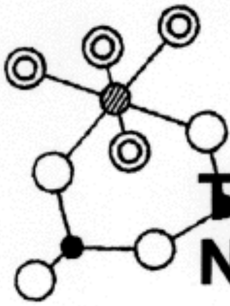
# The Colloidal Nature of Kaolin



# The Colloidal Nature of Kaolinite

*Understanding the colloidal nature of kaolinite is critical to developing a well-controlled, repeatable process.*

Kaolinitic clays are the foundation of whiteware and traditional ceramic industries. Clays account for 95% of the specific surface area of a typical whiteware batch (composed of 45% kaolin and ball clays, 25% quartz and 30% feldspar) and thus dominate the batch rheology.

Since production of whitewares most frequently begins in the slurry stage, understanding the colloidal nature of kaolinite is critical to developing a well-controlled, repeatable process. The commonly held view that kaolinite possesses negatively charged basal plane surfaces and positively charged edges is inconsistent with the mineralogy of kaolinite.

This article proposes that kaolinite particles possess a dual basal surface nature. It further establishes a basis for the evaluation of observed dispersant and rheology data for kaolin suspensions.

Based on the colloidal behavior of silicas (isoelectric point of 2.0–3.5) and aluminas (isoelectric point 8.5–10.4),[1] in the pH range of 3.5–8.5, the silica-like basal plane surface of a kaolinite particle must be negatively charged, and the alumina-like basal plane surface must be positively charged.

## Kaolinite and Kaolins

Kaolinite and other clay minerals are formed by the decomposition of feldspars by geological processes. A typical reaction sequence, e.g., a potash feldspar (microcline or orthoclase) usually found in a granite source rock, can be written:[2]

$$2KAlSi_3O_8 + 3\,H_2O \rightarrow Si_2O_5Al_2(OH)_4 + 4\,SiO_2 + 2K(OH) \quad (1)$$

If the potassium is not properly removed following the weathering process, illitic clays are formed instead of kaolinite.

The term kaolin refers to a rock, or in this case, a clay powder composed of at least 50% of the mineral kaolinite.[3] Kaolin deposits are either primary (i.e., deposited where the weathering process occurs) or secondary (i.e., transported a considerable distance from the source rock).

In commercial kaolin deposits, the most common mineral impurities include quartz, micaceous minerals (micas), smectites (also commonly referred to as montmorillonites), titania (rutile or anatase) and iron oxide.[3,4] Beneficiation of the raw kaolin frequently eliminates all but a small percentage of the impurity minerals.

Kaolinite is a 1:1 sheet silicate composed of a $(Si_2O_5)^{-2}$ tetrahedral layer and an $(Al_2[OH]_4)^{+2}$ octahedral layer.

Minerals such as talc, pyrophyllite, mica, bentonite, etc. are 2:1 sheet silicates in which the octahedral layer is sandwiched between two tetrahedral layers.[5] The presence of 2:1 sheet silicate impurities in commercial clays is easily detected by powder X-ray diffraction as peaks at ~6° and ~8.8° 2θ (using Cu radiation) for montmorillonite and mica, respectively. Similarly, it is routine to demonstrate that the amount of impurity 2:1 minerals is small in industrial kaolins and ball clays.

To understand the colloidal nature of kaolinite, it is essential to recognize that the basal plane surfaces of a kaolinite particle are dif-

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ferent. One will behave as silica does in water and the other as alumina or, more accurately, aluminum hydrate.

Direct evidence regarding the dual surface nature of kaolinite is provided by atomic force microscopy (AFM) studies conducted in conjunction with surface modeling.[6] These results confirm the presence of silanol and hydroxide surfaces on kaolinite particles.

Indirect evidence occurs in the dispersant-clay interactions. The amount of poly acrylic acid (PAA) dispersant necessary to reach the minimum in a viscosity vs. dispersant level curve is ~58% of the amount needed to coat the surface of an alumina powder (to also obtain a minimum in viscosity curve).[7]

In the United States, major ball clay deposits are located on the eastern side of the Appalachian Mountains in western Kentucky and Tennessee. Major kaolin deposits are located on the southeastern side of the mountains in central Georgia and South Carolina. All commercial kaolins and ball clays in the United States are mined from secondary deposits.

Kaolins and ball clays are mineralogically similar—both containing a large fraction of kaolinite. The major differences reside in remaining impurities, usually quartz, montmorillonites, titania and organic matter.

