INVESTIGATION OF ADDITIVES ON DRILLING MUD PERFORMANCE WITH "TØNDER GEOTHERMAL DRILLING" AS A CASE STUDY

Chemical Engineering Department

Aalborg University Esbjerg

Master Thesis

M.Sc. Oil And Gas Technology

January 6, 2014

Author: ***Nwaoboli Awele***

Supervisors: ***Erik Søgaard and Sigurd Solem***

AALBORG UNIVERSITY
DENMARK

Abstract.

The physico-chemical properties and behaviors of 5 different mud samples were investigated to evaluate their performances for use in drilling operation, “Tønder geothermal drilling” as case study.

The project focuses more on the laboratory experiments carried out on the mud samples at different conditions of temperatures and pressures, aging times, quantities of additives e.t.c. Two different water sources,“fresh tap water” and “sea water” from Fanø beach were used as the continuous phase for the experiments. Different additives were employed in evaluating the mud performances. Duo Tec NS, Bentonite and CMC were viscosifiers used, MI PAC Elv, Bentonite, CMC and Starch were the fluid loss additives used, Sodium hexametaphosphate (SHMP) and sodium pyrophosphate decahydrate (SPP) were the polyphosphates applied for thinning effects. Other materials provided include glycol and potassium chloride for inhibition of clay/shale, soda ash and barite for reducing calcium and for weighting the mud respectively. Apart from experiments carried out on the mud directly, experiments were also run on the mud filtrates to determine their properties and how they affect or deter the success of the drilling operation with regards to their interaction with the formation.

Results from the experimental works showed that all mud samples provided had a good swellability and could be used for coating of the side walls of well bore. For the viscosity reduction test, though both polyphosphates presented did their jobs of reducing viscosity, sodium pyrophosphate decahydrate showed more superior thinning effects than sodium hexametaphosphate. Samples 4 and 5 were seen to have the least sand contents both in volume and weight percents, while sample 2 contained the most sand.

Regarding the test with viscosifiers, both CMC and Duo Tec NS have proven they can be used for increasing viscosity effectively, however, Duo Tec showed more superior qualities in terms of mud rheology. It has a higher yield point and and gel strength than CMC which is a property well desired of a viscosifier. In the swell inhibitive test, inhibition was mainly due to the potassium ions present in KCl, and that glycol could not effectively inhibit absorption of water except in combination with KCl.

In addition, CMC has been proven to have very good fluid loss properties compared to other additives used, but MI PAC has also been seen to be another fluid loss agent that can competitively give similar results as CMC. Both would be recommended as fluid loss agents, allowing the mud sample to produce filter cakes of desirable properties.

Filtrate analysis showed that the levels of calcium, magnesium and chlorides present in the filtrates were at acceptable levels and further treatment would not be necessary and alkalinity tests showed the ions present in the filtrate in terms of carbonates and bicarbonates using a stoichiometric classification as well as the amounts of acids needed to reach the phenolphthalein and total alkalinity end points.

The effects of aging were inconclusive from the experiments, but generally, it showed that aging reduced rheological properties. Temperature effects also showed that increasing temperature from ambience to 74^{o}C generally decreased rheological properties. Filter cake was formed with pressure increase, and the concepts of balanced, over balanced and underbalanced holes were verified from the balance between hydrostatic and formation pressures.

Preface.

This thesis is in partial fulfillment of the requirement for the completion of the Master Program in Oil and Gas Technology, Aalborg University, Esbjerg. It was supervised by Erik Søgaard and Sigurd Solem from September 2013 to January 2014. The project is more practical based as a greater part of it was carried out in the university laboratory. Five different mud samples along with various mud additives were provided and the objective of the project was to experimentally investigate the physico-chemical properties and behaviors of these samples at varying conditions with Tønder geothermal drilling as a case study.

The thesis comprises of 8 chapters, the first provides an introduction to the project task giving an insight of what it entails and also projecting drilling mud as an intricate and vital part of any drilling operation, which must be dealt with meticulously should any drilling operation be termed successful.

The next chapter talks more in details about drilling mud with regards to types, functions and additives used to enhance drilling mud performance while chapter 3 describes the properties and functions of drilling mud. These first three chapters make up the theoretical background of the report while the remaining chapters are the practical aspects.

In chapter 4, the different experiments carried out on the mud samples and the additives are documented. The procedures, requirements and results in both tabular and graphical representations are provided. Discussions of each result are given and Conclusions are also drawn based on the results gathered from each of the experiments carried out.

Chapters 5 and 6 include a generalized discussion of the experiments and conclusions reached respectively for each of the experiments.

The limitations of the project work are stated in chapter 7, while for further works on this project path, recommendations which would aid in improving the experimental values are given in chapter 8.

References for works cited and appendix are listed at the end of the report. A CD of the report is also attached at the back cover of the booklet.

Acknowledgment.

Special thanks to my Supervisors, Erik Søgaard and Sigurd Solem for providing majority of the project materials from MI SWACO and for their immense contribution and guidance during the course of the project.

My appreciation to the University laboratory Staff for their assistance in the experimental parts of this project and to everyone who has contributed towards the progress of this project.

To my colleagues in the department of Oil and Gas Technology, especially to my partner in this project, Mikkel Fischer, I would like to say it has been a nice academic journey with you all and the times we spent together have been worthwhile. Thank you.

My gratitude to my family for their love and support during the course of my program and finally, to God Almighty, I say thank you for everything.

Esbjerg, 06.01.2014

Nwaoboli Awele.

Contents

List of Figures.

Figure

List of Tables

Table

1. Introduction.

Every rotary drilling operation implies three systems that work simultaneously in boring a hole; a rotating system which rotates the drill bit, a hoisting system that raises and lowers the drill string into the hole, and a circulating system which performs the function of moving a fluid around from the drill stem, out of the drill bit and up again to the hole at the surface(Van Dyke & Baker 1998). This fluid otherwise called drilling fluid, in its liquid form, may be water or a mixture of water and oil, clay with some additives. This mixture in drilling parlance is termed drilling mud by drilling operators, henceforth, the terms “drilling fluid” and “drilling mud” would be used interchangeably.

A circulating system on any drilling rig is a closed loop of activities consisting primarily of a drilling fluid which is the workhorse of the whole drilling operation and other equipment which aid in the circulation of the drilling fluid. It is quite interesting to know that this system functions in like manner as the circulatory system in the human body. The functions of this fluid can be likened to those of the liquids running or circulating in the blood vessels of the human body, the mud pump equivalent to the heart, and the drilled out cuttings represent the slag products(Skalle 2010). The mud cleaning system which is at the surface represents the kidney and the lungs. A schematic of a circulatory mud system is shown in figure 1.

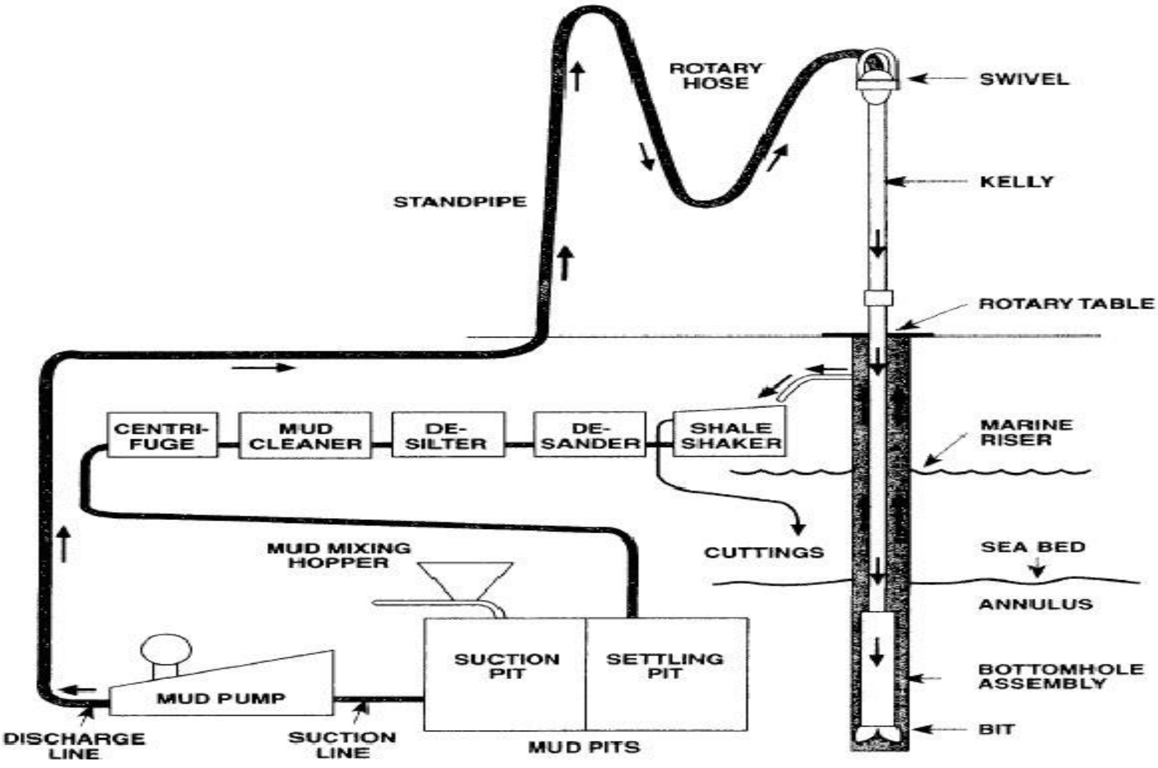


Figure 1 Drilling Mud Circulatory System(Van Dyke & Baker 1998)

Almost every drilling problem has a link, directly or indirectly with the performance of the drilling fluid. This is not to say that the drilling fluid can be traced as the source or solution of all problems encountered during drilling operations, rather, as a tool that can often be used to alleviate a difficult drilling situation.

Therefore in general, a drilling fluid should be seen as a very vital and intricate part of the whole drilling process that should be used to complement other aspects of the operation.

For any drilling operation to be termed successful, care must be taken during the selection and application of the drilling fluid which are key factors that should be considered. Any actions contrary to carefully selection and application of drilling fluids could have very dire consequences ranging from destruction of the drilling rig equipment, non productive time leading to financial losses, damage to environment and loss of lives of crew workers, therefore the properties of drilling fluids must from the onset of the drilling operation, and at regular intervals, be monitored, tested and investigated to ascertain they have the desired qualities all the way, and in most cases, drilling mud agents are added to the muds if needed to necessitate a successful drill operation, hence the title of this write up, **" Investigation of additives on drilling mud performance with Tønder geothermal drilling as a case study**".

1.1 Project Task.

A good drilling fluid has to fulfill some basic requirements, it has to be generally simple with a number of additives, and it is worth knowing that the performance of a drilling fluid should be driven more by engineering than of the product used. Most often, exotic mud systems end up in failed states simply because those operating them lack the basic understanding of such mud systems. The type of fluid chosen for a particular well depends on 3 important factors; cost, technical performance and environmental impact. The cost of products is very important, but should only be considered on a cost-performance basis. Most important of all 3 is the technical performance of the drilling mud(Hawker 2001; Devereux 1999).

In the light of the above, it is of paramount importance to always test the mud properties to make sure they have the right qualities.

For the project under study, investigations are to be carried out on some samples of mud using some additives and chemicals to check the effects on their physico-chemical properties. These mud samples are to be used in geothermal drilling in Tønder in 2014, so they have to meet the requirements of a good drilling mud. These drilling fluid products supplied by MI Swaco include;

- 5 different mud samples
- Bentonite about 25kg.
- Potassium chloride about 25 kg
- Glycol 1 liter solution.
- MI Pac ELV 25 kg Sx
- Duo Tech NS 25 kg Sx
- Soda Ash 25 kg Sx.
- Barite.
- WBM Premix.
- A Fann VG 35 SA viscometer was also provided.

Other materials used from the university laboratory include;

- Carboxy methylcellulose (CMC)
- Sodium Hexametaphosphate (SHMP)

- Sodium pyrophosphate decahydrate (SPP)
- Starch.

The task focuses on investigating the physico-chemical properties of the different mud samples and studying their behaviors when subject to different conditions. In order to do this, they would all be subjected to a number of experiments in order to determine the most appropriate for use. This is necessary as a drilling mud for use has to be multifunctional and a lot of compromises made. In doing so, the above mentioned additives would be used and at certain varying conditions such as varying temperatures and aging times, to help the mud samples perform maximally.

Furthermore, choice of additives performing similar functions would be investigated to know which best suits a particular mud function or property. A description of these different additives and what they perform would be given in later chapters of this report.

Amongst the tests to be carried out are filtration or water loss test, swell tests, inhibitive swell tests, sand content analysis, investigations to determine the rheological properties of the different mud samples, pH tests, aging and temperature tests at ambient and elevated temperature, downhole simulation, as well as determining the chemistry of make-up water and filtrate alkalinity tests.

2. Drilling fluids

The drilling fluid according to the American Petroleum Institute (API) is defined as a circulating fluid used in rotary drilling to perform any or all of the various functions required in drilling operations(Fink 2011). It is the single most essential system in safe, efficient, and economic well drilling. The drilling fluid consists of a mixture of natural and synthetic compounds used for a variety of purposes. This chapter gives an overview of the significance of drilling fluids in drilling operations and details about what it entails.

2.1 Types of drilling fluids.

The challenges met during drilling operations in the petroleum industry have led to the formulation of different types of drilling fluids. Drilling muds are classified based on the continuous phase of the mud and they include;

a) Water Base Muds (WBM) – Also referred to as aqueous drilling fluid, which is 90–95 % of fresh water, salt or sea water and several dissolved substances meaning that water is the continuous phase here(Skalle 2010; Devereux 1999) . It is predominantly used in the industry due to its environmentally acceptable nature, and also because it is relatively cheap to operate with. WBM is the drilling mud type which would be focused on and used in this project. There are several types of WBM as seen below;

  - Dispersed Muds– These mud type are basically used at greater depths requiring higher densities or in problematic hole conditions where heightened treatments are required. The mud system would be dispersed with specific additives to give specific properties to the mud e.g thinners or dispersants.
  - Non – Dispersed Muds - These mud type are basically applied for shallow wells or top hole sections. Clear or native water is used and examples are spud muds, natural muds and other lightly treated systems. The use of thinners or dispersants to disperse drilled solids and clay particles is not required, rather, the water is allowed to react with formations containing shales/clays so that the mud will form solids content and density naturally.
  - Salt water Muds – This could either be a saturated salt system with chlorides concentration around 190,000 mg/l, which is suitable for salt formation drilling in order to prevent dissolving, or a saltwater system where chloride concentration lies between 10,000 and 190,000 mg/l(Van Dyke & Baker 1998; Hawker 2001).
  - Polymer Muds – Long chain polymers such as cellulose and acrylamide are used in mud systems to provide a number of functions; increase viscosity, prevent dispersion by acting as encapsulating agents to drilled solids, minimize fluid loss, and inhibit or prevent sloughing of shales by coating. Example of such is KCl/NaCl muds which are inhibited salts that stabilize shale formations.
  - Low solids Mud – This mud system is significantly used to control or improve the rates of penetration. These are systems where the amounts of solids are intentionally controlled with a range of 6 to 10 % total solids volume and clay volume not more than 3 %. They typically use polymer additives as viscosifier and are non-dispersed.
  - Calcium Muds – The presence of calcium or magnesium in fresh water drilling muds inhibits swelling and hydration of clays and shales, but with higher levels of dissolved calcium, the problems of shale sloughing and hole enlargement are greatly reduced. Calcium treated

muds also resist contamination and are therefore suitable for use in drilling gypsum/anhydrite lithologies. However, they are susceptible to gelling and solidifying at elevated temperatures.

b) Oil Base Muds (OBM) – These muds have oil as their continuous phase, usually diesel oil, mineral oil or low toxicity mineral oil, and although they may pick up formation water, no additional water or brine is added. This is due to the fact that they contain water-emulsifying agents. This system which contains less than 5 % water has a number of advantages compared to WBM, but as seen in table 1, it also has some drawbacks(Van Dyke & Baker 1998; Hawker 2001; Devereux 1999).

Table 1 Comparison between Water and Oil Base Muds.

Advantages	Disadvantages
Good inhibition reducing shale swelling and sloughing	Environmental issues
Thermally stable.	Log formation interpretation problems.
High lubricity reducing torque and drag effect and risk of sticking.	Solids removal due to high plastic viscosity.
High salt tolerance	High cost compared to WBM.
Increased rate of penetration	flammability
Natural permeability and producing zones are preserved due to non-invasion.	

- Invert Emulsion Muds: These are water-in-oil emulsions typically with base oil or diesel as the continuous phase, and up to 50 % brine in the emulsifier phase. They are used in 10-20 % of all drilling jobs and find more application in stable, water sensitive formations and in inclined bore holes. They are very high thermal stabilities and provide excellent corrosion protection. However, their disadvantages are their high price, the great risk if gas reservoirs are bored through and their huge environmental problems. An example of an emulsifier used in these systems is calcium chloride brine.
- Emulsion Muds – In these muds, water is the major continuous phase, with oil now making up the dispersed phase, normally between 5-10 %. Environmental issues and cost are both minimized with water constituting the main phase, but with the addition of oil, the advantages associated with oil base systems are provided, such as improved lubricity, increased rate of penetration, reduced torque and drag effects, reduced filter loss(Hawker 2001).

c) Synthetic-Base Muds – Out of an increased desire to reduce the environment impact of offshore drilling operations, synthetic-base muds were developed but without sacrificing the cost-effectiveness of oil-based systems. They (synthetic oils and mineral oils) provide much of the performance advantages of hydrocarbon oil systems but have none of the associated environmental concerns(Fink 2011). Like OBMs, SBMs can be applied to minimize wellbore stability problems arising from reactive shales, maximize the rate of penetration and increase lubricity in directional and horizontal wells. Examples of synthetic mud systems are esters, ethers and poly or isomerized alpha olefins. These have high biodegradability and low toxicity and as such, are good base fluids for environmental performance.

2.2 Functions of drilling fluids.

Drilling fluids should meet some basic requirements and have the following functions in every drilled well at some point in time.

- Balance of formation pressure to assure proper well control.
- Transport drilled cuttings and sloughing to the surface.
- Provide lubrication and cools the drill string and bit.
- Minimizes drilling damage to the formation.
- Helps to seal permeable formations.
- Cleans beneath the drill bit
- Stabilizes well bore.
- Aids in information about formation evaluation.
- Suspends cuttings when circulation stops.
- Provides hydraulic power to downhole equipment.
- Corrosion control.

For the drilling fluid to perform all these functions, it would require characteristics that may sometimes be contradictory therefore it requires the best overall compromise to create a balance among the numerous needs. This is to say that the most important functions in a particular drilling operation should be given the most preference in the design of the drilling fluid. An in-depth discussion of these functions would be given subsequently as many of these functions are controlled by more than one mud property.

2.2.1 Formation pressure control

The proper restraint of formation pressures depend upon the density or the weight of the mud column in the well. The density of the drilling mud must be such that the hydrostatic pressure exerted by the mud column will prevent flow into the well bore. As the formation pressures increase, the density of the drilling fluid is increased to help maintain a safe margin and prevent “**kicks**” or “**blowouts**.” However, if the density of the fluid becomes too heavy, the formation can break down. If drilling fluid is lost in the resultant fractures, a reduction of hydrostatic pressure occurs. This pressure reduction also can lead to an influx from a pressured formation. Therefore, maintaining the appropriate fluid density for the wellbore pressure regime is critical to safety and wellbore stability.

The well is said to be “**balanced**” if the mud hydrostatic pressure is equal to the formation pressure. It is said to be “**underbalanced**” if the mud hydrostatic pressure is less than the formation pressure and “overbalanced” if the mud hydrostatic pressure is greater than the formation pressure(Van Dyke & Baker 1998; Devereux 1999). The hydrostatic pressure of the drilling mud is a function of the mud weight and the height of mud column given mathematically from the equations 1 to 3 depending on the units of operation(Hawker 2001).

$$P_{Hyd1} = \rho_1 * TVD_1 * 0.052 \qquad (eqn\ 1)$$

$$P_{Hyd2} = \rho_2 * TVD_2 * 0.433 \qquad (eqn\ 2)$$

$$P_{Hyd3} = \rho_3 * TVD_3 * 0.00981 \qquad (eqn\ 3)$$

Where,

$P_{Hyd\,1}$, $p_{Hyd\,2}$ and $P_{Hyd\,3}$ are the hydrostatic pressures in psi, psi and Kpa respectively.
ρ_1, ρ_2 and ρ_3 are mud densities in ppg, SG and kg/m^3 respectively.
TVD_1, TVD_2 and TVD_3 are the True Vertical Depths in feet, feet and meters respectively.

Control of formation pressure remains a very big issue when it comes to drilling mud function because it does not only consist of controlling the formation and hydrostatic pressures in the well bore, it also consists of controlling pressure build dissipated in frictional losses along the entire flow path. As a result, the sum of the hydrostatic pressure and the circulating pressure drop from a particular point to the exit point make up the total pressure in a circulating system.

Equivalent Circulating Density (ECD) represents the total-actual bottom hole pressure exerted on the formation being drilled and is usually given in terms of equivalent density(Skalle 2010). ECD is the cumulative sum of the static density, the density or weight of drill cuttings in the annulus and the effect of pressure drop along the annulus. Figure 2 shows the graphical effects of ECD.

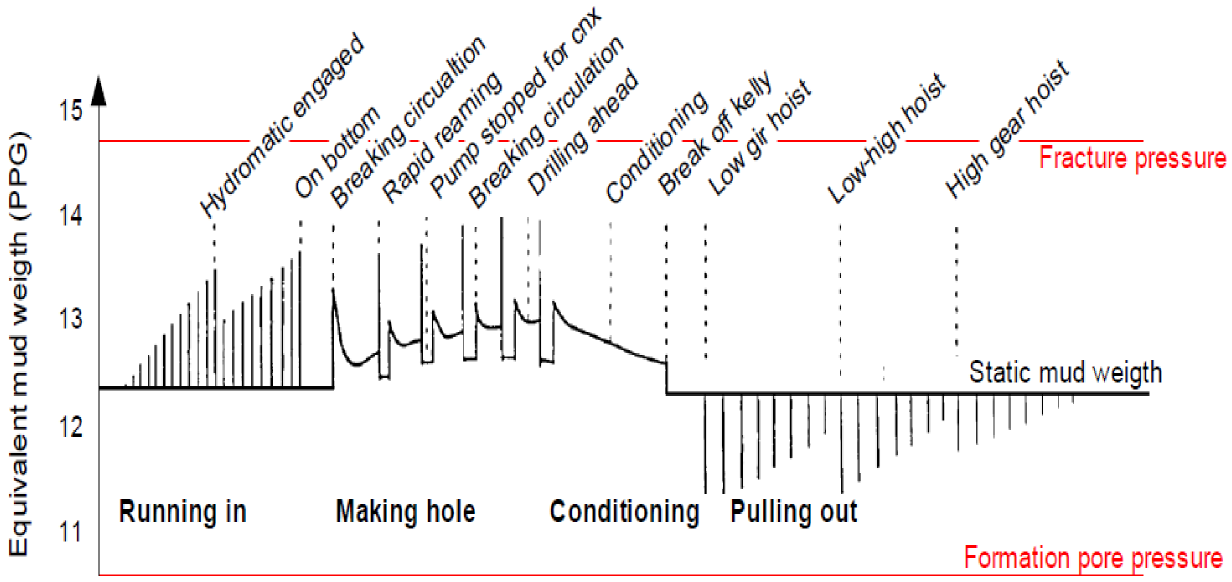


Figure 2 Graphical view of pressure variation during tripping and drilling(Skalle 2010).

Additional weight added due to annular pressure drop maybe of great importance when long and narrow well bores are drilled . Mathematically, ECD can be expressed as equation 4.

$$ECD = \rho_{mud} + \frac{\Delta p_{annular\ friction} + \Delta p_{cuttings} + \Delta p_{surge\&swab} + \Delta p_{rotation} + \Delta p_{acceleration}}{gz} \qquad (eqn\ 4)$$

Where,
g = unit conversion factor and z = True Vertical depth.

When ECD is in ppg, g = 0.052, z is in feet, ρ_{mud} is in ppg and ΔP in psi.
When ECD is in kg/l, g = 0.0981, z is in m, ρ_{mud} is in kg/l and ΔP in bar.

In deeper wells, the ECD is of more significance as the pressure window becomes thinner i.e. it is a critical parameter in avoiding kicks and losses, particularly in wells that have a narrow window between the fracture gradient and pore pressure gradient i.e downhole ECD remains within the given boundaries(Skalle 2010). This is illustrated in figure 3.

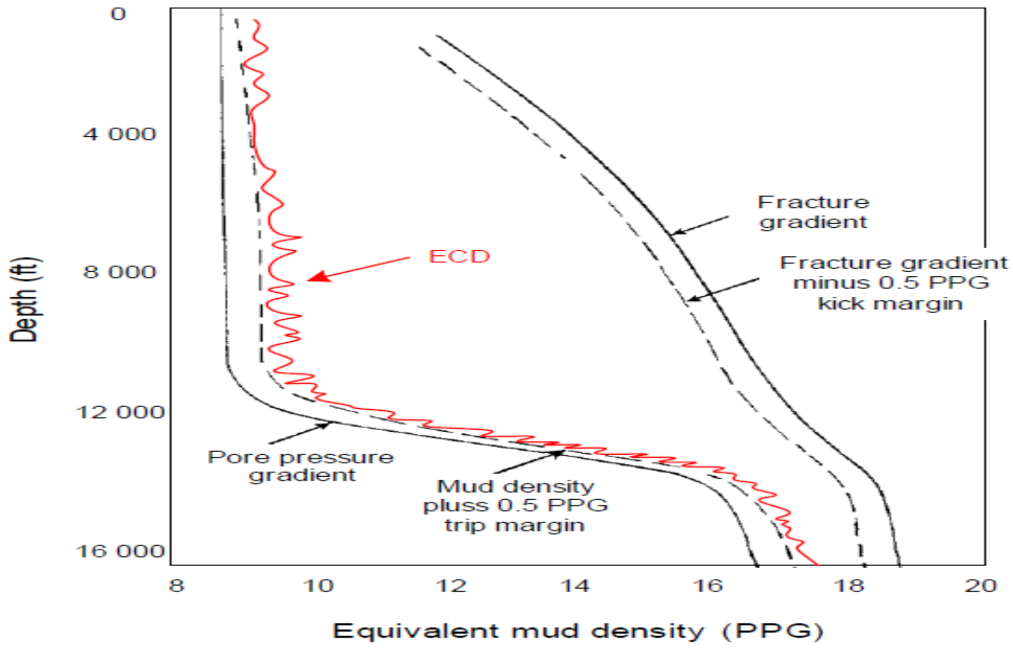


Figure 3 Equivalent pore and fracture density vs Depth(Skalle 2010)

Another factor that affects formation pressure control is **surge and swab pressures**. Figures 4 and 5 show the effects of annular flow during running in and pulling out respectively, the drill string from the wellbore.

During surge operations, the drill string which is run into the hole displaces a volume of fluid causing it to rise up the annulus thereby increasing hydrostatic pressure as a result of increase in frictional pressure. During swab operations involving pulling out of the drill string from the hole, the mud drops under gravity filling up space which was taken by the drill string. This brings about a flowing pressure drop that subtracts from the hydrostatic pressure. In the light of the above, the difference in total pressure at any depth between the hydrostatic and swab or surge lines is the pressure drop caused by pipe movement.

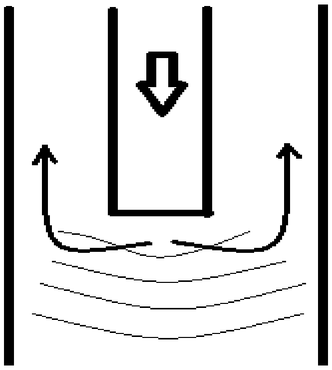


Figure 4 surge action of drill string(Hawker 2001).

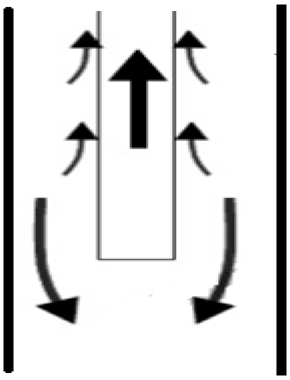


Figure 5 Swab action of drill string(Hawker 2001).

Under swab conditions and in the event that the well bore pressure is lesser than the formation pressure which is an underbalanced situation, then this would cause formation fluid to flow into the well(kicks). Under surge conditions and in the event that at the same depth, the well bore pressure is more than the formation pressure, then formation fracture would be the outcome with an eventual lost circulation occurring leading to unstable hole conditions. This would lead to a decrease in the mud level in the annulus, and a drop in the hydrostatic pressure throughout the wellbore. With reduced hydrostatic pressure in the annulus, a permeable formation at a different point may give way to influx of formation fluid into the well bore. With lost circulation at one point and formation fluid influx at another, then this would certainly lead to an underground blowout. This factor must also be borne in mind when regulating the right density of the mud during drilling operation. In balancing pressures down hole, it is normal practice to have a mud density slightly higher than required to create a kind of allowance or safety margin required to offset excess pressures(Hawker 2001; Devereux 1999).

Controlling the pipe velocity in and out of the hole also has significant effects particularly when this precaution of regulating mud density has been applied, for instance, if it is noticed that swab effect is still greater than the overbalance, then to overcome this, the pipe must be pulled out slowly because there would be lesser quantity of mud in the hole in a very short space of time with a greater pipe velocity pull out, and this would reduce drastically, the hydrostatic pressure causing the well to flow. And in the case that the surge or circulating pressure drop causes the total pressure to surpass the fracture pressure, then the velocity of the pipe or the rate of circulation must be lowered in order to prevent fracturing of formation. Here, increasing the mud density further would not be a good option because this has its own consequences – reduced rate of penetration, ROP, lost circulation and differential pressure sticking. In worst case scenario, when maximum and minimum pressure requirements cannot be met by adjusting circulating rates or pipe velocities, then the remedy becomes casing the hole.

Ways of calculating annular pressure drop.

At least two different methods could be used in calculating the annular pressure loss while circulation of mud is ongoing.

- The first method, which is a more accurate method for finding annular pressure losses, involves the application of an accurate standpipe pressure measurement. Here, the pressure drop down the drill string and through the bit can be accurately calculated using a Reed Slid Rule and subtracted from the standpipe pressure(Potash & Nygren 1993; Max R. Annis 1996). The annular pressure drop is given as the calculated difference as shown in equation 5.

$$P_{sp} = P_{sc} + P_{dp} + P_{dc} + P_b + P_a \Rightarrow P_a = P_{sp} - \left(P_{sc} + P_{dp} + P_{dc} + P_b\right) \qquad (eqn\ 5)$$

$P_{sp} =$ total circulating pressure measured at standpipe.
$P_{sc} =$ pressure loss in surface equipment.
$P_{dp} =$ pressure loss down drill pipe.
$P_{dc} =$ pressure loss down drill collars.
$P_b =$ pressure loss through bit nozzles.
$P_a =$ pressure loss in annulus.

- The second method involves a prediction of the mud flow properties under downhole condition. Once the circulation rate and hydraulic diameter are known, the annular pressure drop can be calculated using the equations 6 and 7 below(Lapeyrouse et al. 2011).

$$v = \frac{(24.5 * Q)}{(D_{h^2} - D_{p^2})} \qquad (eqn\ 6)$$

$$P = \frac{[(1.4327 * 10^{-7}) * MW * L * v^2]}{D_h - D_p} \qquad (eqn\ 7)$$

$v =$ average annular velocity (ft/min)
$Q =$ circulation rate in gpm
$D_h =$ inside diameter of casing or hole size in inch.
$D_h =$ outside diameter of pipe, tubing or collars, in inch.
$L =$ length of annular in ft.
$MW =$ mud weight in ppg.
$P =$ annular pressure losses, psi.

The second method however is not an easy approach as there are several factors limiting its uses, they include;

a) A precise knowledge of the flow properties of mud in usually not known.
b) Inaccurate knowledge of the hole diameter either caused by washing out or filter cake deposition.
c) Positioning of the pipe in a central position which is best for calculating annular pressure drops but not usually the case(Max R. Annis 1996).

2.2.2 Cooling and lubricating drill string and bit

The circulation of mud down the drill string cools the bottom of the well bore. The mud should have sufficient thermal properties (heat capacity and thermal conductivity) to absorb heat down hole by convection, convey this absorbed heat to the surface and release it to the atmosphere by radiation. As the geothermal bottom-hole temperature is higher than the maximum mud temperature during circulation, it is important to know that the point of maximum circulating temperature is not at the bottom of the hole as many would imagine, but say about two-thirds the way down the hole. This fact is particularly important when additives which are influence by temperature are used, because it could be possible to have a mud additive which may perform satisfactorily at circulating temperatures, but at the geothermal bottom-hole temperature, becomes absolutely unstable or vice-versa(Potash & Nygren 1993; Max R. Annis 1996).

Furthermore, the circulating mud also gets rid of frictional heat produced in large quantities by the drill bits and string and provides some lubricating effects as well which is aimed at increasing drilling efficiency and improving the bit's life. When using a diamond bit for example which happens to be very expensive, then it is very essential to keep the temperature below a certain critical value because at higher temperatures, graphitization of diamond could be induced which would lead to the destruction of the diamond structure hence reducing tool life and drilling efficiency. In the absence of abrasive materials as sand or fine drilled cuttings in the drilling mud, then the problem of lubrication would not surface because the mud would only contain solids that are softer in texture than the piping and casing. Attempts to improve this basic lubricating quality of a mud have proved abortive – they are in most cases expensive and ineffective(Max R. Annis 1996).

Why the need for lubrication?

Lubrication is a very difficult case area especially as it applies to drilling operations. Generally, what lubrication does in a drilling operation is to improve drilling efficiency and increase tool life. The following factors are reasons lubrication is very important;

- Excessive torque and drag: The drill string, during drilling, may develop an unacceptable rotational torque and drag, often caused by key seats, improper hole cleaning and bit balling, which would make twisting and rotating very difficult thereby limiting horizontal displacement of the hole. This would give rise to a very high COF (Coefficient of friction) hence the need for lubricant effect.
- Stuck pipe: In this case, the drill string cannot be rotated, neither can it be raised or lowered. This problem could be caused by a number of factors:
    - Unexpected differential formation pressure
    - Build up of drill cuttings or sloughing in the well bore.
    - Embedding of part of the drill string into wall cakes caused by irregular well bore development.
    - An under gauge borehole.

In the event that the drill pipe becomes embedded or stuck in the mud wall cake opposite a permeable zone, then this is termed "**Differential Pressure Sticking**". The pipe gets stuck in place as a result of difference between the hydrostatic pressure in the drill pipe and the formation pressure. Differential pressure sticking could be prevented and a stuck pipe freed with the use of oil based mud or water based surfactant composition(Max R. Annis 1996). This composition performs functions as permeating drilling mud wall cake, reducing differential pressure, reducing friction resistance and destroying binding wall cake. Unfortunately, the uses of these are severely limited by environmental concerns and high costs.

Mechanism of lubrication.

The success rating of a lubricant with regards performance is related to its film strength in relation to the contact pressure at the surface being lubricated. A lubricant performs badly if its lubricating film is squeezed out. Lubricants especially in the liquid state form a film that is thick enough to engulf surface roughness and strong enough to withstand high compression forces. The performances of these lubricants tend to depend on their concentration simply because they compete with other surface-active components in the drilling mud(Fink 2011).

In addition, at high shear rates, these lubricants can become tightly emulsified and so stable that adsorption is inhibited. Lubricants compatible with water based mud and capable of reducing drill string/well bore COF as effectively as oil based or synthetic based muds have proved elusive. During a test, a material that seems to be a good lubricant at low contact pressure may perform very poorly in real application due to higher contact pressures, higher rotating speeds, e.t.c. The only sure test confirming a lubricants performance is under exact conditions that exist where lubrication is desired, but sadly, these downhole conditions are unknown.

2.2.3 Seal permeable formations.

Drilling mud should possess the quality of depositing filter cake on the wall of the well bore to consolidate the formation which is almost always permeable and to retard the flow of well bore fluid into the formation. This fluid is often referred to as "**fluid loss or filtrate loss**". As the cake becomes thicker, sealing occurs thus decreasing the flow rate into the formation. This causes a reduction of the amount of fluid lost to the formation, with the filter cake progressively building up causing some other problems. For this reason, the filtration properties of mud should be measured and controlled.

In summary, a good mud must keep the loss of fluid to the formation as minimal as possible while preventing excessively thick filter cake. Thinner and less permeable are thus the desired characteristics of a good filter cake. The following are some of the problems associated with thick filter cakes;

- **Differential pressure sticking**: With increase in the wall cake thickness comes this problem of differential pressure sticking. Here, the contact area of pipe and the wall cake is increased resulting in decreased hole diameter and increased sticking force. The incidence of pipe sticking would be drastically reduced if thin and low permeable cakes durable enough are deposited on the wall of the hole.
- **Lost circulation**: With increased wall cake thickness to an appreciable extent comes an increment in the circulating pressure drop due to the decreased clearance between the wall and the pipe. During swabbing or pulling out of the drill string, there would be an increase in pressure and even greater problems with increased surge pressure which could lead to a fractured formation resulting in escape of mud into the formation.
- **Logging problems**: The feedback of some logging tools are affected by thick wall cakes as the tendency for the tools to be stuck is heightened and in some cases, the tools cannot be lowered down because of drag on a thick wall cake.

Other problems created by thick wall cakes include torque and drag, difficulty in running casing in the whole and poor cement jobs(Max R. Annis 1996).

Drilling problems associated with fluid loss include;

- **Caving or sloughing**: This is particularly peculiar with shale formations as some shales are very sensitive to water. They absorb water entering the formation, swell up, become weakened and then fall off or slough causing caving in the formation.

- **Formation damage**: par venture liquid is lost into the producing zones, then during production, this may affect flow rate, reducing the produced amount of oil. This phenomenon is possible because, like shales, some producing zones are sensitive to water. The surrounding rocks swell as water escapes into tiny pore spaces, thus reducing the interconnectivity between these pores spaces or blocking permeability. This blocked permeability is referred to as "**formation damage**".
- **Stuck drill string**: As fluid is lost to the formation, filter cakes are left behind. Accumulation of these becomes thick enough that they reduce the diameter of the hole, creating tight spots where the drill string can get stuck in place.

In general, sealing the walls of the borehole is more involved than just reducing the amount of filtrate that flows into the formation.

2.2.4 Well bore stability

A good combination of chemical composition and mud properties would provide a stable well bore. Also, pressure is a key player when it comes to well bore stability as the formation pore pressure must be balanced. Most peculiar with instability issues are shale formations as they are water-sensitive.

Mechanism of shale destabilization

Failure of shale formation is caused by a combination of 2 effects(Fink 2011; Skalle 2010);

- **Stress induction**: With the absorption of water by a shale formation, stress is induced into the formation. Increased absorption leads to a corresponding increase in the stress level until it eventually overcomes the peak strength of the rock. This yield in rock strength gives way to failure of the formation.
- **Weakening effects**: Absorption of water goes into the grain boundaries and eventually penetrates the grain interstitials causing softening of the grains of the formation and an increased stress level. This weakening accelerates the occurrence of the rock failure.

In general, well bore instability is caused by reaction between drilling fluid and the formation due to discrepancies in their chemical make-up. Shale formations have a high affinity for water therefore they tend to be destabilized much easier than any other type of formation. Below are some of the causes of instability and some that aid instability as well.

- **Erosion**, which involves washing away a part of the shale formation by drilling fluid, may cause an already weakened formation to slough enlarging the hole. By reducing the annular velocities, these erosion effects can be lowered because there would be a change in the flow regime from turbulent to laminar.
- **Swabbing** can also cause sloughing in an already weakened zone because during swabbing, hydrostatic pressure is reduced adding more stress imbalance at the wall. This pulling out action of the drill string causes the fluid motion to act downwards on its own weight which is a deviation from normal. This may lead to displacement of rock particles in the drilled hole causing hole enlargement.

How can wellbore instability be reduced or prevented?

One of the ways in which well bore stability can be improved is by “**increasing mud density”**. To aid in the balancing of the wellbore stress caused by water absorption is the hydrostatic pressure in the well bore. Increasing mud density would increase hydrostatic pressure, but as more water absorption continues, the stress imbalance would increase and thus weaken the formation until its yield point is exceeded causing failure. The density of mud would have to be further increased each time it is suspected that failure would occur as a result of instability(Max R. Annis 1996). This method is particularly applicable in areas of abnormal pressure where the initial stress surpasses the formation strength, when no other means of salvaging the situation is available. For this reason, it can be concluded that increasing mud density is only a temporary deterrent to most shale formation instability and has as of course, some negative consequences.

Use of special water muds: Since instability is mainly as a result of reaction with drilling mud and formation, services of some special water mud can be employed. Here, the content of the electrolyte is adjusted to reduce its reactivity with the shale slowing down the rate of absorption and hence delay the onset of sloughing, but this method again has its draw back – it can only be used for specific shale types, that is, it is not universal with regards performance in all types of shales therefore it is not a permanent solution.

Use of balanced-activity oil muds: This is at present, the best and only means of preventing absorption of water sensitive shale formations.

Use of additives: Well bore stability mud additives do not solve the primary problem at hand, which is preventing or reducing instability. They however do a number of things – aid in reducing erosion effects, removal of sloughed formation and reduce disintegration and dispersion rates of the shale particles into the mud.

Reduction of water absorption: This remains the most important means of controlling shale sloughing, in other words, it is the best option in controlling wellbore instability, but the question to be answered is this, “**how can this be achieved?”** Two very important factors are considered here for making this action possible,

- Rate of absorption of water by formation.
- Length of time formation is exposed to water from the drilling mud.

Considering the rate of absorption, sometimes, this can be controlled by applying the right type of mud, using some additives, or some plugging action, but if this is practically impossible, then reducing the duration of exposure of shale to the mud would be the next option and this would only mean one thing, drilling the formation and then casing as fast as it can possibly be done.

Some would actually think that “**fluid loss control”** could be a way of reducing wellbore instability and this might seem so in a way as fluid loss control is all about preventing filtrate loss into permeable and porous formation, but absorption of water is not controlled by filtration characteristics of a mud, rather by the chemical constituents and composition of the formation in relation to the fluid mud, hence reduced filtration should not be a criteria for shale control mud, neither should it be a remedy for instability of wellbore(Max R. Annis 1996).

To summarize, in order to maintain well bore stability, the drilling fluid must be able to perform the following:

- Prevent formation caving by preventing formation pressures.
- Prevent dissolution of salt sections by using salt saturated or oil base muds.
- Prevent erosion of wellbore.
- Stop swelling and sloughing especially of shale formations(Hawker 2001).

2.2.5 Drilled cuttings removal from the annulus and bit.

This is the most basic function of mud which involves the mud being able to lift cuttings of various sizes out of the drilling hole. For this to be achieved, the mud must possess a high suspension capacity to ensure that during moments of non circulation, the cuttings and commercially added solids as barite, do not sink to the bottom, the mud circulation rate must be adequate to prevent excessive increase in mud viscosity or density as a result of drilled solids being dispersed into it especially when they become finer. This would give rise to an increase in equivalent circulating density of the mud in the annulus exceeding the fracture gradient causing lost circulation. To reduce the effect of increased density and viscosity by these drilled solids, the rated of circulation can be increased, but this would in turn increase the ECD. In the event that the ECD is greater than the fracture gradient, the rate of drilling must be reduced. The chemical properties of the mud should be such that it helps to prevent or minimize dispersion of drilled solids to they can be efficiently be rid off at the surface.

It is very vital that cuttings are being removed from the annulus because of reasons listed below(Max R. Annis 1996; Hawker 2001);

- Maintaining minimum annular pressure
- Permitting the drill string to move and rotate easily.
- Preventing loading of the annulus.
- Transporting drilled cuttings to the surface in proper conditions to aid in formation evaluation by geologists.

The annular velocity, the yield point and gel strength of the mud are the key determinants of cuttings removal with other factors as pipe rotation, hole inclination, size, colour, shape and density of drilled cuttings being secondary.

The ability of the mud to lift cuttings or sloughing and convey them to the surface poses a very big challenge to mud. This problem is particularly difficult to identify as the larger cuttings with much heavier weights settle at the hole bottom and the finer ones come out at the top. The sizes coming out with the mud would give an indication of the extent of hole cleaning. Furthermore, hole fill or fill on bottom after a trip would signify inadequate cleaning, but absence of this would not necessarily mean that there are no cleaning problems. It is possible to have a sloughed hole with lots of cuttings collecting in. Another hole cleaning problem is drag experienced during swabbing. Swabbing effects may be just adequate to displace cuttings lodging in washed out sections of the hole. This could cause severe drag or sticking.

2.2.6 Cleaning beneath the bit

At high speeds and pressures, the rock surface is crushed by the drilling bit and in order to maintain the tempo of crushing, the cuttings must be removed in an efficient manner at the same or even greater rate than they are produced. Two types of energy namely mechanic and hydraulic energy are brought from the surface to the rock surface and the former takes care of the rock crushing process, while the latter, the cuttings removal process. Investigations have shown that drilling rate is increased significantly with increased hydraulic energy which could be as jet velocity through the bit nozzles or hydraulic horse-power.

The methods of hydraulic program design can be divided into two groups;

- Determining the level of bottom hole cleaning energy required in order to balance the mechanical energy level.
- Maximize criterion of estimation e.g. jet impact force.

Field tests would be required for methods in the first group which are based on the idea that, "if the bottom hole cleaning is sufficient, then the drilling rate is proportional to bit weight". Figure 6 shows the proportionality curve for the ROP (Rate of Penetration) against the WOB (Weight on Bit).

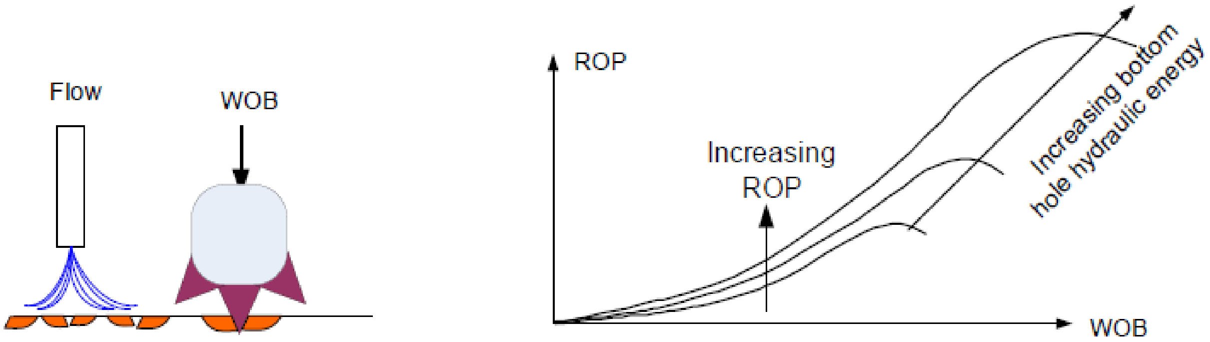


Figure 6 ROP vs. WOB for different bit hydraulic energy levels(Skalle 2010).

From this curve, the minimum energy for bottom hole cleaning to avoid bit balling at that level of WOB is determined when at some point, there starts a deviation from its increasing trend. For methods in the second group, optimum hydraulics is the proper balance of the hydraulic elements (flow rate, bit nozzles diameter) which satisfy some criterion of estimation (the objective function) e.g. maximizing the jet impact force. A suggested mathematical model from past experiments and observations demonstrated through figure 6 is given by equation 8. This equation relates the ROP and the hydraulic objective function.

$$ROP = A * (q/d_{nozzle})^{a_8} \qquad (eqn\ 8)$$

A is a constant term which includes the effect of all other parameters (other than q, d_{nozzle} and a_8) having an influence on ROP, while the quantity (q/d_{nozzle}) represents the bit hydraulic objective function. It can be seen from the figure 6 above that with increase in the hydraulic energy, the trend shows a general increase in the ROP. The points where the curves are turning and pointing downwards are called bit balling point(Skalle 2010).

2.2.7 Formation evaluation.

This function of mud which focuses on discovering and evaluating potential reservoir zones unfortunately is not being given so much focus as should be as attentions are being shifted to the drill rates and costs, which often lead to programs being implemented that have a detrimental side blow on formation evaluation. The drilled cuttings brought up the surface by the drilling mud are analyzed for information gathering about the formation.

Cutting Analysis

For accurate geological analysis, the best cuttings should be aimed at being transported out of the hole. This is one of the areas where the mud viscosity plays a very vital role as it determines how well the cuttings are being lifted and transported from the hole. Smooth laminar flows are preferred to turbulent flow patterns to reduce the degree of erosion and structural alteration of the cuttings(Hawker 2001). Typically, for production of high quality cuttings, then it is advisable to use oil bas muds as water base systems can react with most of the clay minerals.

Wireline logs and production Tests.

It is necessary that both formation evaluation and mud programs are synchronized to be consistent with one another. Regardless of mud type, logs which can be run would be affected when in the well bore. The salinity of water base muds as well as the degree of flushing of the zone around the wellbore are important evaluation considerations.

In an overbalanced wellbore, filtrate will normally invade a permeable formation displacing formation fluid around the wellbore. This type of water invasion depending on the depth of invasion, can affect the accuracy of wireline log analysis. If the depth of filtrate invasion is greater than the depth of investigation of an electric logging tool, the log will give misleading information. This depth of invasion is a function of the porosity, the amount of filtrate lost, and fingering of filtrate due to heterogeneity of some formations. Both low porosity and filtrate fingering may permit deep invasion which would in turn affect formation evaluation and little or nothing can be done about this in most cases. Many of the deep invasion problems are as a result of little or no filtration control. With necessary actions to stop the problem of filter cake in terms of thickness reduction in solving drilling problems, then filtrate invasion would no longer be a major issue. The amount of filtrate lost to a formation is as a result of 2 key factors – the dynamic filtrate rate and the filtration time under dynamic conditions, therefore efforts to limit or control fluid loss to a formation should be geared at minimizing dynamic filtration.

To reduce the dynamic filtration rate, an increase in the amount of colloidal solids in the mud or a decrease in the annular velocity would help as both methods will reduce the filtration rate due to increased thickness of the filter cake. It is advisable not to use API fluid loss as the criteria for limiting filtrate invasion because application of fluid loss control agents that reduce the permeability of filter cake and consequently the static fluid loss, have barely any effect on the rate of dynamic filtration or say just very little. When a fractured formation is pressure induced, loss of whole mud can lead to the same evaluation problems as would be encountered with deep filtrate invasion. With an oil mud, lost returns may totally affect the reliability of a log in the loss zone and the occurrence of this should be prevented by use of recommended pressure control practices.

In general, oil muds are recommended for use in well established areas as they do not seriously interfere with formation evaluation, as they are immiscible with water and unable to mix with formation fluid. However, they have some draw back in that they eliminate the use of some logging tools such as the SP and contact resistivity tools. They also limit severely, sidewall core and wireline test interpretation, show detection from mud logging and eliminate the use of show detection from samples. Because of the above disadvantages of oil mud, they makes its use undesirable in wildcats rigs therefore when drilling conditions require the use of an oil mud, then more tests have to be carried out due to the indefinite nature of other evaluation information(Max R. Annis 1996).

Coring is also a method of formation evaluation that often requires special mud characteristics. The type of mud to be used depends on what is aimed at during coring and the type of measurements to be made on the core will tell the type of filtrate that is good enough. An oil filtrate from an oil mud will eliminate location of oil-water contact, eliminate show detection and oil saturation determinations, therefore, water base muds are best suited for conventional core analysis or show detection. In order to get irreducible water saturation from a core, water base mud would not be appropriate as water filtrate would produce error in the determination, therefore oil mud would be the best coring fluid for use. In the case that the purpose of coring is either to obtain only geologic and lithology environmental data, then there is no problem with whichever type of mud is being used.

2.2.8 Formation Damage

This function of drilling mud is concerned more with the type of filtrate than it is with the amount of fluid loss to a formation. A restriction in permeability will result if there is a reaction between the filtrate and the formation solids or fluids, because this would block the pore throats and pore spaces. Only a very narrow layer of damage around the well bore is sufficient to cause serious restriction of fluid flow, however, if the damaged zone is sufficiently narrow that the pore openings extend beyond it, then, the well could still produce effectively. This problem is normally associated with water sensitive formations which are mainly sands with appreciable clay solids content. Several factors are responsible for the degree of damage; the types of clay present in the pore space, their reaction with the filtrate, and of course, their mobility. On reacting with the filtrate, a change in the salinity or ionic level of the water present in the pores may result to either swelling or shrinking or the clay particles making them mobile. This will certainly cause damage.

In solving the problem of formation damage, there is unfortunately no one best type of mud to prevent damage. This is because the type of clay and ionic content of the residual or connate water differs in a wide range from one formation to another. In some cases, special types of muds are used and they could work effectively in one scenario but badly in others e.g. saturated salt water appears to reduce damage in some sands but may not be appropriate in others. The same can be said of potassium chloride types of muds. Oil muds have been found to be suitable for preventing damage in water sensitive sands, but they have a drawback in that their use is not universal(Max R. Annis 1996).

2.3 Drilling Mud Additives.

Additives are added to mud to enhance its performance by changing its properties and composition particularly when the driller would like the mud to carry out specific function(s) to optimize the drilling operation. Several mud additives exists some performing more than one function, but only a few would be discussed subsequently. Some common mud additives and their functions are given in table 2(Skalle 2010; Hawker 2001).

