8º CONGRESSO BRASILEIRO DE PESQUISA E DESENVOLVIMENTO EM PETRÓLEO E GÁS

TÍTULO DO TRABALHO:

Physical and Chemical Tests of a Mud Contaminated with Calcium Chloride

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Abstract

In this experiment, a WBM was produced using Bentonite and Calcium Chloride ($CaCl_2.H_2O$) as additives. As a main purpose, mud physical properties, such as viscosity, yield point, gel strength, funnel viscosity, pH, water loss, cake thickness, and mud weight, were tested to evaluate the effects of mud contamination by $CaCl_2.H_2O$. In addition, as secondary focus, chemical tests were also performed to measure the chloride concentration, filtrate and mud alkalinity, and hardness determination. The drilling fluid performance, that is, its physical and rheological properties, was affected by the presence of $CaCl_2.H_2O$ in the mud. Low viscosity and yield point, and high water loss and mudcake thickness were recorded. Chemical tests strictly followed the instrument instructions and they were well performed. After analysis, it was possible to conclude the bentonite, a mud viscosifier agent used, loses its functionality in the presence of a mass concentration of 1% of calcium chloride and the chemical tests work well for their determined purposes.

Keywords: Drilling Fluid, Contamination, API Tests.

Introduction

When a foreign material is present in the mud composition and it negatively changes mud density, viscosity, or filtration, it means that the mud is contaminated. Oilfield Glossary (2015) states that it may be caused from material entering the mud during drilling or from overtreatment of the mud with additives. Calcium, which is a major contaminant to freshwater-based mud systems, is encountered in greatest quantity when drilling cement or anhydrite. Calcium ions (Ca^{++}) tend to replace the sodium ions on the clay surface, flocculate bentonite based muds and precipitate anionic polymers. High chloride levels may also flocculate freshwater bentonite muds. These facts change mud properties by losing mud rheology and filtration control due to collapse of the clay structure. The presence of high calcium concentrations may be determined from chemical analysis of the filtrate and the treatment depends on the source of the calcium ion. Some common sources of soluble calcium ions are gypsum, unset cement anhydrite-bearing strata, influx of formation water, and so on. Small quantities of calcium (<400 mg/L) are acceptable and works against the presence of carbonate alkalinity. High concentrations, however, have those undesirable effects mentioned on WBM (Petrowiki, 2015).

According to Drilling Mud Docs and Jobs (2015), in order to avoid mud contamination some steps can be followed. Monitoring pH and mud alkalinity and performing treatments when required to prevent polymer precipitation and clay flocculation, avoiding over treatment with calcium ions, and using correct mud weight to minimize brine influx from formation are some examples. When using a bentonite system, as this experiment, it is possible to provide some short term viscosity and filtration control by pre-hydration of the clay in drill water. Since chloride cannot be reduced by chemical precipitation, dilution with freshwater may be an alternative, but only in low-density muds because of high costs and time to maintain high weight mud.

Chemical tests to measure the soluble chloride ion concentration, filtrate and mud alkalinity and hardness of the mud filtrate may be performed to evaluate the mud characteristics. The chloride ion concentration, which comes from the calcium chloride in this experiment, is estimated by the reaction with silver nitrate forming silver chromate. However, if the pH of the filtrate is lower than 8.3, the reaction will not happen (OFITE, 2014). While mud alkalinity (Pm) measures the alkalinity of the whole mud, filtrate alkalinity (Pf, Mf) measures the alkalinity contributions from soluble mud contents. Pm and Pf are, respectively, phenolphthalein alkalinity of the mud and mud filtrate, and Mf is the Methyl orange alkalinity. Pm, Pf and Mf may be used to estimate the excess amount of lime in a lime based mud, and concentrations of hydroxide ion (OH^-), carbonate ion (CO_3^{-2}) and bicarbonate ions (HCO_3^-). The API diagnostic tests for determination of P_m, P_f, and M_f are reported in cubic centimeters of 0.02N sulfuric acid per cubic centimeter of sample (Nguyen, 2012). The amount of soluble calcium ions in the mud filtrate can be determined by the hardness determination test.