English china clays (also kaolinitic in nature) are obtained from primary and secondary deposits and differ slightly in the types of mineral impurities from kaolins obtained in the United States. Micas are common (almost no montmorillonites are found), and the titania content is lower.

The lower titania content in English clays corresponds to a high whiteness after firing, even though the iron contents are similar. A small amount of ionic substitution of iron in the titania lattice is responsible for the coloration after heat treatment.

## Kaolinite in Water

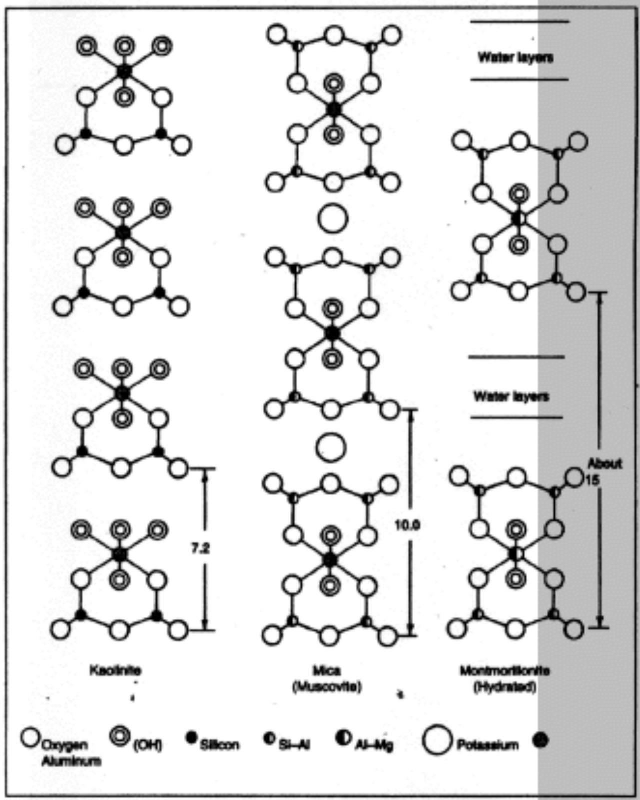
The prevailing perspective regarding the nature of kaolinite in an aqueous medium is that the basal plane surfaces are negatively charged and the edges are positively charged. This view is supported in the literature by studies demonstrating the agglomeration of negatively charged gold particles to the positively-charged edges of clay platelets as observed via transmission electron microscopy (TEM).[8]

The experimental conditions, specifically the pH at which the experiments were performed, however, is unclear. The lack of particles agglomerated to the faces of the kaolinite particles has been used to argue that the faces, therefore, are negatively charged—a conclusion subsequently drawn by other authors.[9]

Several key concepts are essential to deciphering the nature of kaolinite in aqueous suspension. When an oxide particle is suspended in water, a series of acid-base reactions occur that creates charged sites on the particle surface. When the particle surface is in equilibrium with the aqueous suspension medium, the charge at the particle surface is net neutral (i.e., there is an equivalent number of positive and negative charges).

The pH at which neutrality is achieved is called the point of zero charge (PZC). The PZC is unique for each oxide, and is determined by the cation valence and the lattice bond strength.[1]

Colloidal theory introduces the concept of a double layer of ions surrounding a suspended particle to compensate for the potential at the particle surface. Close to the particle surface is a strongly held layer of ions known as the Stern layer. The inter-



*A schematic illustration of the layer structures of kaolinite, mica and montmorillonite, showing the relative spacing between layers (in Å). The kaolinite crystal is a 1:1 sheet silicate, while the mica and montmorillonite are 2:1 sheet silicates.*[8]

face between the Stern layer and the diffuse layer is called the shear plane.

The potential at the shear plane is defined as the zeta-potential ($\zeta$-potential). Similar to the PZC, the pH at which the $\zeta$-potential changes sign is defined as the isoelectric point (IEP). In the presence of an indifferent electrolyte (i.e., anions and cations have similar affinities for the particle surface), the PZC and the IEP are equivalent.[1, 10–11]

In a kaolinite particle, one basal plane surface is composed of a silica-like surface while the other is composed of an alumina-like or aluminum hydroxide-like surface. It is generally recognized that alumina forms an aluminum hydroxide surface in an aqueous medium. The kaolinite particle edge is composed of a mixture of alumina and silica sites.