Table 2 Drilling mud additives, functions and examples.

Type	Purpose	Agents
Alkalinity, pH control	To control acidity and alkalinity of fluid	Lime, caustic soda, soda ash, bicarbonate of soda
Bactericides	Used to reduce bacteria count	Para formaldehyde, caustic soda, lime and starch preservatives.
Calcium removers	To prevent and overcome contaminating effects of anhydrite, gypsum and calcium sulphates.	Caustic soda, soda ash, bicarbonate of soda and certain polyphosphates.
Corrosion inhibitors	Prevent corrosion, pH control, neutralize hazardous acid gases such as H_2S, prevent formation of scale in drilling fluid.	Hydrated lime, amine or phosphate based products.
Defoamers	Reduce foaming action especially in brackish or saturated saltwater muds.	
Emulsifiers	To create a heterogeneous mixture of two insoluble liquids.	Oil based muds – fatty acids, amine-based chemicals. Water based muds – detergents, soaps, organic acids.
Filtrate loss	Reduce water loss from the drilling mud into the formation.	Bentonite clay, CMC, lignite, polyacrylate, pregelatinized starch.
Flocculants	Increase viscosity, improve hole cleaning, de-water or clarify low-solids fluids. Particles in suspension will aggregate into flocs causing solids to settle out.	Salt, hydrated lime, gypsum, soda ash, bicarbonate of soda, polymers.
Foaming agents	Permit air or gas drilling through water-bearing formations.	Surfactants (foamers).
Lost circulation materials	To plug the zone of loss in the formation.	
Lubricants	Increase horsepower transmitted to the bit by reducing the coefficient of friction, also reduces torque and drag.	Oils, graphite, synthetic liquids, glycol or surfactants.
Pipe-freezing agents	Increase lubricity and reduce friction where a pipe sticks and inhibit formation swelling.	Detergents, soaps, oils and surfactants
Shale inhibitors	Reduce shale hydration when drilling water sensitive shales, thereby preventing excessive wellbore enlargement and caving of shale.	Gypsum, sodium silicate and calcium lignosulfonates, lime and salt.

Suface active agents	Reduce interfacial tension between contacting faces (water/oil, water/air, water/solid).	Emulsifiers, de-emulsifiers, wetting agents, flocculants or de-flocculents, depending on the surfaces involved.
Temperature stability	Increase rheological and filtration stability in fluids exposed to high temperatures.	Acrylic or sulphenated polymers, lignite, lignosulphate, tannin
Thinners or dispersants	They modify the relationship between viscosity and solids volume reducing gel strength and increasing the pumpability of a fluid. More specifically, they act as deflocculents to reduce attraction of clay particles that cause high viscosity and gelation.	Tannins, lignite and lignosulphates, polyphosphates.
Viscosifiers	Increase viscosity providing better solid suspension and hole cleaning.	Bentonite, CMC, attapulgite clays and polymers.
Weighting agents	To provide necessary density to control formation pressures, provide hole stability and to prevent u-tubing when pulling the drillpipe.	Barite, lead compounds, iron oxides, calcium carbonate.

3. Mud properties in relation to functions.

It is very important to measure the mud properties (physico-chemical) when trying to design and maintain a mud system to perform a particular function. Since there are various mud properties, it is normal to carry out measurements on these properties by running tests and correlating the results with the functions of the mud. These mud tests are done mainly to simulate closely, downhole conditions or to predict the downhole mud properties from surface condition measurements. Since drilling mud normally have multifunctional requirements, it is necessary to have both physical and compositional tests in order to properly monitor a mud system. Some of the mud properties are discussed in details below.

3.1 Density

Of great importance in a drilling operation is the density of mud. It is necessary for controlling the pressure and all pressure control calculations are done based on the weight of the mud column in the hole. This increased density helps to prevent caving and flow into the hole. As density is increased, the buoyancy effect increases carrying capacity for cuttings but decreases settling rate in the mud pit. A mud balance is used to carry out weight measurements on mud samples during drilling operations. During this measurement, precaution must be taken not to include air or entrained gas in the mud sample as this would give a false density measurement, particularly with muds having high yield points or gel strengths. Therefore, with a degasser or by stirring at an appropriate speed, the entrained gas can be rid off. Temperature and pressure affect density inversely and proportionally in the sense that increased temperature results in decrease in density while increased pressure causes an increase of density. Down hole conditions do not highly affect density, but the effects of increased temperature and pressure oppose each other and tend to equalize(Max R. Annis 1996).

Use of weighting agent helps increase the density of mud. One of such is barite, a commercial grade of barium sulfate, a mineral often found as evaporates or soluble salts (brines). It is used quite often because it is regarded as a standard weighting agent due to its low cost, inertness, high specific gravity and low abrasive tendencies. Pure barium sulfate has a specific gravity of 4.5, and commercial barite, 4.25, the difference owing to the fact that some impurities are present in the commercial grade. Before using barite, quality check must be carried out to ensure that the level of impurities (soluble alkaline earth metals mostly) are beyond detrimental range from API standard or specification with a maximum of 250 mg/l expressed as calcium. Most of the impurities vary by source of barite, calcium being introduced through poor quality control at the grinding plant or during transporting from cement contamination. Solid components such as sand, silt, fine cuttings, e.t.c. also increase density, but are undesirable as they are very abrasive increasing the rate of wear of equipment, forming thicker than required filter cake, retarding drilling rate and increasing power requirements of the mud pump.

However, some problems could arise from using muds maintained at higher densities than required to control formation pressures, they decrease the ROP, increase possibility of lost circulation, increase differential pressure sticking, increase mud costs and an eventual increased in overall well cost, therefore this must be done meticulously even when dealing with unweighted muds, hence solids control must be handled carefully and critically.

In order to weight up mud, the most important consideration is to add the weighting material at a rate that keeps the mud weight constant in the suction tank while circulating. Measurements of density of the mud in the suction tank which have been meticulously carried out, give an idea as to whether the weighting material is being added at the right pace and speed. The following steps through equations 9 to 20 should be followed when calculating the amount of weighting agent needed, and when doing this, two factors must be calculated – the amount of barite to be added and the speed at which it must be added(Van Dyke & Baker 1998).

- **Amount of Barite to add**: To calculate this amount, it has to be determined first how many kilograms of barite are needed for each cubic meter in the circulatory system. Equation xxx should be used when adding barite.

$$amount\ of\ \frac{barite}{m^3}\ of\ mud = \frac{4{,}250(desired\ density{,}kg/m^3 - initial\ density{,}kg/m^3)}{4{,}250 - desired\ density{,}\frac{kg}{m^3}} \qquad (eqn\ 9)$$

- **Volume of mud to be treated**: The number of cubic meters of mud in the system is determined next. The total amount of mud in the system is given as the sum of the volume of mud in the hole and the volume of mud in the mud tanks, i.e. Total volume = hole volume + tank volume.

  - Next, the approximate volume of the hole in cubic meters is calculated by squaring the diameter of the hole and multiplying by the depth. The hole diameter should be converted to meters since its in millimeters.

$$total\ hole\ volume = D^2h \qquad (eqn\ 10)$$

  - The volume of each tank is determined next, the depth of the mud being constant all the time.

$$volume\ of\ tank(m^3) = length(m) * width(m) * depth(m) \qquad (eqn\ 11)$$

  - The cumulative volume is calculated by summation of all active tanks.

$$total\ tank\ volume(m^3) = \sum_{i=1}^{n} volume\ of\ tanks(m^3) \qquad (eqn\ 12)$$

  - The total volume of mud in the circulatory system is determined next by addition of the total hole volume and total tank volume.

$$total\ volume\ of\ mud(m^3) = hole\ volume(m^3) + tank\ volume(m^3) \qquad (eqn\ 13)$$

  - Calculation is made next on how much barite needs to be added.

$$total\ barite(kg) = barite\ per\ m^3(kg) * volume\ of\ mud(m^3) \qquad (eqn\ 14)$$

  - To find this amount of barite in sacks, then conversion from kilograms to sacks is required.

$$sacks\ of\ barite = \frac{kilograms\ of\ barite}{number\ of\ kilograms/sack} \qquad (eqn\ 15)$$

- **Rate of Addition**: The cycle time, which is the required for the mud to make one complete circulation from the suction intake at the pump to the bottom of the hole and back to the suction of the pump, is necessary to be calculated in order to figure out the rate of barite addition. It is also important that the cycle time is known as it is desirable to add all the barite during one circulating cycle.
  - First, the pump output is determined using any of equations 16 or 17 below.

$$pump\ output(m^3/\min) = pump\ output(litres/\min) * 0.001 \qquad (eqn\ 16)$$

OR

$$pump\ output(m^3/min) = \frac{litres}{stroke} * \frac{strokes}{min} * 0.001 \qquad (eqn\ 17)$$

  - Next, the cycle time is calculated.

$$cycle\ time(min) = \frac{total\ volume\ of\ mud(m^3)}{pump\ output(m^3/\min)} \qquad (eqn\ 18)$$

  - Finally, the rate of addition of sacks per minute is determined.

$$sacks\ per\ minute = \frac{total\ number\ of\ sacks}{cycle\ time(min)} \qquad (eqn\ 19)$$

It is worth mentioning that for the addition of every 100 sacks of barite, the mud volume increases by 4,250 kg, so in order to calculate how much increase there would be in total volume, the equation below is applied.

$$volume\ increase(m^3) = \frac{kilogram\ of\ barite\ added}{4{,}250} \qquad (eqn\ 20)$$

3.2 Rheological properties

These properties, otherwise known as flow properties, describe the flow characteristics of a mud under different flow conditions. In order to predict or know the effects of this flow, it is important that the flow behavior of the mud at various points of interest in the mud circulating system are known. The categories of drilling fluid are determined by the fluid behavior when it is subjected to an applied force (shear stress). Based on fluid behavior, then it would be important to know the following;

a) At what point of applied shear stress is movement initiated in the fluid?
b) Once movement has been initiated, what is the nature of the fluid movement (shear rate)?

The shear stress is the frictional drag exerted by a flowing fluid on the surface of a conduit, its magnitude dependent on the frictional drag between adjacent layers of fluid moving at different speeds, and the difference in velocities of adjacent layers next to the wall of the pipe. This difference in the velocities between adjacent layers across a flow path is termed the shear rate and for a driller, the effect of the flow at the wall where both shear stress and shear rate are at a maximum is his area of concern. Based on rheological properties, fluids can be categorized into two types depending on the viscosity of the fluid.

- Newtonian fluids
- Non-Newtonian fluids.

Very simple fluids such as oil or water that have the ratio of the shear stress to shear rate giving a constant are called **Newtonian fluids**. For such, measurement of shear stress at one shear rate is good enough to predict flow behavior at all shear rates. The ratio of shear stress to shear rate is termed the viscosity.

Viscosity, which is a measure of a fluids resistance to flow, is used to characterize flow behavior of Newtonian fluids. It has units of centipoises. Between layers of a liquid, it can be said to be a measure of the internal friction developed as one layer slides over another and shows how thick a fluid is.

Mathematically, viscosity μ = shear stress, τ /shear rate, γ.

Deformation of a Newtonian fluid occurs instantly once a force or shear stress (regardless of magnitude) is applied and thereafter, the degree of movement or flow is proportional to the applied stress. A phenomenon known as "**shear thinning**" occurs when the effective viscosity or the ratio of shear stress to shear rate is high at low shear rates and low at high or increased shear rate. Put differently, with increasing shear rate, the increase in effective viscosity over that of water decreases.

Drilling fluids where the flow relationship between shear stress and shear rate is non-linear are referred to as "**Non-Newtonian fluids**". They require a certain amount of shear stress to initiate flow, and thereafter, additional stress must be added as there is an increase in shear rate. For these kinds of fluids e.g. drilling fluids and cement slurries, they contain solids that connect together to form a structure causing flow to stop when the pressure or shear stress is reduced to a point which is less than the shear strength of the structure. This point at which the shear stress is required to initiate flow is called the fluid's yield stress or point. Allowing these non-Newtonian fluids to stand static for some time would continue to build a semi rigid structure causing the shear stress required to initiate flow to increase. The shear stress at this point is called the gel strength and the structure gains more rigidity with time resulting to increased gel strength. To the driller, 4 important areas where shear rate values are of paramount interest include;

- The annulus, where shear rates are low.
- The bits, having super high shear rates.
- The pits, with almost no shear rate values.
- The drill string and collars, through which hydraulic power is supplied to the bit from a pump.

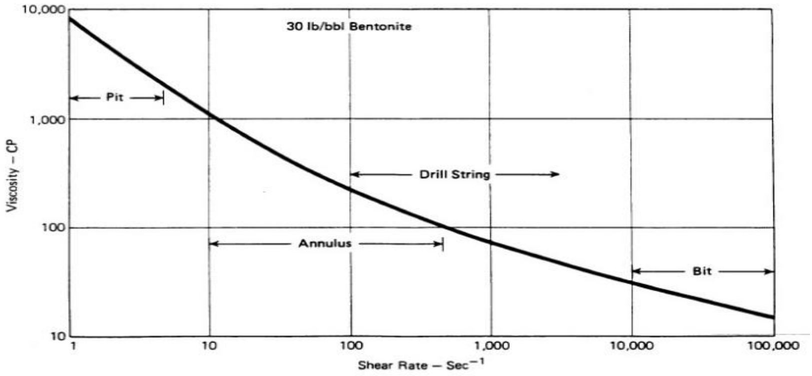


Figure 7 Viscosity curve for Bentonite suspension(Max R. Annis 1996).

Figure 7 shows a graph illustrating the different shear rate ranges in a mud circulating system and the effective viscosity of a bentonite suspension at these shear rates.

Non-Newtonian fluids can be categorized into 2 based on their shear stress/shear rate behaviors;

- Time-dependent fluids: Here, shear stress is dependent on duration of shear as represented in flow curves in figure 8. Examples are thixotropic fluids, rheopectic fluids.
- Time-independent fluids: For these, shear stress is independent of duration or time of shear. Examples include Bingham plastic fluids, pseudoplastic fluids, and dilatant fluids.

A third type of fluid are the viscoelastic fluids which exhibit elastic recovery from the deformation that occur during flow. They portray dual characteristics of being viscous and elastic. Some level of recovery is made after deformation upon removal of the stress. Examples of viscoelastic fluids include flour dough, bitumen, polymer melts. The flow curves for the different fluid types are shown in figure 9.

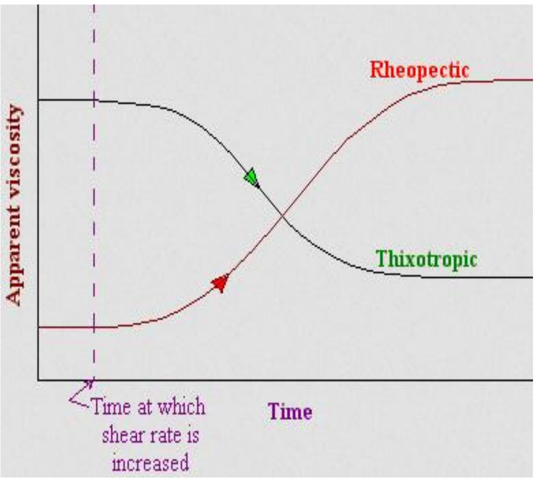


Figure 8 Time dependent fluid flow curves.

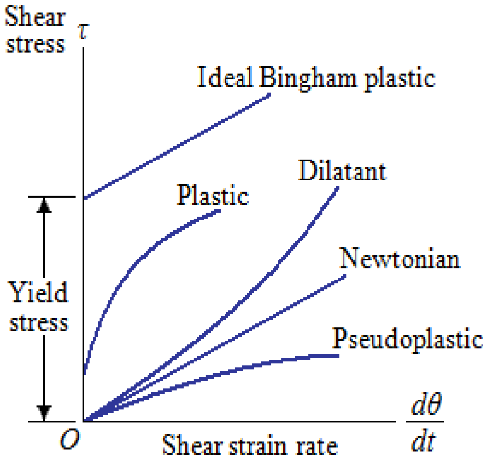


Figure 9 Flow curves for different fluid types.

3.2.1 Plastic viscosity.

It is an important mud property that gives a measure of the internal resistance to flow due to amount, type and size of solids in the mud. Due to collision of solids with one another and with the liquid phase of the mud, mechanical friction is produced deterring movement. The plastic viscosity is essentially a function of the viscosity of the liquid phase and the volume of solids contained in a mud. It describes the expected behavior of mud at the bit. In order to minimize high shear rate viscosity, the plastic viscosity has to be minimized. By decreasing the plastic viscosity, a driller correspondingly reduces the viscosity at the bit giving rise to higher ROP.

Generally, a high plastic viscosity is never desirable as one might think that having a high plastic viscosity would improve the hole cleaning ability of a mud, but this would only cause more harm than good. Actually, an increase in plastic viscosity, which causes a pressure drop increase down the drill string would retard the rate of flow and tend to offset any increase in lifting ability. It is therefore safe practice to keep the plastic viscosity as practically low as possible. The viscosity of the liquid phase is increased by addition of any soluble material.

In a mud, the volume of solid is made up of the sum of the dry volume of solids and the increase in volume caused by hydration which means that the water of hydration actually becomes a part of the solid so far as its effect on viscosity is concerned. As mentioned earlier, plastic viscosity can be increased by adding any type of solid to the mud, but with solids like clays which absorb water and swell, the plastic viscosity in increased further due to hydration. Factors such as time, temperature and agitation tend to disperse and allow hydration of individual clay platelets, which cause increased viscosities. To minimize plastic viscosity, then the amount of drilled solids in the mud must be kept at a very minimal level. However, to increase plastic viscosity, then increasing the percentage by volume of solids in the mud would make this happen, and if the volume percent solids remain constant, reducing the size of the solid would be the next option (Max R. Annis 1996). This can be done by either reducing the concentration of the solid or by adding a flocculant to increase the size of the particles thereby reducing the available surface area.

3.2.2 Yield point

This is a measure of the attractive forces between the particles in a mud as a result of opposite charges existing on the particle surfaces causing initial resistance to flow. This mud property is dependent on the type of solids present and their respective surface charges, the concentrations of these solids, and the type and concentration of other ions or salts that may be present.

Ways by which yield point is increased include;

- Increased solids concentration e.g. addition of bentonite, -as a result of increased surface charges if the solids are in an active mode. This reduces the space between the particles if they are inactive.
- Bit action by grinding of the particles thereby exposing more active surface charges.
- Less chemical treatment as dispersants making some active charges available for interaction.
- Introduction of contaminants such as salt, cement, e.t.c. that cause the mud particles to flocculate.

A fluid with large molecules or colloidal solids tend to have them bumping into one another producing large resistance to flow. With particles that are quite long compared to their thickness, then at low shear rates, the inter-particle interference will be quite large when they are randomly oriented in the flow stream causing them to link together. However, at increased shear rates, the effect of particle interaction is reduced as the particles will be arranged in line in the flow stream. This would lead to the linked bonds being broken and fluidity is increased. The combination of these two effects determines the yield point of a mud. Chemical treatment is used to control the electrical interaction of the solids while the mechanical interaction is controlled by regulating the quantity and type of solids in a mud.

In summary, a high yield point is caused by flocculation of clay solids or high concentrations of colloidal solids. Flocculation may be caused by high temperature, lack of sufficient deflocculent, or contaminants introduction. Flocculating agents or clay extenders are sometimes added to promote linking and cause higher yield points to be achieved. Examples include soda ash, polyacrylates and several calcium compounds. Two important mud functions which are associated with yield point include;

a) Hole cleaning capability and
b) Pressure control capability of the mud.

In terms of hole cleaning, the carrying capacity of a mud and the circulating annular pressure drop is increased by a higher yield point. Due to the fact that an increased yield point is detrimental to the problems of lost circulation and swabbing but good for hole cleaning, then a compromise has to be reached. Since hole cleaning capabilities are improved by increasing mud weights, then, higher yield points are usually not necessary in high weight muds to insure good cuttings carrying capacity. Furthermore, in terms of pressure control, this is often critical where high weight muds are required. As a consequence, the need to get yield point to a minimum usually outweighs any advantages of maintaining a high yield point in high density muds (Max R. Annis 1996).

3.2.3 Gel strength

This is a very vital mud property that measures the shear stress necessary to initiate flow of a fluid that has been quiescent for a length of time i.e. a measure of its thixotropic character. In very plain language, it is the ability of the mud to suspend cuttings when circulation stops. It is as a result of the association between electrically charged particles within the structure causing it to be rigid which means that anything that prevents or promotes the bonding of particles in the mud will decrease or increase respectively, the tendency to gelate. The rigidity of the structure so formed is dependent on factors as the quantity and type of solids in suspension, the chemical environment, time and temperature.

To measure the gel strength of a mud, a V-G meter is used by taking the peak dial deflection when the gel structure breaks, and this is done at selected times of 10 seconds and 10 minutes. These set times are necessary to provide a comparison of gelation qualities of muds and the difference between the two measured values simply represents the rate of gelation. Gel strength is measured in lb/100 sq. ft and for a mud to be able to suspend barite, it is necessary for it to have gel strength between 2 to 4 lb/100 sq. ft(Max R. Annis 1996). At values lower than this, barite will not suspend but settle down in the mud, regardless of its viscosity. A high viscosity would only have the effect of slowing down the settling rate and time. It is easier to have barite suspended in water based muds than oil based mud because the clay particles are very active in water, whereas in oil, they are essentially inert. A mud with a high viscosity will not necessarily have high gel strength as they are two different phenomena and should not be mixed up. As drilling operation takes place, the viscosity and gel strengths will both tend to increase as solids are being introduced e.g. drilled cuttings, barite, e.t.c. into the mud system. This can be reduced by addition of more fluids or surface removal of mud solids.

An increase in gel strength shows that flocculation has just begun as is the case in water base muds, while deflocculating reduces gel strength. Excessive gel strengths are not desirable in a mud as they cause the following problems:

- During tripping, large surge pressures could be encountered while running the pipe in causing possible breakdown of formation.
- During solids separation, it hinders them from settling down.
- Increased problems due to swabbing. This can cause the hole to cave in below the bit.

3.3 Solids Analysis

In order to control the filtration properties and flow behavior of a mud, the amount and types of solids in it are the main areas to concentrate on. This means that the amount of each of the different types of solids present would be determined and this is done by running some tests on the mud. The volume percent water and its specific gravity, the volume percent oil and its specific gravity, the volume percent solids, and the mud density are to be known. The major solids making up drill mud are barite (nonreactive solid) which is a weighting agent, drilled solids (non reactive solid) enjoined in the mud and bentonite (reactive solid or colloidal phase). The mud retort is the equipment used for measuring the volume percent oil and that of distilled water in the mud. With huge amounts of dissolved salt in the mud, the volume percent distilled water from the retort is smaller than the actual volume percent distilled water as these salts increase the volume capacity of water and its specific gravity. Once the actual water volume and oil volume have been established, the amount of suspended solids can be calculated by subtraction. If the mud density has been measured and the volume percent of suspended solids found, then the relative amounts of barite and low gravity solids can be calculated. As different types of solids have different cation exchange capacities, a distinction can be made between bentonite being the major faction of the mud and the low quality drilled solids, which have much lower exchange capacities. Carrying out a methyl blue test would help determine the cation exchange capacity of the clay solids and with knowledge of the volume percent low gravity solids, the percent bentonite and percent drilled solids can be estimated.

For high salt content muds, the following steps 1-4 are relevant for solid analysis;

Step 1: Calculate the volume of salt water in percent.

$$W_s = [(5.88 * 10^{-8} Cl^{1.2}) + 1]W \qquad (eqn\ 21)$$

W_S= volume of salt water in %,
Cl= chloride content measured from the filtrate in ppm
W=volume of water in mud from the retort in %

Step 2: Calculate the volume of the suspended solids in %.

$$S_s = 100 - O - W_s \qquad (eqn\ 22)$$

S_S = volume of suspended solids in %,
O= oil content in %

Step 3: Calculate the Average Specific Gravity (ASG) of the salt water.

$$W_{ASG} = [(1.94 * 10^{-6}) Cl^{0.95}] + 1 \qquad (eqn\ 23)$$

W_{ASG} =Average specific gravity of salt water.

Step 4: Calculate the Average Specific Gravity of the solids suspended in the mud.

$$S_{ASG} = \frac{(12MW) - (W_s * W_{ASG}) - (O * O_{ASG})}{S_S} \qquad (eqn\ 24)$$

S_{ASG} = Average specific gravity of suspended solids in the mud,
O= volume of oil in the mud in %
O_{AGS}= Specific gravity of base oil being used in mud (0.84 for diesel and 0.8 for IO)

For low-chloride muds, solids analysis can be started from step 5.

Step 5: Calculate the Average Specific Gravity of solids without salt in water phase.

$$S_{fASG} = \frac{(12MW) - (1W) - (O * O_{ASG})}{S_S} \qquad (eqn\ 25)$$

S_{FASG}= Average specific gravity of solids without salt in the water phase.

Step 6: Calculate the volume of Low Gravity Solids (LGS) in %.

$$LGS = \frac{S_S * (WM_{SG} - S_{ASG})}{1.6} \qquad (eqn\ 26)$$

LGS= volume % of Low Gravity Solids.

Step 7: Calculate the amount of LGS in lb/bbl.

$$LGS_{ppb} = 9.1LGS \qquad (eqn\ 27)$$

LGS_{ppb}= amount of LGS in lb/bbl.

Step 8: Calculate the volume of the weight material in %.

$$HGS = S_S - LGS \qquad (eqn\ 28)$$

HGS= volume of high specific gravity weight material in %.

Step 9: Calculate the amount of High Specific Gravity Weight material in pounds (lbs).

$$HGS_{ppb} = HGS * (3.5 * SG_{WM}) \qquad (eqn\ 29)$$

HGS_{PPb}= amount of high specific gravity weight material in lb/bbl.

Step 10: Calculate the amount of Bentonite (High-quality LGS) in the mud.

- If the cation exchange capacity (CEC) of the formation clays and the methylene blue test (MBT) of the mud are known.
  a) **Calculate the amount of bentonite in the mud in lb/bbl.**

$$B_{ppb} = \left[\frac{1}{1 - \frac{F_{CEC}}{65}}\right]\left(M_{MBT} - 9\frac{F_{CEC}}{65}\right) * LGS \qquad (eqn\ 30)$$

B_{ppb}= amount of bentonite in the mud in lb/bbl
F_{CEC}= CEC of the formation solids,
M_{MBT}= MBT of the mud

  b) **Calculate the volume of bentonite in the mud in %**

$$B = \frac{B_{ppb}}{9.1} \qquad (eqn\ 31)$$

B = amount of bentonite in the mud in %.

- If the cation exchange capacity (CEC) of the formation clays are not known.
  a) **Calculate the volume of bentonite in %.**

$$B = \frac{M_{MBT} - LGS}{8} \qquad (eqn\ 32)$$

  b) **Calculate the amount of bentonite in the mud in lb/bbl.**

$$B_{ppb} = 9.1 * B \qquad (eqn\ 33)$$

Step 11: Calculate the volume of drill solids in %.

$$DS = LGS - B \qquad (eqn\ 34)$$

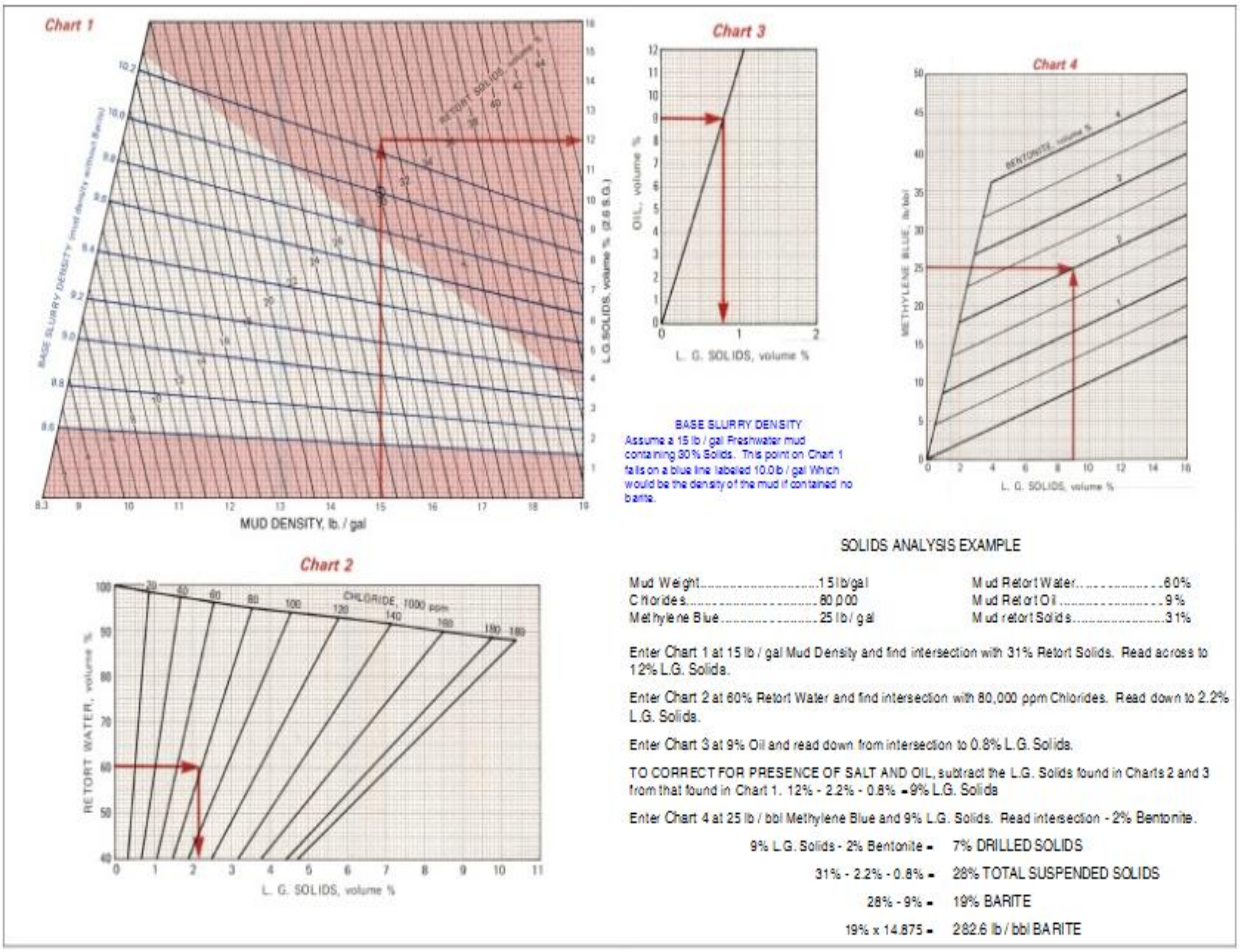
DS = volume of drill solids in %.

Step 12: Calculate the amount of drill solids in the mud in lb/bbl.

$$DS_{ppb} = 9.1 * DS \qquad (eqn\ 35)$$

Alternatively, a large fold-out chart shown in figure 10 could be used graphically to solve some of the preceding equations.

- Chart 1 – This chart is used to solve the simplified equation when it is assumed that the mud contains no oil, but just fresh water.
- Chart 2 – The percent bentonite can be estimated from this chart when the corrected low-gravity solids content has been determined.
- Chart 3 – This shows the percent low-gravity solids that should be subtracted from the value indicated by the first chart.
- Chart 4 – when the mud contains oil, this chart can be used to indicate the percent low-gravity solids that should be subtracted from the original value to correct for the presence of the oil.



BASE SLURRY DENSITY
Assume a 15 lb / gal Freshwater mud containing 30% Solids. This point on Chart 1 falls on a blue line labeled 10.0 lb / gal Which would be the density of the mud if contained no barite.

SOLIDS ANALYSIS EXAMPLE

Mud Weight	15 lb/gal	Mud Retort Water	60%
Chlorides	80,000	Mud Retort Oil	9%
Methylene Blue	25 lb / gal	Mud retort Solids	31%

Enter Chart 1 at 15 lb / gal Mud Density and find intersection with 31% Retort Solids. Read across to 12% L.G. Solids.

Enter Chart 2 at 60% Retort Water and find intersection with 80,000 ppm Chlorides. Read down to 2.2% L.G. Solids.

Enter Chart 3 at 9% Oil and read down from intersection to 0.8% L.G. Solids.

TO CORRECT FOR PRESENCE OF SALT AND OIL, subtract the L.G. Solids found in Charts 2 and 3 from that found in Chart 1. 12% - 2.2% - 0.8% = 9% L.G. Solids

Enter Chart 4 at 25 lb / bbl Methylene Blue and 9% L.G. Solids. Read intersection - 2% Bentonite.

9% L.G. Solids - 2% Bentonite = 7% DRILLED SOLIDS

31% - 2.2% - 0.8% = 28% TOTAL SUSPENDED SOLIDS

28% - 9% = 19% BARITE

19% x 14.875 = 282.6 lb / bbl BARITE

Figure 10 Four fold chart for graphically solving some solids analysis equations(Kranenburg et al. 2011; Max R. Annis 1996).

3.4 Filtration

When mud pressure is higher than formation pressure, filtrate is forced to flow into the formation with deposition of mud solids on the walls of the borehole, thus with filtration, both the filtrate invasion and filter cake deposition could pose problems. The problems posed by filtrate invasion are more of formation evaluation and completion problems. For instance, flushing of the zone around a well bore may be caused by excessive fluid loss to the point that incorrect logging and testing information are gathered. Furthermore, another problem could be a huge reduction of formation permeability by fluid invasion. Consequently, the type of filtrate is of greater significance than the volume of filtrate lost and from the stand point of drilling operation, more focus should be given to the filter cake than the volume of filtrate. This is because it has a direct connection with problems such as lost circulation, differential pressure sticking, torque and drag and poor primary cement jobs. Therefore of primary concern should be ways to minimize the thickness and permeability of the deposited cake.

Two types of filtration could occur –"**dynamic and static filtration**". Dynamic filtration occurs when the fluid is being circulated and when it is at rest, it is static filtration.

Dynamic filtration differs from static filtration in that the flow of mud tends to erode away the cake as it is deposited by the filtration process. As the filter cake piles up, it gets to a point where the rate of deposition equals the rate of erosion. At this equilibrium thickness, the rate of filtration becomes constant. This is not the case with static filtration. In static filtration, the cake grows continually with time increasing in thickness and causing a continuous reduction in filtration rate. Static filtration should be controlled in order to control filter cake thickness and dynamic filtration should be controlled in order to check invasion of filtrate. The erosion rate is a function of annular velocity, mud viscosity and flow regime.

- Increasing annular velocity or mud density would result in an increase in erosion rate, yielding an increased filtration rate.
- Changing the flow from laminar to turbulent will also increase the erosion rate, therefore, it is of great importance that the flow regime in the annulus is laminar and that the velocity is kept practically as low as possible to insure greatly reduced dynamic filtration rates.
- Increasing the viscosity will bring about a proportionate increase in erosion rate. Dynamic filtration rates may be increased also by fluid loss control additives that cause huge increases in mud viscosity.

The deposition rate is a function of the rate at which solids are being transferred to the cake by the filtrate flow. The amount of solids and the type as well play a role in how much filtrate is allowed to pass through the filter cake. Bentonite has been seen to be the most effective additive in reducing dynamic filtration rate. Some materials which are very good for reducing static filtration have been found to have very little effect on dynamic filtration as they cause a decrease in the permeability of the cake thereby causing a decrease in the equilibrium cake thickness rather than a reduction in the rate of filtration, hence, such materials will not function in reducing dynamic filtration rate, but can only reduce the API fluid loss. Examples of such materials include lignosulfonate, starch, oil, CMC, lignite (Kranenburg et al. 2011; Max R. Annis 1996).

Static filtration control on the other hand is important in controlling the properties of the filter cake deposited downhole as the cake is the primary cause of filtration related drilling problems. Of major interest are the cakes thickness, permeability, slickness and texture. The volume of filtrate is important but more important is the cakes characteristics, so both should be looked into critically.

Talking about the characteristics of the filter cake, it is desirable that the cake is thin and of low permeability. The permeability of the cake is proportional to the product of cake thickness and fluid loss. The slickness of a cake is related to the frictional drag that can develop during differential pressure sticking. Using a stickometer, the effect of a mud treatment on this property can be evaluated with the test. This sticking coefficient is increased with increasing mud density due to increased solids content of the cake and to minimize this effect, drilled solids have to be removed, with addition of bentonite or special lubricating additives. The texture of filter cake is a characteristic for which no direct test is run. It is so closely related to the other cake characteristics that it will probably never be a problem if the other cake properties are in good shape. Static filtration tests are normally of two types – a low temperature low pressure test run at surface temperature and 100 psi filtration pressure, and a high temperature high pressure test at 300^oF and 500 psi filtration.

3.5 Rheological Models.

In the drilling sector, the use of the rotational viscometer (Fann VG meter) has influenced the rheology models and measurements to a large extent, with the aim of simplifying rheology control in the oil field. The 6-speed viscometer consisting of 3, 6, 100, 200, 300 and 600 rpm is normally used for higher quality rheology control. To determine rheology constants, three different approaches are presented, they include;

a) 2 data points oil field approach
b) 2 data points standard approach
c) 6 data points regression approach

With plotted values of shear stress against shear rate from a rotational viscometer, flow curves otherwise known as rheograms can be produced. A very important point to note is that the readings obtained from the Fann VG viscometer are usually multiplied by a correction factor of 1.06 to give the true shear stress values(Skalle 2010). This is due to the geometry and calibration of the viscometer.

3.5.1 Newtonian Model.

Once a force or shear stress is being applied, a Newtonian fluid will begin to deform and move. Thereafter, the degree of movement is proportional to the stress applied. A linear relationship exists between the Shear Stress (τ) and the Shear Rate (γ). The graph in figure 11 shows this relationship.

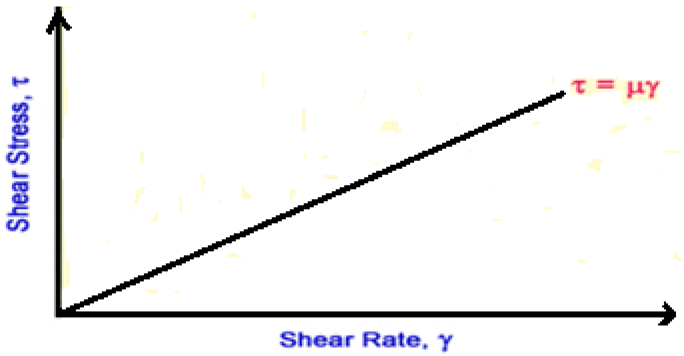


Figure 11 Plot demonstrating Newtonian model.

The Newtonian model is demonstrated mathematically by equation 36.

$$\tau = \mu \gamma \qquad (eqn\ 36)$$

Where, μ is the viscosity.

Using the 2 data points standard approach, one constant is sufficient to describe this model. A reading at 300 rpm is used for Newtonian fluids.

$$\mu_{300} = \frac{\tau_{300}}{\gamma_{300}} \qquad (eqn\ 37)$$

μ_{300} = viscosity at 300 rpm.
τ_{300} and γ_{300} = shear stress and shear rate at 300 rpm respectively.

3.5.2 The Bingham Plastic Model.

This model predicts that fluid movement will take place only after a minimum value of shear has been applied. This minimum value is called the Yield Point, YP of the fluid as seen in figure 12. Once movement has been initiated, the relationship between τ and γ is linear i.e Newtonian, with the constant being called the Plastic Viscosity, PV. PV is dependent on both temperature and pressure.

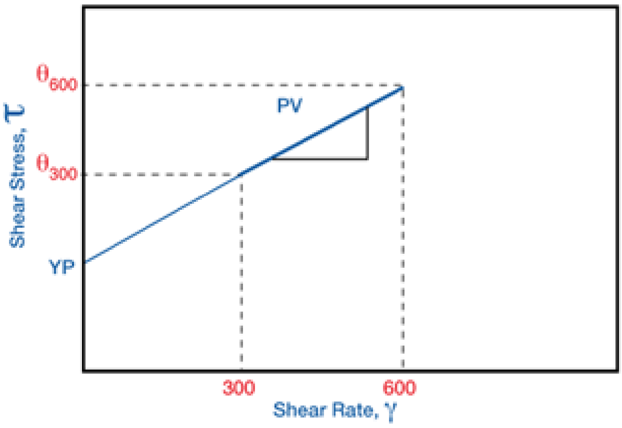


Figure 12 Plot demonstrating Bingham Plastic model.

The Bingham Plastic Model is given mathematically as

$$\tau = PV * \gamma + YP. \qquad (eqn\ 38)$$

This model has two approaches, the oil field approach and the standard approach.

The oil field approach: The fann VG viscometer is calibrated to suit the Bingham model. The shear rate at 300 is designed to be equal to one shear rate unit by getting the difference between the 600 and 300 rpm dial readings. The plastic viscosity and yield point using this model are given by equations 39 and 40 respectively.

$$\mu_{pl} = \theta_{600} - \theta_{300} \qquad (eqn\ 39)$$

$$\tau_y = \theta_{300} - \mu_{pl} \qquad (eqn\ 40)$$

μ_{pl} and τ_y are the plastic viscosity and yield point respectively.
θ_{600} and θ_{300} are the viscometer dial readings at 600 and 300 rpm respectively.

The standard approach: Here, a conversion factor of 1.06 is used to convert the obtained readings to true shear stress after the SI units have also been converted. The viscosity and the yield points are calculated as given by equations 41 and 42 respectively.

$$\mu_{pl} = \frac{\tau_{600} - \tau_{300}}{\gamma_{600} - \gamma_{300}} \qquad (eqn\ 41)$$

$$\tau_y = \tau_{600} - \mu_{pl} * \gamma_{600} \qquad (eqn\ 42)$$

Both the oil field approach and the conventional standard procedure give almost similar results with an error of around 1 % for both constants.

The Bingham Plastic Model represents to a high level, behaviors of such fluids as bentonite, slurries, cement and low gravity oils. A typical Bingham fluid will possess no gel strength but a high viscosity. It is however not suitable for more complex fluids as errors would arise. This model simulates fluid behavior in the high shear rate range (300 to 600 rpm), but would give errors in the low shear range.

3.5.3 The Power Law Model.

This model suits better, the behavior of most fluids particularly polymer based fluids and attempts to improve on the Bingham plastic model at low shear rates. The Power law is more complicated than the Bingham Plastic model in that it does not assume a linear relationship between the shear stress and shear rate. However, it shares a similar feature with Newtonian fluids in that the plots of shear stress against shear rate run through the origin. At zero shear rates, fluids that obey the Power Law rheological model have no shear stress. The disadvantage being that most fluids possess yield stress, but with this model, this cannot be accounted for. Just like the Bingham Plastic model, but to a lesser degree, the Power Law model predicts efficiently, fluid behaviors at high shear rates, but shows a degree of error at the lower shear rates(Skalle 2010). A representation of the Power Law model is given in figure 13.

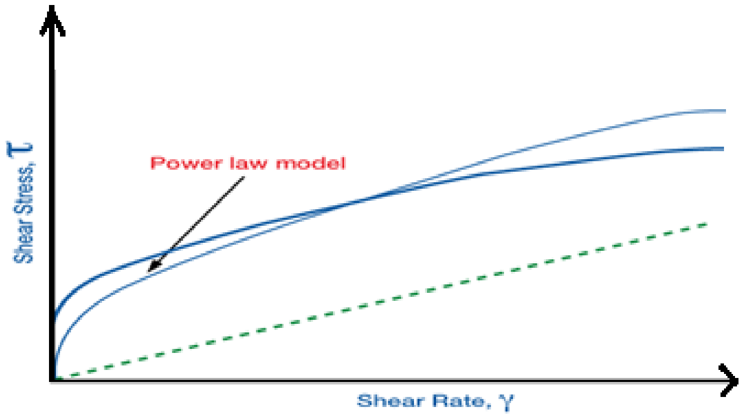


Figure 13 Plot demonstrating the Power law model.

The power Law model best describes a fluid in which the shear stress increases as a function of the shear rate to the power of some index. This model is demonstrated mathematically by equation 43 as

$$\tau = K(\gamma)^n \qquad (eqn\ 43)$$

τ = Shear stress
k = Consistency index
γ= Shear rate
n = Power Law index or flow behavior index.

Figure 14 shows a log-log plot of shear stress vs. shear rate for Power Law fluids giving a linear relationship. The slope of the line is the "n" value and the intercept is the "k" value. The "n" value signifies a fluid's degree of non-Newtonian behavior over a given shear rate range.

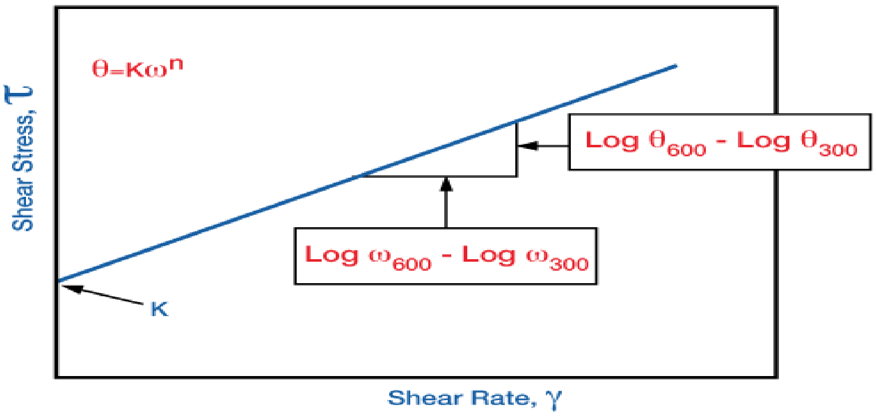


Figure 14 Log-log plot demonstrating Power law model.

Mathematically, the "n" and "K" values are expressed by equations 44 and 45 or 46 respectively.

$$n = \frac{log\tau_{600} - log\tau_{300}}{log\gamma_{600} - log\gamma_{300}} \qquad (eqn\ 44)$$

$$k = 1.067\ \frac{\theta_{300}}{(511)^n} \qquad (eqn\ 45)$$ OR $$k = 5.11\ \frac{\theta_{300}}{(511)^n} \qquad (eqn\ 46)$$

3.5.4 The Modified Power Law

This model is as a result of the combined theoretical and practical aspects of both the Bingham Plastic and the Power Law models. It is also known as the Yield Power Law or Herschel-Bulkley Model. The values of "n and K" are similar to those derived using the Power Law model. Assumptions made by this model are that a certain amount of stress must be applied to fluids to initiate movement and for these fluids having a yield stress, the calculated values of "n and K" will be different.

For Modified Power Law fluids, the relationship exists

$$\tau = \tau_0 + K(\gamma)^n \qquad (eqn\ 47)$$

Where
K= consistency index
n =flow behavior index
τ_0= the fluid´s yield point at zero shear rate. In theory, this value is similar to the Bingham Plastic yield point, though it`s calculated value is different.

With n = 1, the Bingham Plastic Model is formed.
With τ_0 = 0, the Power Law Model is derived.

The Modified Power Law Model is very suitable for both water and oil based drilling muds because both exhibit shear thinning behavior and have a shear stress at zero shear rate. It is however, very complex to find the n, K and τ_0 values. Figure 15 shows the combined view of the flow curves for the different rheological models.

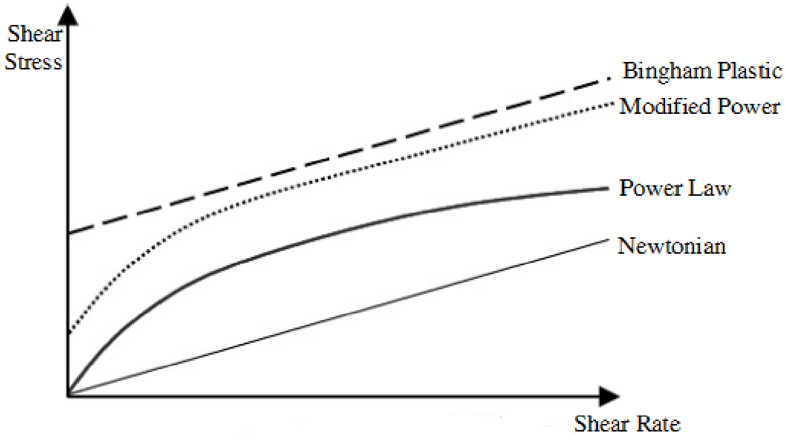


Figure 15 Plots demonstrating the different rheological models (Hawker 2001).

4. Experimental Investigations.

In order to evaluate and enhance mud performance, analysis are required on daily basis, at several times and occasions. As a result, many checks and tests are carried out onsite and some in the laboratory to ensure a proper, smooth running drilling operation. In this chapter, experiments carried out on the makeup water and drilling mud samples would be discussed. Five different mud samples to be used for geothermal drilling in Tønder, would be experimented on to study their properties and which would perform best under different scenarios. Two different sources of water would be used as the continuous phase for mixing the mud – "fresh water from the tap and sea water from the Island Fanø". Comparison would also be made on mud behaviors and properties based on the use of these different water sources for a few of the experiments.

Before going into the experiments, a very brief description of all chemicals and additives used and their functions is outlined below;

- Bentonite: Powdery clay mineral predominantly montmorillonite, which is used as a viscosifying additive and also good for reducing fluid loss.
- Barite: A dense sulfate mineral used to add weight to drilling mud.
- Potassium chloride (KCl): A white crystalline salt of the alkali metal potassium. It is a swell inhibitor at high concentrations, and helps to encapsulate mud particles. It is also a major source of K^+ ions in potassium polymer muds.
- MI PAC ELV: An ultra low viscosity polyanionic cellulose polymer for fluid loss control in water based drilling mud.
- DUO TEC-NS: Duo-vis xanthan gum is a high molecular weight biopolymer used for increasing viscosity in water based system. Small quantities provide viscosity and suspension of weight materials, and it produces a highly shear-thinning and thioxotropic fluid.
- Soda ash (Na_2CO_3): It is a weak base in granular powder form soluble in water and dissociates into Na and CO_3 ions in solution. Its main function is to reduce calcium ion in water base drilling muds and make up waters. It also increases pH of makeup water and flocculates spud mud.
- Glycol: A liquid solution which is viscous and soluble in water at low temperatures belonging to the alcohol series. It is used as effective shale inhibitors and improves lubricity.
- Carboxymethyl Cellulose (CMC): Used primarily as a fluid loss additive. It also gives higher apparent viscosities at low shear rates.
- Starch: A drilling mud additive used to control fluid loss in water muds ranging from freshwater to saturated salt to high-pH lime.
- Sodium Hexametaphosphate (SHMP): Granular white substance used as effective deflocculants for clays in fresh water. Helps to reduce viscosity and overcome cement contamination of fresh water.
- Sodium Pyrophosphate Decahydrate: Crystalline white substance which deflocculates clays in fresh water and acts as a viscosity reducing agent.
- WBM Premix: Viscous water based prepared mud.

4.1 Water Chemistry.

The suitability of water for use during mud mixing is a vital aspect to be considered prior to preparing a mud sample. For the experiments to be carried out, fresh water from the university laboratory tap and sea water from the Island Fanø were used.

a) **pH Determination**: The pH of a solution is a measure of its hydrogen ion concentration. There is an equilibrium hydroxyl ion concentration for each hydrogen ion concentration, so by measuring the hydrogen ion concentration, the concentration of hydroxyl ion is also measured in effect. In measuring pH, a pH paper or pH meter could be used, but a pH meter preferably was used in the experiments as it gives more accurate values. The pH meter is calibrated using two buffer solutions that are of different pH values so the pH of the actual sample to be determined can fall within range. The electrode is rinsed with demineralized water each time after being used in a solution. Figure 16 gives a pictorial view of a standard pH meter.

Figure 16 A standard pH meter.

The pH scale is logarithmic and it is on a scale of 0 to 14 with a neutral point of 7. It is acidic from 0 to 7 and alkaline from 7 to 14. The pH of the tap water was measured at a value of 7 indicating neutrality, while the sea water was measured at a pH of 7.47. Literature has it that for good mixing, pH values above 8.5 and below 10.5 are very suitable (Max R. Annis 1996). Alkaline pH is necessary for a number of reasons;

- Corrosion rates are suppressed more at higher pH values.
- It helps for better mixing of bentonite.

b) **Hardness**: The amount of Ca^{2+} and Mg^{2+} present in water determines if water is hard or not and the atomic absorption spectometry is used to detect their levels. Theoretically, a desirable limit for both cation concentrations in water should be less than 100 mg/l (100 ppm) for it to be considered soft water and above 100 mg/l, water is considered hard. Tests conducted by the university laboratory staff showed that the amount of Ca^{2+} was given as 50 mg/l (conducted in past experiments) and 254.4 mg/l in fresh tap water and sea water respectively. The amount of Mg concentration in fresh water and sea water was found to be 4 mg/l (conducted also in past experiments) and 948.05 mg/l respectively. Caustic soda (NaOH) is used sometimes to suppress the amount of soluble calcium contained in the mud in a mud. Soda ash (Na_2CO_3) is mainly used to precipitate Ca^{2+} ions but care should be taken not to over treat water with soda ash as a carbonate problem would occur. Overtreatment would also pose problems of high yield point, high gel strength and fluid loss therefore the level of Ca^{2+} should be kept at acceptable levels of not more than 100 mg/l.

c) **Chloride Determination**: The salinity of water is determined by the amount of chloride ions present in the water solution and Ion Chromatography is used to detect its level. It is important because increased salinity could have detrimental effects on properties as yield point, gel strength, degree of hydration e.t.c of the mud. Theoretical data shows that a desirable limit of chloride ions should be less than 10,000 mg/l, as fresh water has chloride content between 1 to 250 mg/l. The chloride content of the sea water was found at about 10,500 mg/l by the laboratory staff. The importance of determining the salt content of water cannot be overemphasized because most salts are contaminants in the mixture especially the chlorides of the alkali metals e.g NaCl and KCl. The following will happen if the chloride content is more than 10,000 mg/l;

- Poor hydration resulting to the mud not being able to swell.
- Huge increase in apparent viscosities.
- Increase in yield point and gel strength.
- Water loss increase.
- Loss of thixotropic property.

