



EFFECT OF SURFACTANTS AND GRAFTED COPOLYMER ON STABILITY OF BENTONITE PARTICLES DISPERSION IN BRINE SYSTEM

Abdelazim Abbas Ahmed, Ismail Mohd Saaid and Nur Asyraf Md Akhir

Department of Petroleum Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Perak, Malaysia

E-Mail: abdulazim_abass@yahoo.com

ABSTRACT

A major issue for the oil and gas industry is the production of high water from many fields due to massive water injection. Reducing the water production while improving oil recovery from these fields is a key challenge. Polymer gel has been widely used to shut off water-producing zones, but it is not suitable for high temperature reservoirs ($> 100\text{ }^{\circ}\text{C}$). Recently, developing a thermally stable plugging agent has posed a challenge for oil and gas business. The aims of the present study are to investigate the stability and aggregation rates of 0.1% w/w bentonite particles dispersion in the brine system (1% w/w NaCl) at various conditions. The main objective is to select an effective and suitable method for stabilizing of bentonite colloids for possible propagation in porous media to plug high permeable zones (thief zones). The effects of surfactants (cationic/anionic), and grafted poly(N-isopropyl acrylamide-co-acrylic Acid) on the bentonite colloids aggregation kinetics and stabilities were investigated. In this study, a series of bentonite dispersions stability tests were conducted using light transmission and backscattering measurements by Turbiscan. Time evolution of turbidity was employed to define colloids aggregation rates. The study revealed that surfactants and polymer grafted bentonite had significant impacts on the stability of bentonite particles dispersion. It was observed that anionic surfactant (SDS) has more tendency to stabilize the particles compared to cationic surfactant. However, both surfactants have shown unstable dispersion in 1% NaCl. Also, increasing SDS surfactant concentration decreases aggregation and migration rates, whereas cationic surfactant (DTAB) exhibits an opposite phenomenon. It was also observed from the Turbiscan measurements that the aggregation and sedimentation dynamics fell into two patterns, slow and rapid coagulations. Under studied conditions, grafted bentonite effectively showed excellent dispersion stability.

Keywords: bentonite, grafted polymer, pH, surfactants, stability.

INTRODUCTION

Most of hydrocarbon reservoirs are characterized by complex geologic conditions and high permeability contrasts. High permeability contrasts as a result of inter-layer heterogeneity, geological layering and fractures limited the successful performance of many water or chemical flooding projects. In practice, excess water production is a noteworthy issue prompting early well abandonment and unrecoverable hydrocarbons for mature wells [1]. Commonly, there are many types of conformance problems and several different conformance improvement techniques. The challenge is how to correctly identify and then to choose an appropriate conformance enhancement technique. Recently, in-depth fluid diversion has posed a frequently business need. A new soft solid-particle-like for conformance-improvement techniques were developed and reported as a viable technique for in-depth fluid diversion and/or relative permeability modification for high water production control [2]- [8]. Typically, all of these new soft preformed particles are organic based with different particle sizes and plugging mechanisms [9]. The blocking mechanism of most of the developed gel particles is particle swelling after being triggered by changes in temperature or pH. Unfortunately, polymer gels have an upper temperature limit above which the gels are not stable or useful [10]. Consequently, there is a need to develop a high strength and thermally stable particles for high temperature applications. In the present study, bentonite

has been selected for some unique properties. Firstly, bentonite has a high tendency to swell when it contacts with water.

Secondly, thermally stable at elevated temperature (up to $200\text{ }^{\circ}\text{C}$). Finally, environmentally friendly alternative. Although, the applications of bentonite for underground earth sealing and grouting are not new, its application in the oil industry as in-depth fluid diversion is in its infancy.

