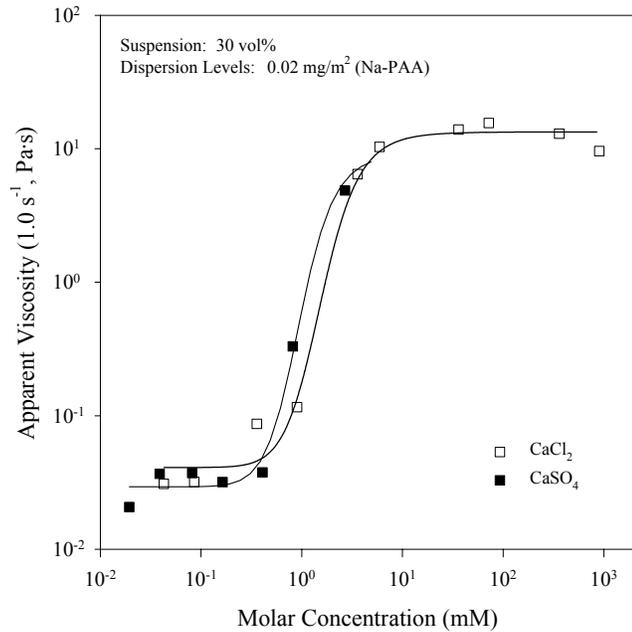


Figure 4-8. The apparent viscosity of the suspension with CaCl₂ and CaSO₄ which are normalized to the cation concentration.

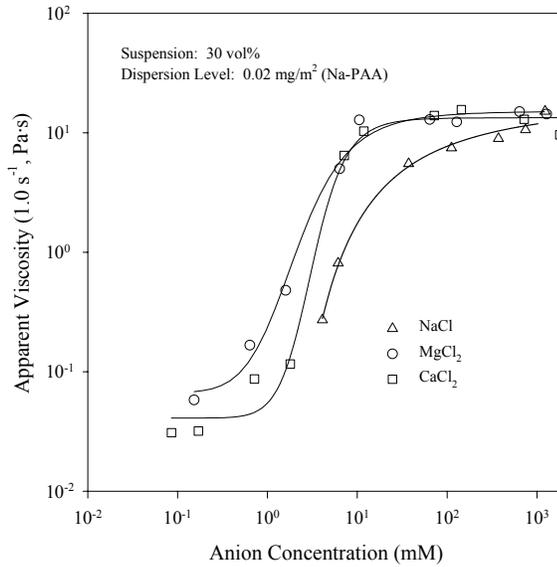


Figure 4-9. The apparent viscosity of the suspension with NaCl, MgCl₂, and CaCl₂ which are normalized to the anion concentration.

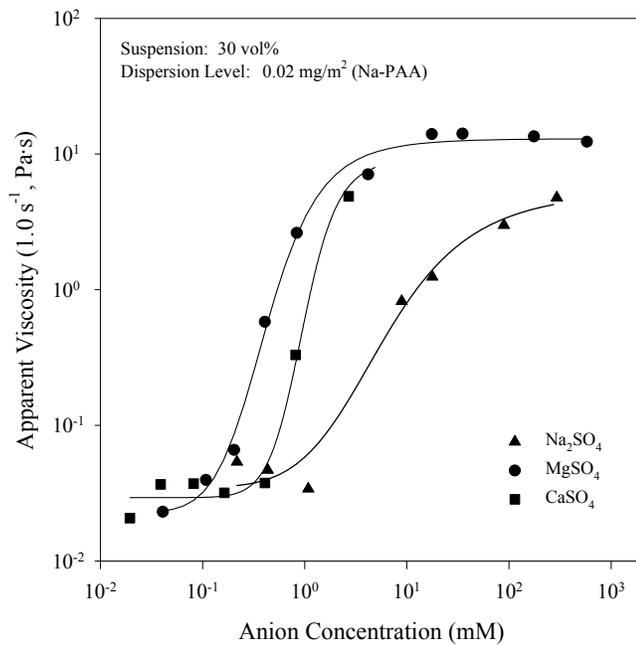


Figure 4-10. The apparent viscosity of the suspension with Na₂SO₄, MgSO₄, and CaSO₄ which are normalized to the anion concentration.

In the chloride salt suspensions that were dispersed at 0.02mg/m², the CCC for the monovalent cation, NaCl, is 6.5 mM and the divalent cations are 1.5 mM and 2.1 mM, respectively. These results agree with the Schultze-Hardy rules that indicate the charge

of the counter-ions dictates the concentration necessary to coagulate a suspension, specifically the higher charge ions require a smaller concentration.^{5, 23} But, the proposed ratio between monovalent and divalent salts necessary to coagulate a negative sol is $\left(\frac{1}{z}\right)^6$, where z is the charge of the cation, specifically, $\left(\frac{1}{1}\right)^6 : \left(\frac{1}{2}\right)^6$, or 100:1.6.^{5, 24} These ratios are higher than that observed with our data, indicating the CCC results are influenced by the experimental techniques used to obtain CCC values. Historically, CCC was determined as a function of electrolyte concentration using turbidity or light absorption in a dilute suspension, which were measured after a chosen time, anywhere from minutes to hours, to allow for kinetic effects.⁵ In contrast, the CCC values presented here were determined by the change in the apparent viscosity as a function of the cation concentration in a 30v/o suspension. Lower ratios of monovalent cations to divalent cations can be justified in this work because the suspension coagulation assessment, apparent viscosity, is a direct measurement of the interactive forces within the suspension and is independent of time. Also, the higher concentration of particles virtually eliminates kinetic effects that were present in dilute suspensions.

Effects of Dispersant Additions

Similar apparent viscosity trends were observed for all six salts at each level of dispersion, Figures 4-2. The figure indicates a decrease in the initial apparent viscosity as the dispersant concentration increases, with the highest dispersant concentration having the lowest initial apparent viscosity. The amount of salt required to attain the CCC increased with the addition of dispersant, specifically a higher cation concentration was

necessary with a higher degree of dispersion, due to the adsorption of the polyanionic species PAA onto the clay surface. Despite these two shifts due to the dispersant addition, lower initial apparent viscosity and higher CCC, the final plateau of Region III remains similar for all three levels of dispersion.

The addition of dispersant lowered the initial apparent viscosity by adsorbing polyanionic species to the clay surface imparting electrosteric stabilization.¹¹ Because the negative potential on the surface was increased by adsorbing anion, an increased cation concentration was required to coagulate the suspension therefore accounting for the shift to higher CCC. Figure 4-2 clearly illustrates higher dispersant concentrations require higher CCC for all six salts. Once a suspension is completely dispersed, indicated by a minimum in the apparent viscosity curve, higher dispersant concentrations cause an increase in the apparent viscosity. This apparent viscosity increase has previously been accounted for by bridging with polymers and polymer-like dispersants.²⁵ However, the apparent viscosity increase in Figure 4-11 is similar to the increase encountered as function of cation concentration in Figure 4-2 except that it is shifted to a higher concentration due to increased charge, with a greater dispersant concentration. These whiteware suspensions are completely dispersed at approximately 0.20 mg/m^2 with sodium carbonate (soda ash), sodium silicate (Na-silicate), and sodium polyacrylic acid (PAA), Figure 4-11.²⁶ Once the minima was reached, indicating complete dispersion, the apparent viscosity values of the three dispersed suspensions increased with increasing dispersant concentration, following the same rheological behavior that is observed with the addition of salt to a clay suspension. Once the suspension was completely dispersed,

further dispersant additions caused the suspension to coagulate due to the increased cation concentration introduced with the dispersant.

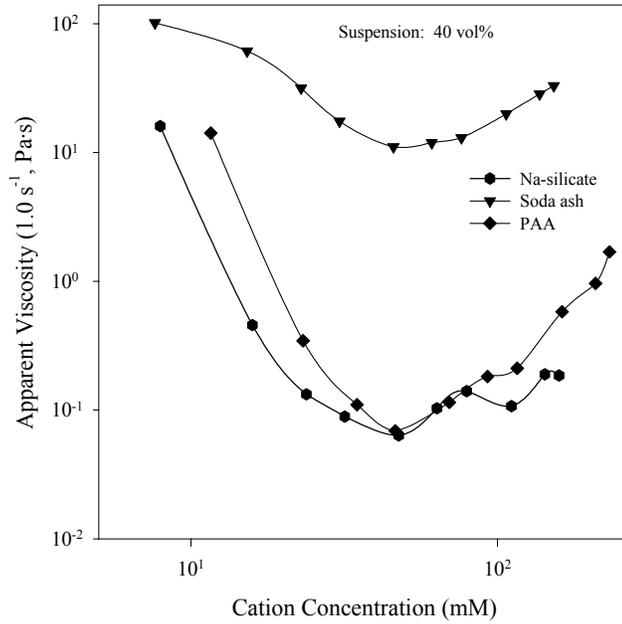


Figure 4-11. The suspension apparent viscosity normalized to the cation concentration over the dispersant concentration range.

