

## THE EFFECT OF ELECTROLYTE CONCENTRATION AND PH ON THE FLOCCULATION AND RHEOLOGICAL BEHAVIOUR OF KAOLINITE SUSPENSIONS

M. S. NASSER<sup>1\*</sup>, A. E. JAMES<sup>2</sup>

<sup>1</sup>Deptment of Chemical Engineering, University of Nizwa ,  
P.O. Box 33, P.C. 616, Sultanate of Oman

<sup>2</sup>School of Chemical Engineering and Analytical Science,  
The University of Manchester, P.O. Box 88, Manchester M60 1QD, U.K.

\*Corresponding Author: mustafa.nasser@unizwa.edu.om

### Abstract

The effects of the electrolyte concentration and pH on the settling behaviour, floc sizes and rheological behaviour of kaolinite suspensions were investigated. The results show that the settling behaviour of kaolinite changes with the ionic strength and pH of the suspension. In the acidic pH range, (pH 2) particles settle in flocculated form regardless of electrolyte concentration, however, in the basic pH range, the particles settle both, in dispersed form (at lower electrolyte concentrations) and in flocculated form (at higher electrolyte concentrations). The Bingham yield stress and time-dependent behaviour for these flocculated and deflocculated suspensions was investigated. In this study, the fundamental of structural kinetic model (SKM) was used to investigate the time-dependent viscosity behaviour of flocculated and deflocculated kaolinite suspensions. It was found that the kaolinite suspensions in the deflocculated form show viscosity time-independent behaviour with negligible Bingham yield stress. While, the flocculated suspensions show marked non-Newtonian time-dependent behaviour. This work has been very successful in establishing the link among particle-particle interactions, floc size, Bingham yield stress, breakdown rate constant, and extent of thixotropy.

Keywords: Kolinite; Ionic strength, pH, Floc size, Bingham yield stress, Structural kinetic model.

### 1. Introduction

In the mineral industry, many of wastes contain colloiddally stable dispersions which are difficult to settle and consolidate. Hence, the effective dewatering of such stable

**Nomenclatures**

$C_{AK}$	Ratio of volume concentration of the aggregates to kaolinite
$d_A$	Average (equivalent) aggregate diameter, microns
$g$	Gravitational acceleration, m/s <sup>2</sup>
$k$	Rate of structural decay, 1/s
$p$	Order of the structure breakdown
$Q$	Settling rate of slurry-supernatant interface, cm/hr
$Q_o$	Initial settling rate, cm/hr
$t$	Time, s
$V_{SA}$	Stake's velocity for single aggregates, cm/hr
$Z$	Interface height, cm

*Greek Symbols*

$\gamma$	Shear rate, 1/s
$\varepsilon$	Void fraction
$\eta$	Transient viscosity, Pa.s
$\eta_B$	Bingham plastic viscosity, Pa.s
$\eta_e$	Equilibrium apparent viscosity, Pa.s
$\eta_o$	Initial apparent viscosity, Pa.s
$\mu_W$	Viscosity of water, 0.893 cp.@ 25°C
$\rho_K$	Density of kaolinite, 2.6 g/cc
$\rho_W$	Density of water, g/cc
$\tau$	Shear stress, Pa
$\tau_B$	Bingham yield stress, Pa
$\phi_A$	Aggregate volume fraction
$\phi_K$	Kaolinite volume fraction

clay dispersions presents a significant challenge for the mining and mineral processing industries and dewatering equipment manufacturers worldwide. Flocculant-assisted, gravity thickening and filtration processes are currently used by industry for dewatering but these are far from efficient, requiring further development for dramatic improvements [1-4]. Consequently, the flocculation behaviour of kaolinite dispersions under different conditions has been investigated intensely by many workers [5-10]. In addition, the rheological behaviour of kaolinite dispersions is of considerable scientific interest and many workers have used rheological techniques to study the microstructure of clay dispersions [11-16].

Most of the references cited above consider either the flocculation of kaolinite dispersions or their rheological behaviour without considering any relationships between them. Linking different types of experimental studies of clays is difficult because even if the clay has the same mineralogy it often comes from different sources and undergoes different treatments prior to experiment. Evidently it is easier to search for links if the same system is used.

Therefore, the aim of this study is to investigate: the effect of electrolyte concentration and suspension pH on the structure and size of kaolinite flocs (edge-face or face-face); the behaviour of flocs during settling and in the

sediment bed; how these structures are related to the rheological behaviour (i.e., Bingham yield stress and time-dependent behaviour) and to contrast the results obtained for flocculated and deflocculated kaolinite suspensions.

## 2. Theory

### 2.1. Background

Kaolinite, a hydrated aluminium silicate of composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , occurs in the form of thin, roughly hexagonal platelets, of length-to-thickness ratio of about 10. Kaolinite layers have amphoteric properties. The faces or surfaces carry a permanent negative charge and depending on the pH, there is positive or negative charge on the edges. Kaolinite platelets can associate in edge-edge (E-E), edge-face (E-F), and face-face (F-F) configurations [17-19]. The easy formation of the different types of association depends on the balance of electrostatic interactions (attractive or repulsive), which are controlled by the chemistry of the dispersions, and the attractive van der Waals forces between the particles [18].

In acidic environments aluminol groups exposed on the edges of the particles apparently bind hydrogen ions in water thus generating positive charge. Thus, edges and faces of particles will mutually attract giving rise to face-edge attraction and coagulation of kaolinite dispersions referred as “card-house” structure. Under alkaline conditions, the edge charge is either absent (neutral charge) or negative and the particles are deflocculated, provided the electrolyte concentration in solution is low. At high electrolyte concentrations electrostatic repulsion (or attraction) between the particles is reduced because of electrical double layers compression or ion shielding of the surface charges. Thus, the particles to adhere to one another along their basal surfaces, forming “card-pack” structure [18]. Association of the F-F type gives small aggregates of higher density whereas E-F and E-E associations lead to lower density aggregates of larger volume [19]. As these different interactions influence the rheology and settling behaviour of kaolinite dispersions, it is necessary to use a number of different rheological techniques to fully characterise their behaviour.

