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Effect of Flocculant on Solid Removal from Drilling Fluids

by

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A thesis submitted for the degree of

Master of Professional Engineering in Petroleum Engineering

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Abstract

Solids Control Systems are a major component in every drilling operation. Drilling Fluids became highly sophisticated and costly fluids with thin window for the properties such as viscosity and density variation, because of that there a constant necessity to keep the drilling fluid in operational conditions for as long as possible with minimum effort. Any improvement to the Solid Control system, such as the chemical aid of a flocculant has a potential to decrease costs in drilling operation and must be evaluated.

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Dear Prof. Masood Mostofi and Prof. Ferial Hakami,

I, Vinicius Cunha de Souza, hereby submit my thesis entitled “Effect of Flocculant on Solid Removal from Drilling Fluids” as part of my requirements for completion of the Master of Professional Engineering in Petroleum Engineering.

I declare that this thesis is entirely my own work with the exception of the acknowledgements and references mentioned.

Yours sincerely,

Vinicius Cunha de Souza
20075716

Declaration of published work

I also acknowledge that parts of the progress report presented at the end of the first semester of this project have been used in the following chapters of this thesis, and the report has been properly referenced:

- Chapter 1.
- Chapter 2.
- Chapter 3.

Acknowledgements

I would like to express my gratitude to my supervisors for the opportunity to work on this project as well as all the support during the execution.

Also, I would like to thank my colleagues that prove to be a source of encouragement throughout this course.

Finally, my deepest gratitude to my family for all the love and care provided, specially during this time in spite of all the physical distance between us their support always reached and helped me in every moment.

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CHAPTER 1

1. INTRODUCTION

1.1 Background

Drilling Fluids are a major aspect to be considered in drilling operations, they control or impact critical parameters such as:

- Cuttings removal
- Fluid loss
- Wellbore stability
- Drill string lubrication and cooling

The performance of drilling fluids, and therefore the drilling operation, is controlled by properties from the formation to be drilled and from the correct drilling fluid selection.

As the drilling operation occur the carefully engineered drilling fluids properties needs to be constantly checked and adjusted, one of the systems involved in this adjustment is the solids-control system. During drilling the cuttings are removed to surface by the continuous circulation of drilling fluid, however the accumulation of solids changes the fluid concentration and affect other properties such as viscosity and density, this can decrease the capacity of the fluid to perform a good cleaning, and consequentially decrease the drilling performance.

Traditionally solids control in drilling mud involved dilution, the use of thinning agents and the subsequent discharge of the used drilling fluid, as technology developed the drilling mud became more expensive and at the same time environmental concerns created more restrictive regulations forcing the development of better solids-control approaches [1]. Since solids present in drilling fluids vary greatly in size, the system is composed of various steps each aiming to remove a specific range of particles. The removal can be further improved by using chemical methods such as coagulants, usually inorganic salts, and flocculants. Flocculants are polymeric molecules usually of synthetic origin, as a polymeric chain these molecules have high molecular weight, although, the molecular weight will vary from the different types of flocculants. The flocculants can be either, cationic, anionic, or non-ionic. Flocculants, absorption is based in different mechanisms, such as

- **Electrostatic:** If the flocculants molecules are anionic or cationic, they will absorb particles of opposing charges.
- **Hydrogen Bonding:** If the proper radical is present in the polymer, it may form hydrogen bonds based on the chemical composition of the solid's particles.

The actual flocculation mechanism will vary for each case and is a factor of the flocculant itself, the fluid medium present and the solids in solution. However, generally the use of flocculants improves solid-liquid separation processes performance creating an interesting approach to drilling mud cleaning method.

1.2 Objectives

This project aims to evaluate the performance of Flocculation of drilling fluids.

The specific drilling fluid to be analysed is Ctrol™, a recently developed drilling fluid. The flocculation performance will be evaluated based on the particle size distribution (PSD) of the flocculated samples, ideally the flocculation will increase particles size turning the mechanical separation process of the Solids-Control System more effective. To better understand how this particular Drilling Fluid behaves different types of flocculants will be applied and compared.

1.3 Significances

Due to the major importance of Drilling Fluids in drilling operations nowadays, high performance drilling muds are continuously being developed improving the operation but adding increasingly costs as well, creating a scenario where the fluid needs to be kept within operational standards for as long as possible.

On the Technical side, as drilling occurs it inherently change the fluids properties, in a detrimental manner, causing efficiency problems and possibly risks to the operation.

Finally, environmental concerns take place regarding the dispose of used waste drilling fluid, although recent advances obtained better performance fluids, in general, the more complex the composition is a more complex dispose method is required in order to prevent water and soil contaminations.

Based on these aspects it is clear that an improvement in the Drilling Fluids properties management, which can be done by an efficient solid control methodology can greatly provide economic, safety and environmental returns.

1.4 Scope of the study

The scope of this project is to evaluate flocculation performance on Drilling Fluid Ctrol™ by considering how the particle size distribution is affected.

A systematic comparison of flocculation experiments and particle size distribution measurements will be carried out aiming the best relationship between particle size increment and flocculant dosage.

By the end of this project two deliverables will be obtained:

- Determine if flocculation is possible in Ctrol™.

- Determine which type of flocculant performs better in Ctrol™.

1.5 Layout of the report

In this thesis a concise Literature Review regarding flocculation of drilling fluids will be carried out in Chapter 2 intending to explain the basis for this project as well as the outlines for Chapter 3 the Methodology which will further explain how the project will be carried out.

Following the Methodology description in Chapter 4 the results are presented and discussed and finally Chapter 5 presents the conclusions and possible future work.

CHAPTER 2

2. LITERATURE REVIEW

Flocculation is a considered a complex process not fully comprehended. However, many studies were carried to investigate the mechanisms behind the formation of flocs.

Flocculants consist of long polymers molecules with high molecular weight either from synthetic or natural origins, presented in a cationic, anionic, or neutral electrostatic form, forming viscous solutions. Three main flocculation mechanism can be presented:

- **Electrostatic Neutralization**: Since flocculants can have electrostatic charges, and, if the solids in solution contain an opposing charge, electrostatic attraction will be in place and solids particle will adhere to the polymer surface. Considering the length of a polymer molecule more than on solid particle can be neutralized by the same molecule.
- **Hydrogen Bonding:** Some radicals presented in a polymer, such as hydroxyl and amine, can from a hydrogen bond depending on the chemical composition of the solid and the medium.
- **Ion Bridging:** Based on the length of the polymer, even after a flocculant molecule is adhered to a solid particle it can be long enough that some areas of its molecule are as far as to be beyond the electrical double layer, this creates the possibility of further interactions with other particles in the solution.

In general, regardless of the mechanism the flocculant will adhere to the solid particle surface, creating a bond that will vary in nature based on the mechanism, continuously more and more flocculant is attached to the solids in solution creating an agglomerate considerably bigger in size when compared to the initial solid particle.

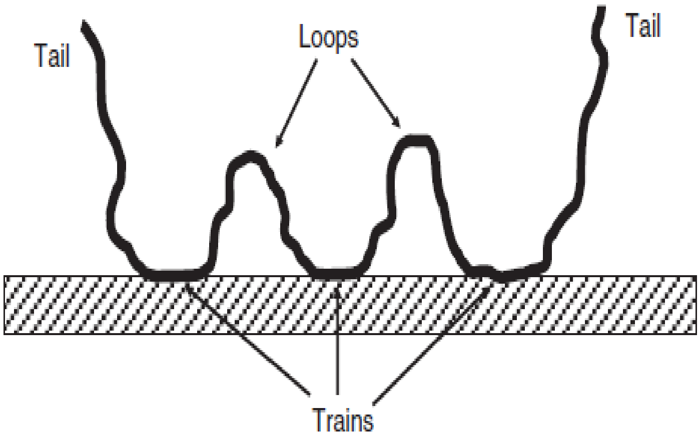

Figure 1 - Flocculant polymer chain and surface.

The process can be described as the flocculant is mixed in the solution contact between molecules will occur, from this contact the polymer molecule can be attached to a solid surface. As showed in Figure 1. more than one region of the flocculant molecule will bond with the surface of the solid, the region of attachment is called Train, in this region, the flocculant is close enough to the surface to be inside the electrical double layer and by this prevented from any other interaction. However, between these Trains other region called Loop will be present, in this region the molecule can be as far from the surface as to attached to a second surface and by doing this create a continuous agglomeration process as showed in Figure 2. A third region can be described, the ends of the polymer molecules, Tail region, since they can also be further enough from the particle it is possible that new bonds are created in the Tails same as the Loops region. Considering the long nature of polymers chain a high number of Trains and Loops regions are present for each flocculant.

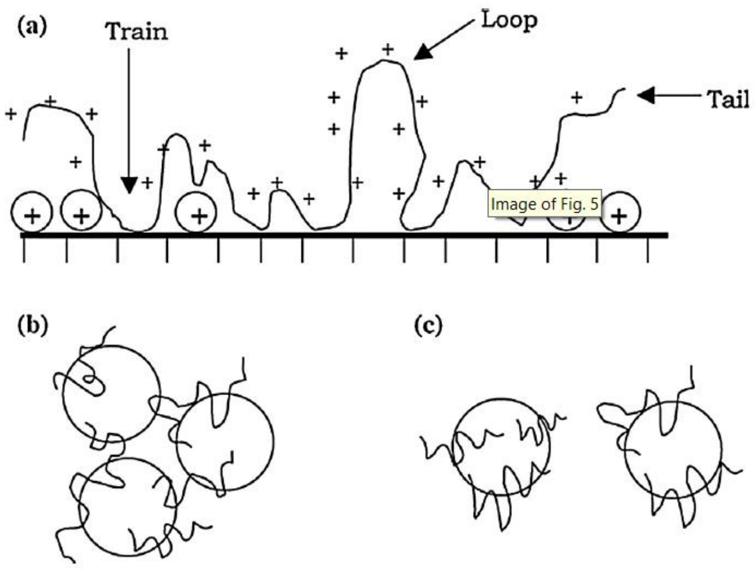

Figure 2 - Flocculant bridging process.

Another major aspect of flocculation is based on its kinetic. From the moment that Flocculant is added to the solution contact can be obtained from the flocculant and the surface and a bond will be created, in this stage, a high number of free polymer molecules and dispersed particles coexist in solution.

Considering the flocculant concentration is enough the process will continue until virtually every solid particle is attached to several polymer particles, creating bigger agglomerates.

Contrary to what could be expected letting the process continue will decrease the agglomerate size. Since the polymer will be continuously attracted by the surface of the solid particle, the molecule will conform as time passes, in practice the Trains regions will increase in length, decreasing the Loops and tails length, to a point where they are fully within the double electrical layer, effectively turning the polymer molecule inactive for further bonding, as represented in Figure 3.

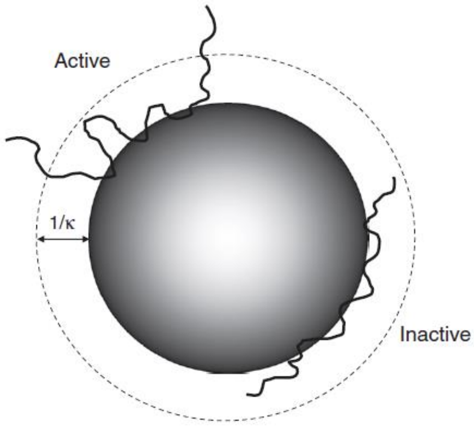

Figure 3 - Flocculant activation

As time passes in a flocculation process an increasingly number of flocculants molecules became inactive, causing the size of agglomerates to decrease, at this point the flocculant concentration have an impact, if too little flocculant is added to the solution the free area around the solid's particles will be enough so that they will became mostly inactive, effectively not creating agglomerates. On the other side, if too much flocculant is added to the solution the competition for contact in the particle surface will be so that not as many different solid's particles can be attached to the same molecule also decreasing the effective size of the agglomerate. The kinetics of the process is summarized in Figure 4.