Double Layer Thickness

The information presented thus far has been based on either the cation or anion concentration of the salt solution. By calculating the thickness of the double layer, both the cation and anion concentration are considered. The calculation of the double layer thickness was shown in equation (1) indicating the ion charge and concentration have the greatest impact on the double layer thickness. These calculations are only valid for symmetrical electrolytes, Figure 4-12 shows the calculated double layer thickness, as a function of the total ionic concentration for NaCl, MgSO₄, and CaSO₄ salts. The calculated thickness values and the apparent viscosity values are plotted against the

apparent viscosity values for the three salts in Figure 4-13 showing similar behavior. The values are listed in Table IX.

The shift in the double layer thickness shown in Figure 4-12 clearly indicates the 2:2 electrolytes, MgSO_4 and CaSO_4 , require less salt concentration to compress the double layer than the 1:1 electrolyte, as predicted by colloidal theory. Because the clay surface has an overall negative charge in the pH range of these suspensions, the cations, Na^+ , Mg^{+2} , and Ca^{+2} are responsible for compressing the double layer. Once the double layer has been sufficiently compressed to reduce the repulsive force, by either the monovalent or the divalent cations, the suspension coagulates, as indicated by the abrupt increase in the suspension viscosity. The CCC of NaCl , MgSO_4 , and CaSO_4 that is shown in Figure 4-13 were calculated at the inflection point to be 9.8, 1.6, and 1.9 mM, respectively, which corresponds to double layer thickness values to be 3.1, 3.8, and 3.5 nm, respectively. The apparent viscosity curves normalized to the calculated double layer thickness show similar behavior, further indicating that coagulation is primarily due to the compression of the double layer, rather than to specific adsorption.

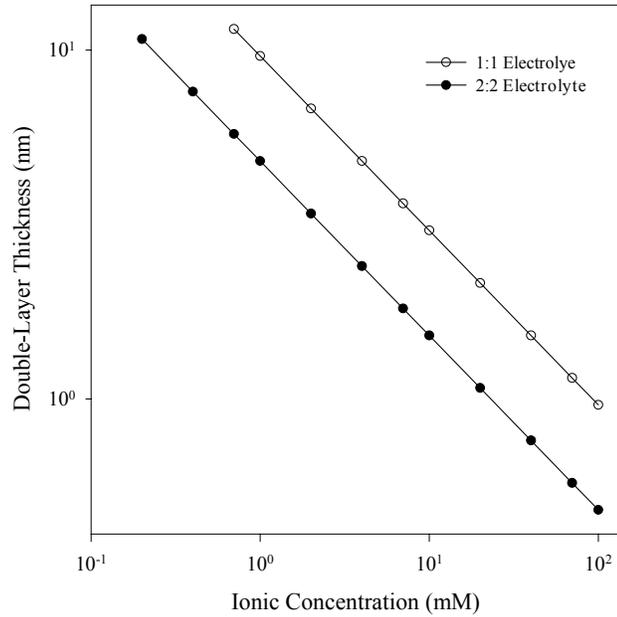


Figure 4-12. The double layer thickness as a function of the ionic concentration due to salt additions for symmetrical electrolytes.

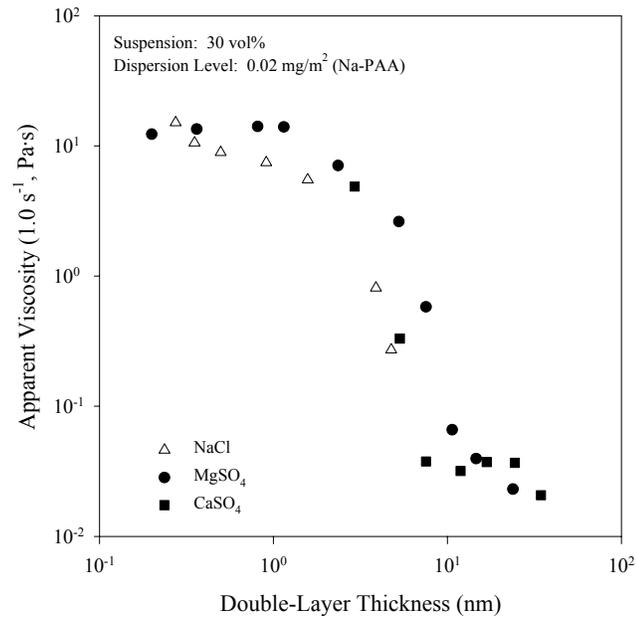


Figure 4-13. The apparent viscosity as a function of the calculated double layer thickness for the symmetrical electrolytes. The CCC determined from the inflection point were 3.1, 3.8, and 3.5, respectively.

Table IX. Calculated double layer thickness (D.L.) for symmetrical electrolytes

Electrolyte	Cation Concentration (mM)	Double Layer Thickness (nm)
NaCl	1.23E+03	2.74E-01
	7.47E+02	3.52E-01
	3.73E+02	4.98E-01
	1.12E+02	9.09E-01
	3.73E+01	1.57E+00
	6.13E+00	3.88E+00
MgSO ₄	4.09E+00	4.75E+00
	5.79E+02	2.00E-01
	1.76E+02	3.63E-01
	3.51E+01	8.12E-01
	1.76E+01	1.15E+00
	4.18E+00	2.35E+00
	8.40E-01	5.26E+00
	4.10E-01	7.53E+00
	2.00E-01	1.07E+01
	1.10E-01	1.46E+01
CaSO ₄	4.00E-02	2.38E+01
	2.69E+00	2.93E+00
	8.20E-01	5.32E+00
	4.10E-01	7.53E+00
	1.60E-01	1.19E+01
	8.00E-02	1.68E+01
	4.00E-02	2.44E+01
	2.00E-02	3.45E+01

Affinity of Salt Species

It is proposed that the difference in cation and anion affinity manifest itself as a shift in the CCC or a change in the shape of the apparent viscosity versus salt concentration curves of the six salts. The affinity of the Ca⁺² ions to the clay surface is indifferent with chloride and sulfate anions indicated by similar concentrations of each salt required to coagulate the suspensions in Figure 4-8. Figure 4-7 indicates the Mg⁺² ion has a greater affinity to the clay when associated with sulfate rather than chloride, while the Na⁺ ions has a greater affinity to the clay with chloride rather than sulfate shown in Figure 4-6.

Furthermore, the shape of the Na_2SO_4 curve has a more gradual change through the coagulation region, suggesting the sulfate has a greater affinity to the clay surface. The affinity of Ca^{+2} and Mg^{+2} ions to the clay surface is similar in the presence of chloride, but the Mg^{+2} ion has a greater affinity than the Ca^{+2} ion in the presence of sulfate shown in Figure 4-4 and 4-5, respectively. Further work is necessary to verify specific ionic affinities to the clay surface.

SUMMARY AND CONCLUSIONS

Aspects of this work support the colloidal theory that indicates cation is responsible for coagulating the clay suspension. First, by normalizing the ionic concentration versus the apparent viscosity values for the divalent and monovalent species to the anion concentration, the apparent viscosity should have been the same if the anion was causing the coagulation. But only when the plots are normalized to the cation are the apparent viscosity values similar. Second, the calculation on the double layer thickness accounts for the total ionic strength: divalent cations are more effective at compensating for the particle surface potential causing the suspension to coagulate at a lower cation concentration. The anions -- chloride and sulfate -- appear to play only a minor role in the viscosity change and slight differences (curve shifts and shape) in the suspension behavior was noted between MgSO_4 and MgCl_2 , and between NaCl and Na_2SO_4 .

Once the CCC has been obtained, the apparent viscosity values plateau, suggesting that the viscosity is independent of further salt additions and the dispersant concentration of the suspension. This plateau is similar for all suspensions indicating the final suspension structure achieved is similar despite the salt type or dispersant concentration. This

change in the apparent viscosity at the CCC increases by a factor of 100-10,000, which is dependent on the salt type and dispersant concentration. The data indicates double layer compression is responsible for the increase in the apparent viscosity as opposed to specific affinity.

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5. ZETA POTENTIAL MEASUREMENTS ON DISPERSED AND COAGULATED SUSPENSIONS

INTRODUCTION

Suspension rheology (defined as the study of flow and deformation) and properties is determined by five factors: 1) particle-particle interaction; 2) particle morphology; 3) particle size and distribution; 4) particle concentration; and 5) rheology of suspension medium.¹⁻³ The particle-particle interaction is the most critical of these parameters, and is directly impacted by the strength of the attractive and repulsive forces between particles in suspension. The source of the particle surface charge can originate from the following mechanisms: preferential dissolution of surface ions, direct ionization of surface groups, substitution of surface ions, specific ion adsorption, or generation of charges derived from specific crystal structures.⁴ By understanding the source of the charge on the particle surface, which impart either attraction or repulsion between the particles, it is feasible to predict the impact chemical changes will have on the suspension behavior.