### 2.2. Floc size measurements

The floc size measurements herein are based on the theoretical and experimental results of Richardson and Zaki [20] with further analysis as suggested by Michaels and Bolger [19]. Richardson and Zaki [20] equation for the group-settling rate for uniform spherical particles can be written

$$Q = V_{sA} \varepsilon^{4.65} \quad (1)$$

Michaels and Bolger [19] suggested that the aggregate diameter,  $d_A$ , is relatively independent of kaolinite concentration over the “dilute” range, and that  $d_A$  does not change once settling has begun. The dilute settling rate should then be given by Eq. (1) in the form

$$Q_o = \frac{g(\rho_A - \rho_W)d_A^2}{18\mu_W} (1 - \phi)^{4.65} \quad (2)$$

From a material balance on the kaolinite, it follows that

$$\rho_s - \rho_w = \phi_A(\rho_A - \rho_w) = \phi_K(\rho_K - \rho_w) \quad (3)$$

Equation (2) is rewritten as

$$Q_o = \frac{g(\rho_K - \rho_w)d_A^2}{18\mu_w C_{AK}}(1 - C_{AK}\phi)^{4.65} \quad (4)$$

where

$$C_{AK} = \frac{\phi_A}{\phi_K} = \frac{\text{Volume of aggregate}}{\text{Volume kaolinite in aggregates}} \quad (5)$$

If  $d_A$  is expressed in microns, density of kaolinite,  $\rho_K$ , is 2.6 g/cm<sup>3</sup> and viscosity of water,  $\mu_w$ , is 0.893 cp@25°C, then  $V_{SA}$ , the Stokes' settling velocity for single aggregate, is

$$V_{SA} = 0.349 \frac{d_A^2}{C_{AK}} \quad (6)$$

Finally, Eq. (4) can be rewritten [19]

$$Q_o^{1/4.65} = V_{SA}^{1/4.65}(1 - C_{AK}\phi_K) \quad (7)$$

Therefore, if one plots  $Q_o^{1/4.65}$  against the corresponding value of  $\phi_K$ , a straight line should result. From the values of the slope and intercept one, can estimate the aggregate size

### 2.3. Rheological behaviour

#### a) Bingham yield stress ( $\tau_B$ )

In a Bingham fluid, the fluid starts to flow after the shear stress exceeds the Bingham yield stress. This phenomenon can be explained as follows: in a three-dimensional structure, the fluid at rest can resist a fixed shear stress and does not flow until the stress exceeds the Bingham yield value [21]. The Bingham Equation for non-Newtonian fluids is shown in Eq. (8)

$$\tau = \tau_B + \eta_B \gamma \quad (8)$$

where  $\tau_B$  is the Bingham yield stress and  $\eta_B$  is the Bingham plastic viscosity.

#### b) Time-dependent rheological behaviour

A literature survey indicates that kaolinite thixotropy is often not taken in to account because of: the complex nature of the material; the lack of quantitative understanding and availability of simple, systematic, and relevant methods of measurements. In order to model the time-dependent behaviour of the

suspensions, we apply the phenomenological structural kinetic model of Nguyen, Jensen, and Kristensen [22] based on an approach initially suggested by Moore [23] and later refined by Chavan et.al. [24] and Cheng and Evans [24,25]. The final form of the model is

$$\left(\frac{\eta - \eta_e}{\eta_o - \eta_e}\right)^{1-p} = (p-1)kt + 1 \quad (9)$$

where  $\eta_o$  is the initial apparent viscosity,  $\eta_e$  is the equilibrium apparent viscosity for the flocculated suspension,  $k$  is the rate of structural breakdown and  $p$  is the order of the structure breakdown. The transient viscosity data for the kaolinite suspensions at constant shear rates is correlated to Eq. (9) using an appropriate  $p$ . Previous authors, Saw [26] and Boger and Walter [27] reported that,  $p = 2$  for concentrated and diluted clay suspensions.

### 3. Material and Methods

#### 3.1. Kaolinite purification

The kaolinite used was 'Supreme' grade china clay provided by courtesy of Imerys, UK. It is well known that some deflocculants are added to the kaolinite for stabilisation purposes and also there is a low level of natural impurity (Imerys Literature). In order to ensure that the kaolinite suspensions used in the experiments were consistent, the surface preparation methods of Williams and Williams [28] were used to prepare homoionic sodium kaolinite suspensions. The technique involved repeated washing of the kaolinite in 1 M NaCl at pH 3, the kaolinite-NaCl suspension was prepared and allow to settle over a 24 hr period, then supernatant was removed and fresh 1 M NaCl was added. The electrophoretic mobility of the kaolinite suspension was checked periodically until consistent measurements were obtained. In our case it was found that the mobility became constant after 6 washes. Following this technique, further washing with distilled water causes the sodium ions to be expelled from the kaolinite by osmotic diffusion. About 8 – 12 washes each wash lasting for 24 hours are required to reduce the supernatant conductivity to 2  $\mu\text{mho}$  and to produce kaolinite particles in their natural unsubstituted form. Subsequently the kaolinite slurries were stored under distilled water.

#### 3.2. Settling tests

Purified kaolinite slurry was used to prepare 50 ml of kaolinite suspension at 4 % by volume in a series of 250 ml flasks. The 2 % by volume suspensions used in the experiments were produced by adding 50 ml of sodium chloride in varying concentrations (0.001-0.1 M) and adjusted to the desired pH using appropriate amounts of 0.1 M NaOH or HCl. Following sodium chloride addition the suspension was mixed for 1 minute and thereafter, the prepared kaolinite suspensions were transferred to 100 ml measuring cylinders (30 mm in diameter). Long-term settling tests (up to 48 hours settlement) were carried out until the equilibrium position of sediment-supernatant interface was reached. Subsequently the thickness of the interface was recorded with settling time.

