

# RHEOLOGY OF AQUEOUS SUSPENSIONS OF CLAY AND PORCELAIN BODIES

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### **ABSTRACT**

The rheology of a series of kaolinitic suspensions, including processed clay and commercial porcelain body compositions, was evaluated in the context of dispersant selection and ionic strength considerations. It is clear from these experiments that the Na<sup>+</sup> ion is not responsible for clay dispersion, but that the anion associated with the Na<sup>+</sup> controls behavior. In addition, the effect of ionic strength is evaluated using Na-, Ca-, and Mg-salts over a broad range of concentration.

Several dispersants were evaluated, including Na-poly (acrylic acid), Na-poly (methacrylic acid), Na-silicate, Na-phosphate, Na-carbonate, and mixtures of Na-silicate and Na-carbonate. To evaluate the behavior of the suspensions, controlled stress rheometry was performed (under steady-state flow conditions); ionic strength contributions were verified through the quantification of soluble ions (via ICP analysis); and surface-charge evolution was determined using zeta-potential measurements (via electrophoretic and acoustophoretic mobility techniques).



## **INTRODUCTION**

There is a great deal of confusion, both in industry and academia, regarding the colloidal nature of kaolinite particles in aqueous suspension largely stemming from a generally incorrect "picture" of the charge distribution on a kaolinite particle. The commonly held view that kaolinite possesses negatively charged basal-plane surfaces and positively charged edges is inconsistent with the mineralogy of kaolinite particles - a 1:1 sheet silicate composed of a  $[Si_2O_5]^{-2}$  tetrahedral layer and an  $[Al_2(OH)_4]^{+2}$  octahedral layer. Based on the colloidal behavior of silica (isoelectric point of 2.3-3.5) and hydrated alumina (isoelectric point 8.5-9.5),<sup>[1]</sup> in the pH range of 3.5 to 8.5 silica surfaces must be negatively charged and alumina surfaces positively charged. 2:1 sheet silicates (i.e., two  $[Si_2O_5]^{-2}$  surfaces sandwiching an octahedral layer), such as talc, pyrophyllite, mica, bentonite, etc., do possess the negatively charged basal-plane surfaces and presumably neutral (or possibly slightly positively-charged) edges, consistent with the mineralogy and the charge character of silicate surfaces in water. Details on the nature of kaolinite are available elsewhere.<sup>[2,3]</sup>

Another problem obstructing the understanding of kaolin\* suspension behavior is the myth regarding the role of sodium. It is incorrect, although widely accepted, that Na<sup>+</sup> functions as a dispersant and is responsible for the reduction in viscosity of clay suspensions. This misconception may stem from the conclusions of Johnson and Norton: (4) "...(a) the charge on the kaolinite particles controls the degree of defloculation and is governed by the type of cation and (b) the stability of system is controlled by the anion of the medium and is governed by the type of anion preferentially adsorbed" (emphasis existing). The intent of these two conclusions is not entirely clear, and while mostly correct, their study focussed on salts of Na and Ca, the common interpretation is that Na<sup>+</sup> causes stability. The large net negative charge on kaolinite particles means that Na<sup>+</sup> is a counterion, and as such, serves to compress the ionic double layer surrounding a colloidal particle, promoting coagulation of the particles. We propose that a revision of Johnson and Norton's statement would appropriately be "(a) the stability of the system is controlled by the charge on the kaolinite particle, which controls the degree of deflocculation and is a function of the type of anion preferentially adsorbed, (b) the cation compresses the double layer promoting coagulation/flocculation and its effectiveness is proportional to the cation charge and concentration." [5]

This research demonstrates that the colloidal nature of kaolinitic clays is consistent with a particle composed of a silica-like and alumina-like surface. The adsorption of dispersants is consistent with that observed for alumina for a large variety of commercial dispersants, and when corrected for specific surface area, supports the dual nature argument. In addition, the impact of ionic strength, specifically altered by the addition of chlorides and sulfates of Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>, clearly indicates that the behavior of Na<sup>+</sup> is consistent with the divalent cations, demonstrating that sodium cannot be viewed as a dispersant for clay-based suspensions.

