

# Settling Behavior of Kaolinite Clay in the Absence of Flocculant.

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## ABSTRACT

Settling behavior of kaolinite clay in the absence of flocculant was investigated at a 4% w/w solid loading. The work was performed between pH range of 3.5 – 8.4. The sample was characterized using Atomic Absorption Spectrophotometer (AAS). Results show that settling rate and aggregate size of kaolinite decreases with increasing pH from 3 cm/min at pH 3.5 to 1.4 cm/min at pH 8.5 and 22  $\mu\text{m}$  at pH 3.5 to 15  $\mu\text{m}$  at pH 8.4 respectively.

Results further reveal that relative final bed height (RBH), increased with increasing pH from 8% at pH 3.5 to 12% at pH 8.4.

Based on data generated in the study, it was concluded that low pH gave a faster settling rate than high pH.

(Keywords: kaolinite, settling behavior, solid loading, edge-face association, face-face association)

## INTRODUCTION

Kaolinite is the most widespread mineral of the kaolin group; which also contains dickite, nacrite, and halloysite. Kaolinite is a member of the clay mineral group of phyllosilicates. It is known that clay exhibits very poor settling behavior in aqueous medium (Obut, 2005). In mineral processing operations, this poor settling behavior is not desired since large quantities of the mineral can be lost as slimes. Kaolinite has a specific-gravity of 2.6, a hardness of 2 (mohs relative hardness scale), with a perfect cleavage in the (001) plane (Klein and Hurlbut, 1985). It is a 1:1 dioctahedral aluminosilicate mineral with the general formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  (Grim, 1968). It has a layered structure, in which each layer consists of a siloxane tetrahedral sheet joined to a gibbsite-like octahedral sheet.

Kaolinite is referred to as a dioctahedral clay because only two out of every possible site in the octahedral layer are occupied by aluminum atoms (Hunter, 1995). Combination of the tetrahedral-octahedral sheets, known as the kaolinite layer, is electrically neutral, theoretically.

Kaolinite layers are held together by van der Waals forces and hydrogen bonding between the octahedral gibbsite-like surface of one layer and the tetrahedral siloxane surface of another layer.

Kaolinite has two very different basal face surfaces, one a siloxane surface consisting of inert -Si-O-Si- links and the other surface consisting of octahedral Al-OH groups, in which the hydroxyl ions are doubly coordinated causing them to exhibit very weak acidic and basic properties (Hiemstra et al., 1989). Theoretically, the basal faces of kaolinite have a neutral charge. However it is accepted that the siloxane surface carries a small negative charge that is almost independent of pH. Three main theories were identified to account for this charge: a negatively charged smectite layer adsorbing to the outermost basal layer; an aluminosilicate gel coating, rich in silica, adsorbing to the basal surface; or the most accepted theory, isomorphous replacement of Si in the siloxane layer by Al (Schofield, 1954; Jepson, 1984).

The objective of this study was to obtain better knowledge of the influence of pH on the settling behavior of kaolinite in the absence of flocculant. Such knowledge is useful in some type of mineral processing operations that includes clays.

## Effect of pH

When kaolinite plates are broken, an edge surface is formed. The broken metal oxide bonds are able to neutralize their charge by dissociating water molecules to produce metal hydroxide (M-

OH) sites. Because of this, the edge surfaces, unlike the basal surface, have pH dependent charges (Figure 1). These edge surfaces are estimated to occupy approximately 26% of the total kaolinite surface area and exhibit a hydrophilic character (Zbik and Smart, 1998).

The edge surface is known to display a positive charge at acid pH values, a negative charge at basic pH values, and an isoelectric point ranging from pH 5.5 to pH 7 (Schofield and Samson, 1954). As a result of this, at acidic pH values an attraction between the constantly negative basal surfaces and the positive edge surfaces of the kaolinite occurs. A voluminous aggregate of low density is usually produced by this interaction.

### The Effect of Electrolyte Upon Clay Behavior

When clays are immersed into an aqueous environment, due to their surface charge, an electrical double layer is formed at the clay-water interface (Zhou et al., 1994). The stability of clay colloids has been investigated using the Derjaguin, Landau, Verway, Overbeek (DLVO) theory, which postulates that the colloidal stability is controlled by electrical double layer repulsion and van der Waals attraction (Van Olphen, 1977).

