A COMPLIMENTARY METHOD OF ASSESSING CLAY STABILIZERS USED IN HYDRAULIC FRACTURING APPLICATIONS

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ABSTRACT

Reservoirs having clays that swell/migrate can potentially impair production. When these clays are present, it is advantageous to use clay stabilizers to mitigate this damage potential. The industry has adopted several clay assessment methods including analytical procedures such as XRD, SEM and performance testing methods such as capillary suction test (CST) and roller oven test. This paper will describe a new performance test method for inhibitors used in shale reservoirs that complements the existing methods. A modified core flow method has been developed using unconsolidated core material that indirectly measures the clay swelling and migration potential. In this procedure, a packed column composed of tightly-sized shale material is used to simulate an infinite fracture network. Treatment fluids are then pumped through the column at constant rate while measuring pressure drop. The relative pressure change, together with the turbidity of the effluent, allows easy assessment of the clay stabilizer.

INTRODUCTION

Clay stabilizers are a class of products used in oil & gas fracturing applications to minimize clay damage. Two key mechanisms for clay damage consist of osmotic hydration (clay swelling) and/or movement of clay in a formation (fines migration) due to interaction of the clays with fluids such as water. Clay stabilizers can work by minimizing clay swelling and/or fines migration improving oil production by maintaining open pores for fluid flow. Being able to select the right clay stabilizer and loading for a given application becomes a critical need. The industry has several methods to assess the potential for clay damage as well as testing clay stabilizers for performance under a given set of conditions. Analytical methods for determining types and quantities of clays present in a formation include use of x-ray diffraction (XRD) and x-ray fluorescence (XRF) instruments. While this is key information, selection of clay stabilizer type and loading cannot be determined solely by this information. Consequently this information is generally paired with performance tests that are run under as realistic conditions as possible. Capillary suction testing (CST) and roller oven testing can use formation rock and water from a given fracturing site. These tests can compare clay stabilizer technologies and loadings needed to minimize effects of swelling and/or fines migration. This paper will describe a new performance test method to compliment the methods mentioned previously. It uses unconsolidated core material that indirectly measures the clay swelling and migration potential. In this procedure, a packed column composed of tightly-sized shale material is used to simulate an infinite fracture network. Treatment fluids are then pumped through the column at constant rate while measuring pressure drop. The relative pressure change, together with the turbidity of the effluent, allows easy assessment of the clay stabilizer.

EXPERIMENTAL

Clay Column Test Station

Figure 1 is a picture of the clay column test station. It is composed of a constant rate chromatography pump connected to a stainless steel line leading to a pressure transducer followed by a ¾ inch diameter, 6 inch long column that holds the material of interest (100 mesh screens keep the material in place). This material can be sand/clay mixtures, shale, sandstone, etc. Exiting the column is a stainless steel line plumbed to a second pressure transducer which then leads to a collection bottle for the effluent. A computer is used to monitor the pressure from the transducers as a function of time.

Column Preparation

Sand/Clay standardized column

Prepare a mixture of 100 mesh sand and bentonite of the desired weight ratio based on the type of formation being mimicked or use of industry standard ratios (standard sand/clay ratios can range from 95/5 to 80/20). Shake for 10 seconds in a sealed container, then rotate 180° shake for 10 seconds rotate 180° shake again additional 10 seconds to ensure homogeneous mixture of the sand and bentonite mixture only. Pack column by filling with single scoops, while simultaneously tapping the side of the column to allow the clay mixture to distribute consistently throughout the column to avoid air entrapment. We then place a 100 mesh screen and ¼" inch tall spacer .590" diameter with ¼" hole on top of the test media to keep the sand or shale pack column stable. Seal open end of the column with end cap and secure the column in place on the apparatus with a torque wrench.

Shale Column

Cuttings are washed in hexanes (if needed: slurry, filter, repeat) and dried in an oven at 50°C overnight. Next they are ground if needed and sized on a sieve shaker. Particles that are collected in the 70 mesh sieve but pass thru a 60 mesh sieve are used for the test. Pack the column by filling with single scoops, while simultaneously tapping the side of the column to allow the shale to distribute consistently throughout the column to avoid air entrapment. We then place a 100 mesh screen and ¼" inch tall spacer .590" diameter with ¼" hole on top of the test media to keep the sand or shale pack column stable. Seal open end of the column with end cap and secure the column in place on the apparatus with a torque wrench.