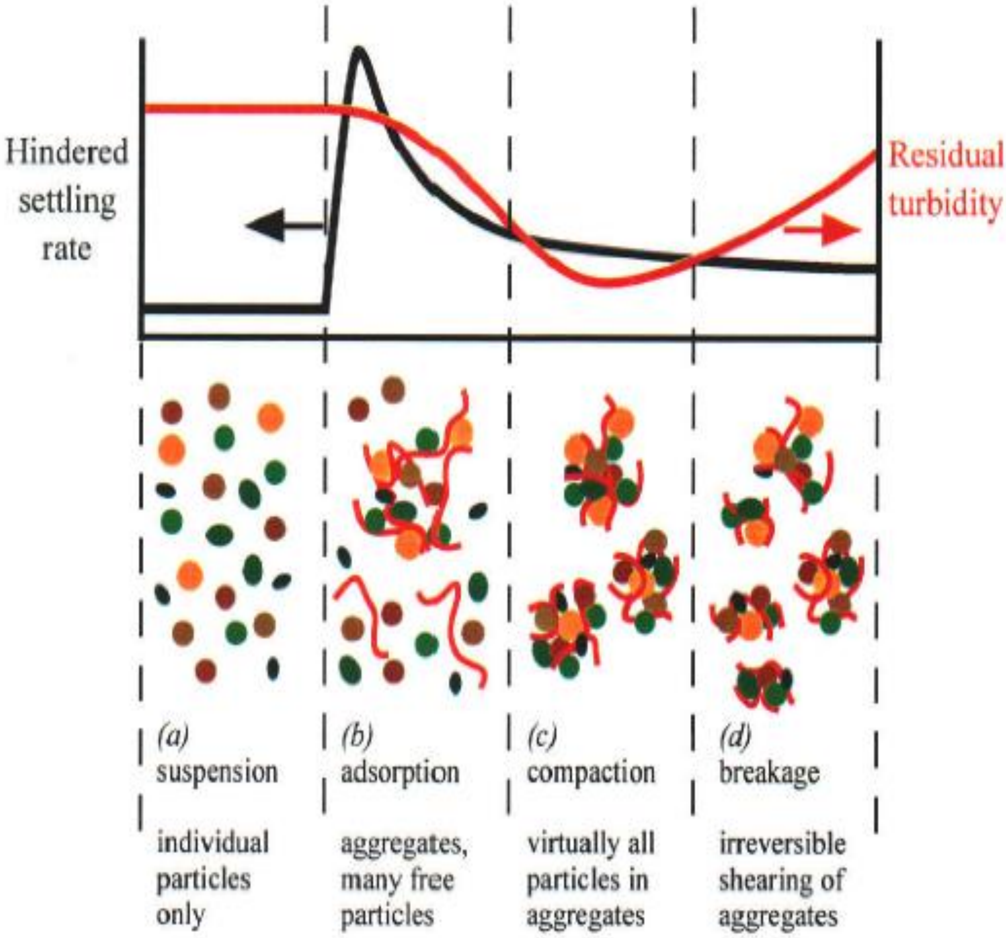

Figure 4 - Flocculation kinetics.

From the basics of the Flocculation process one important aspect can be observed. The bridging process will be dependent on the concentration of flocculant in the solution since it is governed by the contacts between polymer and surface. If Flocculants are underdosed its molecules will reach a maximum absorption while a considerable number of solids remain free in solution. If flocculants are overdosed the surface will be covered by polymer molecules in a way that few bridging can occur also decreasing the effectiveness of the process. Hence, there is an optimal flocculant concentration that must be observed.

Flocculation is an important process used in many industries. Wastewater treatments are one example. Lee et al. (2014) [3] presented a review of flocculation as an alternative to improve wastewater treatment process. Different types of wastewaters were analyzed in various studies and in general the effectiveness of the flocculation to remove solids from solution was observed. Hydrometallurgy also increasingly uses flocculation as a solid-liquid separation process.

For drilling fluids specifically fewer studies were conducted, when compared to other industries. Zhang et al. (2015) [5] analyzed the solid-liquid separation in waste drilling fluids. Polyacrylamide, a common type of polymer used in flocculants, was prepared, and used. The effect on the solid-liquid separation was evaluated by comparing the water concentration present in the solid's precipitates. The experiment consisted in adding different flocs at different concentrations to drilling fluid. Initially low stirring was applied to the solution followed by centrifuge at 3500rpm. A decrease in the water content was observed up until a threshold, as expected, suggesting the effectiveness of the process.

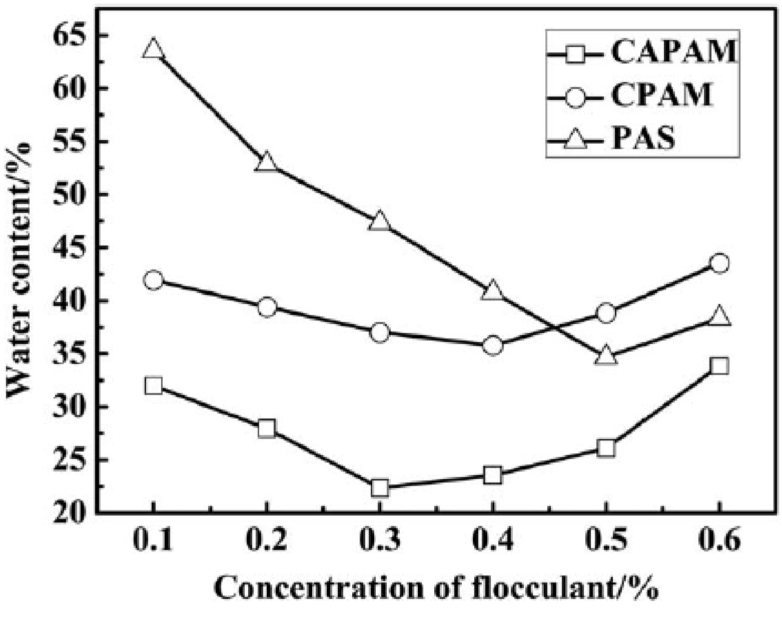

Figure 5 - Agglomerate water content.

Peng, S. et al (2018) [6], considered the application of chitosan-based flocculant. Chitosan was chosen based on the necessity of creating more economically effective flocculants for drilling fluids, since in general commercially available flocculants can be too sensitive to solution PH and solids present in the fluid. In this study the measurement was based in particle size distribution instead of water content. This can be explained as the Solids-control system in Drilling fluids is comprised by different equipment's each one responsible to remove particles in different size range, the main objective of flocculation in this case is to increase the solids size until they can be effectively removed from the system. The methodology in this case involved jar tests for the flocculation, different flocculant concentrations were added to the drilling fluid and stirred for 3min at 300rpm followed by 1 hour of settling. From the measurements the effectiveness of the flocculant in increasing the particle size can be observed.

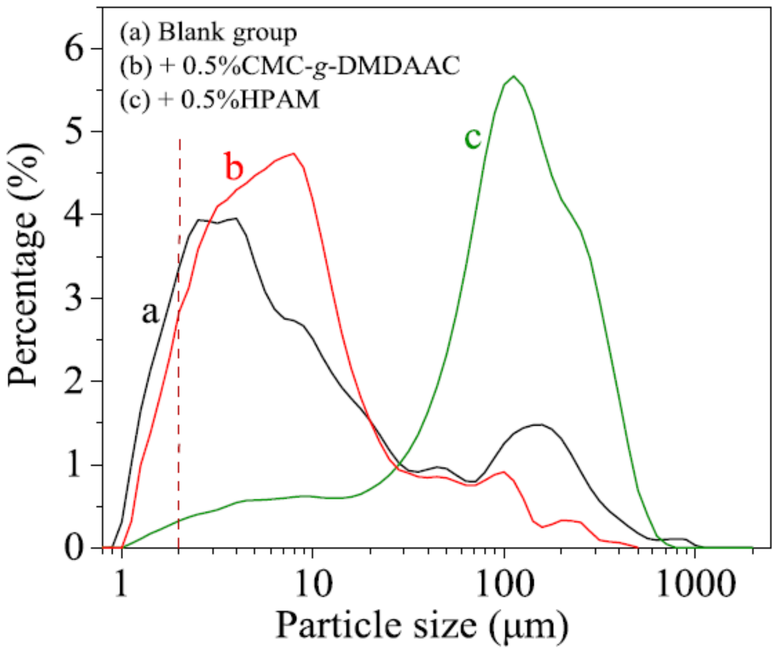

Figure 6 - CMC - g - DMDAAC flocculation.

Finally, Jiang et al. (2018) [7], Starch based flocculant were developed and analyzed in drilling fluid. Similar jar test experiment as used before were conducted, in this case stirring occurred for 5min, again, the flocculation created agglomerates big enough to be easily removed by the Solids-control system.

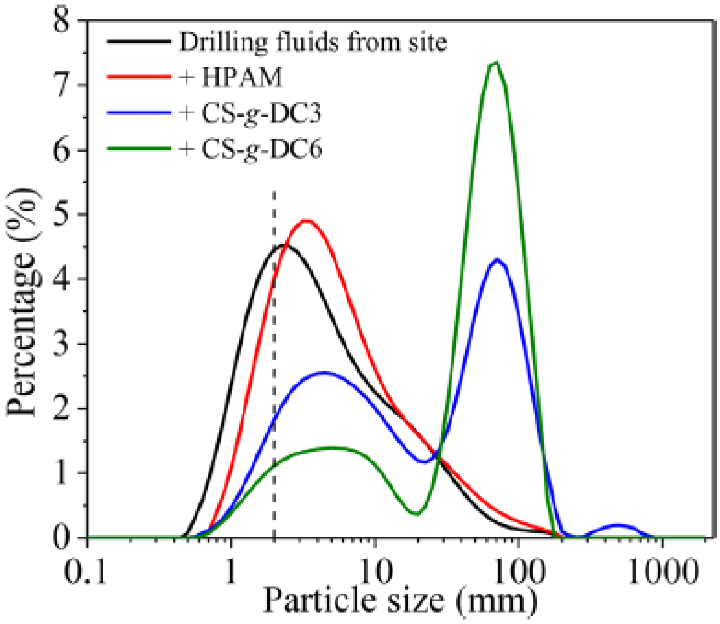

Figure 7 - CS - g - DC flocculation.

From the Flocculation process we conclude that the flocculant type, concentration, and nature of the solids and medium present an important aspect, turning into a highly experimental case by case process, different drilling fluids can behave differently for different types of flocculants and a specific optimum concentration need to be evaluated for increased performance.

CHAPTER 3

3. RESEARCH METHODOLOGY

3.1 Step 1 – Introduction

This Chapter aims to explain the steps that will be part of the thesis experimental methodology with the purpose of obtained information regarding the performance of the flocculation process analyzing the Kaolin solids particle distribution over a period of time after flocculant is added to the solution, the equipment's and methods use will be explained to further clarify the approach.

Based on previous experiments this study will consist in evaluating different flocculant types and dosages based on jar tests experiments.

A graded cylinder containing Ctrol™ drilling fluid will be mixed by a stirrer and solids particles added to the solution. For this experiment Kaolin will be used as solids particles. The mixture will be stirred until the solids are in solution.

After the solution is formed the stirrer will be set for 300rpm and flocculant will be added to the cylinder and the solution will be stirred for another 5 minutes.

The velocity of the stirrer and the time of flocculation were based on previous successful flocculation papers as the ones presented before.

After the mixing time is concluded the stirrer is stopped and the solution left to settle. Samples are taken as the for 10 minutes and analyzed in the Mastersizer 3000. A schematic flowchart is presented in Figure 8.

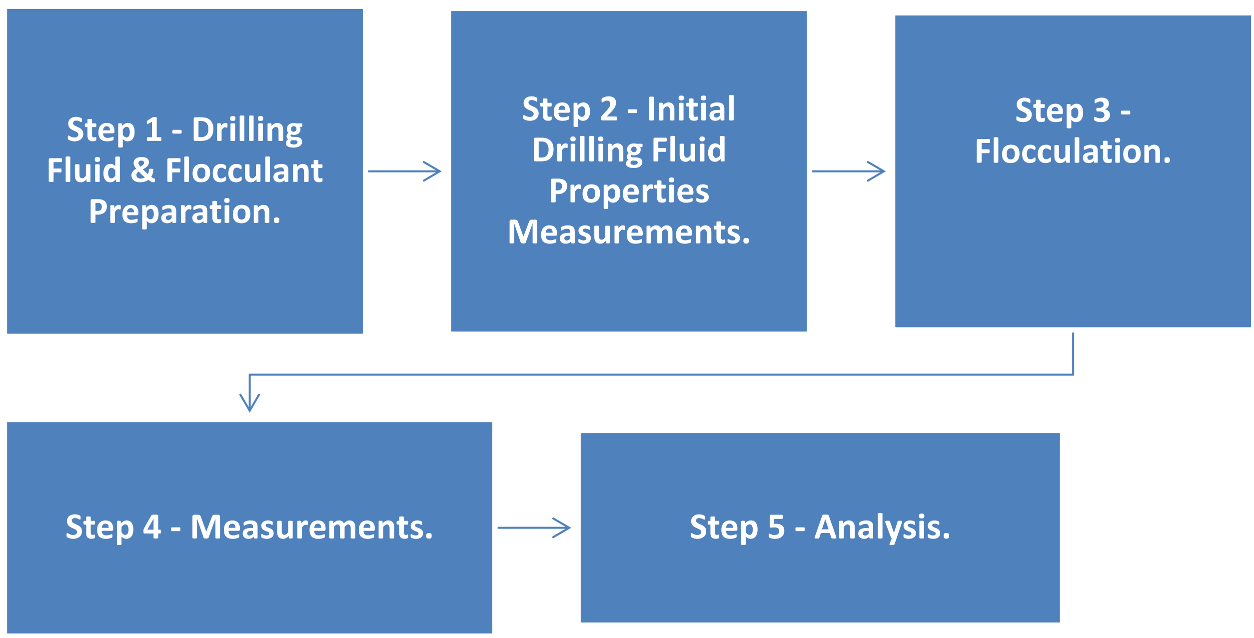

Figure 8 - Methodology.

