

**Improving the Properties of Bentonite as Blocking Agent for Heterogeneous
Reservoirs**

by

Ilaman Gulesenov

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Dissertation submitted in partial
fulfillment of the requirements for the
Bachelor of Engineering (Hons)
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Universiti Teknologi PETRONAS

32610 Bandar Seri Iskandar

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(PETROLEUM)

Approved by,

.....

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January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(Ilaman Gulesenov)

ABSTRACT

It is well known that blocking agents are used in order to boost up the oil production in high water cut wells by injecting the corresponding agents into the wellbore which retard the water influx across the permeable zones. In this project bentonite has been chosen as the best potential agent for plugging water permeable routes, as it acts as a water expandable material in drilling fluid solution which can expand up to several times than its initial size. As a solution for the water production issue the cheaper and more effective blocking agent will be developed. In order to improve the behavior of blocking agent and make it feasible for different reservoir conditions, bentonite was coated with surfactant. The main goal of the project is to examine the bentonite as potential pore block agent, as well as it intends to evaluate performance of bentonite coating by using surfactant and to compare performance of enhanced bentonite with other established blocking agents. The present study reports the effect of anionic surfactant sodium dodecyl sulfate (SDS, $C_{12}H_{25}OSO_3Na$) upon the stability (dispersion) and rheological (viscosity, yield value) properties of the nanoclay, hydrophilic bentonite in presence of NaCl. The SDS dispersant was added in different concentrations in the range of 0.01% w/w to 0.40% w/w. The results show that the viscosity and zeta potential values of bentonite dispersion are affected by the addition of anionic surfactant. The obtained data has shown that stability of the dispersion is greatly affected in higher concentrations of NaCl. It is expected that modified bentonite will perform better in comparison to conventional blocking agents, as it shows a higher plastic viscosity and gel strength in alkaline environment.

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ABBREVIATIONS AND NOMENCLATURES

C	Concentration
Ca	Calcium
CHO ₃	Bicarbonate
cK	Critical Coagulation Concentration
cP	Centipoise
CMC	Critical Micelle Concentration
deg	Degree
FYP	Final Year Project
K	Permeability
Mg	Magnesium
Na	Sodium
NaCl	Sodium Chloride salt
OGC	Oil and Gas Centre
<i>q</i>	Flow rate
rpm	Rotations per minute
S	Sulfur
SDS	Sodium Dodecyl Sulfate
USD	United States Dollar
W	Weight
ZP	Zeta Potential

CHAPTER 1

INTRODUCTION

1.1 Background Study

In recent years, one of the most pressing issues in the oil and gas industry has become the problem of water production, which leads to significant costs, both economically and technically. Due to formations heterogeneity, fluids seek the most permeable paths in order to flow into the wellbore. Since water has lower viscosity it displaces oil, thus the well starts producing water to the surface (Brent, 2003). According to Bailey (2000), price of water treatment during oil production phase is very high; it may vary from 0.10 to 4 USD per barrel, depending on location and technique used for treating the water. Author's estimations have shown that every barrel of oil in average accounts 3 barrels of water, so in worst case scenario each barrel of oil will cost approximately 15 USD of water has been treated.

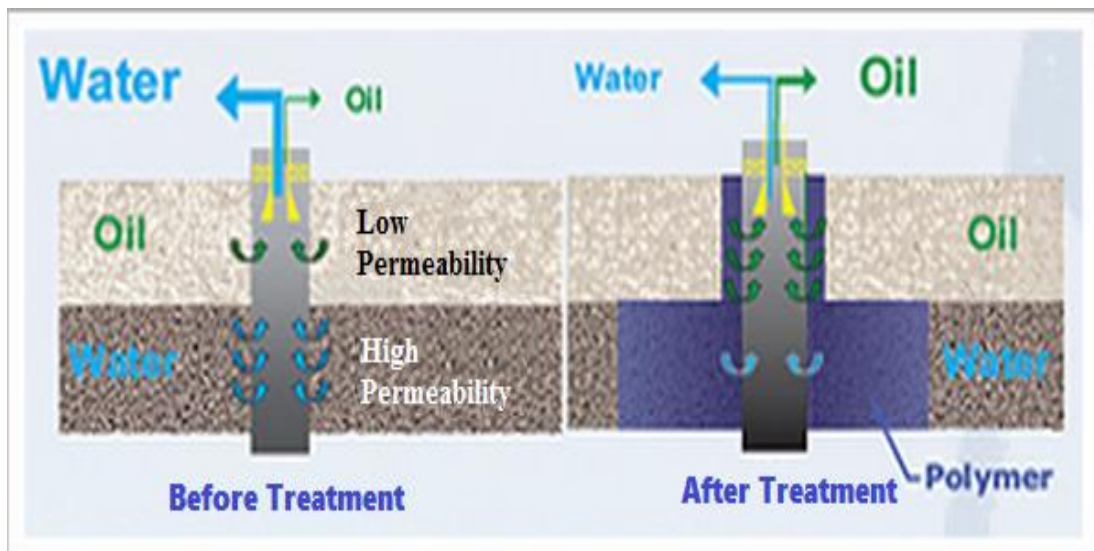


Figure 1.0 - Water flow into the well (OGC Ukraine, 2009)

For solving this problem many solutions has been implemented like cementing, sidetracking and installation of mechanical devices. These methods are time-

consuming and does not guarantee long isolation barrier. Water inflow into the wellbore might be due to the casing leaks, lack of hermeticity of cement ring in the existing perforations interval, pulling up of bottom water, through the breakthrough of the injected water in the formation with maximum permeability (OOO Oil & Gas Centre, 2009). However the project is going to use the method of isolation and restriction of water flow in the channels of productive horizon with an aid of blocking agents.

This project has chosen bentonite as the best potential agent for plugging water permeable routes, as it acts as a water expandable material in drilling fluid solution which can expand up to 30 to 40 times of its initial volume when added up with corresponding additive (Johannes, 2013). Since bentonite is natural clay it's abundant all over the world plus its cheaper when compared to other materials.

The application of modified bentonite as blocking agent can be very beneficial and useful for oil and gas industry. In case of successful application of the project, the oil production can be boosted up. Bentonite particles will have to travel deep into formation; therefore in this project smaller size of nanosize bentonite grains will be coated with surfactant, hence the flow will be much easier. According to the studies were made, the combination of bentonite together with surfactant believed to have improved swelling characteristics (Yalcin, 2002; Gunister, 2002).

1.2 Problem Statement

The major problem is the raising of water aquifers to the level of production horizon. As a solution for this issue the cheaper and more effective blocking agent will be developed. In this project, the potential of bentonite as blocking agent were examined as it is used commercially as additives in drilling mud and polymerization. In order to improve the behavior of blocking agent and make it feasible to different reservoir conditions, bentonite has been coated with surfactant.

1.3 Objectives

1. To examine properties of bentonite for possible pore block agent.
2. To evaluate performance of bentonite coating by using surfactant.
3. To compare performance of enhanced bentonite with other established blocking agent.

1.4 Scope of Study

In this project the smaller size of bentonite were coated using the anionic surfactant (Sodium Dodecyl Sulfate); subsequently the behavior of the solution were observed under different salinities. This project has reviewed only the effects and impacts of bentonite surfactant relationship.

During the experiment, the rheological changes such as elastic modulus, swelling capacity, particle size and other characteristics were recorded. Unfortunately the results of the study have been restricted only for laboratory works. Widely used blocking methods were brought from other sources for comparison purposes.

CHAPTER 2

LITERATURE REVIEW

2.1 Bentonite

Bentonite (named after the field Benton, United States) is a natural clay mineral, which has the ability to swell upon hydration up to 14-16 times of its original size. When material has the confined space for free swelling in the presence of water, a dense gel forms that prevents further moisture penetration. This property, as well as its non-toxicity and chemically resistivity make it indispensable in the oil and gas, manufacturing, construction and many other fields (Hosterman, 1992). According to the Condra (1908) formation of the bentonite is related to volcanic ashes, in his report author mentioned that thin beds of bentonite are considered to be naturally occurred from volcanic ashes.

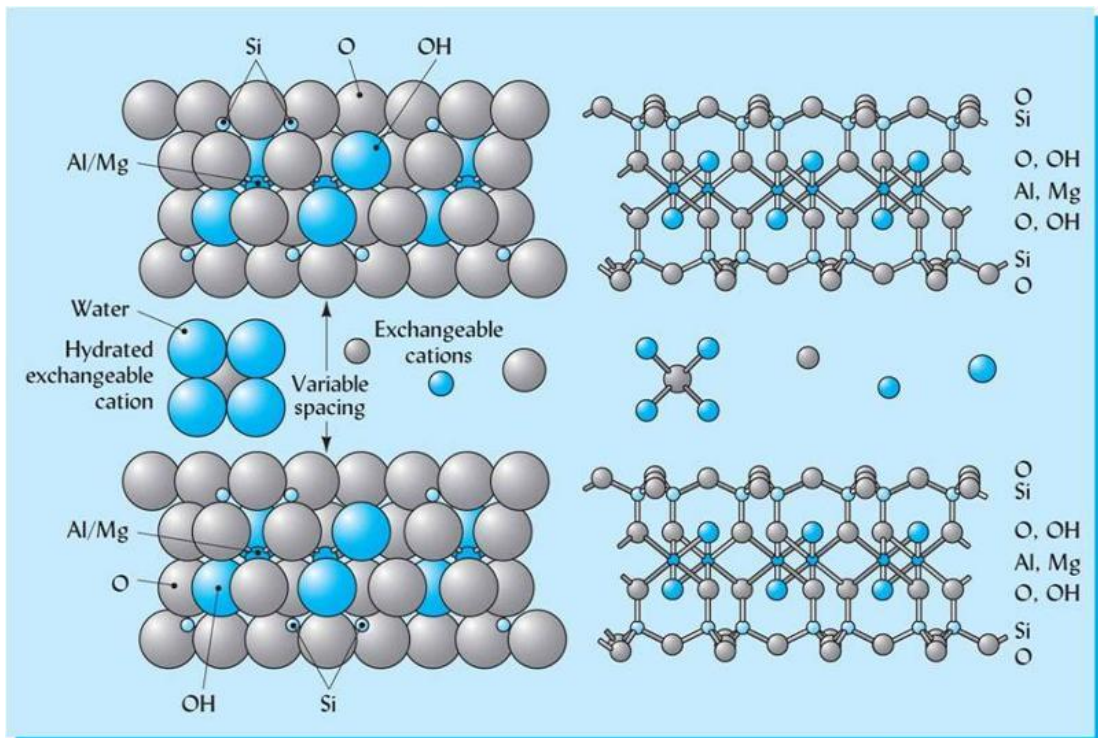


Figure 2.0 – Structure of crystal layers of montmorillonite (Willis, 2008)

Since bentonite is known to be viscosity builder material, it is widely used in oil and gas industry, as it has great swelling abilities which makes it best class clay drilling mud. The main reason of the swelling has been explained by Gunister (2004) who stated that when the Na activated bentonite is being dispersed in water, the clay tend to have unique crystal layers in very fine colloidal particles from dozen to several hundred micrometers, hence its electrostatic attraction between the crystal layers loses its force which results in expansion of clay's size. But the main limitation it cannot be used in saline water environment as the particles of bentonite will flocculate; hence it's used mostly in fresh water wells (Hosterman, 1992). In order to bentonite to perform better in saline water, this project intends to coat the material with surfactant, where it is believed that the mixture of two compounds will result in improved rheological properties of the solution.