<sup>[1]</sup> R. O. James, Characterization of Colloids in Aqueous Systems, Ceramic Powder Science; Advances in Ceramics, Vol. 21, Eds., G. L. Messing, K. S. Mazdiyasni, J. W. McCauley, and R. A. Haber, Amer. Ceramic Soc., Westerville, OH, pp. 401-403, 1987.

<sup>[2]</sup> N. GÜVEN, Molecular Aspects of Clay-Water Interactions, Clay-Water Interface and its Rheological Implications, CMS Workshop Lectures 4, Eds. N. Güven and R. M. Pollastro, The Clay Minerals Society, Boulder, CO, 2-12, 1992.

<sup>[3]</sup> W. M. CARTY, The Colloidal Nature of Kaolinite, Amer. Cer. Soc. Bull., 78 [8], 72-76, (1999).

<sup>[4]</sup> A. L. JOHNSON AND F. H. NORTON, Fundamental Study of Clay: II, Mechanisms of Deflocculation in the Clay-Water System, J. Amer. Ceram. Soc., 24 [6], 189-203 (1941).

<sup>[5]</sup> K. R. ROSSINGTON, U. SENAPATI, AND W. M. CARTY, Colloidal Behavior of Whitewares, I: A Critical Evaluation of Dispersants, submitted to the J. Amer. Cer. Soc.



#### EXPERIMENTAL APPROACH AND PROCEDURES

Properties of the raw materials are listed in Table 1; the suspension medium was distilled water for all experiments. Three separate sets of experiments were performed: 1) dispersion behavior of kaolin suspensions (solely composed of EPK); 2) dispersion of a typical porcelain batch composition; and 3) dispersion of sub-micron alumina suspensions. The dispersants are listed in Table 2. For uniformity, 13 liter clay suspensions were prepared at a higher solids loading without dispersant addition, and a solution of distilled water, plus the appropriate amount of dispersant, was added to 200 ml samples to reduce the solids loading to the desired testing level. All dispersant additions were corrected for the specific surface area of the powders to correlate with surface coverage. Two general preparation routes were followed: 1) the dispersants were added to individual suspensions to create the desired dispersant level; or 2) two suspensions were prepared, one without dispersant and one at the upper limit (1.0 mg/m<sup>2</sup> for the claybased suspensions, or 2.0 mg/m² for the alumina suspensions) that were then blended to create suspensions with the desired concentration of dispersant for testing. The results indicated that the route taken to create the suspensions did not measurably impact the rheology results, i.e., the trends in the data were identical. [6] Although previous experiments have shown little change in rheological behavior with time, it is common for suspensions to "age" prior to use. In these experiments, to avoid potential problems with "aging," suspensions were stored after mixing for at least 14 days prior to rheology measurement. The alumina suspensions were initially prepared at the desired solids concentration and not aged prior to testing.

Raw Materials			$SSA^*$ $(m^2/g)$	Initial (vol%)	Final (vol%)	
Kaolin	EPK; Zemex Minerals	100.0	26.9	35	30	
	(formerly the Feldspar Corp.), Edgar, FL				,	
Typical Porce	elain Batch Suspensions					
Kaolin	EPK; Zemex Minerals Edgar, FL	29.0	26.9			
Ball Clay	Todd Light; Kentucky-Tennessee Clay Co., Mayfield, KY	7.0	25.9			
Nepheline Syenite	A200; Unimin Canada Ltd., Nephton/Blue Mountain, Ontario	22.0	1.1	45 40		
Quartz	Oglebay Norton Industrial Sands, Inc., Glenford, OH	29.5	0.9			
Alumina	A10; Alcoa, Pittsburgh, PA	12.5	1.0			
Alumina Sus	pensions					
A-16 S.G.	Alcoa, Pittsburgh, PA	100.0	8.9		35	
APA-0.5	Ceralox Corp., Tuscon, AZ	100.0	7.8		35	

<sup>\*</sup>Specific surface area measured using Gemini III 2375 Surface Area Analyzer, Micromeritics, Norcross, Georgia.

