

Effects of the Water Quality on the Dispersion Properties of Bentonites Used for Drilling Fluid

시추이수용 벤토나이트의 분산 특성에 미치는 수질의 영향

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ABSTRACT: The dispersion/flocculation behavior of bentonite is a major concern in performance of drilling fluid. We studied the dispersion/flocculation characteristics of three commercial bentonites [two CMC (carboxymethyl cellulose) treated and one untreated] in waters of different pHs and salt concentrations. We also examined changes in the viscosity of bentonite suspensions in such waters as a major rheological property of drilling fluid. The dispersion/flocculation behaviors of bentonites were measured by two methods: colorimetric and light scattering method. Light scattering method allows estimating the floc diameter and flocculation rate. The dispersion and flocculation behaviors were diverse with the different bentonites and water qualities. In distilled water, all the bentonites were well dispersed up to first 10 minutes. After that, the CMC-bearing bentonites were flocculated. In salt waters, all the samples were flocculated and the flocculation rate is varied with salt concentration and polymer content. The volume of settled flocs decreased with increasing salt concentration. The flocculation rate and floc diameter increased with decreasing pH of solutions, whereas the volume of settled flocs increased with increasing pH of solutions. The bentonites of fast flocculation behavior had low viscosity. The results of the present study will be helpful in applying bentonites to drilling fluids in diverse environments.

Key words : bentonite, drilling fluids, dispersion, flocculation, viscosity

요약: 벤토나이트의 분산/응집 거동은 시추이수의 성능에 큰 영향을 줌으로 주요 관심의 대상이 된다. 본 연구에서는 상업적으로 활용되고 있는 3종의 벤토나이트[2종의 CMC (carboxymethyl cellulose)처리 벤토나이트와 1종의 무처리 벤토나이트]에 대하여 pH와 염분농도가 다른 용액에서의 분산/응집 특성을 분석하였다. 또한, 벤토나이트 현탁액의 점성 변화를 시추용이수의 유동학적 측면에서 검토하였다. 벤토나이트의 분산/응집 거동은 비색분석법과 광분산법의 두 방법으로 측정되었으며, 광분산법으로 침전된 입자의 직경과 침전속도도 검토하였다. 벤토나이트의 종류와 수질에 따라 분산/응집 거동은 다양하게 나타났다. 초기 10분 동안에 모든 종류의 벤토나이트는 좋은 분산 특징을 보여주나, 이후에 CMC를 함유한 벤토나이트들은 다소 응집되는 특성을 보여주었다. 염수에서는 모든 시료들이 응집되는 특성을 보이며, 응집속도는 염의 농도와 폴리머의 농도에 따라 변화하였다. 침전된 응집물의 부피는 염의

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농도가 증가됨에 따라 감소하였다. 용액의 pH는 시료의 분산/응집 거동에 주요한 영향을 미치며, 응집 속도와 응집입자의 직경은 용액의 pH가 감소함에 따라 증가하였다. 반면에, 침전된 응집물의 부피는 pH가 증가됨에 따라 증가하였다. 응집 속도가 빠른 벤토나이트 분산용액은 점성이 낮았다. 다양한 환경에서 벤토나이트를 시추이수용으로 적용하고자 할 경우, 본 연구의 결과들은 유용한 자료로 활용될 수 있을 것이다.

주요어 : 벤토나이트, 시추이수, 분산, 응집, 점성

INTRODUCTION

Smectite-group minerals show colloidal property in water because of their internal structure and small particle size. Bentonite, which contains “montmorillonite”, are widely used in various industrial products and processes such as paints, ceramics, pesticides, pharmaceuticals, cosmetics, cement and drilling fluids to modify the rheology and to control the stability of drilling fluid. An important property of bentonite is to provide adequate particles dispersion in such application, which is required to obtain a uniform distribution.

Researches have been done to improve the performance of drilling fluids. Individual additives were developed to affect one or more of the properties that are measured according to the American petroleum institute (API) standard test procedures (Caenn and Chillingar, 1996). Drilling fluid is an essential part of rotary drilling and plays a major role in keeping a safe and efficient well (Australian petroleum production & exploration association limited, 1998). One of the major roles of montmorillonite in drilling fluid is to give viscosity that is adequate for drilling (Bol, 1986). Montmorillonite has the highest swelling capacity, which is responsible for building up viscosity. In practice, bentonites often contain other types of clay and non-clay minerals in appreciable amounts. Their presence would have an adverse effect on the quality of bentonite. The exchangeable ions have a great effect on the swelling capacity of the montmorillonite. By far, the best performance has been obtained with sodium montmorillonite. If the quality of bentonite is not suffi-

cient to accomplish intended viscosity, various additives including salts and polymers should be added to enhance the viscosity of the fluid by flocculating the bentonite suspension (Erdogan and Demirci, 1996; van Olphen, 1977). The addition of polymer or surfactant controls the dispersion and flocculation of the montmorillonite particles. Recently, many researches (Mahto and Sharma, 2004; Gungor, 2000; Isikece *et al.*, 1999; Permien and Lagaly, 1994a) have been performed on the interaction of organic polymers with the montmorillonite surface by means of rheological measurements. Montmorillonite may be dispersed or flocculated, depending on the chemical characteristics and the concentration of the polymers.