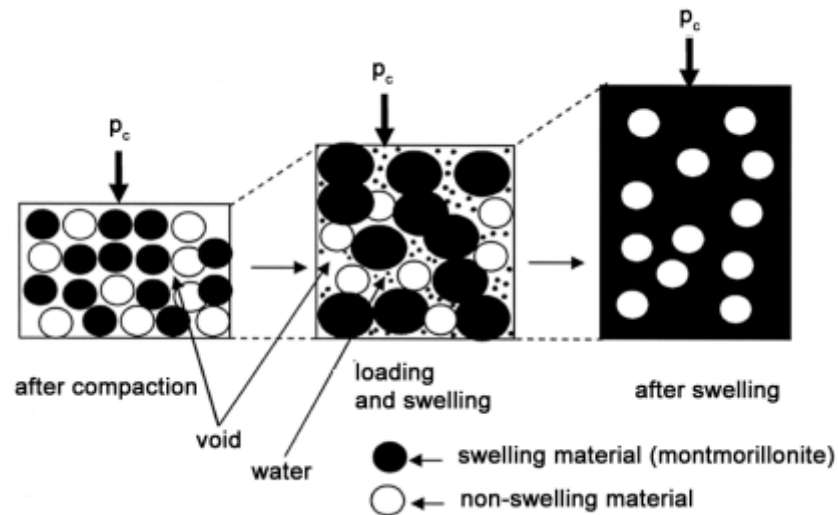


Figure 2.1 – Model of Bentonite clay swelling (Shirazi, 2011)

2.1.1 Properties of Bentonite

Usually bentonite is found in sodium or calcium forms in the environment. The sodium activated bentonite is known to have better swelling, rheological and plastic characteristics, as well as it has greater dispersion than of the calcium bentonite when they are mixed with water. Since sodium bentonite can provide low permeability barrier it is very useful in sealing applications (Bauer, 1993), which confirms the ability of bentonite to be used in applications as blockage of the path of water in reservoirs with water cut problems.

However calcium bentonite is much practical when used as adsorbent of ions in solution, most of the drilling fluid companies use it when the drilling fluid gets polluted by ions like S, Mg and CHO₃ (Bicarbonate). According to the swelling properties the sodium and calcium bentonite can be referred as swelling bentonite and nonswelling bentonite (Inglethorpe, 1993).

Behavior of the bentonite in presence of NaCl in water

As Hosterman (1992) has mentioned before that bentonite has reduction of swelling abilities in presence of salt, Shirazi (2011) has supported this statement with corresponding experiments. It has been proven that the concentration of brine in water strongly effect the rheological properties of the bentonite (Hosterman, 1992; Shirazi, 2011). The experiments were conducted with different concentrations of NaCl.

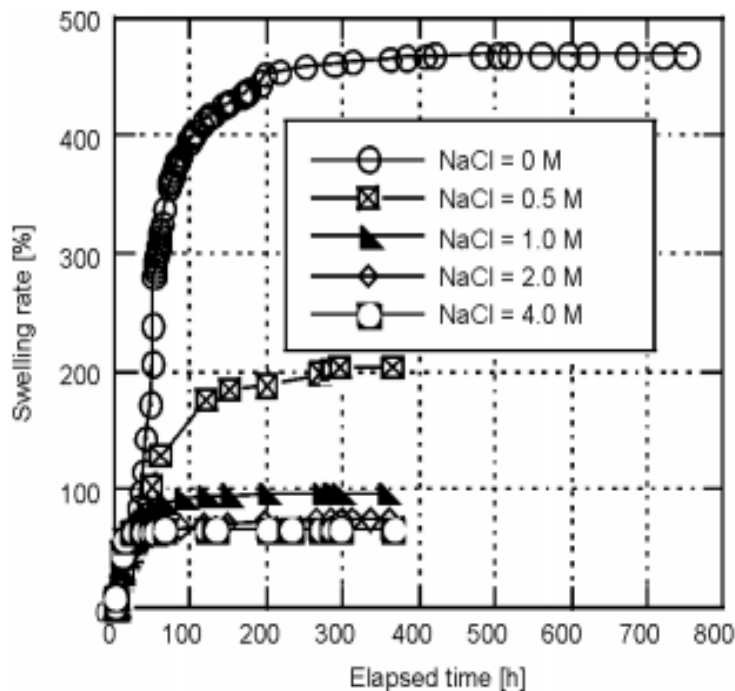


Figure 2.2 - Swelling Rate under various NaCl amount (Shirazi, 2011)

The result of the experiment, where 1.9 g/cm³ of dry bentonite which tested with various types of NaCl concentrations, has shown that with increasing salinity decreases the swelling rate of the bentonite. Shirazi has explained this phenomenon relating to the interparticle forces that exist between clay particles which has the

important role in deciding the liquid restriction of the solution. The interaction forces of the bentonite clay in presence of water have tendency of weakening which results in free movement of particles within the clay paste. In some high swelling clays the major contributor of the interparticle force turns out to be the repulsion forces, this attribute decides the position of each grain in suspension. When some amount of salt is added into the solution, it conduces to decrease the interparticle repulsion which leads to shrinkage of the distance between the particles. The Figure 2.2 presents the differences in swelling rate of bentonite with changing NaCl concentrations.

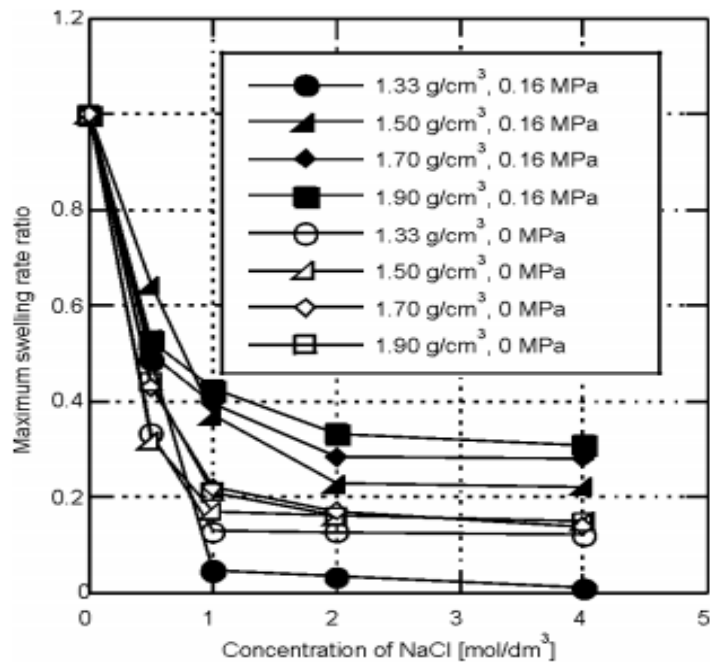


Figure 2.3 – Swelling rate under various pressure loads (Shirazi, 2011)

Behavior of bentonite under the static load

Shirazi (2011) continued his experiments and in his research that compared the swelling rate of bentonite with different applied loads, has revealed the significant importance of the pressure on enhancing the swelling ability of the clay. It shows in Figure 2.3 that pressure boosted up the swelling rate almost in all cases, but again it is clearly seen that brine has severe influence to swelling ratio. However oil and gas reservoirs tend to have very high pressure, therefore a successful expansion of the bentonite particles during its application in real life wells is greatly awaited. Another scholar has denoted the change of the swelling abilities might have occurred due to low expansion of the distance between the quasicrystals, in another

words the particles. It is known that bentonite clay resides the mass of quasicrystals. The void places present between the quasicrystals and the layers inside the quasicrystals (Pusch et al., 1990; Yong, 1999; Suzuki et al., 2001; Suzuki et al., 2004). Pusch (1990) has mentioned that when the clay is mixed with fresh water the void spaces of bentonite aggregate tend to change according to the amount added into mixture. Suzuki (2005) has related the fall of swelling of bentonite to compression of the layers within the quasicrystals, which resulted during the increase of NaCl concentration. It can be concluded as with increasing amount of NaCl in mixture the attraction force between the double layers grows stronger, which reveals that main contributors of bentonite's swelling ability are double layer expansion between particles and crystalline expansions within quasicrystals.

2.1.2 Surfactant

The main quantitative characteristic of the surfactant is its ability to reduce the surface tension at the interface, as the agent contains hydrophilic and at the same time hydrophobic groups (Furse, 2011). There are several types of the surfactant which are classified according to the charge that hydrophilic group of the agent carries. The common types of the surfactants are anionic, cationic, nonionic and amphoteric. The amphoteric surfactants are one of the least mentioned among all, this class of surfactants contain at the same time positive as well as negative charges in their hydrophilic ends, which gives them the net charge of 0. The nonionic surfactants has no any charge on the hydrophilic heads, it is been proven that this type of surfactants are great in emulsifying with oils. However cationic surfactants tend to have positive charges, where it is believed that they perform greatly in antistatic designs (Roach, 2010).

The head of the anionic surfactant is negatively charged, this attribute of the surfactant helps to lower interfacial tension of the reservoir fluids, change the wet ability and control move ability in order to raise the quantity of oil produced from a high water cut wells (Hadi, 2013). The complete coverage of the coating of the bentonite in term of physical and anchoring adsorption can be obtained by using anionic groups of chemical such as anionic surfactant Sodium Dodecyl Sulfate.

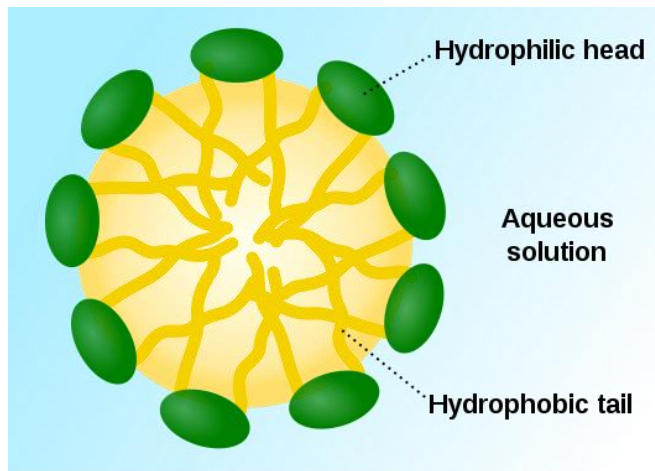


Figure 2.4 – Micelle of oil in aqueous solution (Roach, 2010).

However, Rosen (2012) in his research has highlighted that surfactant has a solubility limit also known as critical micelle concentration or CMC. Critical micelle concentration can be achieved when added to a solution with water where interfacial concentration of surfactant left constant, however simultaneously the molecules of surfactant will start organizing themselves in the dispersion this process is called micelle formation or aggregation. The indication of micelle surfactant is a clouding of the solution, as well as aqueous solutions of surfactants during micellization also acquires a blue tone (gelatinous pattern) due to the refraction of light micelles. Nevertheless, the most important factor to mention about is that formation of micelles will negatively affect the lessening of interfacial tension (Rosen, 2012). According to Furse (2011), micelles has characteristic of trapping the oil which is unkind factor for our project, as the agent might have the possibility of blocking the permeable paths of productive horizon.

2.1.3 Swelling of Bentonite in Presence of Surfactant

The studies done by Gardner (2000) have revealed the permeability reductions of the column which were convened by the various concentrations of the bentonite mixed with nonionic surfactant. In his experiment from 0 to 5 percents of the bentonite has been needed in order to sweep the solution together with surfactant, where the results were distributed respectively, as shown in Figure 2.5. It can be concluded that surfactants do not have negative effect on the properties of bentonite, instead the combination of these mixtures have very good effect in swelling quality of the bentonite.