3.2 Step 1 - Drilling Fluid and Flocculant Preparation

Three different types of flocculants, non-ionic, anionic and cationic, were prepared to a concentration of 0.25%w/v solution, this solution can be stored for a couple weeks without losing its properties. The stirring of the flocculant were carried out until no more power is present and a homogeneous viscous solution is obtained, lower velocities were applied at the end of the mixing to enable the removal of any trapped air bubble.

From the 0.25%w/v flocculant a further dilution is performed on the day of the experiment since the diluted flocculant can not be stored for longer periods. The final concentration were 0.0002%w/v.

Parallel to the flocculant preparation Ctrol drilling fluid were prepared to concentrations of 0.1%, 0.2% and 0.3%. The storage limit for this preparation is about a couple days before the drilling star losing its properties.

3.3 Step 2 - Initial Drilling Fluids Properties Measurements

To guarantee the representativeness of the experiment a number of parameters must be kept constant, although Ctrol and Flocculant were prepared a number of times during the experiments the stirring duration and velocity were kept similar and the fluids visually checked to guarantee complete dissolution. The viscosity was measured each to further assure that the fluids were of similar behaviour. Finally, the fix solid concentration of 1.5% mixed into the drilling fluid at a similar methodology every time collaborating to a representative result.

3.4 Step 3 - Flocculation

A series of jar tests were conducted. For each type and dosage of flocculant combined with each medium fluid, water, Ctrol 0.1%, Ctrol 0.2% and Ctrol 0.3%. Based on the literature after the solids were fully in suspension on the medium the rotation was set to 300rpm, and the flocculant added and left to mix for 5 minutes. After this time the stirrer were stopped and samples collect at specific times: 0 seconds after the mixing, 10 seconds after, 30 seconds, 1 minute, 5 minutes and 10 minutes, ate each the volumetric level of the solids were also measured by the gradings on the cylinder. Figure 9 was taken during one the experiments and represents the methodology applied to all of them.

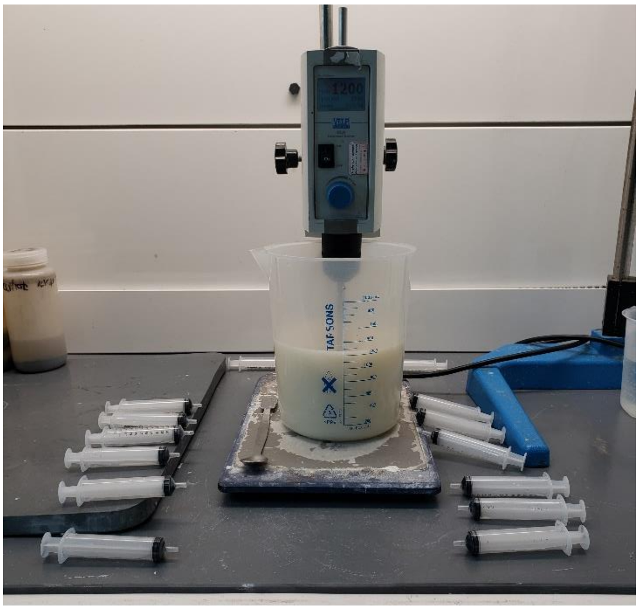

Figure 9 - Flocculation jar test.

3.5 Step 4 – Measurements

The particle size distribution for each sample were measured using a Mastersizer 3000 shown in figure 10. From the measurement a distribution in terms of Volume density in percentage by size in μm is obtained. In addition to the size distribution the kinetics of the process is evaluated by the solids settling rate measured by the solids volumetric occupation of the cylinder.

To create a base of comparison blank tests without flocculant consisting of only medium and solids mixture were conducted to enable comparisons between different experiments run.

3.6 Step 5 - Analysis

The results from the different experiments were first analyzed from the start size of each sample to the final size after 10 minutes of flocculation to check for agglomerations. Since the parameters used in each different experiment are the same it is possible to further compared between the different runs, with different fluids and flocculant types.

3.7 Assumption and Limitations

As stated in the Literature Review many properties affect a flocculation process, in this project the aim is to analyze the flocculant type and dosage impact, so some retrains are in place.

- **Solids Concentration:** to evaluate the impact of flocculant type the solids particles concentration will be kept constant during all experiments at 1.5%.
- **Drilling Fluid properties:** to prevent the impact of variation in the medium the initial properties of Ctrol™ will be measured and kept within the same range.
- **PH and Temperature and other properties:** as stated before the flocculation is acomplex process with man variables such as PH and temperature that might affect the results, however this parameters imacts are out of the scope of this study.

CHAPTER 4

4. Results and Discussion

On this chapter the experiments results are presented and explained in line with the basis obtained in the previous chapters.

4.1 Initial Particle Size Distribution

Before the flocculation experiments were conducted the particle size distribution for a mixture of each medium fluid, Ctrol 0.1%, Ctrol 0.2%, Ctrol 0.3%, Water and Kaolin at 1.5% concentration was measured. The intention was to create a base of comparison for every experiment.

The drilling fluid were prepared using the routine outlined on Table 1, the duration and rotation for each mixing cycle suffered small variation from sample to sample to guarantee the complete mixing, a visual inspection as well as viscosity experiments confirmed the quality of the medium.

Table 1 - Drilling Fluid preparation.

Duration (min)	20	20	20
RPM	1100	900	300

Viscosity measurements were also conducted, and the results presented in Table 2 for Ctrol 0.1%, Table 3 for Ctrol 0.2 % and Table 4 for Ctrol 0.3%.

Table 2 - Ctrol 0.1% viscosity.

Ctrol 0.1%			
RPM	SS (Pa)	µ (cP)	T (c)
600	4.6	4.5	15.8
300	2.8	5.5	15.8
200	2.5	7.5	15.8
100	1.4	8.0	15.8

60	1.2	12.1	15.8
30	1.0	20.0	15.8
20	0.8	23.0	15.8
10	0.7	38.8	15.8
6	0.6	55.0	15.8
3	0.4	80.7	15.8
2	0.4	110.1	15.8
1	0.3	177.3	15.8

Table 3 - Ctrol 0.2% viscosity.

Ctrol 0.2%			
RPM	SS (Pa)	μ (cP)	T (c)
600	8.6	8.4	15.4
300	5.9	11.5	15.4
200	4.8	14.2	15.4
100	3.5	20.3	15.4
60	2.8	27.4	15.4
30	2.1	41.0	15.4
20	1.8	53.8	15.4
10	1.4	84.7	15.4
6	1.2	120.2	15.4
3	0.9	184.9	15.4
2	0.9	268.1	15.4
1	0.8	499.1	15.4

Table 4 - Ctrol 0.3% viscosity.

Ctrol 0.3%			
RPM	SS (Pa)	μ (cP)	T (c)
600	13.0	12.8	17.7
300	8.7	17.1	17.7
200	7.1	20.9	17.7
100	5.2	30.4	17.7
60	4.1	39.7	17.7
30	3.3	63.7	17.7
20	3.0	87.7	17.7
10	2.4	139.3	17.7
6	2.2	210.9	17.7
3	1.7	336.3	17.7
2	1.6	474.6	17.7
1	1.4	837.8	17.7

Again, for each sample minor variations of the viscosity were encountered mainly due to variations of the temperature of the experiment.

The initial PSD for is presented on Figure 10.

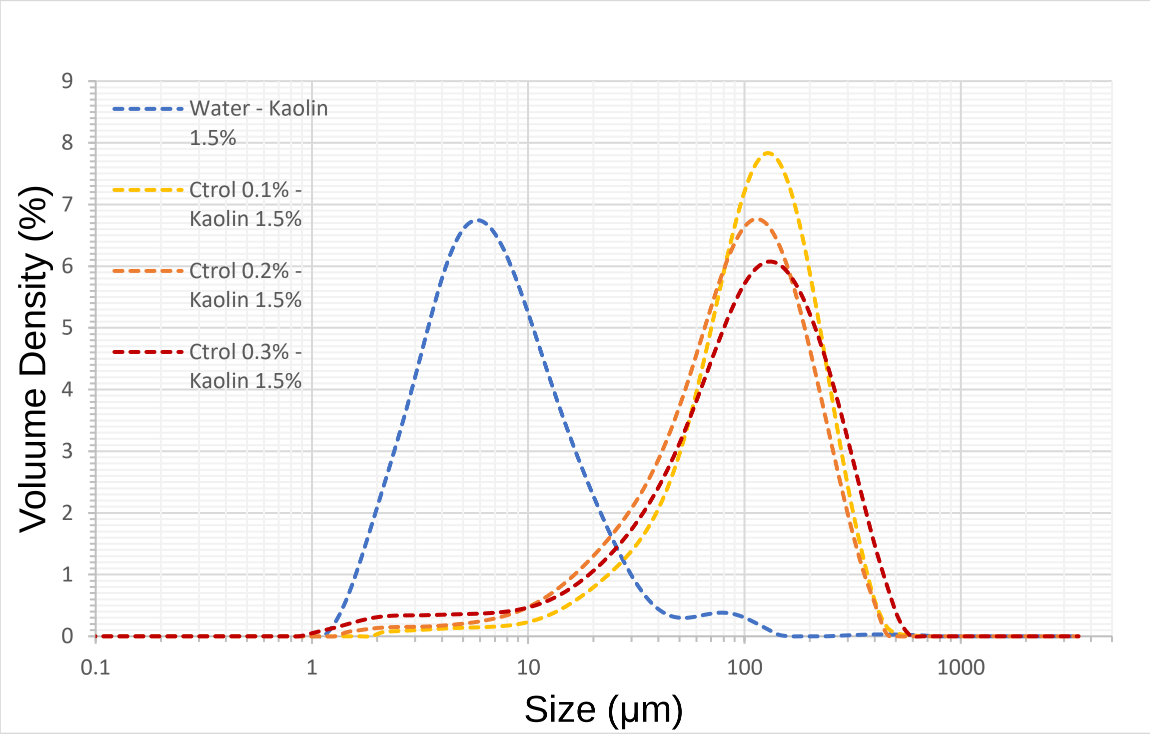

Figure 10 - Kaolin 1.5% PSD.

Observing the plot, the impact of Ctrol medium itself is highly noticeable, while PSD remained fairly lower in Water. This indicates that the polymeric composition of the fluid already creates an agglomeration of solid particles, even without the presence of Flocculants. Figure 11 presents the average particle size for each fluid, from the average 6.9µm for solids particles in water to 119µm in Ctrol 0.1%, proving the agglomeration.

Table 5 - Average Particle Size.

Kaolin 1.5%	Dx (50) (µm)
Water	6.965612263
Ctrol 0.1%	119.6560137
Ctrol 0.2%	100.4589402
Ctrol 0.3%	112.6283168

Contrary to expectation samples of Ctrol 0.1% were more agglomerated than Samples of Ctrol0.3% this variation in the initial particle size will be addressed and further discussed on another section.

4.2 Flocculant Magnafloc 800HP

Flocculation was first evaluated using a non-ionic flocculant Magnafloc 800HP. Next sections presents the flocculation cylinder tests for Water and different concentrations of Ctrol. The flocculant dosage utilized was 250g of Flocculant per Tonne of solids, and the flocculant concentration 0.0002%.