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Test Methodology

Begin test by flowing 7% KCl thru the column at a rate of 3mls/min. to slowly saturate test column until noticeable effluent is gather in fluid beaker, turn pump off and let column sit for 5 minutes to equalize and monitor pressure then zero transducers, change flow rate on pump to 5 ml/min start data collection and establish a stable pressure baseline. 7% KCl was chosen as the baseline fluid as it can wet the column pack while having the minimal impact on clays present. Using 7% KCl also helps to standardize the test so that the results of one test can be compared another. Once the pressure has stabilized the fluid is changed to the fluid comprising the clay stabilizer of interest and it is passed thru the column while monitoring pressure changes over the baseline. Finally de-ionized water is passed through the column to cause maximal swelling of the clay and/or fines migration while monitoring pressure. The performance of the clay stabilizer is determined by measuring the pressure increase over the 7% KCl baseline and the longevity of the stabilizer is measured by noting the time it takes for the fresh water to reach constant pressure. Fines are collected in the effluent at certain intervals. If enough fines are present they can be quantified by measuring %transmittance to light and comparing the results to a fines calibration curve.

X-Ray Diffraction/X-Ray Fluorescence

X-ray diffraction/fluorescence is used to analyze the formation rock and determine types of clay as well as concentration. This method is complimentary to the clay column test method and capillary suction tests as it can give an indication that there could be clay issues but cannot determine which clay stabilizers and at what concentrations are optimal. An example of XRD analysis of drill cuttings from the San Juan Basin is shown in table 1. These cuttings primarily consist of quartz and dolomite with minor amounts of feldspar, clay, and carbonate material. While this analysis is helpful in determining if there could be an issue with swelling and/or fines migration, it cannot be concluded that the issue is significant enough to need a clay stabilizer and what type/loadings are needed.

Capillary Suction Tests (CST)

This method is an industry standard in measuring the potential clay issues. It compares clay stabilizer technologies by measuring the seconds it takes for wicking across a filter paper. Unfortunately it cannot aid in determining the mechanism of clay damage. Another challenge with this method is when comparing different clay stabilizers/loadings the results can sometimes be separated out by only a few seconds. This can make it difficult to select the best clay stabilizer and optimal loading. Graph 1 is an example of this type of data output where 2%KCl, 7%KCl, various polymers and choline chloride are all within 2 seconds of one another.

RESULTS

An example output of the clay column test station where pressure is monitored over time is shown in graph 2. As 7% KCl is pumped into the column the pressure rises and reaches a steady state after several minutes. While some pressure increase is seen, it is generally minimal with no fines migration seen. Once the pressure is stable the 7% KCl fluid is switched to a clay stabilizer laden fluid. The magnitude of the pressure increase and if any fines are seen gives a good indication of the relative performance of the clay stabilizer compared to 7% KCl. After pressure stabilization, the clay stabilizer solution is switched to fresh water. Using fresh water maximizes clay swelling and fines migration. This point is important in the test as it dimensions the sensitivity the clays present in the column have to fluids such as water.

Comparing the performance of clay stabilizers can be done in a variety of ways. One way is shown in graph 3. The graph is a summary of 5 tests. Each test used the same ratio of 85/15 sand/bentonite clay and standardizing using 7% KCl. Clay stabilizers were tested at 2gpt except for the run using a lower concentration of KCl (2%). The data is shown as the pressure difference over baseline pressure generated using 7% KCl. The benefit of using the clay column as a performance indicator is seen in the results in that various clay stabilizer technologies are broken out by differences in pressure. The best performing is the proprietary polymer CB which generated only a 75 psi increase over 7%KCl. Next best performing was 2%KCl at 113psi increase over 7%KCl baseline. Common clay stabilizer technologies such as tetramethyl ammonium chloride (TMAC) and choline chloride performed similar generating a pressure above baseline of 313psi and 361psi respectively. Finally a cationic polymer was used and showed a significant increase in pressure of 772psi.

Another significant piece of data that can be obtained using the clay column test station is being able to measure performance as a function of clay fines migration. This is done by collecting the effluent during select periods of time within the test. Picture 2 shows an example of clay fines where the first bottle on the left has no fines, the middle bottle some fines and the bottle on the far right has significant fines. Qualitative observations can be made or a more analytical determination of clay fines can be done using a Formulation Turbiscan (see picture 3). This instrument measures % transmittance (%T) thru the effluent collection bottle once the fines are dispersed in the fluid. The Turbiscan measures the %T from the bottom to the top of the bottle so one can determine if any settling has taken place in the test. It takes only a minute to run a test so generally clay settling is not an issue. Graph 4 shows a clay fines calibration curve which allows determination of the amount of fines collected in the effluent. Table 2 is an example of quantifying clay fines migration. This test used a 90/10 sand/clay mixture. Adjusting sand/clay mixtures can increase or decrease pressures and amount of fines migration depending on your test needs. The data shows 7%KCl being free of fines migration while 2gpt polymer CB showed minute levels of clay fines. 2gpt choline chloride showed a 15x increase in the amount of fines over polymer CB while switching over to fresh water produced the most fines at 363x increase over polymer CB.