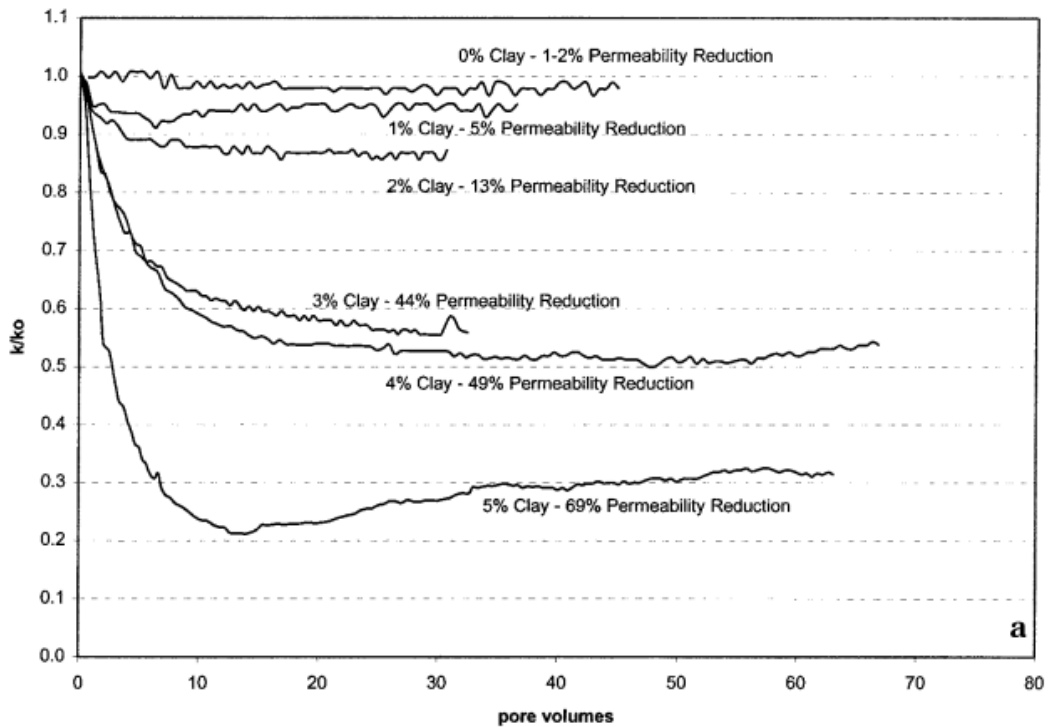


Figure 2.5 – Pore volumes vs K/Ko (Gardner, 2000)

In another experiment conducted by Yalcin (2002) chart shows an increase in viscosity of the bentonite clay in presence of anionic surfactant, Sodium Dodecyl Sulfate (SDS). The study shows the proof of the expansion of the solution, due to the interaction of the negative charges of the surfactant and the positive ends of the bentonite clay that forms the resistant fluid in terms of flowing properties. The anionic surfactant has changed the rheological properties of the clay, particularly it has changed the viscosity value of the clay (Yalcin, 2002; Gunister, 2004). The Sodium Dodecyl Sulfate with 5×10^{-4} mol/l concentration resulted in rapid increase of solution's viscosity, while the higher concentration of Sodium Dodecyl Sulfate has shown a decrease in its viscosity (Gunister, 2004).

The Figure 2.6 represents the adsorption process of the SDS surfactant on bentonite particles, it can be seen as amount of SDS is increased more particles are linked together.

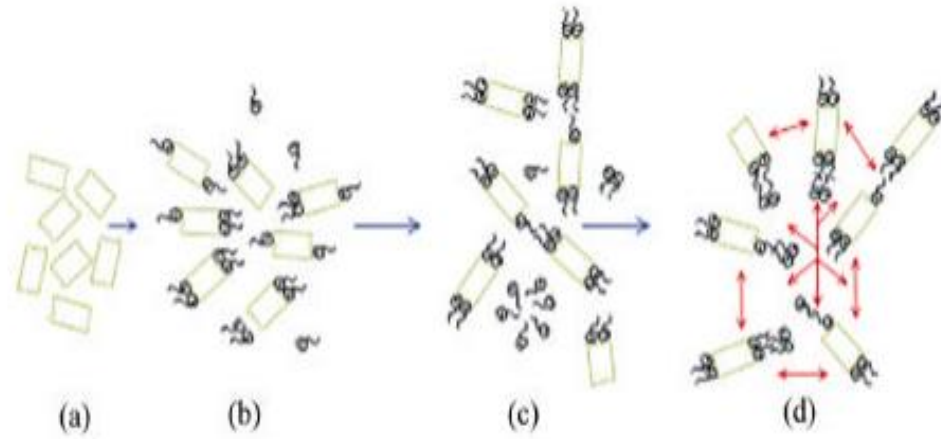


Figure 2.6 – Interaction of SDS with clay particles (Gunister, 2004).

2.1.4 Different Blocking Agents

One of the most common and widely used blocking agents in the heterogeneous reservoirs is gel treatment. The composition of gel treatment is prepared and then injected into the well, the inhibitor prevents the formation of the gel during the injection phase by crosslinking of the polymer molecules in the spatial structure. The viscosity of the prepared composition is not significant and is determined by the concentration of the polymer. This promises more effective pumping of the gelling composition into permeable zones. When the agent contacts with water-saturated seepage channels it starts absorbing on the reservoir rock and ensures the formation of a strong gel, which provides effective blocking water-bearing part of the reservoir (Seright, 1995; Brent, 2003). The characteristics of gel polymer as a blocking agent are depending on the concentration of monomer and crosslinkers of the gel and reservoir conditions (Baojun, et al., 2007).

When the gel treatments were introduced to improve the production in reservoirs with multiple crossflow between layers, it has been believed that the blocking agent will only enter to the high permeability zones and will end up reducing those channels, which will direct the water flow into the less permeable oil bearing channels (Seright, 2012). However this claim did not take into account the probability of gelling agent getting into low permeable strata, where it has been stated that in case of polymer solution going to be gelled in low permeable channels

the reduction of production will be much greater affected than in high permeable channels.

The field experience has revealed that foams perform much better as flow control agents rather than blocking agents. For an instance, in research that has been conducted on vertical well, the results have been compared before and after the foam injection experiment. The test has shown significant change in flow behavior of the well; mainly the flow across the high permeable layers has been retarded while the low permeable layers have increased in their flow rate (Friedmann, 1991). However when the experiment has went further, it has been found that in cases when the lower mobile fluids were injected after foam injection, the wells condition got worse in sense of flow behavior. This attribute has been seen only in heterogeneous reservoirs, which totally contradicts with main function of the blocking agent (Friedmann, 1991).

One of the most challenging issues of foam injection is the agent's dissemination and stability characteristics. It has been predicted that foams stability properties are greatly influenced in case of presence of oil. This kind of response of foam could be favorably used in oil production wells, since foam will successfully block the water zones and fail in blocking the oil zones, but in case if the water containing zone resides some amount of oil most likely the effectiveness of mobility control will collapse (Bernard, 1965). Therefore, it has been suggested to integrate gels or polymers in order to increase the stability of foaming agent in water zones with residual oil. Nevertheless, in case of gel has been used in foam, in order to avoid deterioration of the oil flow, the fluid from the oil zones has to be produced prior to gelation (Seright, 1995).

The studies that have been done have shown none of the indications of emulsions being superior to the usage of gels when their permeability or placement qualities has been compared (Seright, 1995). The emulsions with high concentrations tend to have high viscosity which hampers the placement of the blocking agent deep into reservoir, as well as it retards the reduction of permeability. It is necessary to note that emulsion's confrontation towards the flow of the fluid doesn't increase with increasing permeability of the stratum (Seright, 1995).

CHAPTER 3 METHODOLOGY

3.1 Flow Chart

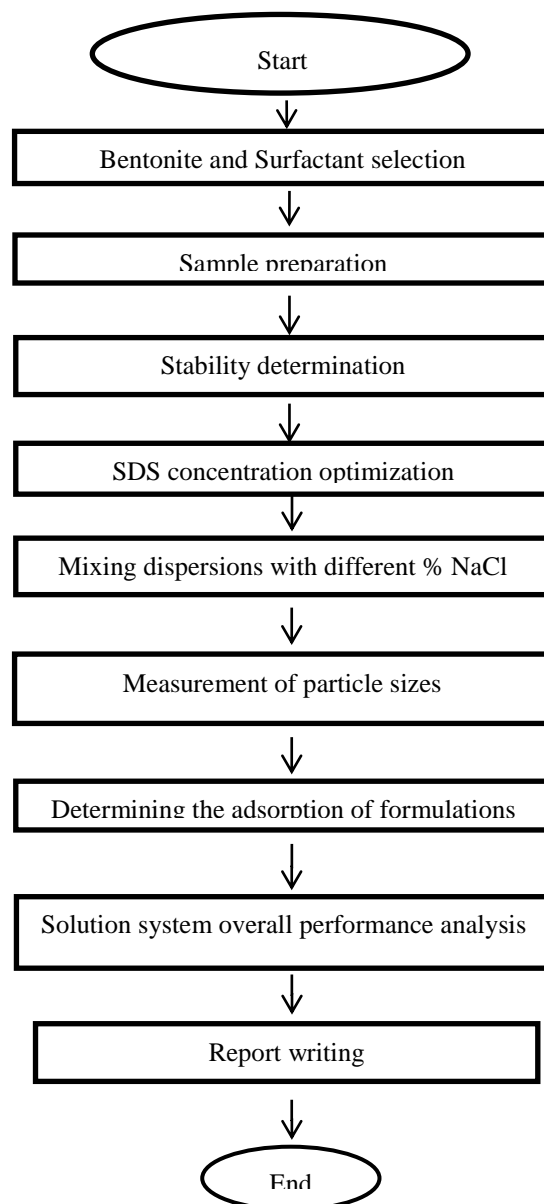


Figure 3.0 – Flow Chart

3.2 Experiment Methodology

The experimental work has been set up after comprehensive literature review on bentonite and surfactant properties and characteristics. The main procedure is sample preparation, which will be mainly about the coating of the bentonite and sample testing, where the rheological properties of the sample will be subjected for the trials.

3.2.1 Sample Preparation

Various concentration of surfactant has been added to the bentonite solution in order to find the most optimized condition of the fluid. As in literature review it has been analyzed that high quantities of the surfactant reduce the stability of the bentonite.

A base solution has been determined and was used for the optimization of SDS surfactant. The solution composed of 0.25 g of bentonite and 250 ml of distilled water. Each base solution has been mixed with different concentrations of SDS surfactant.

3.2.2 Sample Testing

The tests that have been conducted in order to find optimized concentration of SDS are listed below:

- ❖ Stability Test
- ❖ Viscosity measurement
- ❖ Particle size + Zeta Potential

The Particle Size and Zeta Potential of the solutions were determined in presence of different concentration of NaCl in presence of optimized quantity of Sodium Dodecyl Sulfate.

3.2.3 Research Methodology

The critical coagulation concentration was determined in order to find the stable colloidal solution for further tests with NaCl. The term critical coagulation (cK) is defined as the minimum amount of SDS reagent concentration required in order to coagulate the bentonite solution. SDS is an anionic surfactant soluble in water and its molecular weight is 288.3 g/mol. As suggested in the literature (Gunister, 2004), the critical coagulation concentration can be determined visually or using turbidimeter.

The solutions has been prepared at room temperature in test beakers, the bentonite powder has been added slowly in order to get better solubility, consequently SDS surfactant has been added and mixed, the solutions were stirred for 24 hours. The least concentration of surfactant that coagulated the solution has been noted as critical coagulation concentration, cK.

Table 3.0 – Stability Test at different % of SDS

Solution of 0.10% w/w bentonite with	Weight of SDS to be added into 250 mL beaker (g)	Weight of bentonite in 250 mL beaker (g)
SDS 0.00 % w/w	0.00	0.25
SDS 0.01 % w/w	0.025	0.25
SDS 0.02 % w/w	0.05	0.25
SDS 0.04 % w/w	0.10	0.25
SDS 0.08 % w/w	0.20	0.25
SDS 0.12 % w/w	0.30	0.25
SDS 0.20 % w/w	0.50	0.25
SDS 0.40 % w/w	1.00	0.25

The viscosity values of all samples were recorded using the Brookfield LVDV+ viscometer and the stabilities of the dispersions has been determined using turbidimeter. After finding the optimum concentration of SDS below cK, the experiments was continued under various concentrations of NaCl.