Methodology

The main physical parameters discussed and tested in this experiment were MW, pH, Viscosity, Gel Strength, Yield Point, Water Loss, and Cake Thickness. Through those API tests, this current work will focus on how the addition of Calcium Chloride, a mud contaminant, affects those mentioned properties. The performance of chemical tests in order to measure the chloride concentration, filtrate and mud alkalinity and hardness of the produced mud is also in the scope of this report.

In this experiment, one WBM was produced using Bentonite and Calcium Chloride ($CaCl_2.H_2O$) as additives. This mud had a concentration of 20 pounds of gel per barrel of water and 4 pounds of $CaCl_2$ per barrel of water. Thus, this solution was prepared with 4 lab bbl of distilled water, which means 1.4 liter of water after proper conversion (lab bbl x 350 = mL), 80 grams of Bentonite and 16 grams of Calcium Chloride. The water was measured in a graduated cylinder, and then placed in the blender. Bentonite and calcium chloride were taken from their containers, measured in the common mass balance, and displaced in the blender. The blender was turned on at first with water and calcium chloride only to form a brine, then bentonite was added and the mixture was stirred for eight minutes. After these procedures, tests of viscosity, yield point, gel strength, funnel viscosity, pH, mud weight, water loss, and mudcake thickness could be performed without problems. To test those physical parameters cited, the procedures have followed the API methodology instructions.

For chloride ion determination, 1mL of the mud sample was pipetted into titration dish and 3 drops of phenolphthalein indicator were added to verify any change in the color of the sample. Since no change was observed, the test continued by adding 15 drops of potassium chromate indicator to give the filtrate a bright yellow color. Then, silver nitrate was added using a pipette dropwise, while stirring the sample, until the sample's color turns from yellow to orange. The quantity of silver nitrate added was recorded and this test was performed twice.

To measure the alkalinity of the mud produced, the alkalinity determination test was performed. It consisted of adding 1 mL of freshly stirred sample of mud without air bubbles into a titration dish and diluting it with 40 mL of distilled water. Three drops of phenolphthalein were added to verify any change in color. In this case, the sample did not change color, so that the alkalinity of the mud (Pm) was reported as zero. The measurement of filtrate alkalinity (Pf) is similar to the test described before, but without water dilution and more than 3 drops of phenolphthalein need to be added. No color developed again, so the Pf was reported as zero as well. To determinate Mf the same sample used for the Pf test was used and 3 drops of Brome cresol green-methyl red indicator were added to the sample. Then, N/50 sulfuric acid was added until the color changed from blue to pink, and the quantity of sulfuric acid added was recorded and reported as the Mf Alkalinity of the filtrate.

The last chemical test was the Total Hardness determination. For this procedure, 50 mL of distilled water, 30 drops of hardness buffer solution and 12 drops of hardness indicator solution were added into a titration dish. Since a purple color developed, 1.2 mL of total hardness titrating solution was added in order to the water turns to blue. Then, 1 mL of filtrate was pipetted into the titration dish and stirred. The solution was turned to a purple color again, indicating the presence of calcium in the filtrate, and total hardness titrating solution was added and its quantity recorded until the sample turns blue.

Physical experiments were conducted once, while chemical tests were performed twice. At each repetition, the sample of mud was changed and the equipment cleaned before new measurement. At the end of all experiments, the mud was discarded after mixed with wood dust in order to make it solid, and all equipment were cleaned and stored.

Results and Discussion

The following tables (Tables 1A-1D) depict the experimental results obtained from the above procedures.

