

## Kinetic Study on the Sedimentation Behavior of Na- and Ca- kaolinite suspensions in the Presence of Polyethyleneimine

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**Abstract.** Flocculation properties (settling rate, sediment thickness, supernatant clarity) of Na- and Ca- kaolinite suspension have been studied in presence of Cationic polyethyleneimine (PEI) and mixtures of NaCl or CaCl<sub>2</sub> with PEI under controlled conditions of pH. Two Extreme kinds of qualitative sedimentations have been observed: flocculation –sedimentation (at 0, 10 and 50 ppm PEI) and accumulation – sedimentation ( at 200,600 and 1000 ppm PEI). It be conclude that the highest sediment thickness and lowest turbidity was observed for Na-or Ca-kaolinite suspension at 10 ppm PEI, that is to say the critical flocculation concentration occurred at 10 ppm PEI. The sedimentation behaviors of Na -and Ca-kaolinite suspensions in presence of PEI were found dependent on both pH and nature of electrolytes, while their flocculation was enhanced by the addition of low electrolyte concentration (0.001 mol/l) with PEI (10 ppm).

### Introduction

Flocculation is important in many diverse fields, including paper manufacturing, mineral processing, brewing, food processing, pharmaceutical manufacturing, water (drinking and waste) purification, soil conditioning and erosion control. Particles may be flocculated so they can be more easily removed the solids as a “filter-cake” or “sludge” as in wastewater and sewage treatment. The formation of sufficiently large flocs facilitates separation of solids particles from suspension liquid by means of sedimentation the formation of dense flocs allows the solid phase to be removed in a minimal volume; and the formation of open flocs facilitates their removal by filtration. Because Kaolinite is a major raw material for the above applications, the flocculation and dispersion behavior of kaolinite in aqueous media has been studied extensively [Ma, K., and Pierre 1992, 1999, Besra *et al* 2002, Goldberg and Glaubig 1987 and Rossi *et al.* 2003]

Kaolinite is a hydrous aluminosilicate of layer structure comprising silica and alumina sheets stacked on top of each other [Hu and Liu 2003].

Kaolinite has different surface structures between base planes and edge planes. The basal surfaces of kaolinite are believed to carry a constant structural charge due to the isomorphous substitution of Si<sup>4+</sup> by Al<sup>3+</sup>, whereas the charge on the edges is due to the protonation / deprotonation of exposed hydroxyl groups. Depending on the solution pH, the edge surfaces can bear net negative, or positive or no charge. The pH where the net total particle charge is zero is called the point of zero charge (PZC), which is one of the important parameters used to describe variable charge surfaces [Pefferkorn *et al.* 1985] The ability of kaolinite to flocculate is predominantly controlled by coulombic forces between the negative charges on the basal planes and positive charges at the edges surface [Blockhaus *et al* 1997]

When the electrical repulsion of identically charged double layers around kaolinite particles is strong enough, the kaolinite suspension remains dispersed [Amandarajah and Chen 1994]. Flocculation is brought about by the decrease of this repulsion. The use of polymer to control the stability and flocculation behavior of clay suspension have been widely investigated [Luckham and Rossi 1999, Bradenburg *et al.* 1988 and Perezrodriguez 1977] The

nature of the flocculation of kaolinite obtained in polymer solution depends upon a number of factors including polymer characteristics, and solvent properties as well as the hydrodynamic conditions used during the flocculation and preflocculation stages [Luckham and Rossi 1999]. Such factors are important for achieving the desired flocculation state of particular fine particles and are not easy processes [vanOlphen1991]. Many investigators [KJellin 1997, Ma 1997 and Oades 1984] had characterized the behavior of several cationic polymers for flocculation of kaolinite. Polyethyleneimine (PEI) is a cationic polymer and was known to be excellent cationic flocculants. The adsorption of PEI on  $\text{SiO}_2$ ,  $\text{SiC}$  [Pugh and Bergstrom 1994],  $\text{Fe}_2\text{O}_3$  [Radeva and Petkanchin 1997],  $\text{ZrO}_2$  [Wang *et al.* 1999], bentonite [Alemdar *et al.* 2005] surfaces were investigated.