This study was designed to investigate the dispersion and flocculation behaviors of some commercially available bentonites in relation to pH and salt concentration and their applications to the improvement of drilling fluids.

MATERIALS AND METHODS

Three commercially available bentonites, Montigel-F, Bentonil GTC4 and Tixoton were used in this study. These are sodium-type bentonite containing 75% to 85% montmorillonite. According to supplier's report, Bentonil GTC4 and Tixoton contained 0.3% and 0.2% CMC (carboxymethyl cellulose), respectively. Thus, they are polymer bearing samples or treated samples. These polymer bearing samples also contained 4.1% Na_2CO_3 and 0.1% $\text{Mg}(\text{OH})_2$. Montigel-F was untreated with any polymers and chemicals. All Bentonite samples were obtained from the Sud-chemie Korea Co., Ltd. and

Table 1. The physicochemical properties of the bentonite samples obtained from Sud-Chemie Korea Co., Ltd

Properties	Tixoton	Bentonil GTC4	Montigel-F
Polymer content (%)	0.2	0.3	N/A
Moisture (%)	< 12	< 12	< 11
Outer sp. gravity (t/m^3)	0.75~0.85	0.75~0.85	0.75~0.85
pH	10~11	10~11	N/A
Expansion (mL/2 g)	> 22	> 22	> 12
Particle size (200 mesh)	< 25%	< 20%	< 25%
Gel strengt (lbs/100 ft ² *)	> 3	> 3	N/A

N/A: not available.

Table 2. Mineralogical composition of the samples used in this study (Unit: wt%)

Sample name	Montmorillonite	Quartz	Feldspar	Mica	Others
Tixoton	85	1	6	2	6
Bentonil GTC4	83	2	6	2	7
Montigel-F	75	2	7	2	14

used without further treatment. The physicochemical properties of samples obtained from Sud-Chemie Korea Co., Ltd. are listed in Table 1. The mineralogical composition of each sample is indicated in Table 2. The mineral compositions were quantified by XRD analysis with Siroquant version 2.5.

The dispersion and flocculation behaviors of bentonite were measured by two methods. The colorimetric method (HACH DR/8900) depends mainly on the wavelength, while the light scattering method (Turbiscan MA 2000) depends on the photon transport length. Light scattering method is used to study the stability of suspensions and to estimate the dispersed phase properties such as floc diameter and flocculation rate. Colorimeter method, however, often requires a pre-dilution of the dispersion because of a limited measurement range and is unable to give information about the real physical state of dense heterogeneous media. A new technology based on multiple light scattering analyses called TURBISCAN has been recently developed to fill this gap and to characterize both diluted and concentrated dispersions. The experi-

ments were conducted with 3 g of bentonite samples and 100 mL of water of various properties. Homogeneous dispersion was obtained after 1 day. The uppermost 1 cm of solution was taken with 5 mL pipet, and its turbidity was measured with a colorimeter (HACH DR/890) and expressed as NTU (Nephelometric Turbidity Units). The turbidity was measured for estimating flocculation and dispersion rate. The volume of settled flocs was also measured.

The flocs settling behavior was measured in terms of supernatant formation kinetics using a liquid dispersion optical characterization instrument (Turbiscan MA 2000). The samples carefully added into a cylindrical glass cell (about 60 mm). The reading head scans across the height of the sample over time. It reports the percentage of the light either transmitted through (180° from the incident light, transmission sensor) or back scattered (45° from the incident radiation, backscattering detector) from the sample. The light source is an electro luminescent diode in the near infrared ($\lambda_{air} = 850$ nm). The thickness of the supernatant phase was obtained by analyzing the data using a so-called

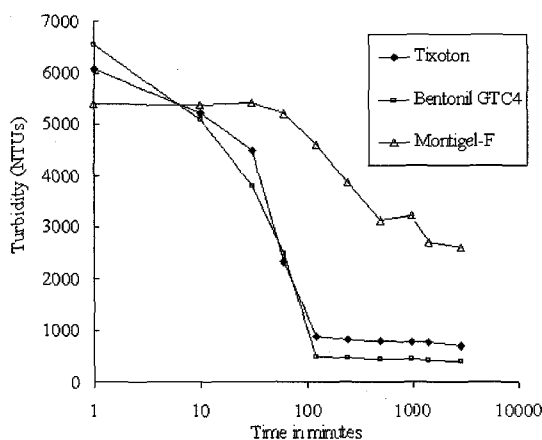


Fig. 1. Variations in turbidity in distilled water.