Table 1A. Viscometer Readings

RPM	Trial #1
300	1 cP
600	8 cP
3 @ 10-sec	1 lbs/100ft2

Table 1 B. Physical Properties

Properties	Trial #1
Mud Weight	8.65 ppg
Funnel Viscosity	27.7 sec/quart
pH	8.2
Cake Thickness	4 in/32

Table 1 C. Filter Press Readings

Time	Water Loss
1.0 min	14.8 mL
2.5 min	24 mL
5.0 min	35 mL
7.5 min	44 mL

Table 1 D. Chemical Tests

Parameters	AVG	Trial #1	Trial #2
Silver Nitrate	0.21 mL	0.23 mL	0.19 mL
Pm	0	0	0
Pf	0	0	0
Mf	0.73 mL	0.73 mL	0.73 mL
Hardness Titrating Solution	46.5 mL	46.2 mL	46.8 mL

The produced mud may be considered a lightweight mud, with **8.65 ppg** (Table 1-B;), and gradient pressure of **0.45 psi/ft**. The pH found was slightly alkaline (**8.2**), being classified as freshwater mud (pH mud between 7 and 9.5), and it does not represent hazard to corrosion of the drilling rig parts.

Using the viscometer readings presented in Table 1- A and the equations below, calculations on the data are given in Table 2;

$$AV: \qquad \mu_a(cP) = \frac{\theta_N}{(\frac{N}{300})} \qquad (1)$$

$$VP: \qquad \mu_p(cp) = \theta_{600} - \theta_{300} \qquad (2)$$

$$YP: \qquad \tau y = \left(\frac{lb}{100\ ft^2}\right) = 2\theta_{300} - \theta_{600} \qquad (3)$$

Table 2. Experiment Rheologies

Apparent Viscosity (AP)	4 cP
Plastic Viscosity (PV)	7 cP
Yield Point (YP)	(-) 6 lbf/100.ft2
Initial Gel Strength	1 lbf/100.ft2

By analysis of Table 2, it is possible to observe that the mud produced and tested has a peculiar rheological profile. Its yield point, for example, presents a negative value, which is unexpected for any fluid. This severe decrease of the drilling mud viscosity, yield point and gel strength is a direct result of calcium ions contamination. Calcium ions, helped by high chloride levels, flocculated the freshwater bentonite mud and collapsed the clay structure. This fact is also evidenced by analysis of the funnel viscosity of the mud (Table 1B), which is close to the water's FV discussed in previous experiments (Gois, 2015), that is, 26.5 sec/quart. It shows that the bentonite, a mud viscosifier agent, loses its functionality in the presence of a mass concentration of 1% of calcium chloride.

High levels of water loss were also notified in this experiment. The API-Water Loss of 30 min is given by the equation below, and the volume of fluid lost is proportional to the square root of the time for filtration ($\sqrt{time}$), since the filter cake volume also develops proportionally to the square root of time.

$$V_{30} = 2(V_{7.5} - V_{sp}) + V_{sp} \tag{4}$$

Therefore, to find the spurt loss (Vsp) is necessary to modify the time to square root of time and predict the Spurt Loss as the interception of coordinate axis ($\sqrt{t}$ = 0). Using the data presented in the Table 1-C, a curve of mud water loss as a function of square root of the time may be plotted (Figure 1).

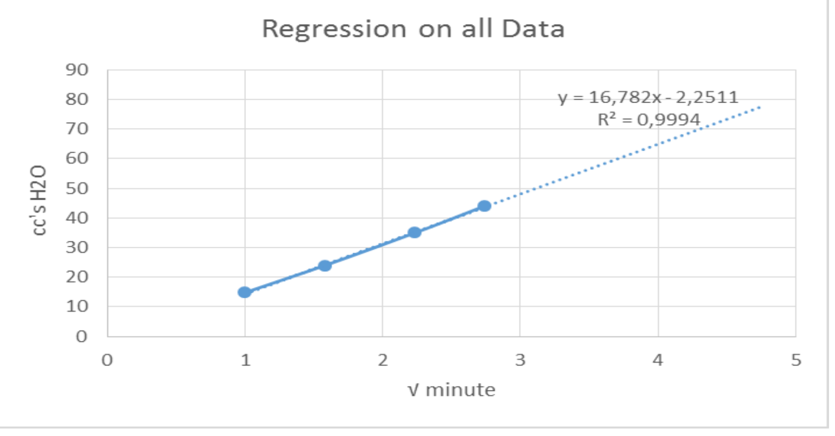

Figure 1: Water loss estimation for mud contaminated by calcium chloride;