An aqueous suspension develops a potential difference between the phases, one being water, which is a polar medium, and the other being the particles.^{5,6} There is a region of charge decay from the surface of the particle to some distance into the water at which point there is no charge imbalance. Near the charged particle, there exist both co- and counter-ions; a higher concentration of counter-ions are present due to the attraction to the particle surface.⁶⁻⁸ This region of charge decay is divided into various planes and

layers, working from the particle surface into the water these include: Stern plane, Stern layer, surface of shear, and diffuse layer. The ζ -potential is a measure of the potential developed between a point some distance from the surface and a point on the shear plane, within the fluid region around the particle.⁸ The exact location and calculation technique used to determine the ζ -potential are a function of the diffuse double layer model used, these include the Helmholtz model, the Stern model, the Gouy-Chapman theory, and the Debye-Huckel theory.^{6, 7, 9, 10}

The suspension ζ -potential can be determined by inducing tangential motion of either the particle or the medium with respect to the other phase, by one of four electrokinetic effects: electrophoresis, electro-osmosis, streaming potential, or sedimentation potential.^{4-7, 11} Electrophoresis induces particle motion with an applied electric field. Electro-osmosis moves the liquid phase with an applied electric field. Streaming potential moves the liquid by an applied pressure. Sedimentation potential uses gravity or a centrifugal field to move the particle. The ζ -potential is then calculated using the electrophoretic mobility, which is an estimate of the net charge on the particle, that is measured from the electrokinetic effects.

Various equipment has been developed in order to determine the ζ -potential values using electrokinetic effects.^{5, 7, 12} Electrophoresis techniques, specifically microelectro-phoretic and electroacoustic, have been the most common and most successful of these effects.

Very dilute solutions are required in order to measure the electrophoretic mobility using the microelectrophoretic techniques. The electroacoustic technique permits suspensions that are opaque to be tested and with higher solids loading. In comparison to the microelectrophoretic technique, it is as much as a thousand times greater.⁷ Higher

concentrations generate a stronger signal with the electroacoustic method. Conversely, some difficulty is encountered while measuring very dilute suspensions and suspensions approaching the isoelectric point (ISE), which would have very low charge and therefore a weak signal.¹² The electroacoustic theory has been applied to concentration levels up to 10% volume fraction for dynamic mobility measurements. Some theory has been developed for spheroidal geometry (discs and rods) that suggests spherical results with radius r are similar to a spheroid with an effective radius of r . This has only been applied, at this time, to dilute suspensions up to 0.1 volume fraction.¹²

Using the electroacoustic technique, the effects of pH, dispersant type and concentration, and electrolyte concentration on the ζ -potential of a clay suspension was examined.

These results should directly apply to higher concentrated suspensions that would generate a greater signal due to more available charge sites. Furthermore, ζ -potential values obtained from suspensions with only clay should correlate to that of a typical whiteware batch in which more than 85% of the surface area, and therefore, charge surface sites, are accounted for by the two types of clays.

EXPERIMENTAL PROCEDURE

Suspension Compositions, Chemistry, and Preparation

All suspensions tested were composed of 5 volume % kaolin (Edgar Plastic Kaolin, EPK, Zemex Industrial Minerals Inc., Edgar, FL) with a specific surface area of 26.9 m²/g, determined using the B.E.T. multi-point method (Gemini III 2375 Surface Area Analyzer, Micromeritics, Norcross, GA). The suspension chemistry was controlled using distilled water in a 10 mM NaCl background electrolyte solution or in a 7.0 X 10³ mM saturated CaCl₂ solution. The clay was gradually added to the liquid while mixing on a stir plate, and the suspensions were tested within 30 minutes.

Three groups of kaolin suspensions were studied that involved: 1) pH sweep; 2) dispersant additions; and 3) electrolyte additions. For the pH sweep group, two suspensions were prepared with clay in the NaCl background electrolyte solution, one of these suspensions also contained 0.05 mg/m² of the dispersant sodium silicate. HCl (6N) and NaOH (6N) were added during testing to initially decrease and then increase the suspension pH, respectively. (All chemicals were reagent grade from Fisher Scientific, Pittsburgh, PA.)

For the dispersant addition group, three suspension were prepared with clay in the NaCl background electrolyte solution, one with each of the three dispersants, polyacrylic acid, sodium silicate, or sodium carbonate (Table III). All dispersant additions were based on the surface area of the clay.

For the electrolyte addition group, the suspension was prepared with clay in distilled water at a dispersion level of 0.20 mg/m² PAA. The ionic concentration was

incrementally increased during testing by adding saturated CaCl_2 solution (7.0×10^3 mM); the solution cation concentration was verified using Inductively Couple Plasma (ICP) Spectroscopy (ACME Analytical Laboratories Ltd., Vancouver, British Columbia, Canada).

Measurement Method (Electrophoretic Mobility)

The ζ -potential values were determined by measuring the electrophoretic mobility (Acoustosizer, Colloidal Dynamics, Warwick, RI) of the kaolin suspensions. The sample chamber contains a stirring blade, two parallel plate electrodes each connected to a glass rod, and probes to measure pH, temperature, and conductivity. This instrument uses the electrokinetic sonic amplitude (ESA) effect that generates sound waves by an applied electric field (alternating current), over a range of frequencies to determine the dynamic mobility.

A Fourier transform, $F(\omega)$, of the ESA pulse is calculated from the original applied signal $f(t)$ by equation (1), where ω is the pulse frequency.¹² The transform gives a linear function to the sinusoidal applied voltage. Using the ESA value from equation (1), the average dynamic mobility, $\langle \mu_D \rangle$, can be calculated from equation (2), where A is an instrument constant, ϕ is the particle volume fraction (5 volume %), $\Delta\rho$ is difference in densities between the particle and the liquid (1.6), ρ is the density of the liquid (1.0), E is the applied field, and Z_s and Z_g are the acoustic impedance of the suspension and the glass rod, respectively.

$$\text{ESA: } F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt \quad (1)$$

$$\text{ESA} = A\phi \frac{\Delta\rho}{\rho} \langle \mu_D \rangle E \frac{Z_s}{Z_g + Z_s} \quad (2)$$

With the average dynamic mobility value, the ζ -potential is then calculated using equation (3), where ε is the dielectric permittivity of the suspension, ζ is the ζ -potential, η is the viscosity of the liquid, a is the particle radius, ν is the kinematic viscosity of the liquid, and G is an inertial term. Equation (3) is identical to the Smoluchowski equation that is used to calculate the dc electrophoretic mobility except for the inertial term G :

$$\langle \mu_D \rangle = \frac{\varepsilon\zeta}{\eta} G \left(\frac{\omega a^2}{\nu} \right). \quad (3)$$

These calculations assume spherical particles, but may be applied if all orientations of suspension particles are equally likely. It can be argued that a kaolin particle, having one positive and one negative basal plane, under an alternating current meets this requirement.¹³

RESULTS AND DISCUSSION

Effects of pH Sweep to the Suspension ζ -Potential

The effects of changing the pH of two suspensions, one with 0.05 mg/m² Na-silicate and one without dispersant addition, on the ζ -potential values are shown in Figure 5-1. Increasing the pH of the two suspensions increased the magnitude of the ζ -potential by increasing the density of negative surface sites or surface charge.⁵ The ζ -potential of the Na-silicate dispersed suspension had a larger increase, (became more negative), than the suspension without dispersant, indicating anion adsorption onto the clay surface. This further supports previous results that indicated similar cation levels do not equally disperse clay suspensions, when the degree of dispersion was measured by the apparent viscosity as a function of the dispersant concentration.¹³

A shift in the isoelectric point (IEP), which would confirm specific adsorption, is not observed with these ζ -potential measurements.⁷ This may be due to the technique used to prepare and test the suspensions. Changing the suspension pH, alters the dissociation of the Na-silicate and would influence the suspension dispersion and ζ -potential values.¹⁴

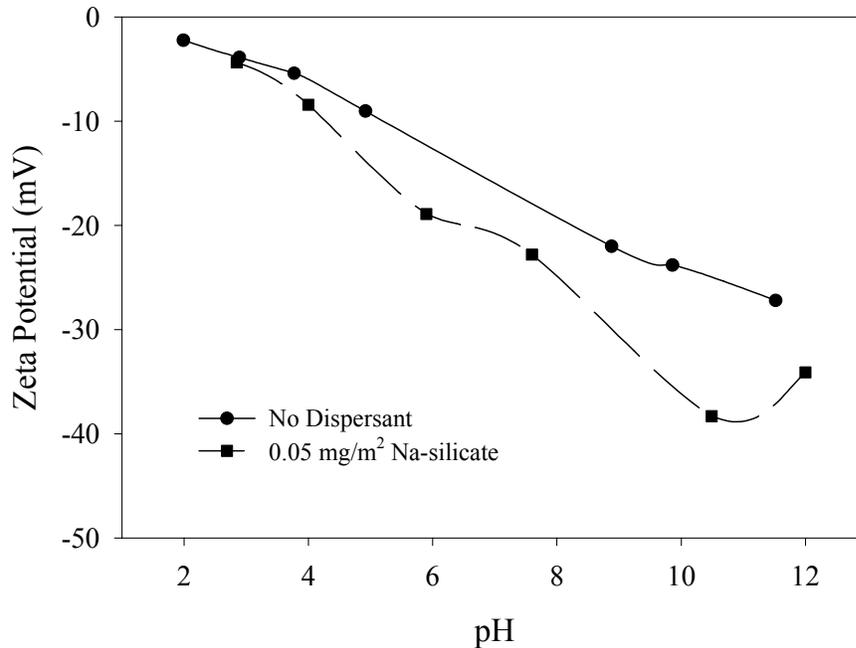


Figure 5-1. The effects of suspension pH on the ζ -potential, in a 5 v/o kaolin suspension, with and without dispersant.