“absolute peak thickness” and the stability of the supernatant phase was obtained by analyzing the data using a so-called “mean values” methods as described in the turbiscan manual. The average floc diameter and the flocculation rate were also calculated.

The viscosity was measured by Brookfield digital (Model RVTD-1) viscometer. The solution pH (range from pH 2 to pH 12) was adjusted with H_2SO_4 and NaOH solutions. The solutions of various salt concentrations (1, 3.5, 10%) were prepared by using NaCl.

RESULTS AND DISCUSSION

DISPERSION/FLOCCULATIONS ANALYSIS

The behavior of bentonite-water system is complex due to unisometric clay particles exposing different crystal faces, on which an electrical double layer can be develop, which differs both in charge and the magnitude of the total surface potential (Singh and Sharma, 1997; Gungor, 2000). In view of that, the dispersion characteristics of bentonite suspensions are achieved by particle-particle and particle-water suspension. Fig. 1 to 9 show the dispersion and flocculation behavior of each sample used in this work. 30 g L^{-1} of bentonite concentration was selected for study. This concentration is the

normal concentration used in oil fields for drilling (Park *et al.*, 1960; Elward-Berry and Darby, 1997). The dispersion and flocculation behaviors of the different bentonite samples were determined according to the property of water. The difference in the behavior of these bentonites was carefully analyzed with relation to their particle size, polymer concentration, as well as montmorillonite content.

Colorimetric Method

In distilled water (Fig. 1), all the samples showed good dispersion until the first ten minutes. The CMC bearing bentonite (Bentonil GTC4 and Tixoton) showed different behaviors compared with untreated bentonite sample (Montigel-F) after 10 minutes. The Bentonil GTC4 and Tixoton were flocculated behavior, but Montigel-F showed good dispersion behavior after 10 minutes. CMC (anionic polymer) dissolves rapidly in water and can control viscosity. Therefore, CMC bearing samples must be dispersed in the solution. But we observed separation between clay and solution that indicated flocculation behavior. This is probably due to the bridging mechanism, which can be explained by the following: In the presence of sodium carbonate and magnesium hydroxide, which contain cations such as Mg^{+2} and Na^{+} . These cations were attached on the middle of the montmorillonite surface and the hydroxyl groups on the polymer and resulted in the aggregation of montmorillonite particles (Gungor, 2000). Both of the treated samples showed same volume of settled flocs of approximately 6.2 cm^3 after 2880 minutes. The untreated sample had much negative charge on their surface that resulted in high dispersion behavior. The untreated sample, however, showed a little sediments nature due to high non-clay mineral contents (0.4 cm^3 after 2880 minutes).

Effect of Salt Concentration

In salt solutions (Fig. 2), all of the samples

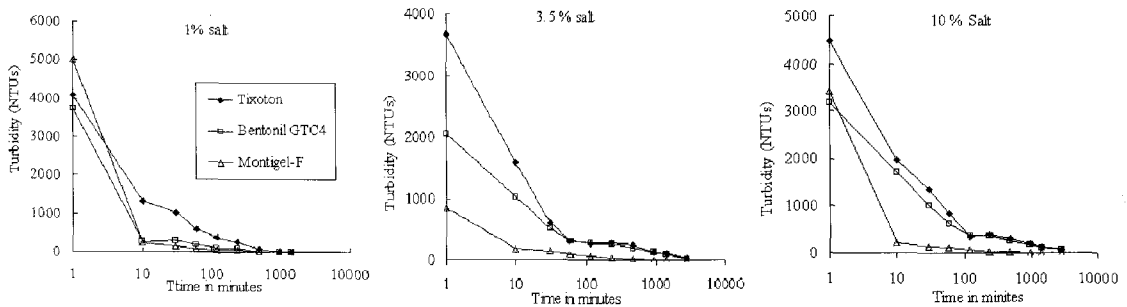


Fig. 2. Variations in turbidity with the different concentration of salt solutions.

showed flocculation behavior in contrasting to distilled water. The treated samples, however, showed slow flocculation behavior compared with untreated sample. For this experiment, we used 1 to 10% salt solutions. Until the first one minute, all of the samples showed more or less good dispersion behavior. The untreated sample was almost completely flocculated within 10 minutes whereas the treated samples showed some turbidity up to 2280 minutes.

There were some changes in flocculation rate with the addition of various concentrations of salt (Fig. 2). With colorimetric analysis, we could not clearly identify the changes in flocculation rate. But it can be determined very clearly by multiple light scattering method. This will be discussed in latter section. The volume of settled flocs decreased with increasing the salt concentration. The volume of settled flocs of untreated sample was approximately 1.9 cm^3 for 1% salt, 0.9 cm^3 for 3.5% salt and 0.6 cm^3 for 10% salt after 2880 minutes. According to van Olphen (1963), the higher the concentration and the higher the valance of the ions of opposite sign, the more the electrical double layer is compressed. With this reason, the volume of settled flocs decreased with increased salt concentrations.