This curve presents a coefficient of determination of 0.9994, which is an accurate fit. According to the linear regression performed, **Vsp is – 2.25 mL**. The value of Vsp, however, should be a positive value since it is a volume measurement. This mathematical contradiction indicates that the test was not well conducted and some water (spurt loss) was not properly collected. This mistake may be explained by the size of the filter press. A possible source of error is that, during this experiment, it was necessary a beaker bigger than usual to collect high volume of fluid lost during the filtration. Since the beaker needed to be change while the experiment was running, the measurement was negatively affected.

Theoretically, the API-Water Loss of 30 minutes is the double of 7.5 -min water loss minus Vsp. Using the data in Table 1-C, API-Water Loss of 30 minutes is:

$$30\,\text{min}\ \ WL\ (cc) = 2 \cdot (7.5\,\text{min}\ WL) - Vsp \tag{5}$$

$$30\,\text{min}\ WL = 2\ x\ 44\ - (-2.25) = \mathbf{90.25\ cc}$$

This API water loss is not acceptable, since it may cause reservoir and formation damage as a result of deep filtrate invasion, changes in mud content, weight and viscosity, also affecting the pump pressure necessary to circulate the mud. Water loss is also responsible to form a filter cake, or mudcake. In this experiment, the mud cake thickness was reported as **4/32''**. An acceptable cake thickness value, however, is 2/32''. Thus, this mud would decrease the annular space of circulation to the mud, damaging the drilling operation.

After discussing the primary focus of the report, that is, the investigation of the effects of calcium chloride, as a mud contaminant, on mud physical parameters, this section will now approach the chemical tests for Chloride concentration, Alkalinity, and Hardness determination.

The chloride concentration, given in parts per million (ppm) chloride, is calculated using the quantity of silver nitrate (mL) used during the titration to turn the sample's color from yellow to orange (Table 1- D) and multiplying this value by 10000. Thus, the chloride concentration of the sample is (EQ. 6):

Ppm Chloride = 0.21 x 10000 = **2100 ppm Cl^-** (6)

During the titration for chloride concentration two chemical reactions are taking place: the formation of silver chloride ($Ag^+ + Cl^- \rightarrow AgCl$) and the formation of silver chromate (Ag_2CrO_4). This last reaction is a result of the interaction between the silver nitrate and chromate that comes from the potassium chromate indicator both added to the sample for titration. No silver oxide precipitated since the pH is not high enough to start this reaction.

The phenolphthalein alkalinity of the mud and mud filtrate, called the P_m and P_f, determines the amount of lime and ion concentrations in the system. The phenolphthalein alkalinity refers to the amount of acid required to reduce the pH to 8.3, the phenolphthalein endpoint. **Pm** and **Pf** were reported as **zero** during the alkalinity tests. This fact agrees with the theory, since the pH of the system is 8.2 and it is already lower than 8.3. The excess lime content, given by (Pm – Pf)/4, was also zero for this experiment. Excess lime may help to stabilize the emulsion and neutralize acidic gases.

Methyl orange alkalinity or M alkalinity of the filtrate, called Mf, refers to the amount of acid in milliliters per volume of filtrate sample required to reduce the pH to 4.3, the Mf endpoint. The M_f is reported as the quantity in ml of 0.02 N sulfuric acid required to reach the M endpoint. Thus, the **Mf** found for this test was **0.73 mL**.