4.2 Experiment 1

Title: **Free standing swell test**.

Aim: To determine the swelling ability of drilling mud samples.

Requirements: mud samples, electronic weigh balance, measuring cylinders, fresh water and spatula.

Procedure

The measuring cylinders were filled with fresh water to the 100 ml mark and 2 grams of each of the samples weighed out using the electronic weigh balance. 0.25 ml of each sample was put in each of the measuring cylinders containing water, using a spatula and allowed to wait until all mud had been absorbed and settled at the bottom. The mud particles settlement was allowed on its own without any stirring. A small batch was added again and allowed some time to be absorbed and settle. This trend was continued until the total mass of mud sample was used up. Following this, they were allowed to stand for 18 hours, and thereafter, the volume of swelled mud measured from the graduated cylinder.

Set up

The experimental set up is a simple one consisting of five graduated cylinders and the mud samples in fresh water as shown in figure 17.

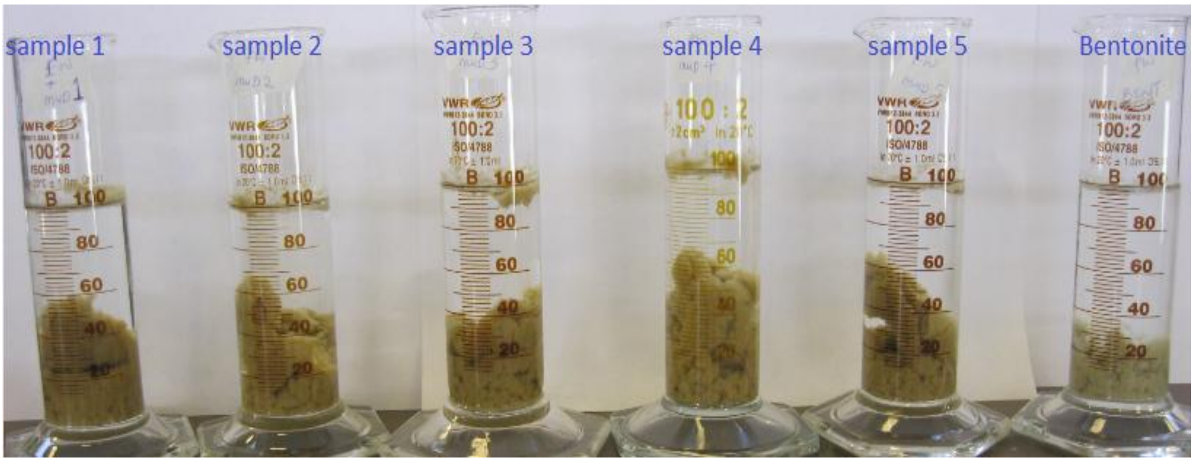


Figure 17 Swell Test for the different mud samples.

Theory

Basically, the swelling type that occurs in most clays is the surface hydration where water molecules are adsorbed on crystal surfaces of the clay. Clay swell ability is attributed to interlayer cation exchange which could be Mg^{2+}, Ca^{2+}, Na^+, k^+ and H^+. Hydrogen bonding holds a layer of water molecules to the oxygen atoms, which are located and exposed on the clay crystal surfaces. Subsequently, layers of water molecules align to form a quasi-crystalline structure between unit layers, which results in increased distance between corresponding planes in adjacent unit layers (c-spacing)(Fink 2011). This leads to an increase in volume and swell of the clay. Figure 18 shows an illustration of this concept.

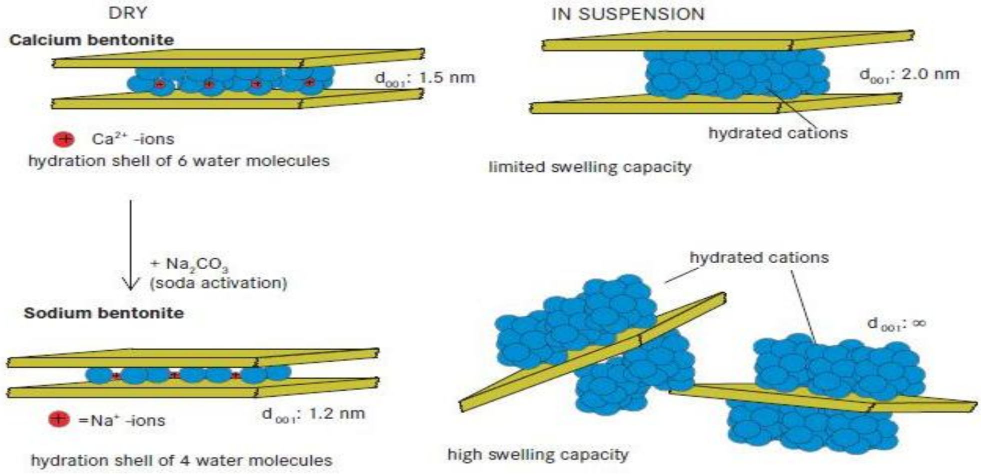


Figure 18 Swell mechanism of mud (Koch, 2008).

Observation

All the mud samples were observed to have swollen but in different capacities. The swellings were irregular in the different cylinders with uneven surfaces which made measurement difficult. However, the highest levels were taken for each and all samples recorded values between 35-70 ml.

Results

The table of results for the free standing swell tests and corresponding chart is presented below;

Table 3 Results of Free Standing Swell Test.

Samples	Mass (g)	Volume of water (ml)	Waiting time(hrs)	Swelled volume (ml)
1	2	100	18	62
2	2	100	18	66
3	2	100	18	60
4	2	100	18	64
5	2	100	18	66
Bentonite	2	100	18	36

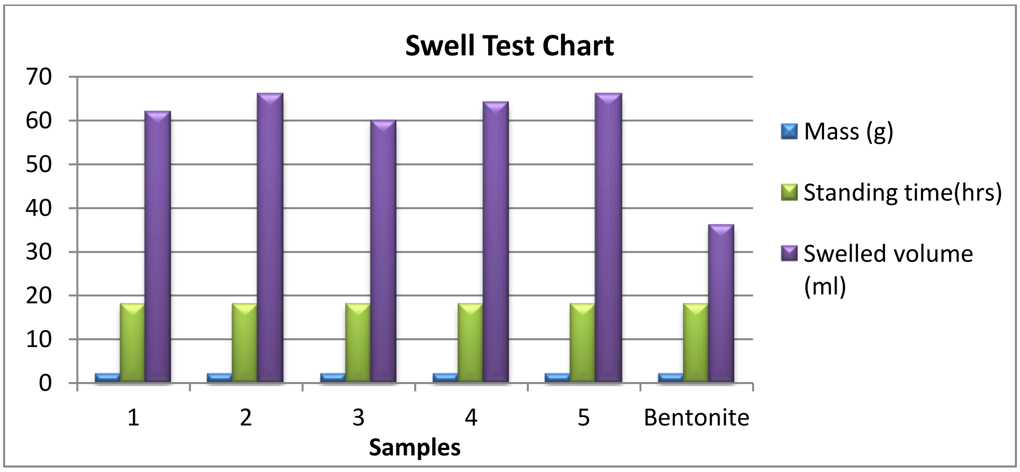


Figure 19 Graphical representation of Swell Test result.

Discussion/Conclusion

From literature, it is reviewed that muds suitable for drilling should have swelled to the 12-16 ml or cm^3 mark or above on the cylinder and if they have swelled less than or equal to the 4-6 ml mark, they are considered ineffective in coating the sides of the borehole during the drilling operation and hence, not suitable as thickening agents. With reference to the swell test chart in figure 19, all mud samples have swollen beyond the 12-16 ml mark, hence, it can be said that they all have good swelling abilities and could be used for coating the side walls of the well bore during drilling.

4.3 Experiment 2

Title: **Swell inhibition Test.**

Aim: To check the swell inhibitive properties of some additives.

Requirement: mud samples, bentonite, graduated cylinders, KCl, glycol, fresh water, electronic weigh balance, and spatula.

Procedure

2 grams of each of the mud samples including the bentonite were weighed out. To the measuring cylinders, fresh water was added until it got to the 100 ml mark.

a) With KCl, 2g of KCl was weighed out and poured into one of each of the cylinders containing the fresh water and stirred vigorously until a homogenous solution was obtained. The 2 g of each mud sample was poured into each of these measuring cylinders in small portions at a time until all 2 grams had settled at the bottom without stirring. The same was applied to the bentonite sample. The resulting mixture allowed standing for 18 hours.
b) With Glycol, 5 ml of glycol was measured out and poured into one of each of the cylinders containing fresh water and stirred vigorously until a homogenous solution was obtained. The 2gram of each mud sample was poured into each of these measuring cylinders in small portions until all were settled at the bottom. The same was done to the bentonite sample. The mixture was allowed to stand for 18 hours.
c) With a mixture of KCl and Glycol, 2 grams of KCl and 5 ml of glycol were added to the fresh water in the cylinders and stirred. Afterwards, the mud samples were added until all 2 grams were poured in, without stirring. The same treatment was given to the bentonite sample. The mixture was allowed standing for 18 hours.
d) With an increased mass of KCl to 4g, this amount was added to the water in the measuring cylinders and the mud samples, each of 2 gram weight were poured in small amounts until all was dissolved and settled. The same was done for the bentonite sample. This was allowed to stand also for 18 hours. After the set period of time, the levels of each sample were recorded from the measuring cylinders.

Theory

Water based glycol (poly glycol) are becoming increasingly popular and are said to have exceptional shale inhibition properties and good lubricity. The high level of inhibition obtained is mainly as a result of shale hardening effect as the shale becomes harder than it was originally. The glycols are strongly adsorbed by the clay, and water is displaced from the clay surface with formation of ordered glycol structures. In combination with a range of salt types, eg KCl, it is said that salt plays an active role in the inhibition mechanism. The nature of these structures and their stability in aqueous fluids is controlled strongly by the presence or absence of potassium cations. The potassium cations from the salt are rapidly consumed by the clay or shale during cation exchange but maintain sufficient k^+ ion to stabilize it by reducing hydration and swelling (McGill et al. 1997).

Results.

Pictorial views of each of the samples with the different additives for the swell inhibition test are given from figures 20-25. A tabular form and chart representation of the performance of the samples under investigation with the different swell inhibitive additives are shown in table 4 and figure 26 respectively.

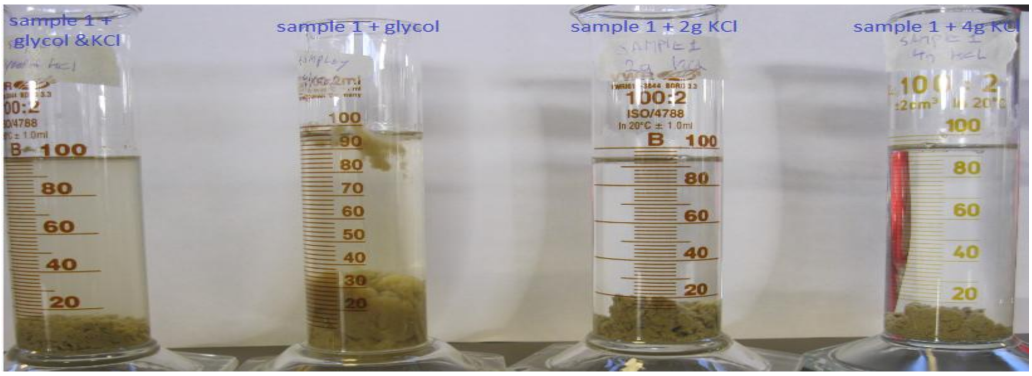


Figure 20 Inhibitive Swell Test Set up for mud sample 1

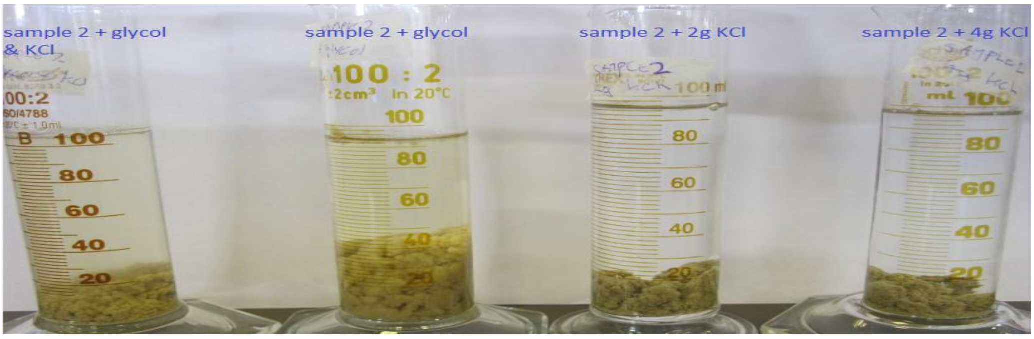


Figure 21 Inhibitive Swell Test Set up for mud sample 2

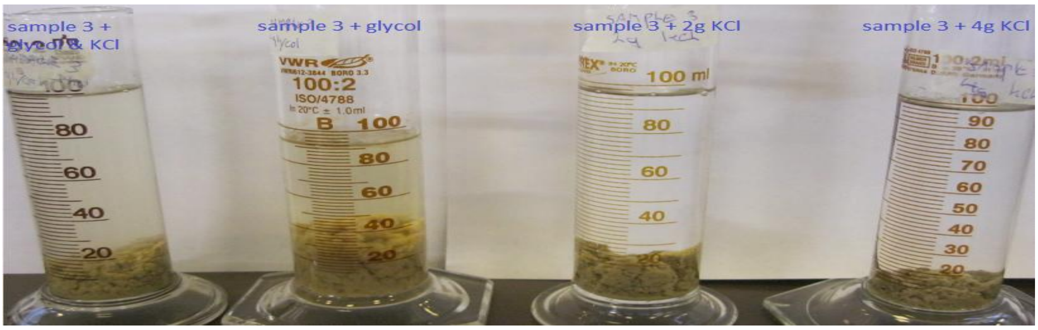


Figure 22 Inhibitive Swell Test Set up for mud sample 3

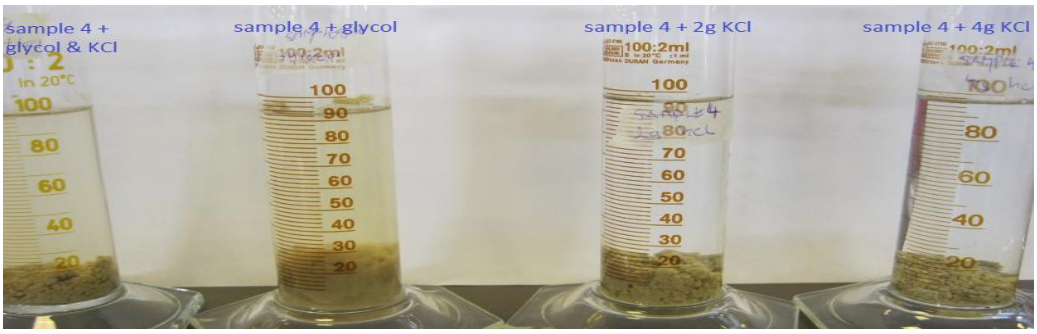


Figure 23 Inhibitive Swell Test Set up for mud sample 4

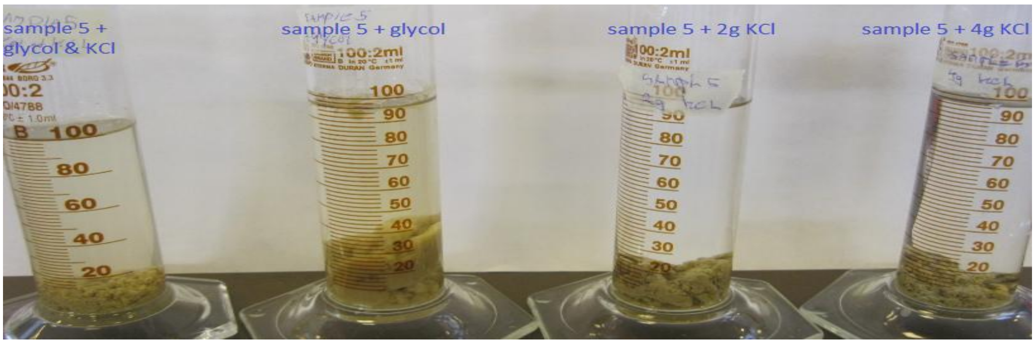


Figure 24 Inhibitive Swell Test Set up for mud sample 5

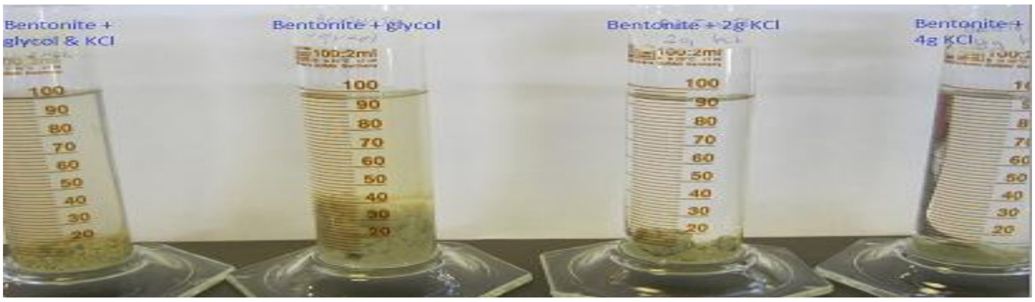


Figure 25 Inhibitive Swell Test Set up for Bentonite sample

Table 4 Results of Inhibitive Swell Test.

Samples	Glycol & 2g KCl (ml)	Glycol (ml)	2g KCl (ml)	4g KCl (ml)	Time of standing (hrs)
1	**14**	**38**	**20**	**18**	**18**
2	**20**	**50**	**22**	**18**	**18**
3	**20**	**46**	**24**	**16**	**18**
4	**24**	**34**	**24**	**18**	**18**
5	**12**	**42**	**22**	**18**	**18**
Bentonite	**18**	**40**	**20**	**14**	**18**

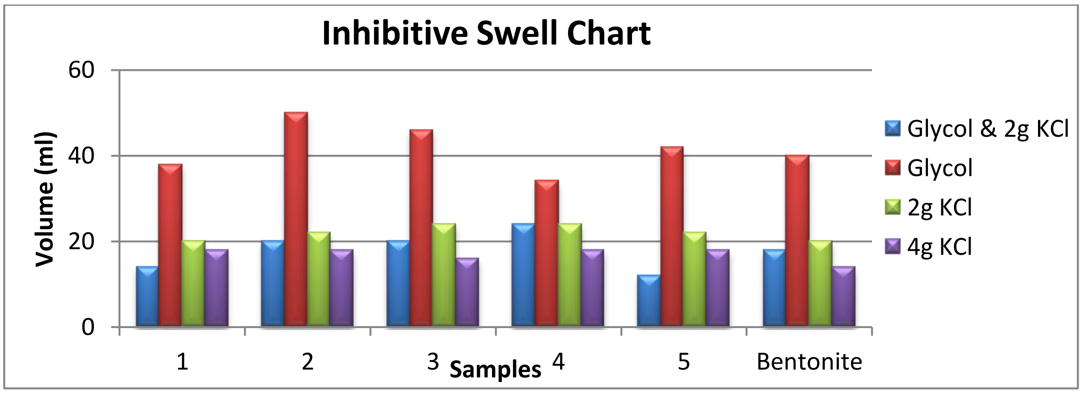


Figure 26 Graphical representation of Inhibitve swell test results.

Discussion and Conclusion.

From the results, it can be said that hydration and swelling of the mud occurred at high volumes when the mud was mixed with glycol alone at ambient temperature. However, with a combination of KCl and glycol, there was not much increase in the clay volume meaning that the KCl added had a major effect on the inhibitive action of the duo additive. Furthermore, with 2 gram KCl alone mixed with the mud, there was also inhibited swelling observed, and this would be traced to the k^+ ions in the mixture causing the mud not to hydrate and swell. This showed that KCl is a major player in the inhibition process. To further verify this, with an increased amount of KCl from 2 gram to 4 gram, further levels of inhibition were observed. To conclude, for glycol to be said to aid in shale inhibition, it would be in combination with KCl as the k^+ ions are the key inhibitive substances and the combination of both forms a stable complex that displaces water from the clay particles. Also, increasing the concentration of KCl will increase the inhibition effect.

Additional Information/Experimentation.

Further experiments were carried out using glycol to experience the cloud point phenomenon. The cloud point is the temperature at which poly glycol changes from being totally soluble to insoluble, and this is the phenomenon responsible for the inhibition and stabilization of shales by glycol. At temperatures above the cloud point, poly glycols form colloidal droplets or micelles resulting in a micro-emulsion. When insoluble poly glycols are adsorbed onto clay/shale formations, they create a protective shield against incoming water and when they are adsorbed on wall cake, they tend to reduce rate of fluid loss reducing the wall cake thickness. The glycol solution was mixed in water (5 ml in 100 ml water) and heated to 110^oC without getting to the cloud point, the concentration was increased by adding another 5 ml glycol, but still could not reach the cloud point so it was assumed it was a high cloud point glycol.

4.4 Experiment 3

Title: **Sand content test**

Aim: To determine the quantity of sand in the mud samples.

Requirement: 200 standard mesh number sieve, 10 ml graduated cylinders, electronic weigh balance, mechanical vibrator, collecting container, mud samples, spatula, funnel.

Procedure

The weights of the 10ml cylinders were measured using the weigh balance. 10 ml of each mud sample was measured out in the measuring cylinders tapping the cylinders regularly to make sure they were well compressed and compacted. The combined weights of sample and cylinder taken and the weights of the mud samples found. The samples were transferred onto the 200 mesh size sieve surface which had a collecting container underneath. With vigorous agitation using the hands and also a mechanical vibrator, the sieve was agitated to allow particles smaller than its size pass through, and larger particles to be retained on it. This was done until it no particles were passing through the sieve. The volume of the sand was measured once transferred into the 10 ml cylinder and the combined weight taken to determine the weight of sand content in the mud. Observations were also made of the nature of the sand sieved from the mud samples.

Set up

In the absence of a standard sand content kit which is the recommended equipment for carrying out a sand content test, a more or less dry test was carried out using a standard 200 mesh size sieve and a vibrator as seen in figure 27.

Figure 27 Sand content test apparatus.

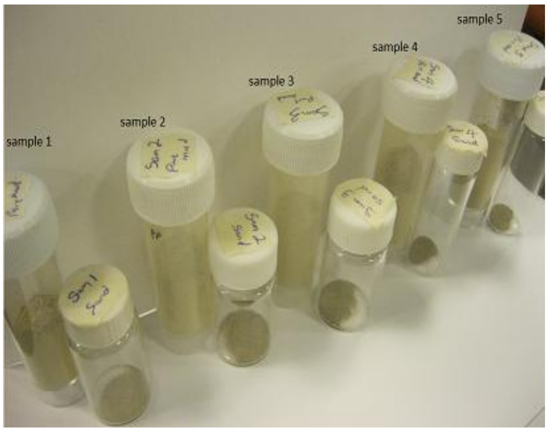


Figure 28 Sieved mud and sand for each sample.

Observation

It was observed that the sand which was sieved out from the mud had a gritty feel on the hand, and contained some other fine particles, mainly black and grey in colour. Also, it is worth mentioning that some mud particles and sand particles were lost due to two different reasons;

- There was adhesion between the mud particles, the sand particles, the funnel, the measuring cylinder and the funnel holding back some of the particles.
- Due to the light particle sizes, some of them were lost to the atmosphere during transfer from one point to another and also during sieving.

Results.

The sand content in the mud was determined both as volume and weight percentages as can be seen in table 5 and the results are also shown graphically in figure 29.

Table 5 Results showing Sand Content Test.

Samples	Wt of cylinder (g)	Wt of cyl. & mud(g)	Wt of mud (g)	Vol. of cylinder (ml)	Wt. of sand (g)	Vol. of sand (ml)	Vol. % sand.	Wt % sand.
1	**32.15**	**41.88**	**9.73**	**10**	**0.52**	**0.39**	**3.9**	**5.3**
2	**31.69**	**43.07**	**11.38**	**10**	**0.68**	**0.50**	**5.0**	**6.0**
3	**31.72**	**43.47**	**11.75**	**10**	**0.51**	**0.38**	**3.8**	**4.3**
4	**31.80**	**43.91**	**12.11**	**10**	**0.47**	**0.30**	**3.0**	**3.9**
5	**31.80**	**44.31**	**12.51**	**10**	**0.47**	**0.30**	**3.0**	**3.8**

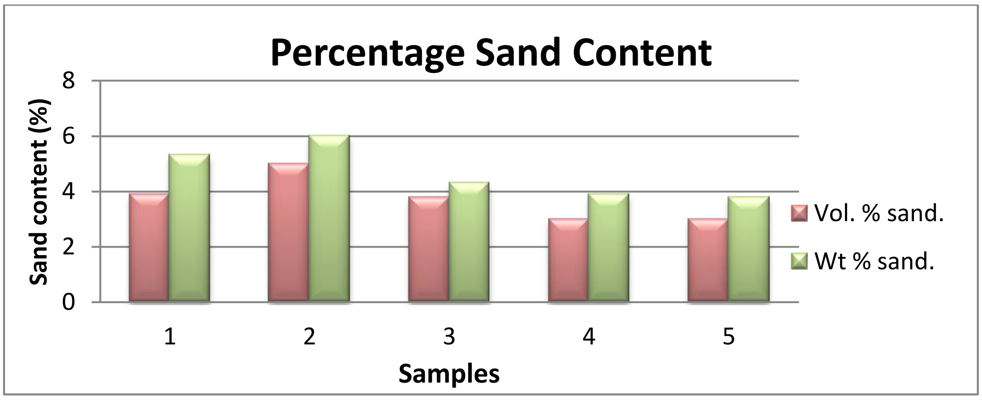


Figure 29 Graphical representation showing sand content in different mud samples.

Discussion and Conclusion

From the chart shown in figure 29, it can be seen that sample 2 had the most sand content both in volume and weight percent, while samples 4 and 5 had the least sand content in both volume and weight percentages of 3.0 and 3.8-3.9 respectively. Therefore, considering amount of sand contents in the different mud samples, samples 4 and 5 would be recommended for use.

It is worth mentioning that there is a generally acceptable level of sand content by volume percent of 2% according to API specification that can be in the mud for drilling. The following results obtained show values higher than this acceptable level, but this is as a result of the method used in conducting the experiment. The standard sand content kit should be used which is more of a wet process, but in this experiment, the standard sand content kit was not used due to its unavailability.

4.5 Experiment 4

Title: **Viscosity reduction test.**

Aim: To check the effect of phosphate thinners or dispersants on mud viscosity.

Requirement: Mud sample 1, fresh water, viscometer, hand mixer, measuring cylinder, electronic weigh balance, thinners – SPP, Sodium pyrophosphate decahydrate ($Na_4O_7PO_2.10H_2O$) and SHMP, Sodium hexametaphosphate $(NaPO_3)_6$.

Procedure

12 grams of the mud sample 1 was measured out and poured into 250 ml fresh water and stirred vigorously to obtain homogeneity and afterwards, the viscometer dial readings obtained. Furthermore, 0.15 gram of SHPP was weighed out in four places and each time one part was added to the mud sample, the viscosity and gel strengths were measured. This was done until all four portions were mixed. The procedure was repeated with SPP and all readings recorded. The viscosity reducing effects of both de-viscosifiers were compared to determine which has a better viscosity reducing potential.

Theory

High viscosity muds are brought about by flocculation of clay particles caused by the positive charge site at the edge of a clay platelet linking to the negative surface of another clay platelet. Polyphosphates upon dissociation would produce phosphate ions (PO_4^{3-}) which would neutralize the positive charges at the edge of the clay platelets, which destroys the ability of the platelets to bond together. This would increase the negative charge density on the platelets and cause them to repel one another resulting in deflocculation and thus reducing the resistance to flow of the suspension(Skalle 2010).

Phosphates are more effective at low temperatures below 82°C and at low concentrations, otherwise, they revert to orthophosphates, which are flocculating in nature. They cannot perform at high salinity concentrations or in high calcium concentrated solutions because they are sequestering agents for calcium and would be degraded in a calcium solution. Generally, thinners are more effective in solutions with pH values greater than 8 as this would increase the number of negative groups on the clay edges and thus stabilize the clay system(Max R. Annis 1996).

Results

Table 6 Viscosity Reduction Test results using SHMP.

Wt. of sample (g)	Wt. Of SHMP (g)	viscosity Dial		PV (cP)	YP (lb/100 sq ft)	Gel Strength (lb/100 sq ft)	
		600 rpm	300 rpm			10 secs	10 mins
12	0	151	127	24	103	31	34
12	0.15	120	89	31	58	26	25
12	0.30	100	75	25	50	23	22
12	0.45	85	65	20	45	20	20
12	0.60	80	60	20	40	18	19

Table 7 Viscosity Reduction Test using SPP

Wt. of sample (g)	Wt. Of SPP (g)	viscosity Dial		PV (cP)	YP (lb/100 sq ft)	Gel Strength (lb/100 sq ft)	
		600 rpm	300 rpm			10 secs	10 mins
12	0	176	138	38	100	34	34
12	0.15	100	69	31	38	15	17
12	0.30	68	46	22	24	8	16
12	0.45	56	37	19	18	5	10
12	0.60	49	32	17	15	3	8

Discussion and Conclusion.

From the tables shown above, it can be seen that both phosphate additives actually reduced the viscosity of the mud, but in different capacities. The reduction in the viscosity dial readings after each 0.15 g added is more with sodium pyrophosphate decahydrate (SPP) than it is with sodium hexametaphosphate (SHMP). Similar effects can also be noticed with the yield points and plastic viscosities. The total percentage reduction in yield point and plastic viscosities after addition of the 0.6 gram of SHMP are 61% and 17% respectively, while that after addition of the 0.6 gram of SPP are 85% and 55% respectively, so SPP shows a higher level of reduction, but generally, both phosphates reduced yield point more than they did plastic viscosity.

Furthermore, the reduction in both 10 seconds and 10 minutes gel strength tests after each addition of 0.15 gram was more with SPP than with SHMP. The total reduction in 10 seconds and 10 minutes gel strengths after the addition of the 0.6 gram of SPP is 91% and 76% while with SHMP, 42% and 44% respectively was reduced. Reduction in these properties were due to deflocculation of the mud particles.

To conclude, from the results gathered, it can be said that sodium pyrophosphate decahydrate (SPP) is a more effective thinner than sodium hexametaphosphate (SHMP). It is also better for reducing the yield point and gel strengths of mud, if these properties are required.

4.6 Experiment 5

Title: **Fluid loss experiment.**

Aim: To determine the extent of fluid loss using various fluid loss additives.

Requirement: B-169 vacuum system, 9 cm filter paper, stopper, retort stand, Buchner funnel, suction beaker, suction pipe, flask, measuring cylinders, beakers, stop clock, viscometer, mud samples, fluid loss additives – CMC (CarboxyMethyl Cellulose natrium salt), starch $(C_6H_{10}O_5)_n$,MI PAC, bentonite, fresh tap water, sea water, pH meter, hand mixer, hot magnetic plates.

Procedure

a) **With fresh tap water.**
   2 grams of each of the 5 mud samples was weighed out and poured out in beakers containing 100 ml water. This was stirred vigorously with a hand mixer and the viscosity measured first without any additives being added. 0.2 gram of starch was weighed out and added to each of the mud samples. The mixture was thoroughly stirred and 50 ml measured out and afterwards, the viscosity and pH values measured. This was done for each of the additives in turn. Next, the vacuum system was turned on and the measured quantity of 50 ml mixture poured into the Buchner funnel containing the filter paper as shown in the set up. This was allowed to stand for 80 minutes and afterwards, the filter cake formed on the filter paper scrapped off and weighed. The filtrate volume was also collected in a measuring cylinder and its volume and pH recorded. Two samples were experimented at the same time as the vacuum system had a provision for 2 simultaneous experiments.

b) **With Sea water.**
   With sea water, a mixture with the mud does not mix as the mud immediately settles down and the water on the top just a few seconds after mixing as shown in figure 30, so the mud was prehydrated first and due to the high amount of Ca^{2+} in the sea water as foretold in the calcium contentration test and its low pH of 7.47, soda ash was added.

Figure 30 View showing mixture of mud in sea water after few seconds of stirring.

5 gram of each mud sample was weighed out and 100 ml of fresh water measured. This was mixed, with temperature of 40^{o}C and agitation and allowed to wait for 6 hours to prehydrate the mud samples. Afterwards, 50 ml of sea water was measured out and 0.3g of soda ash poured in and mixed gently. 0.3g of each of the additives was mixed with the sea water and soda ash solution. After the prehydration time of 6 hours, the mud mix is added to the resulting solution with the seawater, soda ash and additive and stirred thoroughly with a mixer. 50 ml of this grand mix is measured out, and the pH as well as the viscosity determined. The mixture was poured into the Buchner funnel and allowed a standing time of 80 minutes after which the filter cake was scrapped off the filter paper and weighed, the filtrate volume recorded alongside the filtrate pH.

Set up

The experimental set up consists of the water vacuum system as shown in figure 31 and schematically demonstrated in figure 33. The machine helps to produce a suction pressure which exerts a downward pulling effect on the mud and figure 32 shows the agitation and heating of the mud samples using the hot magnetic plates.

Figure 31 Filtration set up using water vacuum system.

Figure 32 Agitation and heating of mud samples.

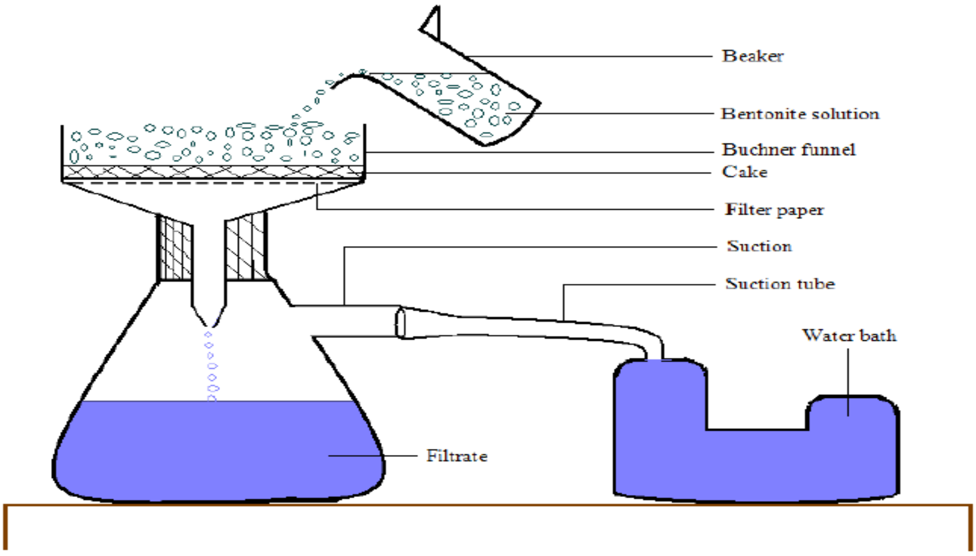


Figure 33 Schematic of filtration set up using water vacuum system(Eghai project, 2004)

Precaution

- Moisten the filter paper with water to adhere to the Buchner funnel for proper filtration.
- At the end of the experiment, disconnect the suction pipe from the suction beaker before turning off the vacuum pump to avoid back flow of water into suction beaker.
- Hold the suction beaker firmly with a clamp to avoid tripping over.
- When mixing the soda ash with salt water, do not mix any other additives at the same time, and mix gently.

Theory

In a porous, permeable formation, hydrostatic pressure compresses the liquid part of a drilling mud forcing it into the formation. The solid part left behind, which is the filter cake or mud or wall cake, should have properties good enough to reduce the loss of liquid called fluid loss, from the mud to the formation at a very low rate. A thin filter cake is most desired as a thick cake continues to grow thicker and causes problems such as reducing the diameter of the hole, causing tight spots where the drill string can get stuck (Van Dyke & Baker 1998). Furthermore, if the fluid loss is high, sloughing and caving of formation would result especially in shale formation. In addition to sloughing, formation damage may occur if the rate of fluid loss is high, as water enters tiny openings in the producing zone and blocking permeability by expansion of surrounding rocks, hence a good filter cake is thin, slick and virtually impermeable. This could be achieved by adding special agents to the drilling mud that pack tightly together and help to improve its ability to form a filter cake or wall-building-ability .

Observation.

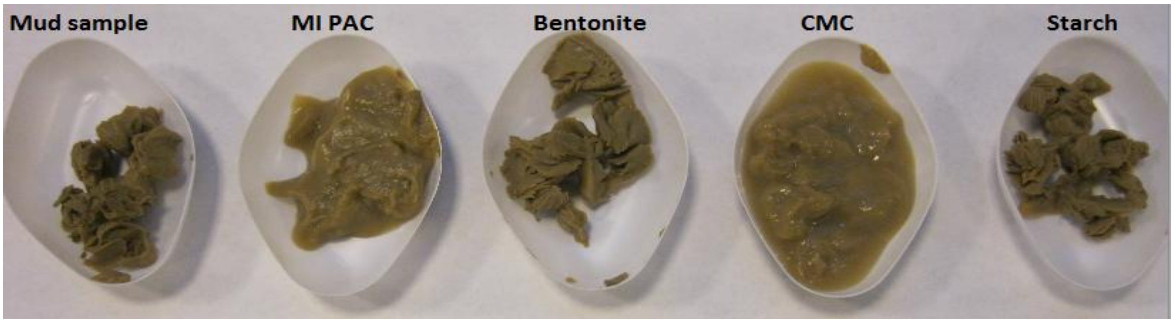


Figure 34 Filter cakes formed using different additives and fresh tap water source.

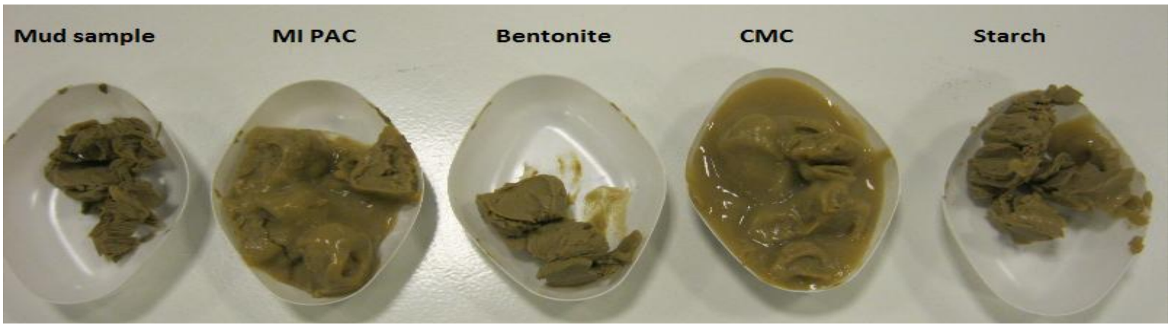


Figure 35 Filter cakes formed using different additives and sea water source.

The views above show the filter cake left on the filter papers which were scrapped off. It was observed that the filter cakes from both fresh tap water and sea water sources using the different additives were very similar. The filter cakes using MI PAC and CMC were thinner, more pastry and weighed more. Those from bentonite, starch and the pure sample were thicker, drier and more solid, and weighed less.

Results.

The results of the fluid experiments are represented in tables 8 through 12 using fresh water as the continuous phase, and represented graphically in figures 36 and 37. For sea water source, tables 13 through 17 show the results and represented graphically in figures 38 and 39.

Table 8 Fluid loss experiment results using fresh tap water for sample 1

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	34	15.12	31	21	10.13	9.81
Starch	30	2.32	32	21	9.64	9.52
CMC	26	11.55	35	25	9.56	9.46
Bentonite	46	5.26	26	17	10.42	10.07

Table 9 Fluid loss experiment results using fresh tap water for sample 2

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	28	13.43	35	24	10.25	9.68
Starch	41	6.77	34	23	10.33	10.03
CMC	26	13.58	46	32	10.08	9.76
Bentonite	36	3.65	25	17	10.24	9.95

Table 10 Fluid loss experiment result using fresh tap water for sample 3

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	32	9.78	37	25	9.27	9.05
Starch	42	4.51	30	20	9.47	9.33
CMC	28	13.95	36	27	9.46	9.11
Bentonite	43	5.15	32	19	9.56	9.33

Table 11 Fluid loss experiment results using fresh tap water for sample 4

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	30	13.78	35	24	10.00	9.66
Starch	40	6.48	40	27	10.24	9.81
CMC	27	18.46	52	37	10.25	9.67
Bentonite	36	4.27	26	18	10.19	10.01

Table 12 Fluid loss experiment results using fresh tap water for sample 5

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	32	8.39	42	22	10.05	9.69
Starch	38	4.85	36	23	10.26	9.78
CMC	26	10.94	38	26	10.31	9.56
Bentonite	40	4.4	27	18	10.26	9.93

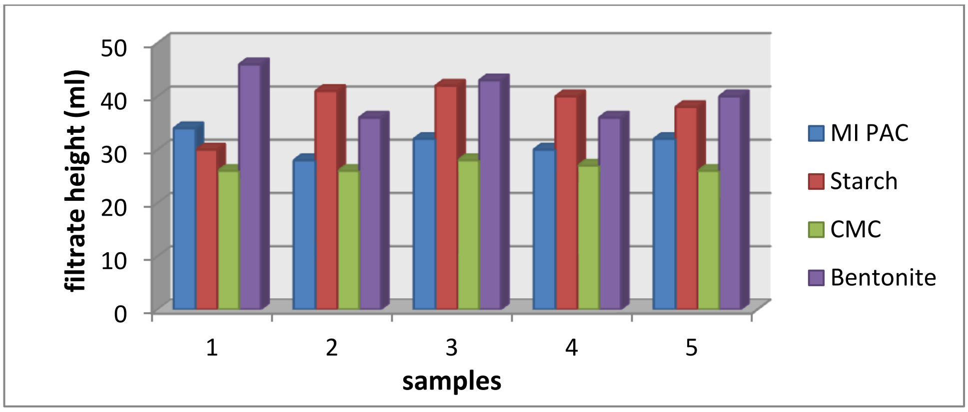


Figure 36 Filtrate levels for the different samples and additives using fresh tap water source.

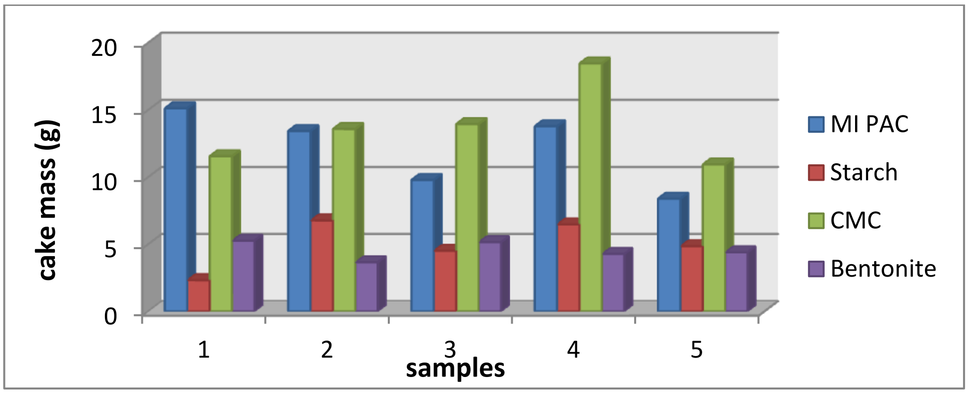


Figure 37 Cake mass for different samples and additives using fresh tap water source.

Table 13 Fluid loss experiment results using sea water for sample 1

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	19	18.87	46	31	9.81	9.7
Starch	41	6.68	32	23	9.78	9.72
CMC	21	19.98	54	34	9.95	9.6
Bentonite	40	5.24	33	23	9.87	9.57

Table 14 Fluid loss experiment results using sea water for sample 2

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	14	19.71	59	41	9.83	9.8
Starch	46	6.2	34	24	9.73	9.75
CMC	16	24.1	45	29	9.76	9.73
Bentonite	43	7.17	38	30	9.74	9.79

Table 15 Fluid loss experiment results using sea water for sample 3

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	24	12.48	46	32	9.65	9.69
Starch	44	5.4	36	25	9.72	9.72
CMC	23	10.03	47	34	9.65	9.64
Bentonite	43	4.71	35	26	9.58	9.59

Table 16 Fluid loss experiment results using sea water for sample 4

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	26	16.51	49	34	9.87	9.83
Starch	37	7.53	46	35	9.86	9.77
CMC	24	22.12	53	36	9.87	9.67
Bentonite	34	4.83	48	36	9.79	9.67

Table 17 Fluid loss experiment results using sea water for sample 5

Additives	**Vol. Of filtrate (ml)**	**Wt. Of cake (g)**	**Viscosity Dial**		**pH**	
			600 rpm	**300 rpm**	**mud mix**	**mud filtrate**
MI PAC	25	13.02	46	30	9.8	9.62
Starch	36	5.75	44	33	9.65	9.61
CMC	20	18.37	50	34	9.73	9.58
Bentonite	37	6.68	43	32	9.71	9.68

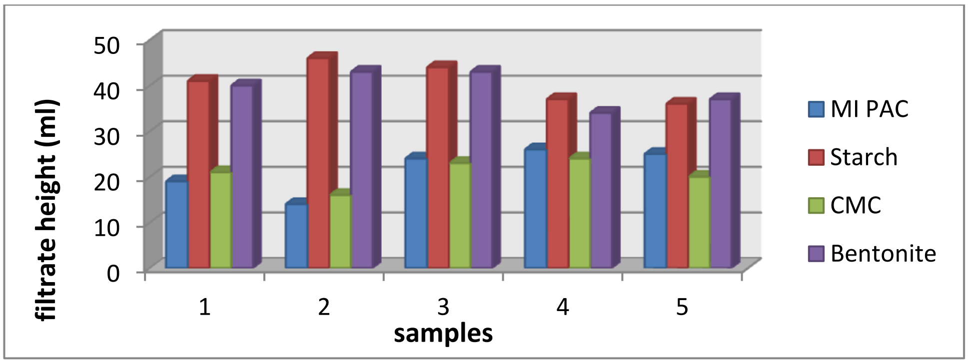


Figure 38 Filtrate levels for different samples and additives using sea water source.

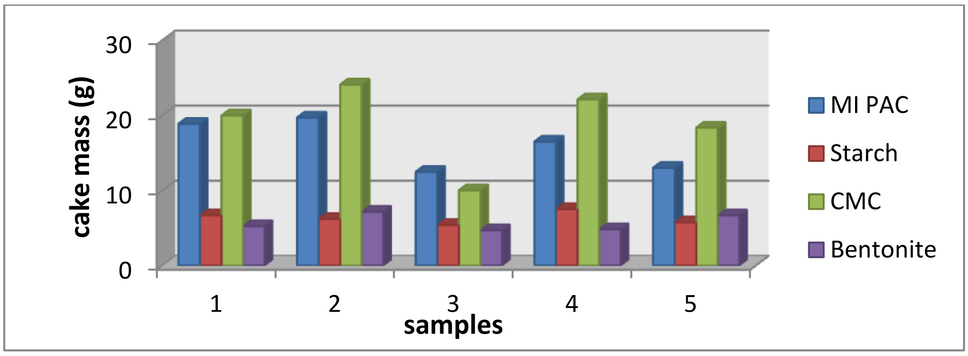


Figure 39 Cake mass for different samples and additives using sea water source.

Discussion and Conclusion.

Starch is a polymer which thickens water thereby making it suitable for fluid loss, and increases plastic viscosity as a consequence. It is unaffected by salinity or hardness, but thins when temperature is increased. CMC is also a polymer which increases viscosity as well, and at higher concentrations, it enhances fluid loss reduction even more. It is however degraded at high temperatures and would be less effective in its fluid loss property in the presence of high salinity water above 50,000 mg/l chloride or Ca concentrations above 100 mg/l. MI PAC, is an ultra low viscosity polyanionic cellulose polymer which also is affected by temperature, but increases viscosity of the fluid part of the mud as they do not react with the solids, becoming an integrated part of the fluid phase which makes it a good fluid loss agent.

Apart from starch, the other additives would be affected by using sea water as the continous phase for the experiment as it contains high amounts of chloride and calcium concentrations, therefore the mud samples were prehydrated first for 6 hours with fresh water, with agitation and heating, to allow for better mix. Also, soda ash was added to the salt water to reduce the concentration of Ca.

From the figure 36 for fresh water source, it can be seen that the filtrate level measured using CMC as fluid loss additive was less than it was with other additives. Furthermore, the mass of filter cake formed using CMC as shown in figure 37 was more than with any other additives. This demonstrates the fact that a thinner and less permeable cake was formed with CMC than with any other additive as it produced the highest resistance allowing the least amount of fluid to pass through it, and its weight was more because it retained more water than the other additives. Similar results were obtained using the sea water source as shown in figures 38 and 39. MI PAC also showed very good fluid loss properties in both water sources as it was the next preferred in performance.

To conclude, both CMC and MI PAC are very good fluid loss additives producing filter cakes with desirable fluid loss characteristics.

4.7 Experiment 6

Title: Effects of viscosifiers on Water Base Mud Premix.

Aim: To determine which viscosifier under study best increases viscosity of the Water Base Premix mud by incremental addition of the viscosifiers.

Requirements: Water Based mud premix, mud samples, viscosifiers – bentonite, CMC, Duo Tec NS, hand mixer, fann viscometer.

Procedure

250 ml of the WBM premix was measured out in a measuring cylinder and its viscosity and gel strengths determined using the viscometer. Subsequently, 1 gram of each viscosifier was measured and mixed with the premix and the viscosities and gel strengths measured. Repeatedly, 1 gram of each viscosifier was added and the viscosities and gel strengths measured until the total amount of added viscosifier for each was 4 grams. The effect of adding these viscosifiers in increased quantities was observed to determine which best increases viscosity.

Results.

The results are presented in tabular form as shown in tables 18 through 20.

Table 18 Results showing effect of increased bentonite mass on WBM premix.

Sample	Mass of Bentonite(g)	Viscosity Dial		PV (cP)	YP (lb/100 sq. Feet)	Gel Strength (lb/100 sq.feet)	
		600 rpm	300 rpm			10 secs	10 mins
WBM Premix	0	93	62	31	31	9	13
	1	85	58	27	31	8	12
	2	83	57	26	31	8	12
	3	84	58	26	32	9	12
	4	81	55	26	29	8	12

Table 19 Results showing effect of increased Duo Tec mass on WBM premix.

Sample	Mass of Duo Tec (g)	Viscosity Dial		PV (cP)	YP (lb/100 sq. Feet)	Gel Strength (lb/100 sq.feet)	
		600 rpm	300 rpm			10 secs	10 mins
WBM Premix	0	93	62	31	31	9	13
	1	98	70	28	42	10	15
	2	137	125	12	113	20	26
	3	245	180	65	115	41	53
	4	> 300		N/A	N/A	66	81

Table 20 Results showing effect of increased CMC mass on WBM premix.

Sample	Mass of CMC (g)	Viscosity Dial		PV (cP)	YP (lb/100 sq. Feet)	Gel Strength (lb/100 sq.feet)	
		600 rpm	300 rpm			10 secs	10 mins
WBM Premix	0	93	62	31	31	9	13
	1	122	85	37	48	10	15
	2	197	142	55	87	15	19
	3	> 300	227	> 73	> 87	22	27
	4	> 300		N/A	N/A	28	38

Discussion and Conclusion.

The viscometer dial gauge has its reading from 0 to 300, so values written greater than 300 indicate that the values went past the highest point and off the scale. Values which are blank on the table indicate that the values were not checked further, and those with N/A indicate that the values could not be found either because one of the values was above 300 or there was a blank reading.

With reference to the tables above, it can be seen that with bentonite on the Premix WBM, its plastic viscosity was reduced on the first addition of bentonite, and on subsequent additions, it remained steady showing there was no effect afterwards. The yield point however showed a somewhat steady trend on increasing the amount of bentonite as was the gel strengths.

With an increasing amount of Duo Tec, the plastic viscosity decreased on adding the first couple of masses, but afterwards, was seen to increase sharply. The yield point however showed an increasing trend from the start of its addition. The Gel strengths also increased with increasing amounts of Duo Tec.

With increased amounts of CMC, it showed both a steady increase in both plastic viscosity and yield point. The same can be said of the gel strengths, but when compared to Duo Tec, its increase in gel strength is not as high as that got from addition of Duo Tec.

To conclude, from the above results, it can be said that both Duo Tec NS and CMC could be used to increase the viscosity of the WBM Premix, but if a lower gel strength is needed, then CMC could be used, and if otherwise, the Duo Tec NS could be applied. The bentonite additive gave the lowest effects on increased rheological properties and would be the least recommended.

4.8 Experiment 7

Title: **Effect of viscosifiers on rheology of drilling mud samples**.