Viscosity properties such as speed of a spindle spinning and dial readings were measured using a Brookfield LVDV+ viscometer for bentonite-surfactant solutions at room temperature which was about 24 °C. Bingham Plastic model was used to determine the viscosity values. Where the Bingham Plastic equation is given as follows:

$$\tau = \tau_y + \mu_p \gamma \quad (1)$$

τ_y = yield point (YP), Pa or lbf/100ft²

μ_p = plastic viscosity (PV), mPa-s or cP

However plastic viscosity of the solutions were calculated using rheological properties through formula:

$$\mu_p = (300/(N_2 - N_1)) * (\theta_2 - \theta_1) \quad (2)$$

θ - Dial reading (° deg)

N - spindle spinning speed (rpm)

The experiment has involved the zeta potential of the bentonite particles, since in the literature it has been stated that electrokinetics forces of the substance has great influence in dispersion of the solution, hence zeta potential of the samples were measured in order to predict the diffusion of the bentonite layering with and without SDS addition. The unstable particles of bentonite tend to be low in stability when compared to stable ones (Min, 2010). Analysis on zeta potential and particle size has been conducted in Central Analytical Lab, total of five samples has been submitted for evaluation, and the temperature of the testing was at 60 °C. In order to complete the experiment each sample's refractive and absorption parameters has been determined as well as the pH range.

Table 3.1 – Particle Size and Zeta Potential

Base Solution - 1 g Clay 100 ml Distilled Water	Temp
Additives	°C
1.0 g NaCl	60
3.5 g NaCl	60
0.5 g SDS 1 g NaCl	60
0.1 g Polymer 1 g NaCl	60
0.5 g Polymer 1 g NaCl	60

The samples above were directed for viscosity measurements as well as they have been centrifuged in order to identify the absorption of solute, where absorption parameters were acquired for each sample by using the Batch technique.

The bentonite concentration retained in the absorbent phase, q_e should be calculated according to

$$q_e = \frac{(C_o - C_e)}{W} \quad (3)$$

where q_e is the amount of bentonite absorbed (mg/g), C_o and C_e are the initial and remaining concentration respectively of bentonite in solution (mg/L) and W is the weight of the bentonite (g) (Desta, 2013; Alagumuthu, 2010).

3.3 Project Activities

Since the beginning of FYP, the project activities were set up as schedule to follow through two semesters. The integration and continuous commitment is important to ensure that the proposed project succeeds. Following plan ensures that the project will be completed within the time scope. Thus, the details of the process are taken as key milestone.

3.4 Key Milestones

Table 3.2 – Milestones for FYP1

No	Description	Week No.
1	Received the approval of FYP project topic. Literature Review to make the title of project to be specified	2
2	Study the sample formulation in order to coat surfactant and bentonite	7
3	Getting familiarized with testing procedure of rheological properties, stability, particle size analysis and zeta potential of the agent.	9
4	Laboratory training prior to conduct the experiment and collection of laboratory booking request form	12
5	Execution of the experiments and collection of results and findings.	15
6	Data Analysis and final draft submission.	25

3.5 Gantt Chart

Table 3.3 - Timeline of FYP 1

No	Activity	week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project title selection	■	■												
2	Literature review			■	■	■	■								
3	Collection of research papers				■	■	■	■							
4	Study on sample formulations				■	■	■	■	■						
5	Study on research methodology						■	■	■	■					
6	Construction of methodology								■	■	■				
7	Continuation of the project									■	■	■	■	■	■
8	Collect laboratory booking request												■	■	

■ → Completed

Table 3.4 - Timeline of FYP 2

No	Activity	week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Submit laboratory booking request	■	■	■											
2	Start the solution optimization			■	■	■	■	■							
3	Identifying SDS cK concentration					■	■	■	■	■					
4	Continue tests with different NaCl						■	■	■	■	■	■			
5	Measurement of particle sizes							■	■	■	■	■	■		
6	Collection of results and findings								■	■	■	■	■	■	
7	Data Analysis											■	■	■	■
8	Submit the final dissertation													■	■

■ → Completed

CHAPTER 4

RESULTS AND DISCUSSION

The influence of surfactants on bentonite swelling depends on various conditions such as the grain size of clay, the charge of the particles, the environment of exchangeable cations and pH values. The cations suspended in the solution may determine the orientation of physical as well as rheological properties of the suspension, such as surface area and volume of each aggregate. It has noticeable effect on the dispersion of the modified solution (Gunister, 2004).

From the literature it has been analyzed that negative charges of surfactant are getting connected to the positive ends of bentonite particles. This phenomenon leads to lowering the electrostatic force of clay, which increases the solutions ability to swell. The viscosity value at the beginning changes very slightly but as amount of SDS approaches to critical coagulation concentration, the sharp increase in viscosity is analyzed. This indicates high resistance to flow of the samples. As experiments continue, it has been found that when the SDS concentration reaches its full coverage the viscosity values decreases again (Gunister, 2004).

In order to determine stable and optimized amount of dispersion, different concentrations of SDS has been mixed with bentonite solution, then the viscosity and turbidity values were recorded.

Table 4.0 – Viscometer Readings

Solution	Spindle speed N1,N2 (rpm)	Dial reading θ_1, θ_2 (deg $^\circ$)	Plastic Viscosity (cP)
Bentonite 0.10% w/w, SDS 0.00 % w/w	(50,100)	(2.45,2.62)	1.05
Bentonite 0.10% w/w, SDS 0.01 % w/w	(50,100)	(2.72,2.90)	1.08
Bentonite 0.10% w/w, SDS 0.02 % w/w	(50,100)	(2.92,3.10)	1.08
Bentonite 0.10% w/w, SDS 0.04 % w/w	(50,100)	(3.23,3.41)	1.11
Bentonite 0.10% w/w, SDS 0.08 % w/w	(50,100)	(3.42,3.60)	1.08
Bentonite 0.10% w/w, SDS 0.12 % w/w	(50,100)	(2.69,2.88)	1.14
Bentonite 0.10% w/w, SDS 0.20 % w/w	(50,100)	(2.79, 3.0)	1.26
Bentonite 0.10% w/w, SDS 0.40 % w/w	(50,100)	(2.75, 2.92)	1.02

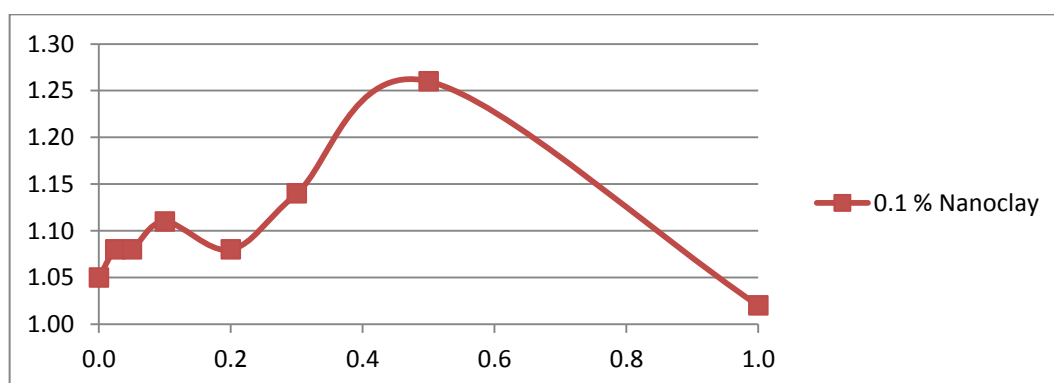
**Figure 4.1 - SDS concentrations (g) as a function of plastic viscosity (cP).**

Figure 4.1 shows that solutions of the bentonite and nanoclay dispersions exhibit nearly Newtonian behavior as their viscosity values, which were determined using the Bingham Plastic model equations, are approximately similar with Newtonian fluid trend line. Plastic viscosity of Nanobentonite solution increases slightly on addition of a small amount of SDS. Surfactant anions are adsorbed on the ends of the bentonite colloids and compensated or neutralized the positive charges of the particles. As seen from the figure, the initial plastic viscosity value of the dispersion remains nearly constant with increasing SDS concentration from 0 to

0.12. This shows very light effect to the bentonite solution in terms of viscosity changing rate. However when the concentration reached 0.2 % w/w, the sharp increase in viscosity has been indicated and with further raise of SDS the plastic viscosity has been declining to its original state again. This phenomenon can be explained with the particles bonding of the solution, when the concentration were increased to 0.2 % w/w the full coverage of the dispersion has been reached, but further addition in concentration led solution to move closer to each other resulting in destabilizing the sample and flocculating the bentonite particles, Vander Waals and Coloumbic forces have the important function in this phenomena (Gunister, 2004).

The results shown in figure 4.1 indicate the increase in viscosity value of the solution, which mainly could be due to gelation of the sample during addition of SDS into nanobentonite dispersion. This gelation might be considered to be due to interaction between alkyl chains of SDS surfactant. The gel state is characterized by the appearance of the shear yield value, which has been identified with an aid of viscometer. Formation of the gel depends on the particle–particle interactions, which are governed by the type and concentration of the surfactants, on the solid content of clay particles and the shape and size of the particles.

After each viscosity measurement in order to determine stability of each sample, then turbidity tests were conducted. Following results were obtained:

Table 4.1 – Stability Test

Solution of 0.10% w/w bentonite with	Turbidity (NTU)			
	0	20min	40min	60min
SDS 0.00 % w/w	333	306	282	273
SDS 0.01 % w/w	334	308	285	277
SDS 0.02 % w/w	341	312	294	285
SDS 0.04 % w/w	347	317	302	291
SDS 0.08 % w/w	362	327	312	292
SDS 0.12 % w/w	361	327	311	290
SDS 0.20 % w/w	357	317	311	309
SDS 0.40 % w/w	235	210	204	197

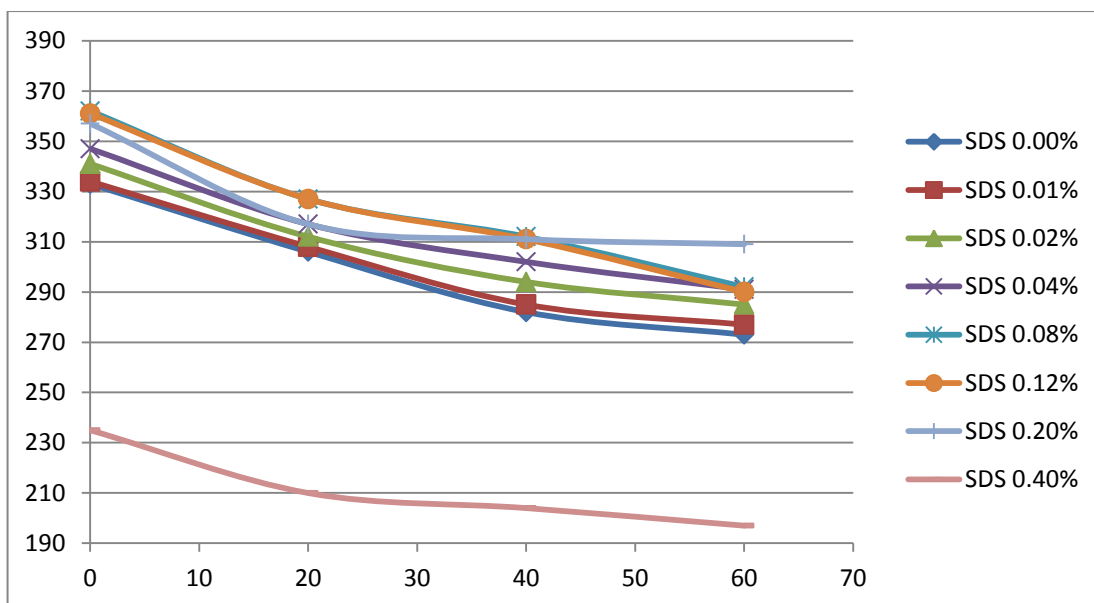


Figure 4.2 – Time (min) versus Turbidity (NTU)

Solution turbidity is a function of particle concentration and size, the stability of solution can be determined by measuring the change in turbidity with time. Figure 4.2 shows the stability of bentonite solution with different concentrations of SDS surfactant. From the results acquired, it can be concluded that all solutions have approximately same stability, as the turbidity parameters decrease following the same pace in all samples. All solutions are stable, except for the 0.4 % w/w concentration of SDS sample, in which it shown significantly low dispersion of the solution. This proved that a higher amount of surfactant leads to coagulation or flocculation of the dispersions.