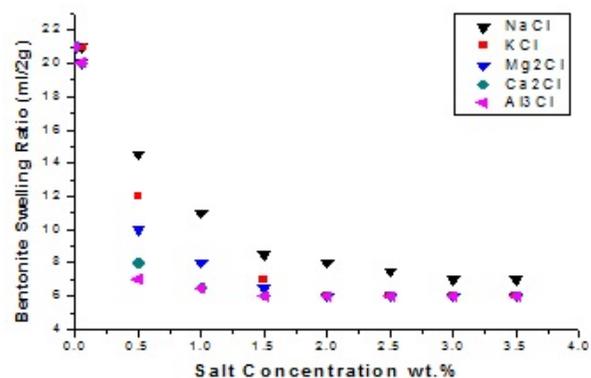


Figure-1. Effect of salinity and cation type on bentonite swelling ration.



The results from previous experiments, bentonite showed various swelling when it contacted with different brines. The free swelling of bentonite decreased with the increased of cation valence and concentration (see Figure-1 above) [11]. This result is consistent with previous studies which have found a similar relationship [12-16]. The results proved that, bentonite swelling properties could be controlled and inhibited by varying solution salinities and/or altering interlayer exchangeable cations. However, the challenge is that dried bentonite particles size used for drilling mud ($<75\mu$) are relatively larger than commercial available rock-matrix diverting fluid agents ($<10\mu$). Furthermore, at high electrolyte concentrations the condition becomes worse. Because bentonite particles have a tendency to form aggregates in brine and rapid settlement due to increase in electrostatic attraction force [17]. Therefore, it is of major importance to determine aggregation rates and stability of bentonite particles, since particles flocculation and cake formation may occur at sand face during injection and preventing particles propagation deep into high water channeling zones. Therefore, Turbiscan was used to characterize dispersion stability of the bentonite colloids in the brine with and without modifications.

In this study, aqueous bentonite colloidal dispersions stability in brine solution (1% NaCl) were studied. Firstly, two types of ionic surfactants, sodium dodecyl sulfate (SDS) and Dodecyltrimethylammoniumbromide (DTAB) are used in addition to a bentonite dispersion (0.1% w/w) in various concentrations. Secondly, stability of grafted copolymer chains (N-isopropylacrylamide-co-Acrylic Acid) on surface of bentonite particles also studied. The changes in the stability of the bentonite-water dispersion systems are studied by means of turbidity (light transmission and backscattering) and particle-particle interactions.

MATERIALS AND METHODS

Materials

The used bentonite, sodium dodecyl sulphate (SDS), N-Isopropylacrylamide (NIPAM), Acrylic Acid (AA) and) were purchased from Sigma-Aldrich while 3-[Dimethyl-[2-(2-methylprop-2-enoyloxy)ethyl]azaniumyl] propane-1-sulfonate (DMAPS) and Dodecyltrimethylammoniumbromide (DTAB) were obtained from Merck (German). Sodium chloride, hydrochloric acid and potassium hydroxide, which were used in preparation of solutions salinities and pH were purchased also from Sigma-Aldrich and used as received without further treatment.

Methods

The stability of bentonite colloids dispersions were investigated using a Turbiscan Classic (Formulation, Figure-2). The Turbiscan head is made out of a pulsed near infrared light source ($\lambda = 850$ nm) and two synchronous indicators: a transmission detector which gets the light going over the sample (at 0° from the

incident beam) and a back scattering detector which gets the light scattered backward by the sample (at 135° from the incident beam). Samples were prepared from dry bentonite (0.1% w/w) to which 1% NaCl brine was added. Two surfactants, SDS (anionic) and DTAB (cationic) were used at three different concentrations 0.001, 0.01 and 0.1 M. The resulting dispersions undergo 24 hours, stirring at a constant shear rate 250 RPM in order to hydrate bentonite and obtain a homogenous and dispersed system. Tests of 7 mL of bentonite dispersion, prepared as previously described, were presented in a round and hollow glass cell. The detection head examined the whole length of the sample gaining transmission (T) and backscattering (BS) data every 40μ and every 1 min over 1 h. The variation of the transmission signal (ΔT) was figured as the distinction between T measured soon after the blending of the bentonite dispersions and T at a given time.