4.2.1 Water

Magnafloc 800HP were added to water and Kaolin 1.5% and the particle size distribution obtained shown in figure 12.

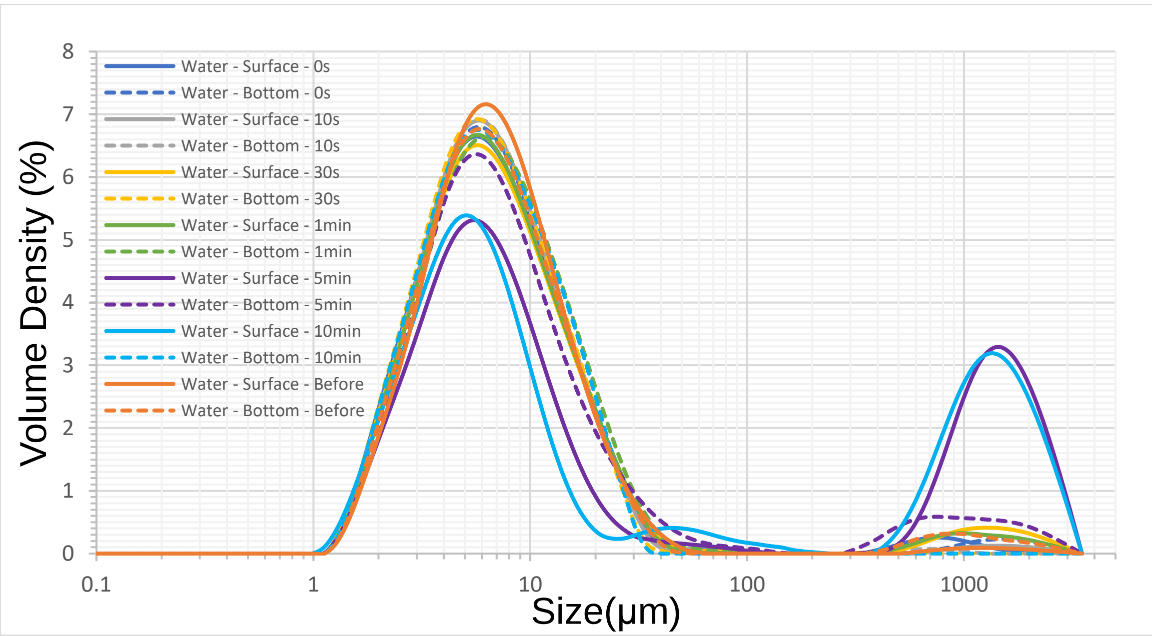

Figure 11 - Water - Kaolin 1.5% - 800HP

Although samples for 5 minutes and 10 minutes in the surfaced showed a significant increment as highlighted in Table 5, this can explained by the settling of solid particles, Table presents the settling rate for this experiments, samples from the surface at these points lacked enough concentration for proper measurements distorting the average, a more relatable result are the bottom samples at those same times which followed the trend of the experiment indicating very little to no effect regarding the flocculant.

Table 6 - Average Particle Size for Water and 800HP.

Water	Dx (50) (µm)
Surface - 0s	6.792555196
Bottom - 0s	6.883000821
Surface - 10s	6.7551597
Bottom - 10s	6.77996939
Surface - 30s	6.992079352
Bottom - 30s	6.575462385
Surface - 1min	6.955740713
Bottom - 1min	7.122233814
Surface - 5min	16.40584664
Bottom - 5min	7.250642821
Surface - 10min	126.0250331
Bottom - 10min	6.707947137
Surface - Before	7.050221291
Bottom - Before	6.993803109

Table 7 - Settling Rate for Water and 800HP.

Settling Rate	
Time	Vol (ml)
0s	49
10s	49
30s	48
1min	47
5min	32
10min	19.5

4.2.2 Ctrol 0.1%

Again, the same parameters were applied, and the cylinder teste executed.

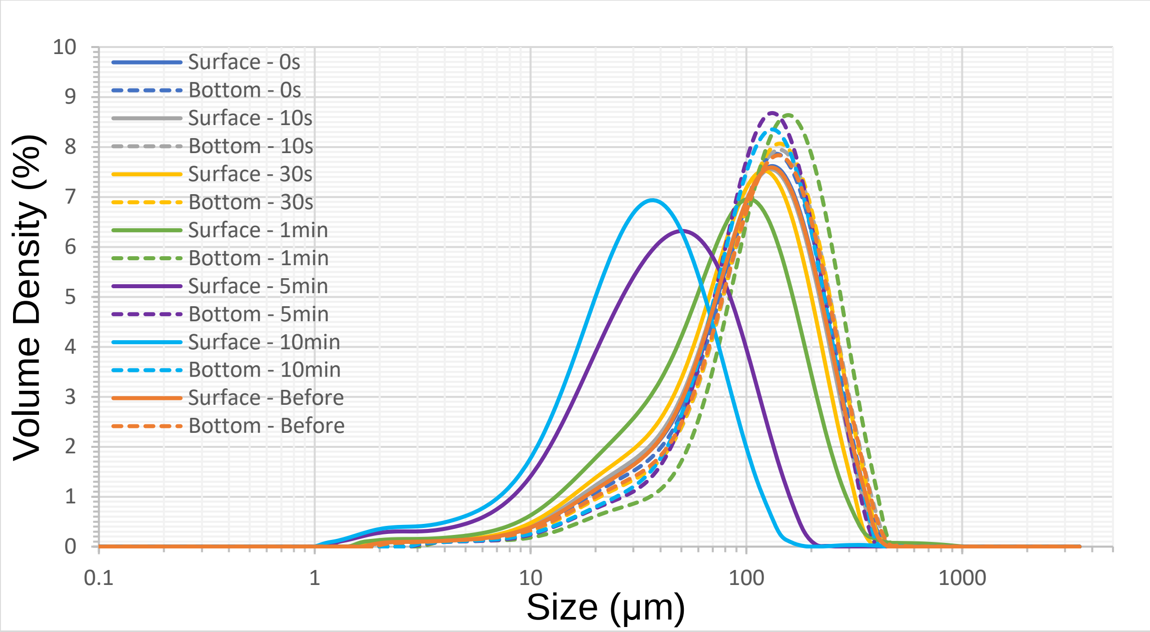

Figure 12 - Ctrol 0.1% - Kaolin 1.5% - 800HP.

Table 8 – Average Particle Size for Ctrol 0.1% and 800HP.

Ctrol 0.1%	Dx (50) (µm)
Surface - 0s	116.3444574
Bottom - 0s	121.19799
Surface - 10s	113.0212524
Bottom - 10s	128.6759631
Surface - 30s	103.7420354
Bottom - 30s	128.2417894
Surface - 1min	86.34466864
Bottom - 1min	147.4972869
Surface - 5min	43.29059158
Bottom - 5min	123.9770093
Surface - 10min	34.27444106
Bottom - 10min	122.9098312
Surface - Before	115.7245262
Bottom - Before	126.5658037

Table 9 - Settling Rate Ctrol 0.1% and 800HP.

Settling Rate	
Time	Vol (ml)
0s	51.5
10s	51
30s	50
1min	49
5min	5
10min	4.5

This medium also provided no effect of flocculation due to the flocculant itself, as the average particle size centered around the initial sample with only the medium impact.

4.2.3 Ctrol 0.2%

Ctrol 0.2% experiment were conducted following the same methodology.

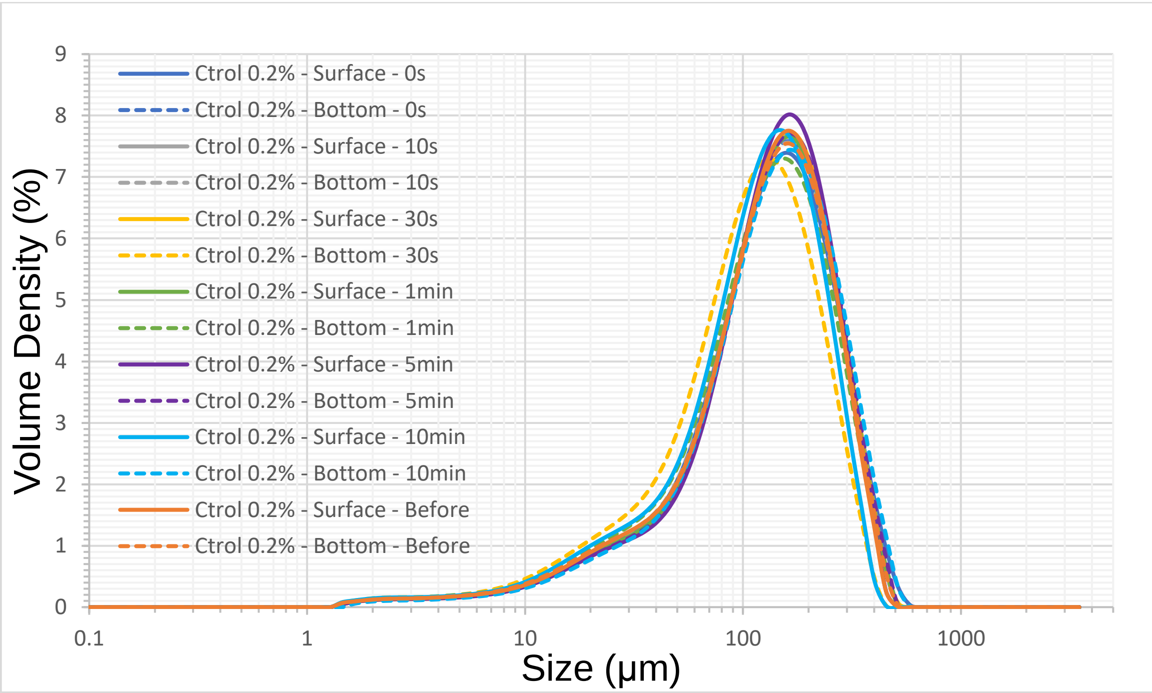

Figure 13 - Ctrol 0.2% - Kaolin 1.5% - 800HP

Table 10 - Average Particle Size for Ctrol 0.2% and 800HP.

Ctrol 0.2%	Dx (50) (µm)
Surface - 0s	141.3709175
Bottom - 0s	141.1604113
Surface - 10s	142.8134156
Bottom - 10s	140.6926826
Surface - 30s	144.745128
Bottom - 30s	116.0294755
Surface - 1min	142.9010532
Bottom - 1min	134.602973
Surface - 5min	145.5406174
Bottom - 5min	146.1660082
Surface - 10min	128.4317138
Bottom - 10min	148.0830505
Surface - Before	140.6645992
Bottom - Before	140.585904

Table 11 - Settling Rate Ctrol 0.2% and 800HP.

Settling Rate	
Time	Vol (ml)
0s	51
10s	51
30s	50.5
1min	50.5
5min	50
10min	49.5

As the viscosity of the medium increase considerable in this experiment the experiment proved to be less significant, the average ranges were small and fairly similar for every time and the viscosity of the fluid prevented settling to occur avoiding concentration discrepancies between surface and bottom samples.

4.2.4 Ctrol 0.3%

The final experiment with this flocculant were conducted for Ctrol 0.3%.

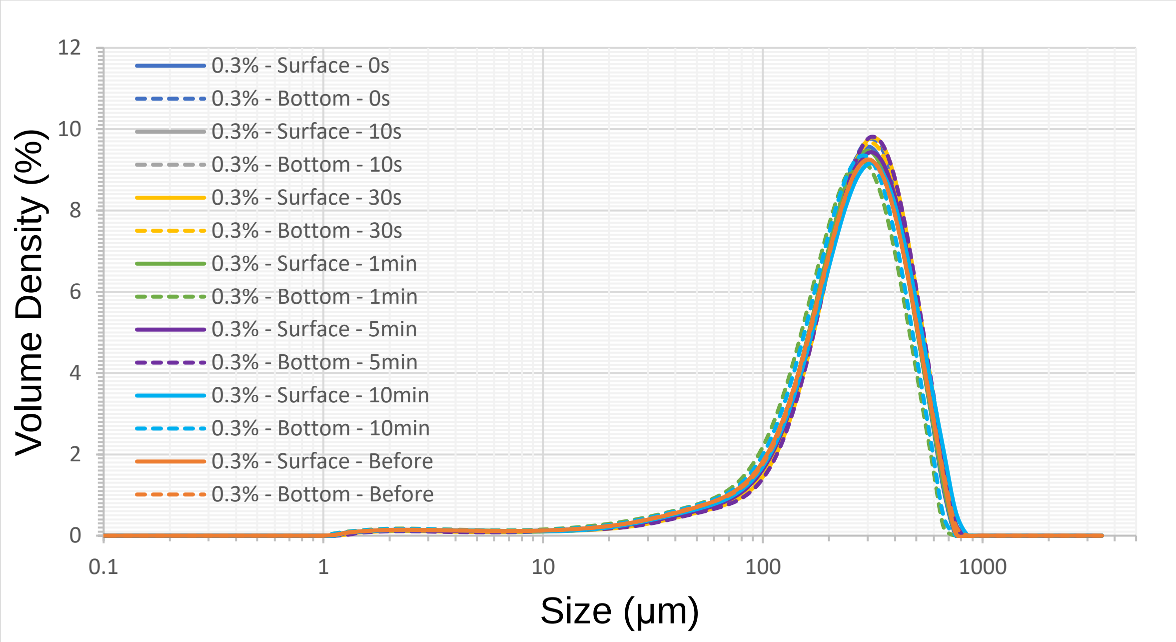

Figure 14 - Ctrol 0.3% - Kaolin 1.5% - 800HP.