### 3.3. Floc size

Purified kaolinite slurry was used to prepare a number of aliquots comprising 500 ml of kaolinite suspension but having different volume fractions in the range 0.005-0.015. The samples were prepared using different sodium chloride (NaCl) concentrations (0.001 and 0.1 *M*) and pH to produce different kaolinite flocs structures (i.e. Edge-Face or Face-Face structures). Each suspension was mixed for 1 minute, and thereafter the prepared kaolinite suspensions were transferred to 500 ml measuring cylinders (5.5 cm in diameter). Subsequently, the settling rate was recorded as a function of time. Therefore, considering Eq. (7), if one plots the initial settling rates  $Q_o^{1/4.65}$  as a function of the corresponding kaolinite volume fractions  $\phi_k$  a straight line should result and from the slope and intercept one can estimate the floc size.

### 3.4. Rheological measurements

The rheological measurements were performed at the controlled temperature of  $20.0 \pm 0.1^\circ\text{C}$  using a controlled stress and controlled strain instrument (Bohlin C-VOR rheometer, Malvern Instruments, UK) with a cone and plate sample geometry (4° cone, 40 mm diameter plate, 150  $\mu\text{m}$  truncation gap). Since the structure of kaolinite suspensions is quite sensitive to its shear deformation history, samples were carefully loaded on the rheometer platen with a spatula and then the cone was slowly lowered until the correct measurement gap was reached.

For the Bingham yield stress measurements, 10 % by volume suspensions were sheared by increasing the shear stress linearly from 0.01 to 1.0 Pa using a ramp time of 150 seconds. Once the curve of shear stress versus shear rate was obtained for kaolinite suspensions under the given experimental conditions, the value of the extrapolated  $\tau_B$  was determined from the intersection of the extrapolated linear portion of the flow curve with the stress axis (Eq. (8)). The method of least squares was used to determine the values of this intersection.

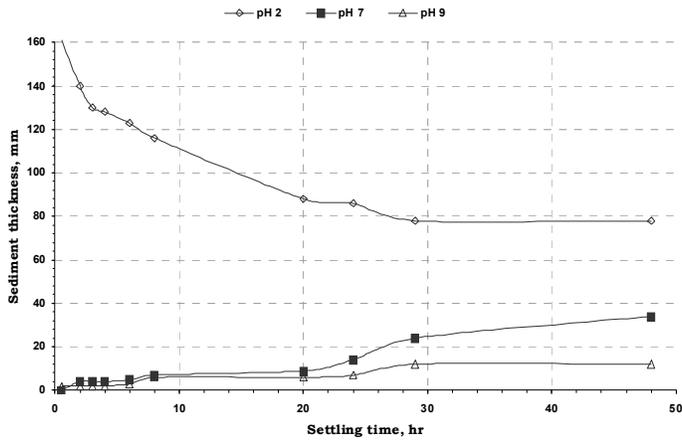
The time-dependent behaviour of 10% by volume kaolinite suspensions were characterized by apparent viscosity measurements as function of time at constant shear rate. In transient measurements a fresh sample was sheared at constant shear rates, namely at 5 and 20  $\text{s}^{-1}$ , and the apparent viscosity was measured as a function of shearing time until equilibrium state was reached. A fresh sample was used for each trial and at least three replications were made for each sample used.

## 4. Results and Discussion

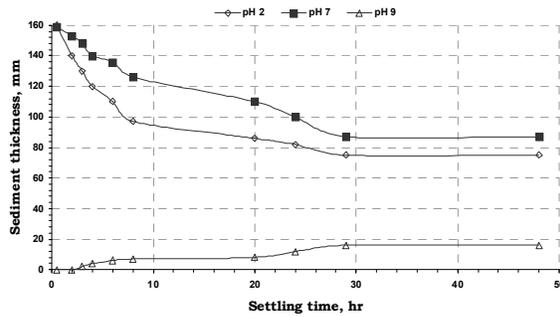
### 4.1. Effect of pH and ionic strength on settling behaviour

The final sedimentation thicknesses as a function of settlement time for kaolinite suspensions in water, 0.001 *M* NaCl, and 0.1 *M* NaCl at different pH are presented in Figs. 1 through 3. Based on electrolyte concentration and pH, the kaolinite particles settle either in flocculated or dispersed form. An increase in the sediment thickness with time to a maximum, which remained unchanged when settlement was complete, indicated that the particles or primary flocs had settled in dispersed form. On the other hand, a decrease in the sediment thickness with time indicated

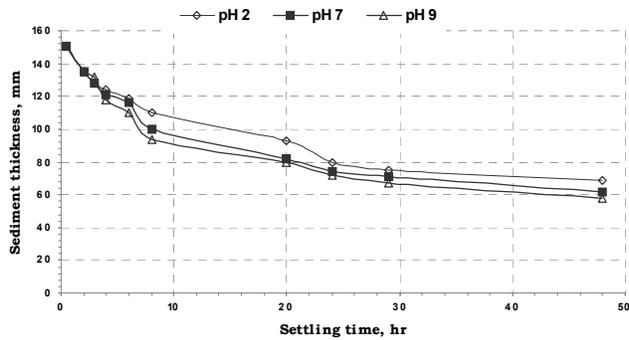
that flocs had settled in flocculated form. The settling behaviour of the flocculated and dispersed forms of kaolinite is schematically illustrated in Fig. 4.