The different properties of the flocculated systems can be the determining criterion in different process. For example, whereas supernatant clarity, sediment thickness will be important when water is to be important in effluent treatment. It is well known that the flocculation of fines particles is very difficult. Therefore in this study the effect of PEI adsorption on selected flocculation parameters, such as settling rate, sediment thickness and supernatant clarity is studied for kaolinite fines. The settling rate is mainly a measure of the size of the flocs and in latter stages the compressibility of flocs and floc networks, and supernatant clarity is a measure of the size distribution of flocs and size dependent capture of the particles and flocs by the polymer. Also the study aims to investigate the influence pH and electrolyte ( $\text{NaCl}$  and  $\text{CaCl}_2$ ) in presence of PEI on flocculation behavior of Na- and Ca- kaolinite suspension.

### Experimental Work

#### Material

The studied kaolinite samples were chosen from Ymama regions in the Saudi Arabia. X-ray analysis showed the characteristic pattern of kaolinite (the distance between a certain plane in the unit layer of kaolinite and corresponding plane in the next unit layer) of about  $7.2 \text{ \AA}$ , which indicate that the clay sample is mainly kaolinite, not another clay. Chemical analysis obtained from by X-ray fluorescence are represented in table 1. The cationic polyethyleneimine (PEI) was used. It has a molecular weight of  $2 \times 10^4 \text{ g mol}^{-1}$ . Analar salts of  $\text{NaCl}$  and  $\text{CaCl}_2$  are from VWR were used.

### Methods

#### Clay separation and saturation

This work aims to study the effect of PEI adsorption on flocculation of fine kaolinite (The average particle size was  $2 \mu\text{m}$ ) which are not easily flocculated which will be important in water treatment. Therefore, about 1 Kg of kaolinite was suspended in graduated cylinder of volume 5 liter of deionizer water, the  $2 \mu\text{m}$  fraction was separated and this can be done by choosing a height 10 cm to collect a decant and by applying Stock's law which by:

$$D = 14.29 (h/t)^{1/2}$$

Where (D) is the radius of separated particles (in this work  $D = 2 \mu\text{m}$ ), (h) is the height of a decant and (t) is the time for collecting this height. About 100 g of fine particles each of effective diameter of  $2 \mu$  were obtained by this method. According to the method of Schofield and Samson [Schofield and Samson 1954]. These fine particles ( $2 \mu\text{m}$ ) were treated with 0.5 molar  $\text{NaCl}$  or  $\text{CaCl}_2$  solution to convert the kaolinite to the sodium form (Na- or Ca-kaolinite). The Cation Exchange capacity (CEC) of Na-kaolinite was determined by using ammonium acetate (1M) as described by Black and Hannah 1961. The cation content was determined by atomic absorption spectrophotometer, Shimadzu Corporation, AA-6701/6601 Series. The obtained CEC value is 15 meq/100g clay. The point of zero charge (PZC) was determined by potentiometric titration according Bolland *et al.* method [Bolland *et al* 1980], the PZC at pH 4. Also the ignition loss percentage (represent the organic compounds on kaolinite surface) was determined for the kaolinite sample, the obtained value is about 10%.

#### Sedimentation test

To carried out the sedimentation tests, each suspension of Na- kaolinite or Ca- kaolinite with a median size of  $2 \mu\text{m}$  was prepared in a graduated cylinder with an inside diameter of 30 mm, which was large enough to neglect the wall effect [ Ma, K., and Pierre 1992]. Then, distilled water and proper amounts of different concentrations of a polymer (1000, 600, 200, 50, 10 ppm) were added to get an initial suspension volume of 100ml each, having 6.5 of pH value. The cylinders were turned upside down many times to uniformly distribute the components inside the suspension. To study the effect of pH on flocculation of Na- and Ca-kaolinite suspensions, the pH in all of the suspensions was adjusted with dilute

HCl or NaOH to have the pH range from 3 to 12. Also the sedimentation tests were carried for Na- or Ca- kaolinite in presence of PEI with NaCl or CaCl<sub>2</sub>. All experiments were performed at room temperature and cylinders were covered with a piece of Para film to prevent water evaporation.