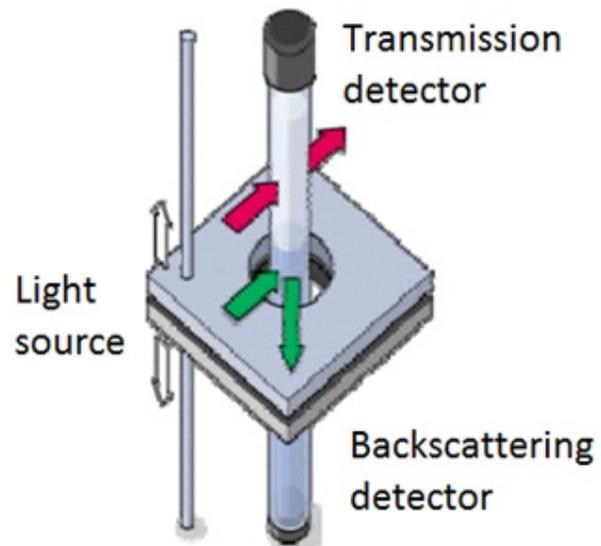


Figure-2. Principle of Turbiscan measurement.

RESULTS AND DISCUSSION

When surfactants added to bentonite dispersion, surfactants molecules interact with dispersed particles based on cationic or anionic character and bentonite particles charge nature. Bentonite particles have negative charges on basal surfaces as a result of isomorphous substitutions of low cations valence (i.e. Mg^{+2} or Fe^{+2}) replacing high cations valence (i.e. Al^{+3} or Fe^{+3}) and pH dependent charge on edges [18, 19 and 20]. The potential interactions of anionic surfactant are electrostatic with a positive charge on edge or physical adsorption [21]. The cationic surfactants also induce an electrostatic interaction by cation exchange mechanism and replacing cations attached to bentonite particle [19]. This part discusses stability analysis of four dispersions of bentonite in 1 % NaCl brine solution using Turbiscan.