**Fig. 1. Sedimentation Characteristics of Kaolinite Suspensions in Water at Different pH.**

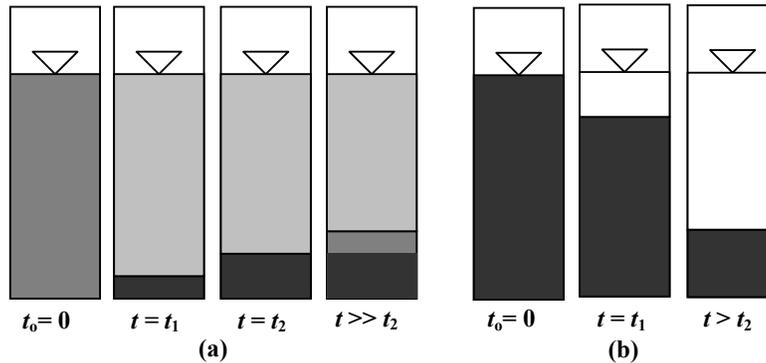


**Fig. 2. Sedimentation Characteristics of Kaolinite Suspensions in 0.001 M NaCl at Different pH.**



**Fig. 3. Sedimentation Characteristics of Kaolinite Suspensions in 0.1 M NaCl at Different pH.**

When the particles settle in dispersed form the gravitational force is the governing force and both primary flocs and particles settle individually until they reach their lowest possible position to form a closely packed arrangement without building a network. In these conditions, there is no distinct interface between the accumulated sediment bed and the overlying water (see Fig. 4a). When the particles are flocculated the van der Waals and other attractive colloidal forces are dominant and the flocculated particles settle together forming a network with a sharp interface between the flocculated sediment and supernatant (see Fig. 4b).



**Fig. 4. The Settlement Characteristics of Kaolinite in (a) Deflocculated or Dispersed Form, and (b) Flocculated Form.**

Figures 1 through 3 also show that the settling behaviour of the suspensions depends on the electrolyte concentration and pH. When the pH of the solution is 2, kaolinite suspensions are highly flocculated and the particles settle in flocculated form for all concentrations of NaCl. In contrast, at pH 9, only suspensions in 0.1 M NaCl settle in the flocculated form, whereas kaolinite suspensions with the NaCl concentration < 0.001 M settles in deflocculated form. Similarly at pH 7, the only sediments that settle in flocculated form do so in 0.1 and 0.001 M NaCl.

In acidic conditions, the edge carries a positive charge; promoting an electrostatic attraction between edges and faces in addition to the van der Waals attraction leading to E-F associations. However, the edge positive charges gradually decrease with increasing pH and become neutral or negatively charged at higher pH and consequently the flocs will breakdown (see Table 1). At high electrolyte concentration both the face and edge surfaces are negative leading to F-F association.

**Table 1. Floc Size of Kaolinite Suspensions Obtained from Dilute Settling Rate Data at Different Ionic Strengths and pH.**

NaCl Concentration (M)	$d_A$ (micron)		
	pH 2	pH 7	pH 9
0.1	102.88	83.20	83.35
0.001	115.20	73.30	deflocculated
Zero	117.58	deflocculated	deflocculated

The effects of pH on surface charge can be clearly seen in Figs. 1 to 3. Note that only 0.1 M NaCl produces settlement in the flocculated form at pH 9, whereas particles settle in the flocculated form even in water at pH 2 at all concentrations. On the other hand, at high electrolyte concentration (i.e. 0.1 M NaCl) the settling behaviour was improved by increasing the pH from 2 to 7 and 9. One is tempted to immediately conclude that the E-F interactions between particles are more probable at low pH, and F-F interactions are more probable at high pH. This result agrees with Raveendran [29] and Mahmood et al. [30] who used calculations of total interaction forces between the clay particles to demonstrate different types of particle interactions. In addition, the thicknesses of the sediments are greater when the particles settled in flocculated form than when they are settled in dispersed form indicating that the flocculated settled sediment are more porous and form a network than dispersed settled sediment.

#### 4.2. Effect of pH and ionic strength on floc size

Kynch theory of batch sedimentation analysis was used to estimate the initial settling rates by plotting the height,  $Z$ , of the interfacial plane between the slurry and the supernatant as a function of time [19]. Figure 5 shows the sediment as a function of time for different volume fraction for kaolinite suspension in water at pH 2. The floc size,  $d_A$ , is estimated from the relationship between the initial settling rate and volume fraction of kaolinite suggested by Eq. (7) which should be used only within the dilute limit (see Fig. 6). Volume fractions of kaolinite in the range of 0.005–0.015 are found to delineate the limits of the dilute region for all flocculated kaolinite-NaCl suspensions. Average floc sizes estimated using Eq. (7) for kaolinite suspensions experiencing different electrolyte conditions are summarized in Table 1.

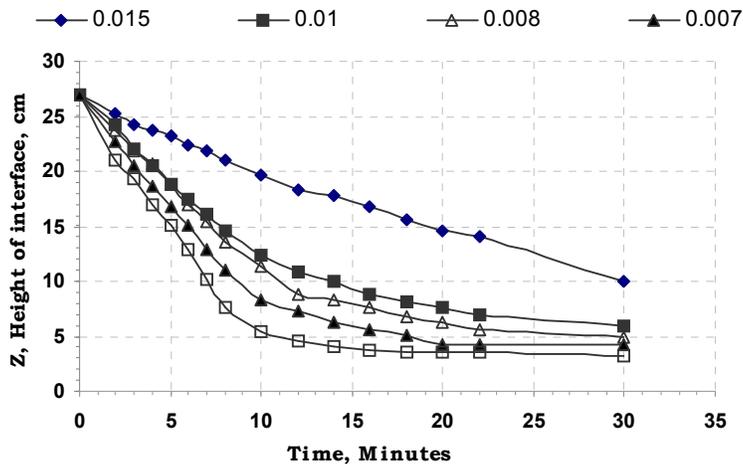
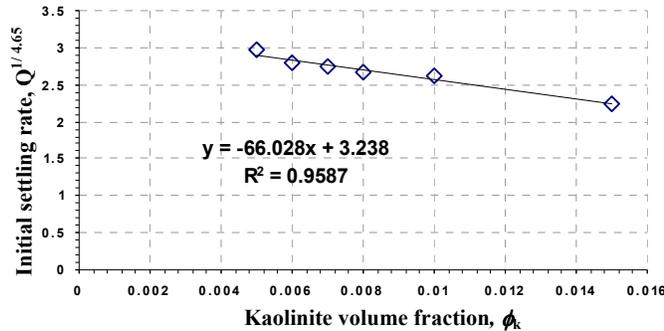


Fig. 5. Settling Rate as a Function of Volume Fraction for a Kaolinite Suspension in Water at pH 2 using a 500 ml Measuring Cylinder (5.5 cm in diameter).