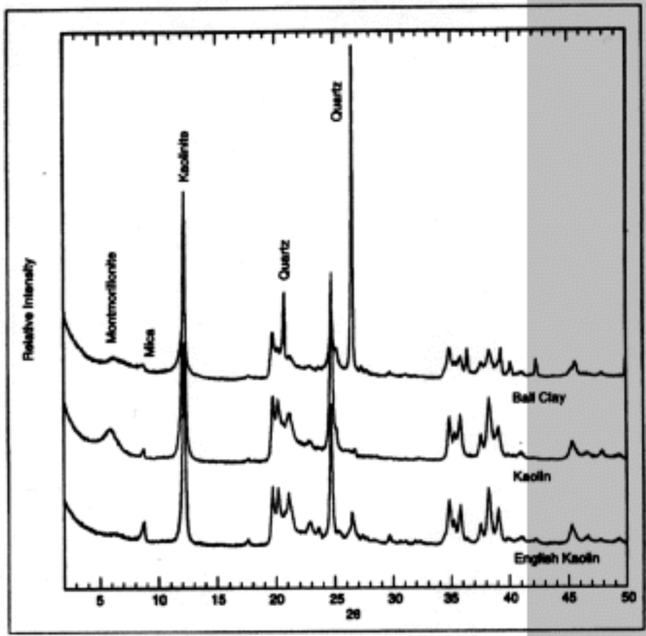
It is proposed here that one basal surface should behave like silica while the other behaves like alumina in aqueous suspension.

It is well documented that silica has an IEP of 2.0–3.5, and aluminum hydroxide has an IEP of 8.5–10.4. At suspension pH levels above the IEP, the particle is net negatively charged; below the IEP, the particle is net positively charged. Conservatively, then, the basal plane surfaces should be oppositely charged from pH = 3.5 to pH = 8.5.

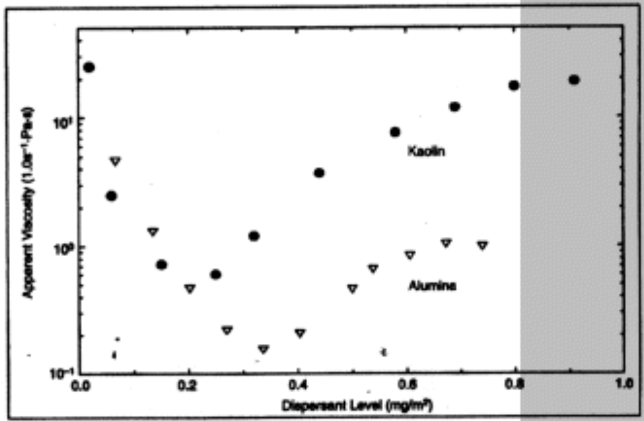
At a neutral pH, therefore, the silica-like basal plane surface must be negatively charged, and the aluminum hydroxide-like basal plane surface must be positively charged. However, 2:1 sheet silicates possessing silica-like surfaces for both basal planes will have negatively charged basal-plane surfaces above pH = 3.5, with the edge charge changing as a function of pH.

Obviously, the prevailing model of both basal plane surfaces as negatively charged cannot be rectified with the mineralogy of kaolinite.

The concept of a silica-like and an aluminum hydroxide-like surface is further supported by the amount of PAA dispersant required to disperse kaolin compared to $\alpha$-$Al_2O_3$. When corrected for the specific surface area of the powder (measured using $N_2$ adsorption), the amount of dispersant required to disperse kaolinite is ~58% of that required to disperse alumina, based on suspension viscosity mea-



*Powder X-ray diffraction patterns for domestic ball clay and kaolin and English kaolin. The diffraction peaks at ~6° and ~8.8° 2θ correspond to the interlayer spacing for mica and montmorillonite, respectively, as illustrated on p.XX. The large reflection at ~12.3° 2θ represents the interlayer spacing for kaolinite. All three of the samples contain impure quartz.*



*Comparison of viscosity vs. Na-PAA dispersant level for 30 vol% alumina and kaolin suspensions at pH = 8.5 (±0.2), corrected for the specific surface area of the powders (9.6 $m^2/g$ and 21.4 $m^2/g$, respectively).[49] The data indicate that approximately 58% as much dispersant is necessary to reach the minimum in the viscosity curve for kaolin compared to that required by alumina.*

surements. Other experimental results have indicated that PAA has a weak affinity for silica surfaces.[12]

Assuming, therefore, that the clay booklets have been dispersed into individual particles, approximately one-half of the available kaolinite particle—proposed to possess the alumina-like basal plane surface—is being coated by the PAA. The common explanation has been that the edge of kaolinite particles is being coated by the dispersant. This explanation, however, is inconsistent with the morphology of kaolinite particles, as will be demonstrated.