Aim: To determine which mud samples have the best viscosifying effects with increased amounts of viscosifiers.

Requirement: Mud samples, fresh water, viscometer, hand mixer, viscosifiers – bentonite, CMC and Duo Tec NS, electronic weigh balance, measuring cylinder.

Procedure

5 grams of each mud sample were measured and mixed in 250 ml fresh tap water, the viscosities and gel strengths measured after mixing vigorously. Following this, 1 gram of each of the viscosifiers under study was added and mixed thoroughly. Repeatedly, 1 gram of each of the viscosifiers was added to the different samples until the total amount of viscosifier for each was 4 grams. The viscosities and gel strengths at each 1 gram increase were measured. The effects of these increments in the quantities of viscosifiers on the mud samples were investigated.

Results.

The results for the 5 different samples are represented in both tabular and graphical forms below;

Results for sample 1.

Table 21 Results showing effect of increased Duo Tec mass on sample 1 properties.

Wt. of sample (g)	Wt of Duo Tec (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	23	15	8	7	2	4
5	1	57	47	10	37	8	12
5	2	84	73	11	62	22	35
5	3	160	133	27	106	52	57
5	4	222	188	34	154	71	77

Table 22 Results showing effect of increased Bentonite mass on sample 1 properties.

Wt. of sample (g)	Wt. Of Bentonite (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	23	15	8	7	2	4
5	1	31	22	9	13	4	5
5	2	39	28	11	17	6	7
5	3	44	31	13	18	9	9
5	4	50	37	13	24	12	10

Table 23 Results showing effect of increased CMC mass on sample 1 properties.

Wt. Of Sample (g)	Wt. Of CMC (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	23	15	8	7	2	4
5	1	71	50	21	29	5	10
5	2	145	100	45	55	8	15
5	3	252	176	76	100	12	25
5	4	>300		N/A	N/A	18	34

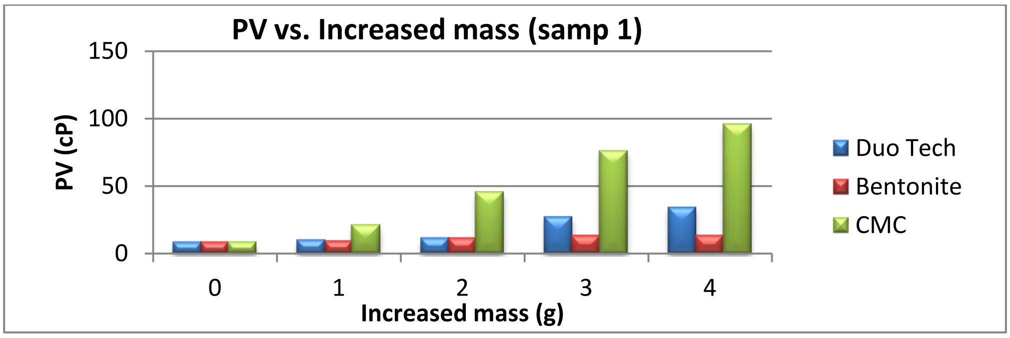


Figure 40 Plot of plastic viscosity vs. increased mass for mud sample 1.

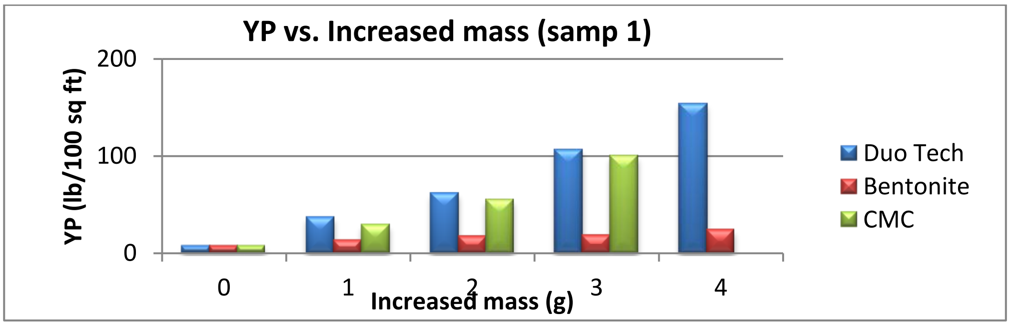


Figure 41 Plot of yield point vs. increased mass for mud sample 1

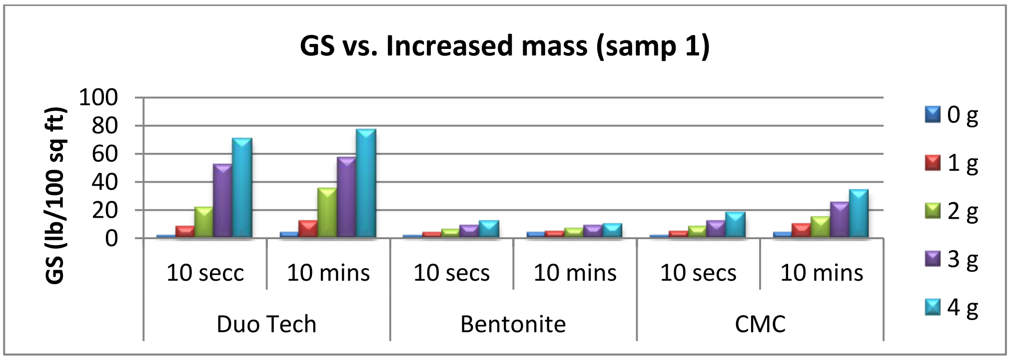


Figure 42 Plot of gel strengths vs. increased mass for mud sample 1

Results for sample 2

Table 24 Results showing effect of increased Duo Tech mass on sample 2 properties.

Wt. of sample (g)	Wt of Duo Tec (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	31	22	9	13	5	5
5	1	70	63	7	56	9	19
5	2	123	100	23	77	35	38
5	3	186	158	28	130	57	62
5	4	246	207	39	168	74	82

Table 25 Results showing effect of increased Bentonite mass on sample 2 properties

Wt. of sample (g)	Wt. Of Bentonite (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	31	22	9	13	5	5
5	1	32	22	10	12	5	7
5	2	35	25	10	15	7	7
5	3	41	30	11	19	9	9
5	4	48	36	12	24	11	9

Table 26 Results showing effect of increased CMC mass on sample 2 properties

Wt. Of Sample (g)	Wt. Of CMC (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	31	22	9	13	5	5
5	1	81	55	26	29	7	13
5	2	182	125	57	68	11	22
5	3	282	199	83	116	17	42
5	4	>300		N/A	N/A	19	46

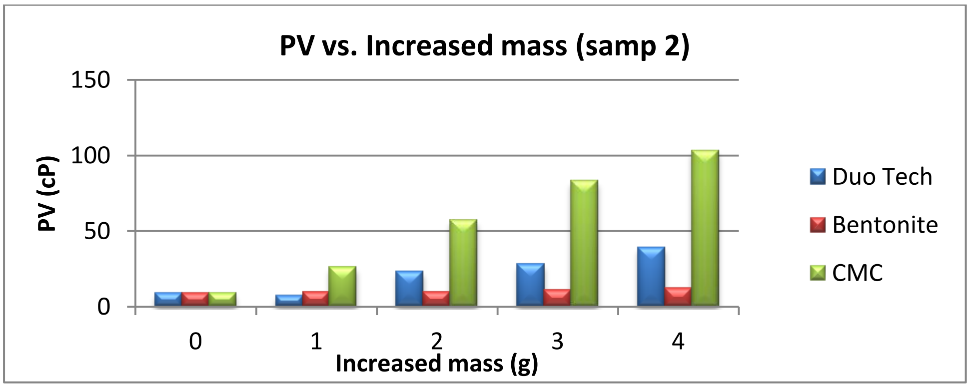


Figure 43 Plot of plastic viscosity vs. increased mass for mud sample 2.

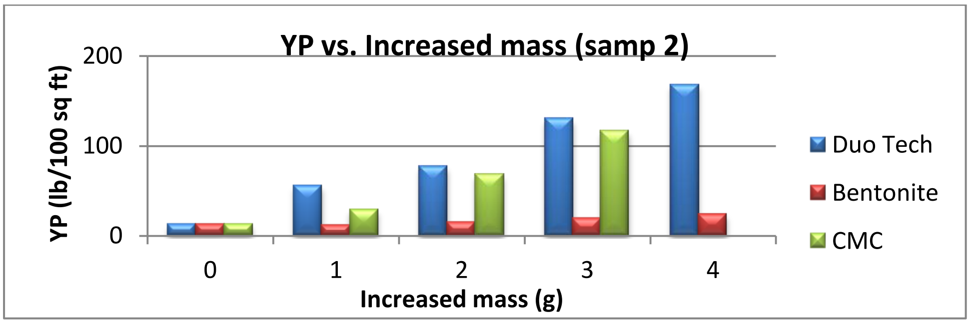


Figure 44 Plot of yield point vs. increased mass for mud sample 2

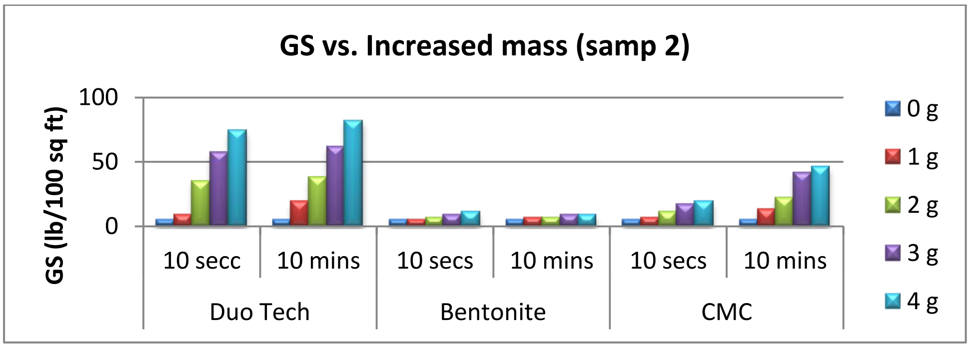


Figure 45 Plot of gel strengths vs. increased mass for mud sample 2

Results for sample 3

Table 27 Results showing effect of increased Duo Tech mass on sample 3 properties.

Wt. of sample (g)	Wt of Duo Tec (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	37	26	11	15	5	5
5	1	73	68	5	63	12	15
5	2	129	102	27	75	34	38
5	3	195	172	23	149	61	71
5	4	250	215	35	180	78	78

Table 28 Results showing effect of increased Bentonite mass on sample 3 properties.

Wt. of sample (g)	Wt. Of Bentonite(g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	37	26	11	15	5	5
5	1	35	24	11	13	4	5
5	2	40	29	11	18	8	8
5	3	48	35	13	22	10	8
5	4	56	41	15	26	12	10

Table 29 Results showing effect of increased CMC mass on sample 3 properties.

Wt. Of Sample (g)	Wt. Of CMC (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	37	26	11	15	5	5
5	1	72	50	22	28	6	13
5	2	150	105	45	60	9	21
5	3	258	186	72	114	14	33
5	4	>300		N/A	N/A	23	48

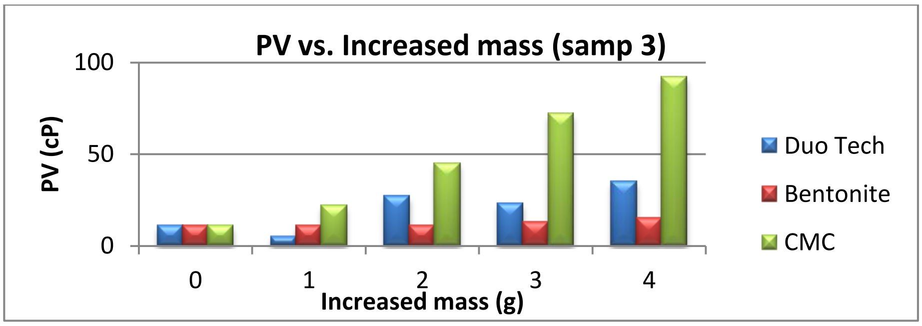


Figure 46 Plot of plastic viscosity vs. increased mass for mud sample 3

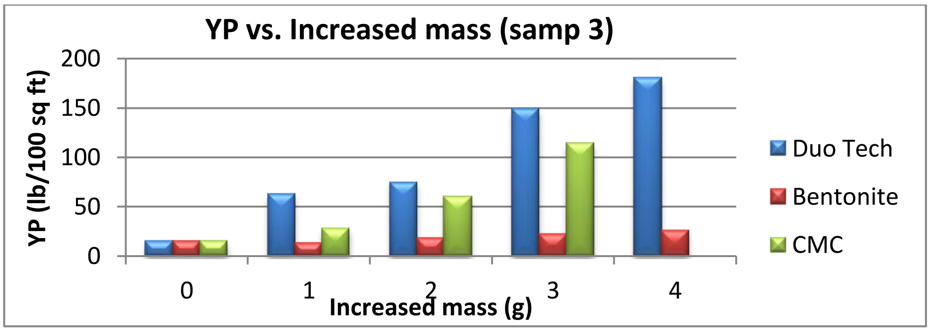


Figure 47 Plot of yield point vs. increased mass for mud sample 3

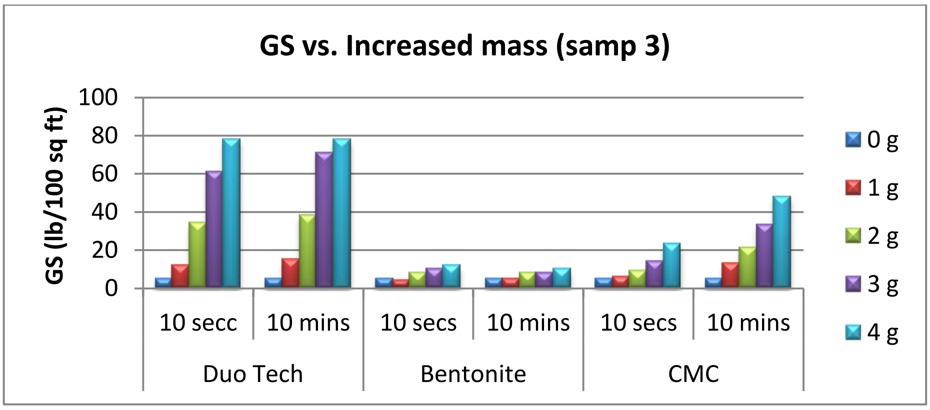


Figure 48 Plot of gel strengths vs. increased mass for mud sample 3.

Results for sample 4

Table 30 Results showing effect of increased Duo Tec mass on sample 4 properties.

wt. of sample (g)	wt of Duo Tec (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	28	19	9	10	3	5
5	1	74	62	12	50	12	16
5	2	133	97	36	61	31	36
5	3	193	168	25	143	60	65
5	4	253	220	33	187	79	83

Table 31 Results showing effect of increased Bentonite mass on sample 4 properties.

wt. of sample (g)	Wt. Of Bentonite (g)	viscosity Dial		PV (cP)	YP (lb /100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	28	19	9	10	3	5
5	1	27	20	7	13	4	7
5	2	37	27	10	17	8	8
5	3	42	31	11	20	9	9
5	4	47	36	11	25	12	10

Table 32 Results showing effect of increased CMC mass on sample 4 properties.

Wt. Of Sample (g)	Wt. Of CMC (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	28	19	9	10	3	5
5	1	85	59	26	33	9	17
5	2	175	123	52	71	12	27
5	3	292	215	77	138	22	44
5	4	>300		N/A	N/A	36	60

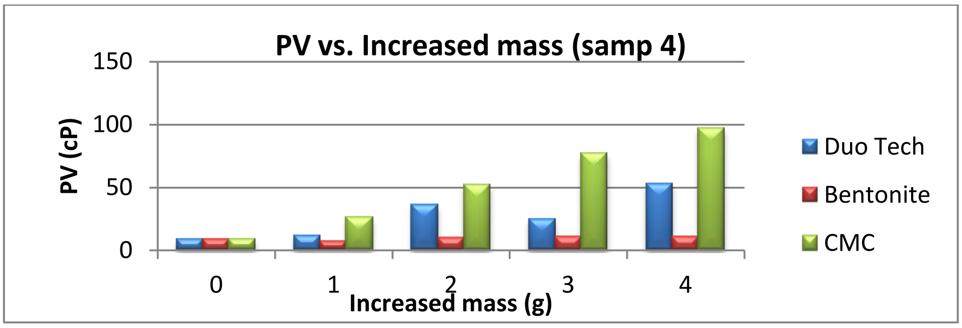


Figure 49 Plot of plastic viscosity vs. increased mass for mud sample 4

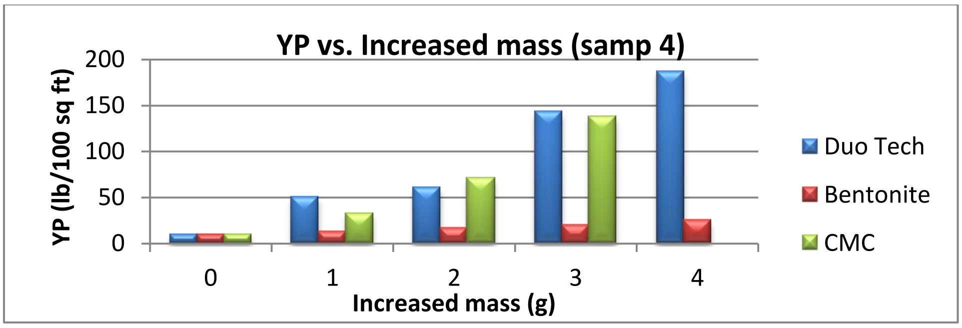


Figure 50 Plot of yield point vs. increased mass for sample 4

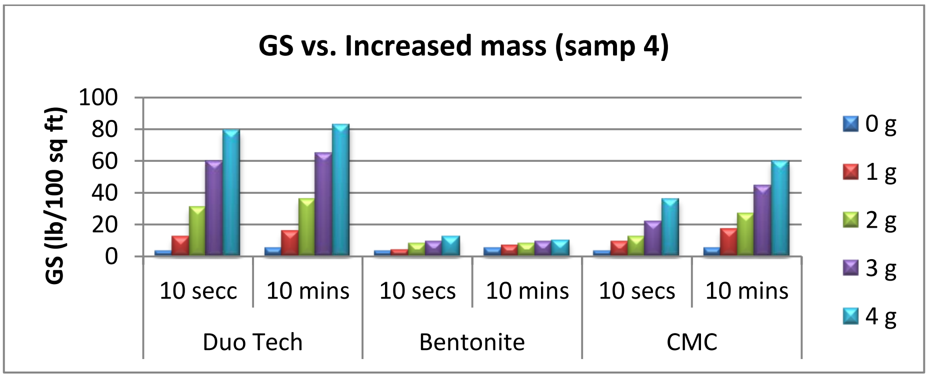


Figure 51 Plot of gel strength vs. increased mass for sample 4

Results for sample 5

Table 33 Results showing effect of increased Duo Tec mass on sample 5 properties.

wt. of sample (g)	wt of Duo Tec (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	31	20	11	9	4	4
5	1	68	58	10	48	9	15
5	2	117	95	22	73	31	40
5	3	180	151	29	122	55	60
5	4	235	207	28	179	75	80

Table 34 Results showing effect of increased Bentonite mass on sample 5 properties.

wt. of sample (g)	Wt. Of Bentonite (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	31	20	11	9	4	4
5	1	33	23	10	13	6	7
5	2	44	31	13	18	9	9
5	3	53	39	14	25	11	11
5	4	60	45	15	30	14	10

Table 35 Results showing effect of increased CMC mass on sample 5 properties.

Wt. Of Sample (g)	Wt. Of CMC (g)	viscosity Dial		PV (cP)	YP (lb/100 sq. feet)	Gel Strength (lb/100 sq. feet)	
		600 rpm	300 rpm			10 secs	10 mins
5	0	31	20	11	9	4	4
5	1	82	54	28	26	6	13
5	2	165	110	55	55	10	22
5	3	265	189	76	113	17	38
5	4	>300		N/A	N/A	30	65

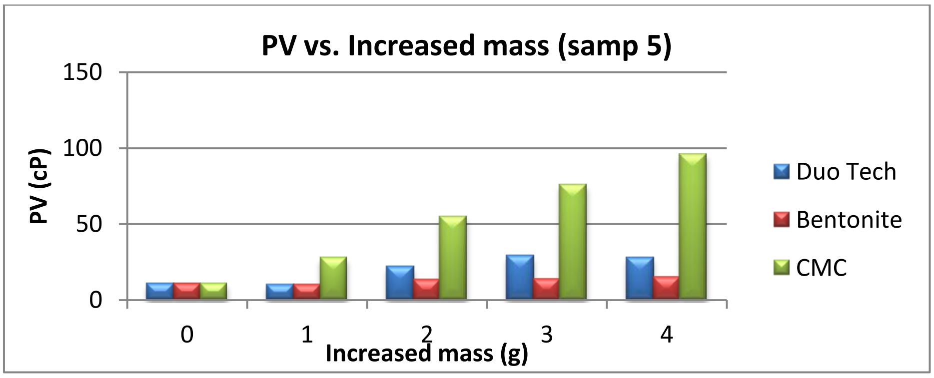


Figure 52 Plot of plastic viscosity vs. increased mass for mud sample 5

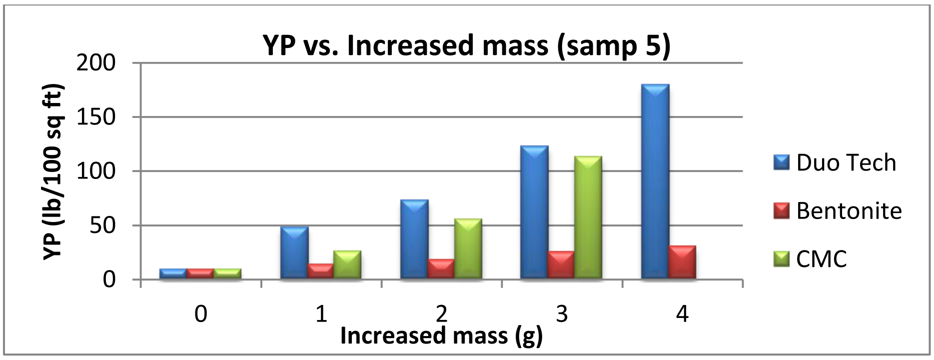


Figure 53 Plot of yield point vs. increased mass for mud sample 5

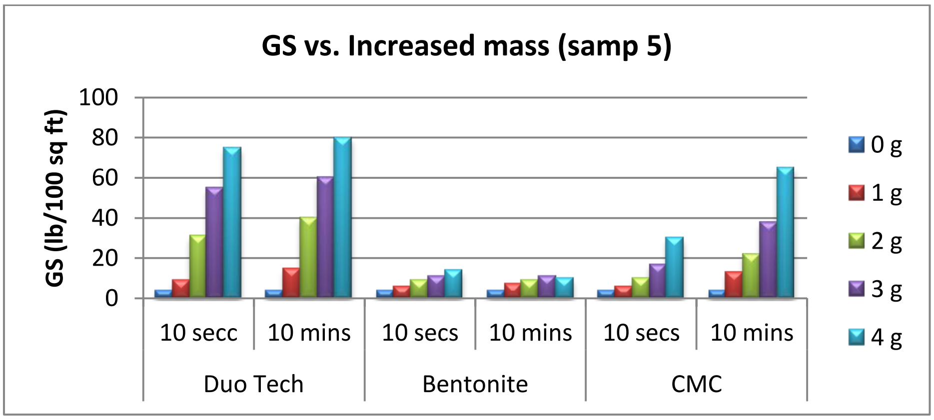


Figure 54 Plot of gel strengths vs. increased mass for mud sample 5

Discussion and Conclusion.

Results shown for all the samples for plastic viscosity, yield point and gel strengths showed a similar trend. With regards to plastic viscosity, increasing the masses of the different additives showed that CMC gave the highest plastic viscosities, followed by Duo Tec, then Bentonite. With regards to yield point, Duo Tec produced the highest yield points, followed by CMC, then Bentonite. The later trend was also observed with regards to gel strengths with increasing mass of additives.

CMC is a natural polymer type material with long chain lengths and is water soluble. At lower concentrations, it deflocculates clay suspensions in much the same manner as lignosulfonate. This results in fluid loss and yield point reductions. As the concentration is increased, the viscosity of the liquid phase (water) is increased since plastic viscosity is primarily a function of both the viscosity of the liquid phase and the volume of solids in the mud, and fluid loss is further reduced. Therefore, addition of more CMC is detrimental if the target is to lower the plastic viscosity and increase the yield point, as it has the natural tendency to deflocculate and to build plastic viscosity.

On the other hand, Duo Tec is a high molecular weight biopolymer that also increases viscosity of the mud. its structure is such that it has long chains, which attract and tangle much easier, increasing the yield point more than plastic viscosity. This is a very desirable quality or characteristic in a viscosifier as it is necessary for good hole cleaning, and lower plastic viscosities are also desirable. With high plastic viscosities as shown with CMC increase, the viscosity at the drill bit is also increased, and this results in a higher rate of penetration (ROP). Furthermoere, high plastic viscosity increases the pressure drop down the drill string which results in a reduction in the available flow rate, hence retards or offsets any increase in lifting abilities of cuttings to the surface.

The gel strengths also are seen to be higher for Duo Tec than for the other two additives. This thioxotropic behavior exhibited by Duo Tec is also a desirable property if for some reason, operation stops, and circulation of the mud seizes for some time. Then, the cuttings suspending ability would be an advantage for this additive unlike with CMC and bentonite. Hence, its ability gelate is a property well desired in drilling operations.

In conclusion, all three are viscosity builders, but CMC and Duo Tec show more superior quality than bentonite as they are special viscosity builders used in areas where bentonite is not well suited for example, when low solids mud are required. CMC, shows a higher PV when increased and a lower YP compared to Duo Tec, but this is not so desirable as a viscosifier property, hence Duo Tec would be recommended for use for increasing the viscosity of the mud. However, CMC shows a better fluid loss characteristic than the other additives.

4.9 Experiment 8

Title: **Aging and Temperature effects on mud sample rheology.**

Aim: To determine the effect of temperature and different aging times on the rheological properties of drilling mud samples.

Requirement: mud samples, fann 35 SA viscometer, oven, viscosifiers – bentonite, CMC and Duo Tec NS, hand mixer, fresh water, sea water, measuring cylinders, thermometer.

Procedure

a) **With fresh tap water from the university laboratory as the continuous phase used.** 5 grams of each of the mud samples were weighed out and mixed in 250 ml fresh tap water. 1 gram of each of the viscosifiers was weighed out and added to the various samples with thorough shearing for 10 minutes afterwards. After mixing properly, the samples were allowed to stand for 16 hours both at ambient temperature and at 74^{o} C in the oven. At the end of the period, the viscosities and gel strengths were measured. The same procedure was repeated for the different samples as they were allowed to age for 20, 24 and 32 hours at both ambient temperatures and 74^{o}C. The viscometer cup was always heated to 74^{o}C when dealing with the samples coming out from the oven to maintain the same temperature. The effects of temperature and aging on their rheological properties were determined from the values of measured viscosities and gel strengths from the viscometer.

b) **With Sea water.**
5 grams of each mud samples were weighed out and poured in 100 ml of fresh tap water in order to prehydrate the mud. This was agitated, slightly heated, then allowed a waiting time of 3 hours. Afterwards, 150 ml of sea water was measured out separately and 0.9 gram of soda ash introduced into the sea water and stirred gently. The pH was noticed to have increased from 7.47 to 9.95. The

prehydrated mud was then mixed with the sea water and stirred to homogenize the mixture, and afterwards, 1 gram of each of the additives added in turns (one additive for one experiment). . After mixing properly, the samples were allowed to stand for 16 hours both at ambient temperature and at 74^{o} C in the oven. At the end of the period, the viscosities and gel strengths were measured. The same procedure was repeated for the different samples as they were allowed to age for 20, 24 and 32 hours at both ambient temperatures and 74^{o}C. The viscometer cup was always heated to 74^{o}C when dealing with the samples coming out from the oven to maintain the same temperature. The effects of temperature and aging on their rheological properties were determined from the values of measured viscosities and gel strengths from the viscometer.

Theory

The concept of aging is important in simulating the properties of drilling mud at bottom hole conditions from the surface conditions as the properties at the surface do not in any way give a true picture of bottom hole conditions. Aging is a process in which drilling fluids previously subjected to a period of shear are allowed to more fully develop their rheological and filtration properties. Aging takes place when the mud is left inactive for a period and is done under conditions which vary from static to dynamic and from ambient to highly elevated temperatures. 74^{o}C was used as the elevated temperature to simulate the temperature down hole in Tønder where geothermal drilling would be carried out.

Set up/Apparatus

Figure 55 Fann 35 SA viscometer.

Figure 56 Aging mud samples at ambient temperature.

Figure 57 Aging samples in the oven at 74 deg. C

Observation.

It was observed that after aging for a period of time, the Mud-Duo Tec mix showed it had swollen more, but showed an uneven dispersion in appearance as if it had patches all over. The Mud-bentonite mix however shows it has been well hydrated, but there is a separate layer of clear water on the top and the mud at the base. The Mud-CMC mix shows a behaviour which is inbetween these two. This observation is more with the sea water source and at ambient temperature.

Results

The results are given in forms of tables and charts for each of the mud samples as shown below;

Results for sample 1

Table 36 Aging results for fresh water at ambient temperature for sample 1

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet)	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	35	23	12	11	5	7	10.22	9.83
	CMC	96	65	31	34	7	13	10.23	9.85
	Duo	58	47	11	36	13	17	9.98	9.11
20	Bent	25	17	8	9	5	7	10.22	9.93
	CMC	95	65	30	35	8	12	10.23	9.93
	Duo	67	54	13	41	16	16	9.98	9.13
24	Bent	37	25	12	13	7	8	10.22	9.69
	CMC	75	52	23	29	5	10	10.23	9.40
	Duo	63	50	13	37	14	15	9.98	8.89
32	Bent	30	20	10	10	5	6	10.22	9.56
	CMC	71	48	23	25	5	10	10.23	9.45
	Duo	58	45	13	32	13	15	9.98	9.06

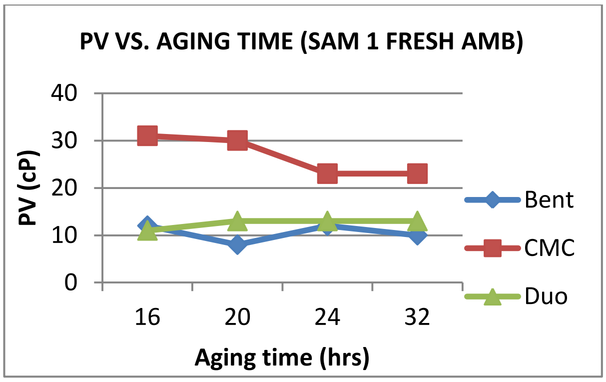


Figure 58 PV vs. Aging time, fresh water ambient, sample 1

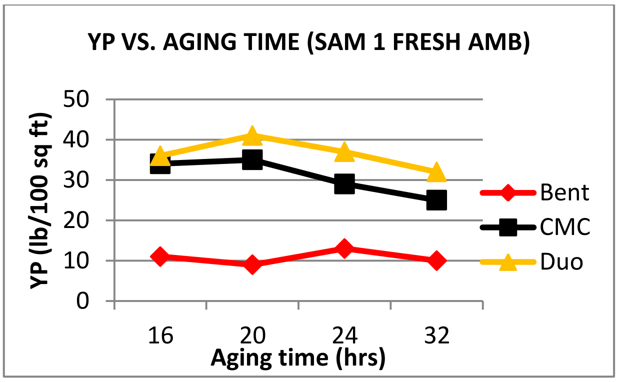


Figure 59 YP vs. Aging time, fresh water ambient, sample 1

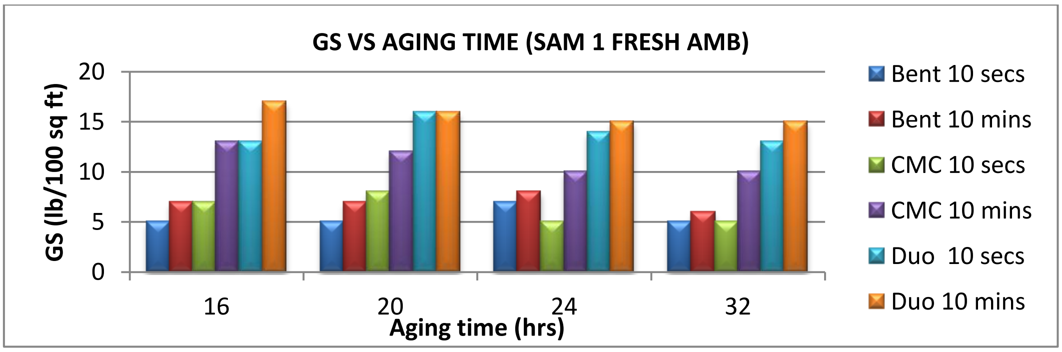


Figure 60 Gel strengths vs. Aging time for fresh water at ambient temperature for sample 1.

Table 37 Aging results for fresh water at 74 degree celcius for sample 1

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet)	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	24	17	7	10	6	6	10.22	9.19
	CMC	35	24	11	13	5	8	10.23	9.50
	Duo	47	38	9	29	10	10	9.98	8.90
20	Bent	19	13	6	7	5	6	10.22	9.57
	CMC	49	34	15	19	8	10	10.23	9.54
	Duo	52	43	9	34	13	13	9.98	8.65
24	Bent	24	15	9	6	4	4	10.22	9.59
	CMC	45	31	14	17	6	9	10.23	9.50
	Duo	50	41	9	32	12	12	9.98	8.25
32	Bent	22	15	7	8	5	5	10.22	9.31
	CMC	36	25	11	14	5	7	10.23	9.17
	Duo	46	37	9	28	9	10	9.98	7.41

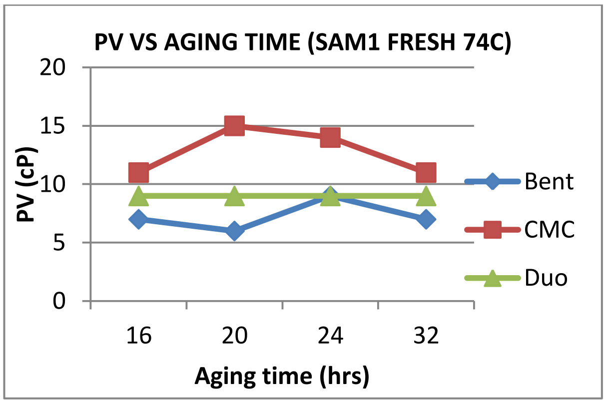


Figure 61 PV vs. Aging time, fresh water 74^{o}C for sample 1

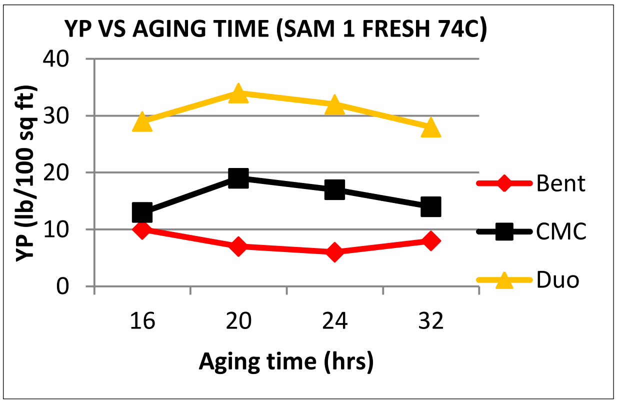


Figure 62 YP vs. Aging time, fresh water 74^{o}C for sample 1

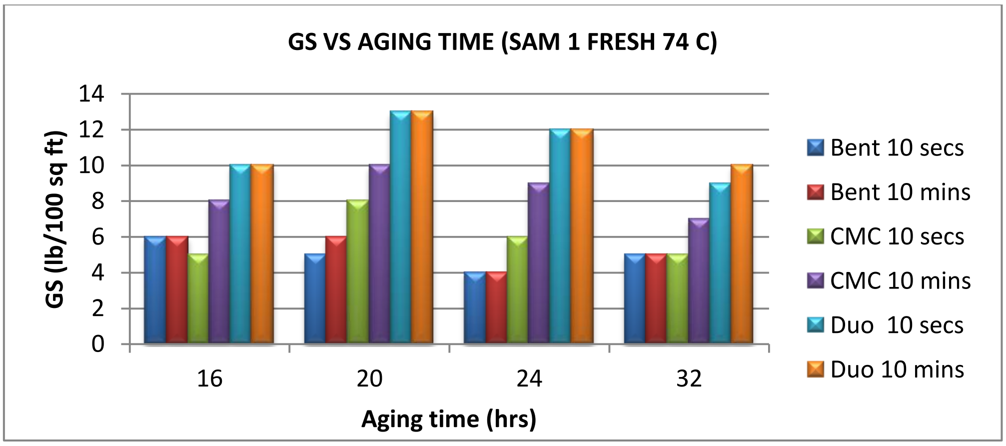


Figure 63 Gel strengths vs. Aging time for fresh water at 74^{o}C for sample 1

Table 38 Aging results for sea water at ambient temperature for sample 1

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq. feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	13	8	5	3	2	3	9.97	9.80
	CMC	31	18	13	5	2	5	9.90	9.85
	Duo	75	61	14	47	10	12	9.80	9.65
20	Bent	18	10	8	2	3	3	9.97	9.77
	CMC	26	15	11	4	2	2	9.90	9.80
	Duo	78	63	15	48	11	13	9.80	9.47
24	Bent	13	8	5	3	2	3	9.97	9.74
	CMC	28	16	12	4	2	4	9.90	9.83
	Duo	74	63	11	52	11	12	9.80	9.50
32	Bent	12	8	4	4	3	3	9.97	9.73
	CMC	24	14	10	4	2	3	9.90	9.78
	Duo	80	66	14	52	12	14	9.80	9.37

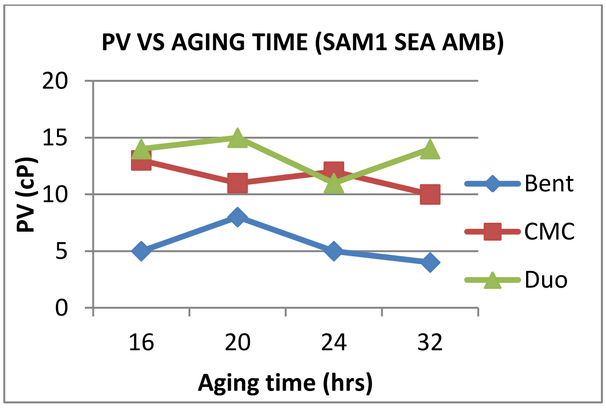


Figure 64 PV vs. Aging time, sea water ambient for sample 1

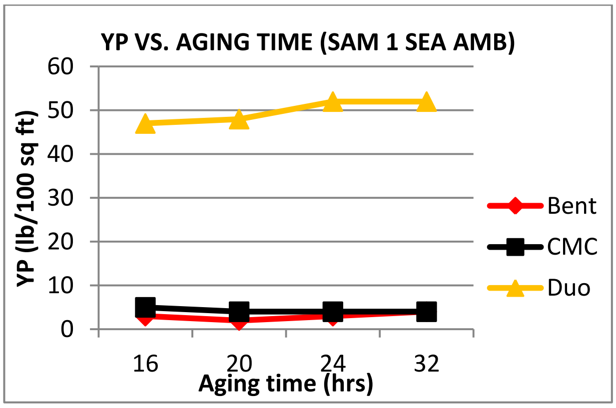


Figure 65 YP vs. Aging time, sea water ambient for sample 1

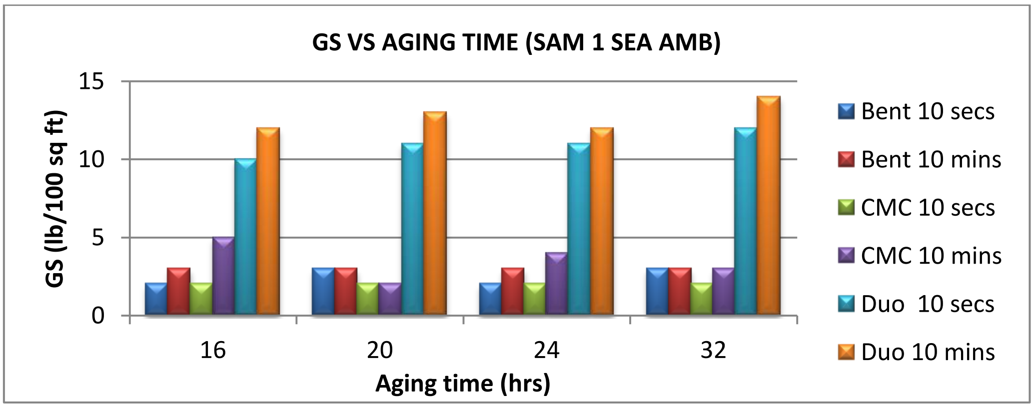


Figure 66 Gel strengths vs. Aging time for sea water at ambient temperature for sample 1

Table 39 Aging results for sea water at 74 degree celcius for sample 1

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.ft)	Gel Strength (lb/100 sq.ft)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	10	7	3	4	3	3	9.97	8.37
	CMC	15	9	6	3	1	3	9.90	8.03
	Duo	68	52	16	36	13	15	9.80	7.83
20	Bent	11	8	3	5	2	2	9.97	7.96
	CMC	17	10	7	3	1	3	9.90	8.06
	Duo	66	52	14	38	12	15	9.80	7.74
24	Bent	10	7	3	4	2	2	9.97	8.19
	CMC	16	10	6	4	3	4	9.90	7.86
	Duo	65	50	15	35	13	15	9.80	7.72
32	Bent	8	6	2	4	3	3	9.97	7.98
	CMC	10	6	4	2	0	3	9.90	7.90
	Duo	65	50	15	35	13	15	9.80	7.73

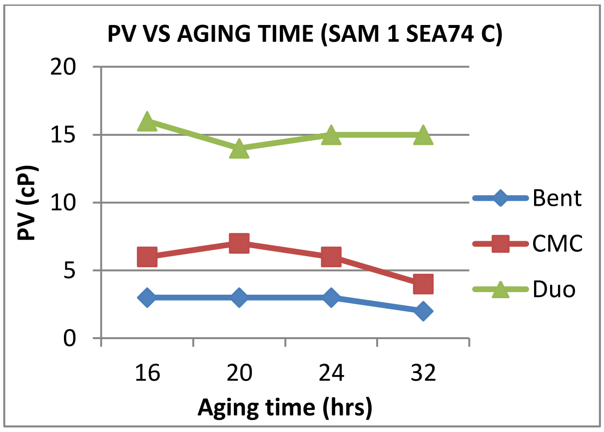


Figure 67 PV vs. Aging time, sea water 74° C for sample 1

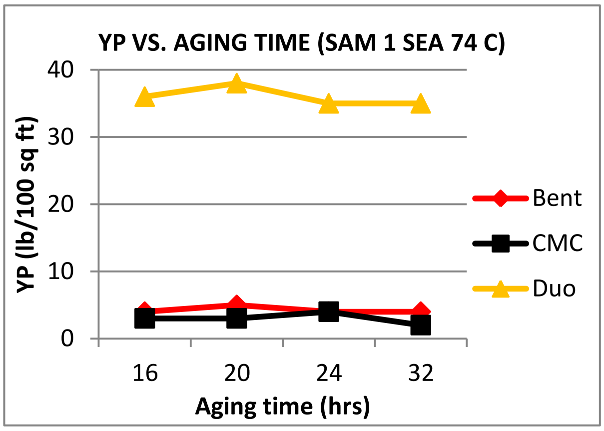


Figure 68 YP vs. Aging time, sea water 74° C for sample 1

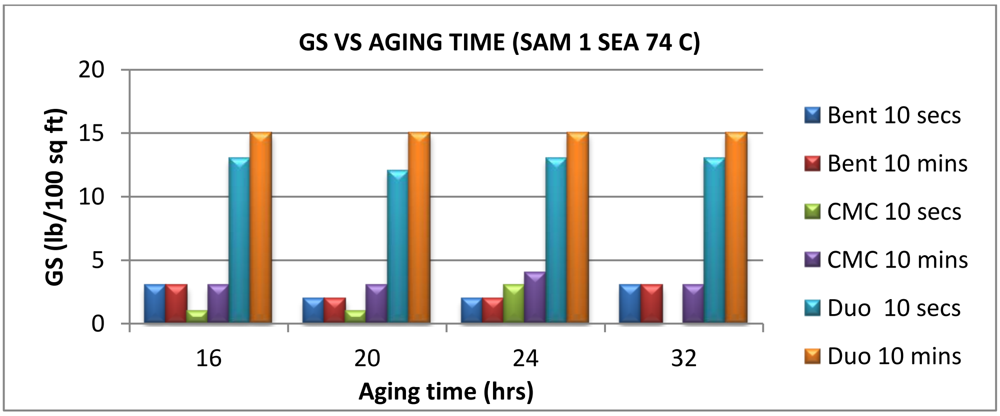


Figure 69 Gel strengths vs. Aging time for sea water at 74° C for sample 1

Results for sample 2

Table 40 Aging results for fresh water at ambient temperature for sample 2

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet)	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	40	26	14	12	6	7	10.24	9.82
	CMC	93	63	30	33	8	14	10.16	9.71
	Duo	60	47	13	34	14	15	9.92	9.21
20	Bent	35	25	10	15	7	7	10.24	9.79
	CMC	101	68	33	35	9	15	10.16	9.40
	Duo	64	51	13	38	15	15	9.92	8.89
24	Bent	35	24	11	13	6	7	10.24	9.82
	CMC	96	64	32	32	8	12	10.16	9.51
	Duo	60	48	12	36	14	15	9.92	8.90
32	Bent	42	28	14	14	5	5	10.24	10.20
	CMC	69	44	25	19	3	5	10.16	10.13
	Duo	52	41	11	30	11	14	9.92	9.27

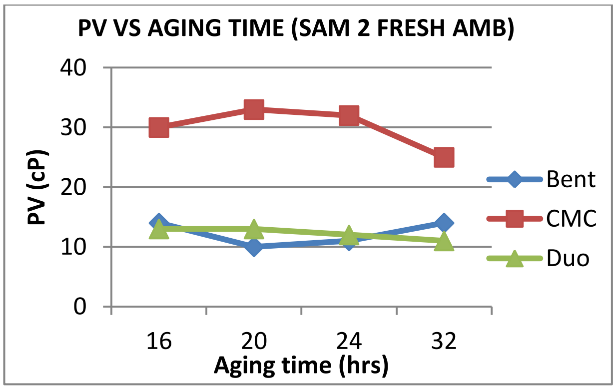


Figure 70 PV vs. Aging time, fresh water ambient for sample 2

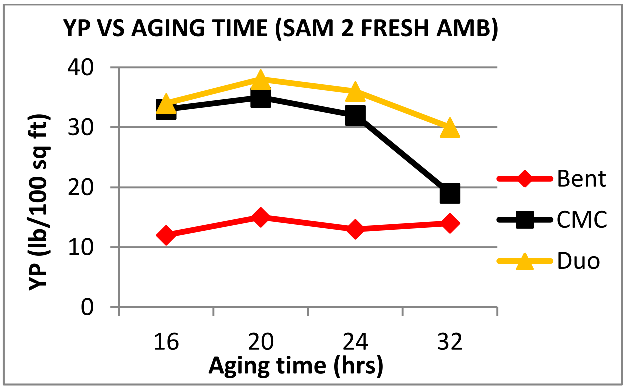


Figure 71 YP vs. Aging time, fresh water ambient, sample 2

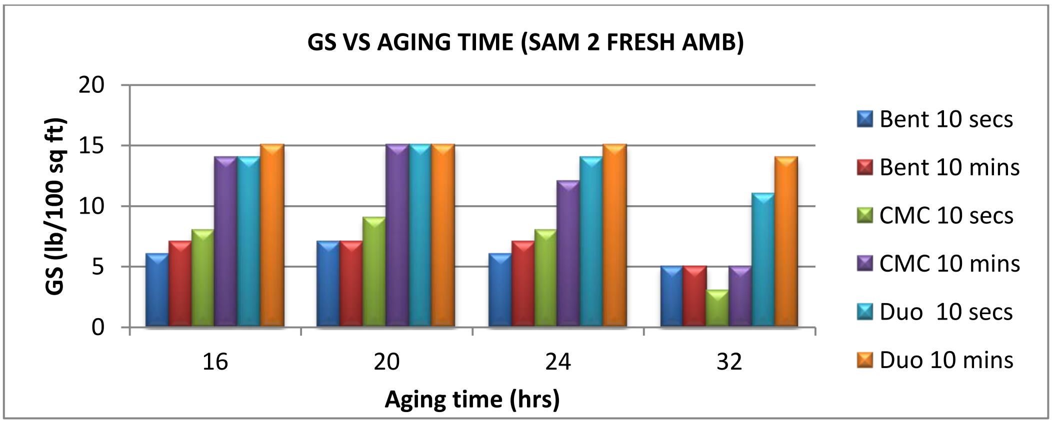


Figure 72 Gel strengths vs. Aging time for fresh water at ambient temperature for sample 2.