In all sedimentation experiments where a clear interface occurred, the position of this interface was read every 10 minutes during the first hour, then every hour for the following two hours, and finally every 24 hours until 360 hours. The rate at which this interface moved was used to measure the accumulation rate, or the settling rate (depending on sample behavior, in mm/hr). After 24 hours of sedimentation experiments, the obtained supernatant was taken and turbidity was measured by using turbidimeter.

## Results and Discussion

### Effect of polyethyleneimine (PEI)

Figure 1a and b show the relationship between sediment thickness of Na- and – Ca kaolinite suspensions and time, at different polymer concentrations. The curves correspond to polymer concentration of 0, 10 and 50 ppm showed that the onset of flocculation is not instantaneous after the addition of PEI. Solutions of high molecular weight polymer are viscous at typical operational concentrations and this can lead to a distinct period of time for thorough distribution through the suspension [Ma, K., and Pierre 1992]. Therefore there is a lag time of about 10 minutes between the addition of the polymer and the onset of flocculation. At this moment, the floc was formed and these flocs joined to each other and created an apparently uniform sediment, separated by a sharp interface from clear supernatant, liquid. The settling rate of kaolinite suspension after 10 minutes is fast. Later on, the settling rate began to slow down progressively, until it reached an aging stage (after 24 hours). This behavior represents the flocculation- sedimentation [Ma, K., and Pierre 1992].

The sedimentation data with high PEI concentrations (200,600 and 1000 ppm) are also represented in figure 1. The sedimentation behavior of Na- or Ca- kaolinite suspension at high polymer concentration is in reverse trend to that of low polymer concentration and represents accumulation-sedimentation behavior [Ma, K., and Pierre 1999]. Its initial volume was zero and it increased slowly by accumulation of new particles. On top of the accumulated layer, the remaining suspension composed of smaller, slower-settling clay particles.

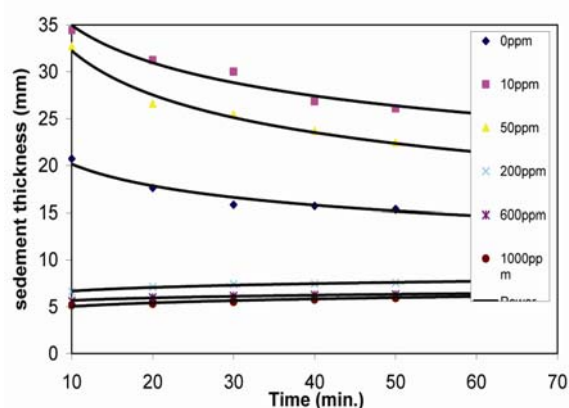


Fig. 1a. Relationship sediment thickness Na-kaolinite suspension and time at different PEI concentration (ppm).

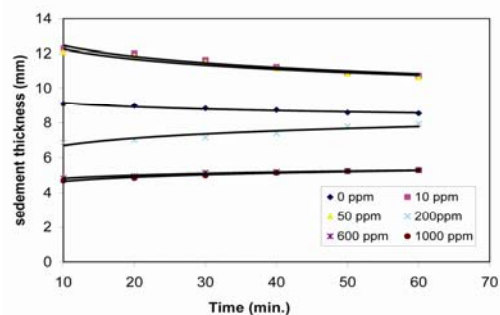


Fig. 1b. Relationship sediment thickness Ca-kaolinite suspension and time at different PEI concentration (ppm).

The final sediment volume in accumulation-sedimentation was much lower than in flocculation-sedimentation. Therefore, the accumulated-sediment was more densely packed than flocculated-sediment [Ma, K., and Pierre 1992].