The stability of a colloidal suspension is highly dependent upon the concentration of electrolyte present (Manahan, 1991). As the concentration of electrolyte increases, the thickness of the electrical double layer decreases and thus the magnitude of the repulsive component decreases. As a result, colloidal particles can be aggregated more easily with higher electrolyte concentrations. It is due to this colloidal behavior that the ionic strengths of clay-based tailing systems are of

extreme importance in controlling the aggregation of the particles.

## MATERIALS AND METHODS

The kaolinite clay used in this work was collected from Agbahara-Nsu, Ehime-Mbano Local Government of Imo State, Nigeria. The lumps ranged between 5mm to 15mm. The clay lumps were crushed, ground, and sieved through a 75µm sieve. This was the particle size used throughout this experiment.

### Atomic Absorption Spectrophotometer (AAS)

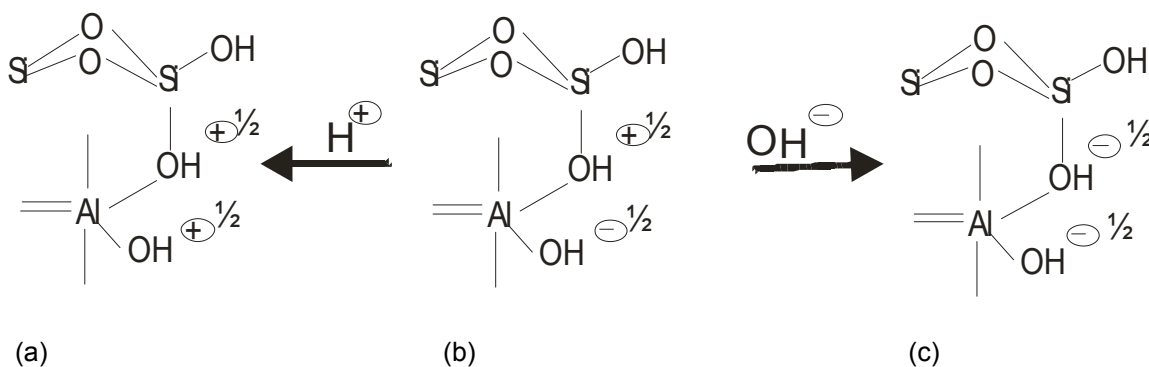
The chemical composition of the clay sample in % wt of (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc.) was determined using AAS Mode 320 carried out at the Chemistry Department of the University of Port Harcourt, Rivers State, Nigeria.

- **Loss on Ignition:** The water content (in % wt) of the clay was determined by measuring the weight loss of a known mass of the sample (1 gram) after firing in a furnace at 1000 C for one hour thirty minutes.

Loss on ignition (LOI) % =

$$\left\{ \frac{W_i - W_f}{W_i} \times 100 \right\} \quad (1)$$

Where  $W_i$  and  $W_f$  are the initial and final weight of the sample, respectively.



**Figure 1:** Charge Characteristics at the Edge Face of Kaolinite Under (a) Acidic, (b) Neutral, and (c) Alkaline Conditions (Schofield et al., 1954)

## Settling Test

To measure the settling rate of the suspended solids, a 50ml measuring cylinder was used at a 4% w/w kaolinite solid loading. Cylinder volumes greater than 50ml displayed no difference in the initial settling rate (Farrow and Swift 1996).

Kaolinite samples were conditioned in a beaker by stirring with magnetic flea for 2 hours at the desired pH.

Conditioning is wetting the 4% w/w kaolinite slurry in 0.01M KCL for some hours. After conditioning of the sample, a known mass of the kaolinite 35ml was poured into the measuring cylinder and topped-up with 0.01M KCL solution.

A strip of graph paper was stuck along the length of the measuring cylinder and numbered in an increasing order from its bottom. The cylinder was then covered and shaken 10 times. Settling was taken to commence as the cylinder was placed upon the bench top and a stop watch was used to time the settling of the suspended solids. The height of fall (cm) for each test under consideration-pH, was recorded against time (sec) Figure 2.

The linear regions of the settling curves display the initial settling region, where the individual aggregates are able to settle without hindrance of others. The settling rates were obtained by taking

the slopes of the linear regions of the settling curves.