Also, it may be inaccurate to assume that all orientations of the clay particle are equally likely. This assumption may allow the ζ -potential results from the Acoustosizer to only illustrate trends in the clay suspension particle charge, but "...even approximate numbers can be useful."⁴ Because kaolinite, the mineral form of kaolin, has one silica-like or quartz-like basal plane and one alumina-like or gibbsite-like basal plane, the IEP of the clay should incorporate the IEP of these two surfaces. The point of zero charge (PZC) for gibbsite has been measured to be 9.8, and the IEP of vitreous silica has been measured to be 2.4.^{15, 16} Therefore, the IEP of kaolin should fall within this range, 2.4-9.8, but the suspension ζ -potential values, determined with the Acoustosizer, remained negative at a pH of less than 2. Electrophoretic mobility of sodium kaolinite with background

electrolyte solutions was found to be zero near a pH of 4 indicating a ζ -potential of zero by using Smoluchoski's equation (4),

$$\text{Smoluchoski Equation: } U = \frac{\varepsilon\zeta}{4\pi\mu} \quad (4)$$

where U is the electrophoretic mobility, ε is the permittivity, and μ is the liquid viscosity.¹⁷

If the IEP of the clay suspension in the background electrolyte in Figure 5-1 was assumed to be at a pH of 4, than the IEP of the suspension with Na-silicate would occur at a lower pH. The shift in the IEP would verify specific adsorption, and indicate the anion is responsible for dispersing the clay suspension.

As the suspension approaches the IEP, the signal generated becomes weaker due to a decrease in the magnitude of the surface charge.¹² Therefore this suggests that, for a region around the IEP, the dynamic mobility is difficult to effectively measured using electroacoustic techniques.

Effect of Three Dispersants to the Suspension ζ -Potential

The effects of incremental additions of three dispersants, PAA, Na-silicate, and soda ash, to the ζ -potential magnitude of the suspension are illustrated in Figure 5-2. The addition of the dispersants increased the ζ -potential of the clay suspensions suggesting that the anion species are responsible for dispersion. The complete dispersion of PAA, Na-silicate, and soda ash, measured by the minima in the apparent viscosity curves, occurs at

a dispersant concentration of approximately 0.20-0.30 mg/m², as shown in Figure 5-3.¹³ This dispersant level also corresponds to a plateau in the suspension ζ -potential values shown in Figure 5-2. Dispersant levels above 0.2-0.3 mg/m² do not contribute additional negative sites, i.e. the ζ -potential magnitude does not increase. This indicates a uniform surface charge has been achieved, further supporting complete dispersion at the apparent viscosity minima. The impact of dispersant addition on the suspension pH and ζ -potential values is shown in Figure 5-4. The suspension pH with no dispersant is 5.2 and increased to 7.9, 10.5, and 10.6, with the addition of 1.0 mg/m² PAA, Na-silicate, and soda ash, respectively.

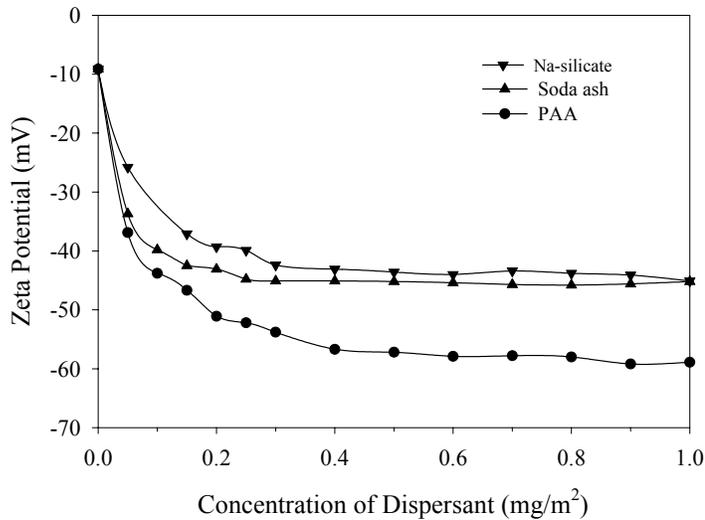


Figure 5-2. The effects of incremental dispersant addition on the 5 v/o kaolin suspension ζ -potentials value for PAA, Na-silicate, and soda ash.

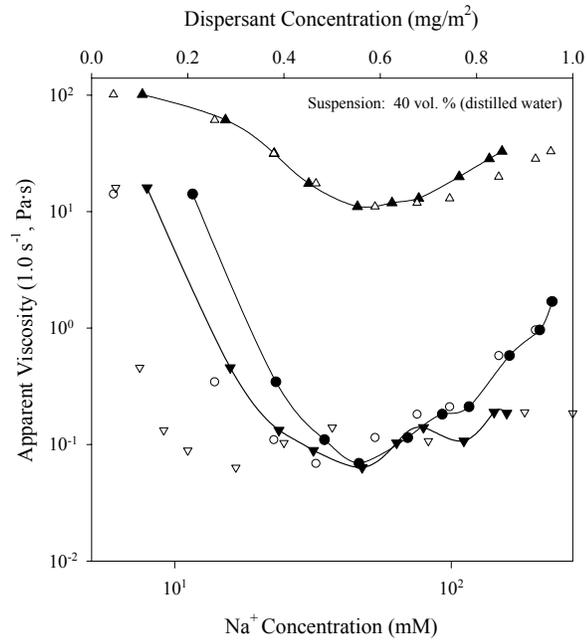


Figure 5-3. The apparent viscosity results of a typical whiteware composition suspension with the addition of Na-silicate, Soda Ash, and PAA as a function of Na^+ concentration ∇ , \blacktriangle , and \bullet , respectively, and dispersant concentration ∇ , Δ , and \circ , respectively.

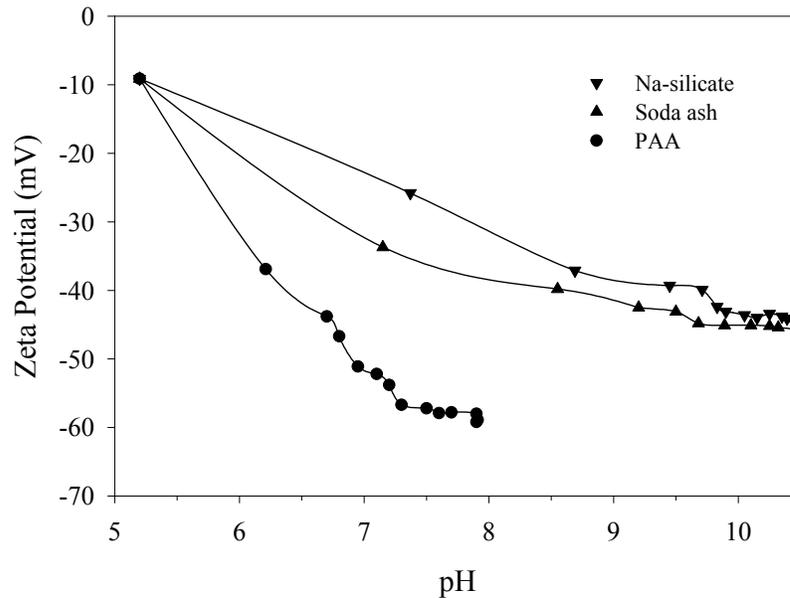


Figure 5-4. The effects of incremental dispersant addition on suspension pH and ζ -potential for the three dispersants in the 5 v/o kaolin suspensions.

A comparison of the suspension behavior measured by ζ -potential, pH, and apparent viscosity between these three dispersants produced some unanticipated results. First, the ζ -potential and pH of the suspension with soda ash was similar to those observed with Na-silicate. But, the apparent viscosity values, which measured the degree of dispersion, with soda ash were 100 times that of the Na-silicate even though the pH of the two suspensions is similar. A parallelism to this observation is that the apparent viscosity of the suspension with PAA additions is similar to that of the suspension with Na-silicate, but the magnitude of the ζ -potential in the PAA suspension is approximately 10 mV greater than that in the Na-silicate suspension. However, the pH of the PAA suspension is lower than that of the Na-silicate suspension, indicating pH does not significantly affect the dispersion of kaolin over this pH range that was investigated. The stability of a suspension, which implies a similar surface charge between the particles sufficient to cause dispersion, is considered to be closely related to the ζ -potential of a colloidal system.¹⁸⁻²¹ These results do not support this general assessment of the relationship between ζ -potential and suspension stability.