The concentration of $6.9 \times 10^{-3} \text{ mol/l}$ of surfactant has been chosen as worthy contender for further experiments since it has shown higher gelation above that the viscosity value of it has remained considerably low, which the main objective in finding the optimum match for the further was testing with NaCl.

Table 4.2 – Stability test with addition of NaCl & SDS

Bentonite 0.1% & SDS 0.2% w/w	Turbidity (NTU)			
	0	20min	40min	1hr
NaCl 0.5 g	408	36.7	26.5	22
NaCl 1.0 g	335	36	25.5	20
NaCl 3.5 g	679	131	147	102

Table 4.3 – Stability test with addition of NaCl

Bentonite 0.1 % w/w	Turbidity (NTU)			
	0	20min	40min	1hr
NaCl 0.5 g	379	80.7	26.6	15.8
NaCl 1.0 g	368	41	23.8	14.4
NaCl 3.5 g	410	39.6	24.4	15.3

Figures 4.3, 4.4 and 4.5 show that SDS has greater stability improvement in highly concentrated amounts of NaCl, however the low concentrations of NaCl has shown very poor performance in keeping the solution dispersed.

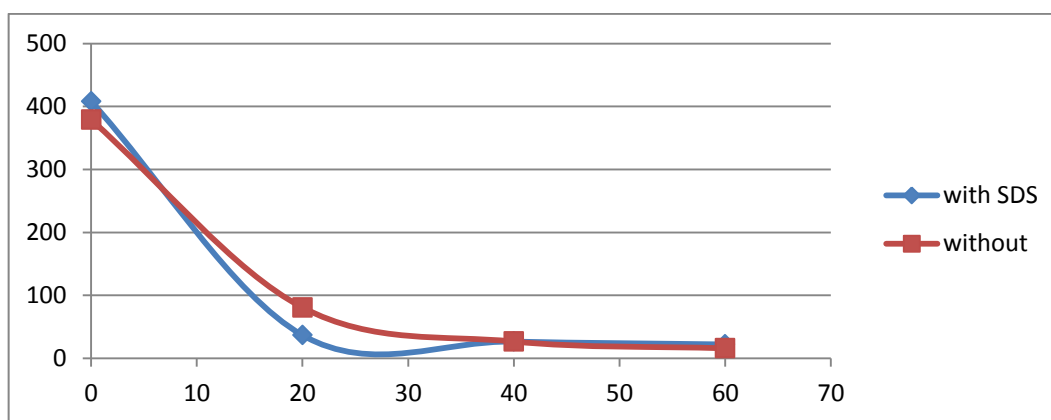


Figure 4.3 – Time (min) vs Turbidity (NTU) with and without SDS at 0.5 g NaCl

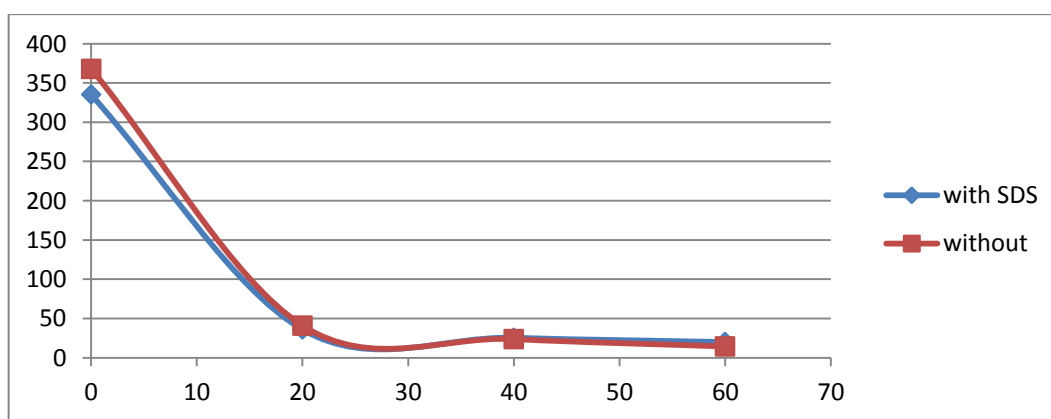


Figure 4.4 – Time (min) vs Turbidity (NTU) with and without SDS at 1.0 g NaCl

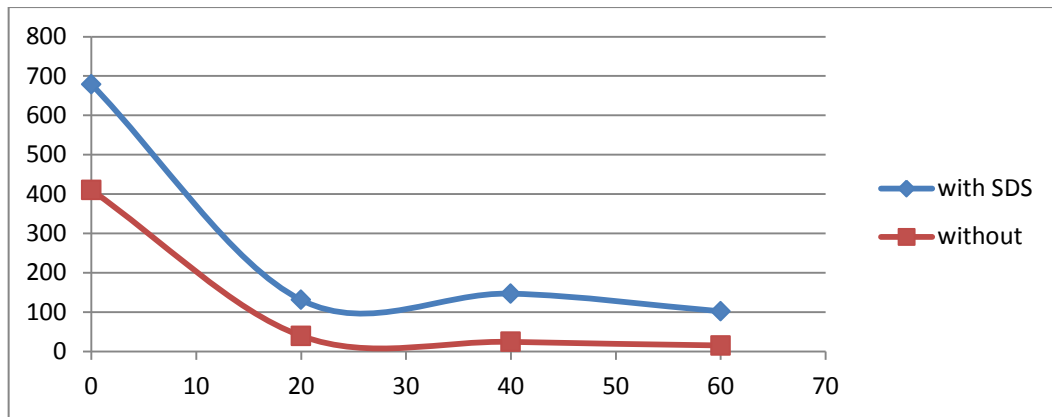


Figure 4.5 – Time (min) vs Turbidity (NTU) with and without SDS at 3.5 g NaCl

In the figure 4.5 can be clearly seen the significant drop in turbidity of the solutions, this behavior of the dispersion can be explained due to a decrease in double layer swelling between quasicrystals by NaCl. As the electronic double layer adjacent to the quasicrystal surface is compressed with increasing NaCl concentration, the aggregate swelling may decrease. Thus, aggregate swelling for NaCl solution is possibly controlled by both crystalline swelling and double layer swelling between quasicrystals. The positive charges of NaCl will get connected with negative charges of bentonite particles which will decrease the electrostatic attraction between clay particles and will lead to sample's flocculation. However in the figure 4.5 the improvement in stability can be explained with an aid of coagulation of the solution, which led the solution to be kept dispersed longer time than the rest of the samples.

Table 4.4 – Zeta Potential Results

Base Solution - 1 g Clay 100 ml Distilled Water	Temperature	Zeta Potential	Particle Size
Additives	°C	mV	d.nm
1.0 g NaCl	60	-6.08	1676.33
3.5 g NaCl	60	-16.37	669.73
0.5 g SDS 1 g NaCl	60	-29.33	1099.03
0.1 g Polymer 1 g NaCl	60	-5.79	85.56
0.5 g Polymer 1 g NaCl	60	-2.02	167.9

Table 4.3 shows that zeta potential values without addition of surfactant were sufficiently low, however when the SDS has been added into the solution the ZP values started increasing in directly proportional order. The presence of surfactant in that solution has indicated a sharp increment of Zeta Potential Value, which were -29.33 mV and -30.7 mV, respectively. The zeta potential value changed in a similar way as a function of surfactant concentration for dispersions. The addition of SDS into the dispersions neutralizes the positive edge charges of the bentonite particles. This results in an increase in the total negative charge of the particles. After the SDS concentration of 0.5g, electrostatic repulsion between the particles becomes higher and dispersions showed higher zeta potential values. The curves indicate a deflocculant system. This result correlates with the trend of viscosity values after the addition of the additives.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The anionic surfactant has changed the rheological properties of the clay; particularly viscosity value and the stability of the clay. The Sodium Dodecyl Sulfate with 0.20 % w/w concentration resulted in rapid increase of solution's viscosity, while the higher concentration of Sodium Dodecyl Sulfate has shown a decrease in its viscosity.

The optimized concentration of SDS surfactant has improved the stability of bentonite solution at high saline amounts of NaCl with considerably low viscosity value, which is good for deeper penetration into reservoir. One of the key parameter that has to be used in heterogeneous reservoirs for blocking agents is that solutions have to be low in viscosity, since high viscous agents tend to pass through the low permeable oil residing layers and slow down the oil production. Hence the water like viscous fluids is more favorable when dealing with reservoirs that contain multiple cross flows between the layers.

It is expected that modified bentonite will perform better in comparison to conventional blocking agents. Besides that, modified bentonite shows a higher plastic viscosity and gel strength in alkaline environment.

It takes more than 100 hours for bentonite to reach its maximum swelling ability. It means bentonite has plenty time for injection as well as penetration into deep formation before reaching the desired place and inflating to its maximum volume and restricting the porous medium. Moreover high pressure boosts bentonite's swelling ability. This is a positive sign since in real case scenario reservoirs' pressure are usually high.

The further studies on bentonite using polymer is believed to perform even much better than SDS, since polymers has greater tendency to keep the solution dispersed regardless of the amount of NaCl added.