**Table 1.** Raw materials, batch composition (for the typical porcelain composition - dry weight basis, d.w.b.), specific surface area, and solids loading information.

Following the first cycle of data generation for the dispersants with clay suspensions using the 1:1 mixture of Na-silicate and Na-ash, other experiments were performed evaluating the first the mixing route, then the effect of the Na-silicate to Na-ash ratio. In the latter experiments, Na-silicate and Na-ash were added to water prior to the addition of the porcelain body slurry (previously mixed without dispersant

<sup>[6]</sup> K. R. Rossington, U. Senapati, and W. M. Carty, *A Critical Evaluation of Dispersants for Clay-Based Systems*, Ceram. Eng. and Sci. Proc., 19 [2], 77-86, (1998).



additions) to dilute the suspensions to 40 volume percent. These suspensions were mixed thoroughly, then allowed to age for two weeks prior to testing. No further blending of the suspensions to achieve alternative dispersant levels was performed.

Dispersant	Chemical Formula	Abbreviation	
Na-Poly Acrylic Acid	H-(NaC <sub>3</sub> O <sub>2</sub> H <sub>3</sub> ) <sub>n</sub> -H	Na-PAA	
Na-Poly Methacrylic Acid	H-(NaC <sub>4</sub> O <sub>2</sub> H <sub>5</sub> ) <sub>n</sub> -H	Na-PMAA	
Na-Hexametaphosphate	(NaPO <sub>3</sub> ) <sub>6</sub>	SHMP	
Na-Silicate $(x=0.22)^*$	xNa <sub>2</sub> O•(1-x)SiO <sub>2</sub>	Na-silicate	
Na-Ash	Na <sub>2</sub> CO <sub>3</sub> •10H <sub>2</sub> O	Na-ash	
Na-Silicate:Na-Ash Blend (1:1)	as noted above	1:1	

<sup>\*</sup>Ratio determined by ICP analysis of the Na-Silicate solution, (Acme Analytical Laboratories Ltd., Vancouver, British Columbia, Canada).

**Table 2.** The dispersants evaluated in the suspensions are listed along with the corresponding chemical formula and the abbreviation used throughout this paper.

The rheological properties of the all the suspensions were measured using a steady-state, stress-sweep test (SR-200 Dynamic Stress Rheometer, Rheometrics Scientific, Piscataway, New Jersey). The stress sweep test descended from high stress to low stress, with a parallel plate testing geometry. The measurements generated apparent viscosity (Pa·s) versus shear rate (s<sup>-1</sup>) data sets, which when plotted on log-log axes, exhibited linear behavior. The reported apparent viscosity values are calculated linear regression intercepts (1.0 s<sup>-1</sup>) of the log-log data sets.

The suspension pH was measured for each suspension at each dispersant level, but was not adjusted. This data is compiled in Table 3. Detailed discussion of the pH data is presented elsewhere.<sup>[5,6]</sup>

Dispersant	Kaolin	Porcelain Batch	A-16 S.G.	APA-0.5
No addition	5.2	7.4	9.6	8.4
Na-PAA	7.2	7.8	9.9	8.5
Na-PMAA	7.2	7.8	9.9	8.5
SHMP	6.2	7.3	6.9	6.4
Na-silicate	11.2	10.9	11.2	11.0
Na-ash	10.4	10.2	Not available	Not available
1:1	Not prepared	10.5	Not prepared	Not prepared

**Table 3.** Change in pH associated with the addition of the dispersants at a level of 1.0 mg/m<sup>2</sup> for the clay-based suspensions and at 2.0 mg/m<sup>2</sup> for the alumina suspensions.