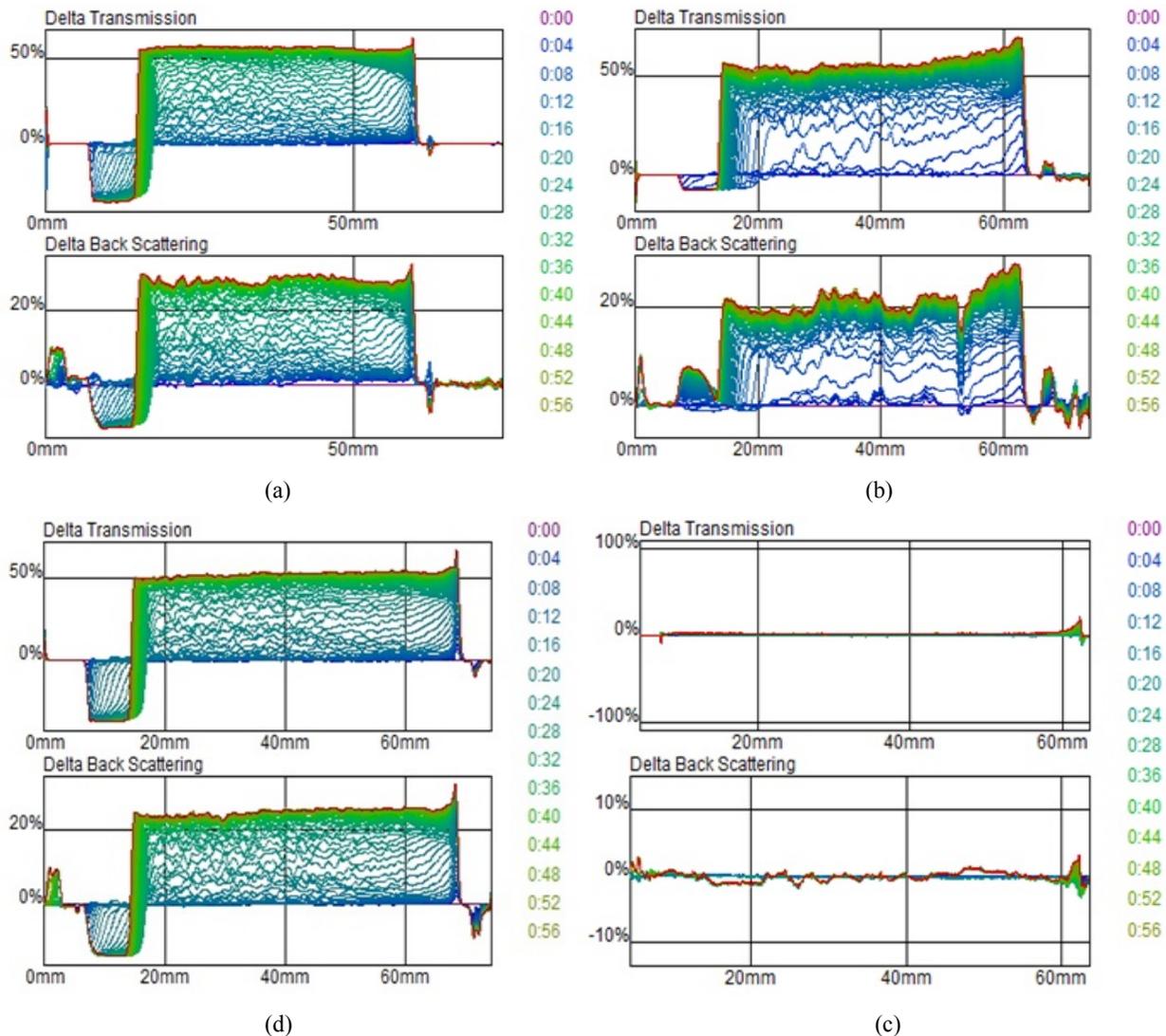


Figure-3. Transmission and backscattering profiles at 1% NaCl of (a) Bentonite (b) Bentonite with 0.1M SDS (c) Bentonite with 0.1M DTAB (d) Grafted Bentonite.

Figure-3 presents transmission (T) and backscattering (BS) intensities as a function of sample height over duration of analysis, for the dispersion cases of an origin bentonite (a), bentonite with 0.1M SDS (b), bentonite with 0.1M DTAB (c) and grafted bentonite (d). These profiles conduct were comparable for the various cases considered aside from grafted bentonite. In cases (a), (b) and (c), both the intensity of the transmitted light (T) and the intensity of the backscattered light (BS) expanded as a function of time. The variation of transmission was large, indicating an aggregation of the particles and hence poor particles stability. At the point when grafted polymer is used, this aggregation is not observed and the bentonite stayed all around dispersed. These findings are consistency with literature findings showing zeta potential of bentonite to generally decrease in absolute value with increasing surfactants concentration [22].

In the case of original bentonite and bentonite with SDS surfactant, the variation of backscattering profiles showed a decrease of the backscattering at the base of the tubing test, as the particle concentration increases because of sedimentation, while it increased in the case of bentonite with DTAB surfactant. The study suggests that BS decrease due to light absorption by bentonite and SDS surfactant. At the top of sample height, both T and BS increases are observed as clarification takes place. The shape of these clarifications phase, as revealed by transmission profile (Figure-3), indicates about the aggregation and sedimentation characteristic of the bentonite particle dispersion. In case (d), the clarification is very less intense and the shape of the profile does not show any packing of the sediment. The use of polymer grafting, is therefore the most appropriate to stabilize this dispersion of bentonite particles.



In order to compare the extent of aggregation and sedimentation kinetics in the three dispersions; it is conceivable to compute the speed of clarification (Table 1) from the slope of the thickness of the clarified layer. Therefore, the sample portion (20 -40 mm) of each mixture was selected to study BS variation.