Table 41 Aging results for fresh water at 74 degree celcius for sample 2

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet)	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	34	22	12	10	6	6	10.24	9.54
	CMC	46	30	16	14	6	8	10.16	9.45
	Duo	47	38	9	29	10	10	9.92	8.35
20	Bent	22	16	6	10	6	6	10.24	9.50
	CMC	46	31	15	16	6	8	10.16	9.50
	Duo	49	41	8	33	10	10	9.92	8.20
24	Bent	25	17	8	9	5	5	10.24	9.43
	CMC	45	31	14	17	5	9	10.16	9.44
	Duo	46	38	8	30	10	10	9.92	8.00
32	Bent	23	16	7	9	5	5	10.24	9.20
	CMC	37	25	12	13	5	8	10.16	9.15
	Duo	46	38	8	30	10	10	9.92	7.41

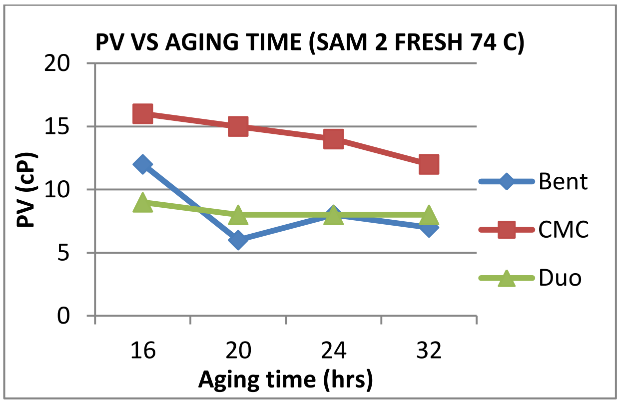


Figure 73 PV vs. Aging time, fresh water 74^{o} C for sample 2

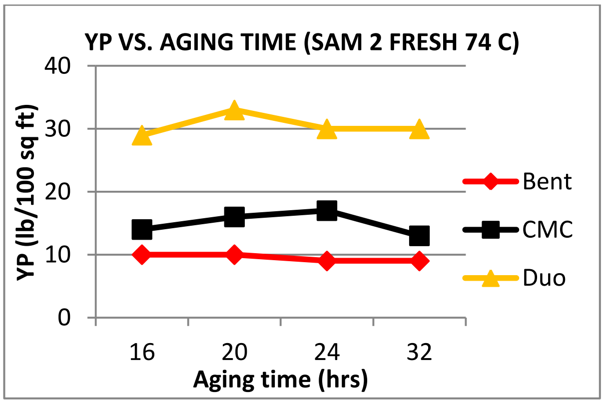


Figure 74 YP vs. Aging time, fresh water 74^{o} C for sample 2

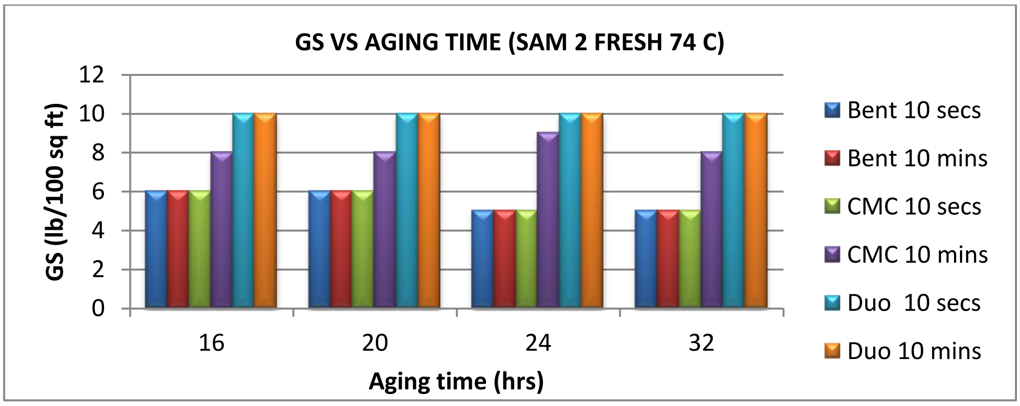


Figure 75 Gel strengths vs. Aging time for fresh water at 74^{o} C for sample 2

Table 42 Aging results for sea water at ambient temperature for sample 2

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100 sq.feet)	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	11	6	5	1	3	3	9.87	9.71
	CMC	23	13	10	3	0	2	9.92	9.71
	Duo	75	60	15	45	11	13	9.81	9.44
20	Bent	13	8	5	3	3	4	9.87	9.72
	CMC	26	15	11	4	1	3	9.92	9.83
	Duo	77	63	14	49	11	14	9.81	9.50
24	Bent	13	8	5	3	3	2	9.87	9.68
	CMC	26	15	11	4	2	4	9.92	9.69
	Duo	80	63	17	46	12	14	9.81	9.39
32	Bent	14	8	6	2	2	3	9.87	9.70
	CMC	31	18	13	5	3	5	9.92	9.77
	Duo	84	67	17	50	12	15	9.81	9.61

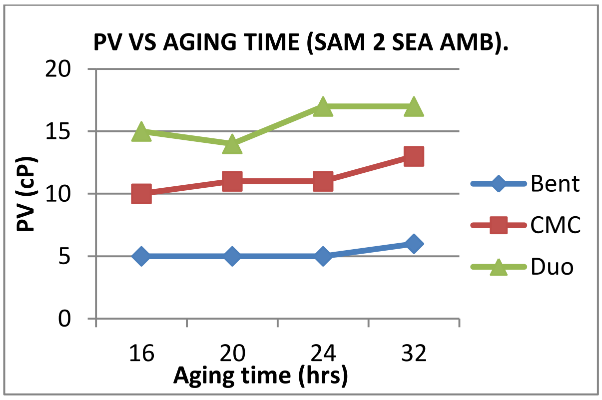


Figure 76 PV vs. Aging time, sea water ambient for sample 2

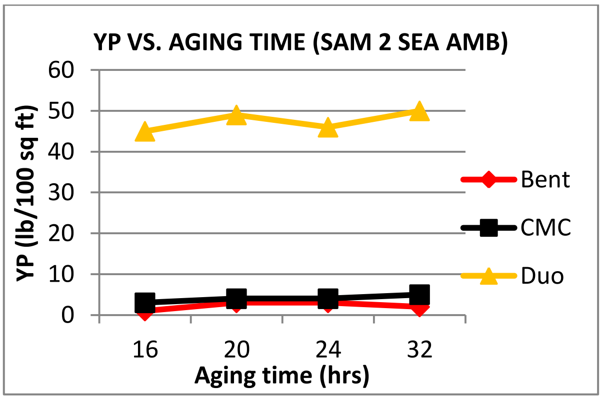


Figure 77 YP vs. Aging time, sea water ambient for sample 2

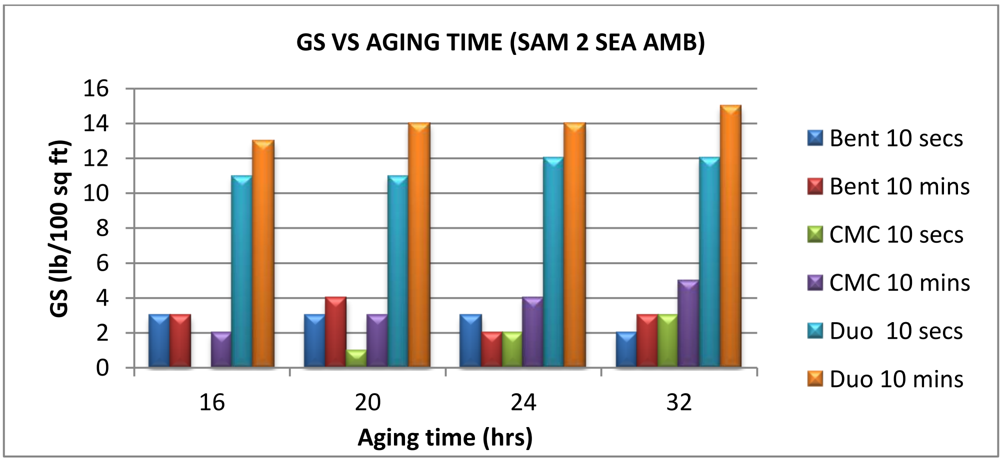


Figure 78 Gel strengths vs. Aging time for sea water at ambient temperature for sample 2

Table 43 Aging results for sea water at 74 degree celcius for sample 2

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	12	9	3	6	3	3	9.87	8.10
	CMC	14	8	6	2	1	2	9.92	7.98
	Duo	70	54	16	38	14	17	9.81	7.79
20	Bent	11	8	3	5	2	2	9.87	8.07
	CMC	15	9	6	3	2	3	9.92	8.10
	Duo	71	55	16	39	14	16	9.81	7.81
24	Bent	12	8	4	4	3	3	9.87	8.10
	CMC	17	10	7	3	3	4	9.92	8.00
	Duo	62	48	14	34	12	15	9.81	7.70
32	Bent	12	9	3	6	3	3	9.87	7.98
	CMC	17	11	6	5	4	4	9.92	8.01
	Duo	69	54	15	39	14	16	9.81	7.60

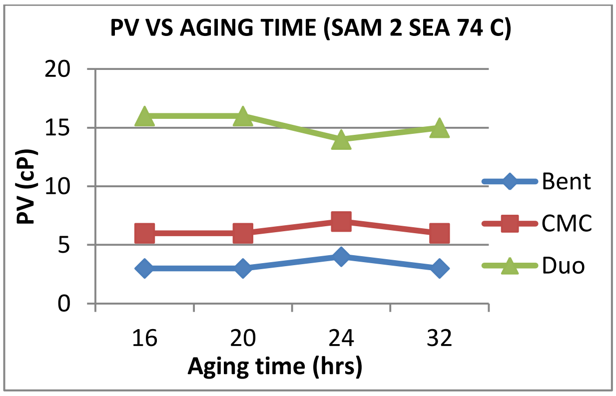


Figure 79 PV vs. Aging time, sea water 74° C for sample 2

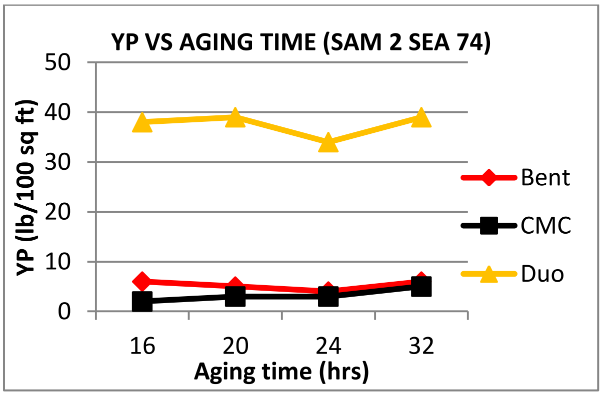


Figure 80 YP vs. Aging time, sea water 74° C for sample 2

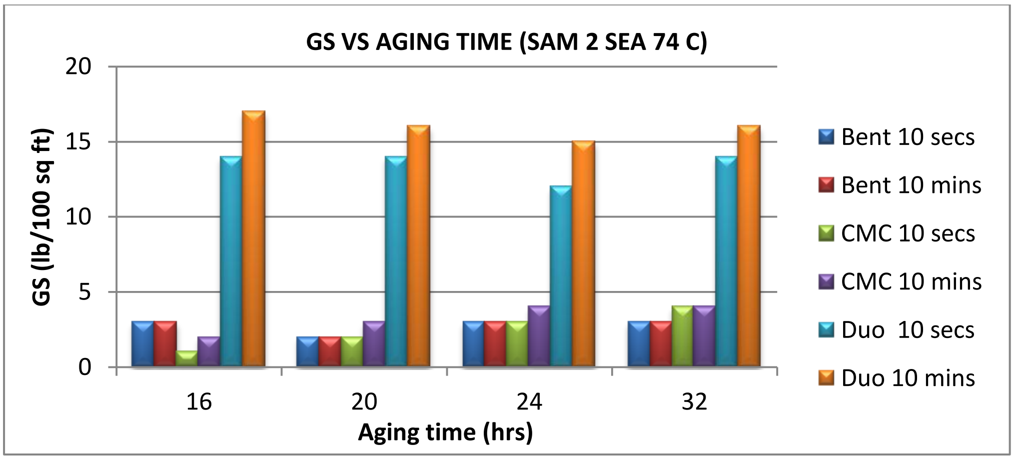


Figure 81 Gel strengths vs. Aging time for sea water at 74° C for sample 2

Results for sample 3

Table 44 Aging results for fresh water at ambient temperature for sample 3

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet)	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	45	30	15	15	8	8	10.35	9.98
	CMC	107	74	33	41	10	18	10.21	10.03
	Duo	66	55	11	44	15	16	9.93	9.29
20	Bent	42	28	14	14	7	7	10.35	10.15
	CMC	100	68	32	36	9	16	10.21	9.71
	Duo	58	47	11	36	13	14	9.93	8.97
24	Bent	43	28	15	13	6	7	10.35	10.06
	CMC	93	63	30	33	8	13	10.21	10.15
	Duo	64	50	14	36	14	15	9.93	9.15
32	Bent	40	26	14	12	5	7	10.35	10.26
	CMC	83	55	28	27	7	10	10.21	10.27
	Duo	57	46	11	35	13	15	9.93	9.10

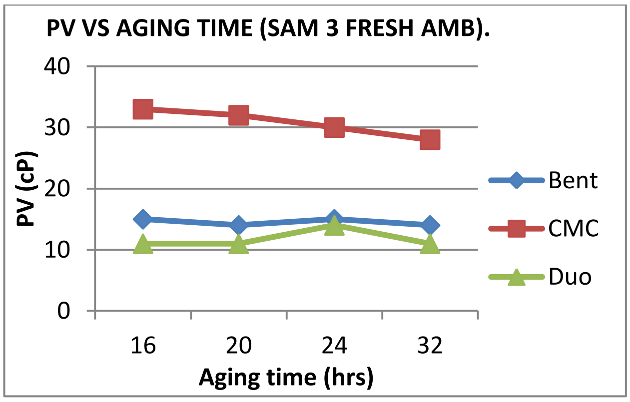


Figure 82 PV vs. Aging time, fresh water ambient for sample 3

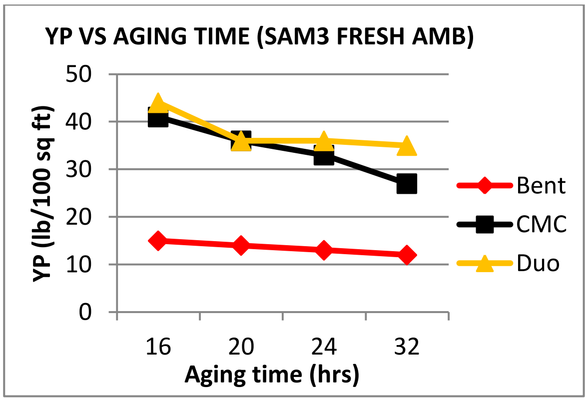


Figure 83 YP vs. Aging time, fresh water ambient for sample 3

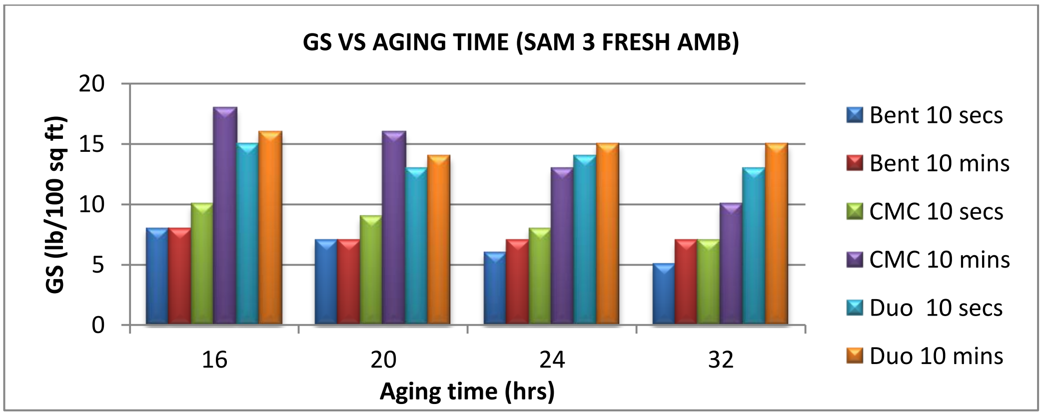


Figure 84 Gel strengths vs. Aging time for fresh water at ambient temperature for sample 3

Table 45 Aging results for fresh water at 74 degree celcius for sample 3

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet)	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	31	19	12	7	5	5	10.35	9.33
	CMC	60	40	20	20	7	8	10.21	9.80
	Duo	50	42	8	34	12	11	9.93	8.46
20	Bent	23	15	8	7	4	5	10.35	9.67
	CMC	48	32	16	16	7	8	10.21	9.81
	Duo	53	45	8	37	13	12	9.93	8.09
24	Bent	26	17	9	8	4	5	10.35	9.86
	CMC	44	30	14	16	5	6	10.21	9.77
	Duo	46	43	3	40	10	10	9.93	8.01
32	Bent	27	18	9	9	6	6	10.35	9.67
	CMC	54	36	18	18	7	9	10.21	9.61
	Duo	51	44	7	37	10	11	9.93	7.64

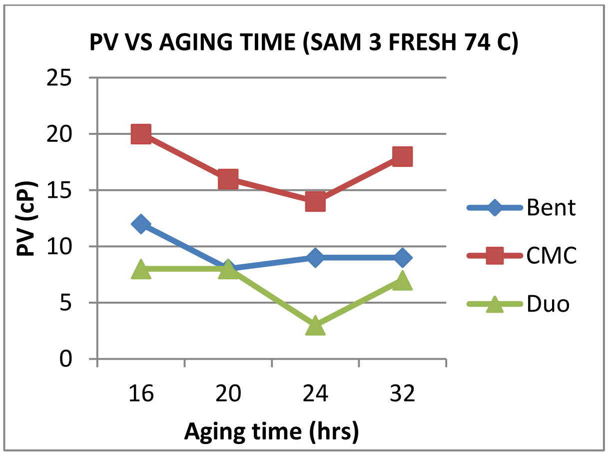


Figure 85 PV vs. Aging time, fresh water 74° C for sample 3

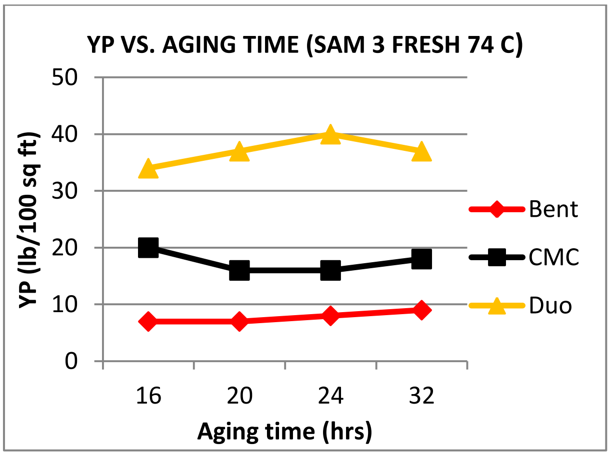


Figure 86 YP vs. Aging time, fresh water 74° C for sample 3

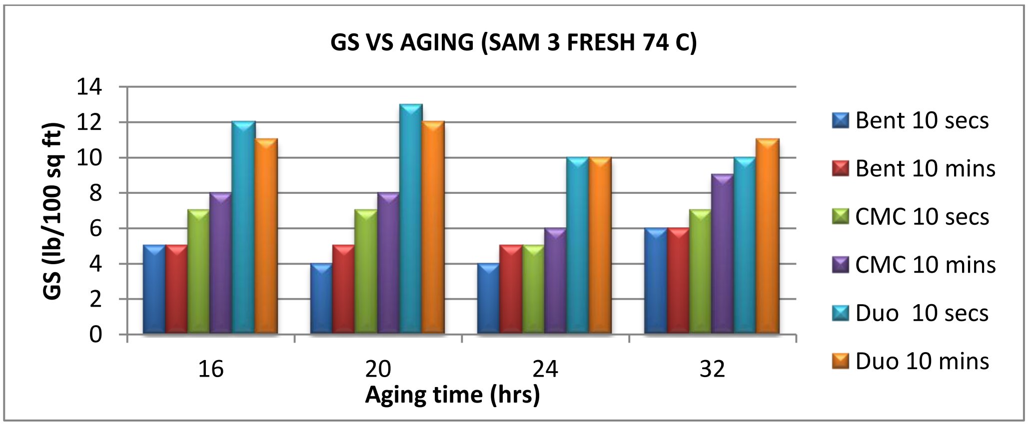


Figure 87 Gel strengths vs. Aging time for fresh water at 74° C for sample 3

Table 46 Aging results for sea water at ambient temperature for sample 3

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	12	8	4	4	3	3	9.88	9.75
	CMC	26	15	11	4	2	3	9.86	9.78
	Duo	72	54	18	36	10	12	9.81	9.55
20	Bent	13	8	5	3	3	4	9.88	9.70
	CMC	25	14	11	3	1	2	9.86	9.69
	Duo	70	53	17	36	10	12	9.81	9.32
24	Bent	12	7	5	2	2	3	9.88	9.66
	CMC	25	14	11	3	2	3	9.86	9.67
	Duo	68	54	14	40	9	13	9.81	9.37
32	Bent	13	9	4	5	4	4	9.88	9.68
	CMC	29	17	12	5	2	5	9.86	9.69
	Duo	89	68	21	47	12	15	9.81	9.40

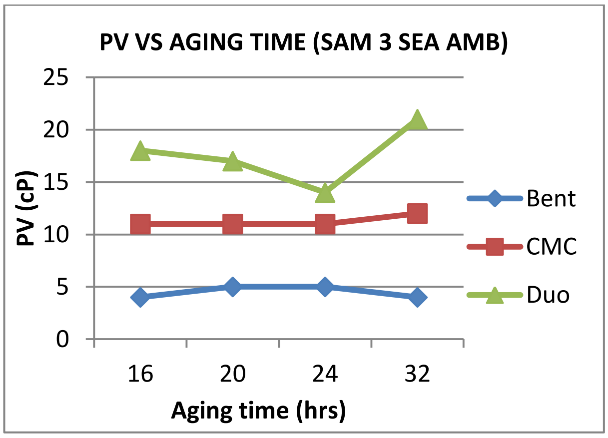


Figure 88 PV vs. Aging time, sea water ambient for sample 3

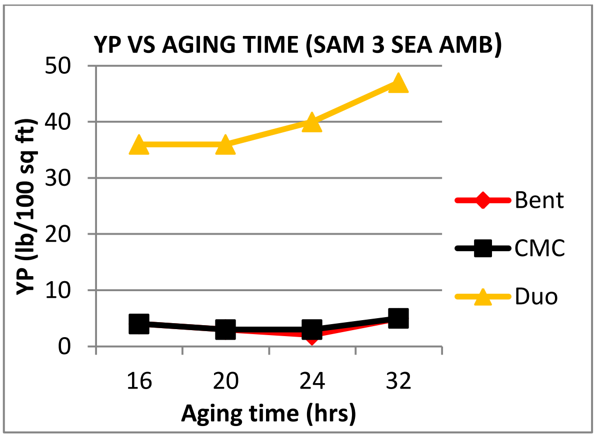


Figure 89 YP vs. Aging time, sea water ambient for sample 3

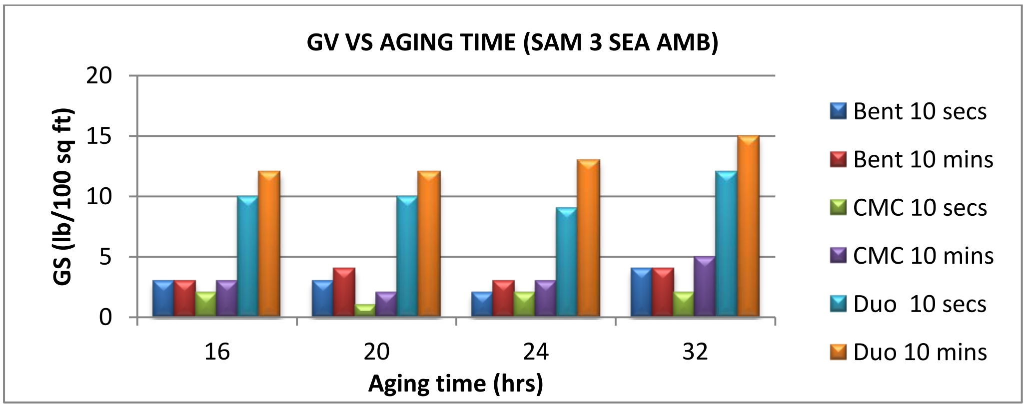


Figure 90 Gel strengths vs. Aging time for sea water at ambient temperature for sample 3

Table 47 Aging results for sea water at 74 degree celcius for sample 3

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	10	7	3	4	2	3	9.88	8.21
	CMC	15	9	6	3	2	3	9.86	8.09
	Duo	63	52	11	41	11	12	9.81	7.86
20	Bent	11	8	3	5	2	2	9.88	8.12
	CMC	17	10	7	3	3	4	9.86	8.09
	Duo	60	46	14	32	10	12	9.81	7.73
24	Bent	11	8	3	5	3	3	9.88	8.05
	CMC	10	6	4	2	0	3	9.86	8.06
	Duo	63	50	13	37	12	14	9.81	7.62
32	Bent	11	8	3	5	2	3	9.88	8.06
	CMC	18	11	7	4	4	4	9.86	7.85
	Duo	66	52	14	38	12	15	9.81	7.67

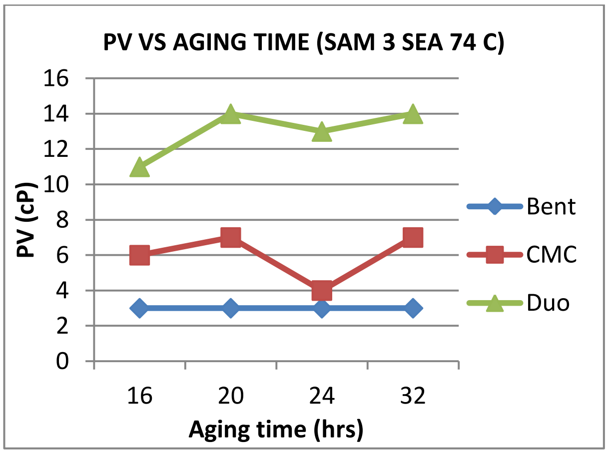


Figure 91 PV vs. Aging time, sea water at 74^{o} C for sample 3

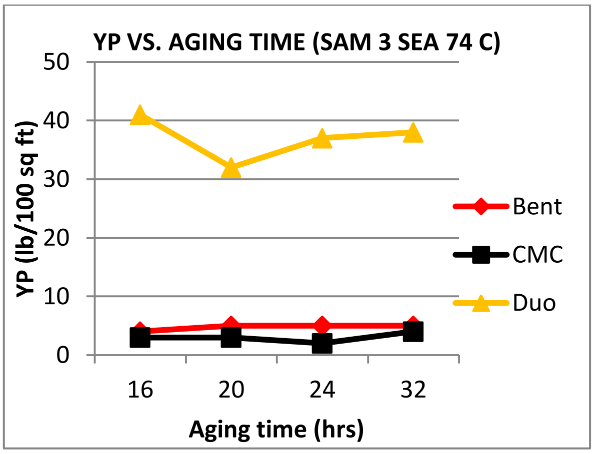


Figure 92 YP vs. Aging time, sea water at 74^{o} C for sample

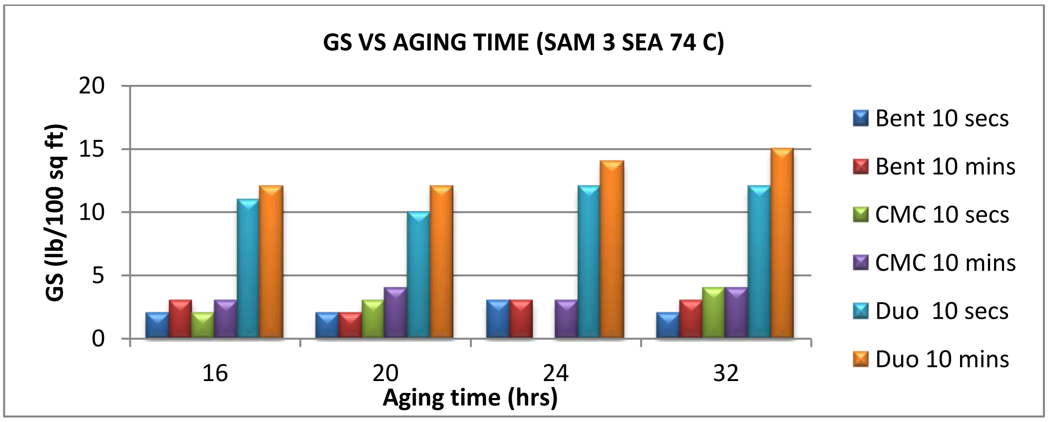


Figure 93 Gel strengths vs. Aging time for sea water at 74^{o} C for sample 3

Results for sample 4

Table 48 Aging results for fresh water at ambient temperature for sample 4

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	36	24	12	12	5	6	10.37	10.24
	CMC	99	68	31	37	9	17	10.29	9.83
	Duo	70	55	15	40	16	17	9.95	9.13
20	Bent	36	25	11	14	6	5	10.37	10.14
	CMC	90	61	29	32	8	13	10.29	10.11
	Duo	73	59	14	45	17	17	9.95	9.16
24	Bent	39	26	13	13	7	8	10.37	10.14
	CMC	94	64	30	34	8	15	10.29	9.82
	Duo	67	59	8	51	14	15	9.95	9.18
32	Bent	45	31	14	17	6	6	10.37	10.25
	CMC	84	58	26	32	7	13	10.29	10.22
	Duo	58	47	11	36	13	15	9.95	8.98

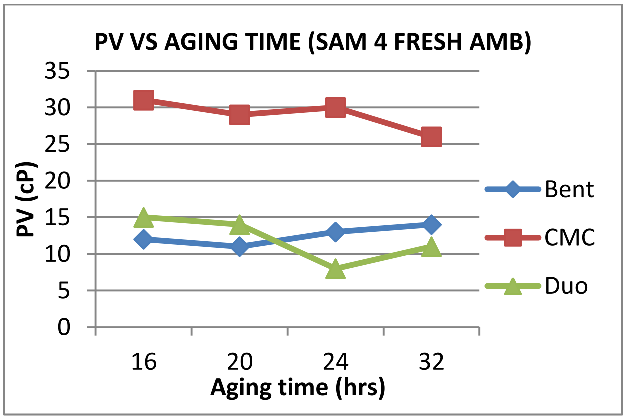


Figure 94 PV vs. Aging time, fresh water ambient for sample 4

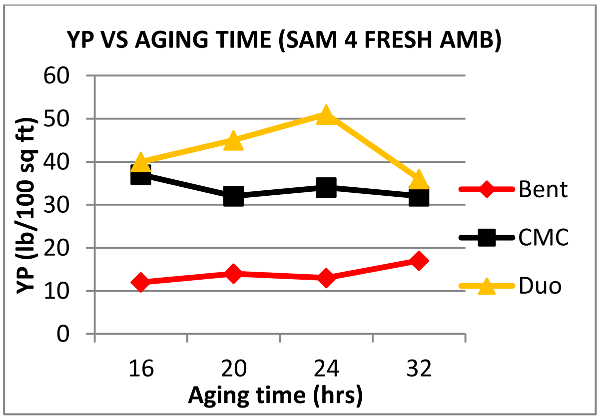


Figure 95 YP vs. Aging time, fresh water ambient for sample 4

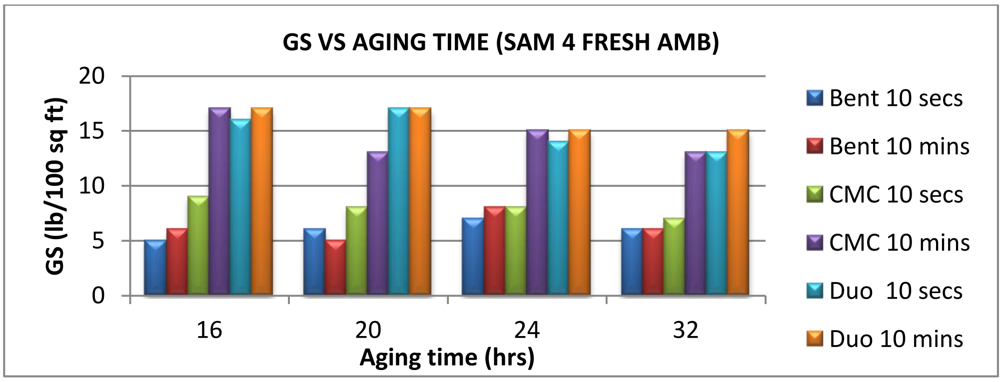


Figure 96 Gel strengths vs. Aging time for fresh water at ambient temperature for sample 4

Table 49 Aging results for fresh water at 74 degree celcius for sample 4

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	28	18	10	8	5	5	10.37	9.71
	CMC	57	39	18	21	8	9	10.29	9.54
	Duo	55	44	11	33	12	12	9.95	8.16
20	Bent	27	18	9	9	5	5	10.37	9.64
	CMC	47	32	15	17	7	7	10.29	9.62
	Duo	52	44	8	36	11	11	9.95	8.71
24	Bent	28	18	10	8	5	5	10.37	9.67
	CMC	47	32	15	17	7	10	10.29	9.56
	Duo	52	44	8	36	12	12	9.95	8.11
32	Bent	26	17	9	8	5	5	10.37	9.58
	CMC	60	41	19	22	8	11	10.29	9.65
	Duo	51	43	8	35	10	11	9.95	7.61

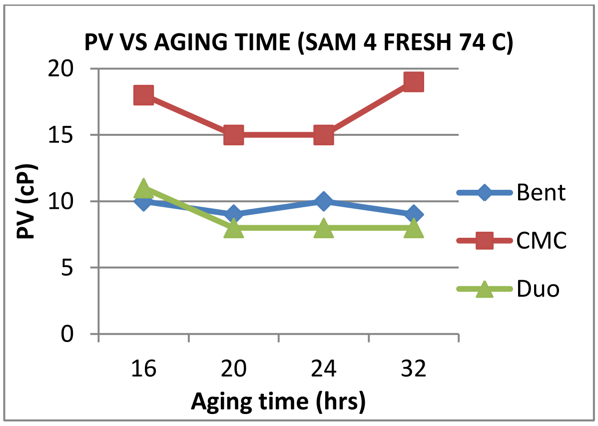


Figure 97 PV vs. Aging time, fresh water 74° C for sample 4

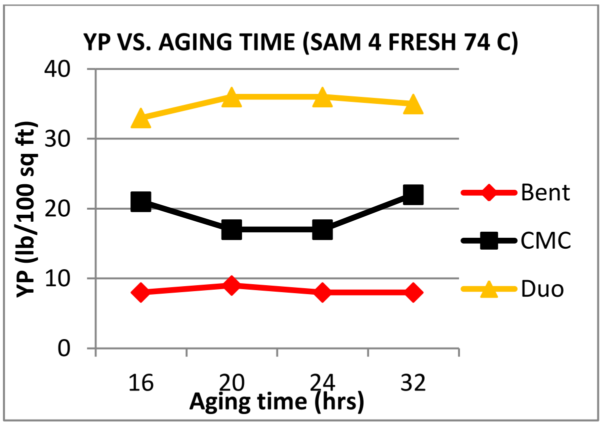


Figure 98 YP vs. Aging time, fresh water 74°C for sample 4

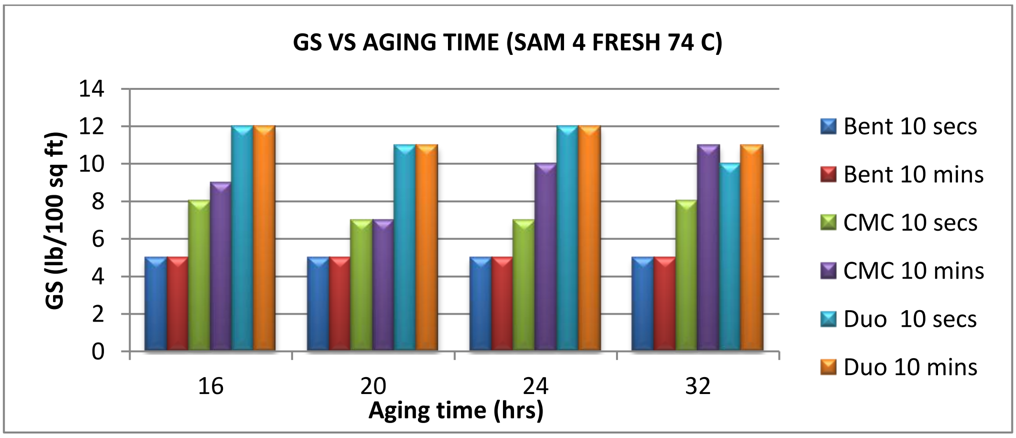


Figure 99 Gel strengths vs. Aging time for fresh water at 74° C for sample 4

Table 50 Aging results for sea water at ambient temperature for sample 4

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	12	7	5	2	3	3	9.89	9.69
	CMC	30	18	12	6	3	6	9.81	9.68
	Duo	82	72	10	62	12	15	9.87	9.45
20	Bent	12	8	4	4	3	3	9.89	9.61
	CMC	28	16	12	4	1	3	9.81	9.64
	Duo	85	68	17	51	12	15	9.87	9.44
24	Bent	14	9	5	4	4	4	9.89	9.52
	CMC	29	16	13	3	2	3	9.81	9.58
	Duo	86	68	18	50	13	16	9.87	9.00
32	Bent	14	9	5	4	4	5	9.89	9.59
	CMC	34	20	14	6	3	7	9.81	9.80
	Duo	76	66	10	56	11	14	9.87	9.42

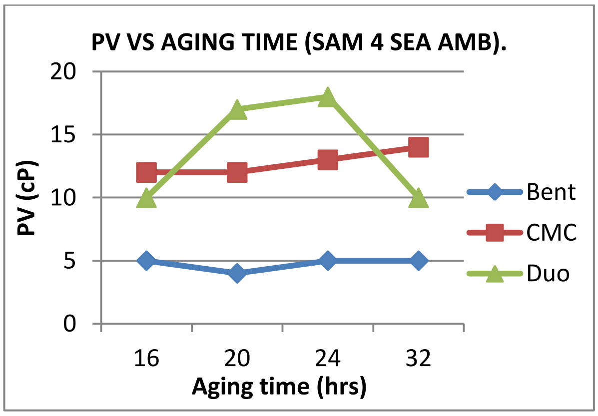


Figure 100 PV vs. Aging time, sea water ambient for sample 4

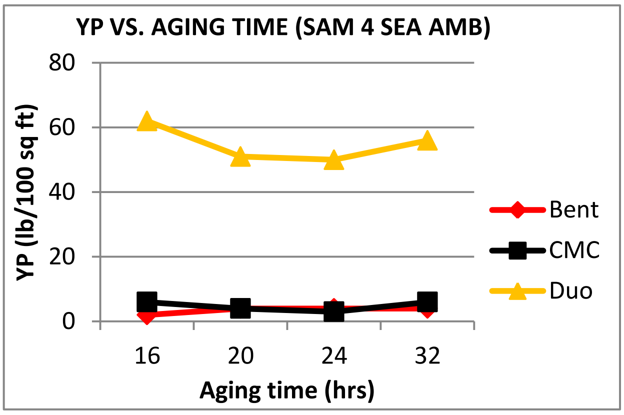


Figure 101 YP vs. Aging time, sea water ambient for sample 4

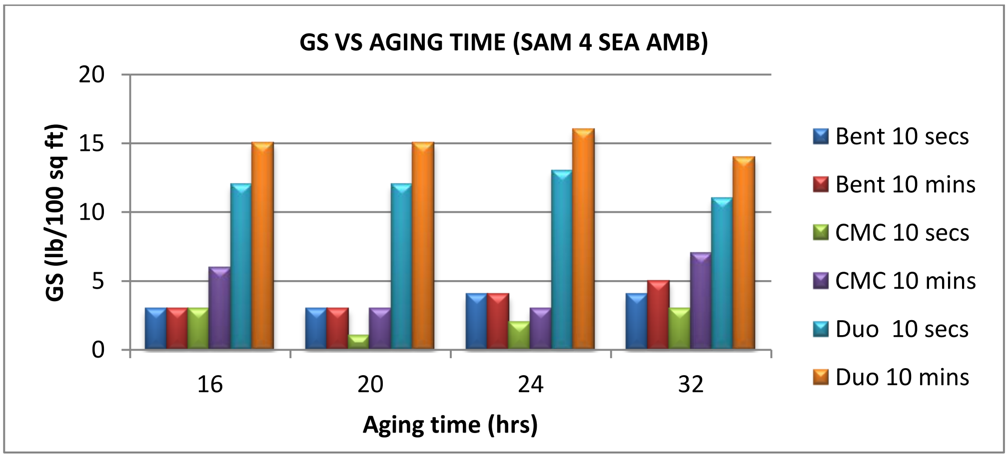


Figure 102 Gel strengths vs. Aging time for sea water at ambient temperature for sample 4

Table 51 Aging results for sea water at 74 degree celcius for sample 4

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet)	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	10	7	3	4	2	2	9.89	7.92
	CMC	19	11	8	3	3	5	9.81	7.99
	Duo	72	55	17	38	14	17	9.87	7.94
20	Bent	11	8	3	5	3	3	9.89	7.96
	CMC	17	10	7	3	2	4	9.81	7.86
	Duo	68	53	15	38	13	15	9.87	7.67
24	Bent	11	8	3	5	3	3	9.89	7.93
	CMC	20	12	8	4	4	6	9.81	7.73
	Duo	68	51	17	34	14	16	9.87	7.60
32	Bent	13	10	3	7	3	3	9.89	7.73
	CMC	23	14	9	5	4	4	9.81	7.70
	Duo	62	48	14	34	13	17	9.87	7.82

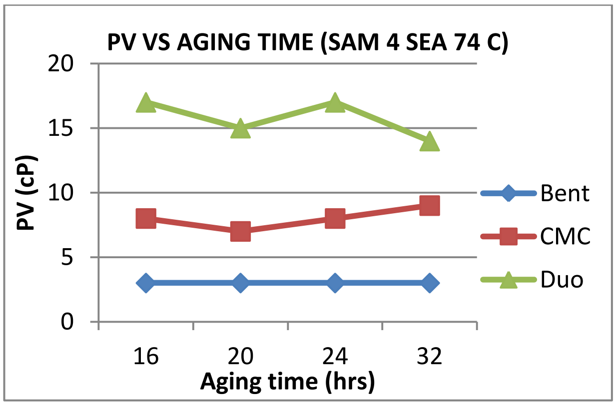


Figure 103 PV vs. Aging time, sea water 74° C for sample 4

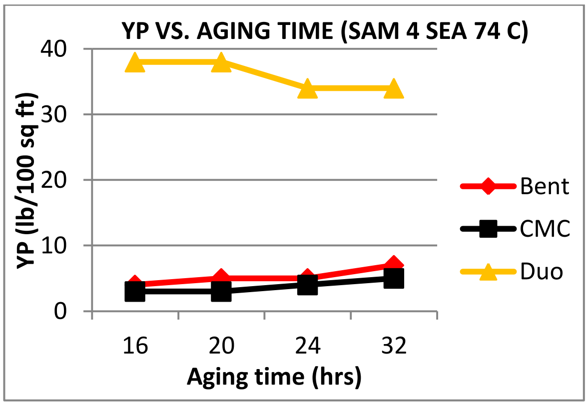


Figure 104 YP vs. Aging time, sea water 74° C for sample 4

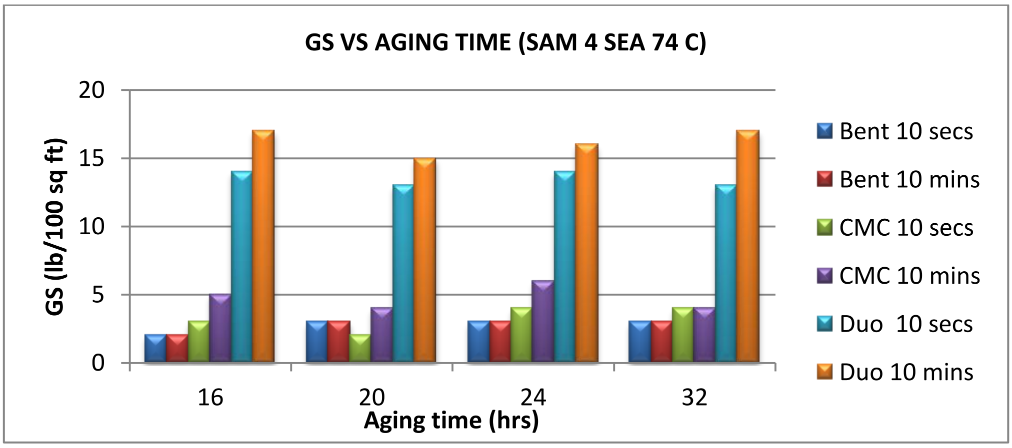
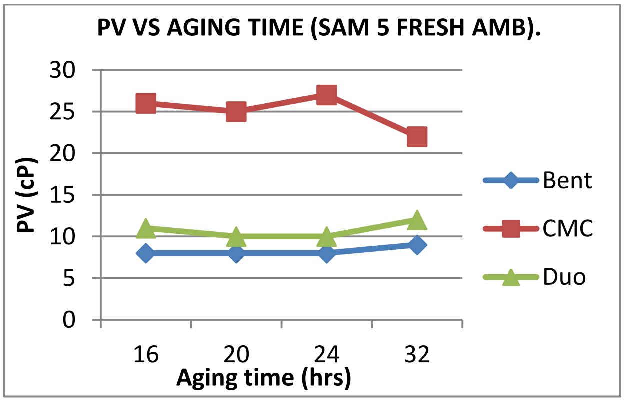


Figure 105 Gel strengths vs. Aging time for sea water at 74° C for sample 4.

Results for sample 5

Table 52 Aging results for fresh water at ambient temperature for sample 5

Aging time (hrs)	Additives	Viscosity Dial		PV (Cp)	YP (lb/100sq.feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	25	17	8	9	4	5	10.32	9.52
	CMC	76	50	26	24	3	7	10.30	9.41
	Duo	52	41	11	30	12	14	9.93	8.74
20	Bent	26	18	8	10	5	6	10.32	8.60
	CMC	75	50	25	25	5	11	10.30	9.32
	Duo	51	41	10	31	12	14	9.93	8.57
24	Bent	26	18	8	10	5	5	10.32	9.24
	CMC	80	53	27	26	6	11	10.30	9.33
	Duo	49	39	10	29	12	14	9.93	8.46
32	Bent	26	17	9	8	4	5	10.32	9.67
	CMC	66	44	22	22	3	7	10.30	9.68
	Duo	62	50	12	38	15	17	9.93	9.08



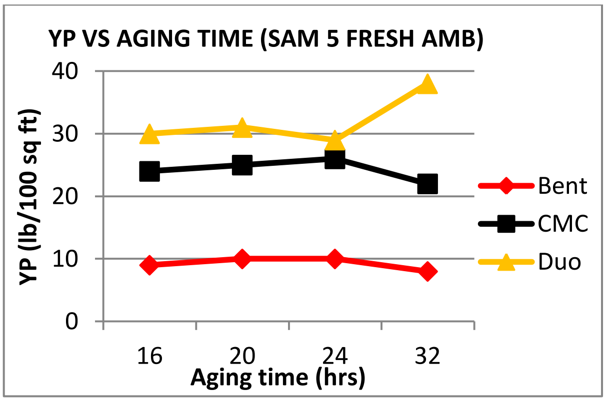


Figure 106 PV vs. Aging time, fresh water ambient for sample 5

Figure 107 YP vs. Aging time, fresh water ambient for sample 5

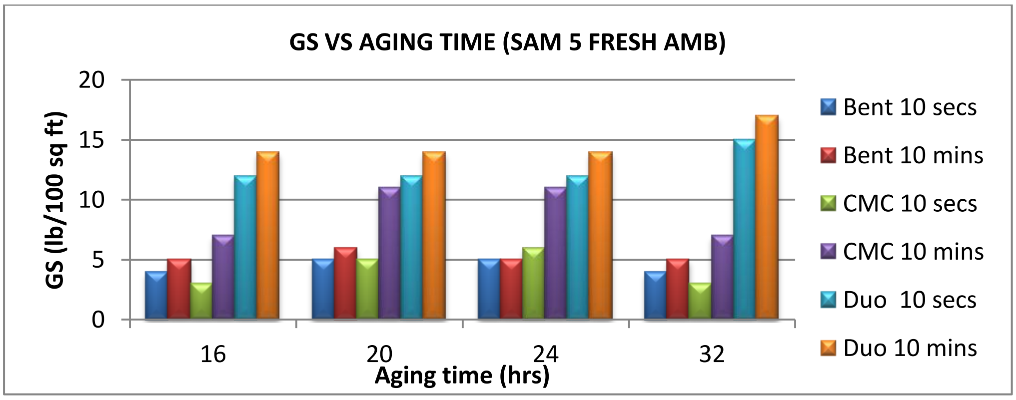


Figure 108 Gel strengths vs. Aging time for fresh water at ambient temperature for sample 5

Table 53 Aging results for fresh water at 74 degree celcius for sample 5

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	17	11	6	5	3	3	10.32	8.29
	CMC	36	24	12	12	3	6	10.30	9.20
	Duo	45	37	8	29	9	10	9.93	7.66
20	Bent	20	13	7	6	3	3	10.32	9.11
	CMC	35	23	12	11	4	4	10.30	9.15
	Duo	43	36	7	29	9	9	9.93	8.11
24	Bent	18	13	5	8	3	3	10.32	9.14
	CMC	37	25	12	13	4	6	10.30	9.28
	Duo	42	35	7	28	10	10	9.93	7.64
32	Bent	19	13	6	7	4	4	10.32	9.50
	CMC	30	24	6	18	3	7	10.30	9.37
	Duo	42	35	7	28	9	10	9.93	7.65

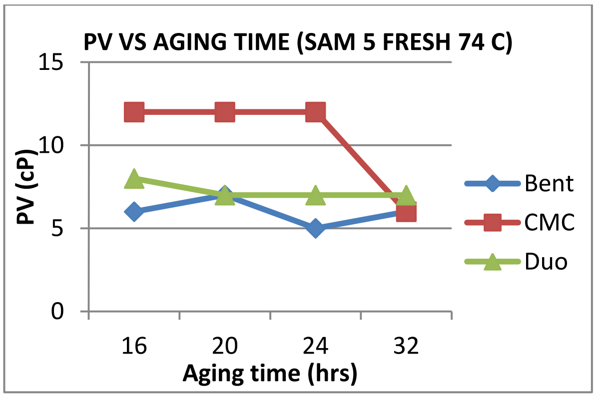


Figure 109 PV vs. Aging time, fresh water 74°C for sample 5

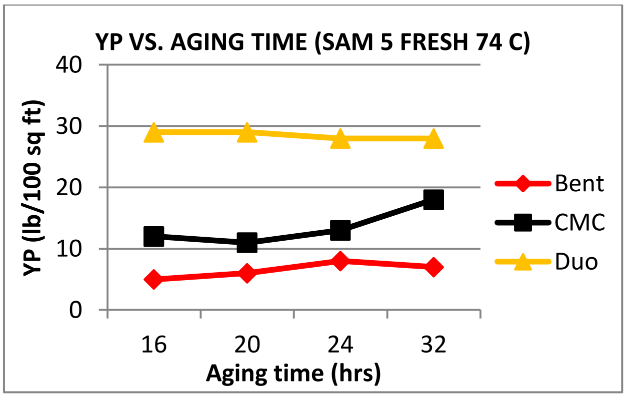


Figure 110 YP vs. Aging time, fresh water 74°C for sample 5

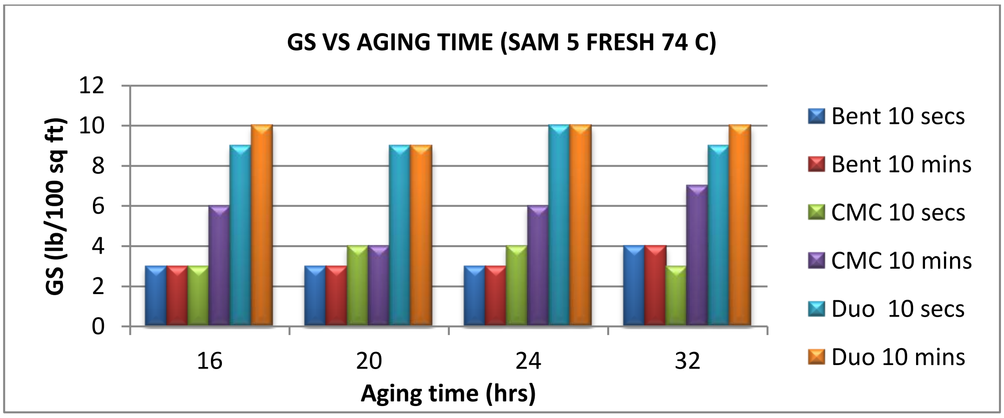


Figure 111 Gel strengths vs. Aging time for fresh water at 74° C for sample 5

Table 54 Aging results for sea water at ambient temperature for sample 5

Aging time (hrs)	**Additives**	**Viscosity Dial**		**PV (cP)**	**YP (lb/100sq.feet**	**Gel Strength (lb/100 sq.feet)**		**Start pH**	**End pH**
		600 rpm	**300 rpm**			**10 secs**	**10 mins**		
16	Bent	13	7	6	1	2	2	9.73	9.54
	CMC	30	17	13	4	1	2	9.78	9.61
	Duo	74	65	9	56	11	12	9.79	9.26
20	Bent	11	6	5	1	2	3	9.73	9.58
	CMC	27	16	11	5	2	4	9.78	9.60
	Duo	82	66	16	50	11	14	9.79	9.35
24	Bent	11	7	4	3	2	4	9.73	9.45
	CMC	16	9	7	2	1	3	9.78	9.42
	Duo	67	59	8	51	11	13	9.79	9.11
32	Bent	12	8	4	4	3	4	9.73	9.69
	CMC	23	13	10	3	0	2	9.78	9.77
	Duo	79	61	18	43	12	15	9.79	9.31

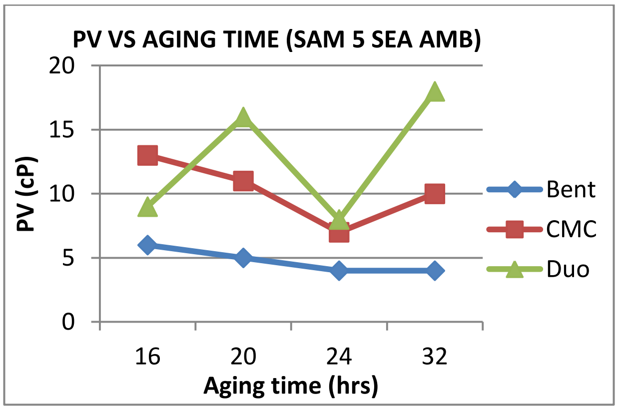


Figure 112 PV vs. Aging time, sea water ambient for sample 5

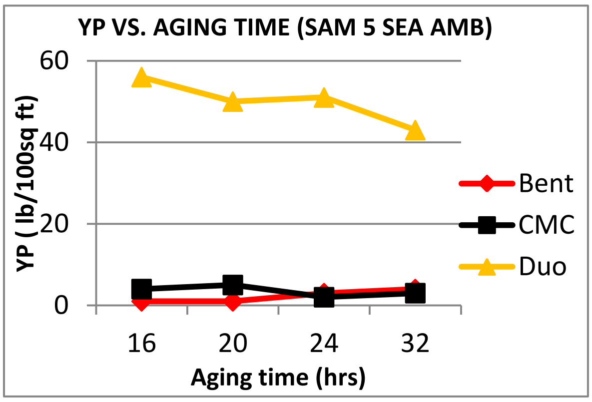


Figure 113 YP vs. Aging time, sea water ambient for sample 5

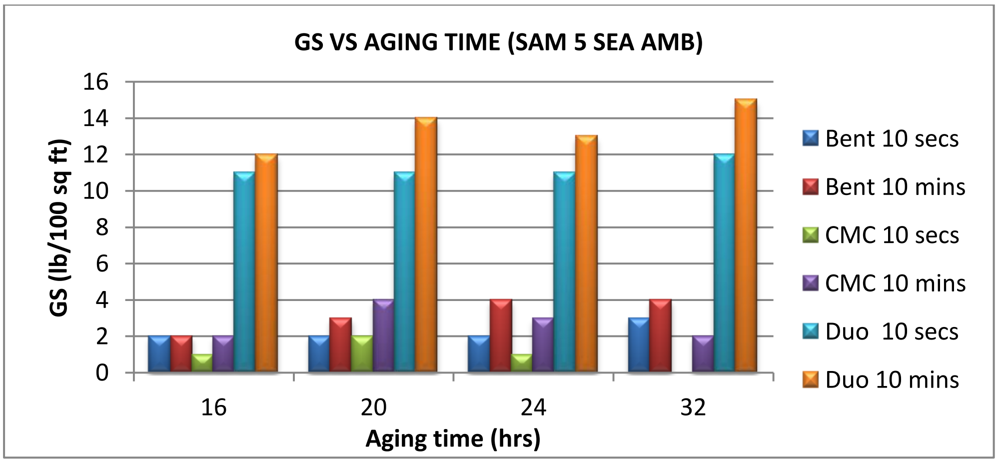


Figure 114 Gel strengths vs. Aging time for sea water at ambient temperature for sample 5

Table 55 Aging results for sea water at 74 degree celcius for sample 5

Aging time (hrs)	Additives	Viscosity Dial		PV (cP)	YP (lb/100sq.feet	Gel Strength (lb/100 sq.feet)		Start pH	End pH
		600 rpm	300 rpm			10 secs	10 mins		
16	Bent	7	5	2	3	2	2	9.73	7.91
	CMC	16	10	6	4	2	3	9.78	7.88
	Duo	63	49	14	35	11	13	9.79	7.66
20	Bent	10	7	3	4	2	3	9.73	7.88
	CMC	17	9	8	1	2	4	9.78	7.89
	Duo	59	47	12	35	11	14	9.79	7.56
24	Bent	13	10	3	7	3	3	9.73	7.82
	CMC	12	7	5	2	2	2	9.78	7.82
	Duo	66	51	15	36	14	16	9.79	7.45
32	Bent	12	9	3	6	2	2	9.73	7.82
	CMC	15	9	6	3	1	3	9.78	7.84
	Duo	61	47	14	33	13	16	9.79	7.74

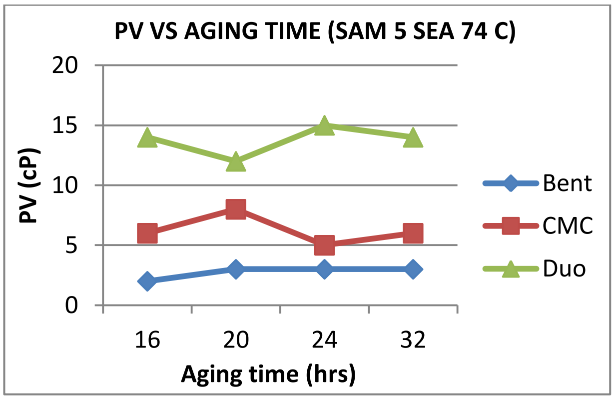


Figure 115 PV vs. Aging time, sea water 74^{o}C for sample 5

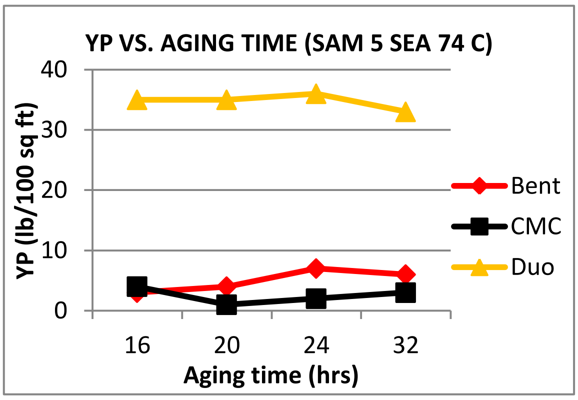


Figure 116 YP vs. Aging time, sea water 74^{o} C for sample 5

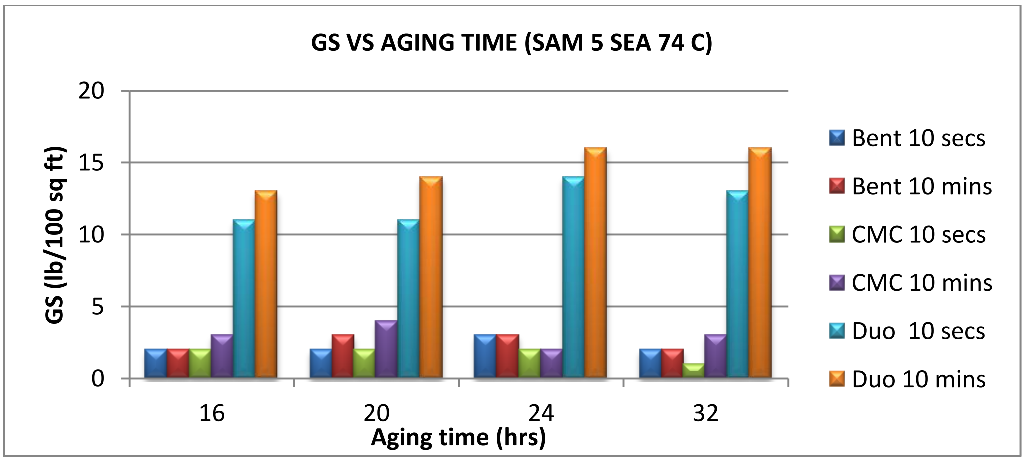


Figure 117 Gel strengths vs. Aging time for sea water at 74^{o} C for sample 5

Discussion and Conclusion

For this experiment, the effect of temperature, salinity and aging are investigated on the rheological properties of the various mud samples and on the additives. Different comparisons would be made to better understand the effects of these parameters incorporating the different water sources and additives.