The clay column test station can also use shale (ground up, cuttings) to test performance of clay stabilizers. Test procedures and results are similar to when using sand/clay columns. The only appreciable difference is generally pressures are lower. This is because many shale formations contain less swelling clay then our standard sand/clay column. Fines migration is possible in many shale formations. Graph 5 shows the performance of clay stabilizer polymer CB on San Juan Basin shale as a function of concentration. This test starts with a high concentration of clay stabilizer and moves to lower concentrations of stabilizer (after pressure stabilization) and the finally switch over to fresh water. The data shows polymer CB is effective at keeping pressures down at loadings as low as 0.5gpt. Another interesting piece of data is that switching to fresh water does not raise the pressure up significantly over 0.5gpt polymer CB. This shows the tenacity the polymer has to the shale surface which is hard to rinse off with fresh water.

Graph 6 shows the performance of choline chloride on shale as a function of concentration. This test starts with a high concentration of clay stabilizer and moves to lower concentrations of stabilizer (after pressure stabilization) and the finally switch over to fresh water. The data shows choline chloride has a slow increase in pressure as the concentration is reduced. This shows choline chloride is not as effective at keeping pressures low at low loadings vs. polymer CB on the San Juan Basin shale used in the test. Switching over to fresh water causes a significant rise in pressure to over 200psi. This shows choline chloride is easily rinsed off the shale surface and has poor tenacity when compared to polymer CB.

Fines in the effluent can also be seen when using shale. Picture 4 and 5 are examples of the type of shale fines seen using the clay column test. Picture 4 shows choline chloride at 1gpt, 0.5gpt then the switch to fresh water. Fines can be seen at both 1gpt and 0.5gpt while the switch to fresh water shows a significant increase in fines. Picture 5 shows polymer CB with no fines at 1gpt and 0.5gpt and the switch to fresh water shows a small amount of fines. These two pictures are good examples of how this method can help to show differences in clay stabilizer performance on various substrates as well as quantifying the sensitivity of the formation is to water. Quantitative analysis of shale fines can also be done in a similar manner to that outlined in the previous section describing fines migration when using a standardized sand/clay column.

CONCLUSION

The method described in this paper has been shown to be an effective complimentary test to classical methods for screening clay stabilizers such as CST and roller oven. Differences in clay stabilizers can be measured as a function of pressure differences as well as quantity of migrating fines. The method can use a standardized column of sand/clay or it can use cuttings or ground up cores from actual rock formations. The data output allows for accurate selection of the optimal clay stabilizer and loadings for a given application.