It was clearly from migration rates and time required to start fast linear aggregation that anionic surfactant (SDS) has more tendency to stabilize the particles compared to cationic surfactant (DTAB) (see Figure-4 and 5). SDS shows little improve in dispersion stability compared to origin bentonite dispersion.

Table-1. Aggregation and Sedimentation Kinetics calculations.

Dispersion Cases	Slope of Linear Region (S ⁻¹)	Slope of Rapid Region (S ⁻¹)	Migration Rate (mm/s)	Equivalent Dynamic Radius (μ)
Bent.	0.075	3.384	5.1	1.283
Bent_SDS_0.001M	0.055	3.364	4.2	1.139
Bent_SDS_0.01M	0.096	2.584	3.1	0.983
Bent_SDS_0.1M	0.113	2.79	3	0.97
Bent_DTAB_0.001M	0.261	11.183	3.2	0.99
Bent_DTAB_0.01M	0.155	8.572	5.9	1.354
Bent_DTAB_0.1M	3.245	3.57	7	1.47
Grafted Bentonite	NA	NA	NA	NA

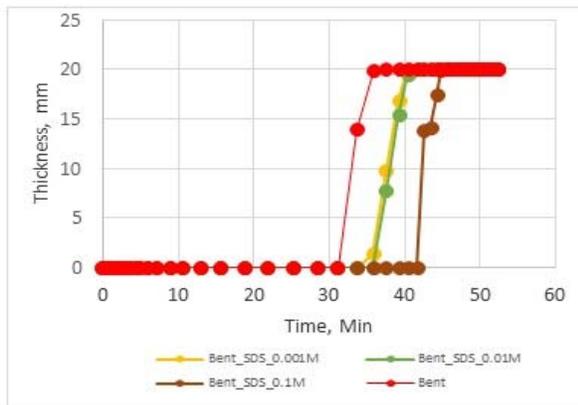


Figure-4. Thickness of clarification layer as a function of time for bentonite with and without SDS surfactant (samples portion 20 to 40 mm).

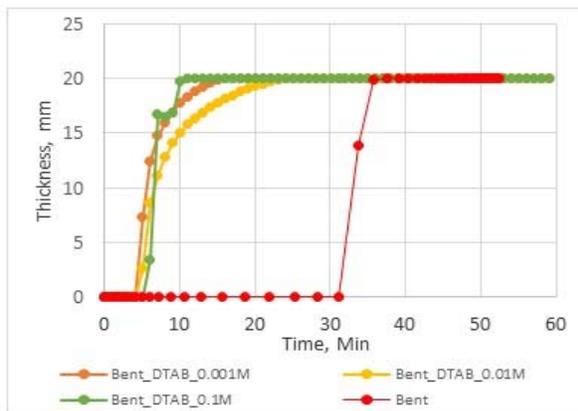


Figure-5. Thickness of clarification layer as a function of time for bentonite with and without DTAB surfactant (samples portion 20 to 40 mm).

In case of cationic surfactant (DTAM), the dispersion stability is lesser than bentonite dispersion alone. This behavior is consistent with DLVO theory. In DLVO Theory [23 and 24], the total interaction energy between particles is the sum of the attractive van der Waals forces and repulsive Coulomb forces. The cationic surfactant is expected to neutralize negatively charged bentonite particles and hence enhancing particles aggregation.