For a polymer to cause flocculation by reducing the electrical repulsion of identically charged double layers around kaolinite particles, it must of necessity be of ionic character, and, furthermore, must carry a charge opposite in sign to that of the solid surface [Besra *et al* 2002]. Cationic polyelectrolyte would be expected to be active flocculants for such systems [Solberg and Wagberg, 2003]. A review by Kitchener 1972 on polymeric flocculants establishes that flocs (aggregated particles) produced with polymers are much stronger than those formed by the addition of electrolytes. Effective bridging flocculation requires that the adsorbed polymer extends far enough from the particle surface to attach to other particles and that sufficient free surface is available for the adsorption of segments of the extended chains. To achieve this, there is an "optimum dosage" for producing the largest flocs where the polymer is practically all adsorbed, but the

surface carries only half of the saturation capacity of the polymer. The flocculation of clays by polymers was first studied by Ruehrwein and Ward [Ruehrwein and Ward 1952] and Michaels [Michaels, A.S. 1954], who both studied the effect of charged polyelectrolytes on the flocculation of clay suspensions. Both emphasized the strong adsorption of the polymer especially at low concentration on the clay and the concept of the formation of strong anchor points for bridges. Koksai *et al.* 1990 found that kaolinite clay is flocculated by very low concentration of polyethylene oxide (PEO) of high molecular weight, this was attributed to the high molecular weight PEO chain being more amenable to the formation of tails and loops that are required for bridging flocculation to occur. Recently Alemdar *et al.* 2005 studied the adsorption of PEI on purified bentonite, they found that the adsorption rate of PEI was very fast and the equilibrium was reached after 5 min, and the adsorption isotherm shows a high-affinity L-type. High affinity means a strong electrostatic interaction between clay particles and PEI. Because of the pH-dependent protonation of the imine groups on the polymer chain, the polymer chains gain a net positive charge.

The high-molecular-weight PEI used in this study has a positive charge over a wide pH range between pH 3 and 11 [Erim 1995]. On the other hand, at the pH values above the point of zero charge (PZC), which is around 4 for kaolinite under study, both edges and surfaces of clay particles are negatively charged. Therefore, the addition of low PEI concentration resulted in neutralized the charge on the kaolinite particles and consequently a reduction in the electrical double thickness, hence electrostatic repulsions between kaolinite particles decreased and the particles were able to approach each other close enough giving chance for short range H-bonding forces between  $-NH_2^+$ -groups of PEI- $H^+$  and negative sites of the kaolinite surface to cause formation of polymer bridges between kaolinite particles and consequently flocculation occurred [Luckham 1999 and Wang 1999]. These flocs joined to each other and extended from wall to wall in the cylinder and formed the flocculated sediment, while the supernatant liquid was free of particles. This flocculated sediment was able to flow. The very open flocs as proved by the initial thickness of the sediment are responsible for a slow initial settling rate. However, the fractal arms of the flocs were flexible and could slowly deform during aging in the final sediment. Consequently, its volume decreased slowly with time.

At high PEI concentrations (200, 600 and 1000 ppm), all available adsorptive sites on the surfaces of

suspended kaolinite particle can be satisfied by adsorption of oppositely charged PEI, and consequently all faces of kaolinite are positively charged. As a result, the repulsive forces between the positively charged particles, preventing them from coming together or flocculation [Alemdar 2005]. Thus, sorption of large amount of PEI to kaolinite resulted in increased stability of kaolinite suspension due to increases of positive charge on kaolinite particles (electrostatic stabilization). This may result in steric stabilization caused by a thermodynamic repulsion that occurs between interpenetrating polymer chains attached to the kaolinite surfaces [Hunter 1986]. Therefore, the chance of formation of polymer bridges between kaolinite particles reduced and consequently, the heaviest particles settled immediately under gravity and formed the accumulated sediment at the bottom of the cylinders.