- **Relative Final Bed Height (RBH) (%):** Is the percent of the initial interface height prior to settling and it was used in calculating the final bed height, shown in Table 1. The final heights of the settled beds were obtained after 24 hours. Relative final bed height (RBH) (%) was calculated using the relation:

$$RBH, \% = \frac{h_f}{h_i} \times 100 \quad (2)$$

where  $h_i$  and  $h_f$  are initial and final bed height respectively.

- **Aggregate size:** Stoke's equation was used in calculating particles size (aggregate size) shown in Table 2. Knowing that the velocity of a particle falling through a fluid is directly proportional to the gravitational force  $g$ , the difference between the density of the particle and the density of the fluid ( $d_s - d_f$ ) and the square of the effective particle diameter  $d^2$  (aggregate size) (Nyle, 1999):

$$V_t = \frac{d^2 g (d_s - d_f)}{18\eta} \quad (3)$$

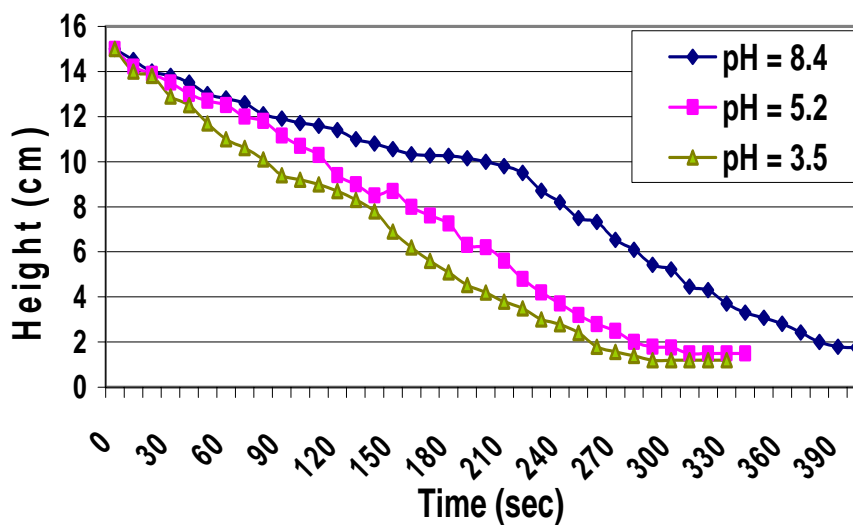


Figure 2: Settling Curves of Kaolinite at Different pH.

where,  $g$ =gravitational force(N/kg)  
 $\eta$ =viscosity of water at 25°C(K/m<sup>3</sup>)  
 $d_s$ =density of the solid particles,(kg/m<sup>3</sup>)  
 $d_f$  = density of the fluid (water)kg/m<sup>3</sup>  
 $V_t$ =terminal velocity of particle (settling rate)  
 $d$ =particle diameter; aggregate size( $\mu$ m)

**Table 1:** Relative Final Bed Height (%) of Kaolinite (4%w/w) at Different pH.

pH	Bed ht(%)
3.5	8
5.2	10
8.4	12

**Table 2:** Aggregate Size of Kaolinite Clay.

pH	Settling rate (cm/min)	Aggregate size ( $\mu$ m)
3.5	3	22
5.2	2.3	19
8.4	1.4	15

## RESULTS AND DISCUSSION

### Chemical Composition

The result according to AAS chemical analysis is presented in Table 3. The clay gave alumina content of 31.32%. The clay is moderately pure based on its alumina/silica ratio ( $Al_2O_3/SiO_2$ ) of 0.68 compared to 0.84 for pure kaolinite.

### Settling Rates

Figure 4 shows the plots of Height of fall (cm) versus time (sec). Settling rates shown in Table 3 were obtained from Figure 4. During the settling process, the destabilized aggregates initially settle very rapidly. This region of rapid settling is commonly called the free settling region as settling kaolinite aggregates are not hindered by any neighboring bodies during their downward movement (Michaels and Bolger, 1962).

**Table 3:** Chemical Composition of the Clay Sample.

Composition	Wt %
$SiO_2$	46.01
$Al_2O_3$	31.32
$TiO_2$	0.34
$Fe_2O_3$	4.78
MnO	2.66
MgO	1.45
$Na_2O$	0.98
$K_2O$	0.61
$H_2O$ (Ignition loss @ 1000C)	10.82
$Al_2O_3 / SiO_2$ ratio	0.68

Furthermore, as the aggregates continue to settle, the density of the settled bed increased and the settling bodies came into contact with one another as a network. In this region, settling is known as hindered settling.