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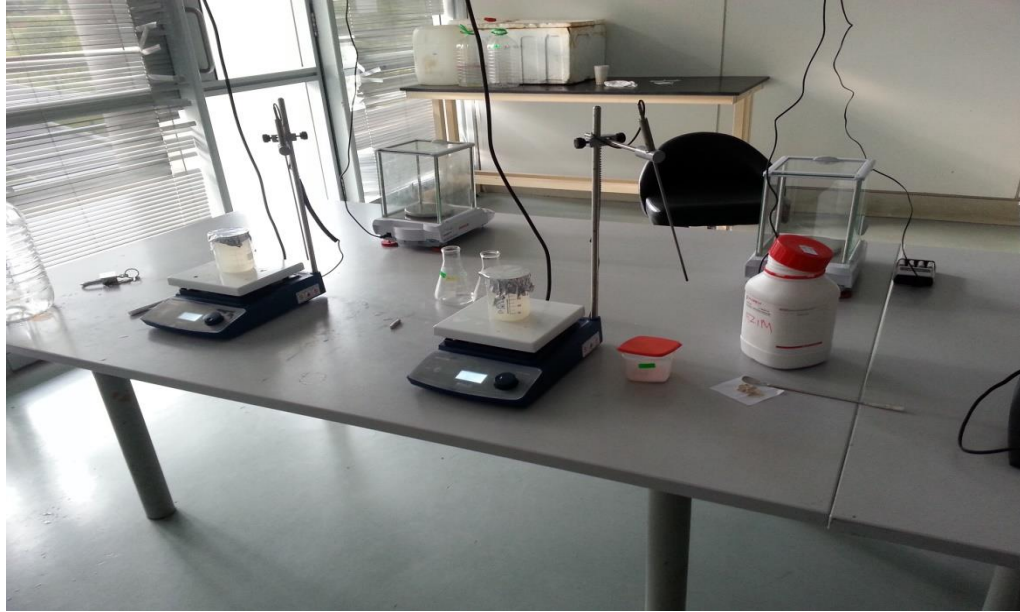
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APPENDICES

Appendix A



A1 – Coating the Bentonite with SDS surfactant



A2 – Viscosity test on prepared sample



A3– Stability test using turbidimeter



A4– Rheology measurement



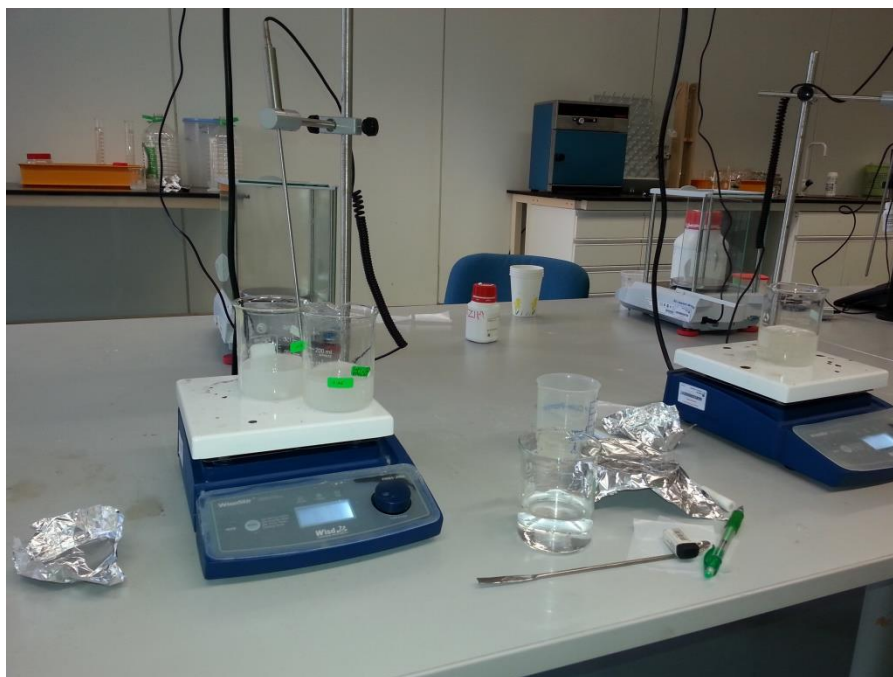
A5 – Rheology measurement



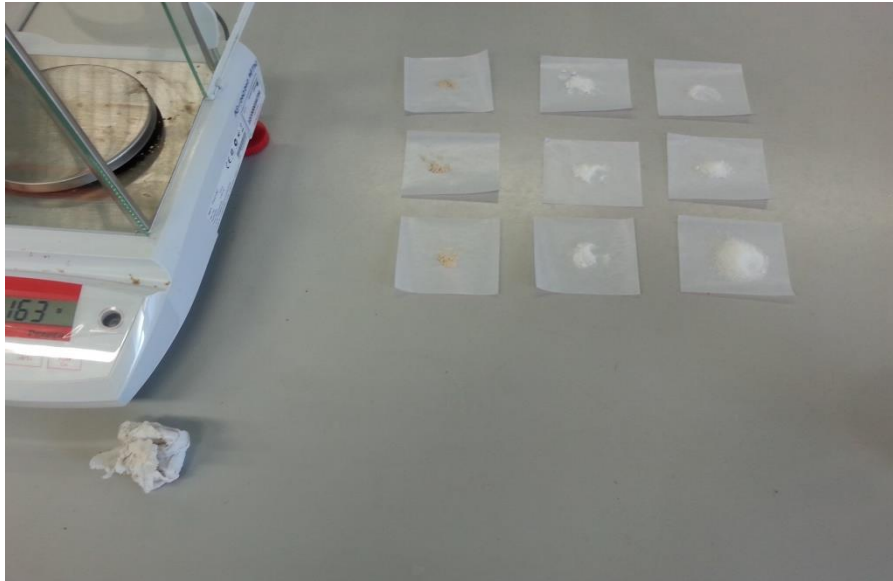
A6– Rheology measurement



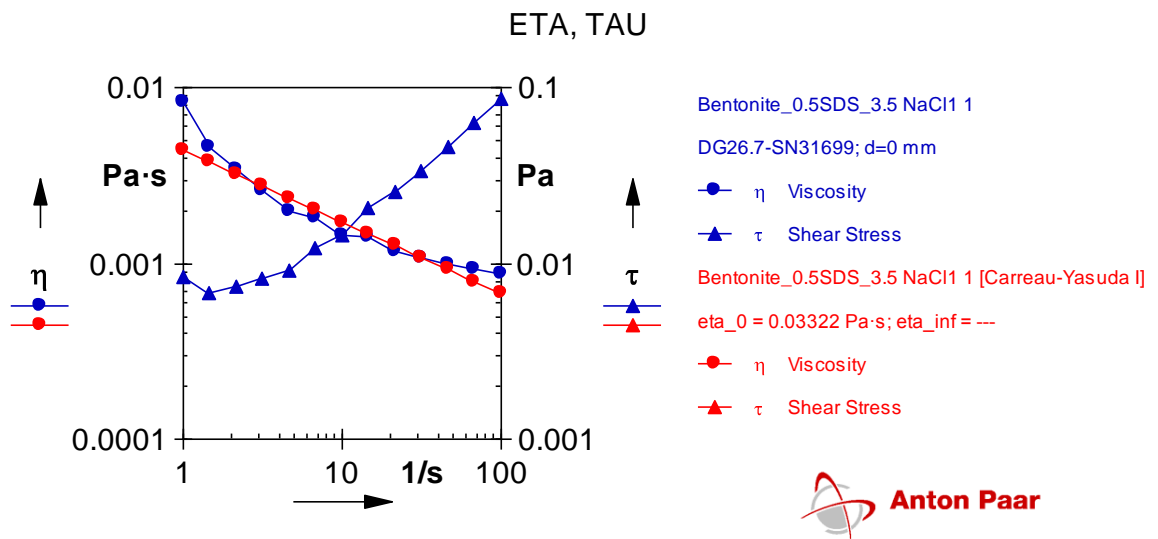
A7 – Stability measurement of Bentonite in presence of NaCl



A8 – Sample preparation

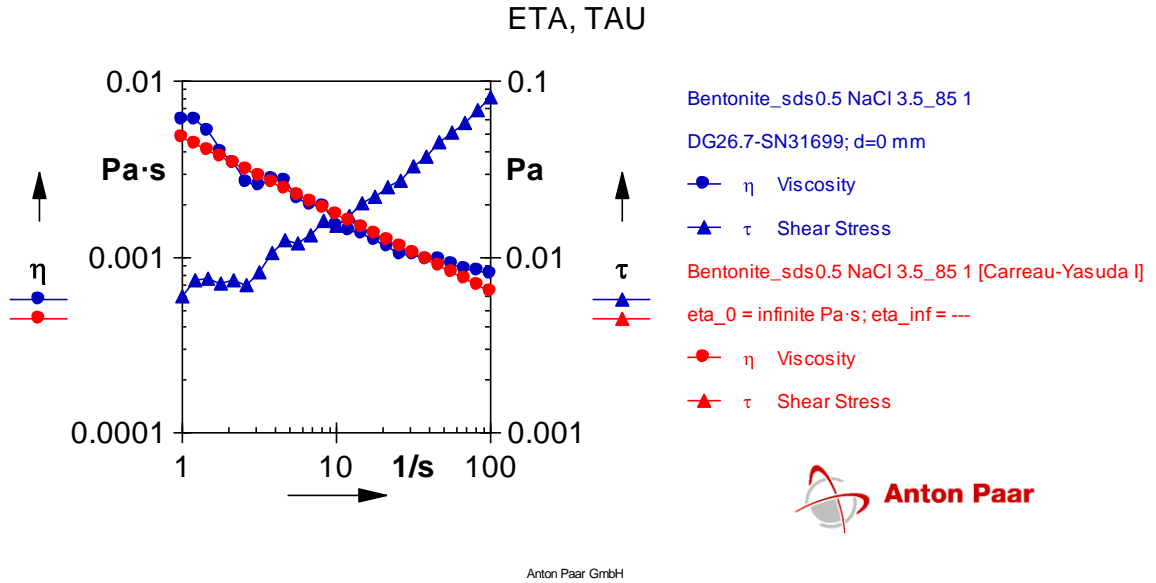


A9 – Sample Preparation

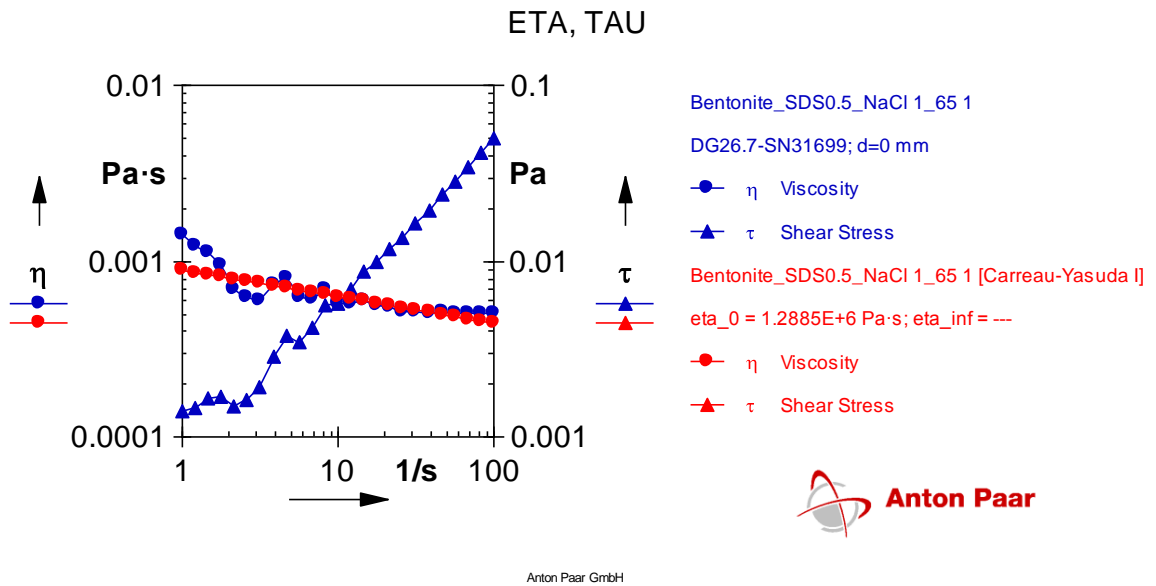


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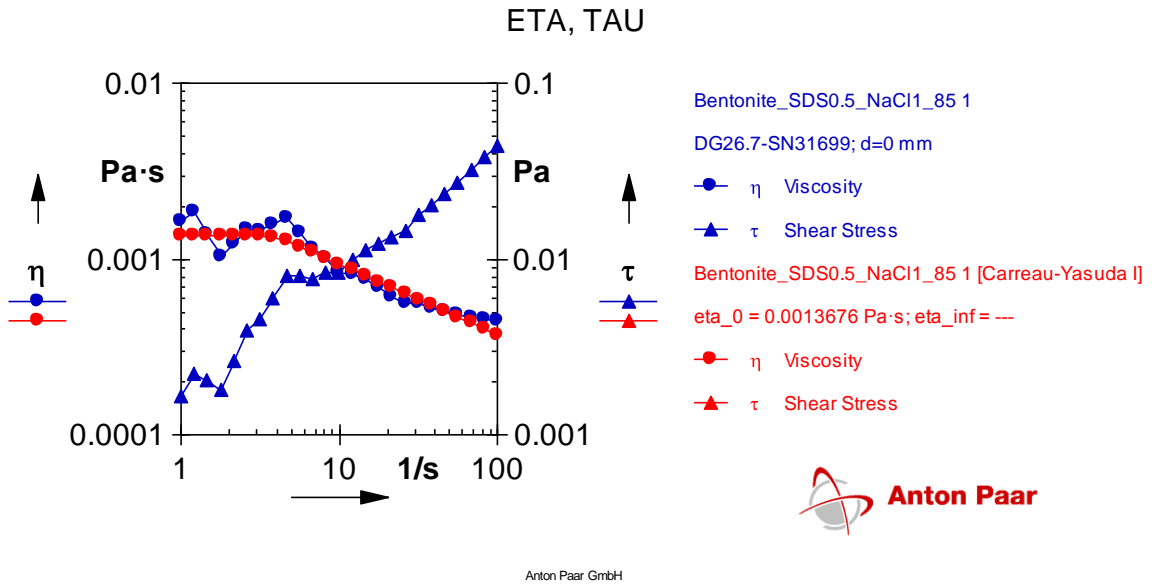
A10 – Rheological model Bentonite_0.5SDS_3.5 NaCl1 1