The final of sediment thickness of Na- and Ca-kaolinite in presence of different PEI concentration at equilibrium (after 24 hours) were shown in Fig. 2. The highest sediment thickness was observed for Na- or Ca-kaolinite at 10 ppm PEI. The results of sedimentation were confirmed by measuring the turbidity of the obtained supernatant as shown in Table 1. The result indicate that, the turbidity of the supernatant decreased from 23 and 9.03 Ntu for Na- and Ca-kaolinite suspension respectively in absence of PEI to 12.5 and 6.595 of Ntu after addition of 10 ppm PEI. From Fig. 2 and Table 2 it could be conclude that the highest sediment thickness and lowest turbidity was observed for Na- or Ca-kaolinite at 10 ppm PEI. But with increasing polymer concentration the final sediment thickness decreased to a very small value and turbidity increases, That is to say the critical flocculation concentration occurred at 10 ppm PEI.

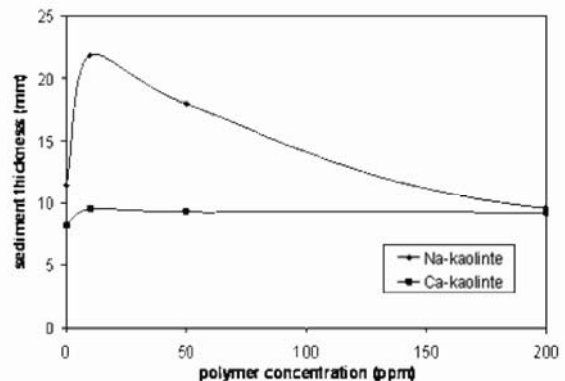


Fig. 2. Sediment thickness Na- and Ca-kaolinite suspension at different polymer concentration.

**Table 1. The turbidity (Ntu) of Na- or Ca- kaolinite suspension at different concentration of PEI after 24 hour**

Polymer concentration (ppm)	Turbidity (Ntu)	
	Na-kaolinite	Ca-kaolinite
0	23	9.03
10	12.5	6.595
50	12.9	8.91
200	755	303.5
600	875.5	370
1000	<1000	754

**Table 2. The maximum sediment thickness (mm) and turbidity (Ntu) of Na or Ca- kaolinite suspension in presence of different electrolytes concentration at 10 ppm PEI at equilibrium (after 24 hour)**

Electrolyte concentration (mol/l)	Na-kaolinite		Ca-kaolinite	
	Sediment thickness (mm)	Turbidity (Ntu)	Sediment thickness (mm)	Turbidity (Ntu)
0*	25.5	12.5	10.75	6.6
0.001	20	8.12	9.7	5.3
0.01	17.5	14.8	9.5	10.4
0.1	18	19.5	9.3	12

Results showing that the sedimentation behavior of Na-kaolinite was similar to Ca-kaolinite at different polymer concentration, but there is variation in sediment thickness and turbidity values of Na-and Ca-kaolinite suspension at different PEI concentration. The behavior is some what complex. Particles in Ca-kaolinite settle more slowly at the start than those in Na-kaolinite as shown in Figs. 1a, b. For example, the slope of the curve of sedimentation for Na-kaolinite is steeper than the slope of the curve of Ca-kaolinite. After a certain period of time (60 minute), the settling rate of particles in Na-or Ca-kaolinite becomes constant.

Sediment thickness of kaolinite suspension decreases with an increasing the valence of saturating cation at the same polymer concentration. This result, due to the double layer of surface face and edge face on Ca-kaolinite, is more compressed and becomes very thin compared to Na-kaolinite. Therefore, the repulsion force between the electrical double layer around kaolinite particles decreases and attractive force increases, face- face domain can be formed easily in the sedimentation experiment and these domain associate into aggregates [Luckham 1999]. This association leads to lower sediment voids between the Ca- kaolinite particles , very closed flocs were formed (lower sediment thickness) and consequently lower turbidity values of the supernatant solution were obtained compared to very open flocs formed ( high sediment thickness ) and

higher turbidity in Na-kaolinite [Ma and Pierre 1992]. Thus , higher valence of saturating cation become more effective in reducing sediment thickness and consequently turbidity of Ca-kaolinite in presence of PEI compared to Na-kaolinite.