For the treated samples, flocculation rate decreased with increasing concentrations of salt. This can be explained as following: when small amount of salts are added with bentonite suspension, first flocculation occurs, but upon the

further addition, stability of the suspension is restored because the suspension particles have become positively charged. Finally, with an excess of the salt, the positively charged suspended particles are flocculated (van Olphen, 1963). The volume of settled flocs decreased as the salt concentration increased from 1% to 10%. This is probably due to more double layer compression in solution of high salt concentration. The volume of settled flocs was approximately 3.3 cm^3 in 1% salt, 1.4 cm^3 in 3.5% salt and 1.1 cm^3 in 10% salt for Tixoton and 3.0 cm^3 in 1% salt, 1.6 cm^3 in 3.5% salt and 1.5 cm^3 in 10% salt for Bentonil GTC4 after 2880 minutes.

Effect of pH

The solution pH significantly affects the dispersion and flocculation behaviors of the samples. Clay minerals exhibit two types of electric charges. The permanent charges are structural charges originated from isomorphous substitutions and do not vary with the pH. The surfaces of edges carry surface groups (Al-OH and Si-OH) that can be protonated or deprotonated depending on the solution pH and can have variable charges. With this reason, the pH of aqueous solution has two specific roles. One is the high affinity of H^+ ions to neutralize the permanent negative charges of dominant electric double layer on surfaces, and the other is providing chemical species (H^+ and OH^-) to the surface protolytic reactions on edge sites in which the

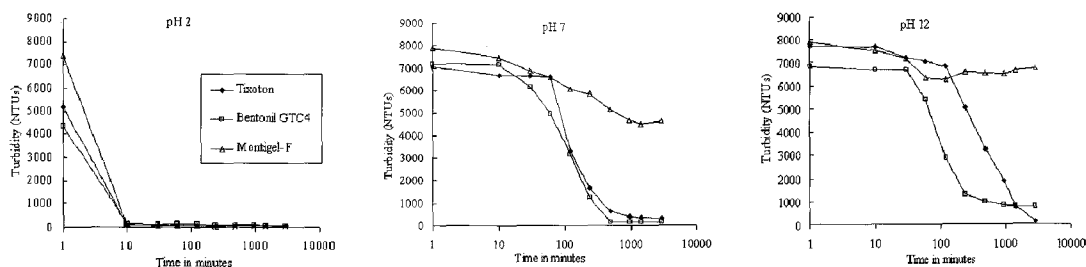


Fig. 3. Variations in turbidity with the solutions of different pH.

pH dependent hidden electric double layer forms (Tombacz and Szekeres, 2004). Fig. 3 represents the flocculation and dispersion behaviors of the samples in different pHs of solutions.

The untreated sample (Montigel-F) showed dispersion behavior with a little sediments (caused by non-clayey minerals in sample) nature in alkaline conditions. In acidic condition (pH 2), the sample showed dispersion nature for the first one minute. After one minute van der Waals attraction become predominant and flocculation started. This is probably due to the presence of hydrated ions at low solution pH. The broken edge of montmorillonite is also positively charged in acidic condition. So, the particles are flocculated by electrostatic force between positive charged edges and negative charged surface of montmorillonite. The volume of settled flocs of the untreated sample was 1.9 cm^3 . Since amphoteric sites are conditionally charged, and variable either positive or negative charges can develop at the edges by direct H^+ / OH^- (anions/cations) transfer from aqueous phase depending on the pH. For this reason, in acidic condition the attraction between the oppositely charges resulted in flocculation of the untreated sample. In alkaline conditions, the electrostatic repulsion between the same charges resulted in dispersion of the untreated sample.

The treated samples showed flocculation behavior at the ranges of pH 2 to pH 12. Due to the anionic nature of polymer, the treated samples must have to show dispersion behavior in alkaline conditions. But we observed the clear

separation of clay and solution, which indicated flocculation behavior. This is probably due to the presence of sodium carbonate or magnesium hydroxide. In acidic conditions, the polymer works as a flocculation agent primarily by the bridging mechanism where segments of the same polymer molecule are attached to more than one particle (Heath and Todars, 1983). Both of the polymer bearing samples showed similar flocculation rate at the all pH. And the volume of settled flocs of treated samples increased with increased solution pH. Because of settled flocs in alkaline solutions were loosely packed. The loose packing of the flocs probably due to the strong charge repulsion by the anionic polymers against negative charges of clay surface and edges in the alkaline solutions (Theng., 1979). And in acidic condition, polymer attached directly with positively charged of clay particles. The volume of settled flocs was 2.5 to 6.9 cm^3 for Bentonil GTC4 and 3.6 to 7.9 cm^3 for Tixoton. These slight changes of the volume of settled flocs were due to the double layer compression. The degree of double layer compression depended on polymer concentration (Tixoton: 0.2% and Bentonil GTC4: 0.3%), particle size (200 mesh, Tixoton: <25% and Bentonil GTC4: <20%) and percentage of montmorillonite (Tixoton: 85% and Bentonil GTC4: 83%) of the samples.