Two models are proposed to explain the suspension behavior due to the addition of these dispersants. The similar ζ -potential measurements of the soda ash and Na-silicate would indicate the anion species of the two dispersants are equally adsorbed onto the surface of the clay particles, thus creating equivalent number of negative sites. The cation concentration introduced with the soda ash could be sufficiently high to compress the double layer and cause coagulation. This would be denoted by higher apparent viscosity values with soda ash over those of the Na-silicate. But, it has been shown that the

apparent viscosity with soda ash is still two orders of magnitude higher than that with the Na-silicate, after normalizing to the Na^+ cation concentration.^{13, 22}

A second model proposes that the mechanism of dispersion, (electrostatic, steric, or electrosteric), impacts the ζ -potential measurements.^{7, 23, 24} The suspensions with PAA and Na-silicate are dispersed by electrosteric stabilization and have similar ζ -potential measurements and nearly identical apparent viscosity values. The suspension with the soda ash is dispersed by electrostatic stabilization. The results suggest that in suspensions dispersed by electrosteric stabilization one may not be able to directly relate the stability results, measured by apparent viscosity, to the ζ -potential results. Conversely, in suspensions dispersed by electrostatic stabilization, one may relate ζ -potential directly to the suspension stability. Due to the uncertainty of the relationship between the two parameters, stability and ζ -potential, the rheological results can be further explained with ζ -potential measurements, but suspension stability can not be predicted by ζ -potential measurements alone.

Effect of Salt Addition to the Suspension ζ -Potential

Changes in the suspension ζ -potential value due to the addition of CaCl_2 to the clay suspension, dispersed with 0.20 mg/m^2 PAA, are illustrated in Figure 5-5. By increasing the salt concentration, the magnitude of the ζ -potential decreased. This implies that the cation is responsible for coagulating the suspension by compressing the double layer. These ζ -potential measurements are shown in conjunction with the rheological behavior

of a typical whiteware batch composition suspension at three PAA addition levels, 0.00, 0.02, and 0.05 mg/m².²² The suspension ζ -potential with only clay can be correlated to the batch rheological behavior because the clay accounts for 94% of the batch surface area. The greatest drop in the magnitude of the ζ -potential occurred from -33.1 to -13.6 at approximately the same cation concentration required to coagulate the batch suspensions, which is indicated by an abrupt increase in the apparent viscosity values. Below a threshold ζ -potential value, the repulsive force between the particle is insufficient to prevent agglomeration by van der Waals attractive forces, and the suspension coagulates. It has been shown that a minimum ζ -potential magnitude in the range of 25-35mV is necessary to insure a stable well dispersed clay suspension.^{10, 25}

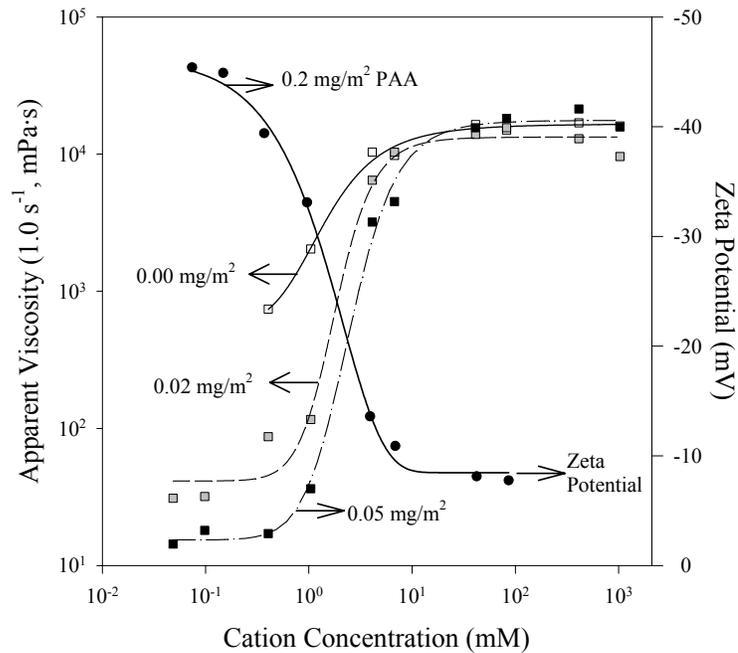


Figure 5-5. The effect of CaCl₂ additions on the ζ -potential values of a 5 v/o kaolin suspension dispersed with 0.2 mg/m² PAA, as a function of CaCl₂ concentration in conjunction with the apparent viscosity of three whiteware batch composition suspensions, which are dispersed at three levels, 0.00, 0.02, and 0.05 mg/m².

It has been demonstrated that coagulation of a clay suspension is due to the cation species but the mechanism, either compression of the double layer or specific adsorption, was not isolated. Figure 5-6 illustrates the ζ -potential results from Figure 5-5 in a clay suspension dispersed with 0.20 mg/m^2 and the ζ -potential results due to the addition of PAA from Figure 5-4. These curves, PAA additions and PAA with CaCl_2 additions, suggest coagulation due to the compression of the double layer because there is no shift in the IEP.

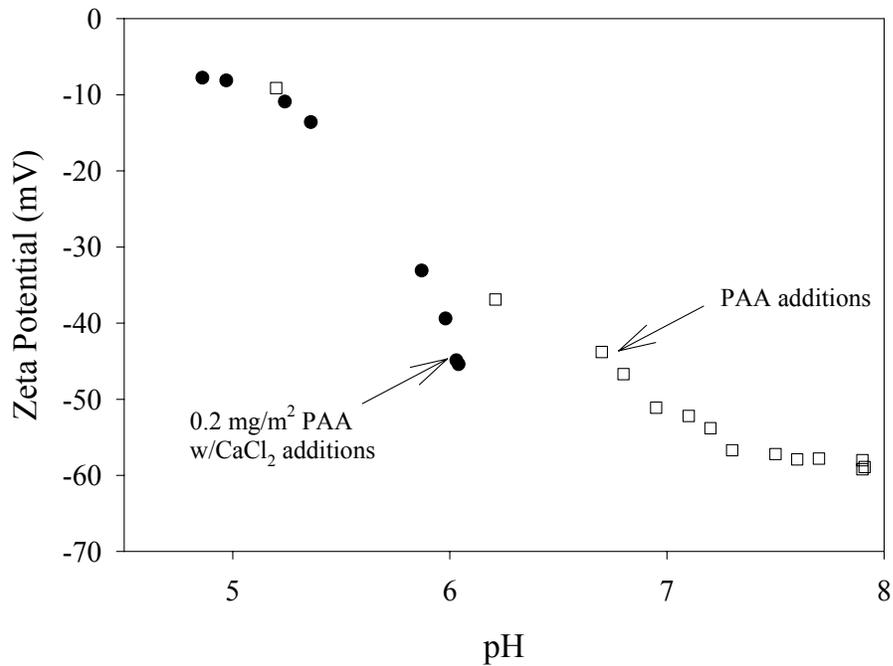


Figure 5-6. The ζ -potential values for the 5 v/o kaolin suspension with salt additions, which is dispersed with 0.20 mg/m^2 PAA, and with incremental PAA additions.

SUMMARY AND CONCLUSIONS

The anion species control dispersion in a clay suspensions and specific adsorption is the likely mechanism. Based on the ζ -potential measurements and the nature of the clay particle geometry and charge, a shift in the IEP was not observed, which would confirm specific adsorption. ζ -Potential and suspension stability are not interchangeable parameters and these results suggest the dispersion mechanism impacts the magnitude of the ζ -potential measurements. Rheological behavior can be explained further with ζ -potential measurements, but ζ -potential measurements can not predict rheological behavior. Cation species are responsible for the coagulation of a clay system, and suggest compression of the double layer as the responsible mechanism.

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6. EFFECT OF CATION CONCENTRATION ON PLASTICITY

INTRODUCTION

The cation concentration in a whiteware suspension has been clearly shown to be responsible for coagulation.¹ According to colloidal theory, the cations compress the double layer, which reduces the repulsive force between particles, imparting agglomeration in a clay suspension. The impact of increasing the concentrations of monovalent and divalent cations on the suspension behavior was measured. By increasing the solids loading from 60% to greater than 80%, the role of the cation concentration on a plasticity body can be evaluated.

Characterizing the plastic body presents a challenge due to the lack of standardized testing procedures and a definitive understanding of the mechanisms responsible for plastic behavior. Furthermore, the definition of plasticity is frequently linked with how a material performs rather than a material property.²⁻⁵ Various techniques have been proposed to evaluate the plasticity of a clay body.^{3, 4, 6-8} The technique utilized to determine the impact of cation concentration on the plasticity was a High Pressure Annular Shear Cell (HPASC), which was previously used to evaluate changes in clay-water systems^{9, 10} and pseudo-boemite systems.¹¹

The HPASC measures a shear stress, due to imposed shear rate under an applied force. From these results, the applied pressure dependence is determined, which is a function of the water content of the plastic body, and the critical shear stress, or cohesion stress of the plastic body. The plasticity measurements, pressure dependence and cohesion stress, are shown as a function of water content of a plastic body in Figure 6-1.⁹ The results clearly

indicate that increasing the water reduces the pressure dependency of the plastic body. The cohesion stress of a plastic body increases as the water content is reduced up to a maximum stress, and then gradually reduces upon further water reduction.