### Effect of pH

Figure 3 shows the sediment thickness for Na- and Ca-kaolinite at 10 ppm of PEI with different pH values (3, 7 and 12) after 24 hours time sedimentation. Sedimentation data similar to Fig. 1.a (which corresponds to what is called flocculation-sedimentation here). As was observed with Increased the pH, the sediment thickness increases, but the reverse trends were observed for turbidity results as shown in Fig. 4. At pH 3, the flocculated sediment thickness was smaller compared to that at pH 7 and 12. For kaolinite, the reported values for the point of zero charge (ZPC) are between 2.5 and 3.8, depending on the conditions [Hu and Liu 2003]. Below the ZPC, the edge surfaces (E) of kaolinite particles are considered to be charged positively and the face surfaces (F) are charged negatively. Above the ZPC, the edges also become negatively charged. Depending on the pH values, three different modes of particle association may occur: face to face (FF), or edge- to- face (EF) and edge-to-edge (EE) [Luckham 1999]. The electrical interaction energy for the three types of associations is governed by three different combinations of the two double layers. Also, the rate of diffusion of the particles as they approach each other in these ways is not the same. FF association leads to thicker and larger flacks, and EF and EE association leads to three-dimensional voluminous "house- of- cards" structures. The extent to which the particles become flocculated depends upon the degree of compression of the double layer. When the edges are positive, the platelets flex towards a negative face [Zaman 2000]. When the edges are negative, the platelets are forced to assume a more parallel type orientation (face-to face, FF). for this reason, the pH of the medium is an important parameter to flocculation and sedimentation of clay suspension. Brandenburg and Lagaly 1988 proposed that in the PH region 5- 7.5 edge -to-face (EF) contacts are destroyed due to the low positive charged density.

In our study, the PZC of kaolinite was about at pH 4. This value agreed closely with that of Hu and Liu (2003)[6] and not agree with PZC of kaolinite edge surfaces reported in the literature that ranges from pH 5 to 9, depending on the kaolinite used and the method used for its determination [Herrington 1992 and Melton and Rand 1977].

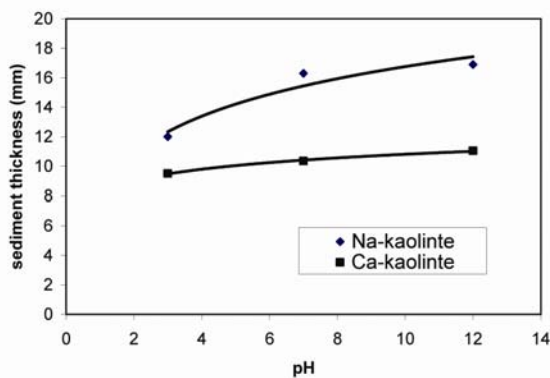


Fig. 3. Sediment thickness Na-and Ca-kaolinite suspension in presence of 10 ppm PEI at different pH After 24 hours.

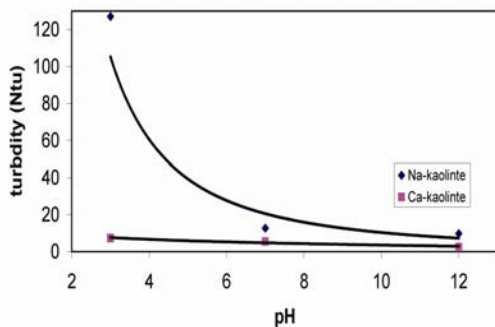


Fig. 4. Turbidity of Na-and Ca-kaolinite suspension in presence of 10 ppm PEI at different pH.