Zeta-potential (ζ-potential) values were measured using acoustophoretic mobility (Acoustosizer, Colloidal Dynamics, Warwick, Rhode Island) in five volume percent kaolin suspensions as a function of pH against a background ionic strength of 10 mM NaCl.

To evaluate the contribution of ionic strength, batch suspensions were prepared with dispersant levels of 0.00, 0.02, and 0.05 mg/m $^2$  Na-PAA (based on the batch specific surface area) at 35 vol% solids. Saturated suspensions of six salts: NaCl, Na $_2$ SO $_4$ , CaSO $_4$ , MgCl $_2$ , and MgSO $_4$  were diluted to the desired level with distilled water and added to the

<sup>[5]</sup> K. R. Rossington, U. Senapati, and W. M. Carty, Colloidal Behavior of Whitewares, I: A Critical Evaluation of Dispersants, submitted to the J. Amer. Cer. Soc.

<sup>[6]</sup> K. R. Rossington, U. Senapati, and W. M. Carty, A Critical Evaluation of Dispersants for Clay-Based Systems, Ceram. Eng. and Sci. Proc., 19 [2], 77-86, (1998).



batch suspensions bringing the final solids loading to 30 vol%. Similar to the dispersant studies, the suspensions were aged for a minimum of 14 days prior to testing. Adding the salt as a saturated solution eliminated localized coagulation around individual salt crystals, but also limited the cation concentration, noticeably in the case of CaSO<sub>4</sub>. Chemical analysis (ICP) was performed to verify the cation concentration levels in the suspensions and to determine the cation concentration due to raw material dissolution; pH was also monitored and showed a decrease in pH with increasing ionic strength. [7]

#### **RESULTS AND DISCUSSION**

## ALUMINA SUSPENSION BEHAVIOR - ESTABLISHING A BASELINE FOR COMPARISON

If the basal-plane surfaces of a kaolinite particle are silica-like and alumina-like, to affect strong dispersion, it should only be necessary create a negatively charged alumina surface through the adsorption of anionic species, such as the polyelectrolytes PAA and PMAA, or possibly SiO<sub>3</sub><sup>2-</sup> or the poly-phosphate species. The affinity for PAA and PMAA has been clearly demonstrated by Cesarano, *et al*,<sup>[8]</sup> but to establish a benchmark, the behavior of alumina was evaluated under similar conditions to those used to evaluate clay suspensions. Examples of the alumina dispersion results for the five primary dispersants are presented in Figure 1 for APA; A-16 S.G. results were similar.<sup>[9]</sup> The effect of Na-silicate, SHMP, and Na-ash dispersants are also presented in Figure 1.

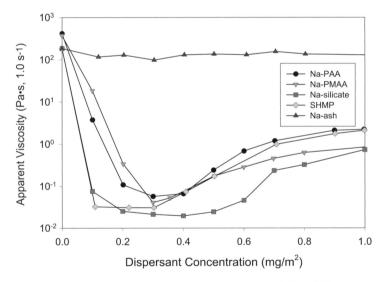


Figure 1. Dispersion of 35 vol% APA alumina suspensions using the five Na-based dispersants. Note the amount of dispersant necessary to reach the minimum in the viscosity curve. It is also clear that Na-ash is an ineffective dispersant for alumina, but that Na-silicate and SHMP are slightly more effective than Na-PAA or Na-PMAA.

The amount of dispersant is corrected for the surface area of the suspended particles. To properly evaluate the dispersion effectiveness with comparison to clays, these results should be compared at equivalent pH levels because the dissociation behavior of PAA and PMAA is highly dependent on pH. The Na-silicate and SHMP

<sup>[7]</sup> K. R. O'CONNOR AND W. M. CARTY, The Effect of Ionic Concentration on the Viscosity of Clay-Based Systems, Ceramic Engineering and Science Proceedings, 19 [2], 65-76, (1998).