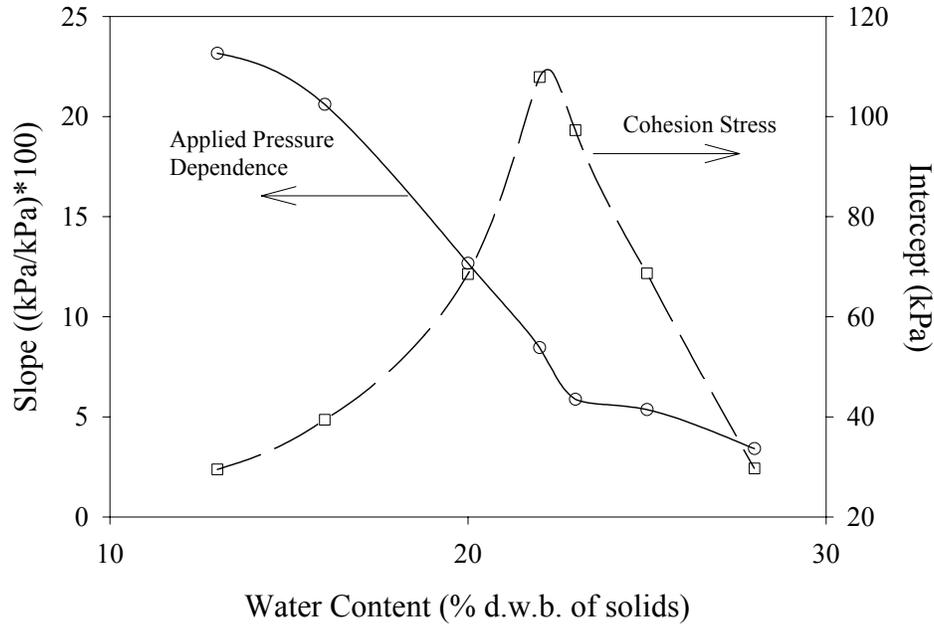


Figure 6-1. The applied pressure dependence and cohesion stress as a function of water content for a ball clay and water plastic body.⁹

The influence of cation concentration, via CaCl_2 additions, on the plasticity of a generic triaxial porcelain body was evaluated at a water content of 16%; these results were correlated with the coagulation behaviors of a clay suspension. Using an industrial porcelain body, the plasticity of a coagulated body and dispersed body were compared. The effects of aging on the plasticity were examined with the industrial body.

EXPERIMENTAL PROCEDURE

Plastic Body Composition

The plasticity of two whiteware bodies was evaluated, *Body A* and *Body B*. *Body A* is a generic triaxial porcelain composition, i.e. clay, quartz, and feldspar. The composition of *Body A* is listed on a dry weight basis (d.w.b.) in Table X along with the corresponding specific surface area measurements for each raw material. The surface area was measured using the B.E.T. multi-point method (Gemini III 2375 Surface Area Analyzer, Micromeritics, Norcross, GA).

Body B is an industrial triaxial porcelain composition prepared by a whiteware manufacturing facility using production raw materials. The composition of *Body B* is listed in Table XI on a d.w.b. along with the corresponding surface area of the raw materials.

Plastic Body Chemistry

Body A was prepared using distilled water to control batch chemistry. The ionic concentration of *Body A* batches was adjusted using saturated CaCl₂ solution; the cation concentration of the CaCl₂ solution (6.30×10^3 mM) was verified by Inductively Coupled Plasma (ICP) Spectroscopy (ACME Analytical Laboratories Ltd., Vancouver, British Columbia, Canada).

Table X. *Body A* composition of standard triaxial porcelain plastic body

Raw Material	Supplier	Wt. % (d.w.b.)	Specific Surface Area (m²/g)	% of Batch Surface Area
Kaolin	Edgar Plastic Kaolin (EPK) Zemex Miniearls, Inc., Edgar, FL	50.0	26.9	95.2
Quartz	Ogledbay Norton Industrial Sands, Inc. Glenford, OH	25.0	0.9	1.6
Feldspar	K200, Zemex Miniearls, Inc., Monticello, GA	25.0	1.8	3.2

Table XI. *Body B* composition of industrial triaxial porcelain plastic body

Raw Material	Supplier	Wt. % (d.w.b.)	Specific Surface Area (m²/g)
Kaolin	Kingsley, Rogers, Kentucky-Tennessee Clay Co., Mayfield, KY	10.0	13.5
			27.8
Ball Clay	Weldon/Victoria, United Clays, Inc., Brentwood, TN	34.0	23.3
			27.5
			45.0
	M& D, Kentucky-Tennessee Clay Co., Mayfield, KY		
Quartz	Ogledbay Norton Industrial Sands, Inc. Glenford, OH	23.0	0.9
Feldspar	K200, G200, Zemex Miniearls, Inc., Monticello, GA	33.0	1.8
			1.1

Body B was prepared with the manufacture's regular process water that is received from the local municipal water treatment facility. The dispersant and coagulant that was used in production are CaCl_2 and sodium polyacrylic acid (PAA) (Dispex®, Ciba Specialty Chemicals, Basel, Switzerland, formerly Allied Colloids), respectively.

Plastic Body Preparation: *Body A*

Individual batches were prepared at 16% water content and were comprised of 250 g of powder and 47.6 of liquid. The liquid included distilled water and the necessary amount of saturated CaCl_2 solution in order to generate batches over a broad range of ionic concentrations, (1.31×10^{-2} - 1.32×10^2 mM). All dry materials were placed into the sample chamber (Plastosizer Prep-Mixer, C. W. Brabender Instruments, Inc., South Hackensack, NJ) and mixed with twin screw roller blades at 60 rpm. The liquid was gradually added and the plastic body was mixed for 15 minutes. The sample chamber was water cooled to eliminate heating the sample and evaporating the liquid during mixing.

Plastic Body Preparation: *Body B*

Four varieties of *Body B* were prepared. A portion of the standard industrial suspension was removed from production prior to filter pressing to create the first two plastic body samples. The first *Body B* sample suspension was highly dispersed with excess dispersant (PAA) above the typical industry levels. The second *Body B* sample suspension was highly coagulated with CaCl_2 , above the typical industry levels. After

thoroughly mixing, the suspensions were filter pressed offline, and filter cakes were collected for plasticity testing.

The third and fourth plastic *Body B* samples were removed from production after the filter pressing process. One sample 'Standard' was tested within hours after filter pressing, and the other sample 'Aged Standard' was aged for two weeks in a sealed container prior to testing.

The effects of de-watering, which occurs during forming and drying, on the plasticity of four *Body B* samples were evaluated by systematically reducing the water content. Plastic *Body B* samples were received at an approximate water content of 19%. Water content values were obtained using the general procedure outlined in ASTM method C324-82. Variations to this procedure included using a smaller sample size and measuring water content of five representative samples to calculate an average and a standard deviation. Each water content level was generated by drying 300 g samples of plastic *Body B* and then placing them into the Plastosizer Prep-Mixer sample chamber. The samples were mixed for 10 minutes to homogenize the sample moisture content prior to measuring the plasticity. Drying times were varied to generate a range of moisture levels. The moisture level was measured immediately after homogenizing to correlate plasticity with water content.

Plasticity Measurement Method

The plasticity of all samples was measured using the HPASC. The *Body A* samples were tested immediately after mixing so the effects of aging the plastic body would be

minimized. The *Body B* samples were tested upon receipt from the production facility except for the ‘Aged Standard’ *Body B* sample. Each test required 75 g of a plastic body to be placed into the test fixture. All tests were conducted at a shear rate of 0.5 rpm with incremental weight additions: 22.9, 34.0, 45.4, 56.7, and 68.0 kg (50.0, 75.0, 100, 125, and 150 lbs.). Between each weight addition, there was an equilibration period prior to measuring sample properties. The typical data generated from these measurements are shown in Figure 6-2, and the slope and y-intercept values were extracted from these results. The slope is a measure of the applied pressure dependence, and the intercept is a measure of the cohesion stress of the plastic body.⁹⁻¹¹