Temperature Effects.

A comparison for fresh water source and at both ambient and increased temperature of 74°C showed that the plastic viscosity, yield point and gel strengths generally decreased for all samples and additives with increase in temperature.

A comparison between sea water sources at both ambient and increased temperature of 74°C showed that with increase in the temperature, the plastic viscosities reduced for all mud samples and additives, and the yield point almost showed similar results, but with very negligible increase with Bentonite additive. The gel strength increased for Duo Tec, but reduced for both Bentonite and CMC.

Salinity Effects.

A comparison between fresh water source at ambient temperature and sea water source (higher salinity) also at ambient temperature showed that an increase in salinity caused the plastic viscosity and yield points reduced with CMC and Bentonite, but increased with Duo Tec. The gel strengths however increased for the 3 mud additives used when salinity was increased.

A comparison between fresh water source at elevated temperature of 74°C and sea water source also at 74°C for all mud samples showed that plastic viscosity, yield point and gel strengths increased for Duo Tec, but reduced for Bentonite and CMC.

Aging Effects.

Unfortunately, the values were not all consistent for this part of the experiment, and it was very difficult to say what the effects of aging are on the mud sample rheologies and on the additives used. It could be as a result of the aging times being too close to each other and needed to be spaced a little futher from each other, or that more aging times were needed to be able to get a trend on the effectiveness of aging.

Some points which were very clear though, were observed from the results of tables and graphs, they include;

- For all 5 mud samples, using fresh water source and at both ambient temperature and 74°C, CMC gave the highest plastic viscosity.
- For all 5 mud samples, using sea water source and at both ambient temperature and 74°C, Duo Tec gave the highest plastic viscosity.
- For all 5 mud samples, using both sea water and fresh water sources, and for both ambient temperature and 74°C, Duo Tec dominated showing the highest yield point all over, CMC next, then bentonite.

- For all 5 mud samples, using only sea water sources at ambient temperature and 74°C, the yield point effects of Duo Tec were very conspicuous compared to when fresh water was used for both temperatures, that is, the gap between the yield points of Duo Tec as against those of bentonite and CMC was very huge.
- Just like the point immediately mentioned above, the same can be said for the gel strength. For all 5 mud samples, using only sea water sources at ambient temperature and 74°C, the gel strengths of Duo Tec were very conspicuous compared to when fresh water was used for both temperatures, that is, the gap between the gel strengths of Duo Tec as against those of bentonite and CMC was very huge.

To conclude, the following facts were established from the experimental results;

a) Generally, increase in temperature reduces plastic viscosity and yield point for both fresh and sea water sources.
b) With sea water, Duo Tec would gelate when temperature is increased, it has a high gel strength, while CMC and bentonite have reduced gel strengths with increase in temperature.
c) Duo Tec gave more superior gel strengths and yield points in sea water than any other additive.
d) CMC only has an advantage over Duo Tec in fresh water, if high plastic viscosity is desired, otherwise, Duo Tec shows more superior rheological properties especially in sea water where salinity is higher, than CMC and bentonite.
e) Aging effects were inconclusive, but a greater part generally showed that increasing the aging time decreased rheological properties.

4.10 Experiment 9

Title: **Filtrate Analysis**.

Aim: To determine the alkalinity, calcium and magnesium, and chloride content of the different filtrates of mud sample 5.

Requirement: mud sample 5 filtrates using different additives from both sea and fresh water sources from fluid loss experiment, phenolphthalein indicator, methyl orange indicator, hydrochloric acid.

Procedure

The filtrates of mud sample 5 obtained from the filtration experiments using the different additives – bentonite, CMC, MI PAC and starch and also using the two water sources – fresh tap water and sea water, were analyzed in the laboratory by the laboratory staff in the University for the above mentioned tests. The results were analyzed and compared.

Theory

a) Alkalinity is a measure of the combining power of a base with an acid. It is a detection of the amount of acid required to reduce the pH of a solution to a specified value. Different amounts of acids are required to reduce the pH of different solutions due to the presence of buffering ions and substances that react with the acid in addition to the hydroxyl ions in solution. Two filtrate alkalinities namely the phenolphthalein filtrate alkalinity, P_F and methyl orange filtrate alkalinity, M_F otherwise known as total alkalinity, are normally measured. The phenolphthalein alkalinity is the number of cubic centimeters of 0.02 normal H_2SO_4 or HCl necessary to reduce the pH of 1 cc of filtrate to 8.3, which is the colour change end point of phenolphthalein indicator solution. The methyl orange alkalinity is a measure of the amount of the same acid needed to reduce the pH of the filtrate to 4.5, which is the colour change end point of methyl orange indicator solution. The presence of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions in the mud filtrates is the reason for titrating to these specific end point values. The carbonate ion reacts with acid to form bicarbonate. This reaction is completed when the pH is reduced to 8.3. Furthermore, neutralization reaction of all the OH^- ions is essentially complete at this pH. Therefore, phenolphthalein alkalinity is a measure of the combined contributions of hydroxyl and carbonate alkalinities.

$$H^+ + OH^- \rightarrow H_2O \qquad (eqn\ 48)$$

$$H^+ + CO_3^{2-} \rightarrow HCO_3^{2-} \qquad (eqn\ 49)$$

As the pH is further reduced to 4.5, the bicarbonates are being converted to CO_2 and water when they react with acid.

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \qquad (eqn\ 50)$$

Stoichiometry classification ascribes the entire alkalinity to bicarbonate, carbonate and hydroxide and assumes the absence of other (weak) inorganic or organic acids such as silicic, phosphoric, and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalkinities.

Based on this classification;

- Carbonate (CO_3^{2-}) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.
- Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.
- Bicarbonate (HCO_3^-) alkalinity is present if phenolphthalein alkalinity is less than half the total alkalinity.

These relationships may be calculated using the following scheme, where P is phenolphthalein alkalinity and T is total alkalinity. Select the smaller value of P or (T-P). Then, carbonate alkalinity equals twice the smaller value. When the smaller value is P, the balance (T-2P) is bicarbonate. When the smaller value is (T-P), the balance (2P-T) is hydroxide (Arnold. E et al, 1992). All results are expressed as $CaCO_3$.

b) Salinity is another vital aspect of mud filtrate analysis. It is measured by titration of the filtrate for chloride ion concentration and is reported as chloride concentration in mg/l or as sodium chloride (NaCl) concentration in mg/l. The chloride content is measured using Ion Chromatography method. The sodium chloride concentration is equal to 1.65 times the chloride concentration. The degree of hydration of mud is reduced by increased salinity due to increased flocculation which inturn reduce plastic viscosity and increases fluid loss. The yield point and gel strength will also tend to increase. Monitoring the chloride content of a mud filtrate is a means of detecting a salt water flow or the drilling of salt. Make up water should also be titrated for chlorides in order to determine whether an increase in filtrate chlorides has come from the formation water or from the makeup water.

c) Calcium and magnesium ions in a mud have serious effects on clay behavior. They cause a reduction in the degree of hydration and promote flocculation and aggregation of the clay particles as they replace the sodium ions on the clays. This would result to increases in yield point, gel strength and fluid loss of the mud. Lots of organic treating agents are also sensitive to calcium and magnesium concentrations therefore, it is necessary to monitor the concentration of these ions in the mud filtrate. In summary, an increasing trend of total hardness or sudden increase to values above 200 mg/l signals the presence of calcium or magnesium in the filtrate. The harmful effects on mud properties will be increased fluid loss, yield point, ang gel strength. The pH will decrease, especially from addition of magnesium, and the plastic viscosity will tend to decrease as the hardness ions reduce the hydration of the clay platelets. The atomic absorption spectrometry is used for determining the calcium and magnesium contents of the mud filtrate in the laboratory.

Results.

Results from the filtrate analysis are shown below in the tables 56 through 60 below;

Table 56 Filtrate alkalinity results using the different additives and fresh tap water source.

samples	start pH	vol. Acid for P_f (ml)	vol. Acid for M_f (ml)	P_f (meq/l)	M_f (meq/l)	CO_3^- (meq/l)	HCO_3^- (meq/l)	OH^- (meq/l)
MI PAC	9.199	0.177	1.522	0.4419	3.3633	0.8838	2.4795	N/A
CMC	9.492	0.261	1.189	0.8703	3.0933	1.7406	1.3527	N/A
Starch	9.834	0.631	1.921	1.2623	2.5803	2.5246	0.0557	N/A
Bentonite	9.710	0.479	1.573	1.1963	2.7370	2.3926	0.3444	N/A

Table 57 Filtrate alkalinity results using the different additives and sea water source.

samples	start pH	vol. Acid for P_f (ml)	vol. Acid for M_f (ml)	P_f (meq/l)	M_f (meq/l)	CO_3^- (meq/l)	HCO_3^- (meq/l)	OH^- (meq/l)
MI PAC	9.706	1.326	4.502	6.6306	15.8780	13.2612	2.6168	N/A
CMC	9.889	1.361	4.414	6.8059	15.2651	13.6118	1.6533	N/A
Starch	9.870	1.491	4.771	7.4555	16.3975	14.9110	1.4865	N/A
Bentonite	9.898	1.503	4.959	7.5136	17.2828	15.0272	2.2556	N/A

Table 58 Chloride concentration results using different additives for both fresh and sea water sources.

Cl concentration.		
	Sample	concentration (mg/l
Fresh water	pure sample	28.705
	MI PAC	255.520
	CMC	25.490
	starch	16.570
	Bentonite	18.365
Sea water	pure sample	4070.000
	MI PAC	4260.000
	CMC	4256.000
	Starch	3986.000
	Bentonite	3872.000

Table 59 Magnesium concentration results using different additives for both fresh and sea water sources.

Mg concentration.		
	Sample	concentration (mg/l
Fresh water	pure sample	0.612
	MI PAC	1.250
	CMC	1.291
	starch	0.983
	Bentonite	1.111
Sea water	pure sample	193.353
	MI PAC	185.925
	CMC	156.205
	Starch	188.708
	Bentonite	164.693

Table 60 Calcium concentration results using different additives for both fresh and sea water sources.

Ca concentration.		
	Sample	concentration (mg/l
Fresh water	pure sample	2.920
	MI PAC	11.120
	CMC	8.894
	starch	2.243
	Bentonite	2.880
Sea water	pure sample	8.519
	MI PAC	33.197
	CMC	5.980
	Starch	10.033
	Bentonite	4.258

Discussion and Conclusion

a) Filtrate Alkalinity test

Filtrate Alkalinity tests are carried out mainly to determine, the amount of acid in ml needed to neutralize the filtrate to a pH of 8.3 and afterwards to 4.5 and also to check the hydroxyl, carbonate or bicarbonate ions present in the filtrate. The pH of filtrates got using sea water, are higher than those got using fresh water, hence a higher amount of acid is needed for neutralization to the end point pH for both phenolphthalein and total alkalinity as evident in tables 56 and 57. The meq/l has also been given for all the various additives. In terms of the amounts of hydroxyl, carbonate and bicarbonate ions present, using the stoichiometry classification, only carbonates and bicarbonates are present in these filtrates.

b) Chloride concentration.

Increase in salinity results to a decrease in the degree of hydration, and the flocculation tendency is also increased, affecting the filtration and flow properties of mud in a huge way. The yield point, gel strength and fluid loss will have increased tendencies. The pH would also be decreased and a slight increase in total hardness may be observed. Increased salinity will also cause dehydration of the mud particles, which in turn reduces the plastic viscosity and increases fluid loss. For concentrations of chloride above acceptable levels, lignosulfonate concentrations should be increased, as it protects the mud particles from dehydration effects of high salinity. It would also cause deflocculation thereby reducing yield point and gel strengths.

For the results shown in table 58, the chloride ion in sea water for all additives used is more than for fresh water, however, the range is within acceptable levels of not more than 10,000 mg/l, which is desirable.

c) **Ca and Mg concentration**.

When these are present in base water for drilling mud mix, they replace the sodium ions in the mud consequently, reducing the hydration degree, enhancing flocculation and aggregation of the mud or clay platelets, which would lead to increases in yield point, gel strength and fluid loss of the mud. As the pH of mud filtrates got from the fluid loss experiment are less than 10.5 for both sea and fresh water, it shows that Ca and Mg are both present. Values of these above 200 mg/l shows the existence or presence of calcium or magnesium in the filtrate and the above harmful effects would be expected. With addition of magnesium especially, the pH will decrease and the plastic viscosity will tend to decrease as the hardness ions reduce hydration of the clay platelets. They also affect some additives, for example, starch will perform quite well at high calcium concentrations, but CMC will lose its ability to hydrate as calcium concentration is increased. At 1000 mg/l, it becomes inactive. If both are found in excess, then treatment for both would be differently, first of all, trying to maintain a mud with a minimum clay solids content for both types of contaminant as the effect of the contaminant on the clay solids is responsible for the changes in mud properties that occur. Using soda ash to precipitate calcium is a very good method of eliminating calcium as it increases the pH and reduces the solubility of calcium. Caustic is applied for precipitating magnesium as it increased the pH,and when it gets to 10, precipitation begins and stops when it gets to a pH of 10.5.

For the results shown in figures 59 and 60, the values of both calcium and magnesium were more in sea water source than in the fresh water source filtrates. However, all values of calcium and magnesium showed that they were less than 200 mg/l, which is desirable.

To conclude, the amounts of chloride, calcium and magnesium are within acceptable range and further treatment would not be needed in the mud.

4.11 Experiment 10

Title: **Downhole Simulation Test**.

Aim: To simulate downhole pressure effects.

Requirement: Bentonite sample, reactor, clean sand from Fanø beach, pressure gauge, fresh water, hand mixer.

Procedure

Attach the necessary fittings and accessories to the reactor as shown in the schematic set up. Next, measure out 100 g of mud, and mix with water until homogeneity is obtained.

Scenario 1: Pour dry sand half way up the reactor, and then add the mud to spread all over the sand. Allow for a period of 30 minutes to develop, then, increasing the pressure gradually in 0.2 bar and observe. When the pressure reaches 2 bar, bleed off the pressure and observe with the tap at the bottom closed initially and later opened. The start time was 11:00 hours and the experiment was for a duration of 90 minutes. It was left to develop further and at 11:00 hours the next day, observations of any developments would be noted.

Scenario 2: Pour dry sand half way up the reactor, and then add water into the reactor. Actively mix the sand and water to uniform mass, then, remove excess water in the reactor. Pour in already mixed mud and allow waiting for 30 minutes and afterwards, apply pressure incrementally in 0.2 bar and observe for any changes. With the bottom tap initially closed and later opened continue with pressure increase and observe.

Precaution.

Care was taken not to exceed 2.5 bar because of the ill-nature of the reactor as some internal cracks were noticed around its structure.

Set up.

The schematic of the reactor fitted with the necessary accessories is presented below;

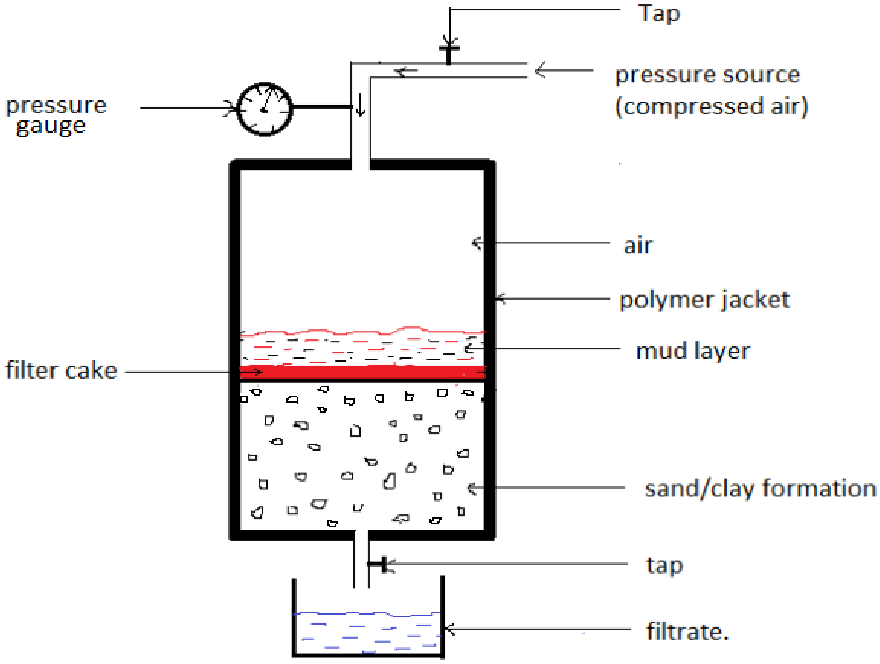


Figure 118 Schematic of downhole simulation experiment equipment.

Results and Observation.

Scenario 1: After 30 minutes of waiting, a thin distinctive layer developed separating the mud from the sand formation as can be seen in figures 119 and 120. It had a height of 3mm when measured.

Figure 119 Formation of thin layer of filter cake.

Figure 120 Section showing thin filter cake layer.

With increase in pressure to 2 bar, it was observed that the distinctive layer thickness separating the mud from the sand formation had increased to 20 mm. This remained steady even when pressure was bled off. After a wait period of 24 hours, it was observed that the thickness again had increased just slightly by 2 mm. Just a few drops of filtrate were got when the tap at the bottom was open.

Figure 121 Formation of thicker layer of filter cake.

Figure 122 Section showing thicker filter cake layer.

10 minutes after a wait time of 24 hours, which was 11:10 hours the next day, pressure was again increased gradually, and a crack was observed all around, just between the distinctive layer and the sand formation as can be seen in figure 123. This was with the bottom tap closed. With further increase in pressure, the crack expanded causing the sand formation to be separated from the other parts as shown in figure 124.

Figure 123 Crack between filter cake and formation

Figure 124 Expansion of crack due to pressure.

With this large gap produced, the pressure was bled off, with no significant reduction in the gap, but once the tap below was open, both parts separated by the gap were reunited again, lapping perfectly. Additionally, the distinctive layer was poked by passing a long metallic object through the mud layer to this layer, and a hard surface was met.

Scenario 2: After waiting for 30 minutes and pressure was increased gradually, the filtrate kept dropping from the bottom part but no distinctive layer was seen like in the case where the formation was dry as shown in figures 125 and 126.

Figure 125 Set up with wet sand formation.

Figure 126 Section showing mud and formation layers.

Further increase in pressure kept the filtrate pouring from the bottom, and the mud height or layer was reduced in thickness and progressively became thinner as seen in figures 127 and 128. The distinctive layer was however not seen easily due to the fact that it was a wet formation, but when poked with a hard metallic object, it showed a very hard surface had also developed just beneath the mud layer as shown in figure 129.

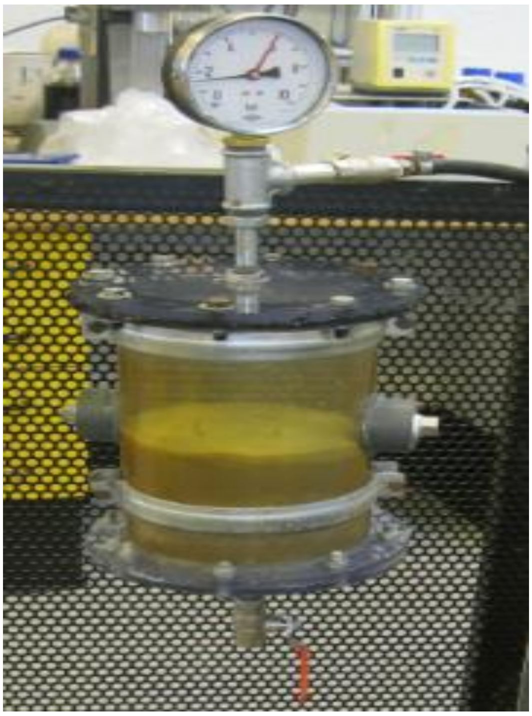


Figure 127 Reduced mud layer in wet formation

Figure 128 Section showing reduced mud layer.

Figure 129 Ascertaining filter cake development on the wet sand formation by poking with a hard metallic object.

Discussion and Conclusion.

Scenario 1: As clean sand from Fanø beach was used, the particles are large, well rounded and well sorted, which indicates a high porosity, and after allowing to stand for 30 minutes without any pressure increase, it can be said that the developed thin distinctive layer, which would otherwise be referred to as the mud or filter cake, was formed by reaction between the mud and the sand. At the time, no filtrate was seen even with the bottom tap open meaning that the hydrostatic pressure in the reactor was either less than or equal to the formation pressure which denotes an under balanced or balanced hole respectively. With increase in pressure to 2 bar, it was noticed that little drops of filtrate were seen from the bottom tap and the thickness of the distinctive layer, which is the filter cake, increased. Here, the increased pressure caused the liquid part of the mud to mix and penetrate further into the filter cake layer already established to increase its thickness. At this junction, it can be said that the hydrostatic pressure of the mud in the reactor was greater than the sand formation pressure, representing an over balanced hole. With increased waiting time of 24 hours, the thickness of the filter cake only slightly increased by a few millimeters which shows that an impermeable layer of filter cake had been formed which restricted much passage or loss of fluid through it.

The crack observed from figure 123 above is a result of compressed air escaping through the sides of the reactor and straight into the sand formation which then separated it from a well formed impenetrable filter cake layer. With increased pressure, and the bottom tap closed, the crack size was seen to increase. Reducing the pressure by bleeding off the pressure supply and allowing some of it to escape by opening the bottom tap sealed off the gap.

Scenario 2: Unlike in the first scenario, the sand formation in the second was a wet formation. Increasing the pressure caused the filtrate to drip from the bottom tap hole, meaning that the hydrostatic pressure was higher than the formation pressure. The height of the mud column in the reactor was also seen to reduce more meaning it had lost some of its volume, in this case, its liquid part, to the wet formation. Visibility of this distinctively filter cake layer was difficult and not obvious, but it was proven after some time that the pressure increase had caused the formation of a hard layer when the layer was poked with a hard metallic object as shown above in figure 129.

To conclude, a hole can be balanced, underbalanced or overbalanced depending on the balance between the hydrostatic pressure and the formation pressure as proven in the experiment. Also, a filter cake layer is formed with increased pressure until a certain thickness is reached after which it becomes impenetrable. A good filter cake should be thin, slick and virtually impermeable.

Additional Information.

In reality, a balance must be struck between these various pressures (hydrostatic and formation pressures) so as to avoid downhole problems, for example, with the formation pressure greater than the hydrostatic pressure of the drilling mud, if not checked, then formation fluid enters into the well causing a kick, which if not controlled quickly, could result to a blow out.

5. Discussion

A typical drilling operation can vary in cost ranging from about $20,000 for a small land rig in an established area to more than $150,000 a day for a modern offshore rig. About U.S $40,000,000 or more can be used for exploration in deep water. These values show that a drilling operation is a very expensive venture which should be handled in the best and most efficient manner possible, as returns on investment are affected significantly depending on performance effectiveness. The drilling fluid plays several fundamental roles in drilling wells. The safety and economics of the drilling operation could be highly compromised if the mud properties (physical, chemical and rheological) are inaccurate. The drilling mud can be said to be the single most essential system in safe, efficient and economic drilling, therefore, its significance cannot be overemphasized. Its performance must be monitored and mud properties tested frequently and results documented in order to have a successful operation. There is no room for error, as a little miscalculation could be very negative, even fatal in some extreme cases, therefore a mud program which has been carefully planned must be in place.

For the purpose of this project, 10 different experiments have been carried out on 5 different mud samples to investigate the effects of various drilling mud additives on their properties and performances. The rheological properties (plastic viscosity, yield point and gel strength) as well as physical properties as fluid loss, sand content, are very important in mud property and performance evaluation as they give an indication of what actions are to be taken in the case that adjustments of the mud properties are required.

As WBM was used, experiments were carried out on both types of base water (fresh tap water and Fanø sea water) to check their suitability for use as the continuous phase for mud mixing. The concentrations of contaminants, in this case, chloride ions, calcium and magnesium ions, were determined as they affect mud and additive performance.

Muds that have a high tendency to absorb water and increase in volume are said to possess good swell abilities and are desirable for coating the sidewalls of the well bore. A free standing swell test was performed on all mud samples to determine their swell abilities. The mud samples were allowed an equal waiting time of 18 hours in water, and their swell volumes checked afterwards. A swell volume above the 12-16 ml mark on a graduated cylinder is said to be desirable, while below or equal to the 4-6 ml mark signifies a poor swell ability.

When clay or shale formations are being drilled, tendencies are high that shale would absorb water as they have strong affinity for water molecules, and when this happens, the result is sloughing of the shale formation. Swelling clays and shales can also impede drilling, cause hole enlargement, increase viscosity and damage oil-producing zones. In order to avoid this, additives are used that inhibit the flow of water into the shale formations. Most of them act by encapsulating the mud, forming a protective coating around them, so the flow of water is inhibited. Glycol and KCl were used for this purpose, but other combinations such as KCl and a polymer such as polyacrylamide, have gained large popularity for use as inhibitive agents.

Solids present in the mud in very high amounts can increase wears on downhole equipment and other mud circulatory equipment such as pumps and valves. The abrasive nature of these sand particles causes friction when it moves against the surfaces of these equipment, therefore the sand content should be as reduced as possible which can be achieved by use of proper solids control equipment. A sand content test was carried out using a 200 standard mesh size sieve to obtain the volume percent of sand contained in the mud. API specification indicates that sand content below 2 % is desirable, and above this value, it has to be controlled.

For muds which are very thick and viscous, they make pumping very difficult around the mud circulatory system and also bring about high pressure losses. This in turn will not allow for good bottom hole cleaning since there is not enough pressure to lift the cuttings. In this case, dispersants or deflocculants are added to thin out the muds. They are mainly anionic in nature and act by deflocculating the clay particles by neutralizing the positive charge on the edge and increase the negative charge density on the clay platelets. Sodium pyrophosphate decahydrate, SPP and sodium hexametaphosphate, SHMP were the two polyphosphates used as thinners in this project to reduce viscosity of drilling mud. Another common polyphosphate commonly used is sodium acid pyrophosphate, SAPP. However, more popularly used and applied thinners are lignosulfonate, lignites and tannins.

For the purpose of increasing viscosity of drilling mud, different viscosifiers were put to the test. Viscosifiers used include bentonite, Duo Tec NS and CMC. With increased amounts of these additives progressively, their effect on viscosity and rheological properties was determined.

Varying the temperature at ambient temperature and at elevated temperature of 74^{o}C which is the temperature in Tønder for geothermal drilling was done to investigate the effects on the mud samples and additives. Since application of heat causes a lot of changes in mud samples and additive, effects could be attributed to the complicated interplay of several causes, some of which are more dominant than others. Factors such as reduction in the degree of hydration of the counter ions, changes in the flocculation and aggregation of clay particles, changes in the dispersion of associated clay micelles and increased thermal energy of the clay micelles could cause a lot of variations since all are happening simultaneously when temperature is varied. Determination of the mud conditions at the surface may be easy, but it is no where near telling the real story or giving a true representation of what happens downhole, and to get an idea of bottom hole conditions at the surface, the concept of aging was applied, which is the process by which mud samples previously sheared are allowed some hours, normally from 16 hours and above, to develop fully, their rheological and filtration properties. It is done when mud is left inactive, for example during tripping. For this project, it was difficult to tell the effects of aging as the trend could not easily be ascertained, so facts on the aging aspects were inclusive, but generally, aging tends to reduce rheological properties of the mud. More aging times and longer aging times should have been tested to give a better understanding of the effects of this concept on mud sample properties and on additives as well.

Filtrate analysis was carried out in order to determine the alkalinity of the mud filtrates, and also to determine the level of calcium and magnesium concentrations present. This analysis is important as these contaminants affect mud performance downhole, it gives an idea of what treatments should be given to the mud to get the contaminants to acceptable levels that would not cause any form of problems down in the well bore.

Pressure variations downhole could also cause a lot of differences in the behaviors of mud. Simulation of downhole pressures in order to determine effect on fluid loss, and filter cake formation was carried out. The results showed the relationship between a balanced, underbalanced and overbalanced hole, as functions between the hydrostatic pressure and formation pressure balances. Pressures of not more than 2.5 bars were used for this experiment, but it would have been more interesting to have varied pressures above this value to get a better understanding of the concepts mentioned. The development of filter cakes were also seen when the formation was dry, and felt when the formation was wet, which made visibility of the filter cake very difficult.

6. Conclusion.

Within the limits of experimental error, investigations have been carried out to determine the effects of additives on the physico-chemical properties of 5 different mud samples at varying conditions. The findings from this study showed that all mud samples used had a good swellability and could be used for coating of the side walls of well bore. In the swell inhibitive test, inhibition was mainly due to the potassium ions present in KCl, and that glycol could not effectively inhibit absorption of water except in combination with KCl. Even though both polyphosphates presented did their jobs of reducing viscosity, sodium pyrophosphate decahydrate showed more superior thinning effects than sodium hexametaphosphate.

Furthermore, samples 4 and 5 were seen to have the least sand contents both in volume and weight percents, while sample 2 had the highest sand content. With regards to viscosity, both CMC and Duo Tec NS have shown that they can increase viscosity well enough, however, Duo Tec would be recommended more for use as its plastic viscosity is not as high as that got using CMC and it has better yield points and gel strengths which are desirable of a viscosifier.

In addition, CMC has been proven to have very good fluid loss properties compared to other additives used, but MI PAC has been seen to be another fluid loss agent that can competitively give similar results as CMC and should be used as an alternative. Both would be recommended as fluid loss agents, allowing the mud sample to produce filter cakes of desirable properties.

The effects of aging were difficult to tell from the experiments, but generally, it showed that aging reduced rheological properties. Temperature effects also showed that increasing temperature generally reduced rheological properties. Filtrate analysis showed that the levels of calcium, magnesium and chlorides present in the filtrates were at acceptable levels and further treatment would not be necessary.

With increase in pressures downhole, filter cake development occurs, and when the hydrostatic pressure is greater than the formation pressure, the hole is said to be over balanced. Reversing this shows that the hole is underbalanced, and both pressures are equal, then it is said to be balanced.

To conclude, drilling muds are meant to perform multiple functions at the same time, so the mud sample to use and additives to apply rest on the shoulders of the mud engineer. He determines what is to be done depending on the operational conditions he faces during the drilling process.

7. Limitations of project.

Some challenges were met during the course of this project work which in one way or the other, cut short and affected some experimental values that would have been significant parts of the project.

Unavailability of most of the standard equipment used in mud tests was a key limitation. The mud balance which is used to measure mud density was unavailable, the sand content kit, for measuring the sand content in the mud was also not available. Other standard equipment such as the filter press and retort kit were also unavailable. Availability of these would have made the project more informative as more tests would have been carried out. However, a fann 35 SA viscometer was provided which is a key equipment in mud tests.

Some key additives such as lignosulphates, lignosulfonates, polyacrylamides solutions and a host of others which would have made for better comparison, more enriching information and provided more results were also not at hand, so what was available was used.

Finally, time was a challenge to this project. More could have been done if the time was available, but within the time frame set for this project, not so much more could have been achieved.

8. Recommendation.

To give a clearer picture of the interpretation to most of the experimental results, the elemental make up or constituents of each of the muds sample should be sought after as this information was not provided along with the mud samples. This would to a large extend tell more about the behaviors of the mud samples when different additives and conditions are applied on them, especially if they are from different sources.

Furthermore, a wider range of additives, polymers and inorganic salts should be used in the experiments, as this would give a better and broader understanding of drilling mud additives and their effects on drilling muds.

In addition, for future works on the aging and temperature experiments, I would suggest using a number of aging temperatures unlike only ambient temperature and 74 degree Celsius used in this project, and also giving more gaps between the aging times possibly aging for days and weeks to get more accurate and clearer results.

For experiments on the downhole simulation tests, superior quality reactors made of materials that can withstand pressure to at least 6 bars should be used to fully appreciate the effects of pressure variation downhole. Also, more should be done mathematically in terms of calculations downhole meaning that the height of mud column, density of mud, diameter of reactor and some other dimensions and parameters should be obtained.

Finally, projects of this nature should be done as a joint 9th and 10th semester project as the experiments were time consuming, and to achieve better results, longer waiting times are required to simulate downhole conditions.

Bibliography

Addison, P.S., 2010. *The illustrated wavelet transform handbook: introductory theory and applications in science, engineering, medicine and finance, CRC Press.*

Arnold E. Greenberg, Lenore S. Clesceri, Andrew D. Eaton, 1992. Standard methods for the examination of water and waste water. American public health Association, American water works Association, Water Environment Federation.

Devereux, S., 1999. *Drilling Technology: In Nontechnical Language*, PennWell Books.

Dr Dietrich Koch, 2008. European Bentonites as alternative to MX-80, Science and Technology series 334(2008) Andra.

Eghai project, 2004. The investigations the physico-chemical effects of additives on drilling mud.

Van Dyke, K. & Baker, R., 1998. *Drilling Fluids, Mud Pumps, and Conditioning Equipment*, Univ of Texas at Austin Petroleum.

Fink, J., 2011. *Petroleum engineer's guide to oil field chemicals and fluids*, Access Online via Elsevier.

Growcock, F. et al., 1999. Novel lubricants for water-based drilling fluids. In *SPE International Symposium on Oilfield Chemistry*.

Handbook, O.O., 2006. US Department of Labor. *Includes information on specific jobs, working conditions, training and education requirements, earnings projections and job prospects*.

Harvey, R.W. & Garabedian, S.P., 1991. Use of colloid filtration theory in modeling movement of bacteria through a contaminated sandy aquifer. *Environmental science \& technology*, 25(1), pp.178–185.

Hawker, D., 2001. Drilling Fluid Hydraulics.

Horsch, R. et al., 1985. A simple and general method for transferring genes into plants. *Science*, 227, pp.1229–1231.

Kranenburg, W. et al., 2011. SWAN-Mud: Engineering model for mud-induced wave damping. *Journal of hydraulic engineering*, 137(9), pp.959–975.

Lapeyrouse, N.J. et al., 2011. *Formulas and Calculations for Drilling, Production, and Workover: All the Formulas You Need to Solve Drilling and Production Problems*, Gulf Professional Publishing.

Leniger, H.A., Beverloo, W. & others, 1975. Food process engineering. *Food process engineering.*

Lienau, P.J., Lunis, B.C. & Center, G.-H., 1989. *Geothermal direct use engineering and design guidebook*, Geo-Heat Center, Oregon Institute of Technology.

Makinde, F. et al., 2011. Modelling the effects of temperature and aging time on the rheological properties of drilling fluids. *Petroleum \& Coal*, 53(3), pp.167–182.

Max R. Annis, M.V.S., 1996. Drilling Fluid Technology Exxon Manual.

McGill, M. et al., 1997. Drilling severely depleted sands in the Gulf of Mexico: the benefits of cloud point glycols. In *SPE Annual Technical Conference and Exhibition*.

MUDS, O.-B., 2000. Stabilizing boreholes while drilling reactive shale formations with silicate-base drilling fluids. *Drilling Contractor*.

Naik, G., 2003. Tight Gas Reservoirs-An Unconventional Natural Energy Source for the Future. *www. sublette-se. org/files/tight_gas. pdf. Accessado em*, 1(07), p.2008.

Olatunde, A. et al., 2012. IMPROVEMENT OF RHEOLOGICAL PROPERTIES OF DRILLING FLUID USING LOCALLY BASED MATERIALS. *Petroleum \& Coal*, 54(1), pp.65–75.

Petrides, D. et al., 1989. Bioprocess simulation: an integrated approach to process development. *Computers \& Chemical Engineering*, 13(4), pp.553–561.

Potash, M.S. & Nygren, R.T., 1993. Multiple integrated document assembly data processing system.

Sifferman, T., 1979. Flow properties of difficult-to-handle waxy crude oils. *Journal of Petroleum Technology*, 31(8), pp.1042–1050.

Skalle, P., 2010. *Drilling Fluid Engineering*, Bookboon.

Taiwo, A. & Joel, O., Investigation of local polymer (cassava starches) as a substitute for imported sample in viscosity and fluid loss control of water based drilling mud.

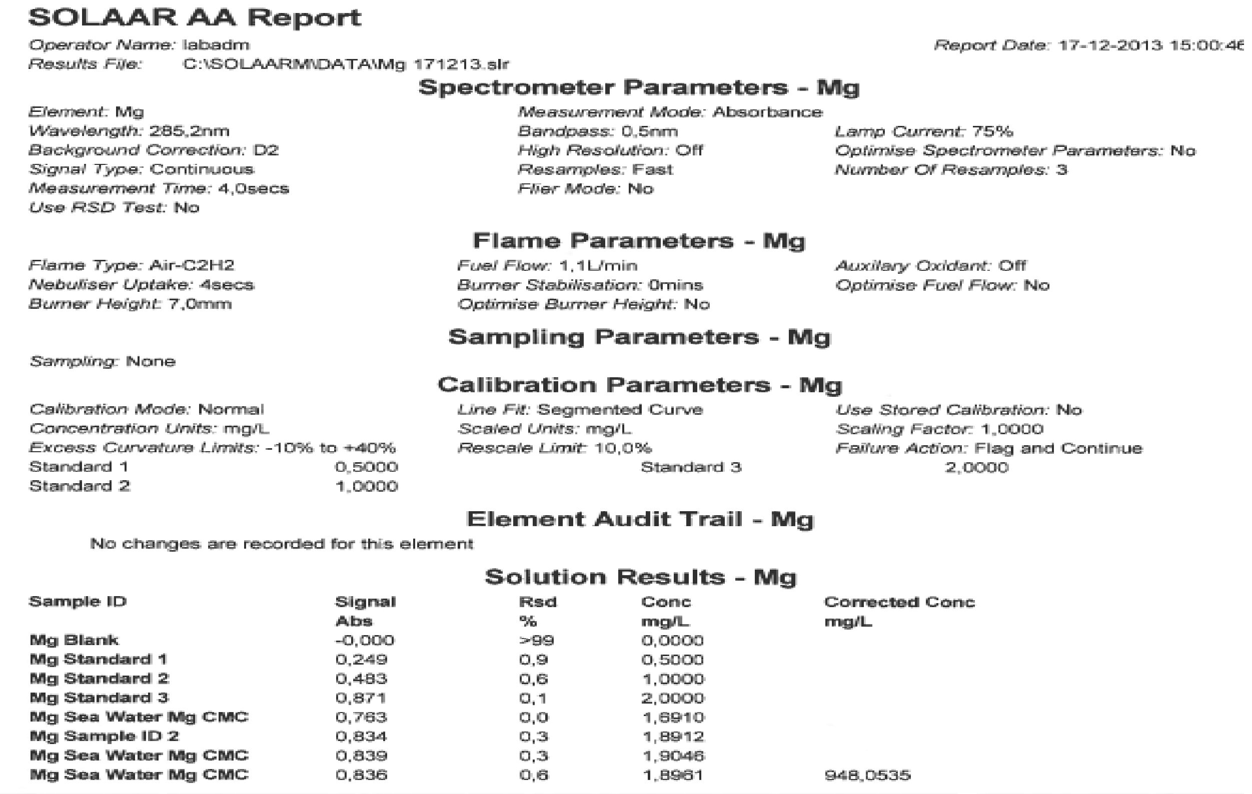
Tan Nguyen, Drilling fluid field tests, chapter 2, drilling engineering, PE 311 for figures 11, 12, 13 and 14.

http://imk209.wikispaces.com/file/view/graph.png/266396260/graph.png for figure 9 accessed 10 Dec, 2013.

http://www.tececo.com/files/newsletters/Newsletter34_files/TimeDependentFlow.gif for figure 8 accessed 10 Dec, 2013.

Appendix

A1. Magnesium concentration for Fanø sea water.



SOLAAR AA Report

Operator Name: labadm
Results File: C:\SOLAARM\DATA\Mg 171213.slr
Report Date: 17-12-2013 15:00:4

Spectrometer Parameters - Mg

Element: Mg
Wavelength: 285,2nm
Background Correction: D2
Signal Type: Continuous
Measurement Time: 4,0secs
Use RSD Test: No
Measurement Mode: Absorbance
Bandpass: 0,5nm
High Resolution: Off
Resamples: Fast
Flier Mode: No
Lamp Current: 75%
Optimise Spectrometer Parameters: No
Number Of Resamples: 3

Flame Parameters - Mg

Flame Type: Air-C2H2
Nebuliser Uptake: 4secs
Burner Height: 7,0mm
Fuel Flow: 1,1L/min
Burner Stabilisation: 0mins
Optimise Burner Height: No
Auxilary Oxidant: Off
Optimise Fuel Flow: No

Sampling Parameters - Mg

Sampling: None

Calibration Parameters - Mg

Calibration Mode: Normal
Concentration Units: mg/L
Excess Curvature Limits: -10% to +40%
Line Fit: Segmented Curve
Scaled Units: mg/L
Rescale Limit: 10,0%
Use Stored Calibration: No
Scaling Factor: 1,0000
Failure Action: Flag and Continue

Standard 1	0,5000	Standard 3	2,0000
Standard 2	1,0000		

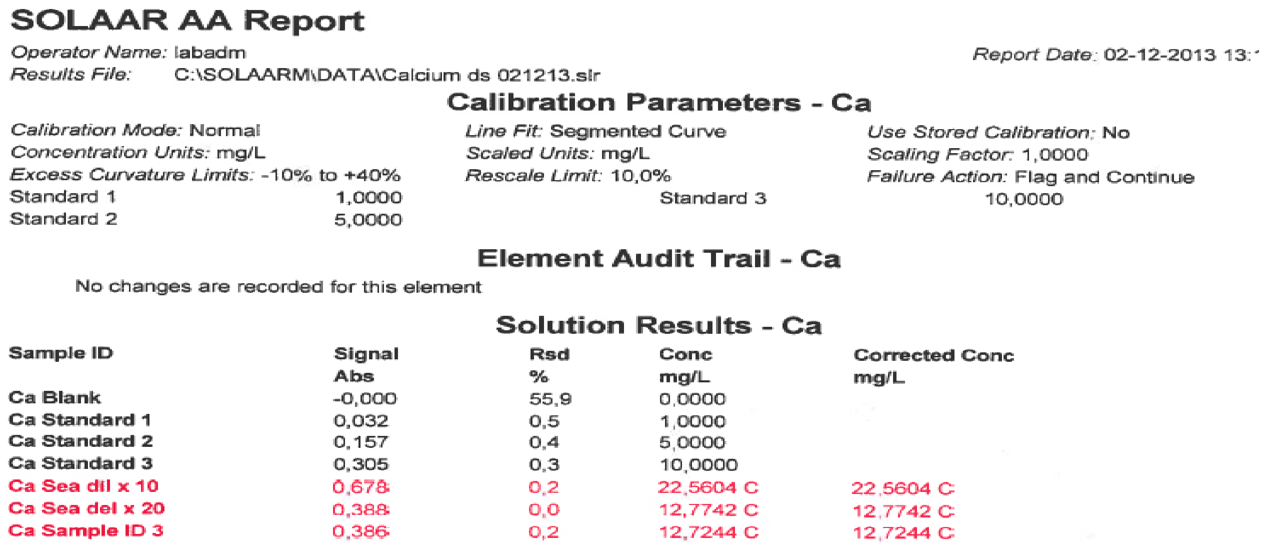
Element Audit Trail - Mg

No changes are recorded for this element

Solution Results - Mg

Sample ID	Signal Abs	Rsd %	Conc mg/L	Corrected Conc mg/L
Mg Blank	-0,000	>99	0,0000	
Mg Standard 1	0,249	0,9	0,5000	
Mg Standard 2	0,483	0,6	1,0000	
Mg Standard 3	0,871	0,1	2,0000	
Mg Sea Water Mg CMC	0,763	0,0	1,6910	
Mg Sample ID 2	0,834	0,3	1,8912	
Mg Sea Water Mg CMC	0,839	0,3	1,9046	
Mg Sea Water Mg CMC	0,836	0,6	1,8961	948,0535

A2. Calcium concentration for Fanø sea water.