Therefore at pH =3 (below point of zero charge, PZC), the edges (E) surfaces of kaolinite are positively charged. Also at this pH, the protonation degree of PEI increased and consequently the positive charge on the polymer chains increases, the face surface (F) of kaolinite becomes positive due to polymer adsorption. As a result, the association by edge – to-face (EF) contacts are destroyed, due enhancement of electrostatic repulsion between the edges surface and face surface of kaolinite, thus preventing the kaolinite particles from coming together or flocculated [Conway 2002]. Therefore lower sediment thickness and higher supernatant turbidity for Na- or Ca-kaolinite suspensions were obtained at pH = 3. But At high pH 7 or 12 (above point of zero charge), the edges of kaolinite particle becomes negative, and the face surfaces are positively charged due to adsorption of PEI, therefore the EF association enhanced again, leading to an increase of the mean aggregate radius and consequently higher sediment thickness and lower supernatant turbidity were obtained.

#### Effect of electrolyte

Table 2 shows the final sediment thickness and

turbidity of Na- or Ca- kaolinite suspension in presence of 10 ppm PEI at different NaCl or CaCl<sub>2</sub> concentrations after equilibrium (24 hours). The kaolinite sediments relatively decreased in presence of 10 ppm PEI, by the addition of NaCl or CaCl<sub>2</sub> electrolytes. The lower turbidity was obtained where the electrolyte concentration 0.001mol/L. This behavior could be attributed to the polymer- kaolinite interactions, which was affected by the presence of electrolyte. This result can be explained by examining the physicochemical properties of both the adsorbed polymer and the electrolyte. Flocculation of Na- or Ca-kaolinite by PEI was enhanced by the addition of the electrolyte. This electrolyte (coagulant) reduced the thickness of the diffuse double layer of adjacent kaolinite particles, thus reducing the interparticle clay particles, where as PEI (a flocculent) is able to span the interparticle distances between these aggregated kaolinite particles by the formation of bridges through the hydrogen bond mechanism [Mekhamer Assaad 1999]. These two process may act individually or together to affect the sedimentation of kaolinite, leading to the initial stages of aggregation especially at low electrolyte concentration. Then a network structure could be produced through the polymer molecules attachment at many points of adsorption sites on the kaolinite surface. This stage accompanied by the formation a large flocs with minimum voids between the aggregates [Ma and Pierre 1999] (that is, the minimum turbidity for the supernatant of Na- or Ca-kaolinite could be obtained). But at high electrolyte concentration, NaCl or CaCl (0.01 and 0.1), the kaolinite surface becomes more positive, leads to retardation of PEI adsorption (which has positive charge on its chains) on kaolinite surface. Therefore the chance of bridge formation between kaolinite particles by the polymer decreased, smallest flocs were obtained (lower sediment thickness and consequently higher turbidity).

#### Data Fitting

In this section, we address the problem of constructing parametric models which approximate the behavior of the empirically gathered data. If the data fit is sufficiently accurate, it is anticipated that the parametric model will provide further insight into the characterization of the phenomenon from which the measured data came.

A basic approach to obtaining a model for a given data  $(y(x_k))_{k=1}^L$  where L is the number of data points, is to assume that:

**Table 3. The maximum sediment thickness (mm) and turbidity (Ntu) of Na or Ca- kaolinite suspension in presence of different electrolytes concentration at 10 ppm PEI at equilibrium (after 24 hour)**

Polymer concentration (ppm)	0	10	50	200	600	1000
C <sub>1</sub>	0.7022	0.0247	6.7123	-2.0025	-1.5890	0.0000
C <sub>2</sub>	9.2215	37.2352	0.0000	7.2642	6.0833	4.9466
λ <sub>1</sub>	0.6696	-0.0791	3.2645	0.1010	0.1103	-0.1662
λ <sub>2</sub>	0.0013	0.0083	0.0057	-0.0008	-0.0007	-0.0037

$$y(x_k) = f(x_k) + w(x_k) \quad (1)$$

Where  $f(x_k)$  is a given function that is obtained from  $f(x)$  in the following manner  $f(x_k) = f(x)|_{x=x_k}$ , and  $w(x_k)$  represents a random error sequence. The objective is to select the parameters of the function  $f(x_k)$  in such a manner that  $w(x_k)$  is a zero-mean error sequence of minimum possible variance. One of the most common forms of  $f(x)$  is as follows:

$$f(x) = \sum_{j=1}^N c_j e^{-\lambda_j x} \quad (2)$$

Where  $\{c_i\}$  and  $\{\lambda_i\}$  are unknown parameters and N is the number of exponentials. Note that the function  $f(x)$  may represent the sediment thickness while as the independent variable x may represent time. Similarly, we can assign  $f(x)$  to represent the initial setting time or turbidity and x to represent polymer concentration. Eq. (1) in conjunction with (2) can be solved for the unknown parameters  $\{c_i\}$  and  $\{\lambda_i\}$ . One possible approach to perform such a task is by minimizing the following function:

$$j = \sum_{k=1}^L |w(x_k)|^2$$

$$= \sum_{k=1}^L |y(x_k) - f(x_k)|^2$$

The parametric model (2) that provides the best fit is selected using the MATLAB routine SIMPLEX SEARCH. In this computations, we have set N=2. The estimated parameters are given in Table (3) It is evident from the figures that the proposed parametric models well fit the empirically gathered data

### Conclusion

The sedimentation behavior of Na- or Ca-kaolinite suspension in the presence of PEI can be classified into two types: (i) Sedimentation by settling of a flocculated kaolinite particles which forms a wall- to wall network structure in the cylinder at low PEI concentrations (0, 10 and 50 ppm), (ii) Sedimentation by accumulation of individual kaolinite particles at high PEI concentration (200,600, and 1000 ppm) .highest sediment thickness was observed for Na- or Ca-kaolinite suspension of PEI concentration of 10 ppm , i.e the critical flocculation concentration occurred at 10 ppm of PEI. The action of Ca<sup>+2</sup> as a saturating cation has a more pronounced effect on flocculation of kaolinite than Na<sup>+</sup> as a saturating cation. The flocculated sediment thickness of Na- or Ca- kaolinite by PEI was enhanced when the kaolinite has initially been coagulated by the addition of 0.001 mol/l NaCl or CaCl<sub>2</sub>. The lower flocculated sediment thickness and the higher turbidity were obtained at pH= 3 compared to that at pH 7 and 12.

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## دراسة حركية سرعة ترسيب الكاولينيت المشبع بالصوديوم والكالسيوم في وجود تراكيز مختلفة من متعدد الأيثيلين أمين الكاتيوني

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ملخص البحث. تم دراسة خواص التلبد (سرعة الترسيب - سمك الراسب و صفاء السائل فوق الراسب) لمعلق الكاولينيت المشبع بالصوديوم والكالسيوم في وجود تراكيز مختلفة من متعدد الأيثيلين أمين الكاتيوني ، وجود خليط من متعدد الايثيلين وكلوريد الصوديوم ووجود خليط من متعدد ايثيلين امين وكلوريد الكالسيوم. لوحظ نوعين عن سلوك الترسيب: ترسيب تلبدى لمعلق الكاولينيت سواء المشبع بالصوديوم أو الكالسيوم عند اضافة صفر، ١٠ و ٥٠ جزء في المليون من متعدد الايثيلين أمين، ترسيب تراكمي عند اضافة ٢٠٠، ٦٠٠ و ١٠٠٠ جزء في المليون من متعدد الايثيلين أمين. كان أعلى سمك راسب وأقل عكارة لمعلق الكاولينيت المشبع بالصوديوم أو الكالسيوم عند اضافة ١٠ جزء في المليون من متعدد الايثيلين أمين. لذلك يعتبر ١٠ جزء في المليون من متعدد الايثيلين أمين الترسبي لمعلق الكاولينيت يعتمد على تركيز الألكتروليت والأس الهيدروجيني. حيث كان أفضل تلبد لمعلق الكاولينيت عند اضافة تركيز من ٠.٠٠١ مول/ لتر مع ١٠ جزء في المليون من متعدد الأيثيلين أمين.