**Fig. 6. Correlation of Settling Rate as a Function of the Volume Fraction of Kaolinite using Eq. (7) for Kaolinite Suspension in Water at pH 2.**

Table 1 allows one to suggest that a higher degree of E-F interaction leads to larger  $d_A$  (i.e. high water content or less dens). In addition increasing the ionic strength weakens the E-F but strengthens the F-F. At low pH (i.e. pH 2), as mentioned before; the electrostatic attraction between edges and faces will produce E-F structure. The E-F interactions result in voluminous three dimensional, card-house flocs having high void ratios (high water content). As the pH increases the positive charge on the edge gradually decreases and become neutral or negative, subsequently, the flocs breakdown as seen here for kaolinite flocculated in water at pH 7 and 9, provided the electrolyte concentration in the solution is low. At pH 7, increasing the NaCl concentration from zero up to 0.001 M allows the suspension particles to be flocculated. This increase in the electrolyte concentration reduces the electrostatic repulsion (or attraction) between the particles and will produce F-F flocs. These F-F flocs are found to be relatively small and dense (see Table 1 where the floc size for kaolinite in 0.001 M NaCl at pH 2 is bigger than at pH 7). A concentration of 0.001 M of NaCl at pH 9 is not enough to compress the electrical double layer sufficiently to induce flocculation and all particles remain discrete. At pH 9, increasing the NaCl concentration from 0.001 to 0.1 M again allows the suspended particles to be flocculated.

Table 1 also shows a very important feature in that the size of card-house flocs for kaolinite suspension at pH 2 is reduced as the electrolyte concentration increases. This is because when electrolyte is added to card-house flocculated kaolinite suspensions, preferential adsorption or 'charge shielding' by the electrolyte at the positive edge of the flakes results in either elimination of charge or sign reversal of the surfaces, with consequent card-house collapse [5, 31].

#### 4.3. Effect of pH and ionic strength on Bingham yield stress, $\tau_B$

The effects of changes in pH and ionic strength on  $\tau_B$  are summarised in Table 2. The Bingham yield stress decreases with an increase in pH at low ionic strength (i.e. at zero and 0.001 M NaCl). This is expected here because at low pH, in the absence of salt, the edge has a higher positive charge and face has constant negative charge and this leads to greater force of attraction between the kaolinite particles in E-F

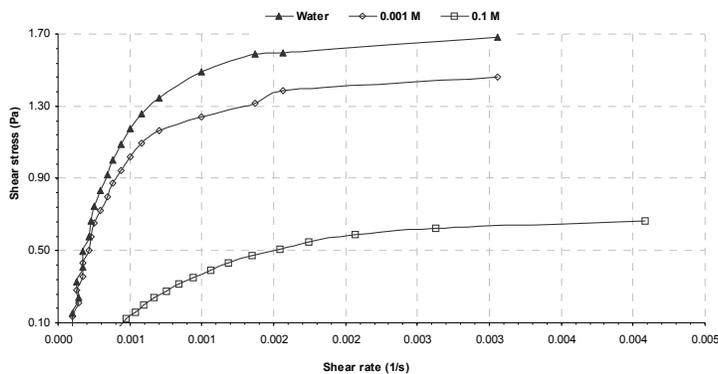
flocculation structure. Hence the stress required to fully disrupt the flocs,  $\tau_B$ , is higher as well. In addition, as the pH increase, the flocs break up and the suspension deflocculates. Hence the stress required to break these primary flocs is low but not zero, i.e.  $\tau_B \rightarrow 0$ ,  $\tau_B \neq 0$ . The existence of small  $\tau_B$  for the deflocculated/dispersed suspensions suggests that the kaolinite suspensions in deflocculated/dispersed form are not totally dispersed, but contain some small flocs which are bigger than the individual particles. The combination of small flocs and particles causes the suspension to settle in dispersed form and the existence of  $\tau_B$  indicates that the suspension does not comprise discrete particles (see Section 4.1).

Table 2 also shows that the value of  $\tau_B$  decreases with an increase in ionic strength at low pH and increases with an increase in ionic strength at high pH. The increase in the electrolyte concentrations reduces the electrostatic repulsion between the particles because of electrical double layer compression. This reduces the E-F interaction at low pH resulting in a weaker interparticle bond. The net effect is to weaken the floc strength (see Fig. 7). However, at pH 7 and 9 there is no E-F interaction but the F-F interaction is now stronger at higher ionic strength which results in an increase in an  $\tau_B$ . All these findings are in agreement with work concerning the compressive yield stress, static yield and particle erosion reported by Nasser and James [5] James and Williams [20, 21], and Saw [26] respectively.

**Table 2. Bingham Yield Stress for 0.1 Volume Fraction Kaolinite Suspensions at Different Ionic Strengths and pH.**

NaCl Concentration (M)	$\tau_B$ (Pa)		
	pH 2	pH 7	pH 9
0.1	0.237	0.115	0.162
0.001	0.572	0.110	0.053
Zero	0.592	0.0546	0.0512

The remarks concerning the Bingham yield stresses are in agreement with those made concerning the other floc size measurements made in this study. That is larger flocs correspond to higher  $\tau_B$  and smaller flocs correspond to smaller  $\tau_B$ , or in other words the breakdown the strong and voluminous E-F flocs required higher shear stress than the relatively small and weak F-F flocs.