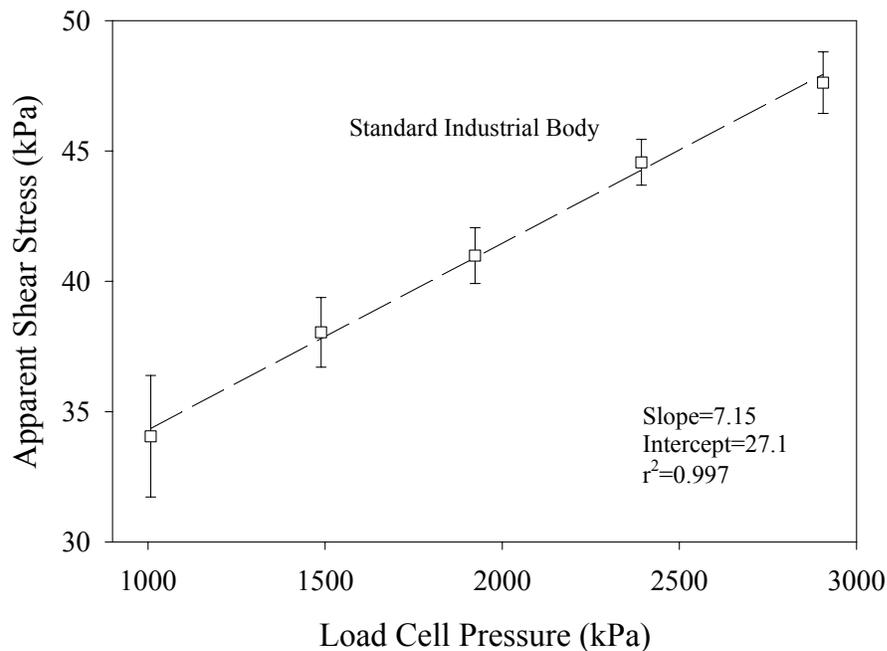


Figure 6-2. The data generated from the HPASC at on shear rate (0.5 rpm) and incremental increasing applied pressure. The slope as a measure of the pressure dependence and the intercept is a measure of the cohesion stress. Error bars indicate ± 2 standard deviation.

RESULTS AND DISCUSSION

Effect of Cation Concentration on *Body A* Plasticity

The effect of cation concentration, Ca^{+2} , on plasticity of *Body A* is shown in Figure 6-3. At low cation levels, the cohesion stress is high, but decreases at a concentration of approximately 1.0 mM, in the 16% water content plastic body. It is proposed that the lower cohesion stress will improve the formability of a plastic body by allowing the particles to flow past each other more easily. The cation concentration that is necessary to reduce the cohesion stress in plastic *Body A* is similar to the critical coagulation concentration (CCC) for a typical whiteware composition suspension, that was previously studied, both are shown in Figure 6-4.¹

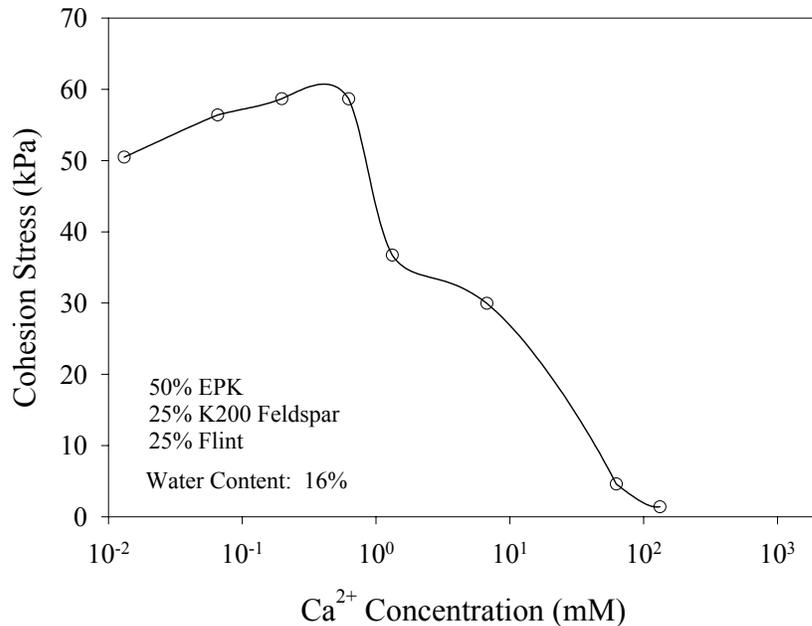


Figure 6-3. The effect of increasing cation concentration on the plasticity of the generic triaxial body. At approximately 1.0 mM of Ca^{+2} the cohesion of the body drops rapidly.

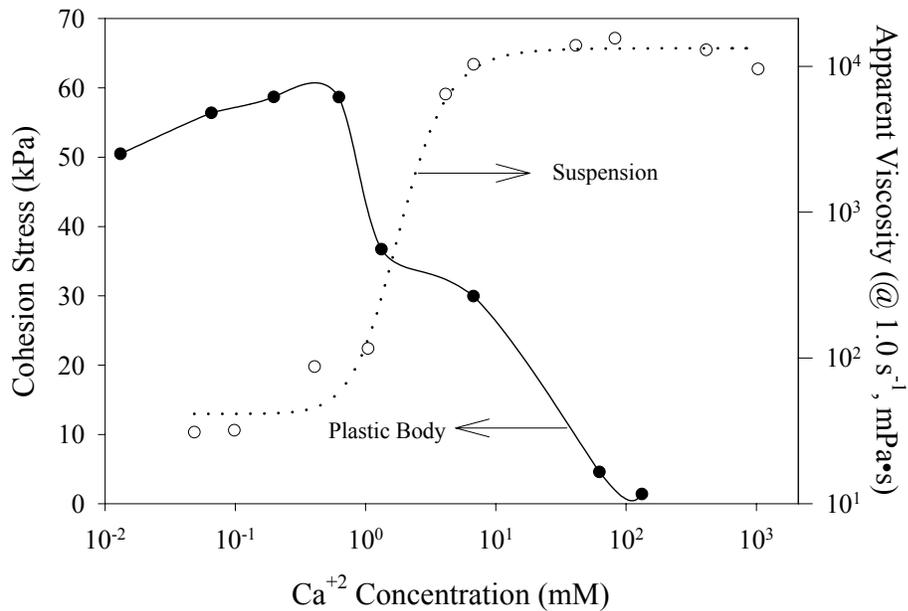


Figure 6-4. The plasticity of the triaxial body is shown with the suspension behavior, both with an increasing Ca^{+2} concentration. The critical coagulation concentration of the suspension, which is indicated by the sharp apparent viscosity increase and the decrease in the cohesion stress, occur at similar Ca^{+2} concentration.

This suggests that the lower cohesion stress is directly impacted by the coagulation and particle-particle interaction. Therefore, the attractive forces between the particles in a suspension play a role in the plastic body behavior. Furthermore, it suggests that by controlling the suspension chemistry, the plastic body behavior during forming and drying can be improved by reducing the cohesion stress. The plastic body is produced by de-watering the suspension, but maintaining the cation concentration. This process is illustrated in Figure 6-5 showing the shift in the solids loading and the rapid increase in the effective cation concentration after filter pressing.

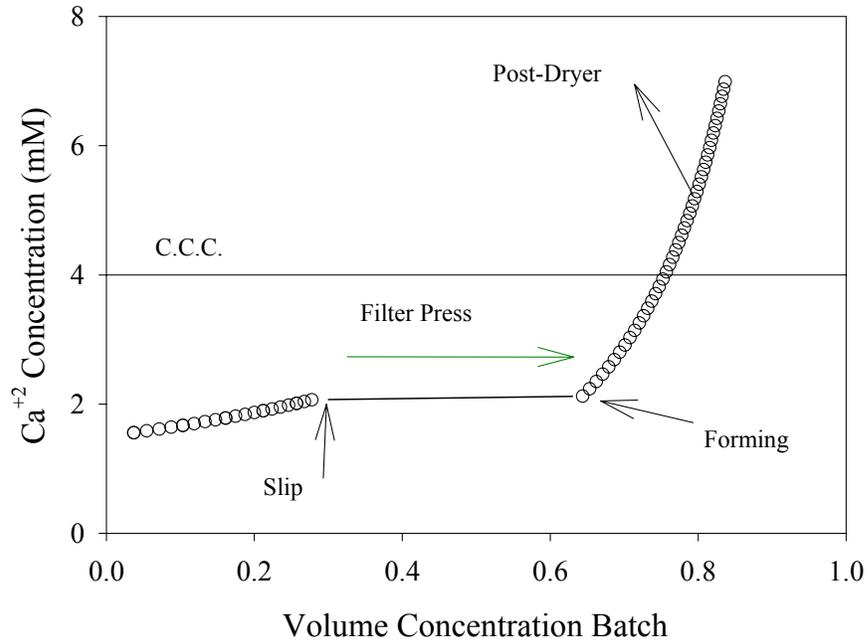


Figure 6-5. The Ca^{+2} concentration as a function of the solids loading change encountered during production stages. Immediately following the de-watering process, the apparent Ca^{+2} concentration increases sharply causing the plastic body to become coagulated.

Effect of Aging and Non-Aging on *Body B* Plasticity

The plasticity, as measured by cohesion stress, of *Body B*, for both aged and non-aged sample is shown in Figure 6-6. The maximum cohesion stress in the aged standard *Body B* is lower than that of the non-aged *Body B*, 116 and 156 kPa, respectively. The aging process increases the cation concentration due to the dissolution of the raw materials, the clays and the feldspar, which further supports lower cohesion stress with a greater cation concentration.