The point at which all aggregates are in contact with one another as a continuous, 3-dimensional network, is known as the gel-point. The settling process then continued beyond the solid loading of the gel-point as compaction of the settled bed occurred. The height of the settled bed then continued to decrease until the bed achieved sufficient density to support its own weight. This point is known as the final bed height.

Figure 3 shows the settling rate of kaolinite as a function of pH. Kaolinite produced a settling rate that was dependent upon pH in the absence of flocculant. It is known that kaolinite particles display a pH-dependent edge-surface and a basal surface that is pH-independent (Schofield and Samson, 1954).

This figure shows that the slow settling rate of kaolinite decreases with increasing pH from 3cm/min at pH 3.5 to 1.4cm/min at pH 8.4. Taylor, 2002, made similar observations. The settling rate of kaolinite is faster at a low pH 3.5 than at high pH 8.4 value. This is attributed to the enhanced edge-face association (Figure 4a), attraction between the positively charged edge surfaces and the negatively charged basal surfaces, resulting in the growth of larger aggregates.

But at higher pH values, some level of repulsion seemed to exist between all kaolinite surfaces (negatively charged edge and basal), hence opposing the process of aggregation and

therefore only permitting smaller, face-face associated aggregates to form (Figure 4b), which in turn produced a slower settling rate.

**Aggregate size**

Figure 5, shows the aggregate size as a function of pH. The figure shows that the aggregate size decreases with increasing pH.

Michaels and Bolger (1962), measured edge-face associated kaolinite aggregates to be larger than face-face associated aggregates, thereby accounting for their different settling rate. The aggregate size of KGa-1b kaolinite in 0.01MKCL was determined to be ~18µm at pH 4.5 as opposed to ~5µm at pH 8.5 measured using a Laser diffraction technique-Malvern Mastersizer (Taylor, 2002). However, Stoke's equation used

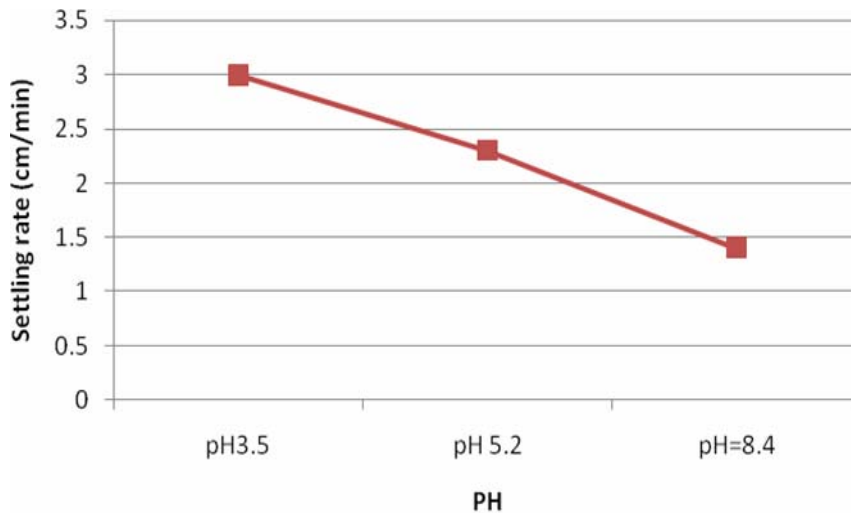
in this work gave an aggregate size of 22µm at pH 3.5 and 15µm at pH 8.4.

**Relative bed height (RBH) %**

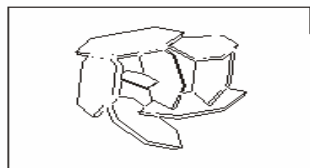
Figure 6 shows that the kaolinite final bed height increases with increasing pH. The bed height increases from 8% at pH 3.5 to 12% at pH 8.4.

At low pH values, large, low density aggregates are proposed to form in a card house structure (edge-face), leading to higher settling rate and a low bed height. This is because the edge-face associated aggregates are very prone to collapse under the stress of the settled bed.

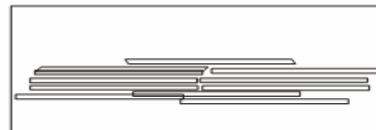
The face-face associated particles are less prone to collapse, hence the higher bed height achieved at high pH.