<sup>[8]</sup> J. CESARANO III, I. A. AKSAY, AND A. BLEIER, Stability of Aqueous α-Al<sub>2</sub>O<sub>3</sub> Suspensions with Poly(methacrylic acid) Polyelectrolyte, J. Amer. Ceram. Soc., 71 [4], 250-255 (1988).

<sup>[9]</sup> B. R. Sundlof and W. M. Carty, Organic and Inorganic Dispersion of Alumina, Ceram. Eng. and Sci. Proc., 20 (1999), in press.



results are similar in pH, however, and require almost exactly one-half as much dispersant to disperse clay as to disperse alumina as discussed in the next section. Previous work has demonstrated that PAA and PMAA have a limited affinity for silica surfaces, such as the silica-like basal plane of kaolinite particles. To create sufficient repulsion forces, it should only be necessary to coat the alumina-like side of a kaolinite particle, which accounts for approximately one half of the total specific surface area of the suspension, consistent with the amount of dispersant necessary to create a stable suspension.

#### DISPERSION OF CLAY SUSPENSIONS

The effectiveness of the dispersants was similar for the clay and batch suspensions, <sup>[5,6]</sup> and, as shown in Figure 2, Na-PAA, Na-PMAA, Na-silicate, and SHMP are all efficient dispersants. Even though the batch is composed of only 36% (d.w.b.) clay, the clay accounts for 93.7% of the available surface area and therefore dominates the batch dispersion behavior. Industry commonly uses a blend of Na-silicate and Na-ash. Figure 3 shows that Na-ash is a poor dispersant, and that when mixed with Na-silicate, the viscosity of the suspension follows the behavior of Na-ash, then behaves at low concentrations as an intermediate, and finally as Na-silicate. This result seemed odd, and not entirely consistent with the industrial observations, warranting further experiments.

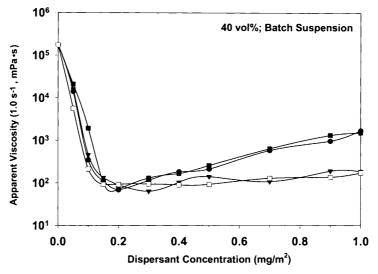


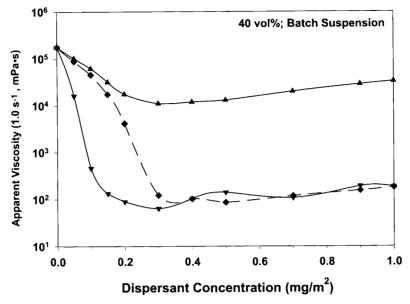
Figure 2. The effect of Na-PAA (●), Na-PMAA (■), Na-silicate (▼), and SHMP (□) on the rheology of the porcelain batch. There is effectively no difference between the four dispersants, each has reduced the apparent viscosity by a factor of nearly 1000 at a level of 0.2 mg/m².

To evaluate the interaction between Na-silicate and Na-ash, three additional suspensions were prepared, in which the dispersant addition sequence was altered: 1) Na-silicate added first, followed by Na-ash; 2) Na-ash added first, followed by Na-silicate; and 3) Na-silicate and Na-ash were blended and added together. In all three cases, the suspensions followed the Na-silicate curve exactly. In the suspensions

<sup>[5]</sup> K. R. ROSSINGTON, U. SENAPATI, AND W. M. CARTY, Colloidal Behavior of Whitewares, I: A Critical Evaluation of Dispersants, submitted to the J. Amer. Cer. Soc.

<sup>[6]</sup> K. R. ROSSINGTON, U. SENAPATI, AND W. M. CARTY, A Critical Evaluation of Dispersants for Clay-Based Systems, Ceram. Eng. and Sci. Proc., 19 [2], 77-86, (1998).