Multiple Light Scattering Method

The turbiscan Ma 2000 depends mainly on

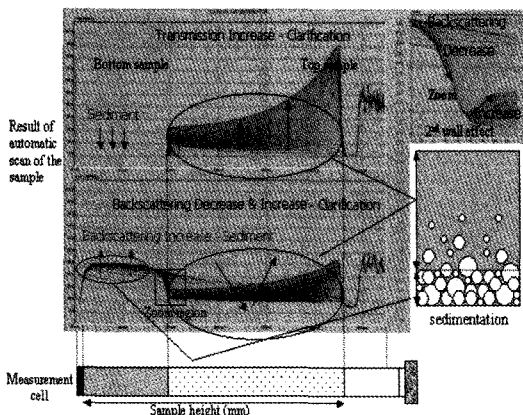


Fig. 4. This figure shows how to identify sedimentation & clarification of a concentrated sample by multiple light scattering method. This result comes from the analysis of Tixoton in 1% salt solution (Kinetic duration = 1 h).

the proton transport length, which permits breaking phenomena to be detected at a very early stage in the concentrated dispersion. Compared with colorimeter, it has the advantage of being a nondestructive method (no sample dilution). This method gives kinetic information on the process leading to phase separation. We can calculate two kinds of destabilization by using multiple light scattering. One is particle migration (creaming, sedimentation) and another one is particle size variation (coalescence, flocculation) (Mengual *et al.*, 1999).

Sample Analysis Methods

We used multiple light scattering methods in order to obtain accurate results. Most of the samples showed flocculation behavior. Fig. 4 is an example that can represent all behavior of the samples. In this figure, the backscattering increased at the bottom of the sample due to the increased concentration of particles, which generally called “**sedimentation**”. The transmitting flux increased at the top of the sample due to the decreased concentration of particles in this part, which we generally mentioned as “**clarification**”. Basically all samples showed the typical sedimentation phenomena (our case was

flocculation since we conducted experiment with clay particles). Transmission increased significantly at the top of the sample and no transmission at the bottom of the sample because of flocculated particles. And also, backscattering increased at the bottom of the sample, but at the top of the sample backscattering decreased at first as typically shown in sedimentation phenomena. In later time, backscattering increased again as shown in figure. This resulted from “**2nd wall effect**” caused by the glass vial. “**2nd wall**” effect (borosilicate glass vial effect) occurred when the concentration at the top of the sample decreased sharply. In this case, almost all the lights passed through the glass vial, and then reached the transmission detector. But parts of lights are reflected mainly due to **2nd wall effect**, and then backscattered lights reached the backscattering detector and resulted in the increased backscatter in later time (from Turbisoft classic user guide).

Among our samples, some showed only typical flocculation behavior, others showed flocculation behavior and **2nd wall effect**.

The Characteristics of Flocculation

We compared the settling behaviours of flocs in the solutions with different salt concentrations and pH. These behaviours were characterized in terms of clarification phase thickness. The change in thickness of the clarification phase (supernatant of solution) may be related with their average floc diameter (Yan *et al.*, 2004). The average floc diameter may be correlated with particle size (Table 1), polymer concentration (Tixoton: 0.2% and Bentonil GTC4: 0.3%) and/or montmorillonite content (Table 2) of the samples. By using the general law of sedimentation (Stokes law), we calculated floc diameter and flocculation rate of the samples. The results are given in Table 3. Fig. 5 to 7 represent the change in thickness of the clarification phase as a function of floc settling time.

In distilled water, the flocs formed in treated samples (Fig. 5). The untreated sample, how-

Table 3. Average floc diameter and flocculation rate of the samples used in this study

Suspension solution	Tixoton	Bentonil GTC4	Montigel-F	Tixoton	Bentonil GTC4	Montigel-F
	Floc diameter (μm)			Flocculation rate (mm/min)		
Distilled water	1.11	0.61	Uncountable	0.03	0.01	0.00
1% salt	2.66	5.79	5.86	0.22	1.09	1.10
3.5% salt	3.75	2.73	5.88	0.46	0.24	1.13
10% salt	2.48	3.09	4.88	0.22	0.33	0.84
pH 2	1.87	5.7	5.87	0.11	1.20	1.15
pH 7	1.77	1.94	0.84	0.09	0.11	0.01
pH 12	1.38	1.74	Uncountable	0.06	0.10	0.00

Uncountable: The floc diameter depend on flocculation rate. Uncountable floc diameter indicates that flocculation rate is zero.