Table 12 - Average Particle Size for Ctrol 0.3% and 800HP.

Ctrol 0.3%	Dx (50) (μm)
Surface - 0s	277.7798838
Bottom - 0s	292.135107
Surface - 10s	279.2436155
Bottom - 10s	280.3882504
Surface - 30s	296.4524612
Bottom - 30s	289.6088657
Surface - 1min	276.8036965
Bottom - 1min	251.716288
Surface - 5min	287.8836316
Bottom - 5min	297.7151265
Surface - 10min	287.2958095
Bottom - 10min	260.9971519
Surface - Before	275.8913963
Bottom - Before	277.5022707

Table 13 - Settling Rate Ctrol 0.3% and 800HP.

Settling Rate	
Time	Vol (ml)
0s	50
10s	50
30s	50
1min	50
5min	50
10min	50

Similar conclusion for Ctrol 0.3% as Ctrol 0.2%, the higher viscosity of the medium prevented the settling of particles, and the drilling fluid agglomeration effect was the only one observed with particle size distribution ranging for very similar values in all times.

4.3 Flocculant Magnafloc 336

From the non-ionic experiments lack of results the analysis moved for an anionic flocculant, Magnafloc 336, from the research this type of flocculant is the most indicated one and was expected to provide the best results, most industrial applications of flocculants use anionic versions.

The experiments were also conducted in Water and Ctrol following the same methodology and the results demonstrated in this section.

4.3.1 Water

The Flocculation test is presented on Graph X.X, the average particle size on Table X.X and settling rate on Table X.X.

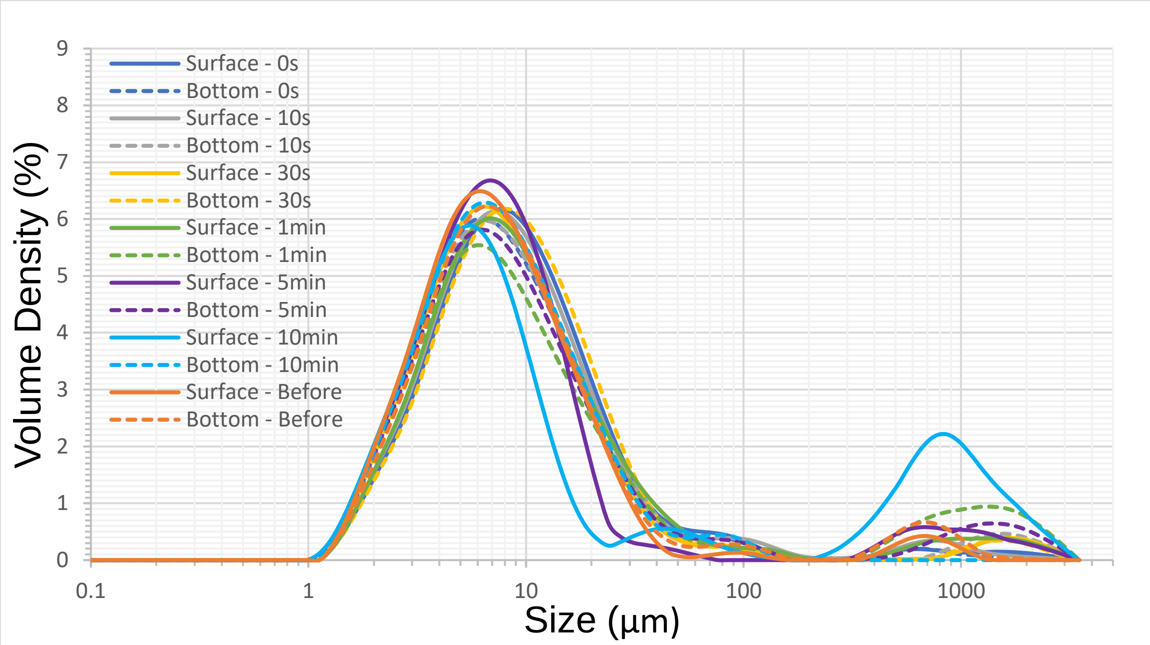

Figure 15 - Water - Kaolin 1.5% - Magnafloc 336.

Table 14 - Average Particle Size for Water and Magnafloc 336.

Water	Dx (50) (µm)
Surface - 0s	8.968107061
Bottom - 0s	7.955079273
Surface - 10s	8.666679137
Bottom - 10s	8.211408115
Surface - 30s	7.859460604
Bottom - 30s	9.157132296
Surface - 1min	8.672203818
Bottom - 1min	8.744984584
Surface - 5min	7.567215156
Bottom - 5min	8.220674149
Surface - 10min	15.61710525
Bottom - 10min	7.692604045
Surface - Before	7.37476814
Bottom - Before	8.094128925

Table 15 - Settling Rate Water and Magnafloc 336.

Settling Rate	
Time	Vol (ml)
0s	51
10s	51
30s	50
1min	49
5min	26
10min	16

Water proved unable to agglomerate particles with the presence of the anionic flocculant similar to the non-ionic experiment, and the spike for the 10 minutes sample is related to lack of solids concentration disturbing the measurement due to solids settling in lower region of the cylinder.

4.3.2 Ctrol 0.1%

Although the water experiment failed to increase the particle size drilling fluid experiments were carried and presented in Figure 16, Table 16 and Table 17.

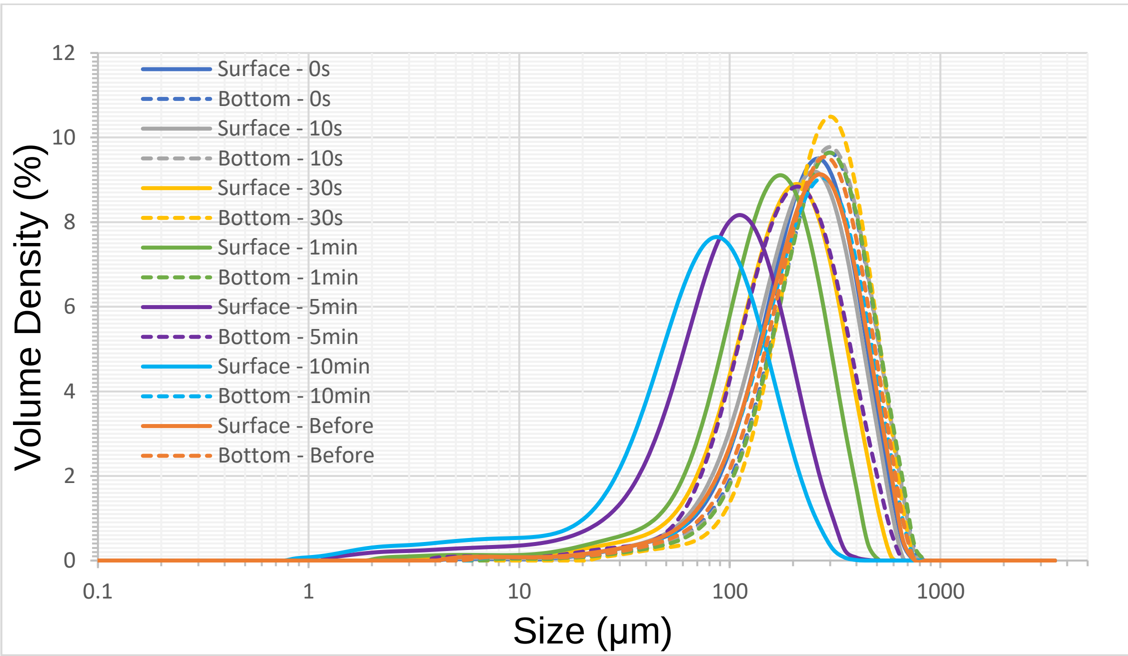

Figure 16 - Ctrol 0.1% - Kaolin 1.5% - Magnafloc 336.

Table 16 - Average Particle Size for Ctrol 0.1% and Magnafloc 336.

Ctrol 0.1%	Dx (50) (μm)
Surface - 0s	248.9540628
Bottom - 0s	284.1161434
Surface - 10s	235.0486211
Bottom - 10s	285.6192024
Surface - 30s	195.5400506
Bottom - 30s	293.545676
Surface - 1min	164.4258724
Bottom - 1min	286.9658722
Surface - 5min	104.0414284

Bottom - 5min	204.2361817
Surface - 10min	80.02411318
Bottom - 10min	257.1435537
Surface - Before	249.7587179
Bottom - Before	269.1971226

Table 17 - Settling Rate Ctrol 0.1% and Magnafloc 336.

Settling Rate	
Time	Vol (ml)
0s	51
10s	50
30s	49
1min	48
5min	4.5
10min	4.5

This experiment indicated the action of flocculant on the experiments with a slight move to the right in the plot as time goes in the experiment with the most significant change occurring at 30 seconds, the analysis of the average particle sizes confirms this as an increment of approximately 13% is observed.

4.3.3 Ctrol 0.2%

Mixture of Ctrol 0.2% and Kaolin 1.5% were then subjected to the cylinder test. Figure 17, Table 18 and Table 19 describe the experiment.

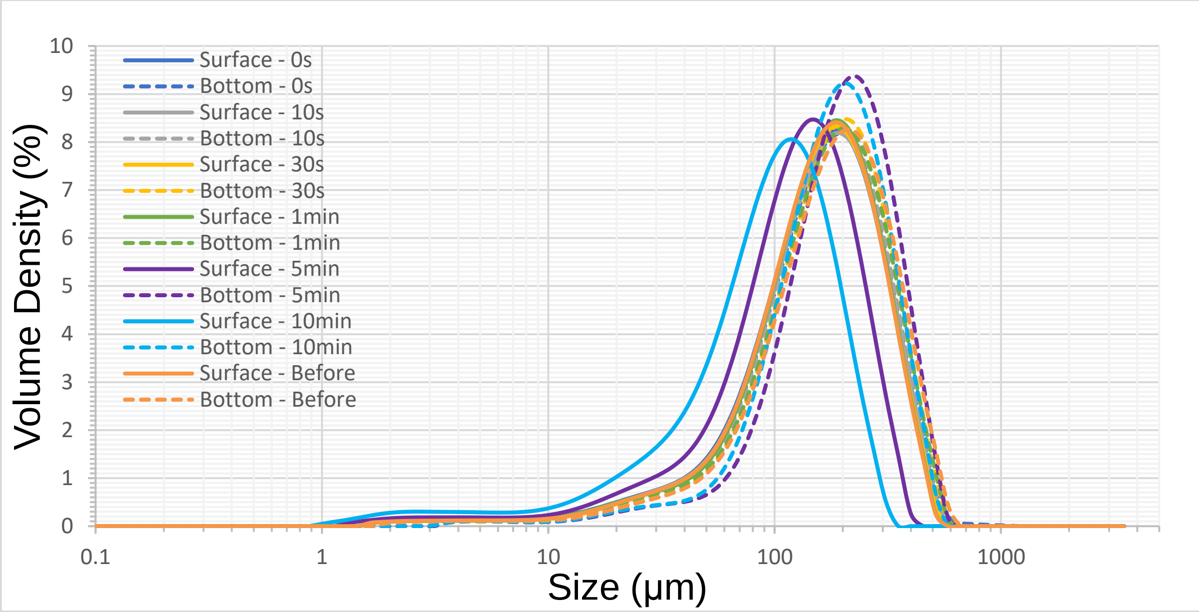

Figure 17 - Ctrol 0.2% - Kaolin 1.5% - Magnafloc 336.