**Figure 3:** Settling Rate of Kaolinite as a Function of pH in the Absence of Flocculant.

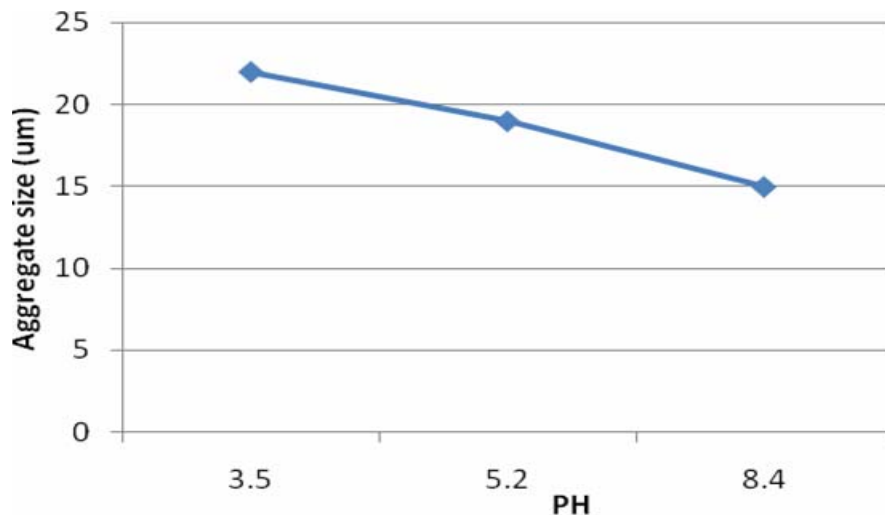


a card-house structure

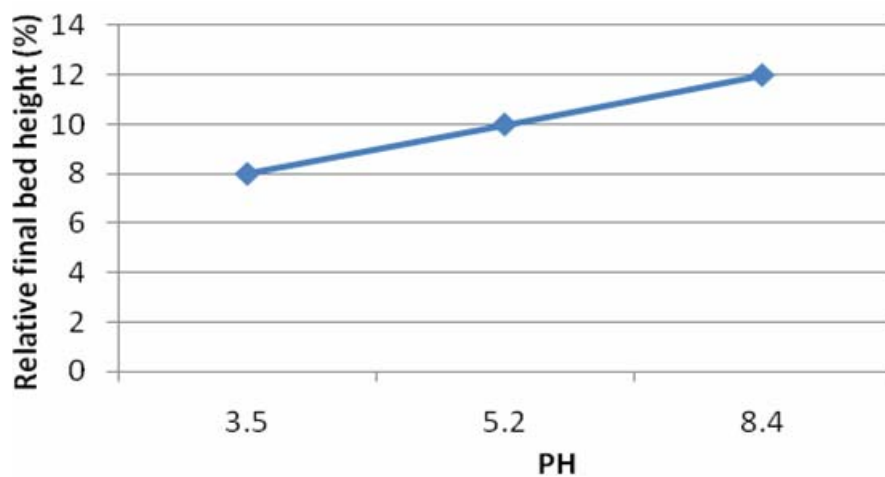


**Figure 4a:** Edge Face Association.

**Figure 4b:** Face-Face Association.



**Figure 5:** Aggregate Size of Kaolinite as a Function of pH.



**Figure 6:** Relative Final Bed Height (RBH), % of Kaolinite against pH.

## CONCLUSION

In this study, it was shown that settling behavior of kaolinite clay in the absence of flocculant is depended upon pH. While the settling rate and aggregate size decreased with increasing pH, the final bed height increased with increasing pH. Generally, low pH gave faster settling rate than high pH.

## ACKNOWLEDGEMENTS

I am greatly indebted to Engr. Prof. O.O. Onyemaobi, Dean, School of Engineering and Engineering Technology (SEET) at the Federal University of Technology, Owerri (FUTO) for his support throughout this work. My best thanks also goes to Mr. Anyika of the chemistry laboratory FUTO and Mr. Okele, U of the chemistry laboratory University of Port Harcourt,

for their assistance in executing this work, I cannot thank them enough.

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## SUGGESTED CITATION

Chukwudi, B.C. 2008. "Settling Behavior of Kaolinite Clay in the Absence of Flocculant". *Pacific Journal of Science and Technology.* 9(1):212-218.