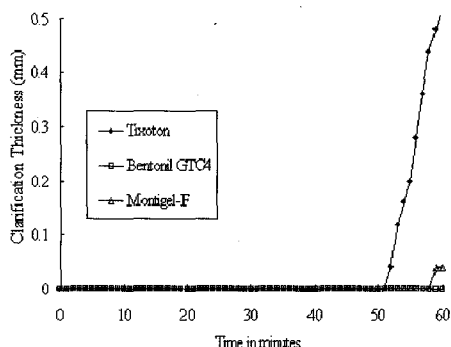


Fig. 5. The thickness of clarification phase (supernatant of solution) of the samples in distilled water.

ever, showed dispersion behaviour which indicating uncountable floc diameter of the sample (Table 3). This result supported our previous colorimeter result. The flocs of Tixoton (1.11 μm) were bigger than those from the Bentonil GTC4 (0.61 μm). For this reason, Tixoton settled much faster than Bentonil GTC4 (Fig. 5).

In salt solutions (Fig. 6), both the treated and the untreated samples showed flocculation behaviour compared with distilled water. The treated samples showed slow flocculation behaviour compared with untreated sample. Simply, it is expected that flocculation rate increased with increasing salt concentration but we observed different flocculation behaviour. The flocculation initiated at earlier time in the solutions of low salt concentration than in solutions of higher

salt concentration. This fact indicates that the flocculation initiating time is increased with increasing salt concentration and the flocculation rate decreased with increasing salt concentration (Fig. 6). The complete flocculation of sample was observed only for the untreated sample within 60 minutes in the solutions of 1% and 3.5% salt concentrations, but was not observed in the treated samples (except Bentonil GTC4 in 1% salt solution). The similar result was observed with in colorimeter experiments although the almost complete flocculation occurred after 48 hrs (Fig. 2). With the multiple light scattering method, it can be clearly demonstrated the early flocculation characteristics. In the solutions with 1 to 10% salt, flocs from the untreated sample (Montigel-F) settled much faster than those from the treated (Bentonil GTC4 and Tixoton) samples. This result was expected by considering the average floc diameter and the rate of flocculation (Table 3). In Table 3, the flocculation rate of suspended particles varied markedly upon the addition of salt, which is closely related with their floc diameter. The flocculation rate increases with increasing floc diameter.

In general, the more polymers contained in bentonite sample, the more stable suspension is expected in salt solution. But this was not observed in our experiments (except 3.5% salt). According to the concentrations of polymer, we

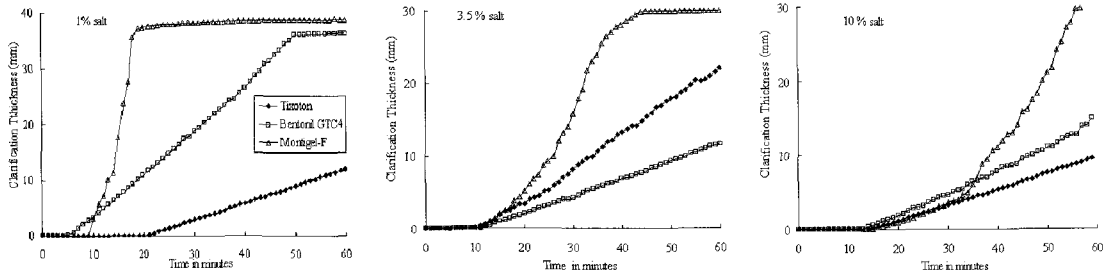


Fig. 6. The thickness of clarification phase (supernatant of solution) of the samples with the different concentration of salt solutions.

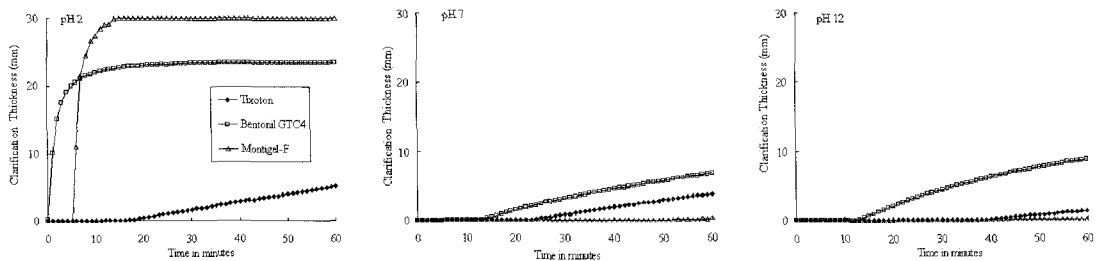


Fig. 7. The thickness of clarification phase (supernatant of solution) of the samples with the solutions of different pH.

expected less flocculation rate with Bentonil GTC4 (0.3% polymer) than Tixoton (0.2% polymer). But we observed opposite results. The one possible reason is polymer degradation by time passed after manufacturing (personal communication with manufacturer). Another possible reason is that the other factors such as particle size (Table1) and/or the content of montmorillonite are more significantly affected on dispersion. The uncertainty will be analysed by future study.

