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

W.K. Mekhamer, N. AL Andis^{*} and M. EL Shabanat

Chemistry Department, College of Science, King Saud University, P.O. Box 2455 Riyadh 11451, Saudi Arabia nadis@ksu.edu.sa

(Received 29/11 /1428H; accepted for publication 28/07/1429H)

Key words: flocculation, sedimentation, polyethyleneimine, kaolinite, Turbidity.

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 CaCl₂ 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 Kaolinte 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⁺⁴ by Al⁺³, 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 coulomic 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 [Amandarajiah 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 [vanOlphen1991].Many processes investigators [KJellin 1997, Ma 1997 and Oades 1984] had characterized the behavior of several cationic polymers for flocculation of kaolinite. Polyethleneimine (PEI) is a cationic polymer and was known to be excellent cationic flocculants. The adsorption of PEI on SiO₂, SiC[Pugh and Bergstrom 1994], Fe₂O₃[Radeva and Petkanchin 1997], ZrO₂ [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 (NaCl and CaCl₂) 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 A°, 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 x10⁴ g mol⁻¹. Analar salts of NaCl and CaCl₂ 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 $2\mu m$) 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 μm 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 $D = 2\mu m$), (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 2µ were obtained by this method. According to the method of Schofied and Samson [Schofield and Samson 1954]. These fine particles (2µm) were treated with 0.5 molar NaCl or CaCl₂ 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 meg/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 2μ 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 CaCl₂. 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 turbdimeter.

Results and Discussion

Effect of polyethyleneimine (PEI)

Figure 1a and b show the relationship between sediment thickness of Na- and - Ca kaolinite and time, at different polymer suspensions 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].

sedimentation with high The data 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 accumulationsedimentation 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 accumulationsedimentation was much lowers that 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 Kitchener1972 on polymeric flocculants establishes that flocs (aggregated particles) produced with polymers are much stronger than those formed by the addition electrolytes. Effective of 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], both studied the effect of charged who 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. Koksal 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 highaffinity 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 gains 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 kaolinte 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 -NH₂⁺-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 Cakaolinite in presence of different PEI concentration at equilibrium (after 24 hours) were shown in Fig. 2. The highest sediment thickness was observed for Naor Ca-kaolinte 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 Naand 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-kaolinte 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)	Turbdity (Ntu)			
	Na-kaolinte	Ca-kaolinte		
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 different PEI at concentration. The behavior is some what complex. Particles in Ca-kaolinite settle more slowly at the start than those in Na-kaolinte 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 Cakaolinite 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 Naand 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 flocculationsedimentation 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 three-dimensional FF association leads to 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 flocculation important parameter to 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 kaolinte, thus preventing the kaolinte particles from coming together or flocculated [Conway 2002]. Therefore lower sediment thickness and higher supernatant turbidity for Na- or Ca-kaolinite suspnsions 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 increases 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 CaCl₂ concentrations after equilibrium (24 hours). The kaolinite sediments relatively decreased in presence of 10 ppm PEI, by the addition of NaCl or CaCl₂ electrolytes. The lower turbidity was obtained where electrolyte concentration 0.001mol/L. the 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 Cakaolinite 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 Cakaolinite 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:

Polymer concentration (ppm)	0	10	50	200	600	1000
C1	0.7022	0.0247	6.7123	-2.0025	-1.5890	0.0000
C2	9.2215	37.2352	0.0000	7.2642	6.0833	4.9466
1λ	0.6696	-0.0791	3.2645	0.1010	0.1103	-0.1662
2λ	0.0013	0.0083	0.0057	-0.0008	-0.0007	-0.0037

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)

$$y(x_k) = f(x_k) + w(x_k)$$
 (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:

$$f(x) = \sum_{j=1}^{N} c_j e^{-\lambda i x}$$
(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-kaolinte suspension in the presence of PEI can be 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-kaolinte suspension of PEI concentration of 10 ppm, i.e the critical flocculation concentration occurred at 10 ppm of PEI. The action of Ca⁺² as a saturating cation has a more pronounced effect on flocculation of kaolinte than Na⁺ as a saturating cation. The flocculated sediment thickness of Na- or Ca- kaolinte by PEI was enhanced when the kaolinte has initially been coagulated by the addition of 0.001 mol/l NaCl or CaCl2. The lower flocculated sediment thickness and the higher turbidity were obtained at pH=3 compared to that at pH 7 and 12. Acknowledgment. The authors would like to thank professor Saleh alshubili for his fruitful discussion.