SOLAAR AA Report

Operator Name: labadm
Results File: C:\SOLAARM\DATA\Calcium ds 021213.slr
Report Date: 02-12-2013 13:

Calibration Parameters - Ca

Calibration Mode: Normal
Concentration Units: mg/L
Excess Curvature Limits: -10% to +40%
Line Fit: Segmented Curve
Scaled Units: mg/L
Rescale Limit: 10,0%
Use Stored Calibration: No
Scaling Factor: 1,0000
Failure Action: Flag and Continue

Standard 1	1,0000	Standard 3	10,0000
Standard 2	5,0000		

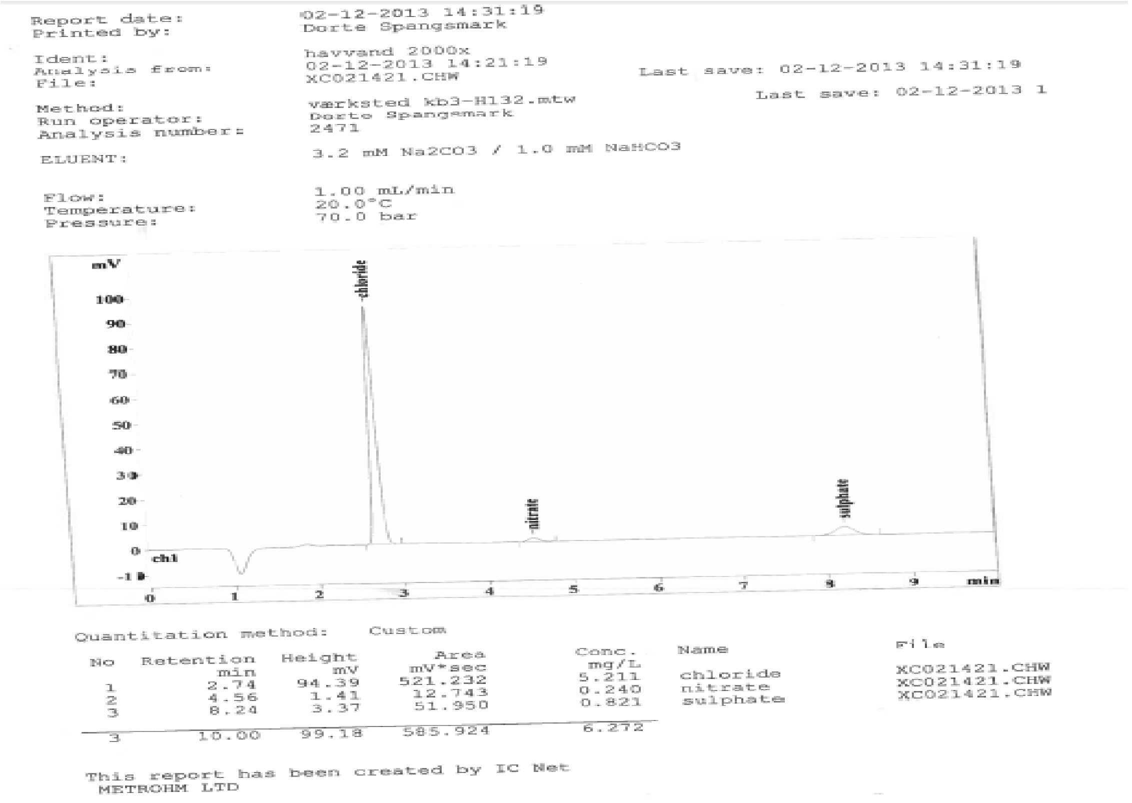
Element Audit Trail - Ca

No changes are recorded for this element

Solution Results - Ca

Sample ID	Signal Abs	Rsd %	Conc mg/L	Corrected Conc mg/L
Ca Blank	-0,000	55,9	0,0000	
Ca Standard 1	0,032	0,5	1,0000	
Ca Standard 2	0,157	0,4	5,0000	
Ca Standard 3	0,305	0,3	10,0000	
Ca Sea dil x 10	0,678	0,2	22,5604 C	22,5604 C
Ca Sea del x 20	0,388	0,0	12,7742 C	12,7742 C
Ca Sample ID 3	0,386	0,2	12,7244 C	12,7244 C

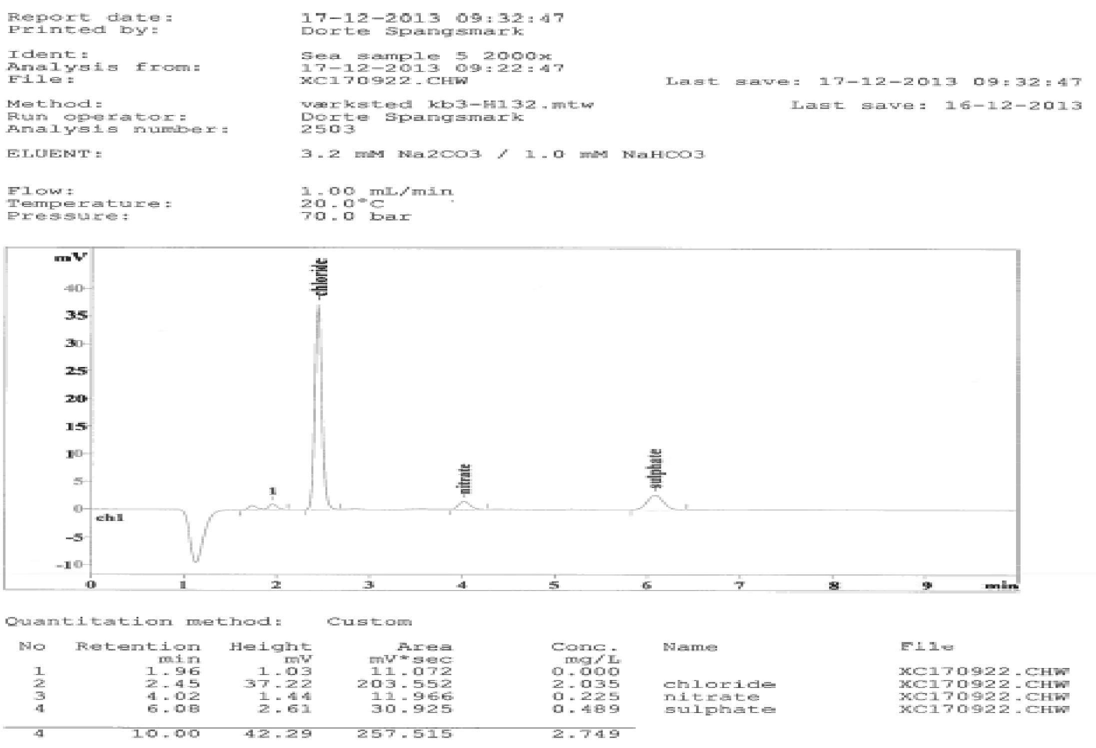
A3. Chloride concentration for Fanø sea water.



```
Report date:            02-12-2013 14:31:19
Printed by:             Dorte Spangsmark

Ident:                  havvand 2000x
Analysis from:          02-12-2013 14:21:19        Last save: 02-12-2013 14:31:19
File:                   XC021421.CHW
                                                            Last save: 02-12-2013 1
Method:                 værksted kb3-H132.mtw
Run operator:           Dorte Spangsmark
Analysis number:        2471

ELUENT:                 3.2 mM Na2CO3 / 1.0 mM NaHCO3

Flow:                   1.00 mL/min
Temperature:            20.0°C
Pressure:               70.0 bar
```

```
Quantitation method:    Custom

 No  Retention   Height      Area        Conc.   Name             File
           min       mV   mV*sec         mg/L
  1       2.74    94.39  521.232        5.211   chloride         XC021421.CHW
  2       4.56     1.41   12.743        0.240   nitrate          XC021421.CHW
  3       8.24     3.37   51.950        0.821   sulphate         XC021421.CHW
 ---------------------------------------------
  3      10.00    99.18  585.924        6.272

This report has been created by IC Net
 METROHM LTD
```

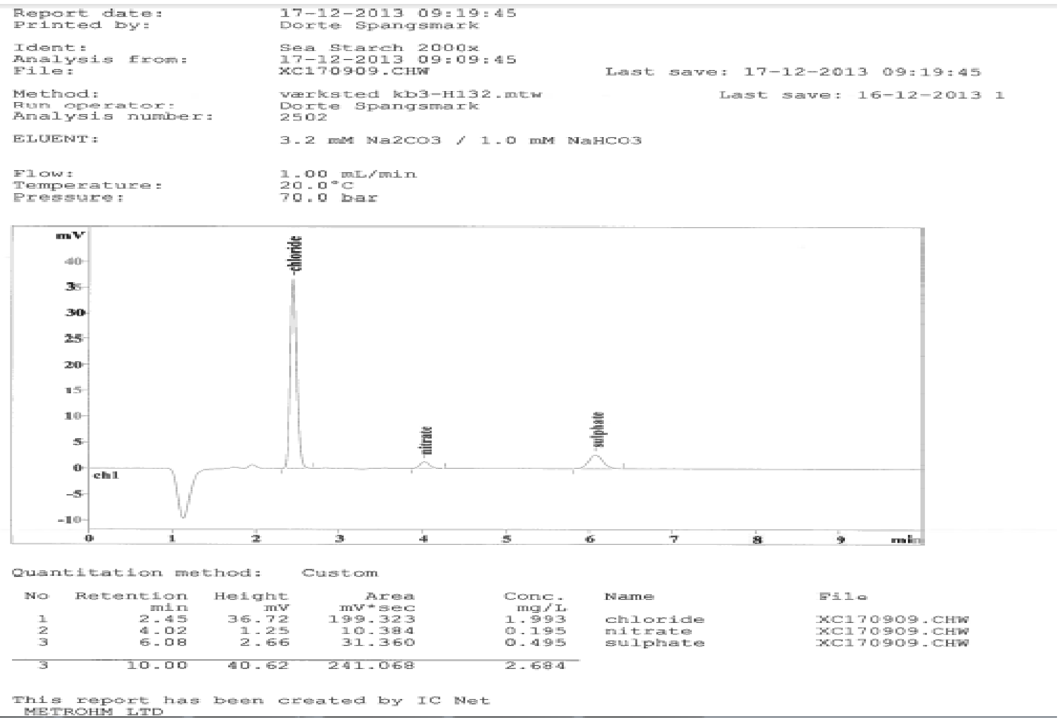
B1. Chloride concentration for sea water, pure sample 5



```
Report date:            17-12-2013 09:32:47
Printed by:             Dorte Spangsmark

Ident:                  Sea sample 5 2000x
Analysis from:          17-12-2013 09:22:47
File:                   XC170922.CHW             Last save: 17-12-2013 09:32:47

Method:                 værksted kb3-H132.mtw             Last save: 16-12-2013
Run operator:           Dorte Spangsmark
Analysis number:        2503

ELUENT:                 3.2 mM Na2CO3 / 1.0 mM NaHCO3

Flow:                   1.00 mL/min
Temperature:            20.0°C
Pressure:               70.0 bar
```

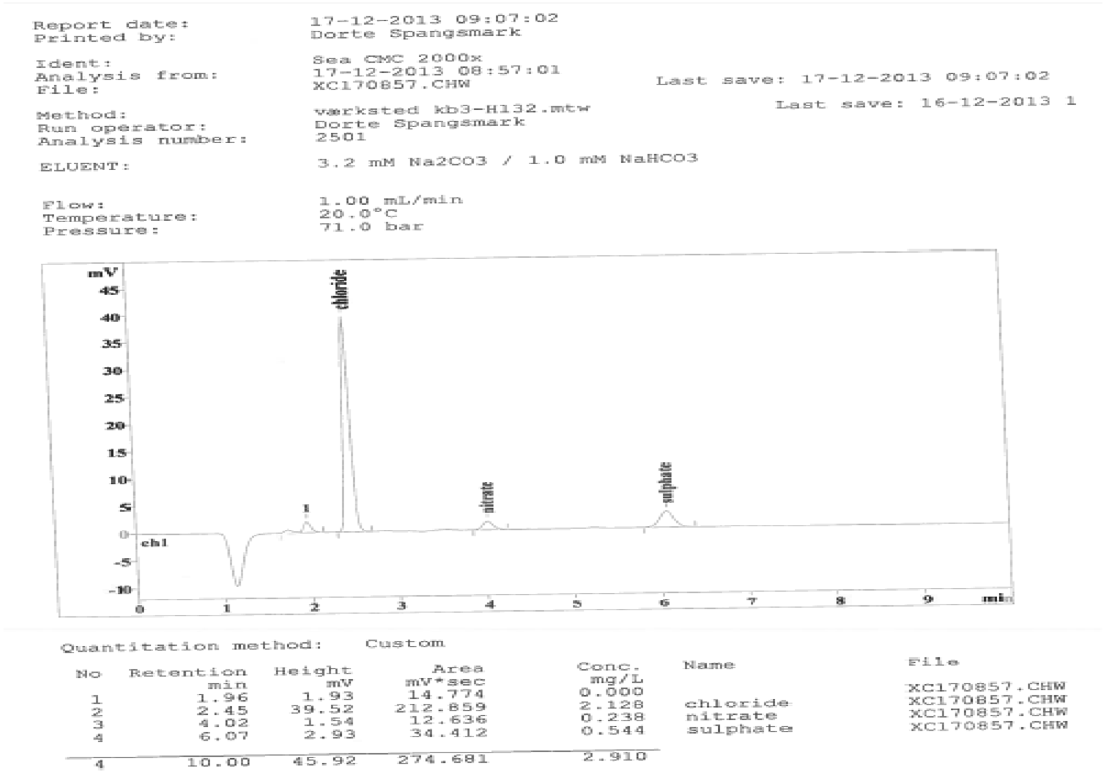
```
Quantitation method:    Custom

 No   Retention   Height      Area         Conc.    Name            File
            min       mV    mV*sec         mg/L
  1        1.96     1.03    11.072        0.000                     XC170922.CHW
  2        2.45    37.22   203.552        2.035    chloride         XC170922.CHW
  3        4.02     1.44    11.966        0.225    nitrate          XC170922.CHW
  4        6.08     2.61    30.925        0.489    sulphate         XC170922.CHW
 ----------------------------------------------------
  4       10.00    42.29   257.515        2.749
```

B2. Chloride concentration for sea water filtrate with starch and sample 5.



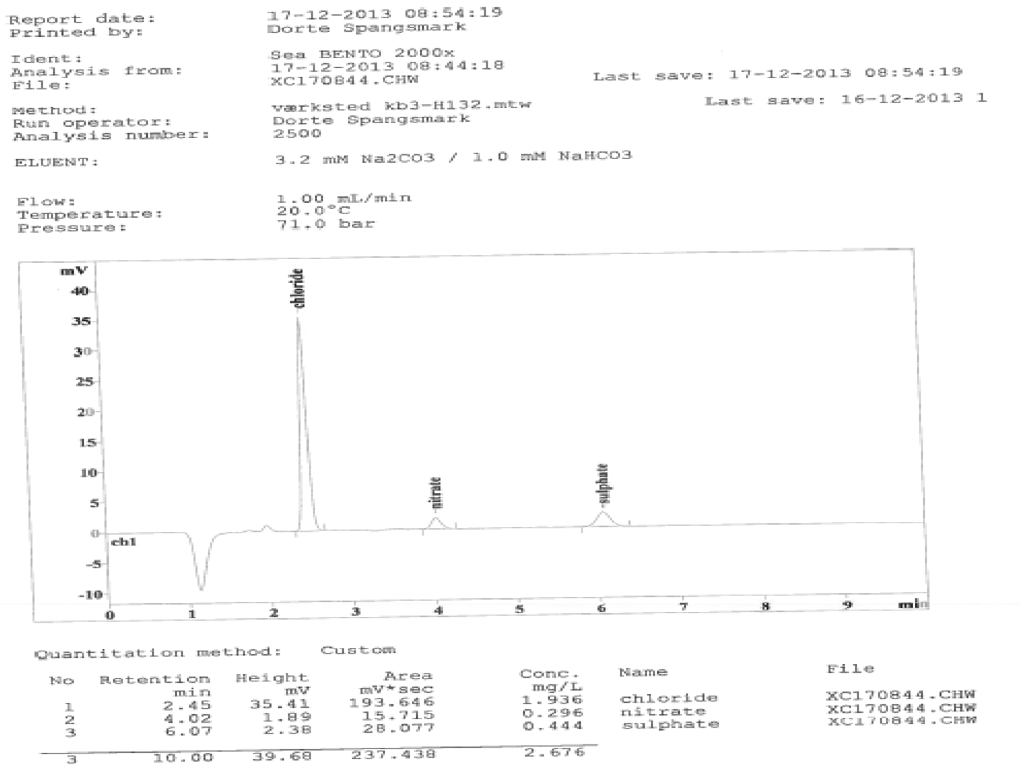
```
Report date:              17-12-2013 09:19:45
Printed by:               Dorte Spangsmark

Ident:                    Sea Starch 2000x
Analysis from:            17-12-2013 09:09:45
File:                     XC170909.CHW              Last save: 17-12-2013 09:19:45

Method:                   værksted kb3-H132.mtw              Last save: 16-12-2013 1
Run operator:             Dorte Spangsmark
Analysis number:          2502

ELUENT:                   3.2 mM Na2CO3 / 1.0 mM NaHCO3

Flow:                     1.00 mL/min
Temperature:              20.0°C
Pressure:                 70.0 bar

Quantitation method:    Custom

 No   Retention   Height      Area        Conc.    Name              File
            min       mV   mV*sec         mg/L
  1        2.45    36.72  199.323        1.993    chloride          XC170909.CHW
  2        4.02     1.25   10.384        0.195    nitrate           XC170909.CHW
  3        6.08     2.66   31.360        0.495    sulphate          XC170909.CHW
-------------------------------------------------
  3       10.00    40.62  241.068        2.684

This report has been created by IC Net
 METROHM LTD
```

B3. Chloride concentration for sea water filtrate with CMC and sample 5.



```
Report date:              17-12-2013 09:07:02
Printed by:               Dorte Spangsmark

Ident:                    Sea CMC 2000x
Analysis from:            17-12-2013 08:57:01
File:                     XC170857.CHW              Last save: 17-12-2013 09:07:02

Method:                   værksted kb3-H132.mtw              Last save: 16-12-2013 1
Run operator:             Dorte Spangsmark
Analysis number:          2501

ELUENT:                   3.2 mM Na2CO3 / 1.0 mM NaHCO3

Flow:                     1.00 mL/min
Temperature:              20.0°C
Pressure:                 71.0 bar

Quantitation method:    Custom

 No   Retention   Height      Area        Conc.    Name              File
            min       mV   mV*sec         mg/L
  1        1.96     1.93   14.774        0.000                      XC170857.CHW
  2        2.45    39.52  212.859        2.128    chloride          XC170857.CHW
  3        4.02     1.54   12.636        0.238    nitrate           XC170857.CHW
  4        6.07     2.93   34.412        0.544    sulphate          XC170857.CHW
-------------------------------------------------
  4       10.00    45.92  274.681        2.910
```

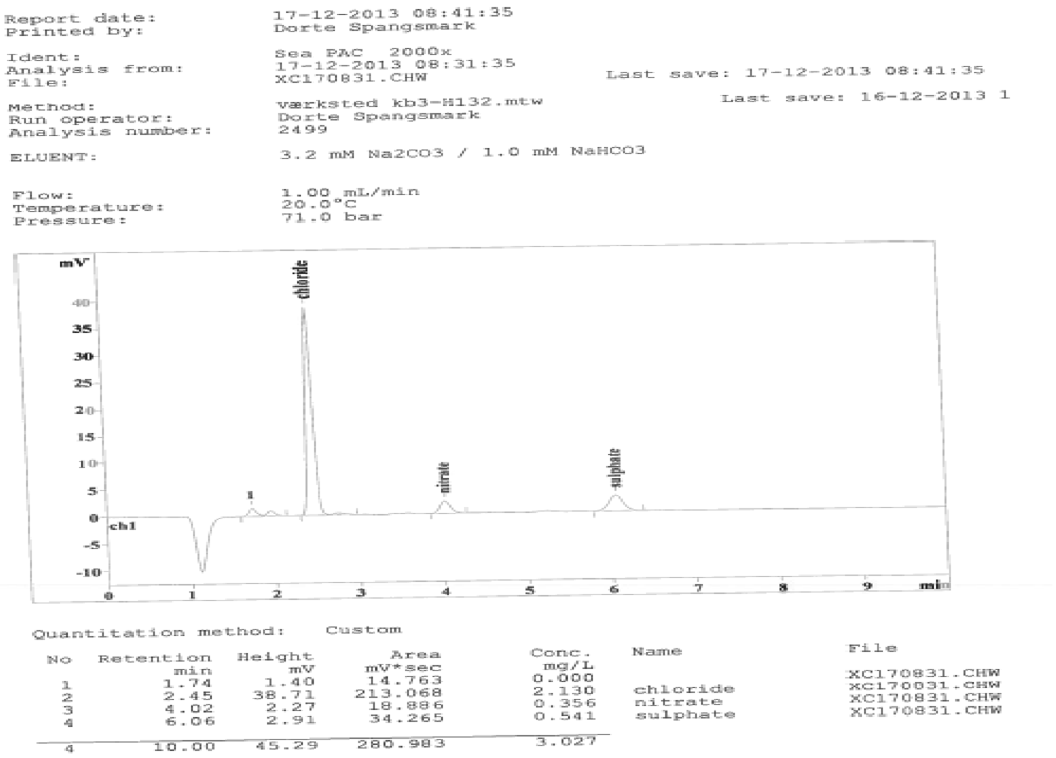
B4. Chloride concentration for sea water filtrate with Bentonite and sample 5.



```
Report date:            17-12-2013 08:54:19
Printed by:             Dorte Spangsmark

Ident:                  Sea BENTO 2000x
Analysis from:          17-12-2013 08:44:18
File:                   XC170844.CHW              Last save: 17-12-2013 08:54:19

Method:                 værksted kb3-H132.mtw              Last save: 16-12-2013 1
Run operator:           Dorte Spangsmark
Analysis number:        2500

ELUENT:                 3.2 mM Na2CO3 / 1.0 mM NaHCO3

Flow:                   1.00 mL/min
Temperature:            20.0°C
Pressure:               71.0 bar
```

```
Quantitation method:    Custom

No  Retention   Height      Area       Conc.    Name        File
       min        mV      mV*sec       mg/L
1      2.45     35.41    193.646      1.936    chloride    XC170844.CHW
2      4.02      1.89     15.715      0.296    nitrate     XC170844.CHW
3      6.07      2.38     28.077      0.444    sulphate    XC170844.CHW

3     10.00     39.68    237.438      2.676
```

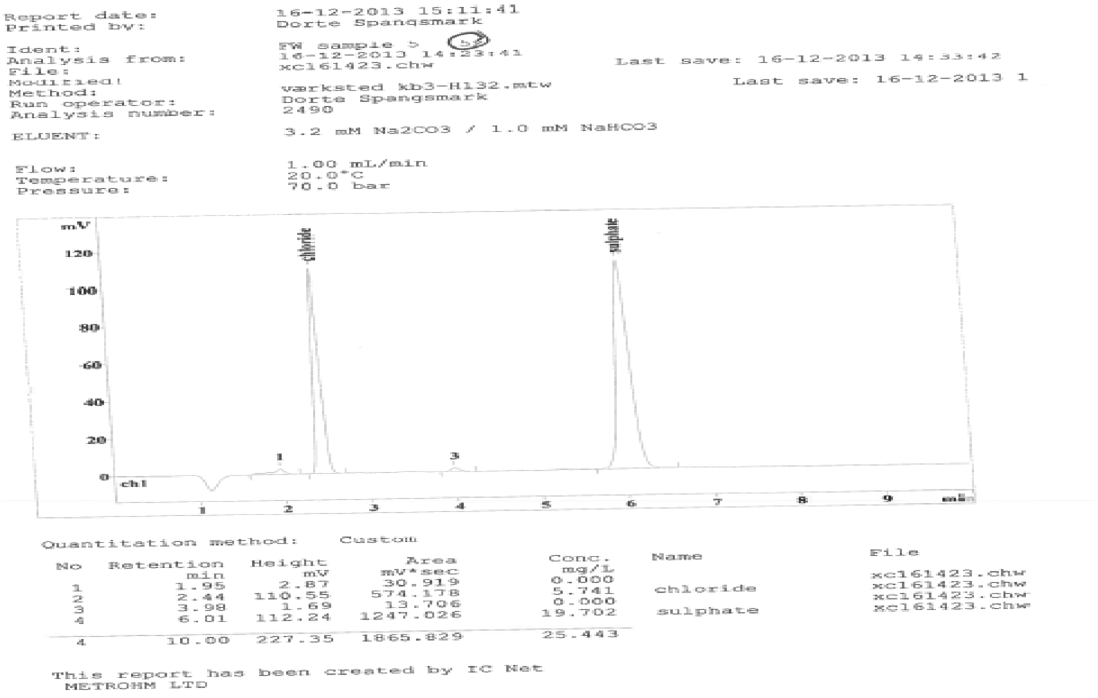
B5. Chloride concentration for sea water filtrate with MI PAC and sample 5.



```
Report date:            17-12-2013 08:41:35
Printed by:             Dorte Spangsmark

Ident:                  Sea PAC  2000x
Analysis from:          17-12-2013 08:31:35
File:                   XC170831.CHW              Last save: 17-12-2013 08:41:35

Method:                 værksted kb3-H132.mtw              Last save: 16-12-2013 1
Run operator:           Dorte Spangsmark
Analysis number:        2499

ELUENT:                 3.2 mM Na2CO3 / 1.0 mM NaHCO3

Flow:                   1.00 mL/min
Temperature:            20.0°C
Pressure:               71.0 bar
```

```
Quantitation method:    Custom

No  Retention   Height      Area       Conc.    Name        File
       min        mV      mV*sec       mg/L
1      1.74      1.40     14.763      0.000                XC170831.CHW
2      2.45     38.71    213.068      2.130    chloride    XC170831.CHW
3      4.02      2.27     18.886      0.356    nitrate     XC170831.CHW
4      6.06      2.91     34.265      0.541    sulphate    XC170831.CHW

4     10.00     45.29    280.983      3.027
```

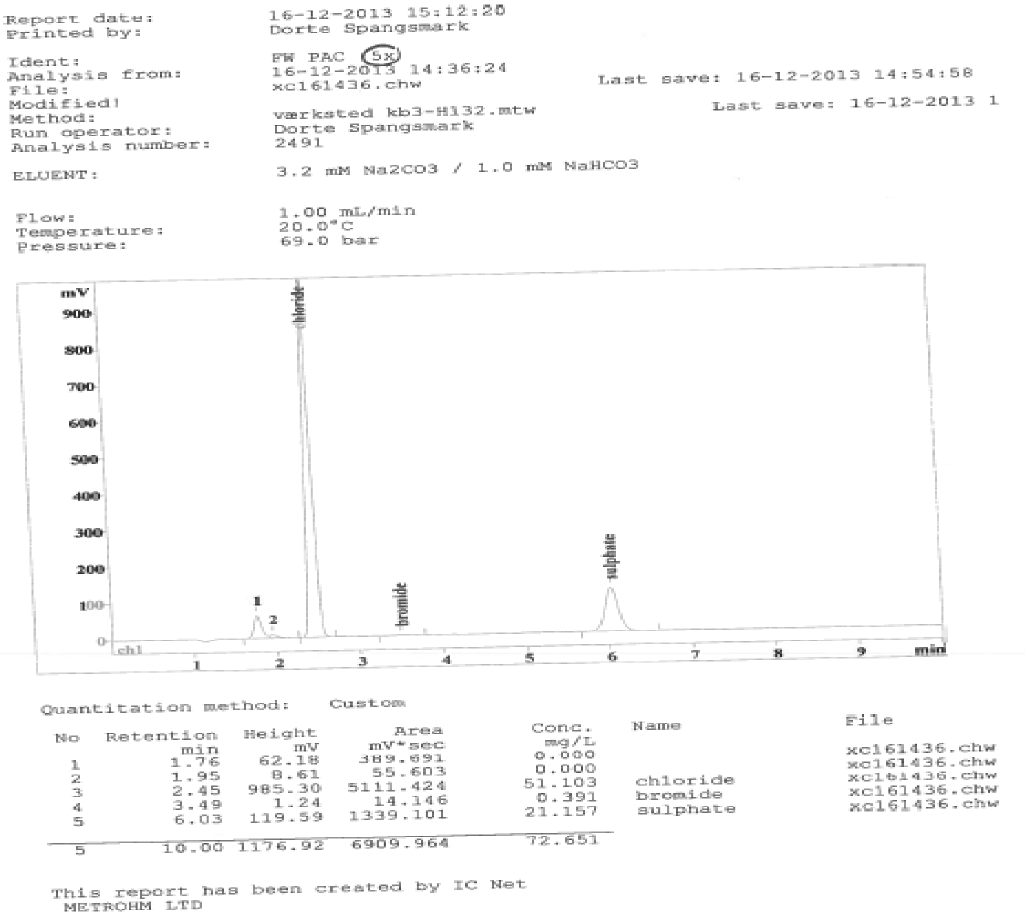
C1. Chloride concentration for fresh water filtrate with pure sample 5.



```
Report date:           16-12-2013 15:11:41
Printed by:            Dorte Spangsmark

Ident:                 FW sample 5  5x
Analysis from:         16-12-2013 14:23:41
File:                  xc161423.chw                Last save: 16-12-2013 14:33:42
Modified!                                                 Last save: 16-12-2013 1
Method:                værksted kb3-H132.mtw
Run operator:          Dorte Spangsmark
Analysis number:       2490
ELUENT:                3.2 mM Na2CO3 / 1.0 mM NaHCO3

Flow:                  1.00 mL/min
Temperature:           20.0°C
Pressure:              70.0 bar
```

```
Quantitation method:    Custom

No  Retention   Height      Area        Conc.    Name          File
          min       mV    mV*sec         mg/L
1        1.95     2.87    30.919        0.000                  xc161423.chw
2        2.44   110.55   574.178        5.741    chloride      xc161423.chw
3        3.98     1.69    13.706        0.000                  xc161423.chw
4        6.01   112.24  1247.026       19.702    sulphate      xc161423.chw
------------------------------------------------
4       10.00   227.35  1865.829       25.443

This report has been created by IC Net
 METROHM LTD
```

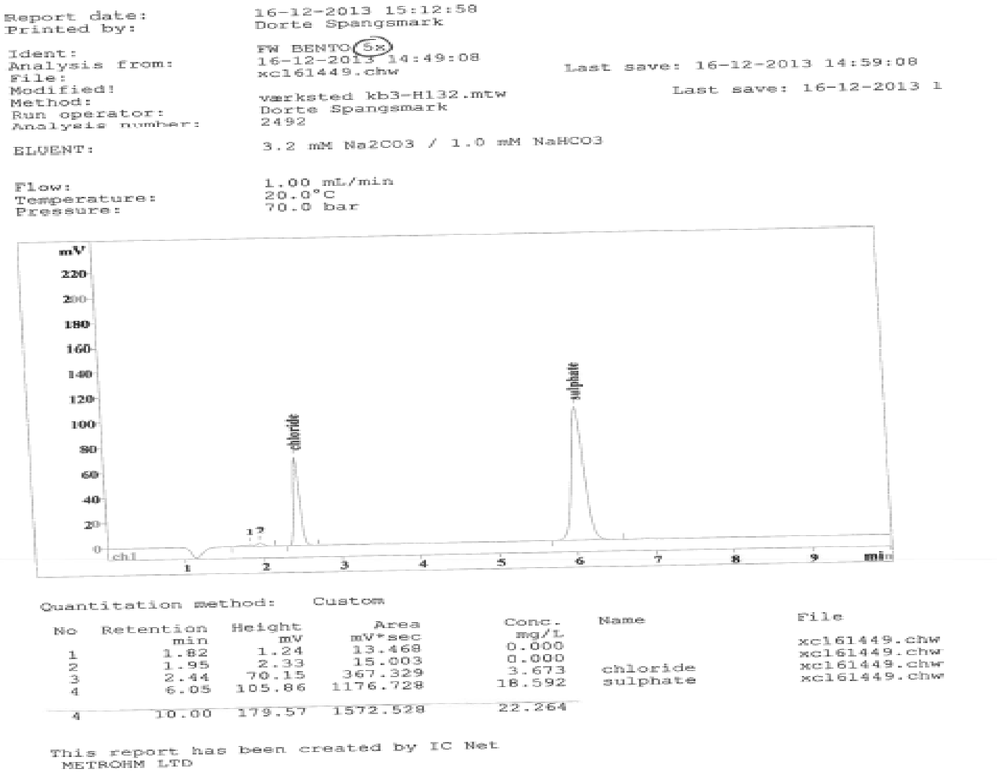
C2. Chloride concentration for fresh water filtrate with MI PAC and sample 5.



```
Report date:           16-12-2013 15:12:20
Printed by:            Dorte Spangsmark

Ident:                 FW PAC  5x
Analysis from:         16-12-2013 14:36:24
File:                  xc161436.chw                Last save: 16-12-2013 14:54:58
Modified!                                                 Last save: 16-12-2013 1
Method:                værksted kb3-H132.mtw
Run operator:          Dorte Spangsmark
Analysis number:       2491
ELUENT:                3.2 mM Na2CO3 / 1.0 mM NaHCO3

Flow:                  1.00 mL/min
Temperature:           20.0°C
Pressure:              69.0 bar
```

```
Quantitation method:    Custom

No  Retention   Height      Area        Conc.    Name          File
          min       mV    mV*sec         mg/L
1        1.76    62.18   389.691        0.000                  xc161436.chw
2        1.95     8.61    55.603        0.000                  xc161436.chw
3        2.45   985.30  5111.424       51.103    chloride      xc161436.chw
4        3.49     1.24    14.146        0.391    bromide       xc161436.chw
5        6.03   119.59  1339.101       21.157    sulphate      xc161436.chw
------------------------------------------------
5       10.00  1176.92  6909.964       72.651

This report has been created by IC Net
 METROHM LTD
```

C3. Chloride concentration for fresh water filtrate with Bentonite and sample 5.



Report date: 16-12-2013 15:12:58
Printed by: Dorte Spangsmark

Ident: FW BENTO 5x
Analysis from: 16-12-2013 14:49:08
File: xc161449.chw Last save: 16-12-2013 14:59:08
Modified!
Method: værksted kb3-H132.mtw Last save: 16-12-2013 1
Run operator: Dorte Spangsmark
Analysis number: 2492

ELUENT: 3.2 mM Na2CO3 / 1.0 mM NaHCO3

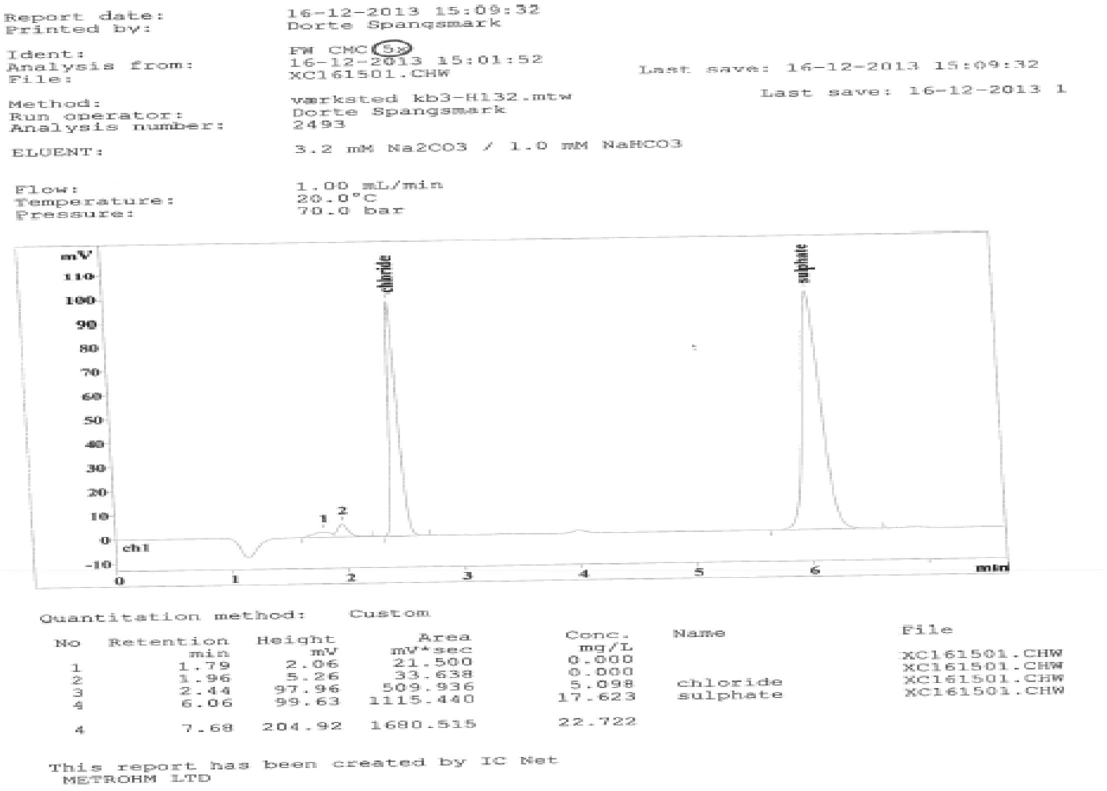
Flow: 1.00 mL/min
Temperature: 20.0°C
Pressure: 70.0 bar

Quantitation method: Custom

No	Retention min	Height mV	Area mV*sec	Conc. mg/L	Name	File
1	1.82	1.24	13.468	0.000		xc161449.chw
2	1.95	2.33	15.003	0.000		xc161449.chw
3	2.44	70.15	367.329	3.673	chloride	xc161449.chw
4	6.05	105.86	1176.728	18.592	sulphate	xc161449.chw
4	10.00	179.57	1572.528	22.264		

This report has been created by IC Net
METROHM LTD

C4. Chloride concentration for fresh water filtrate with CMC and sample 5.



Report date: 16-12-2013 15:09:32
Printed by: Dorte Spangsmark

Ident: FW CMC 5x
Analysis from: 16-12-2013 15:01:52
File: XC161501.CHW Last save: 16-12-2013 15:09:32

Method: værksted kb3-H132.mtw Last save: 16-12-2013 1
Run operator: Dorte Spangsmark
Analysis number: 2493

ELUENT: 3.2 mM Na2CO3 / 1.0 mM NaHCO3

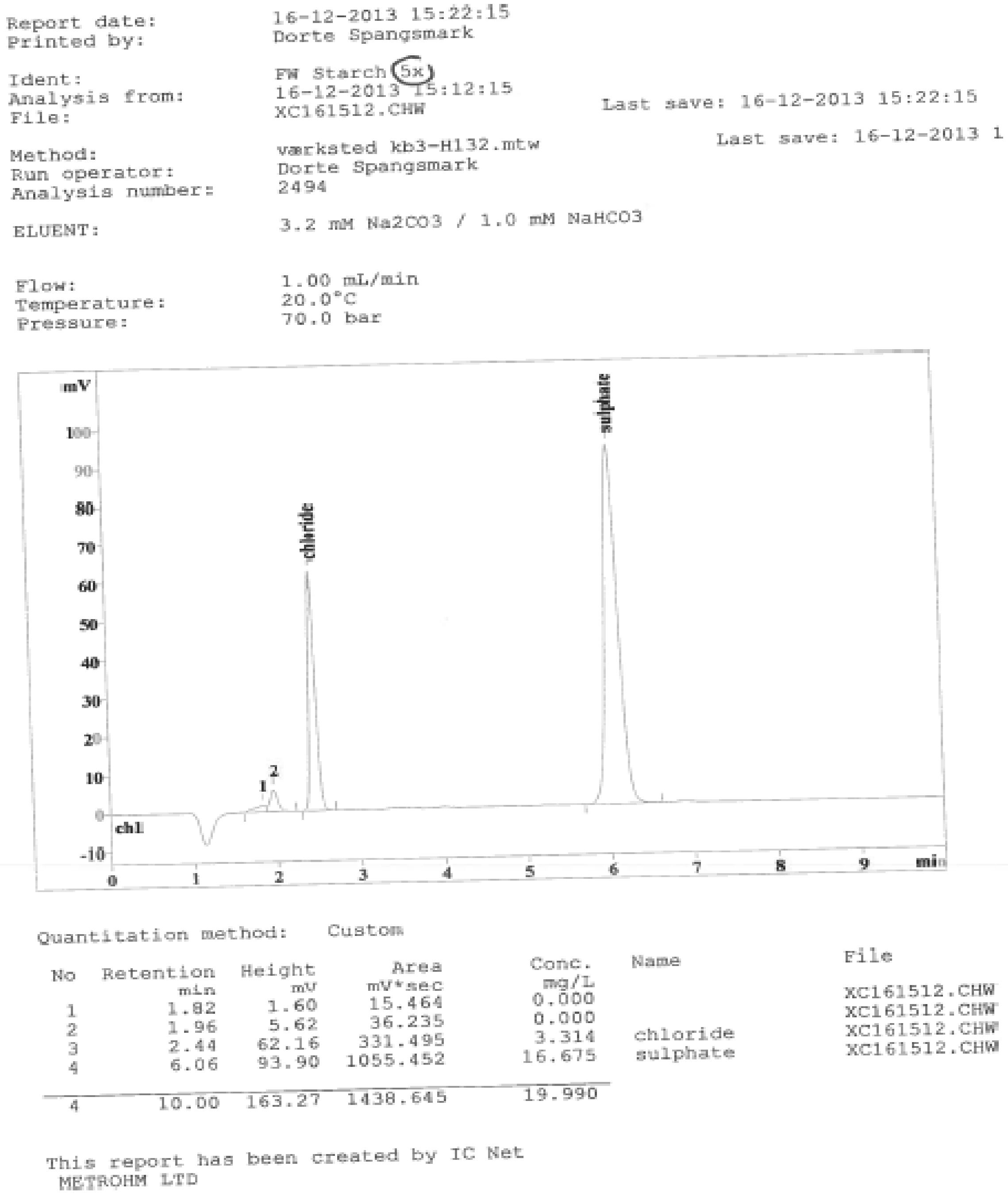
Flow: 1.00 mL/min
Temperature: 20.0°C
Pressure: 70.0 bar

Quantitation method: Custom

No	Retention min	Height mV	Area mV*sec	Conc. mg/L	Name	File
1	1.79	2.06	21.500	0.000		XC161501.CHW
2	1.96	5.26	33.638	0.000		XC161501.CHW
3	2.44	97.96	509.936	5.098	chloride	XC161501.CHW
4	6.06	99.63	1115.440	17.623	sulphate	XC161501.CHW
4	7.68	204.92	1680.515	22.722		

This report has been created by IC Net
METROHM LTD

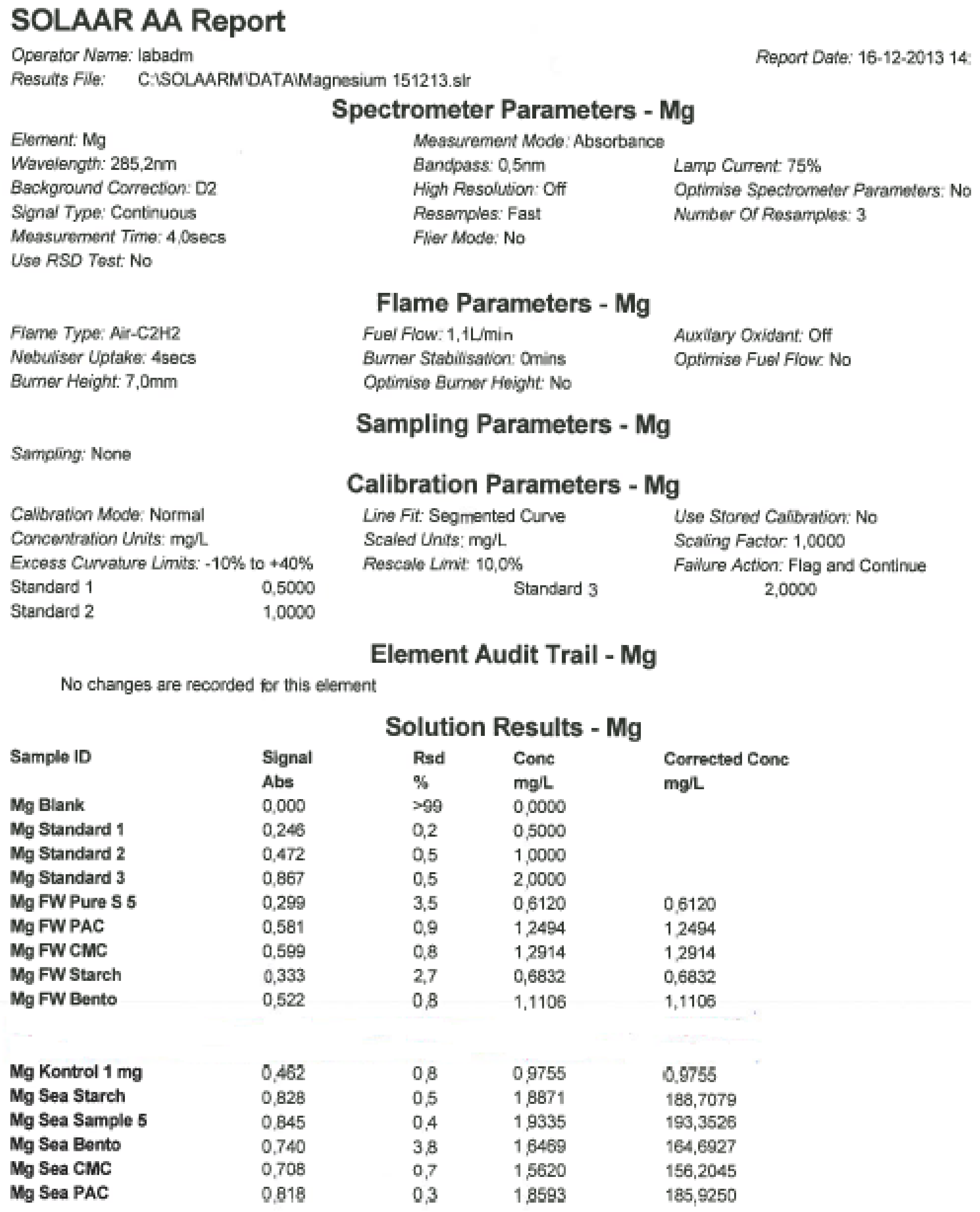
C5. Chloride concentration for fresh water filtrate with starch and sample 5.



```
Report date:          16-12-2013 15:22:15
Printed by:           Dorte Spangsmark

Ident:                FW Starch 5x
Analysis from:        16-12-2013 15:12:15
File:                 XC161512.CHW            Last save: 16-12-2013 15:22:15

Method:               værksted kb3-H132.mtw            Last save: 16-12-2013 1
Run operator:         Dorte Spangsmark
Analysis number:      2494

ELUENT:               3.2 mM Na2CO3 / 1.0 mM NaHCO3

Flow:                 1.00 mL/min
Temperature:          20.0°C
Pressure:             70.0 bar
```

```
Quantitation method:    Custom

No   Retention   Height      Area        Conc.    Name          File
           min       mV   mV*sec         mg/L
 1        1.82     1.60    15.464        0.000                  XC161512.CHW
 2        1.96     5.62    36.235        0.000                  XC161512.CHW
 3        2.44    62.16   331.495        3.314    chloride      XC161512.CHW
 4        6.06    93.90  1055.452       16.675    sulphate      XC161512.CHW
-------------------------------------------------------
 4       10.00   163.27  1438.645       19.990

This report has been created by IC Net
 METROHM LTD
```

D1a. Magnesium concentration of fresh and sea water filtrates with all additives.



SOLAAR AA Report

Operator Name: labadm
Results File: C:\SOLAARM\DATA\Magnesium 151213.slr
Report Date: 16-12-2013 14:

Spectrometer Parameters - Mg

Element: Mg
Wavelength: 285,2nm
Background Correction: D2
Signal Type: Continuous
Measurement Time: 4,0secs
Use RSD Test: No

Measurement Mode: Absorbance
Bandpass: 0,5nm
High Resolution: Off
Resamples: Fast
Flier Mode: No

Lamp Current: 75%
Optimise Spectrometer Parameters: No
Number Of Resamples: 3

Flame Parameters - Mg

Flame Type: Air-C2H2
Nebuliser Uptake: 4secs
Burner Height: 7,0mm

Fuel Flow: 1,1L/min
Burner Stabilisation: 0mins
Optimise Burner Height: No

Auxilary Oxidant: Off
Optimise Fuel Flow: No

Sampling Parameters - Mg

Sampling: None

Calibration Parameters - Mg

Calibration Mode: Normal
Concentration Units: mg/L
Excess Curvature Limits: -10% to +40%

Line Fit: Segmented Curve
Scaled Units: mg/L
Rescale Limit: 10,0%

Use Stored Calibration: No
Scaling Factor: 1,0000
Failure Action: Flag and Continue

Standard 1	0,5000	Standard 3	2,0000
Standard 2	1,0000		

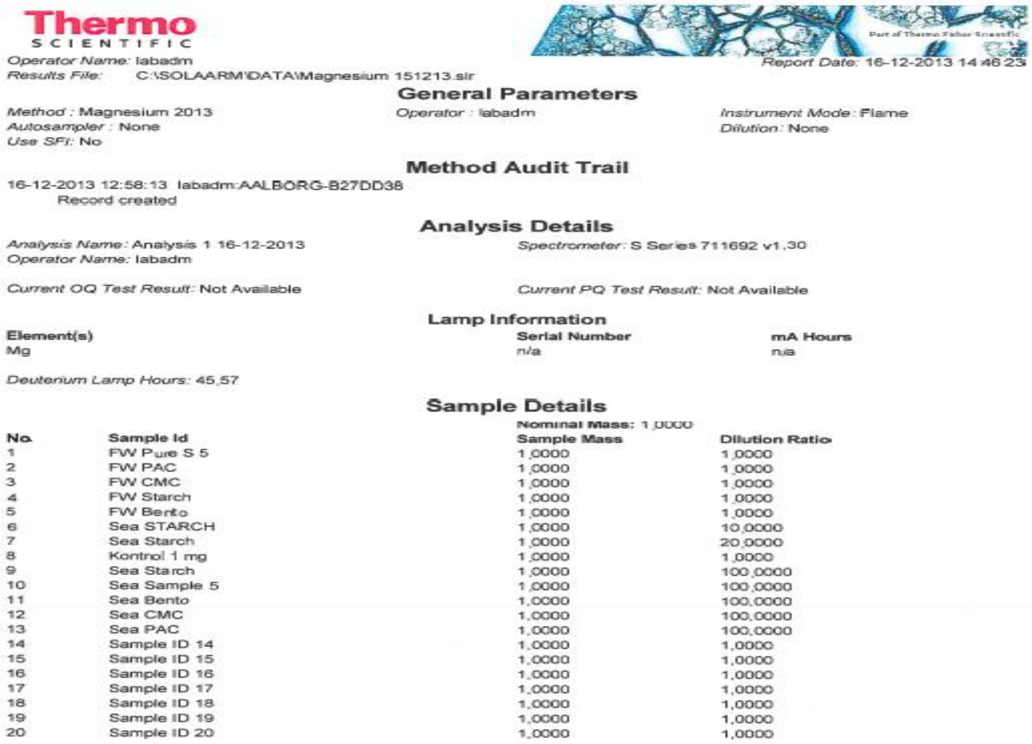
Element Audit Trail - Mg

No changes are recorded for this element

Solution Results - Mg

Sample ID	**Signal** **Abs**	**Rsd** **%**	**Conc** **mg/L**	**Corrected Conc** **mg/L**
Mg Blank	0,000	>99	0,0000	
Mg Standard 1	0,246	0,2	0,5000	
Mg Standard 2	0,472	0,5	1,0000	
Mg Standard 3	0,867	0,5	2,0000	
Mg FW Pure S 5	0,299	3,5	0,6120	0,6120
Mg FW PAC	0,581	0,9	1,2494	1,2494
Mg FW CMC	0,599	0,8	1,2914	1,2914
Mg FW Starch	0,333	2,7	0,6832	0,6832
Mg FW Bento	0,522	0,8	1,1106	1,1106
Mg Kontrol 1 mg	0,462	0,8	0,9755	0,9755
Mg Sea Starch	0,828	0,5	1,8871	188,7079
Mg Sea Sample 5	0,845	0,4	1,9335	193,3526
Mg Sea Bento	0,740	3,8	1,6469	164,6927
Mg Sea CMC	0,708	0,7	1,5620	156,2045
Mg Sea PAC	0,818	0,3	1,8593	185,9250

D1b. Magnesium concentration of fresh and sea water filtrates with all additives.



Thermo SCIENTIFIC

Part of Thermo Fisher Scientific

Operator Name: labadm
Results File: C:\SOLAARM\DATA\Magnesium 151213.slr
Report Date: 16-12-2013 14:46:23

General Parameters

Method : Magnesium 2013
Autosampler : None
Use SFI: No
Operator : labadm
Instrument Mode: Flame
Dilution: None

Method Audit Trail

16-12-2013 12:58:13 labadm:AALBORG-B27DD38
Record created

Analysis Details

Analysis Name: Analysis 1 16-12-2013
Operator Name: labadm
Spectrometer: S Series 711692 v1.30

Current OQ Test Result: Not Available
Current PQ Test Result: Not Available

Lamp Information

Element(s)	**Serial Number**	**mA Hours**
Mg	n/a	n/a

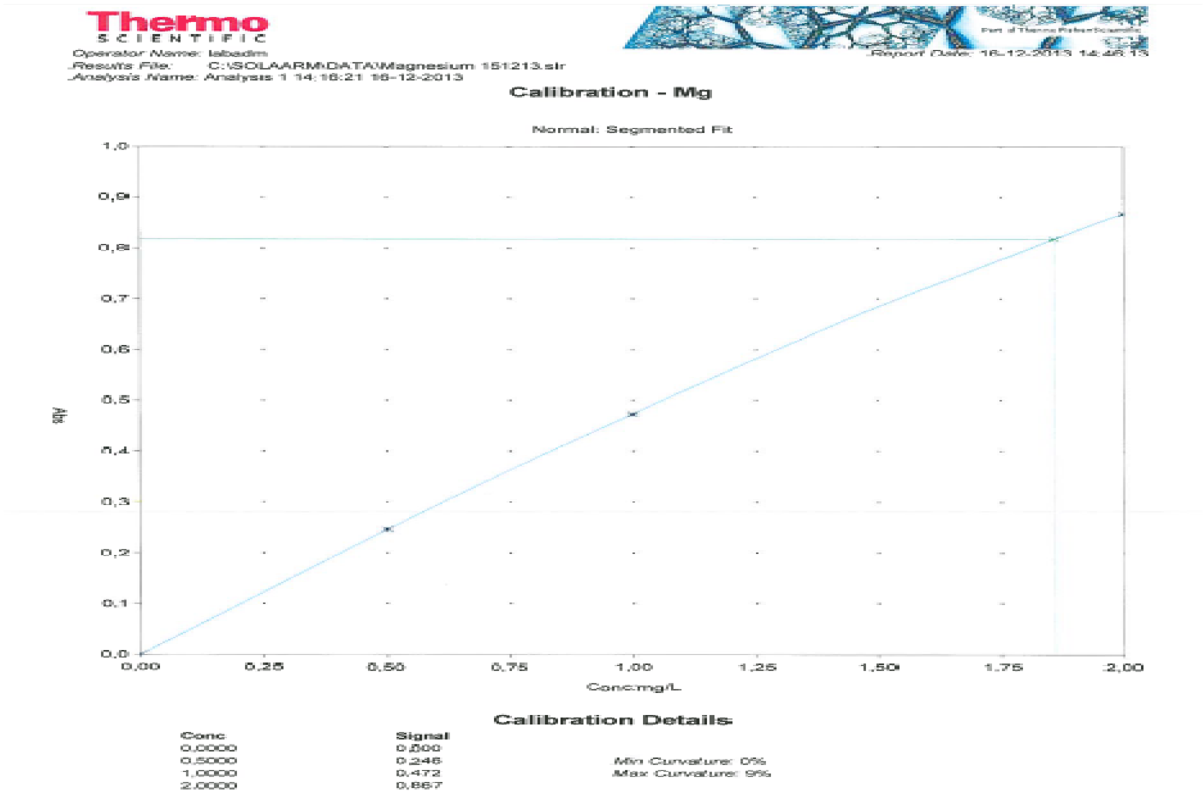
Deuterium Lamp Hours: 45,57

Sample Details

Nominal Mass: 1,0000

No.	**Sample Id**	**Sample Mass**	**Dilution Ratio**
1	FW Pure S 5	1,0000	1,0000
2	FW PAC	1,0000	1,0000
3	FW CMC	1,0000	1,0000
4	FW Starch	1,0000	1,0000
5	FW Bento	1,0000	1,0000
6	Sea STARCH	1,0000	10,0000
7	Sea Starch	1,0000	20,0000
8	Kontrol 1 mg	1,0000	1,0000
9	Sea Starch	1,0000	100,0000
10	Sea Sample 5	1,0000	100,0000
11	Sea Bento	1,0000	100,0000
12	Sea CMC	1,0000	100,0000
13	Sea PAC	1,0000	100,0000
14	Sample ID 14	1,0000	1,0000
15	Sample ID 15	1,0000	1,0000
16	Sample ID 16	1,0000	1,0000
17	Sample ID 17	1,0000	1,0000
18	Sample ID 18	1,0000	1,0000
19	Sample ID 19	1,0000	1,0000
20	Sample ID 20	1,0000	1,0000

D1c. Magnesium concentration of fresh and sea water filtrates with all additives.