In Fig. 7, the main difference in settling behaviour of the samples was found in the low solution pH. In this acidic condition (pH 2), all of the samples showed flocculation behaviour. The particles of the untreated sample were flocculated faster than those of the treated samples. The flocculation rate was closely related with the average floc diameter as shown in Table 3. But we don't know the exact reason why the two treated samples of clarification phase resulted in the big difference in average floc di-

ameter and flocculation rate.

In alkaline condition, the treated samples showed flocculation behaviour and the untreated sample showed dispersion behaviour (Table 3 and Fig. 7), which is the same result as that observed with the colorimeter experiments. In general, anionic polymer increases the dispersion of bentonite in alkaline condition, but our experiments showed reverse result. This may be due to the presence of sodium carbonate and magnesium hydroxide that contain cations such as Mg^{2+} or Na^+ . These cations can cause flocculation through bridging or charge neutralization mechanisms.

Stability Analysis

Light transmittance of clarification phase (supernatant of solution) was characterised with mean value kinetics (variation of the transmission level with time). The mean value kinetics was determined for all of the samples according to the salt concentration and solution

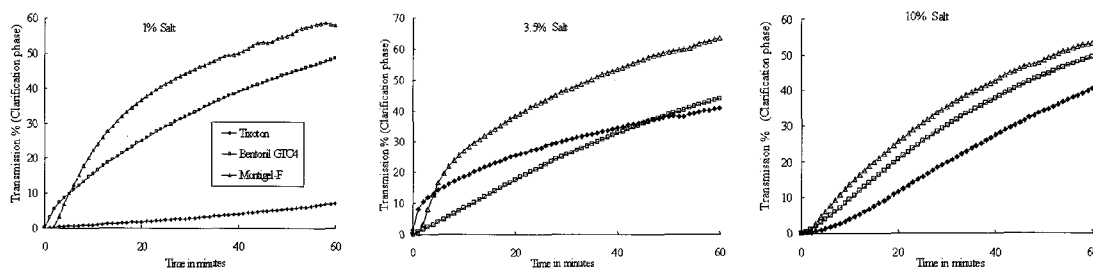


Fig. 8. The transmission % of clarification phase (supernatant of solution) of the samples with the different concentration of salt solutions.

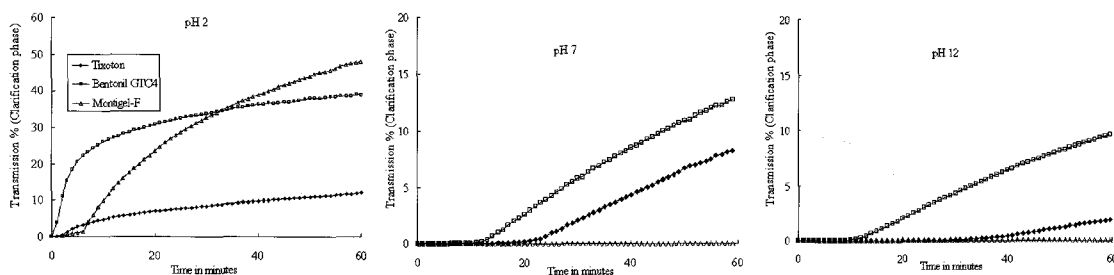


Fig. 9. The transmission % of clarification phase (supernatant of solution) of the samples with the solutions of different pH.

pH. The stability of the samples was measured by mean kinetics. Since stable and “unstable” differ only in their rate of flocculation, the degree of stability or instability may be defined and measured in terms of flocculation rates (van Olphen, 1963). In our experiment, we considered flocculation as unstable state and dispersion as stable state.

Table 3, Fig. 8 and Fig. 9 demonstrate the stability comparison based on the mean kinetics for all of the samples according to the properties of water. In distilled water, all of the samples maintained stable suspension. As shown in Fig. 8, all of the samples were essentially unstable in all salt solutions although the treated samples showed just a little stable nature than the untreated sample.