## The Morphology of Kaolinite

Kaolinite particles have a hexagonal habit, and the perfection of the platelets is dependent on the crystallinity of the particle. Well-crystallized kaolinite particles are clearly hexagonal with sharp corners and edges; poorly-crystallized kaolinites have hexagons with rounded corners and edges.

If a perfect hexagonal parallelepiped is assumed, the basal plane to edge surface areas can be calculated and plotted as a function of the aspect ratio of the platelet thickness (h) to the point-to-point dimension (2L) across the basal plane surface. Thus, the total surface area ($A_{tot}$) of a hexagonal platelet is:

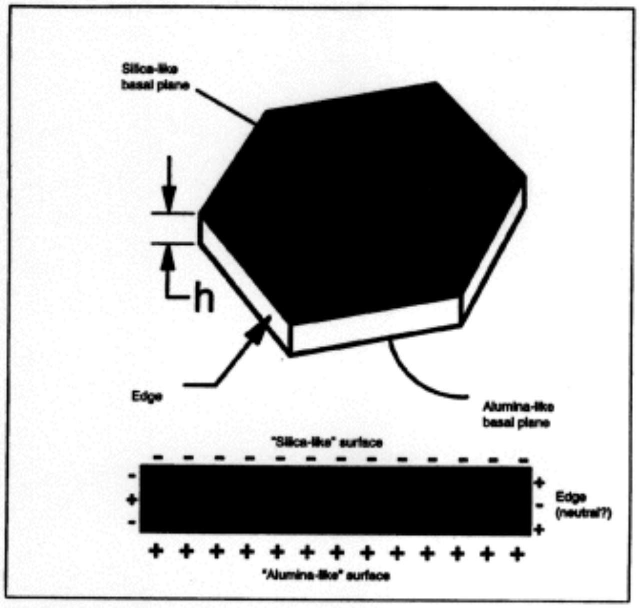
$$A_{tot} = A_{edge} + 2A_{basal} = 6hL + 2\left(\frac{3\sqrt{3}}{2}(L^2)\right) \quad (2)$$

To calculate the ratio of edge to basal plane surface areas, L is defined as 1, and the aspect ratio is defined as x = h/2L. Thus, the fraction of surface area due to the edge ($f_{edge}$) is:

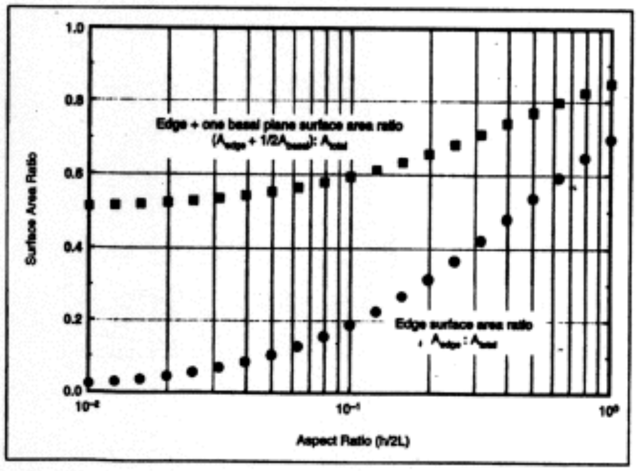
$$f_{edge} = \frac{A_{edge}}{A_{tot}} = \frac{12x}{12x + 3\sqrt{3}} \quad (3)$$

If the dispersant addition only adsorbs on the edge surfaces, significantly thicker kaolinite particles are necessary. For example, if a 50% dispersant level is required to disperse a kaolin sample compared to that needed to disperse alumina, $f_{edge} = 0.5$, producing a calculated edge thickness of 0.866L (or 0.433-2L).