<sup>[10]</sup> G. G. Hong, H. Lee, B. R. Sundlof, and W. M. Carty, Evaluation of Kaolin Surface by Rheological Behavior of Suspensions in the  $Al_2O_3$ -SiO<sub>2</sub> System, to be submitted to the J. Amer. Cer. Soc.



**Figure 3.** Na-ash ( $\triangle$ ) functions poorly as a dispersant, reducing the batch suspension viscosity by only a factor of  $\simeq$ 10. Combining Na-ash with Na-Silicate ( $\nabla$ ) in a 1:1 ( $\spadesuit$ ) mixture, requires additional Na-silicate to disperse, and at low concentrations, the mixture behaves like Na-ash.

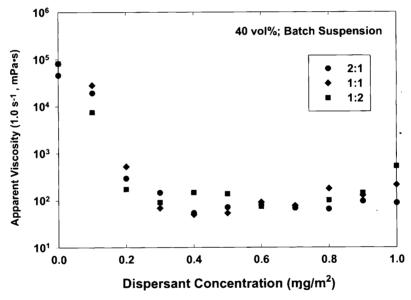


Figure 4. The effect of Na-silicate:Na-ash blends on suspension rheology at ratios 2:1 (♠), 1:1 (♠), and 1:2 (■). Within the range of both repeatability and detection, all three blends basically behave identically, and as Na-silicate does by itself, even though the Na-silicate level is significantly reduced.

measured in Figure 3, suspensions of Na-silicate and Na-ash were blended at each dispersant level *after* aging as separate suspensions for 14 days. These results indicate that Na-silicate and Na-ash are competing for adsorption sites on the particle surface, but that Na-silicate is favored, except in cases where a steady-state adsorption condition is developed, such as that obtained by aging the suspensions. These results also strongly refute the concept of Na<sup>+</sup> as a dispersant, since the effect of the anion is clearly dominating the dispersion behavior.

Questions regarding the nature of blended dispersants remained, however, since the dispersant level at which the minimum in viscosity occurred was the same for a 1:1 mixture of Na-silicate and Na-ash as for a suspension prepared from Na-silicate alone. It would be expected that if one-half as much Na-silicate was added (with the balance Na-

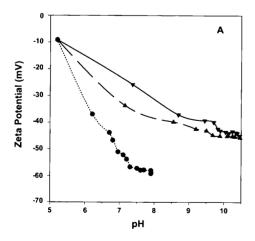


ash) the minimum in viscosity would occur at a dispersant addition level twice that necessary for Na-silicate alone. Therefore, there must be some positive interaction between Na-silicate and Na-ash that augments the dispersing properties. To evaluate this hypothesis, three additional experiments were performed blending Na-silicate and Na-ash at 1:2, 1:1, and 2:1 (the ratio denoting Na-silicate:Na-ash on a weight basis). The additions were added to a stock suspension (as described earlier) at appropriate quantities of a 40.5% Na-silicate solution (d.w.b.) and a 20% Na-ash solution. Figure 4 demonstrates that the results are basically identical regardless of the ratio of Na-silicate to Na-ash. Even with these preliminary results, it seems obvious that Na-ash plays a critical role, perhaps as a polymerizing agent for Na-silicate, producing results that would not be predicted from the behavior of the dispersants alone.

# **ζ-POTENTIAL MEASUREMENTS**

To further support the adsorption of anionic species on the kaolinite surfaces, the  $\zeta$ -potential of kaolin suspensions were measured and the results are presented in Figure 5. The substantial increase in the negative  $\zeta$ -potential indicates strong adsorption of anionic species. A shift in the isoelectric point should be expected if specific adsorption is occurring (these experiments are underway). These  $\zeta$ -potential results generate some interesting issues which are still under investigation - primarily the fact that Na-silicate and Na-ash have effectively the same  $\zeta$ -potential over a broad pH range. This result may indicate that  $\zeta$ -potential does not always correlate with suspension stability, but further testing is necessary for verification. Also based on the  $\zeta$ -potential results, it might be expected that the PAA suspension would have a lower viscosity than the Na-silicate suspension, but this was not observed.