In general, the degree of stability increased with increasing solution pH. Only Tixoton was stable in low pH condition. At pH greater than 7, all the samples showed stable suspension (Fig. 9). The untreated sample, however, show-

ed much stable behaviour than the treated sample at alkaline condition. The same results were shown with the colorimeter experiment as shown in earlier. The untreated sample showed high dispersion property compared with the other two treated samples under alkaline condition. The untreated sample was dispersed by electrostatic repulsive force, because the layer surfaces had permanent negative charge and pH-dependent charge was negatively developed on the edges site of montmorillonite in alkaline condition (Tombacz and Szekeres, 2004). The treated samples are shown unstable behavior compared with the untreated sample (Table 3 and Fig. 9). This is probably due to the presence of sodium carbonate and magnesium hydroxide of the samples.

VISCOSITY ANALYSES

Bentonite is usually used in most drilling fluid, because it can give adequate viscosity for

Table 4. Viscosity of the samples used in this study (unit: centipoises)

Suspension solution	Tixoton	Bentonil GTC4	Montigel-F
Distilled water	20.0	18.0	5.4
1% salt	7.2	3.4	3.9
3.5% salt	3.2	3.1	3.0
10% salt	3.6	3.3	3.2
pH 12	22.0	24.0	6.0
pH 7	33.2	22.0	5.4
pH 2	9.2	3.3	3.9

drilling fluid. High viscosity of drilling fluid is needed for better hole cleaning for rock fragments produced by drilling process under high temperature and pressure applications. It is, however, difficult to control viscosity without polymer under high temperature and pressure. Therefore, various proportion of polymer used with bentonite to maintain proper viscosity for high temperature and pressure applications. According to API (American petroleum institute), 15 centipoises (cp) viscosity is assumed to be an acceptable value for drilling fluid.

The test results are given in Table 4. The treated samples are showed acceptable viscosity under alkaline condition and distilled water whereas the untreated samples showed unacceptably low viscosity under same conditions. This fact indicates that the polymer (CMC) is highly effective to increase the viscosity of bentonite suspension in neutral and alkaline conditions. According to Heller and Keren (2002), anionic polymer bearing samples can build up inter-particle bonds between the polymer and clay particle. In acidic and salt solution, however, the polymer seems not to be very effective in obtaining acceptable viscosity. The viscosity of treated sample was not significantly increased compared with the untreated sample. Even with 1% salt solution, the polymer treated samples could not have desired viscosity.

According to Abend and Lagaly (2000), sodium chloride decreases the viscosity by re-

ducing the electro viscous effect (effect of charge on viscosity is referred as an electro viscous effect). Acids influence the viscosity in the same way (Permien and Lagaly, 1994b).

Our experimental results indicate that the addition of polymer is very effective on increasing the viscosity of bentonite only under in neutral and alkaline conditions. The polymer-bearing drilling fluid will be useful for deep well drilling, such as oil and gas wells, where high viscosity are required to maintain stable suspension of drilling fluid in high temperature and pressure applications. The untreated bentonite can only apply at very shallow depths, where desired viscosity (15cp) is not required for low temperatures and pressures applications.

CONCLUSIONS

We have analyzed the dispersion and flocculation behaviors of three commercial bentonites in waters of different pHs and salt concentrations. From the analyses, we can conclude that:

- 1) The multiple light scattering analysis was very effective to give detail data such as floc diameter and flocculation rate at the early stage of flocculation.
- 2) The volume of settled flocs decreased with increasing salt concentration. This is probably due to more double layer compression in the solutions of high salt concentrations.
- 3) The floc diameter of the treated samples increased with decreasing solution pH. So the flocculation rate increased with decreasing solution pH. In alkaline conditions, the settled flocs of the treated samples were loosely packed than in neutral and acidic conditions. The loose packing of the flocs was likely due to the result of the strong charge repulsion by the anionic polymers against negative charge of clay surface and edges in the alkaline solutions. But in acidic condition, polymer attached directly with positively edge charge of clay particles. For these reason, the volume of settled flocs of treated samples increased with increasing solution pH.

4) Due to the anionic nature of polymer, dispersion behavior was expected in distilled water and in alkaline conditions. But we observed separation between clay and solution which indicating flocculation behavior. This may be due to the presence of sodium carbonate or magnesium hydroxide that contain Mg^{+2} or Na^{+} . These cations attached in the middle of the montmorillonite surface and the hydroxyl groups of the polymer resulting in the aggregation of montmorillonite particles.

5) We found polymer treated bentonite samples showed acceptable viscosity under neutral and alkaline condition. It indicates that polymer (CMC) is very effective in increase the viscosity of bentonite based drilling fluids only under in neutral and alkaline conditions.

6) With consideration of the polymer concentration, we expected good result from Bentonil GTC4 that contains higher amount of polymer. But, Tixoton showed better result than Bentonil GTC4 in many cases. This is probably due to the degradation of polymer. Because of organic compound can be degraded with time. It is considered that the manufacturing time should be considered to ensure better performance.

7) These results can be used for the application of bentonites as drilling fluids for the diverse environments.

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