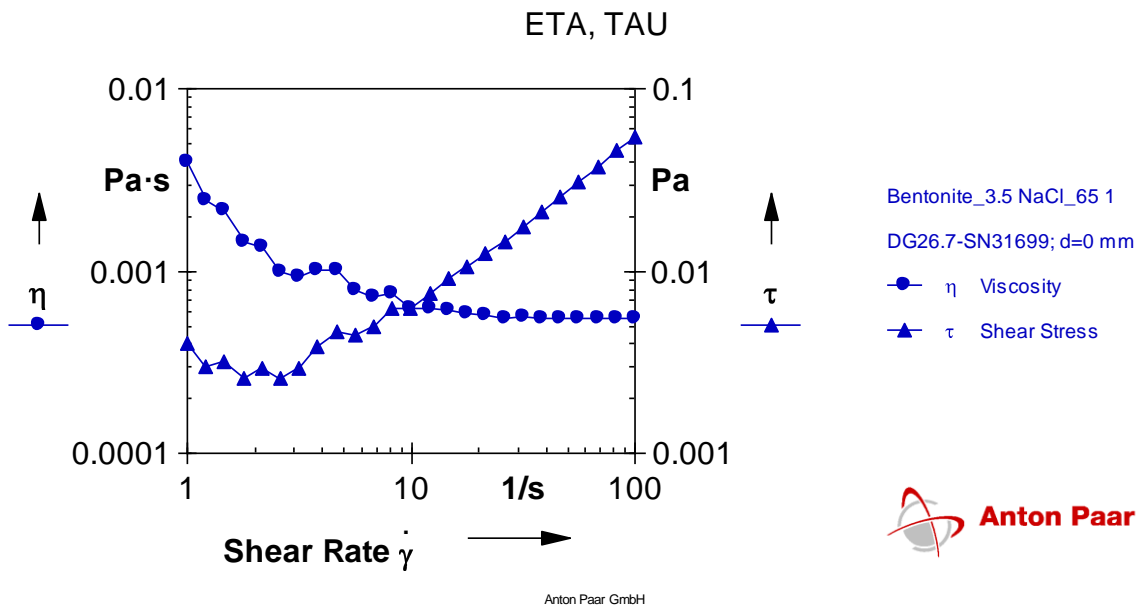
A11 – Rheological model Bentonite_sds0.5 NaCl 3.5_85 1



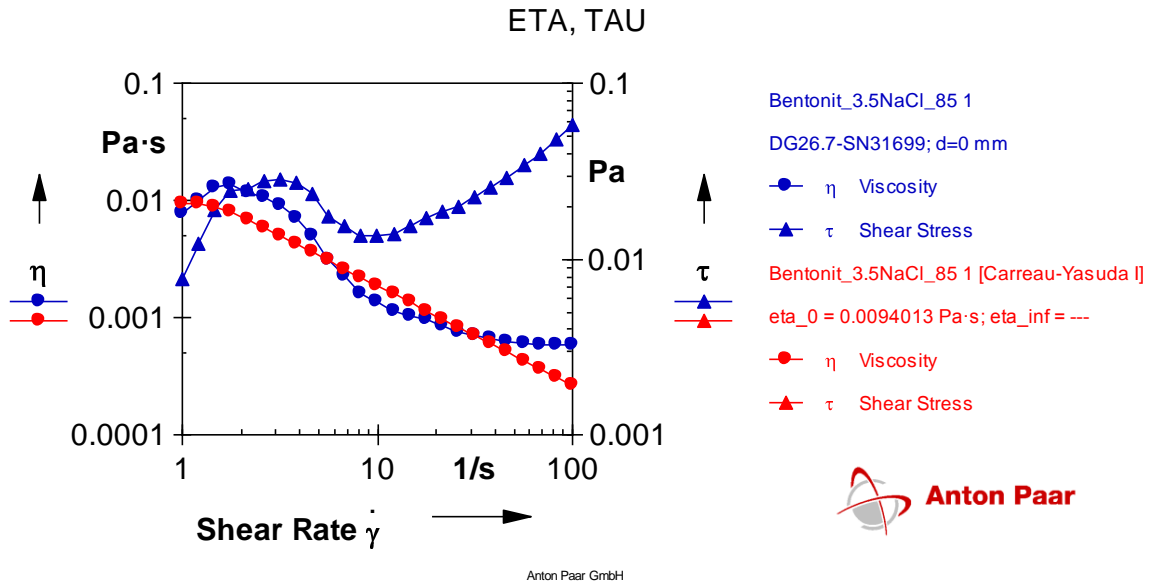
A12 – Rheological model Bentonite_SDS0.5_NaCl 1_65 1



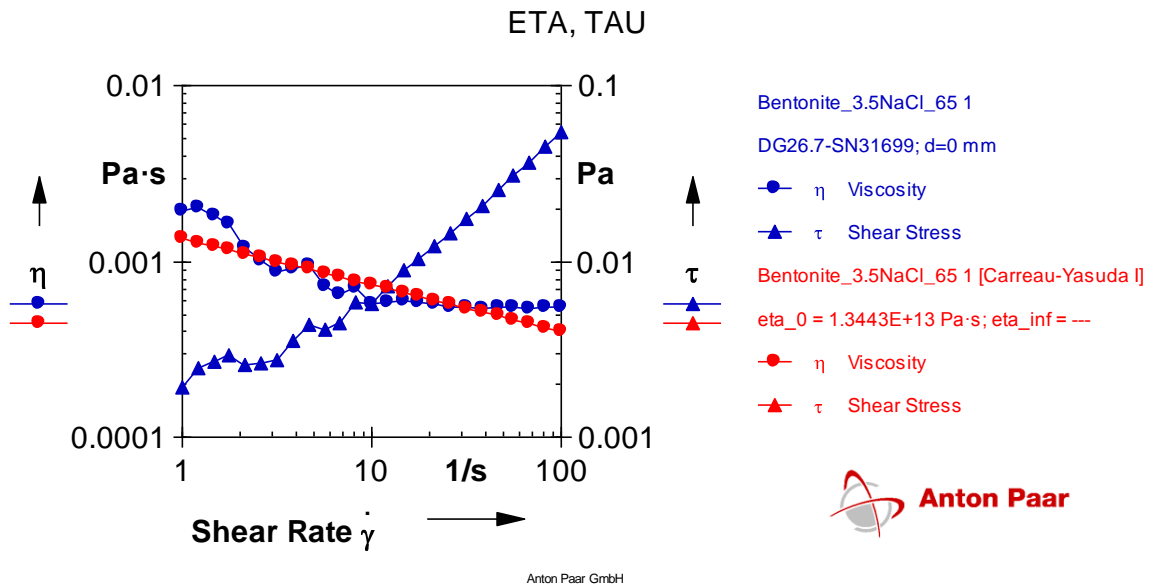
A13 – Rheological model Bentonite_SDS0.5_NaCl1_85 1



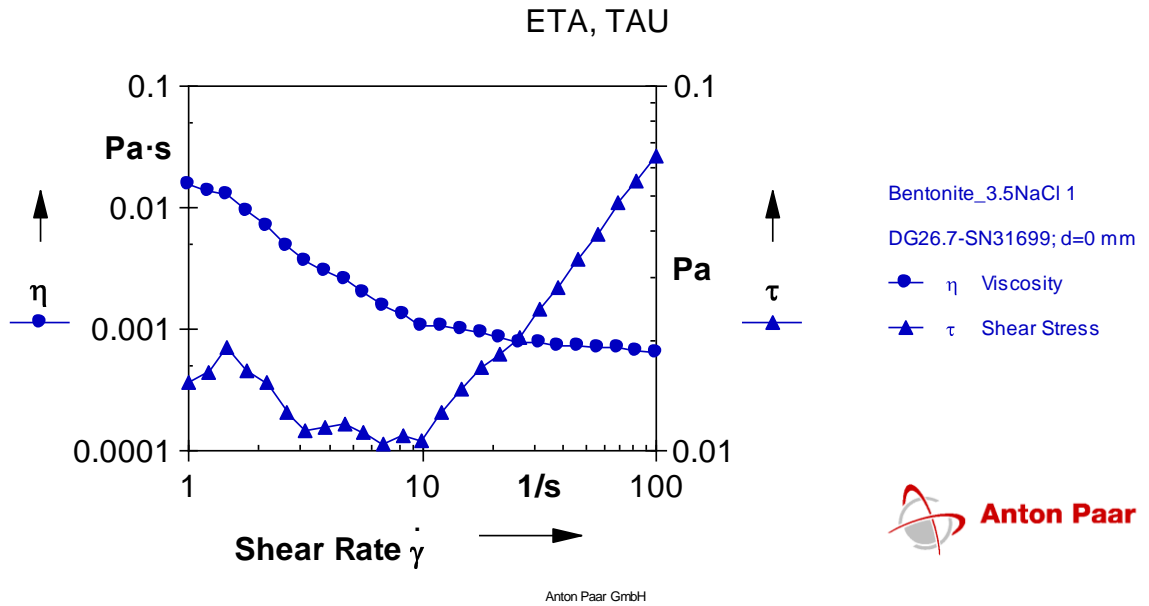
A14 – Rheological model Bentonite_3.5 NaCl_65 1