Table 18 - Average Particle Size for Ctrol 0.2% and Magnafloc 336.

Ctrol 0.2%	Dx (50) (μm)
Surface - 0s	170.1213539
Bottom - 0s	176.7094871
Surface - 10s	173.6832072
Bottom - 10s	178.538262
Surface - 30s	171.654634
Bottom - 30s	188.5032664
Surface - 1min	172.4460601
Bottom - 1min	185.3614811
Surface - 5min	134.3848806
Bottom - 5min	212.4250747
Surface - 10min	102.6547776
Bottom - 10min	194.9468479
Surface - Before	170.9187086
Bottom - Before	194.5877248

Table 19 - Settling Rate Ctrol 0.2% and Magnafloc 336.

Settling Rate	
Time	Vol (ml)
0s	50
10s	50
30s	50
1min	49.5
5min	49
10min	45

Following the same trend as before the Ctrol 0.2% medium also observed the effect of flocculant, more evident with 5 minutes of experiment where about 16% increment were encountered.

4.3.4 Ctrol 0.3%

Finally, Ctrol 0.3% experiment were performed for the anionic flocculant. Figure 18, Table 20 and Table 21 provide the summary for the experiment.

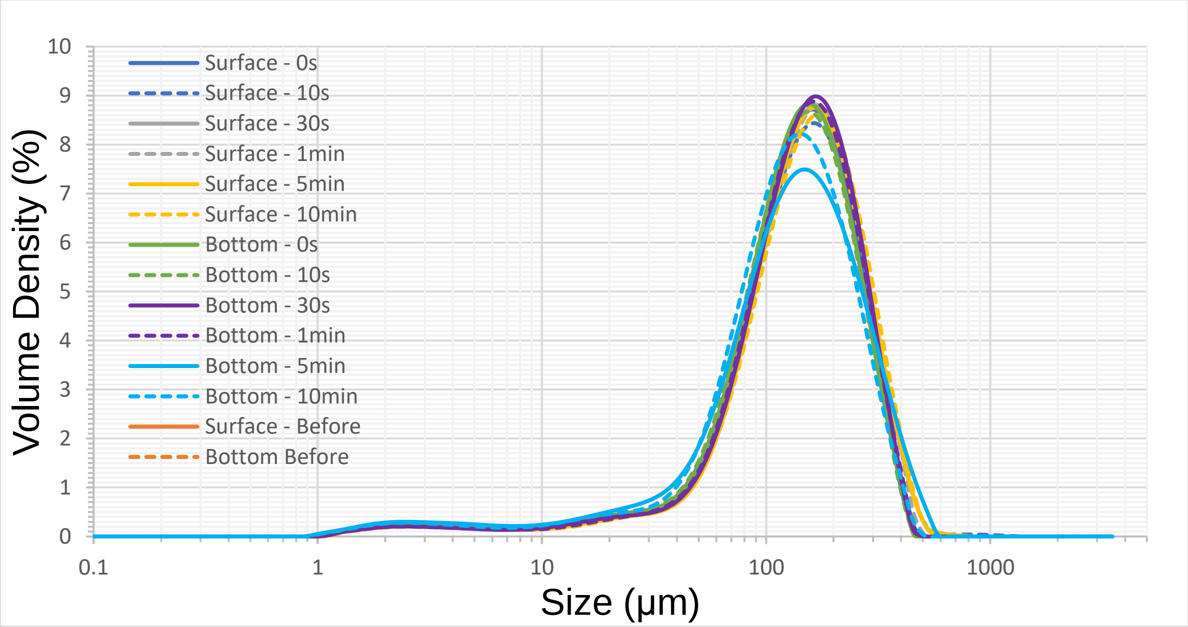

Figure 18 - Ctrol 0.3% - Kaolin 1.5% - Magnafloc 336.

Table 20 - Average Particle Size for Ctrol 0.3% and Magnafloc 336.

Ctrol 0.3%	Dx (50) (µm)
Surface - 0s	150.847888
Bottom - 0s	148.4248882
Surface - 10s	155.8500802
Bottom - 10s	146.0172197
Surface - 30s	155.5126252
Bottom - 30s	156.746664
Surface - 1min	160.934571
Bottom - 1min	154.5963358
Surface - 5min	159.6783504
Bottom - 5min	143.8571677
Surface - 10min	163.4521335

Bottom - 10min	137.8344465
Surface - Before	112.6283168
Bottom - Before	119.6560137

Table 21 - Settling Rate Ctrol 0.3% and Magnafloc 336.

Settling Rate	
Time	Vol (ml)
0s	32
10s	31
30s	30
1min	30
5min	30
10min	30

In line with rest of the experiments Ctrol 0.3% medium were also affected by the anionic flocculant proving this type of flocculant effectiveness.

4.4 Flocculant Superfloc C-493

The last type of Flocculant to be evaluated is the cationic, the same parameters as before were applied in this experiment and the results presented in same manner.

4.4.1 Water

Water experiments were the first conduct as for the other flocculants, Figure 19, Table 22 and Table 23 provide the results.

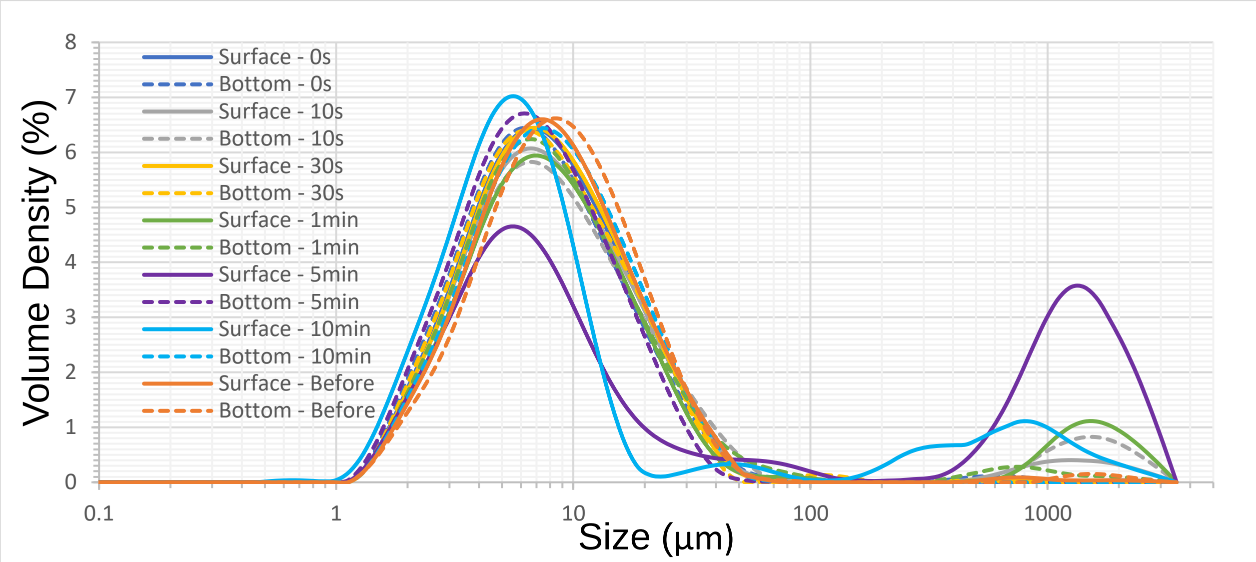

Figure 19 - Water - Kaolin 1.5% - Superfloc C493.

Table 22 - Average Particle Size for Water and Superfloc C493.

Water	Dx (50) (µm)
Surface - 0s	7.893081949
Bottom - 0s	7.540814598
Surface - 10s	8.323369882
Bottom - 10s	8.857651287
Surface - 30s	8.000087288
Bottom - 30s	7.694980152
Surface - 1min	8.969593966
Bottom - 1min	8.174719407
Surface - 5min	189.0554457
Bottom - 5min	7.119802982
Surface - 10min	6.931467442
Bottom - 10min	8.342700314
Surface - Before	8.409023904
Bottom - Before	9.081648866

Table 23 - Settling Rate Water and Superfloc C493.

Settling Rate	
Time	Vol (ml)
0s	51.5
10s	50
30s	49
1min	37
5min	14
10min	11

Similar to the rest of the flocculants Water appears to be incapable to provide the right medium for any Kaolin agglomeration to be observed and the spikes are simply lack of enough concentration due to settling.

4.4.2 Ctrol 0.1%

Ctrol 0.1% experiments for Superfloc C-493 were performed similar to the rest of the experiments.

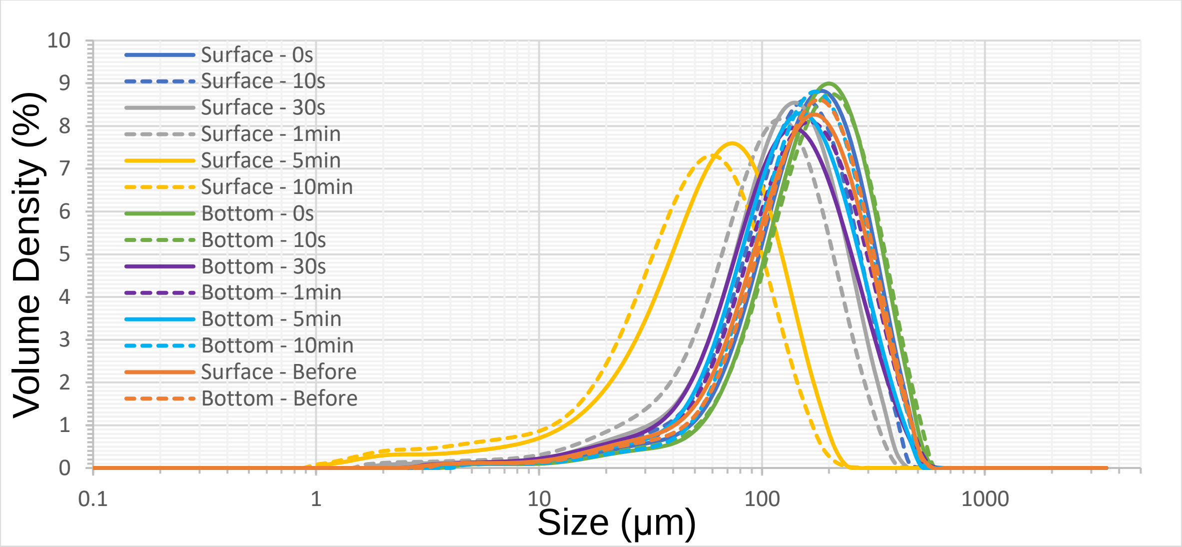

Figure 20 - Ctrol 0.1% - Kaolin 1.5% - Superfloc C493.

Table 24 - Average Particle Size for Ctrol 0.1% and Superfloc C493.

Ctrol 0.1%	Dx (50) (µm)
Surface - 0s	175.9024199
Bottom - 0s	189.933173
Surface - 10s	148.3602035
Bottom - 10s	192.4799835
Surface - 30s	132.1204976
Bottom - 30s	136.8191867
Surface - 1min	112.0381167
Bottom - 1min	157.9920487
Surface - 5min	63.86335067
Bottom - 5min	167.5439501
Surface - 10min	52.42277757
Bottom - 10min	169.2460725
Surface - Before	162.8358969
Bottom - Before	170.9866054

Table 25 - Settling Rate Ctrol 0.1% and Superfloc C493.

Settling Rate	
Time	Vol (ml)
0s	52
10s	50
30s	49
1min	47.5
5min	5
10min	5

Analyzing the cationic flocculant an increase in the PSD were also observed in a similar way as anionic type, with about 15% increment for 10 seconds experiment.

4.4.3 Ctrol 0.2%

The Figure 21, Table 26 and Table 27 shows the results for Ctrol 0.2% experiment.