**Fig. 7. Shear Stress as a Function of Shear Rate for 10 % (v/v) Kaolinite Suspensions in Electrolytes having Different Ionic Strengths at pH 2.**

#### 4.4. Effect of pH and ionic strength on rheological time-dependent behaviour

The kaolinite suspensions used in this investigation were subjected to a long period of shearing at constant shear rate to ensure that the floc structure was eventually reduced to an equilibrium structure appropriate to the particular shear rate employed and where the rheological behaviour was no longer dependent on shearing time. Note that the flocs are never reduced to primary particles since the apparent viscosity found under equilibrium conditions is different for each electrolyte concentration. It was found that, using a second order SKM model, the flocculated kaolinite suspensions shows the viscosity time dependent behaviour. In contrast, the deflocculated/dispersed form of kaolinite suspensions shows time-independent behaviour and the SKM does not apply. The time-dependent apparent viscosity of kaolinite suspensions was measured at constant shear rates of 5.0 and 20.0 s<sup>-1</sup>. Typical experimental results are presented in Figs. 8 through 10. At a constant shear rate, the apparent viscosity for all the flocculated suspensions decreases rapidly with time within the first 5 min of shearing, becoming nearly constant and corresponding to an equilibrium state after approximately 15 min. The time-dependent behaviour of the viscosity can be related to changes occurring in the microstructure of the suspension arising from particle interactions which are sensitive to pH and ionic strength. There is excellent comparison between model-fitted and experimental viscosity–time data for flocculated suspensions and this is seen in Figs. 8 through 10. If the rate constant,  $k$ , is a measure of the rate of thixotropic breakdown then the ratio of the initial to equilibrium viscosity,  $\eta_0/\eta_e$ , can be considered as a relative measure of the amount of structural breakdown or in other words as a relative measure of the extent of thixotropy. The values of  $k$  and  $\eta_0/\eta_e$  as a function of the applied shear rate, pH and ionic strength are summarised in Table 3.

At low pH and in the absence of salt, kaolinite suspensions produces E-F structure flocs, the  $k$  generally increases with increasing shear rate, as we would expect for a thixotropic structured material. Alternatively, at constant shear rate, the rate constant,  $k$ , and extent of thixotropy,  $\eta_0/\eta_e$ , increased with ionic strength. As mentioned above the increase in the ionic strength reduces the electrostatic repulsion between the particles because of electrical double layers compression. This reduces the E-F interaction at low pH resulting in a weaker interparticle bond having high  $k$  and  $\eta_0/\eta_e$ . The results confirm that the strong E-F structure is favoured at low pH and ionic strength.

Figures 8 through 10 and Table 3 also show time independent behaviour for kaolinite-water suspension at pH 7. As mentioned before increasing the pH from 2 to 7 causes the flocs to breakdown. However, increasing NaCl concentration to 0.001 M causes the particles in suspension at pH 7 to be flocculated, resulting in increased non-Newtonian behaviour, with the  $k$  and  $\eta_0/\eta_e$  being significantly larger than at pH 2. The increases of  $k$  and  $\eta_0/\eta_e$  with pH arise from the change in floc structure from strong E-F at pH 2 to weak F-F at pH7 which is related to the thickening of the electrical double layer. Further increase in pH from 7 to 9 for 0.001 M ionic strength suspensions leads to floc-breakdown. As mentioned previously 0.001 M NaCl at pH 9 does not compress the electrical double layer sufficiently to induce flocculation, hence, the viscosity is reduced. Similar trends were observed in the Bingham yield stress measurements.

**Table 3. Structural Breakdown Parameters for the 2<sup>nd</sup>-Order Irreversible Kinetic Model.**

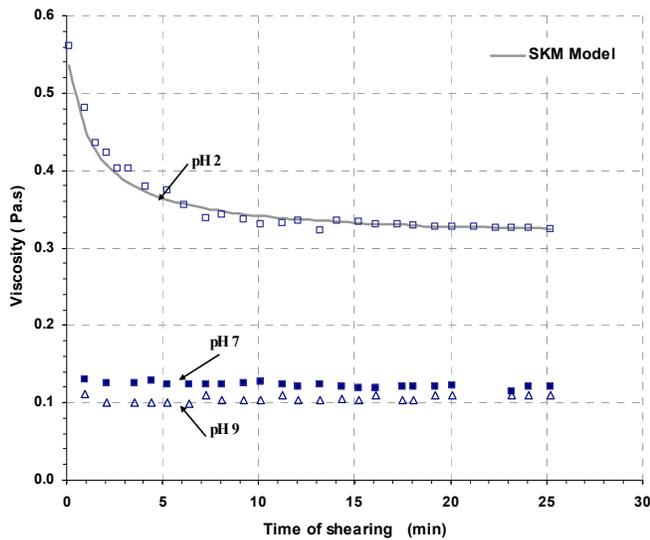
<b>(a) pH = 2</b>				
Electrolyte Concentration (M)	$\dot{\gamma} = 5 \text{ s}^{-1}$		$\dot{\gamma} = 20 \text{ s}^{-1}$	
	$k \text{ (hr}^{-1}\text{)}$	$\eta_0/\eta_e$	$k \text{ (hr}^{-1}\text{)}$	$\eta_0/\eta_e$
<b>0.1</b>	71.97	2.081	167.35	2.556
<b>0.001</b>	48.17	1.879	125.90	1.998
<b>Zero</b>	43.97	1.653	102.09	1.998