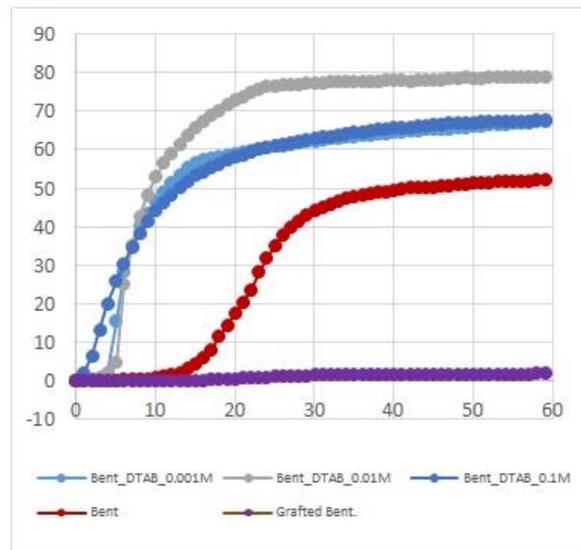


Figure-6. Mean value of transmission for bentonite with and without DTAB surfactant.

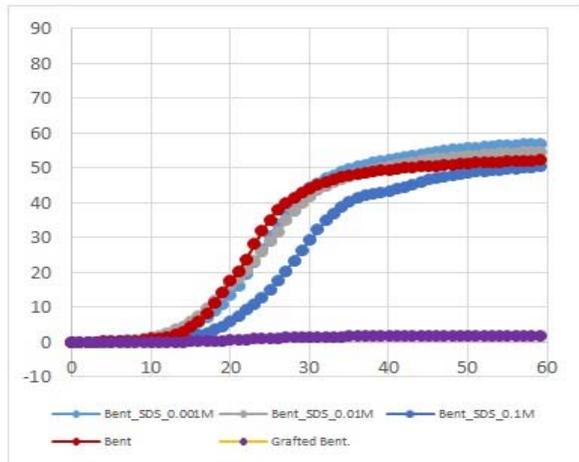


Figure-7. Mean value of transmission for bentonite with and without SDS surfactant.

Figure-6 and 7 represent the mean transmission value for the middle part of the samples (20-40 mm). The particle aggregations dynamics have seen follow two different patterns, i.e. linear growth and rapid growth before reaching a stable end point. For all experiments except grafted bentonite, mean transmission increased linearly over a period of a few minutes, after which increased more rapidly. The slope of leaner and rapid aggregation regions are calculated as shown in Table-1. It clearly indicates that cationic surfactant rapidly coagulate bentonite dispersion. Results revealed that increasing surfactants concentration, aggregation rates decreased. Also migration rate decreased with increased in SDS concentration, while it increased in case of DTAM surfactant.

Conclusions

The light transmission and backscattering were very useful in the study of stability and sedimentation characteristics of bentonite dispersion. It gives the phase clarification thickness, migration rate and expected particle hydrodynamic radius. In brine system (1% NaCl) bentonite dispersion with or without surfactants were aggregated and showed unstable systems. Also, increasing SDS surfactant concentrations decrease aggregation rate, whereas increasing DTAB surfactant concentration enhanced aggregation rate. The grafted bentonite with polymer at same brine salinity showed significant stability and less sensitive to the brine system used. Therefore, grafted bentonite is a suitable and effective method of stabilizing bentonite particle dispersion in the studied brine system.

REFERENCES

[1] P. Moreau. 2010. An Integrated Workflow for Chemical EOR Pilot Design. Paper SPE 129865-MS. (IFP). Source SPE Improved Oil Recovery Symposium, 24-28 April, Tulsa, Oklahoma, USA.