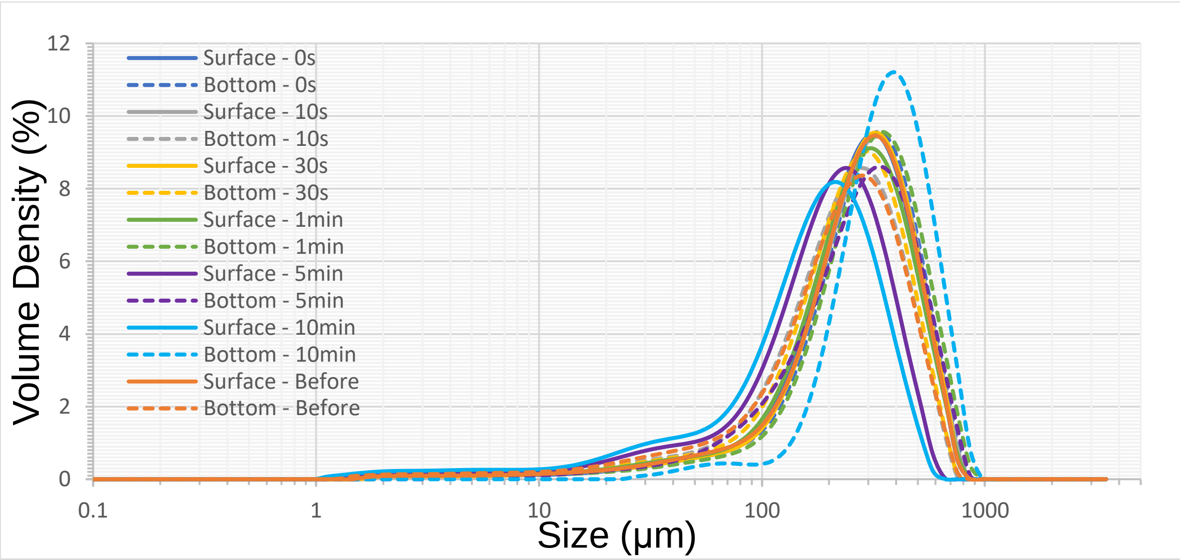

Figure 21 - Ctrol 0.2% - Kaolin 1.5% - Superfloc C493.

Table 26 - Average Particle Size for Ctrol 0.2% and Superfloc C493.

Ctrol 0.2%	Dx (50) (μm)
Surface - 0s	295.0329962
Bottom - 0s	309.8167233
Surface - 10s	302.9126226
Bottom - 10s	252.9561206
Surface - 30s	300.9011417
Bottom - 30s	267.9368768
Surface - 1min	285.5040304
Bottom - 1min	326.7062445
Surface - 5min	212.314024
Bottom - 5min	390.0708958
Surface - 10min	187.2913406
Bottom - 10min	386.7751325
Surface - Before	296.4792939
Bottom - Before	250.0088194

Table 27 - Settling Rate Ctrol 0.2% and Superfloc C493.

Settling Rate	
Time	Vol (ml)
0s	50
10s	50
30s	50
1min	50
5min	47
10min	4

A very significant impact on PSD is observed on this experiment where the 10 minutes sample produces an increment of approximately 41%.

4.4.4 Ctrol 0.3%

Finally, the cationic flocculant is tested on Ctrol 0.3% again following the same procedures. The summary of the experiments are encountered on Figure 22, Table 28 and Table 29.

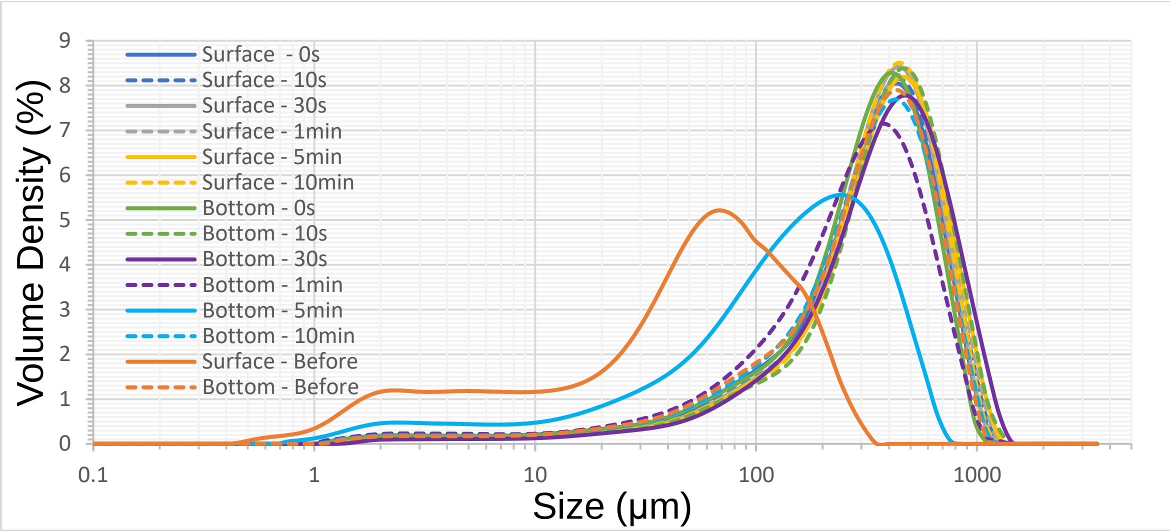

Figure 22 - Ctrol 0.3% - Kaolin 1.5% - Superfloc C493.

Table 28 - Average Particle Size for Ctrol 0.3% and Superfloc C493.

Ctrol 0.3%	Dx (50) (µm)
Surface - 0s	362.954857
Bottom - 0s	347.6195455
Surface - 10s	377.9733237
Bottom - 10s	411.2110757
Surface - 30s	380.1796972
Bottom - 30s	410.5761853
Surface - 1min	391.8272098
Bottom - 1min	301.2872046
Surface - 5min	399.6630145
Bottom - 5min	160.8236554
Surface - 10min	387.529332
Bottom - 10min	351.1788943
Surface - Before	67.87090622
Bottom - Before	351.8834458

Table 29 - Settling Rate Ctrol 0.3% and Superfloc C493.

Settling Rate	
Time	Vol (ml)
0s	52
10s	52
30s	51
1min	51
5min	50
10min	49

Although less significant than Ctrol 0.2% Ctrol 0.3% also presented an increament in the PSD of about 17% considering the 10 seconds sample, in a similar way as the Ctrol 0.1% experiment.

Analyzing the three types of flocculants the non-ionic proved incapable of causing any effect in the particle size distribution and was considered ineffective. Both the cationic and the anionic types were further studied increasing the dosage to better understand the effects.

4.5 Flocculant Superfloc C-493 increased dosage

Superfloc C-493 were tested using Ctrol 0.1% in a dosage of 1000g of flocculant per Tonne of solids the goal of this experiment was to understand if the apparent effect observed before could be potentialized, Figure 23, Table 30 and Table 31 provide the results.

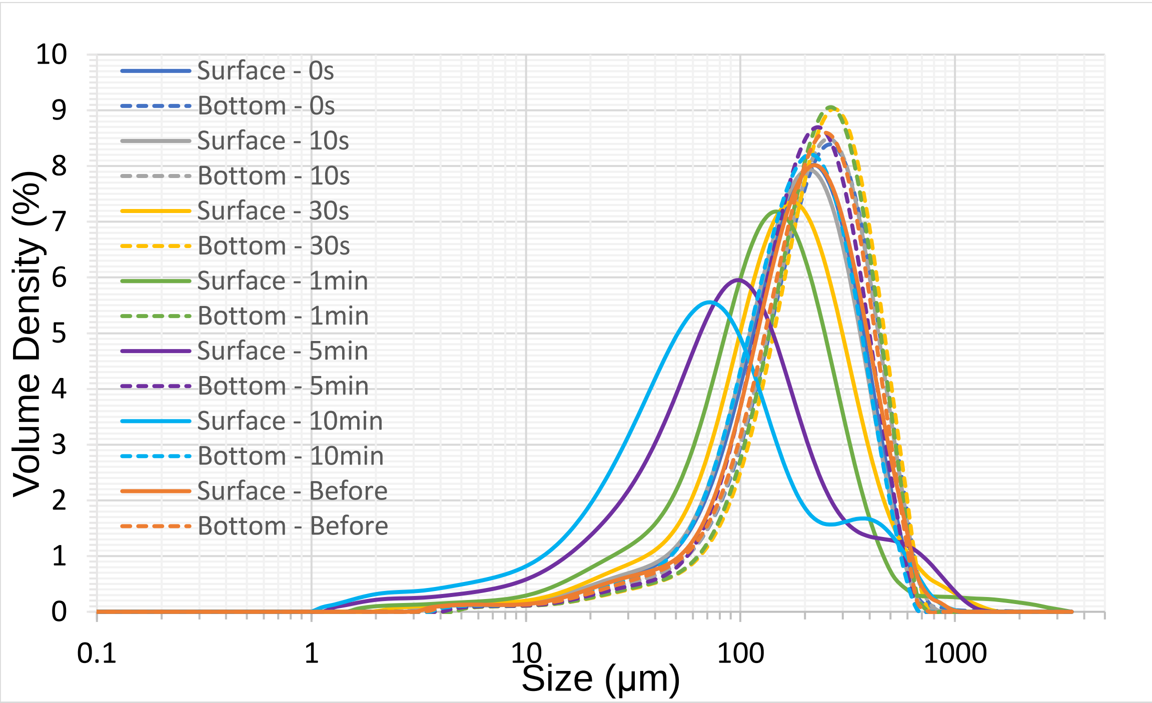

Figure 23 - Ctrol 0.1% - Kaolin 1.5% - Superfloc C493.

Table 30 - Average Particle Size for Ctrol 0.1% and Superfloc C493.

Ctrol 0.1%	Dx (50) (μm)
Surface - 0s	199.6755842
Bottom - 0s	237.4734372
Surface - 10s	192.4059471
Bottom - 10s	234.7162759
Surface - 30s	171.2726343
Bottom - 30s	253.5598858
Surface - 1min	140.7533628
Bottom - 1min	243.5573301
Surface - 5min	95.29736965
Bottom - 5min	214.665167
Surface - 10min	70.83471616
Bottom - 10min	195.5524301
Surface - Before	211.3589734
Bottom - Before	226.225144

Table 31 - Settling Rate Ctrol 0.1% and Superfloc C493.

Settling Rate	
Time	Vol (ml)
0s	50
10s	50
30s	49
1min	46.5
5min	11
10min	11

The analysis of this experiment shows that looking at the average PSD a small increment can be observed for 1 minute sample however a detrimental effect can also be perceived for greater times where the solids were smaller that the initial sample. Studying the graph, the curves for the initial and the 1 minute sample are similar to a point that an increased dosage of this flocculant can not be recommended.

4.6 Flocculant Magnafloc 336 increased dosage

4.6.1 Ctrol 0.1%

Starting with the Ctrol 0.1% comparison the PSD distribution is presented on Figure 24, the average sizes in Table 32 and finally the settling rate on Table 33.

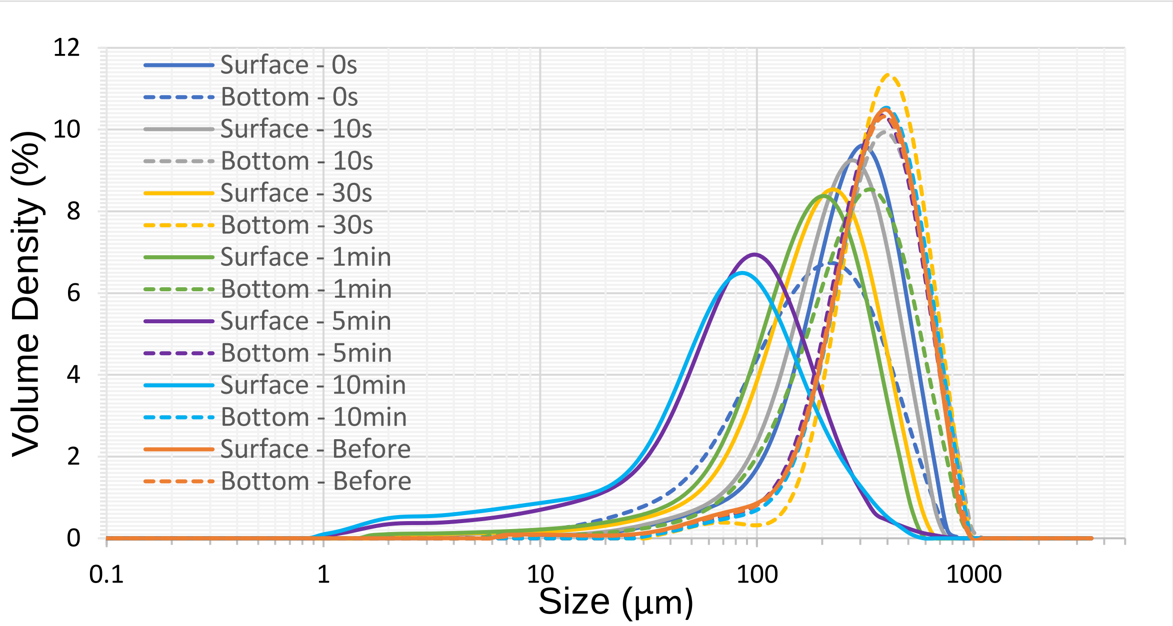

Figure 24 - Ctrol 0.1% - Kaolin 1.5% - Magnafloc 336.