<b>(b) pH = 7</b>				
Electrolyte Concentration (M)	$\dot{\gamma} = 5 \text{ s}^{-1}$		$\dot{\gamma} = 20 \text{ s}^{-1}$	
	$k \text{ (hr}^{-1}\text{)}$	$\eta_0/\eta_e$	$k \text{ (hr}^{-1}\text{)}$	$\eta_0/\eta_e$
<b>0.1</b>	73.06	2.119	102.41	2.667
<b>0.001</b>	125.89	2.080	129.99	2.104
<b>Zero</b>	Newtonian		Newtonian	

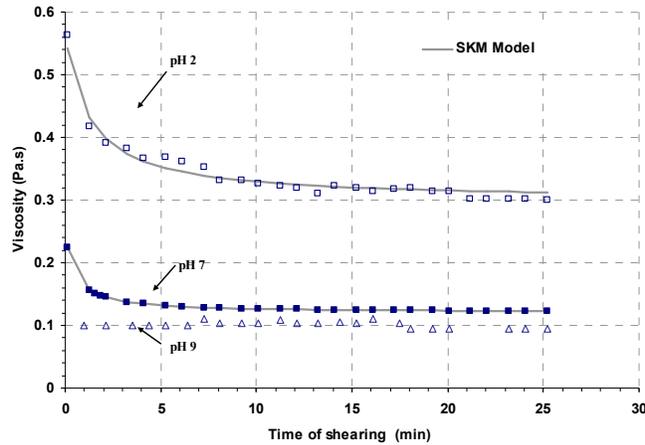
<b>(c) pH = 9</b>				
Electrolyte Concentration (M)	$\dot{\gamma} = 5 \text{ s}^{-1}$		$\dot{\gamma} = 20 \text{ s}^{-1}$	
	$k \text{ (hr}^{-1}\text{)}$	$\eta_0/\eta_e$	$k \text{ (hr}^{-1}\text{)}$	$\eta_0/\eta_e$
<b>0.1</b>	72.25	2.115	102.01	2.629
<b>0.001</b>	Newtonian		Newtonian	
<b>Zero</b>	Newtonian		Newtonian	



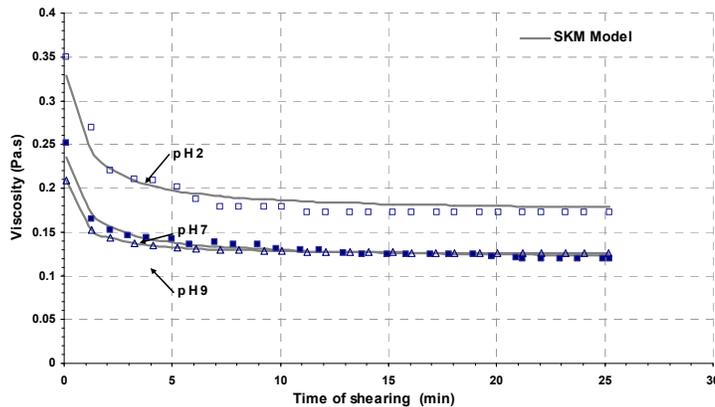
**Fig. 8. Effects of pH on the Time-dependent Viscosity of 10 % (v/v) Kaolinite-water Suspension at a Shear Rate of 5.0 s<sup>-1</sup>. The Continuous Line is the Kinetic Model (p=2).**

For high ionic strength (i.e. 0.1 M NaCl), kaolinite suspensions were found to be flocculated and show non-Newtonian behaviour for all pH investigated in this study. The parameters  $k$  and  $\eta_0/\eta_e$  increase with increasing the pH from 2 to 7 and slightly decreasing as the pH is increased from 7 to 9. This increase in  $k$  and  $\eta_0/\eta_e$  in the range  $2 \leq \text{pH} \leq 7$  is linked to the structural change from strong E-F flocs to weak F-F flocs. However, in the range  $7 \leq \text{pH} \leq 9$  there is no E-F interaction but only the F-F interaction so that the decrease in  $k$  and  $\eta_0/\eta_e$  is linked to the strengthening F-F interaction which is favoured at higher pH.

Finally, it is important to note that this work has been very successful in establishing the links between kaolinite particle-particle interactions and floc sizes,  $d_A$  with the Bingham yield stress,  $\tau_B$ , the breakdown rate constant,  $k$ , and extent of thixotropy,  $\eta_0/\eta_e$ .



**Fig. 9. Effects of pH on the Time-dependent Viscosity of 10 % (v/v) Kaolinite-0.001 M NaCl Suspension at a Shear Rate of  $5.0 \text{ s}^{-1}$ . The Continuous Line is the Kinetic Model ( $p=2$ ).**



**Fig. 10. Effects of pH on the Time-dependent Viscosity of 10 % (v/v) Kaolinite-0.1 M NaCl Suspension at a Shear Rate of  $5.0 \text{ s}^{-1}$ . The Continuous Line is the Kinetic Model ( $p=2$ ).**

## 5. Conclusions

The results show that the settlement characteristics, floc size and rheological behaviour of kaolinite suspensions change significantly with both electrolyte concentration and solution pH. It was found that, the flocculated kaolinite suspensions settled in the flocculated form and produces larger flocs size,  $d_A$ , and Bingham yield stress,  $\tau_B$ , than those settled in deflocculated /dispersed form. The results also show that, the effect of pH and ionic strength on the structural breakdown rate constant,  $k$ , and extent of thixotropy,  $\eta_o/\eta_e$ , was found to be in agreement with the results of the Bingham yield stress,  $\tau_B$ .