When the alkalinity test presents no Pf reading, it indicates the presence of bicarbonate ions (HCO_3^-) only (OFITE, 2014). This concentration is given by EQ. 7;

Mf x 1220 = 0.73 x 1220 = **890.6 ppm HCO_3^-** (7)

The last chemical test, that is, the total hardness determination, measured the level of soluble hardness ions (Ca^{+2}) in the mud filtrate (brine) by titration using versenate hardness titrating solution. The result is reported in mg/L or ppm Calcium given by the EQ. 8 below;

$$\text{ppm Calcium} = \text{EPM total hardness} \times 20 \tag{8}$$

EPM total hardness or hardness titrating solution is reported in mL and it is present in Table 1-D. Thus, ppm Calcium or the hardness ions is:

$$46.5 \times 20 = \mathbf{930\ ppm\ Ca^{+2}} \tag{9}$$

Actually, this value refers not only to the calcium concentration, but also several metal ions at the same time (iron, lead, magnesium, aluminum, zinc). However, the quantity of the other metal ions is usually negligible. The total hardness should be below 400 ppm (Nguyen, 2012). Thus, the total hardness found is 132.5% higher than acceptable values. Figure 2 illustrates ions concentration measurements from the chemical tests performed.

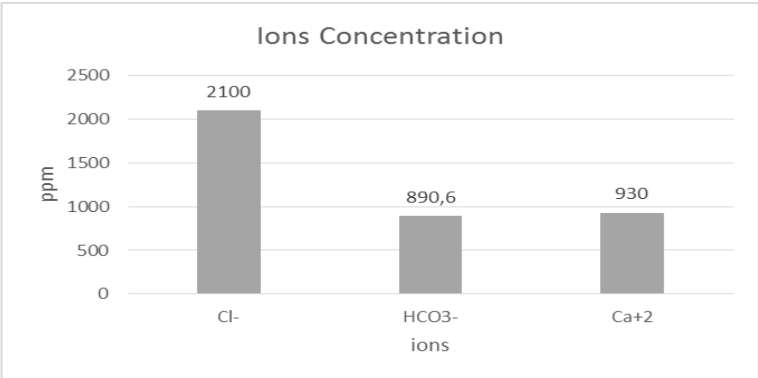

Figure 2. Ion concentration estimated from chemical tests;

The presence of these ions may be considered detrimental to the drilling mud performance, since they directly affect the physical and rheological parameters as previously discussed. High levels of hardness and chloride flocculate bentonite and collapse the clay structure, changing its functionality.

Conclusions

Using a WBM containing bentonite and calcium chloride as additives, this lab was primary meant to examine the mud physical properties, such as viscosity, yield point, gel strength, funnel viscosity, pH, water loss, cake thickness, and mud weight in order to evaluate the effects of $CaCl_2.H_2O$ as mud contaminant. The secondary focus of this report was the practice and measurement of chloride concentration, filtrate and mud alkalinity, and total hardness of the mud sample produced by performing chemical tests. It has been seen that calcium chloride is a harmful contaminant since it changes the drilling fluid performance by reducing the mud viscosity, yield point and gel strength, and significantly increasing the water loss and mudcake thickness when compared with mud samples presented in previous reports. It does not affect, however, the mud weight. Chemical tests were well performed and estimation of ion concentrations was possible from these procedures. After analysis, it was possible to conclude that the bentonite, which works as a viscosifier agent, loses its functionality in the presence of a mass concentration of 1% of calcium chloride, and the ions concentrations in the mud and filtrate are significantly higher than the acceptable. The contamination of mud system by salt can easily occur when drilling salt formations or when saline formation water enters the wellbore.

Thus, it is necessary to monitor pH and mud alkalinity in order to perform treatments as soon as possible to avoid drilling operation risks and unwanted costs.

Acknowledgments

We thank the instructor Paulo Hoyer and his class assistant Ahmed Elgohary for their invaluable support in procedure supervision and research topic idea, and the lab partners Bryson Jones and Jonathan Arndt for their assistance in data acquisition We also owe thank to the University of Wyoming, which provides all equipment and material necessary to run experiments at the Drilling Fluids Laboratory.

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