When comparing Na-silicate and SHMP in terms of effectiveness to Na-PAA and Na-PMAA, and in contrast to the behavior of Na-ash, it is evident that the dispersion behavior may not be due solely to charge generation on the particle surface. It is proposed that the silicate and phosphate ions oligomerize on the particle surface to create steric hindrance as well as electrostatic repulsion. This may also suggest that steric contributions to stability are essentially ignored in  $\zeta$ -potential measurements.



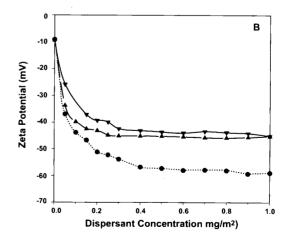


Figure 5. ζ-potential as a function of (A) pH and (B) dispersant concentration for Na-PAA (●), Na-carbonate (▲) and Na-silicate (▼) in a 5.0 vol% kaolin suspension with a 10 mM NaCl ionic strength background. The ζ-potential of the Na-PAA dispersed suspension is significantly lower then the Na-silicate (even though the viscosities of the two suspensions were nearly identical). The Na-silicate and Na-carbonate suspension ζ-potentials are nearly identical, but the suspension viscosities were dramatically different.



## EFFECT OF IONIC STRENGTH ON SUSPENSION RHEOLOGY

Increasing ionic strength compresses the electrical double-layer surrounding a colloidal particle in suspension. It is generally accepted that the counter-ion, e.g., the ion oppositely charged to the net particle surface charge, is the more important species. The co-ion can usually be ignored, except in cases in which the co-ion has a specific affinity for the particle surface. The  $\zeta$ -potential data demonstrates that the kaolin particles are strongly negatively charged, and that charge increases until surface coverage is achieved. These experiments had two goals: 1) to demonstrate that sodium is not a dispersant; and 2) to determine the critical coagulation concentration (CCC), or the ionic concentration necessary to cause a noticeable change in suspension rheology. As stated earlier, six salts were evaluated over a broad concentration range.

As illustrated in Figure 6, the effect of salt addition is dramatic. Na-PAA was added at three levels to impart varying degrees of stability. Under the most dispersed condition evaluated (0.05 mg/m²), the suspension viscosity increases by a factor of nearly 1000 as the ionic concentration exceeds the CCC. Even in samples to which no dispersant has been added, increasing ionic concentration causes an increase in suspension viscosity. In the case of the  $Na_2SO_4$  additions, it is clear that even at small sodium additions, stability is not improved.

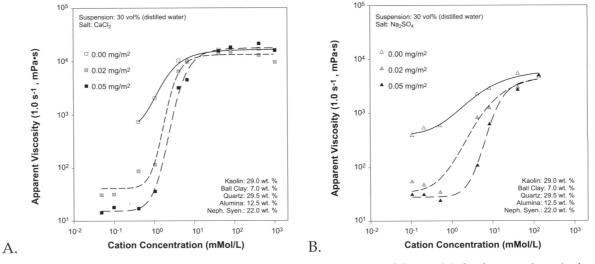


Figure 6. Effect of (A) CaCl<sub>2</sub> and (B) Na<sub>2</sub>SO<sub>4</sub> salt additions on the viscosity of the porcelain batch suspensions. As the dispersant level increases, the amount of salt necessary to induce coagulation increases (albeit slightly), consistent with colloidal theory. In the suspensions containing CaCl<sub>2</sub>, a plateau is reached; greater salt additions do not further increase viscosity. In the Na<sub>2</sub>SO<sub>4</sub> samples, the plateau has not yet been achieved. Note that even small amount of sodium does not impart suspension stability, further supporting the idea that Na<sup>+</sup> is not responsible for dispersion.