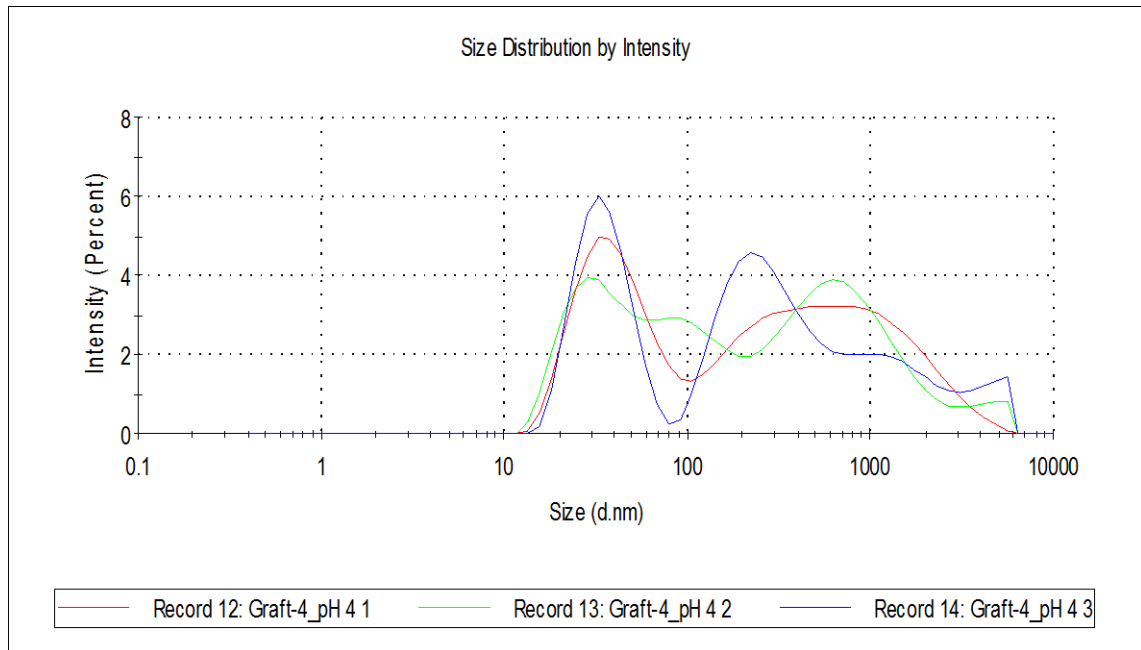
A15 – Rheological model Bentonit_3.5NaCl_85 1



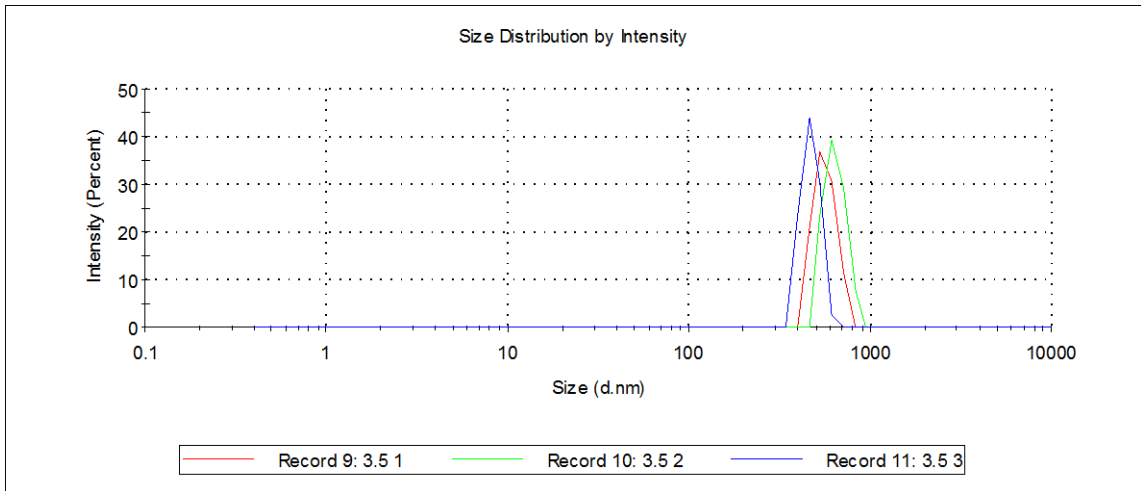
A16 – Rheological model Bentonite_1.0NaCl_65 1



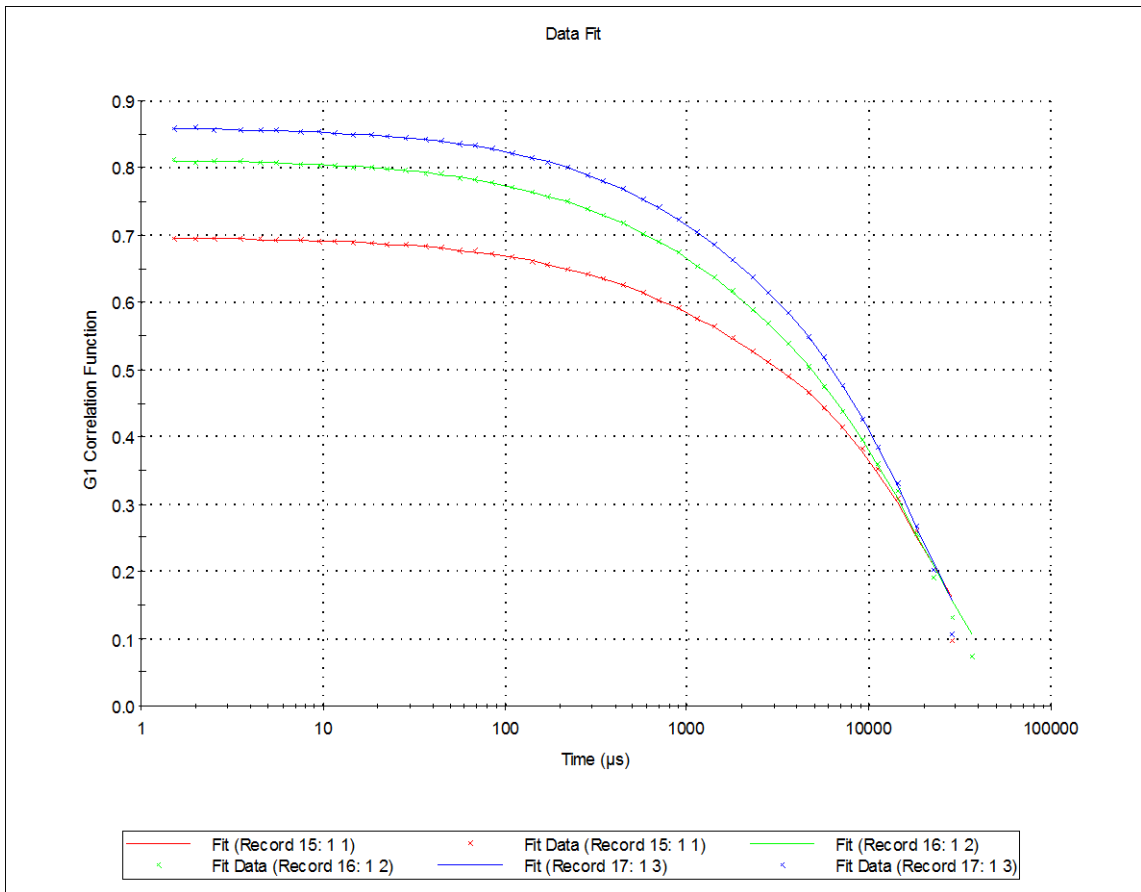
A17– Rheological model Bentonite_1.0NaCl 1



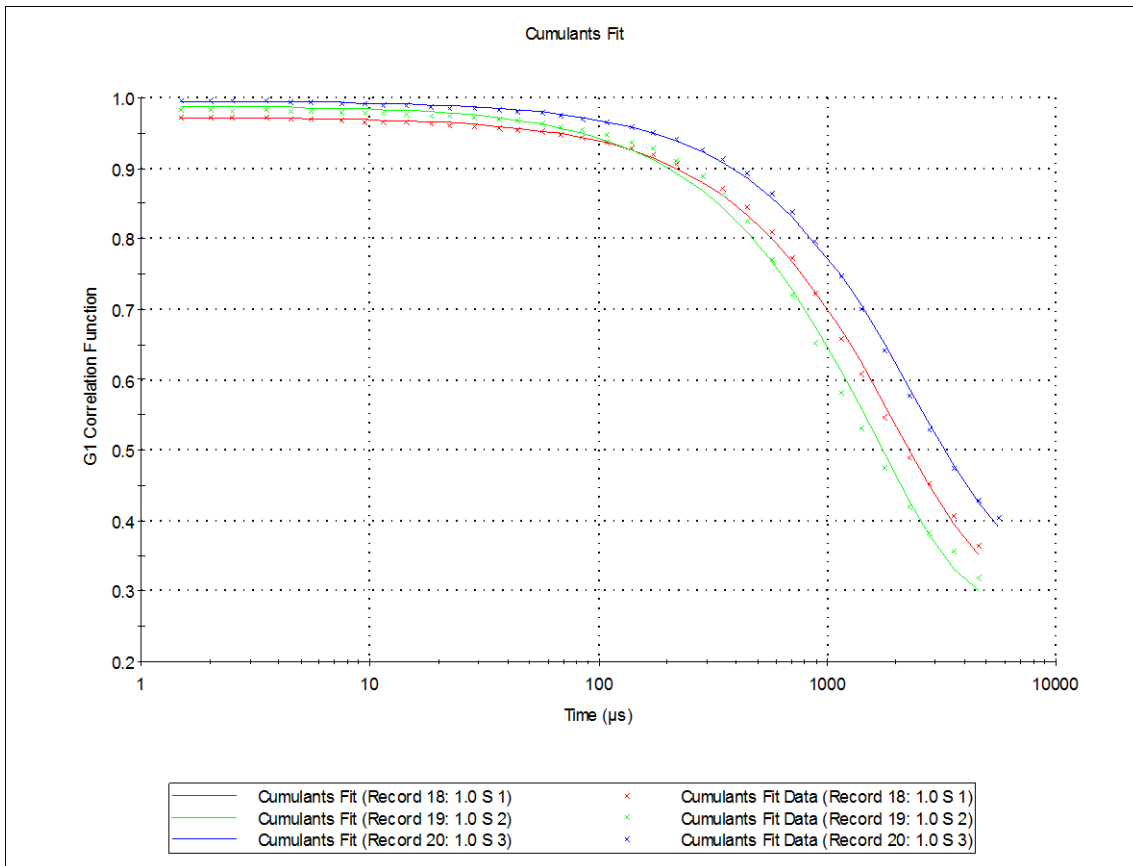
A18– Size Distribution by Intensity



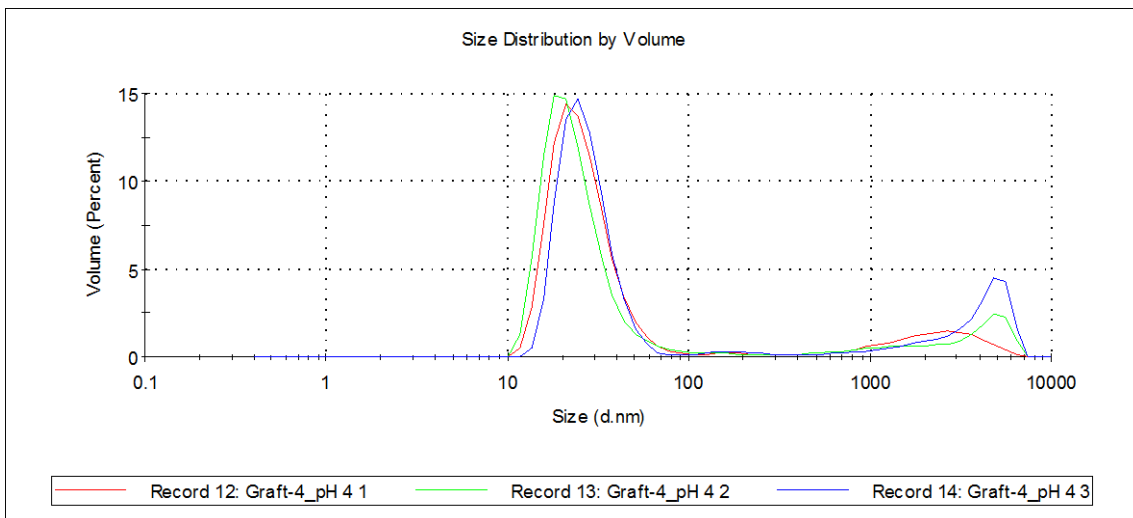
A19 – Size Distribution by Intensity



A20 – Data Fit



A21 – Cumulants Fit



A22 – Size Distribution by Volume