Reference

- Ma, K., and Pierre, C.A. Sedimentation behavior of a fine kaolinite in the presence of fresh Fe electrolyte, Clay and Clay Minerals, 40, (1992), 586-592.
- Ma ,K and Pierre, C. A. Clay sediment-structure formation in aqueous kaolinite suspensions, Clay and Clay Minerals 47, (1999), 522-526.
- Besra,L., Sengupta, D.K, Roy,S.K., and Ay, P. Polymer adsorption: its correlation with flocculation and dewatering of kaolin suspension in the presence and absence of surfactants, International Journal of Mineral Processing, International Journal of Mineral Processing, 66, (2002), 183-202 Goldberg, S., and Glaubig., R.A. Effect on saturating cation, pH, and aluminum and iron oxide on the flocculation of kaolinite and montmorillonite, Clay and Clay Minerals 35, (1987), 220-227.
- Rossi, S., Luckham, P.F., Tadros, T.F. Influence of non-ionic polymers on the rheological behaviour of Na⁺-montmorillonite clay suspensions. Part II. Homopolymer ethyleneoxide and polypropylene oxide-polyethylene oxide ABA copolymers, Colloids and surfaces A: Physicochem. Eng. Aspects 215, (2003), 1-10
- Hu, Y., Liu, X. Chemical composition and surface property of kaolins, Minerals Engineering 16, (2003), 1279-1284

- Pefferkorn, E., Nabzar, L., and Carroy, A., J. Adsorption of polyacrylamide to Na kaolinite: Correlation between clay structure and surface properties, Colloid and Interface Sci. 106, (1985), 94-103
- Blockhaus, F., Sequaris, J.M., Narres, H.D., and Schwuger, M.J. Adsorption-Desorption Behavior of Acrylic-Maleic Acid Copolymer at Clay Minerals, J. Colloid and Interface Sci. 186, (1997), 234-247
- Amandarajiah, A., Chen, J. Double-Layer Repulsive Force between Two Inclined Platy Particles According to the Gouy-Chapman Theory, J. Colloid Interface Sci. 168, (1994), 111-117.
- Luckham, P.F. and Rossi, S. The colloidal and rheological properties of bentonite suspensions, Advances in Colloid and Interface Science 82, (1999), 43-92,
- Bradenburg, U., Lagaly, G. Rheological properties of sodium montmorillonite dispersions, Applied Clay Science, 3, (1988), 263-279
- Perezrodriguez, J.L., Weiss, A., and Lagaly, G. A natural clay organic complex from Andalusian black earth, Clays and Clay Minerals. 25, (1977), 243.
- van Olphen, H., " An Introduction to Clay Colloid Chemistry", 2nd ed. Krieger Publishing, Florida, 1991.
- KJellin, M. U.R., Claesson, p.M. and Audebert, R. Interactions between Adsorbed Layers of a Low Charge Density Cationic Polyelectrolyte on Mica in the Absence and Presence of Anionic Surfactant, J. of Colloid and interface Sci. 190, (1997), 476-484
- Ma, K., and Pierre, A.C. Effect of interaction between clay particles and Fe (super 3+) ions on colloidal properties of kaolinite suspensions., Clays and Clay Minerals 45, (1997), 733-744.
- Oades, J..M. Interactions of polycations of aluminum and iron with clays, Clays and Clay Minerals 32, (1984), 49-57.
- Pugh, R. J. and Bergstrom, L. Surface and Colloid Chemistry in Advanced Ceramics Processing, Dekker, New York ,1994.
- Radeva, T., and Petkanchin, I. Electric Properties and Conformation of Polyethylenimine at the Hematite-Aqueous Solution Interface, J. Colloid Interface Sci. 196, (1997), 87.
- Wang, J L. Gao, J. Sun and Q. Li. Surface Characterization of NH₄PAA-Stabilized Zirconia Suspensions, J. Colloid Interface Sci. 213, (1999), 552.
- Alemdar A. Oztekin N., Gungor N. Ece O.I., Erim F.B. Effects of polyethyleneimine adsorption on the rheological properties of purified bentonite suspensions, Colloids and Surfaces A: Physicohem. Eng. Aspects, 252, (2005), 95-98