The addition of salts to colloidal suspensions always raises the question of specific adsorption of one or both of the soluble ionic species. If specific adsorption occurs, the CCC should decrease substantially, or if a multi-valent counter-ion strongly adsorbs on the particle surface, charge reversal can occur (within the Stern layer) causing an increase in stability. To prove (or disprove) specific adsorption,  $\zeta$ -potential measurements are necessary to document a shift in the isoelectric point. Figure 7 indicates that the CCC is independent of the anionic species involved in the case of CaCl<sub>2</sub> and CaSO<sub>4</sub> additions. The limited solubility of CaSO<sub>4</sub> prevents further addition without adding solid.

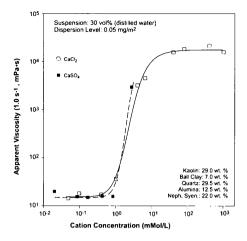


Figure 7. The concentration of Ca<sup>+2</sup> required to reach the CCC is the same for both CaCl<sub>2</sub> and CaSO<sub>4</sub> Both curves appear to be approaching the same plateau, but CaSO<sub>4</sub> concentration level is limited by the solubility of CaSO<sub>4</sub>. The dispersant level is 0.05 mg/m<sup>2</sup>.

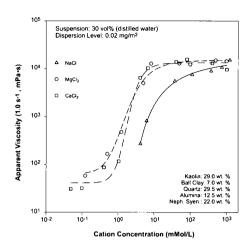


Figure 8. Additions of CaCl<sub>2</sub> and MgCl<sub>2</sub> produce identical CCC values at levels approximately eight times lower than that required for NaCl. All suspensions were prepared at a dispersant level of 0.02 mg/m², but reached a similar viscosity plateau above the CCC.

Figure 8 indicates that the CCC for Ca<sup>2+</sup> and Mg<sup>2+</sup> are identical in samples in which chloride salts have been added, and are approximately eight times lower than the CCC for NaCl. It is clear that above a certain ionic strength level, the viscosity reaches a stable plateau, that appears to be at an intrinsic limit. It has been suggested that this may be an instrumental limitation, however, the data in Figure 2 clearly shows viscosity values well above 10<sup>4</sup> mPa·s.

#### SUMMARY AND CONCLUSIONS

Kaolinite is a 1:1 sheet silicate composed of a  $[Si_2O_5]^2$  tetrahedral layer and an [Al<sub>2</sub>(OH)<sub>4</sub>]<sup>+2</sup> octahedral layer. This structure requires that the basal-plane surfaces are oppositely charged throughout a majority of the pH range. As such, it is only necessary to impart a negative charge on the alumina-like surface to induce suspension stability and reduce the suspension viscosity. These results indicate that the rheological behavior of kaolin and typical porcelain batch compositions mirror those of colloidal alumina, but require only approximately one-half of the dispersant necessary to disperse alumina, thus supporting the colloidal "picture" of a kaolinite particle based on kaolinite mineralogy. In addition, the data clearly indicates that the anionic species strongly adsorbs on the kaolinite particles, not Na<sup>+</sup>, and that Na<sup>+</sup> actually is a coagulant instead of a dispersant. There is also a positive interaction between Na-silicate and Naash that substantially improves the dispersion effectiveness - the underlying mechanisms need to be determined. Finally, the correlation between ζ-potential and rheology suggests that ζ-potential may not be a reasonable estimate of suspension stability and may ignore steric contributions to dispersion. Additional studies are necessary to determine specific adsorption tendencies of the dispersants and ionic species added to cause coagulation.

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<sup>\*</sup> Kaolinite is a mineral. Kaolin refers to a rock, or in this case, a clay powder, composed of at least 50% kaolinite