Thermo SCIENTIFIC

Part of Thermo Fisher Scientific

Operator Name: labadm
Results File: C:\SOLAARM\DATA\Magnesium 151213.slr
Analysis Name: Analysis 1 14:16:21 16-12-2013
Report Date: 16-12-2013 14:46:13

Calibration - Mg

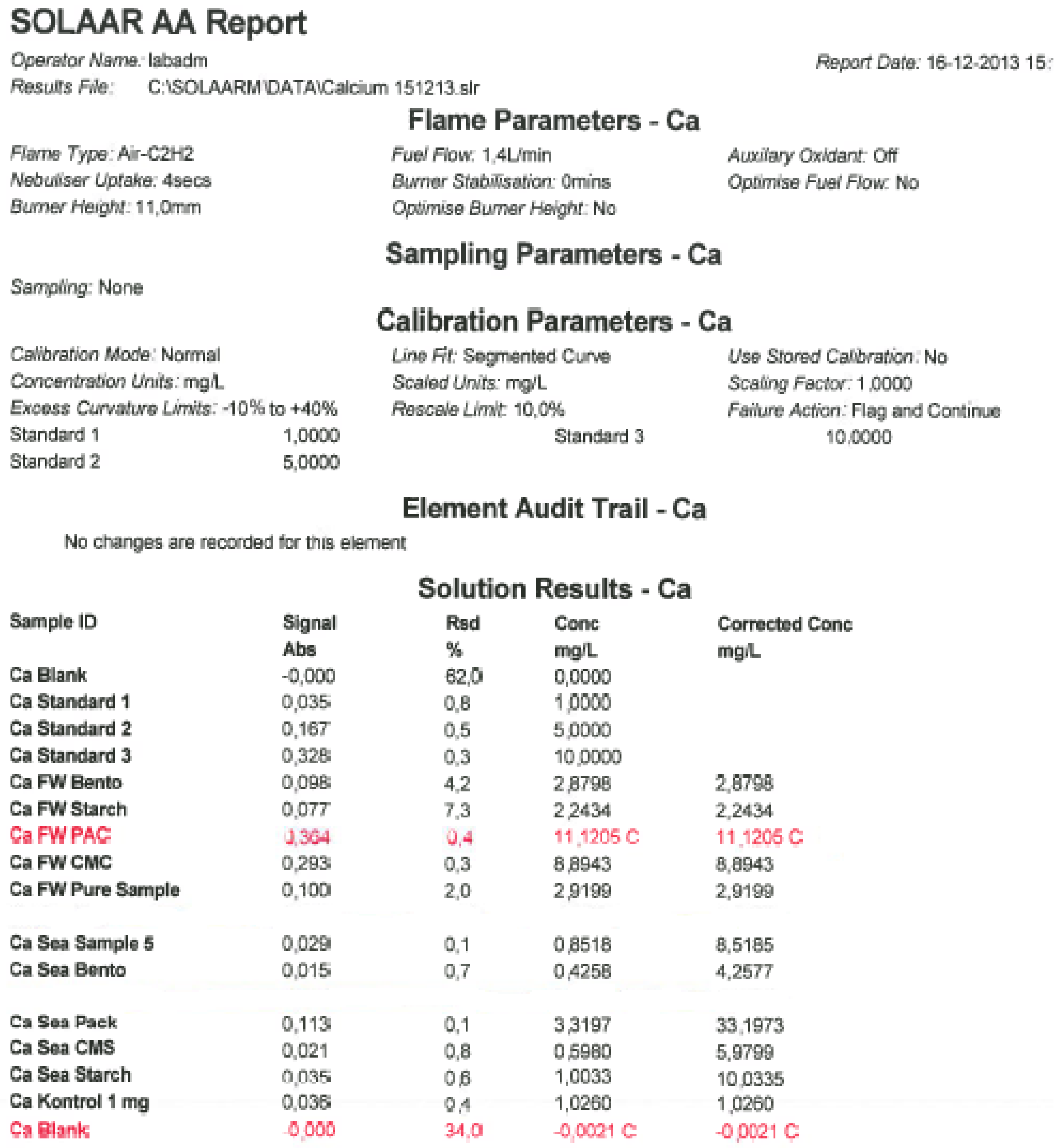
Normal: Segmented Fit

Calibration Details

Conc	Signal
0,0000	0,000
0,5000	0,246
1,0000	0,472
2,0000	0,867

Min Curvature: 0%
Max Curvature: 9%

D2a Calcium concentration of fresh and sea water filtrates with all additives.



SOLAAR AA Report

Operator Name: labadm
Report Date: 16-12-2013 15:
Results File: C:\SOLAARM\DATA\Calcium 151213.slr

Flame Parameters - Ca

Flame Type: Air-C2H2
Fuel Flow: 1,4L/min
Auxilary Oxidant: Off
Nebuliser Uptake: 4secs
Burner Stabilisation: 0mins
Optimise Fuel Flow: No
Burner Height: 11,0mm
Optimise Burner Height: No

Sampling Parameters - Ca

Sampling: None

Calibration Parameters - Ca

Calibration Mode: Normal
Line Fit: Segmented Curve
Use Stored Calibration: No
Concentration Units: mg/L
Scaled Units: mg/L
Scaling Factor: 1,0000
Excess Curvature Limits: -10% to +40%
Rescale Limit: 10,0%
Failure Action: Flag and Continue

Standard 1	1,0000
Standard 2	5,0000
Standard 3	10,0000

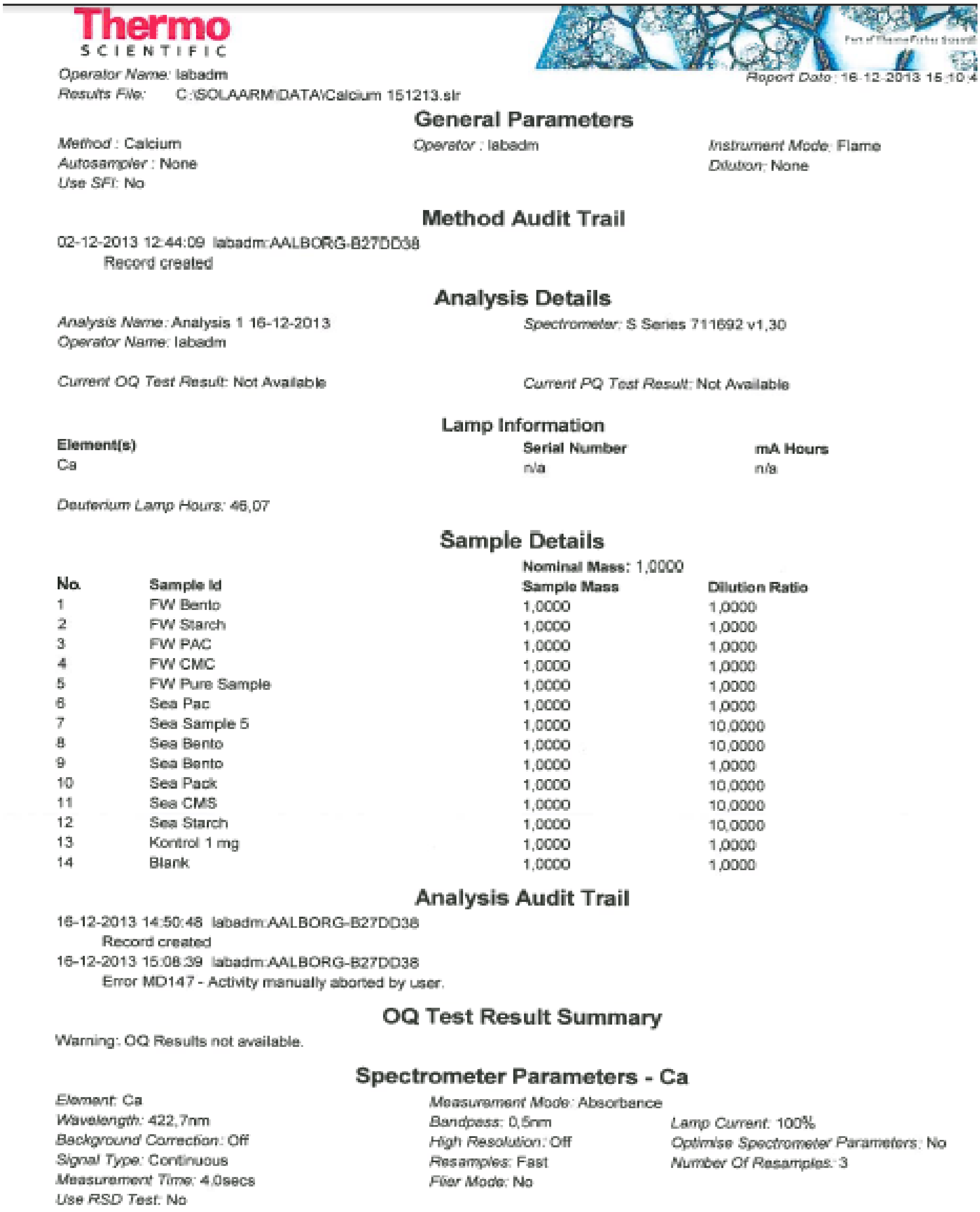
Element Audit Trail - Ca

No changes are recorded for this element

Solution Results - Ca

Sample ID	**Signal** **Abs**	**Rsd** **%**	**Conc** **mg/L**	**Corrected Conc** **mg/L**
Ca Blank	-0,000	62,0	0,0000	
Ca Standard 1	0,035	0,8	1,0000	
Ca Standard 2	0,167	0,5	5,0000	
Ca Standard 3	0,328	0,3	10,0000	
Ca FW Bento	0,098	4,2	2,8798	2,8798
Ca FW Starch	0,077	7,3	2,2434	2,2434
Ca FW PAC	0,364	0,4	11,1205 C	11,1205 C
Ca FW CMC	0,293	0,3	8,8943	8,8943
Ca FW Pure Sample	0,100	2,0	2,9199	2,9199
Ca Sea Sample 5	0,029	0,1	0,8518	8,5185
Ca Sea Bento	0,015	0,7	0,4258	4,2577
Ca Sea Pack	0,113	0,1	3,3197	33,1973
Ca Sea CMS	0,021	0,8	0,5980	5,9799
Ca Sea Starch	0,035	0,6	1,0033	10,0335
Ca Kontrol 1 mg	0,036	0,4	1,0260	1,0260
Ca Blank	-0,000	34,0	-0,0021 C	-0,0021 C

D2b. Calcium concentration of fresh and sea water filtrates with all additives.



Thermo SCIENTIFIC

Operator Name: labadm

Results File: C:\SOLAARM\DATA\Calcium 151213.slr

Report Date: 16-12-2013 15:10:4

General Parameters

Method : Calcium
Autosampler : None
Use SFI: No

Operator : labadm

Instrument Mode: Flame
Dilution: None

Method Audit Trail

02-12-2013 12:44:09 labadm:AALBORG-B27DD38
Record created

Analysis Details

Analysis Name: Analysis 1 16-12-2013
Operator Name: labadm

Spectrometer: S Series 711692 v1,30

Current OQ Test Result: Not Available

Current PQ Test Result: Not Available

Lamp Information

Element(s)	**Serial Number**	**mA Hours**
Ca	n/a	n/a

Deuterium Lamp Hours: 46,07

Sample Details

Nominal Mass: 1,0000

No.	**Sample Id**	**Sample Mass**	**Dilution Ratio**
1	FW Bento	1,0000	1,0000
2	FW Starch	1,0000	1,0000
3	FW PAC	1,0000	1,0000
4	FW CMC	1,0000	1,0000
5	FW Pure Sample	1,0000	1,0000
6	Sea Pac	1,0000	1,0000
7	Sea Sample 5	1,0000	10,0000
8	Sea Bento	1,0000	10,0000
9	Sea Bento	1,0000	1,0000
10	Sea Pack	1,0000	10,0000
11	Sea CMS	1,0000	10,0000
12	Sea Starch	1,0000	10,0000
13	Kontrol 1 mg	1,0000	1,0000
14	Blank	1,0000	1,0000

Analysis Audit Trail

16-12-2013 14:50:48 labadm:AALBORG-B27DD38
Record created
16-12-2013 15:08:39 labadm:AALBORG-B27DD38
Error MD147 - Activity manually aborted by user.

OQ Test Result Summary

Warning: OQ Results not available.

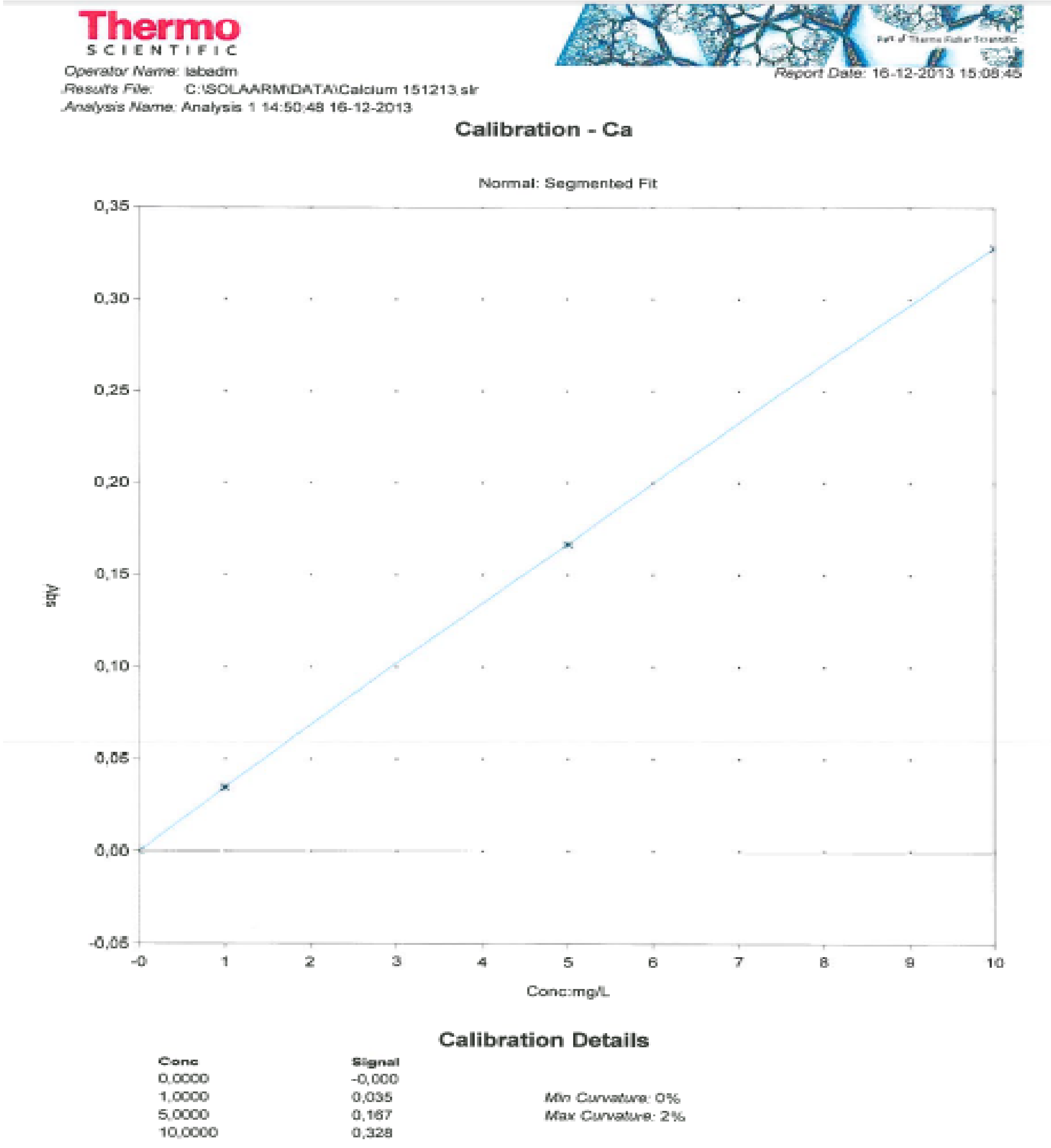
Spectrometer Parameters - Ca

Element: Ca
Wavelength: 422,7nm
Background Correction: Off
Signal Type: Continuous
Measurement Time: 4.0secs
Use RSD Test: No

Measurement Mode: Absorbance
Bandpass: 0,5nm
High Resolution: Off
Resamples: Fast
Flier Mode: No

Lamp Current: 100%
Optimise Spectrometer Parameters: No
Number Of Resamples: 3

D2c. Calcium concentration of fresh and sea water filtrates with all additives.



Operator Name: labadm

Results File: C:\SOLAARM\DATA\Calcium 151213.slr

Analysis Name: Analysis 1 14:50:48 16-12-2013

Report Date: 16-12-2013 15:08:45

Calibration - Ca

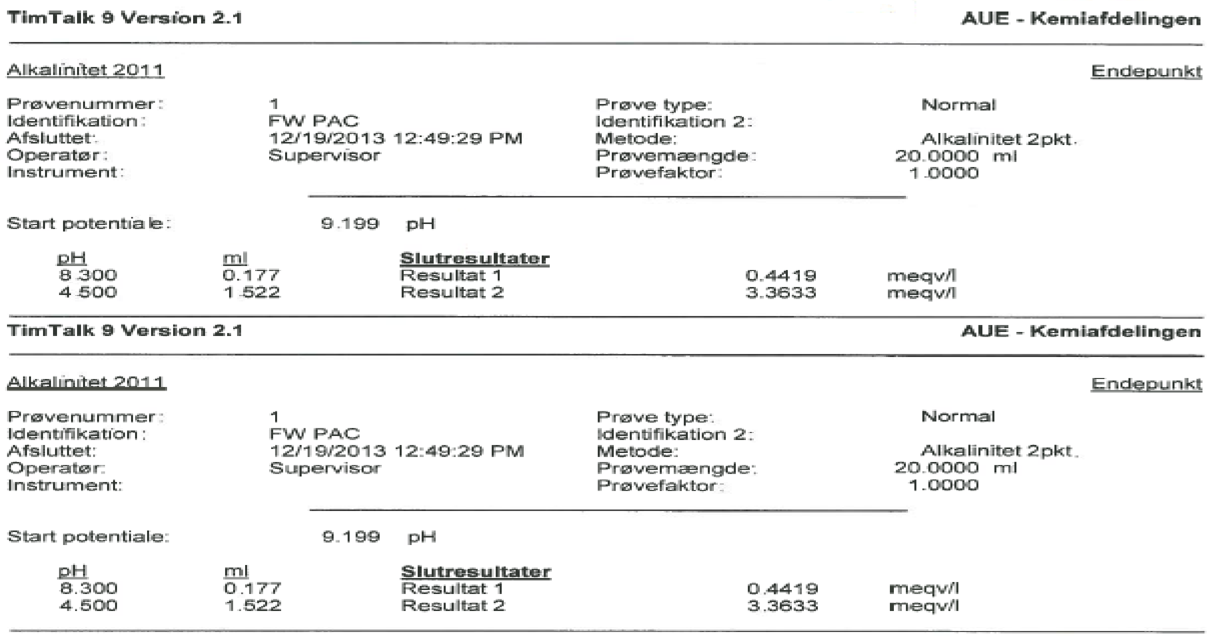
Calibration Details

Conc	Signal
0,0000	-0,000
1,0000	0,035
5,0000	0,167
10,0000	0,328

Min Curvature: 0%

Max Curvature: 2%

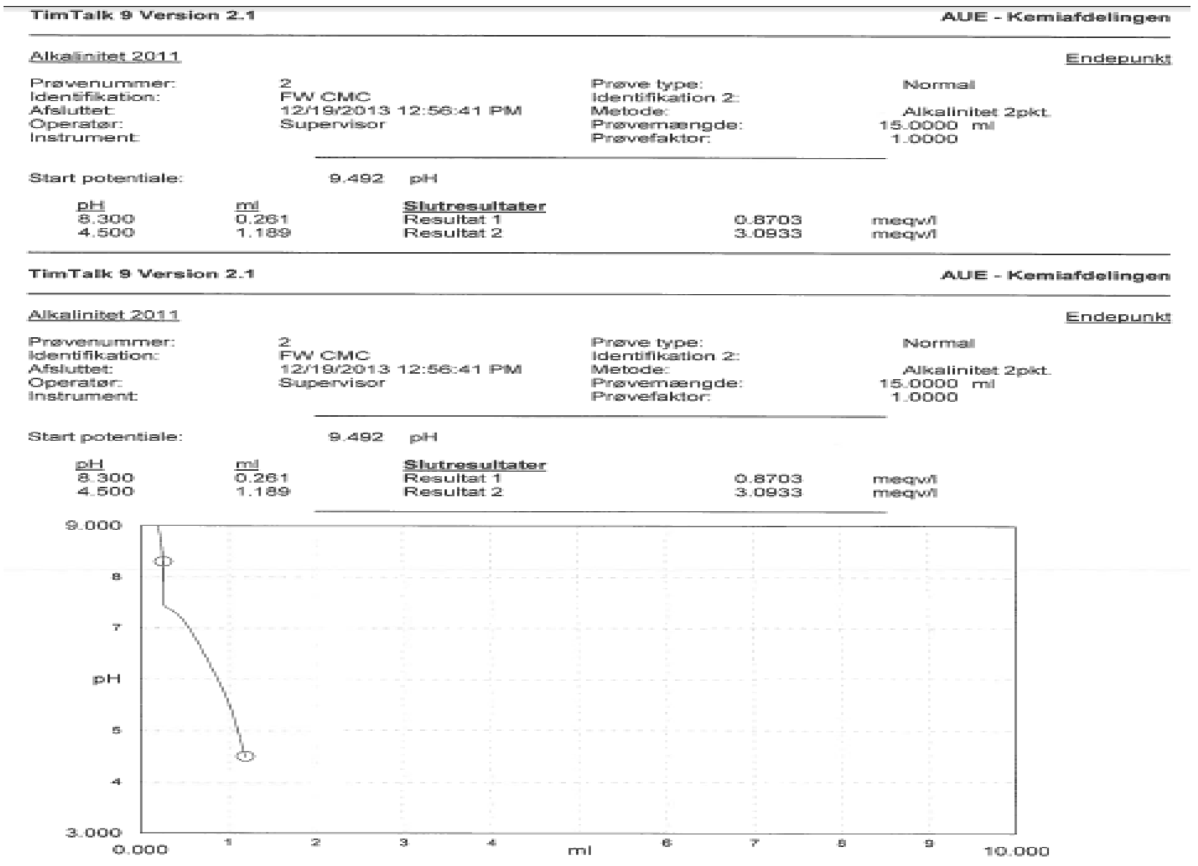
E1. Filtrate alkalinity test for fresh water using MI PAC with sample 5



```
TimTalk 9 Version 2.1                                              AUE - Kemiafdelingen

Alkalinitet 2011                                                             Endepunkt

Prøvenummer:          1                          Prøve type:              Normal
Identifikation:       FW PAC                     Identifikation 2:
Afsluttet:            12/19/2013 12:49:29 PM     Metode:                  Alkalinitet 2pkt.
Operatør:             Supervisor                 Prøvemængde:          20.0000  ml
Instrument:                                      Prøvefaktor:            1.0000

Start potentiale:                9.199    pH

   pH           ml            Slutresultater
   8.300        0.177         Resultat 1                  0.4419       meqv/l
   4.500        1.522         Resultat 2                  3.3633       meqv/l
```

```
TimTalk 9 Version 2.1                                              AUE - Kemiafdelingen

Alkalinitet 2011                                                             Endepunkt

Prøvenummer:          1                          Prøve type:              Normal
Identifikation:       FW PAC                     Identifikation 2:
Afsluttet:            12/19/2013 12:49:29 PM     Metode:                  Alkalinitet 2pkt.
Operatør:             Supervisor                 Prøvemængde:          20.0000  ml
Instrument:                                      Prøvefaktor:            1.0000

Start potentiale:                9.199    pH

   pH           ml            Slutresultater
   8.300        0.177         Resultat 1                  0.4419       meqv/l
   4.500        1.522         Resultat 2                  3.3633       meqv/l
```

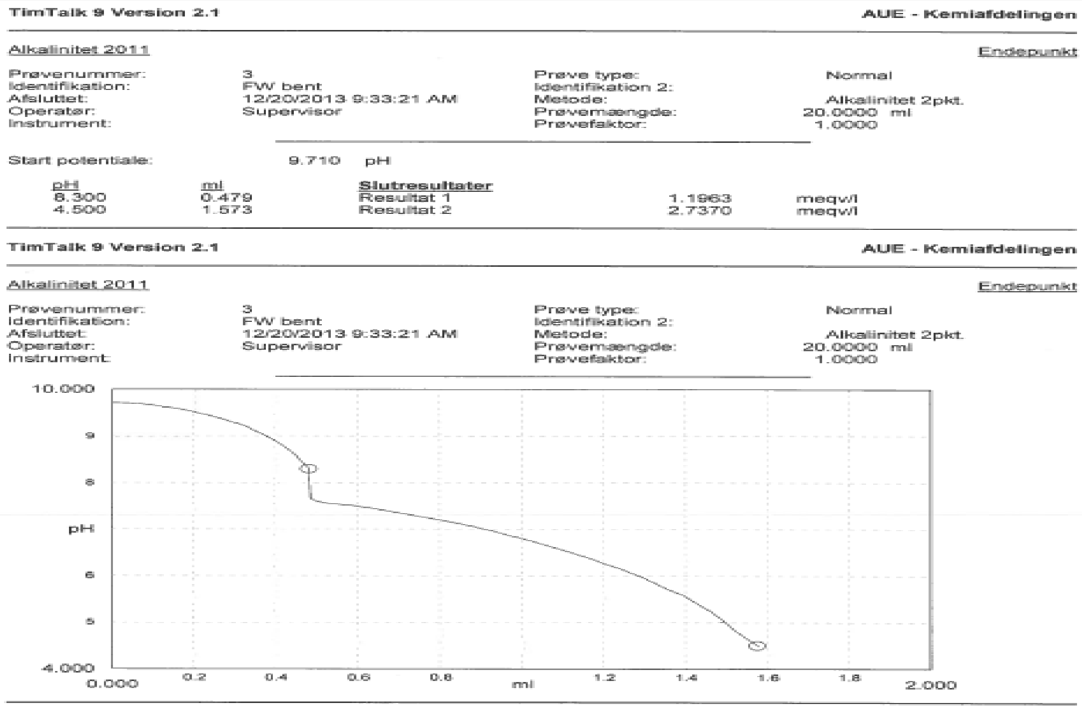
E2. Filtrate alkalinity test for fresh water using CMC with sample 5.



```
TimTalk 9 Version 2.1                                              AUE - Kemiafdelingen

Alkalinitet 2011                                                             Endepunkt

Prøvenummer:          2                          Prøve type:              Normal
Identifikation:       FW CMC                     Identifikation 2:
Afsluttet:            12/19/2013 12:56:41 PM     Metode:                  Alkalinitet 2pkt.
Operatør:             Supervisor                 Prøvemængde:          15.0000  ml
Instrument:                                      Prøvefaktor:            1.0000

Start potentiale:                9.492    pH

   pH           ml            Slutresultater
   8.300        0.261         Resultat 1                  0.8703       meqv/l
   4.500        1.189         Resultat 2                  3.0933       meqv/l
```

```
TimTalk 9 Version 2.1                                              AUE - Kemiafdelingen

Alkalinitet 2011                                                             Endepunkt

Prøvenummer:          2                          Prøve type:              Normal
Identifikation:       FW CMC                     Identifikation 2:
Afsluttet:            12/19/2013 12:56:41 PM     Metode:                  Alkalinitet 2pkt.
Operatør:             Supervisor                 Prøvemængde:          15.0000  ml
Instrument:                                      Prøvefaktor:            1.0000

Start potentiale:                9.492    pH

   pH           ml            Slutresultater
   8.300        0.261         Resultat 1                  0.8703       meqv/l
   4.500        1.189         Resultat 2                  3.0933       meqv/l
```

E3. Filtrate alkalinity test for fresh water using Bentonite with sample 5



TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer:	3	Prøve type:	Normal
Identifikation:	FW bent	Identifikation 2:	
Afsluttet:	12/20/2013 9:33:21 AM	Metode:	Alkalinitet 2pkt.
Operatør:	Supervisor	Prøvemængde:	20.0000 ml
Instrument:		Prøvefaktor:	1.0000

Start potentiale: 9.710 pH

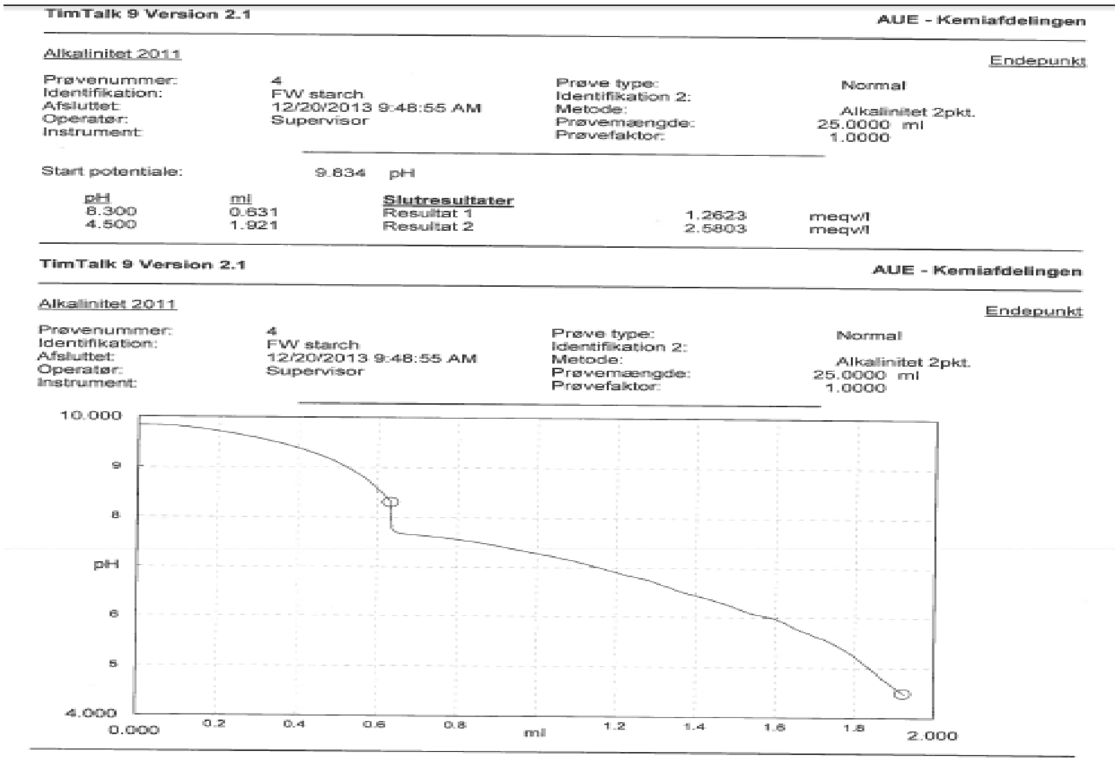
pH	ml	Slutresultater		
8.300	0.479	Resultat 1	1.1963	meqv/l
4.500	1.573	Resultat 2	2.7370	meqv/l

TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer:	3	Prøve type:	Normal
Identifikation:	FW bent	Identifikation 2:	
Afsluttet:	12/20/2013 9:33:21 AM	Metode:	Alkalinitet 2pkt.
Operatør:	Supervisor	Prøvemængde:	20.0000 ml
Instrument:		Prøvefaktor:	1.0000

E4. Filtrate alkalinity test for fresh water using starch with sample 5



TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer:	4	Prøve type:	Normal
Identifikation:	FW starch	Identifikation 2:	
Afsluttet:	12/20/2013 9:48:55 AM	Metode:	Alkalinitet 2pkt.
Operatør:	Supervisor	Prøvemængde:	25.0000 ml
Instrument:		Prøvefaktor:	1.0000

Start potentiale: 9.834 pH

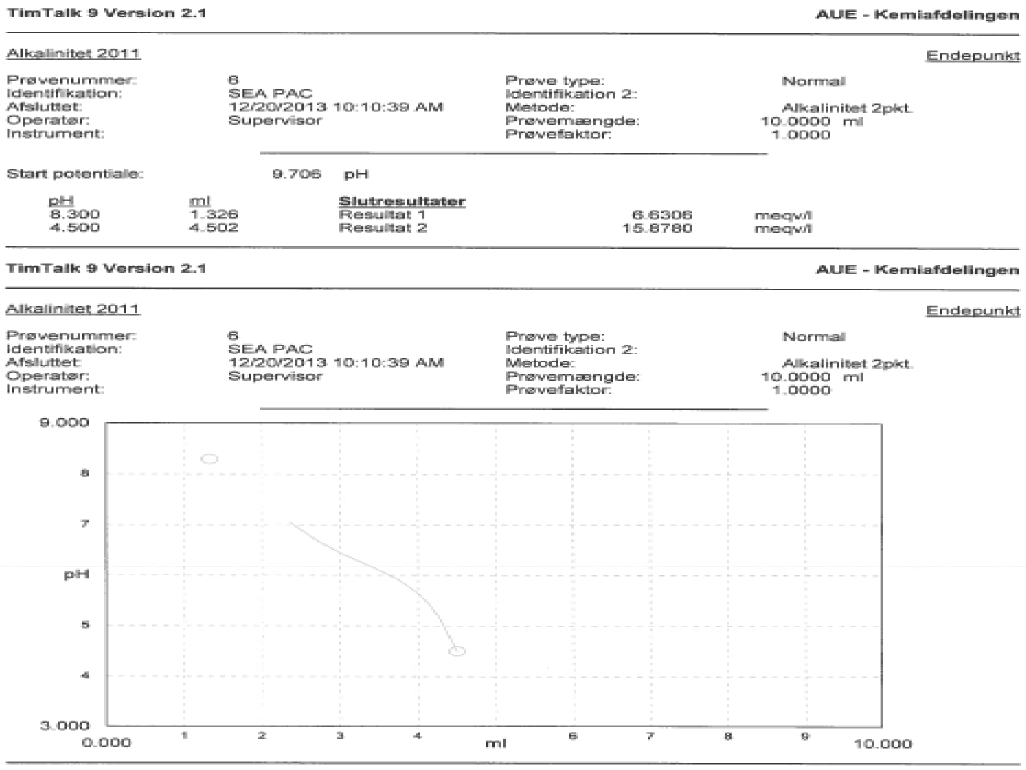
pH	ml	Slutresultater		
8.300	0.631	Resultat 1	1.2623	meqv/l
4.500	1.921	Resultat 2	2.5803	meqv/l

TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer:	4	Prøve type:	Normal
Identifikation:	FW starch	Identifikation 2:	
Afsluttet:	12/20/2013 9:48:55 AM	Metode:	Alkalinitet 2pkt.
Operatør:	Supervisor	Prøvemængde:	25.0000 ml
Instrument:		Prøvefaktor:	1.0000

F1. Filtrate alkalinity test for sea water using MI PAC with sample 5.



TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer: 6
Identifikation: SEA PAC
Afsluttet: 12/20/2013 10:10:39 AM
Operatør: Supervisor
Instrument:

Prøve type: Normal
Identifikation 2:
Metode: Alkalinitet 2pkt.
Prøvemængde: 10.0000 ml
Prøvefaktor: 1.0000

Start potentiale: 9.706 pH

pH	ml	Slutresultater		
8.300	1.326	Resultat 1	6.6306	meqv/l
4.500	4.502	Resultat 2	15.8780	meqv/l

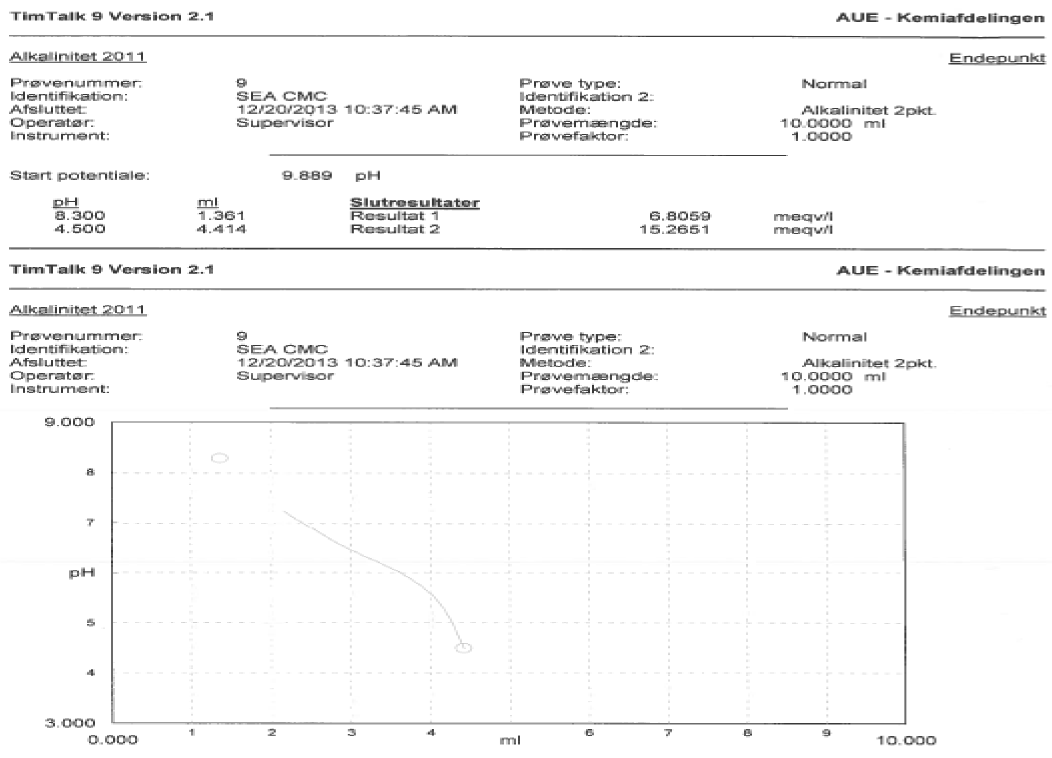
TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer: 6
Identifikation: SEA PAC
Afsluttet: 12/20/2013 10:10:39 AM
Operatør: Supervisor
Instrument:

Prøve type: Normal
Identifikation 2:
Metode: Alkalinitet 2pkt.
Prøvemængde: 10.0000 ml
Prøvefaktor: 1.0000

F2. Filtrate alkalinity test for sea water using CMC with sample 5.



TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer: 9
Identifikation: SEA CMC
Afsluttet: 12/20/2013 10:37:45 AM
Operatør: Supervisor
Instrument:

Prøve type: Normal
Identifikation 2:
Metode: Alkalinitet 2pkt.
Prøvemængde: 10.0000 ml
Prøvefaktor: 1.0000

Start potentiale: 9.889 pH

pH	ml	Slutresultater		
8.300	1.361	Resultat 1	6.8059	meqv/l
4.500	4.414	Resultat 2	15.2651	meqv/l

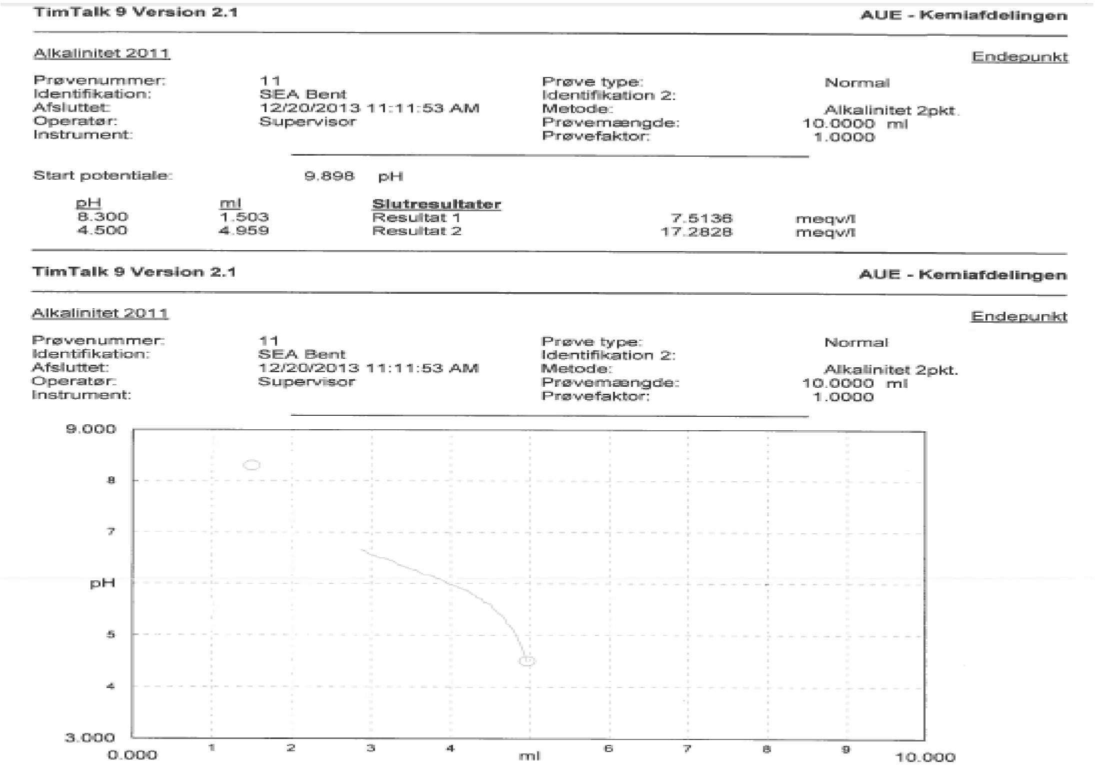
TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer: 9
Identifikation: SEA CMC
Afsluttet: 12/20/2013 10:37:45 AM
Operatør: Supervisor
Instrument:

Prøve type: Normal
Identifikation 2:
Metode: Alkalinitet 2pkt.
Prøvemængde: 10.0000 ml
Prøvefaktor: 1.0000

F3. Filtrate alkalinity test for sea water using Bentonite with sample 5.



TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer: 11
Identifikation: SEA Bent
Afsluttet: 12/20/2013 11:11:53 AM
Operatør: Supervisor
Instrument:

Prøve type: Normal
Identifikation 2:
Metode: Alkalinitet 2pkt.
Prøvemængde: 10.0000 ml
Prøvefaktor: 1.0000

Start potentiale: 9.898 pH

pH	ml	Slutresultater		
8.300	1.503	Resultat 1	7.5136	meqv/l
4.500	4.959	Resultat 2	17.2828	meqv/l

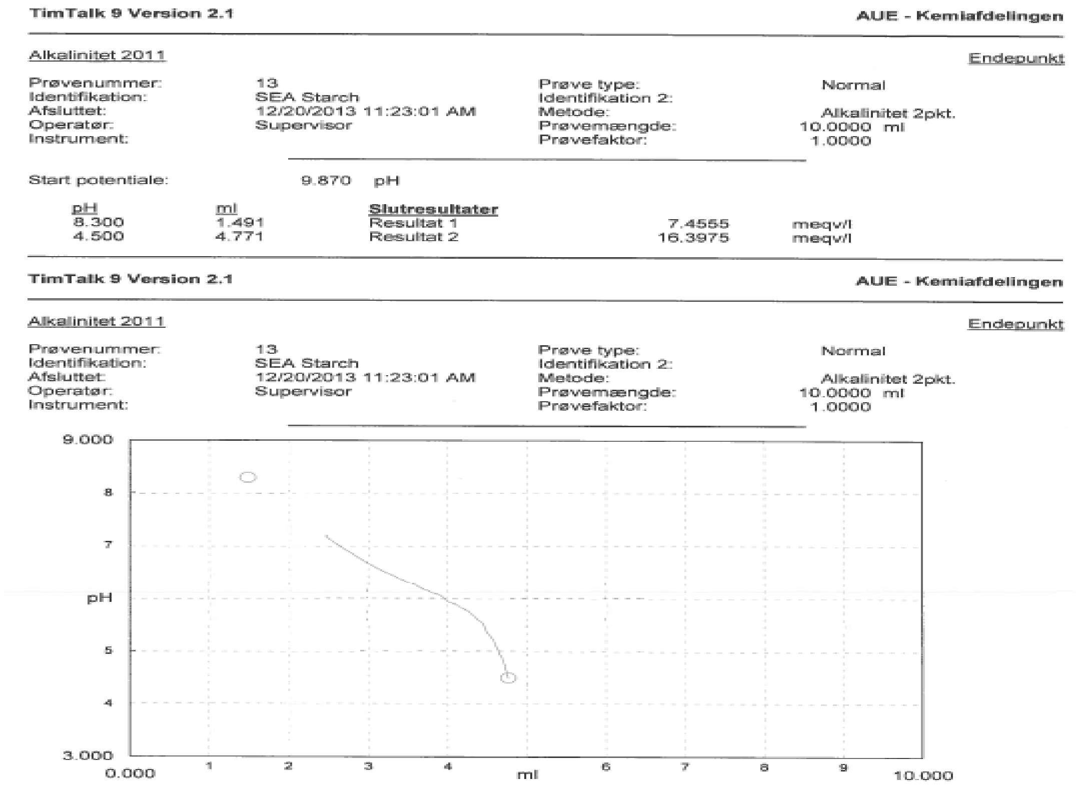
TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer: 11
Identifikation: SEA Bent
Afsluttet: 12/20/2013 11:11:53 AM
Operatør: Supervisor
Instrument:

Prøve type: Normal
Identifikation 2:
Metode: Alkalinitet 2pkt.
Prøvemængde: 10.0000 ml
Prøvefaktor: 1.0000

F4. Filtrate alkalinity test for sea water using Starch with sample 5.



TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer: 13
Identifikation: SEA Starch
Afsluttet: 12/20/2013 11:23:01 AM
Operatør: Supervisor
Instrument:

Prøve type: Normal
Identifikation 2:
Metode: Alkalinitet 2pkt.
Prøvemængde: 10.0000 ml
Prøvefaktor: 1.0000

Start potentiale: 9.870 pH

pH	ml	Slutresultater		
8.300	1.491	Resultat 1	7.4555	meqv/l
4.500	4.771	Resultat 2	16.3975	meqv/l

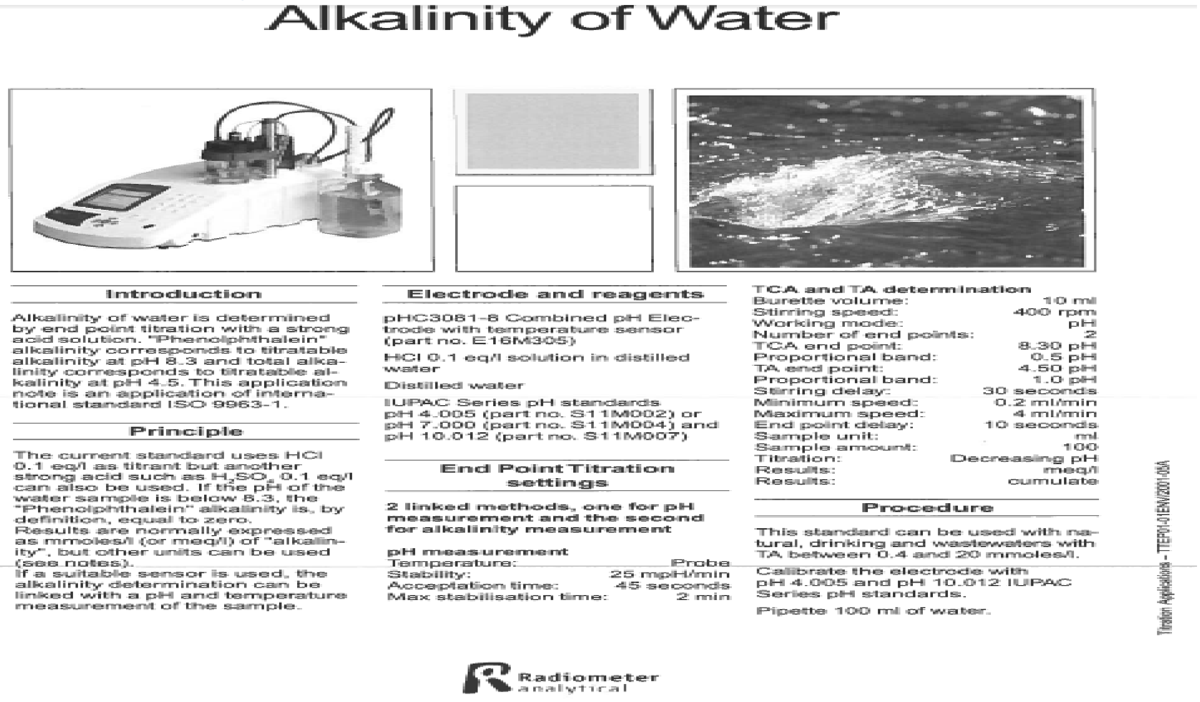
TimTalk 9 Version 2.1 **AUE - Kemiafdelingen**

Alkalinitet 2011 Endepunkt

Prøvenummer: 13
Identifikation: SEA Starch
Afsluttet: 12/20/2013 11:23:01 AM
Operatør: Supervisor
Instrument:

Prøve type: Normal
Identifikation 2:
Metode: Alkalinitet 2pkt.
Prøvemængde: 10.0000 ml
Prøvefaktor: 1.0000

G1a. Filtrate alkalinity test.



Alkalinity of Water

Introduction

Alkalinity of water is determined by end point titration with a strong acid solution. "Phenolphthalein" alkalinity corresponds to titratable alkalinity at pH 8.3 and total alkalinity corresponds to titratable alkalinity at pH 4.5. This application note is an application of international standard ISO 9963-1.

Principle

The current standard uses HCl 0.1 eq/l as titrant but another strong acid such as H_2SO_4 0.1 eq/l can also be used. If the pH of the water sample is below 8.3, the "Phenolphthalein" alkalinity is, by definition, equal to zero.
Results are normally expressed as mmoles/l (or meq/l) of "alkalinity", but other units can be used (see notes).
If a suitable sensor is used, the alkalinity determination can be linked with a pH and temperature measurement of the sample.

Electrode and reagents

pHC3081-8 Combined pH Electrode with temperature sensor (part no. E16M305)

HCl 0.1 eq/l solution in distilled water

Distilled water

IUPAC Series pH standards
pH 4.005 (part no. S11M002) or
pH 7.000 (part no. S11M004) and
pH 10.012 (part no. S11M007)

End Point Titration settings

2 linked methods, one for pH measurement and the second for alkalinity measurement

pH measurement
Temperature: Probe
Stability: 25 mpH/min
Acceptation time: 45 seconds
Max stabilisation time: 2 min

TCA and TA determination
Burette volume: 10 ml
Stirring speed: 400 rpm
Working mode: pH
Number of end points: 2
TCA end point: 8.30 pH
Proportional band: 0.5 pH
TA end point: 4.50 pH
Proportional band: 1.0 pH
Stirring delay: 30 seconds
Minimum speed: 0.2 ml/min
Maximum speed: 4 ml/min
End point delay: 10 seconds
Sample unit: ml
Sample amount: 100
Titration: Decreasing pH
Results: meq/l
Results: cumulate

Procedure

This standard can be used with natural, drinking and wastewaters with TA between 0.4 and 20 mmoles/l.

Calibrate the electrode with pH 4.005 and pH 10.012 IUPAC Series pH standards.

Pipette 100 ml of water.

Titration Applications - TTEP01-01ENV/2001-06A

Radiometer analytical

G1b. Filtrate alkalinity test.

Dip electrode and delivery tip in the sample.

Start method by pressing the RUN key.

Results

Expressed as milliequivalents/l (or millimol/l) of OH⁻ alkalinity

R = V(titr) * C(titr) * 1000 / V(smp)

-V(titr) = Total volume of titrant in ml, delivered to reach the end point (pH 8.3 or pH 4.5)
-C(titr) = titrant concentration in eq/l (currently 0.1)
-V(smp) = Volume of the sample (currently 100 ml)

For a result in mmol/l

Enter

The sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display

The Titration Manager gives a result according the above formula.

Results for 5 determinations in milliequivalents/l
Mean: 3.6
Standard deviation: 0.038
Relative standard deviation: 1%

Working range

The sample size and titrant concentration depend on the quality of the water.
Using the application note settings

V sample = 100 ml
Burette volume = 10 ml
Titrant concentration = 0.1 eq/l

For the best accuracy and reproducibility, the result range is between 3.5 meq/l (or 175 mg/l $CaCO_3$) for 35% of the cylinder burette capacity and 10 meq/l (or 500 mg/l $CaCO_3$) for the burette capacity.

With the same conditions, the "experimental" limit corresponding to a titrant volume of 0.5 ml is 0.5 meq/l (or 25 mg/l $CaCO_3$).
For alkalinity below this value, it is recommended to use a low alkalinity method with 0.02 eq/l titrant and 200 ml for sample volume, using the calculation above.

Notes

1) The results are normally expressed in mmoles/l (or meq/l) of alkalinity.
1 ml of 0.1 eq/l of strong acid represents 0.1 meq or mmol of alkalinity.

2) Depending on the country, many other units can be used for the results

-mmol/l $CaCO_3$ (= meq/l * 0.5)
(CO_3^- has 2 alkalinity functions per molecule)

-mg/l $CaCO_3$ (= meq/l * 50)
(MW of $CaCO_3$ is 100.09 g/mol with 2 alkaline functions per molecule)

-mg/l HCO_3^- (= meq/l * 61)
(MW of HCO3- is 61 g/mol with 1 alkaline function per molecule)

-Clark degree (= meq/l * 3.50)

-German degree (= meq/l * 2.80)

-French degree (= meq/l * 5.0)

-U.S. degree (= meq/l * 2.90)

It is easy to express results in all these units thanks to the equation features of the Titration Manager.

Bibliography

International standard ISO 9963

EPA method number 310.1

Standard methods for water and wastewater 18th edition (1992) 2-25 part 2320

Titration Applications - TTEP01-01ENV/2001-06A

RADIOMETER ANALYTICAL S.A.
72 rue d'Alsace, 69627 Villeurbanne Cedex, France
E-mail: radiometer@nalytical.com Web: www.radiometer-analytical.com
Tel. : +33 (0)4 78 03 38 38 - Fax : +33 (0)4 78 68 88 12