- Schofield, R.K., and Samson, H.R. Flocculation of kaolinite due to the attraction of oppositely charged crystal faces, Discuss. Faraday Soc. 18, (1954), 135-145.
- Black, A.P., and Hannah, S.A. Electrophoretic studies of turbidity removal by coagulation with aluminum sulfate, J. Am. Water Works Assoc. 53, (1961), 438
- Bolland, M.D.A., Posner, A.M., and Quirk, J.P. pH-independent and pH-dependent surface charges on kaolinite, .Clays and Clay Minerals 28, (1980), 412-418,
- Solberg, D.and Wagberg, L. Colloids and surfaces A: Physicochem. Eng. Aspects 219, (2003), 161-172.
- Kitchener, J.A. Principles of Action of Polymeric Flocculants, Polym. J., (1972), 217-229
- Ruehrwein, R.A., Ward, D.W. Mechanism of Clay Aggregation by Polyelectrolytes. Soil Sci, 73, (1952), 485
- Michaels, A.S. Aggregation of suspensions by polyelectrolytes , Ind. Eng.Chem. 46, (1954), 1485
- Koksal, E., Ramachandran, R., Somasundaran, P., Maltesh, C. Flocculation of oxides using polyethylene oxide, Powder Tech.62, (1990), 253-259
- Erim, F.B. Cifuentes, A. Poppe, H. and Kraak, J.C. Performance of a physically adsorbed high-molecular-mass polyethyleneimine layer as coating for the separation of basic proteins and peptides by capillary electrophoresis, J. Chromatogr. A. 708, (1995), 356-361.
- Hunter, R.J. Foundation of Colloid Science. Oxford: Oxford University Press, 1986.
- Zaman, A.A., Bjelopavlic, M., and Moudgil, B.M. Effect of Adsorbed Polyethylene Oxide on the Rheology of Colloidal Silica Suspensions, J. of Colloid and interface Sci., 226, (2000), 290-298.
- Herrington, T.M., Clarke, A.Q., and Watts, J.C. The surface charge of kaolin Colloids surf.68, (1992), 161-169
- Melton, I.E., and Rand, B. Particle interactions in aqueous kaolinite suspensions : II. Comparison of some laboratory and commercial kaolinite samples .J.Colloid Interface Sci.60, (1977), :321
- Conway, B.E. Electrical double-layer and ion adsorption behavior at solid /solution interface; Encyclopedia of Surface and Colloid Science, Marcel Dekker Inc., New York ,2002.
- Mekhamer, W.K., Assaad, F.F. Flocculation and Coagulation of Ca- and K-saturated Montmorillonite in the presence of Polyethylene Oxide, Journal of Applied Polymer Science, Journal of Applied Polymer Science.73, (1999), 659-662.

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

وفاء بنت قطب مخيمر، ناصر بن محمد العندس*، مشاعل الشبانات كلية العلوم ، قسم الكيمياء، جامعة الملك سعود ص.ب ٢٤٥٥ الرياض ١٤٤١ ممانيش فه ١٤٢٨/١١/٢٩هـ ؛ وقبل للنشر في ١٤٢٩/٧/٢٩هـ)

ملخص البحث. تم دراسة خواص التلبد (سرعة الترسيب - سمك الراسب و صفاء السائل فوق الراسب) لمعلق الكاولينيت المشبع بالصوديوم والكالسيوم فى وجود تراكيز مختلفة من متعدد الأيثيلين أمين الكاتيونى ، وجود خليط من متعدد الايثلين وكلوريد الصوديوم ووجود خليط من متعدد ايثلين امين وكلوريد الكالسيوم. لوحظ نوعين عن سلوك الترسيب: ترسيب تلبدى لمعلق الكاولينيت سواء المشبع بالصوديوم أوالكالسيوم عند اضافة صفر، ١٠ و ٥٠ جزء فى المليون من متعدد الايثيلين أمين، ترسيب تراكمى عند اضافة ٢٠٠، ٢٠٠ و ١٠٠ جزء فى المليون من متعدد الايثيلين أمين. كان أعلى سمك راسب وأقل عكارة لمعلق الكاولينيت المشبع بالصوديوم أو الكالسيوم عند اضافة ٢٠٠ ، ٢٠٠ و ١٠٠ جزء فى المليون من متعدد الايثيلين أمين. كان أعلى سمك راسب وأقل عكارة لمعلق الكاولينيت المشبع بالصوديوم أو الكالسيوم عند اضافة ١٠٠ منه المليون من متعدد الايثيلين أمين. كان أعلى سمك راسب وأقل عكارة لمعلق الكاولينيت المشبع بالصوديوم أو الكالسيوم عند اضافة ١٠٠ منه. المليون من متعدد الايثيلين أمين. كان أعلى سمك راسب وأقل عكارة لمعلق الكاولينيت المشبع بالصوديوم أو الكالسيوم عند اضافة ١٠ منه. المليون من متعدد الايثيلين أمين. كان أعلى سمك راسب وأقل عكارة لمعلق الكاولينيت المشبع بالصوديوم أو الكالسيوم عند اضافة ١٠ جزء فى المليون من متعدد الايثيلين أمين. عن أمين ١٠ محبود فى المليون من متعدد الاثيلين أمين التركيز الحرج لتلبد معلق الكاولينيت المشبع ألفون من متعدد الايثيلين أمين. عند اللك يعتبر ١٠ جزء فى المليون من متعدد الاثيلين أمين التركيز الحرج لتلبد معلق الكاولينيت المشبع بالصوديوم أو الكالسيوم . لوحظ أن السلوك الترسيبى لمعلق الكاولينيت يعتمد على تركيز الألكتروليت والأس الهيدروجيني.