## References

1. Farinato, R.S.; Huang, S. and Hawkins, P. (1999). *Colloid-polymer interactions: from fundamentals to practice*. John Wiley & Sons, Inc., New York.
2. Besra, L.; Sengupta, D.K.; Roy, S.K. and Ay, P. (2002). Studies on flocculation and dewatering of kaolin dispersions by anionic polyacrylamide flocculant in the presence of some surfactants. *International Journal of Mineral Processing*, 66(1-4), 1-28.
3. Mpofo, P.; Addai-Mensah, J. and Ralston, J. (2003). Influence of hydrolyzable metal ions on the interfacial chemistry, particle interactions, and dewatering behaviour of kaolinite dispersions. *Journal of Colloid and Interface Science*, 261(2), 349-359.
4. Mpofo, P.; Addai-Mensah, J., and Ralston, J. (2003). Investigation of the effect of polymer structure type on flocculation, rheology and dewatering behaviour of kaolinite dispersions. *International Journal of Mineral Processing*, 71(1-4), 247-268.
5. Nasser, M. S., and James, A. E. (2006). Settling and sediment bed behaviour of kaolinite in aqueous media. *Separation and Purification Technology*, 51(1), 10-17.
6. Nasser, M.S. and James, A.E. (2006). The effect of polyacrylamide charge density and molecular weight on the flocculation and sedimentation behaviour of kaolinite dispersions. *Separation and Purification Technology*, 52(2), 241-252.
7. Itami, K and Fujitani, H. (2005). Charge characteristics and related dispersion/flocculation behavior of soil colloids as the cause of turbidity. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 265(1-3) 55-63.
8. McFarlane, A.; Bremmell, K. and Addai-Mensah, J. (2006). Improved dewatering behaviour of clay minerals dispersions via interfacial chemistry and particle interactions optimization. *Journal of Colloid and Interface Science*, 293(1), 116-127.
9. Žbik, M. and Horn, R.G. (2003). Hydrophobic attraction may contribute to aqueous flocculation of clays. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 222(1-3), 323-328.
10. Taylor, M.L.; Morris, G.E.; Self, P.G. and Smart R.C. (2002). Kinetics of Adsorption of high molecular weight anionic polyacrylamide onto kaolinite: The flocculation process. *Journal of Colloid and Interface Science*, 250(1), 28-36.

11. Nasser, M.S. and James, A.E. (2007). Effect of polyacrylamide polymers on floc size and rheological behaviour of kaolinite dispersions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 301(1-3), 311-322.
12. Laxton, P.B. and Berg, J.C. (2006). Relating clay yield stress to colloidal parameters. *Journal of Colloid and Interface Science*, 296(2), 749-755.
13. Baird, J.C. and Walz, J.Y. (2007). The effects of added nanoparticles on aqueous kaolinite dispersions: II. Rheological effects. *Journal of Colloid and Interface Science*, 306(2), 411-420.
14. McFarlane, A.J.; Bremmell, K.E. and Addai-Mensah, J. (2005). Optimising the dewatering behaviour of clay tailings through interfacial chemistry, orthokinetic flocculation and controlled shear. *Powder Technology*, 160(1), 27-34.
15. Penner, D. and Lagaly, G. (2001). Influence of anions on the rheological properties of clay mineral dispersions. *Applied Clay Science*, 19(1-6), 131-142.
16. Rand, B. and Melton, I.E. (1977). Particle interactions in aqueous kaolinite suspensions: I. Effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions. *Journal of Colloid and Interface Science*, 60(1), 308-320.
17. Bergaya, F.; Theng, B.K.G. and Lagaly, G. (2006). *Handbook of clay science, developments in clay science*. Elsevier, Amsterdam.
18. Van Olphen, H. (1963). *Introduction to clay colloid chemistry*. Interscience, New York.
19. Michaels, A.S. and Bolger, J.C. (1962). Settling rate and sedimentation volumes of flocculated kaolin dispersions. *I & EC Fundamentals*, 1(1), 24-33.
20. Richardson, J.F. and Zaki, W.N. (1954). Sedimentation and fluidization: Part I. *Trans. Instn. Chem. Engrs.*, 32(1), 35-53.
21. James, A.E. and Williams, D.J.A. (1982). Particle interactions and rheological effects in kaolinite suspensions. *Advances in Colloid and Interface Science*, 17(1), 219-232.
22. Nguyen, Q.D.; Jensen, C.T.B. and Kristensen, P.G. (1998). Experimental and modelling studies of the flow properties of maize and waxy starch pastes. *Chemical Engineering Journal*, 70(1), 165-171.
23. Moore, F. (1959). The rheological of ceramics slip and bodies. *Trans. Br. Ceram. Soc.*, 58(1), 470-494.
24. Chavan, V.V.; Deysarkar, A.K. and Ulbrecht, J. (1975). On phenomenological characterization of thixotropic behaviour. *Chemical Engineering Journal*, 10(1), 205-214.
25. Cheng, D.C.H. and Evans, F. (1965). Phenomenological characterization of the rheological behaviour of inelastic reversible thixotropic and anti thixotropic fluids. *British Journal of Applied Physics*, 16(1), 1599-1617.
26. Saw, L.C. (1997). *An investigation of the relationship between the properties of a settled cohesive bed and the eroded flocs*. M.Sc. Thesis, Department of Chemical Engineering, UMIST.
27. Boger, D.V. and Walters, K. (1993). *Rheological phenomena in focus*. Elsevier Science Publisher, New York.
28. Williams, D.J.A. and Williams, K.P. (1987). Electrophoresis and zeta potential of kaolinite. *Journal of Colloid and Interface Science*, 65 (1), 79-87.

29. Raveendran, P. and Amirtharajah, A. (1989). Role of short-range forces in particular detachment during filter backwashing. *Journal of Environmental Engineering*, 121(2), 860-868.
30. Mahmood, T.; Amirtharajah, A.; Sturm, T. W. and Dennett, K. E. (2001). A micromechanics approach for attachment and detachment of asymmetric particles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 177(2-3), 99-110.
31. Schofield, R.K. and Samson H.R. (1954). Flocculation of kaolinite due to the attraction of oppositely charged crystal faces. *Faraday Discuss. Chem. Soc.*, 18(1), 135-145