- [2] B. Bai., 2007. Conformance Control by Preformed Particle Gel: Factors Affecting its Properties and Applications. Paper SPE 89468, August, pp. 415-421.
- [3] A. Zaitoun, and Tabary, R., 2007. Using microgels to shutoff water in gas storage wells. Paper SPE106042 presented at the SPE International Symposium on Oilfield Chemistry, 28 February–2 March, Houston,
- [4] D. Rousseau, and G. Chauveteau., 2005. Rheology and Transport in Porous Media of New Water Shutoff/Conformance Control Microgels. Paper SPE 93254 presented at the 2005 SPE Int. Symp. On Oilfield Chemistry, February 2-4, Houston, TX, USA.
- [5] H. Frampton. 2004. Development of a Novel Waterflood Conformance Control System. Paper SPE 89391 presented at the 2004 SPE/DOE 14th Symposium on IOR, April 17–21, Tulsa, OK, U.S.A.
- [6] J. Pritchett, and Frampton, H. 2003. Field Application of a New In-Depth Waterflood Conformance Improvement Tool. Paper SPE 84897 presented at 2003 International Improved Oil Recovery Conference in Asia Pacific, 20-21 October, Kuala Lumpur, Malaysia.
- [7] G. Chauveteau. 2003. Method for preparing microgels of controlled size. US Patent 6579909 B1, 17 June.
- [8] G. Chauveteau., 2004. Disproportionate permeability reduction by soft preformed microgels. Paper SPE 89390 presented at the 14th SPE/DOE Improved Oil Recovery Symposium, 17–21 April, Tulsa, USA.
- [9] A. Goudarzi, H. Zhang; A. Varavei; Y. Hu; M. Delshad; Baojun Bai; and K. Sepehrnoor, 2013. Water Management in Mature Oil Fields using Preformed Particle Gels. paper, SPE 165356, presented at SPE Western Regional & AAPG Pacific Section Meeting, 2013 Joint Technical Conference, 19-25 April, California, USA.
- [10] R. D.Sydansk, and G. P. Southwell., 2000. More Than 12 Years of Experience with a Successful Conformance-Control Polymer Gel Technology. SPE Prod & Fac. 15 (4): 270. SPE-66558-PA.
- [11] Ahmed.A. A.,2015. . Influence Of Various Cation Valence, Salinity, Ph And Temperature On Bentonite Swelling Behaviour., presented at ICASET 2015, Penang, Malaysia.
- [12] Laird, D. 2006. Influence of layer charge on swelling of smectites. Appl. Clay Sci 34, pp. 74-87.
- [13] Madsen, F., and Müller-Vonmoos, M. 1989. The swelling behavior of clay, Appl. Clay Sci, 4, pp. 143–156.



- [14] Norrish, K. 1954. Faraday Discuss, 18, pp. 120–134.
- [15] Van Olphen, H. 1977. An Introduction to Clay Colloid Chemistry for Clay Technologists, Geologists, and Soil Scientists (2) John Wiley & Sons, New York, Warkentin, B. (1961) Nature. 190, 287.
- [16] Sridharan A. And Rao G. 1975. Mechanism controlling liquid limit of clays. In: Proc. the Istanbul Conf. Soil Mechanics and Foundation Engineering. p. 75.
- [17] P. Singla, R. Mehta, and S. Nath. 2012. Clay Modification by the Use of Organic Cations, paper, Green and Sustainable Chemistry, India.
- [18] F. Paul, R. Sylvia. 1992. The colloidal and rheological properties of bentonite suspensions. Advances in Colloid and Interface Science. 82 (1999): 43-92.
- [19] N. Gungor, A. Alemdar, O. Atici, I.O. Ece. 2001. The effect of SDS surfactant on the flow and zeta potential of bentonite suspensions, Materials Letters 51 (2001) 250–254.
- [20] H. Van Olphen. 1977. An Introduction to Clay Colloid Chemistry, Wiley Interscience, New York, USA.
- [21] Zhang, J. 2008. Polymerically Modified Layered Silicates: An Effective Route to Nanocomposites. Journal of Nanoscience and Nanotechnology Vol. 8, 1597-1615.
- [22] Yalcin, T., Alemdar, A., Ece, I., Gungor, N. 2002. The viscosity and zeta potential of bentonite dispersions in presence of anionic surfactants. Materials Letters. 57: 420–424.
- [23] Derjaguin, B. and Landau, L. 1941. Theory of stability of strongly lyophobic sols and of the adhesion of strongly charged particles in solution of electrolytes A. Physico. 14: 633-662.
- [24] Verwey EJW, Overbeek JThG. 1948. Theory of the stability of lyophobic colloids. Elsevier, Amsterdam.