It is proposed that by decreasing the maximum cohesion stress of a plastic body, the behavior of the plastic body will be more favorable during drying. Specifically, the

moisture gradient that will naturally occur during the drying process will establish lower stress gradients, as measured by cohesion stress, if the cation level is sufficiently high. This can be accomplished via deliberate batch alteration and aging. By reducing stress gradients, differential shrinkage should also be reduced thereby minimizing cracking during drying.¹²

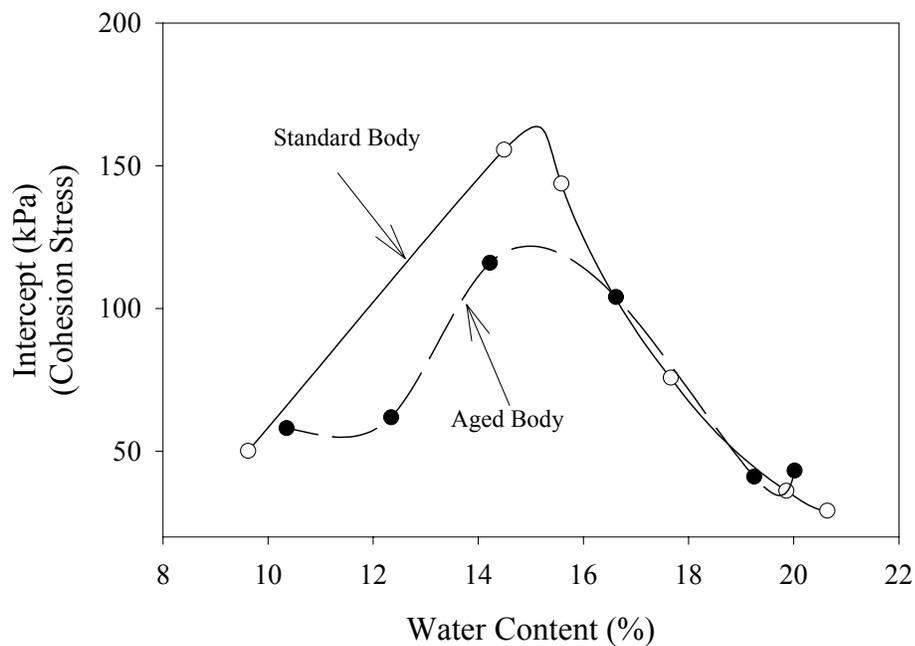


Figure 6-6. The cohesion stress as a function of water content for a standard body and an aged body. The effect of aging on a plastic body, dissolution of ions from the raw materials, on the plasticity, which is metered by the cohesion stress, are compared with a non-aged plastic body sample.

Effect of Dispersed and Coagulated *Body B* on Plasticity

The plasticity behavior of *Body B* samples, one highly dispersed with PAA and the other highly coagulated with CaCl₂, on the plasticity measured by cohesion stress and pressure dependency are shown in Figure 6-7. At high moisture levels, the applied pressure

dependence of the two samples are similar indicating the water has saturated the particles and the pores. Therefore, the water in the plastic body controls the material behavior. As the moisture content decreases, the particle-particle interaction dominates the plastic body behavior, which is impacted by the chemistry, i.e. dispersant or coagulant, due to the water layer around the individual particles. The peak in the cohesion stress for the coagulated sample is lower than that of the dispersed sample, 170 and 241 kPa, respectively, again indicating higher cation concentration decreases the cohesion stress of the plastic body.

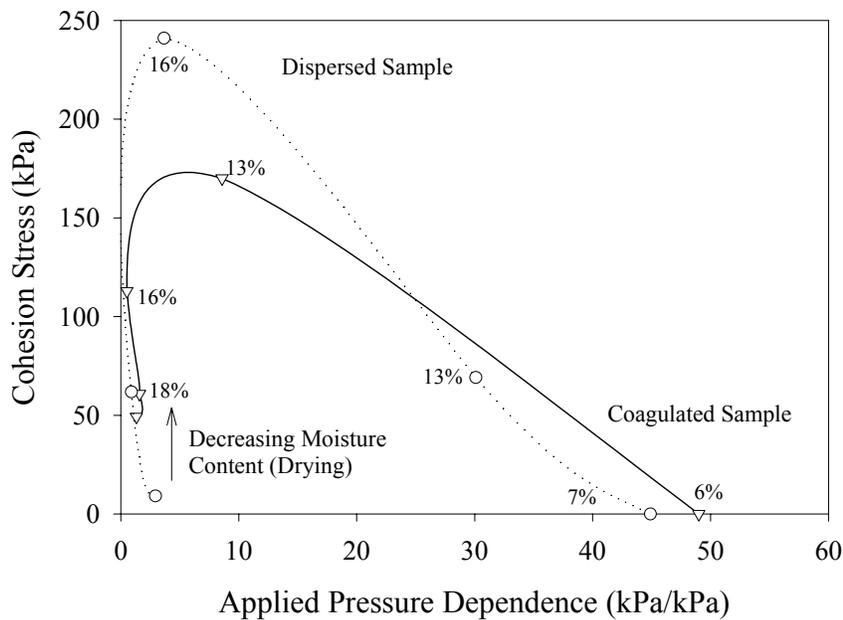


Figure 6-7. The plasticity of a dispersed and coagulated plastic body is compared using the cohesion stress and applied pressured dependence. The cohesion stress peak is lower in the coagulated (CaCl_2) plastic body.

SUMMARY AND CONCLUSIONS

Increasing the cation concentration in a plastic body decreases the cohesion stress measured by the HPASC. The cation level necessary to reduce the cohesion stress corresponds with the critical coagulation concentration of the suspensions. These results suggest that by controlling the chemistry of the suspension one can improve the plastic body behavior and reduce production losses during forming and drying. The level of dispersion during forming and drying should be low. Conversely, the level coagulation should be sufficiently high to reduce the cohesion stress.

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7. CONCLUSIONS

This research investigated the colloidal behavior of kaolinitic clay in aqueous suspensions. The foundation for the understanding of most current clay suspension behavior is based on early studies conducted prior to the application of colloidal concepts in ceramic systems and also when many of the colloidal theories were being developed. Advances in colloid science and the application of the theories greatly enhance the interpretation of the clay suspension behavior. The nature of the clay particle perceived in most literature was re-examined in light of the clay mineralogy and shown to have one silica-like surface and one gibbsite-like surface. With this approach, the previous colloidal nature of the two negative basal planes is altered to be one negative basal plane, silica-like layer, and one positive basal plane, gibbsite-like layer.

The impact of dispersant and electrolyte additions were analyzed by measuring rheological changes in the clay suspension and plastic clay bodies. The mechanisms and ionic species responsible for dispersion and coagulation of the clay suspension were determined. Specifically, the role of the sodium ion as both a dispersing and coagulating agent was explored. Electrophoretic mobility and calculated ζ -potential values in clay suspensions supported the rheological results. The influence of chemistry changes, i.e., dispersant and electrolyte additions, to a clay-water system in the form of a plastic body were examined with HPASC that characterized the plasticity of the material.

Outcome of Dispersant Study

From this work, it is clear that the Na^+ ion is not responsible for dispersing the clay suspension. The anionic species controls the dispersion of the clay suspension, likely due to specific adsorption. Within the pH range that was examined, the dispersion effectiveness, measured by the apparent viscosity, does not correlate with the suspension pH. The magnitude of the ζ -potential can not predict the suspension stability consistent with the apparent viscosity of a clay suspension.

An interactive dispersing effect occurs when soda ash and Na-silicate are blended. The blend produces a highly effective dispersion inconsistent with the amount of Na-silicate added to the suspension. This effect was present at soda ash:Na-silicate ratios of 1:2, 1:1, and 2:1.

Normalizing with respect to the surface area of the clay suspension the amount of PAA and PMAA necessary to completely disperse the suspension was 0.20 mg/m^2 . Work by Cesarano, et.al.¹ indicated that approximately 0.45 mg/m^2 was necessary to disperse alumina with PAA and PMAA, at the same pH as the clay suspension. Based on the surface area available on a clay particle, these two studies support one positive (octahedral surface) and one negative (tetrahedral surface) basal planes on a kaolin particle.

Outcomes of Coagulation Study

The cation is responsible for coagulating the clay suspensions. Lower concentrations of divalent cations are required to coagulate the clay suspension than of monovalent cations; sodium ions do cause the clay suspension to coagulate. Once coagulated, the apparent

viscosity of the clay suspension is independent of the electrolyte and dispersant concentration.

The results suggest coagulation due to compression of the double layer rather than specific affinity. The anionic species have a minor impact on the coagulation that is observed by small shifts and the shape of the coagulation curves. The minor affinity of the anion is influenced by the associated cation.

Outcomes of Plasticity Study

Altering the chemistry of a plastic body, via dispersant and coagulant additions to suspension prior to filter pressing, influences the plasticity. The results suggest that by increasing the cation concentration, coagulating the clay body, the cohesive stress decreases thereby improving the forming capabilities and drying yields.

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