Table 32 - Average Particle Size for Ctrol 0.1% and MagnaFloc 336.

Ctrol 0.1%	Dx (50) (µm)
Surface - 0s	288.5023707
Bottom - 0s	189.958883
Surface - 10s	257.5906123
Bottom - 10s	378.8578376
Surface - 30s	205.2869994
Bottom - 30s	409.8538261
Surface - 1min	183.2152173
Bottom - 1min	303.9755119
Surface - 5min	88.40686048
Bottom - 5min	368.5627037
Surface - 10min	78.2588963
Bottom - 10min	387.1488001
Surface - Before	372.9413685
Bottom - Before	373.554126

Table 33 - Settling Rate Ctrol 0.1% and Magnafloc 336.

Settling Rate	
Time	Vol (ml)
0s	50
10s	49
30s	45
1min	30
5min	4
10min	4

Contrary to the cationic experiment in this case although the effect of flocculant was lower than in the previous concentration it was still present to point that a study in other concentrations of Ctrol were conducted.

4.6.2 Ctrol 0.2%

The same methodology was applied, and the results showed on Figure 25, Table 34 and Table 35.

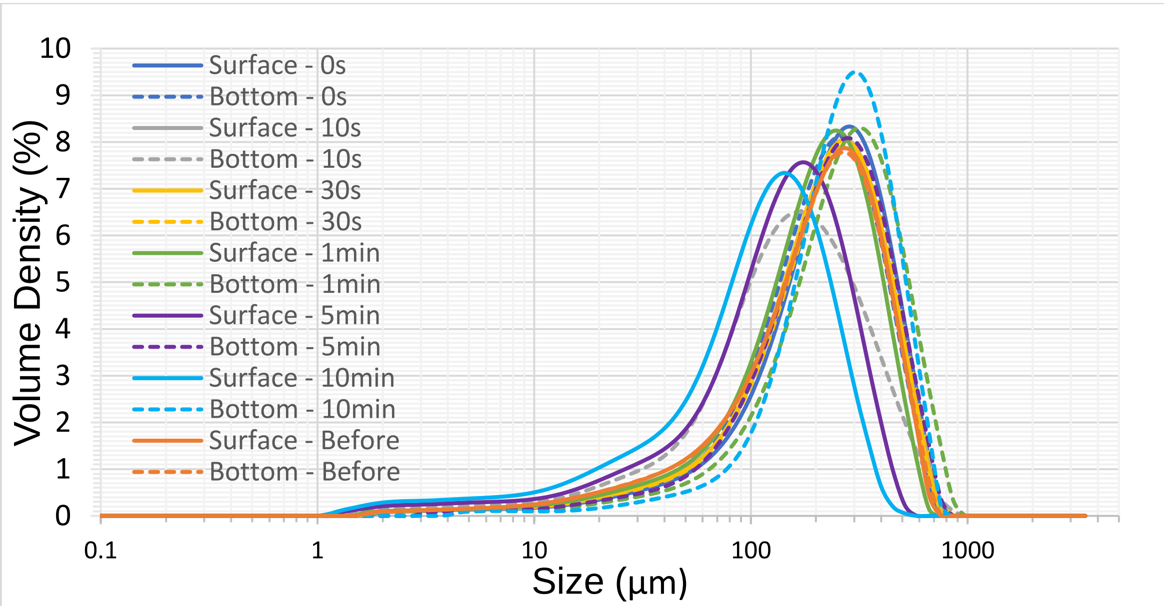

Figure 25 - Ctrol 0.2% - Kaolin 1.5% - Magnafloc 336.

Table 34 - Average Particle Size for Ctrol 0.2% and MagnaFloc 336.

Ctrol 0.2%	Dx (50) (μm)
Surface - 0s	250.6642381
Bottom - 0s	227.5601391
Surface - 10s	237.3052774
Bottom - 10s	163.536408
Surface - 30s	234.8871946
Bottom - 30s	242.8929294
Surface - 1min	215.6827208
Bottom - 1min	285.1332095
Surface - 5min	149.9799575
Bottom - 5min	247.8283873
Surface - 10min	121.016852
Bottom - 10min	285.7649361
Surface - Before	225.2149272
Bottom - Before	224.7109075

Table 35 - Settling Rate Ctrol 0.2% and Magnafloc 336.

Settling Rate	
Time	Vol (ml)
0s	50
10s	50
30s	49.5
1min	49.5
5min	10
10min	10

A significant increase in the average article size of more than 25% were detected in this experiment for 10 minutes sample indicating the possible effectiveness of a higher dosage.

4.6.3 Ctrol 0.3%

Based on the previous experiments Ctrol 0.3% were tested and results can be observed on Figure 26, Table 36 and Table 37.

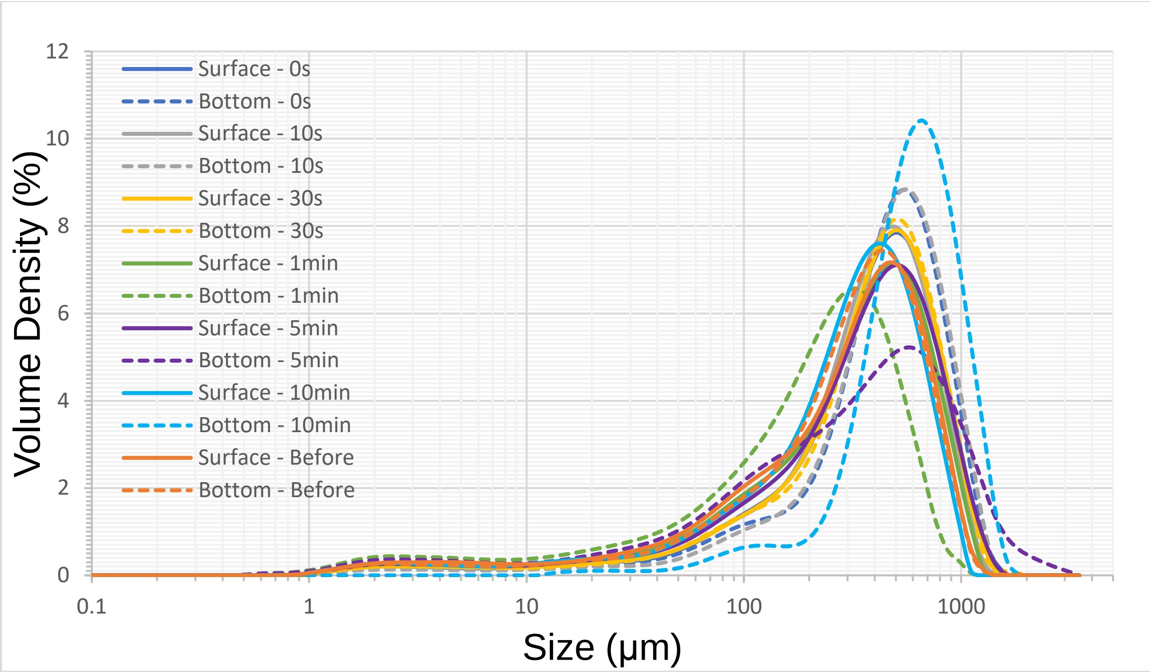

Figure 26 - Ctrol 0.3% - Kaolin 1.5% - Magnafloc 336.

Table 36 - Average Particle Size for Ctrol 0.3% and MagnaFloc 336.

Ctrol 0.2%	Dx (50) (µm)
Surface - 0s	429.2457561
Bottom - 0s	486.9619182
Surface - 10s	411.8312793
Bottom - 10s	499.8888264
Surface - 30s	427.2065298
Bottom - 30s	432.6134364
Surface - 1min	367.4570668
Bottom - 1min	241.0666946
Surface - 5min	399.5305226
Bottom - 5min	382.953489
Surface - 10min	342.4157931
Bottom - 10min	642.0367231
Surface - Before	350.1456669
Bottom - Before	352.4351194

Table 37 - Settling Rate Ctrol 0.3% and Magnafloc 336.

Settling Rate	
Time	Vol (ml)
0s	50
10s	50
30s	50
1min	50
5min	48
10min	49

The most effective result in terms of flocculation the average particle size increased more approximately 83% when compared to the initial sample with a strong shift to the right in the curve.

4.7 Cationic versus Anionic

Although in lower dosages both types seemed to have an impact in the PSD the anionic flocculant showed a better performance in increased dosages over the cationic, indicating that better results are possible with the anionic flocculant.

A point can be made related to settling rate for the cationic and anionic types, both flocculants settled almost completely in Water and Ctrol 0.1% and longer times, showing a similar behaviour, the Ctrol 0.2% experiment shows that solids completely settled at the end of experiment for the cationic type while in the anionic they remained mostly in suspension indicating the maintenance of the high viscosity of the drilling fluid in the anionic experiment. An explanation for this difference is that the cationic flocculant is bonding not only with solids in suspension but with the polymers in the drilling fluid as well breaking the agglomerations created by the drilling fluid alone and removing polymers from the solution and by this decreasing the viscosity. The fairly constant settling in the anionic case for higher drilling fluid concentrations proves that the viscosity of the fluid remained high enough to prevent solids from settling.

Since the main objective of the addition of flocculants in a drilling fluid is to increase the solids removal but to keep the fluid itself in condition to be recirculated again, after the parameters are readjusted, the use of the cationic flocculant can prove to be a problem.

At lower Ctrol concentration both flocculants caused the solids to completely settle at the bottom of the cylinder, but Ctrol 0.1% is considerably less viscous and the settling process were also observed when no flocculant were added indicating that the agglomeration by the drilling fluid itself causes particles to increase to a point where suspension is no longer possible with or without the action of any external factor.

Ctrol 0.3% kept very low settling rates for both types, indicating that the viscosity is such that even a possible interaction between the medium and the flocculant were not enough to cause precipitation. But even in this situation the discrepancy between cationic and anionic can be perceived with cationic experiments showing a slightly higher settling rate.

4.8 Considerations

After the experiments were analyzed two observations can be made. The first one is related to initial particle size. Although the general particle size before the flocculation remained similar between the experiments some differences were encountered. The quantities, mixing rate and duration methodology remained constant throughout the various experiments and the visual inspection of each sample never indicated any dissolution problem. This suggests that the origin of these differences might be on out-of-scope parameters such temperature of the experiment and humidity of the solids prior to the solution.

The experiments were conducted spanning various months and weather significantly changed between them, further experiments taking in account both of these parameters might help to determine the cause.

The one observation is the concentration of flocculant used in this experiments 0.0002% were selected based on the size of the drilling fluid batches and the equipment's were the experiments were performed, although the results showed a good perspective regarding the effectiveness of the solid liquid separation using the flocculants in this case a further dynamic test might be indicated with increased concentrations.

CHAPTER 5

5. CONCLUSIONS

5.1 Conclusions

The experiments proved the effect of flocculant on the particle size distribution in Ctrol drilling fluid. Three different concentrations of drilling fluid and water were analyzed as a medium for flocculation of Kaolin solid particles at 1.5% concentration. Non-inioc flocculant failed to cause any perceivable effect in the solid's particle size distribution at any medium. Water proved to be an issue for any type of flocculant since no experiment showed significant results in it.

Cationic flocculant performed well in lower dosages for the three concentrations of Ctrol, however there is indications that it might have a detrimental effect in the drilling fluid itself.

Anionic flocculant showed the best observed results, being effective in both tested dosages, with the considerably best result provided by it, while the viscosity of the medium appears to be kept at similar values.

5.2 Future work recommendations

The variation on the initial sample particle size although not important enough to disprove the results might indicate that some other factor, temperature and humidity being the most probable ones, can have an impact on the flocculation process, the evaluation of these properties can provide a better understand of Ctrol and Kaolin solution flocculation.

This studied will also be related to a further study where the Flocculation process will be studied in Ctrol™ considering the use of a centrifuge and the results from this study. The higher volume and the dynamic condition from the next study can be a good opportunity to further increase not only the dosage but also the concentration of the flocculants to see its impact.

Chapter 6

6. REFERENCES

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