Analysis of SEM images of well-crystallized kaolinite particles indicates the average edge thickness



*Schematic of an idealized kaolinite particle. The point-to-point dimension across the basal plane surface is defined as 2L; h is the platelet thickness. In aqueous suspension, the silica-like basal plane surface charge should be negative and the alumina-like basal plane surface charge should be positive over a broad pH range. The charge on the edge may be neutral.*



*Calculated surface area ratios for a) $f_{edge}$ ($A_{edge}$:$A_{tot}$) and b) ($A_{edge}$ + $\frac{1}{2}A_{basal}$):$A_{tot}$ as a function of aspect ratio (h/2L). These calculations assume a value for L of unity.*

*SEM photomicrographs of K-Ga1b, a well crystallized Georgia kaolin from the Clay Minerals Society. The well-formed hexagonal platelets and sharp corners and edges are indicative of well-crystallized kaolins. The measured edge thickness average is 103 nm (±30 nm), and the average point-to-point dimension is 1.1 µm (±430 nm). Using the average values for thickness and width, the calculated aspect ratio is 0.095.*

(measured on 350 particles) to be 103 nm (±30 nm) and the average point-to-point dimension (measured on 250 particles) to be 1.1 µm (±430 nm).

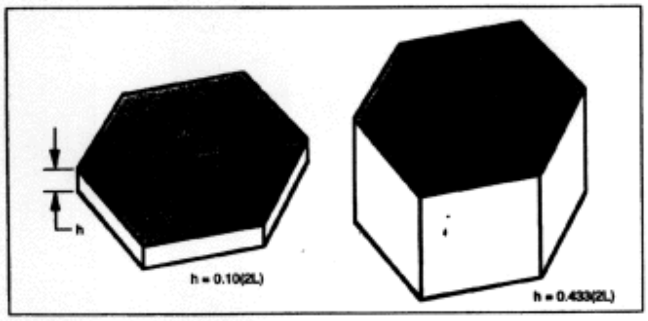
Using the average values for thickness and width, the estimated aspect ratio is 0.095. This produces an $f_{edge}$ value of 18%, indicating that edge adsorption cannot account for the dispersant adsorption levels observed for kaolins.

Clearly, dispersant is adsorbing on a surface other than the edge. With the calculated aspect ratio of 0.095, the area ratio of one basal plane to the total surface area of a clay particle is 41%. The ratio of the edge area plus one basal plane surface, however, accounts for 59% of the total surface area. This is consistent with the observed dispersant demands for kaolin compared to alumina (58%) based on viscosity measurements.

**Typical Chemical Analysis**

(kaolinite, a Georgia kaolin, an English kaolin and a Ball Clay)

| Component (%) | Kaolinite Theoretical | Kaolin Georgia | Kaolin English | Ball Clay Kentucky |
|---|---|---|---|---|
| $SiO_2$ | 46.55 | 45.30 | 46.77 | 44.70 |
| $Al_2O_3$ | 39.50 | 38.38 | 37.79 | 38.30 |
| $Fe_2O_3$ | | 0.30 | 0.36 | 0.60 |
| $TiO_2$ | | 1.44 | 0.02 | 2.40 |
| MgO | | 0.25 | 0.24 | 0.10 |
| CaO | | 0.05 | 0.13 | 0.10 |
| $Na_2O$ | | 0.27 | 0.05 | 0.10 |
| $K_2O$ | | 0.04 | 1.49 | 0.10 |
| L.O.I. (950°C) | 13.95 | 13.97 | 12.97 | 13.60 |



*Schematic illustration of the aspect ratios of two kaolinite particles. The left drawing shows an average particle using a value similar to that obtained from the SEM images. The drawing to the right shows the aspect ratio necessary to allow the edge to account for one-half of the total particle surface area.*

## Summary and Conclusions

Kaolinite, a 1:1 sheet silicate, is composed of a $(Si_2O_5)^{-2}$ tetrahedral layer and an $(Al_2[OH]_4)^{+2}$ octahedral layer, a structure requiring that the basal plane surfaces be oppositely charged over a broad range of pH. It also is observed that, when corrected for specific surface area, one-half as much dispersant is necessary to disperse kaolins compared to alumina.

Finally, calculations of the basal plane and edge surface area ratios for idealized hexagonal platelets indicate that significantly thicker kaolinite particles are necessary to justify adsorption of dispersants on the particle edges alone. However, adsorption of dispersions on one of the two basal plane surfaces and the edge fits both the dispersant data and the mineralogy, supporting the proposal that there are two distinctly different basal plane surfaces on kaolinite particles. ■

### Acknowledgements

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**Author's Note:** This is the first in a series of articles addressing the nature of kaolinite in suspension relative to dispersion, the role of sodium in dispersion, ionic strength effects, plasticity and aging effects. Both kaolin suspensions and whiteware bodies will be discussed in subsequent articles.

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