LIST OF REFERENCES

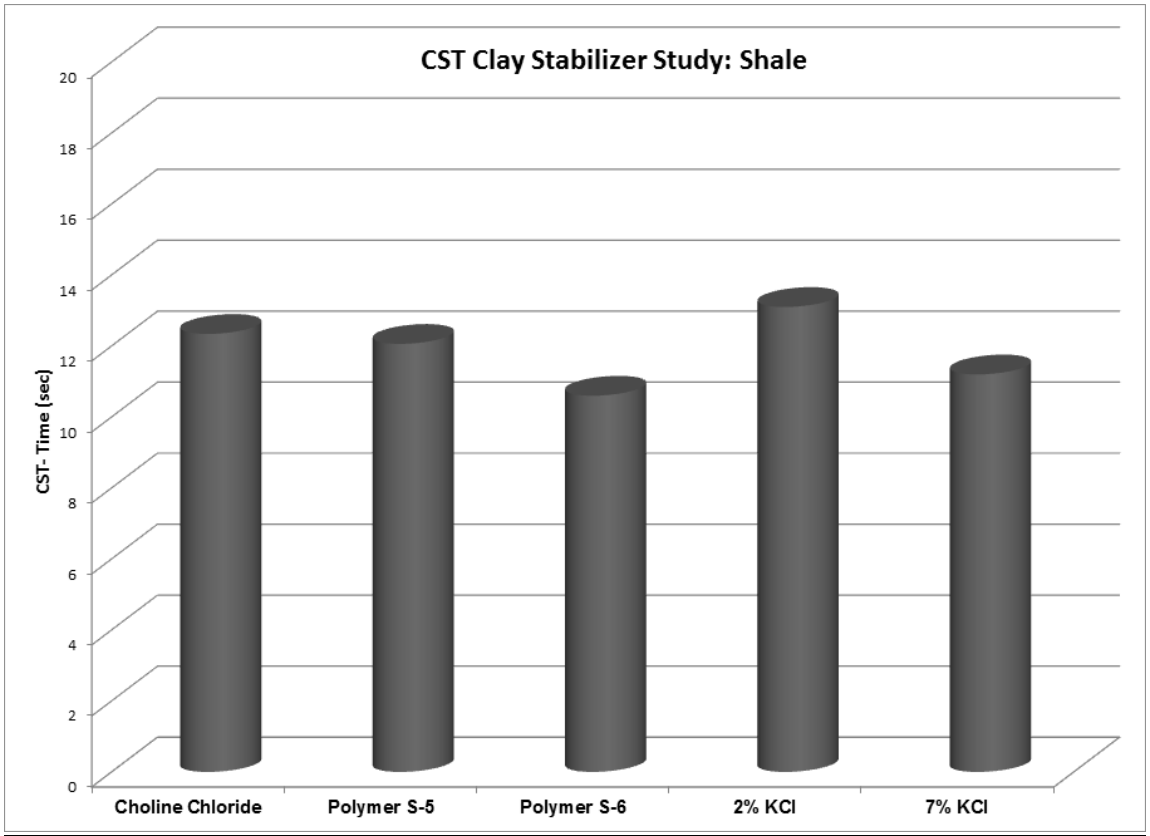
Johnston, Norris, “Role of Clay in Oil Reservoirs”, Clays and Clay Minerals, Vol 1, pp 306-313

Nasr-El-Din, H.A., et al, “Evaluation of Clay Stabilizers for a Sandstone Field in Central Saudia Arabia”, Society of Petroleum Engineers, 1999, vol 14, pp253-259

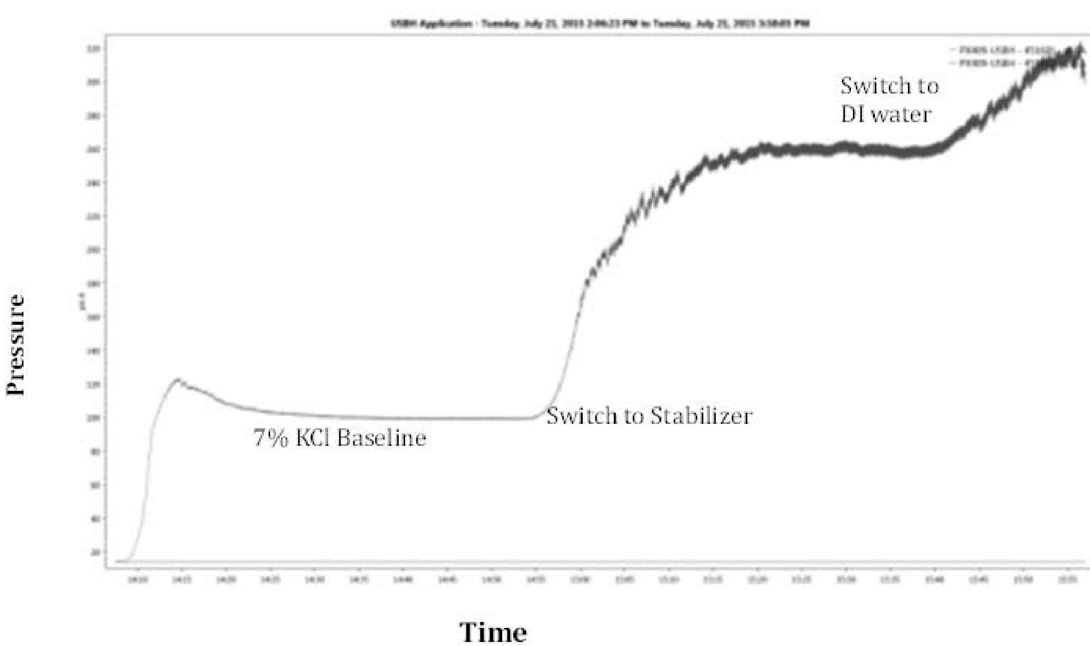
Fink, Johannes K., (2011), Petroleum Engineer’s Guide to Oil Field Chemicals and Fluids, Gulf Professional Publishing

Nanda, et al, “Evaluation of Reactive Clay in Indian Shale”, Offshore World, July 2014, pp 14-18

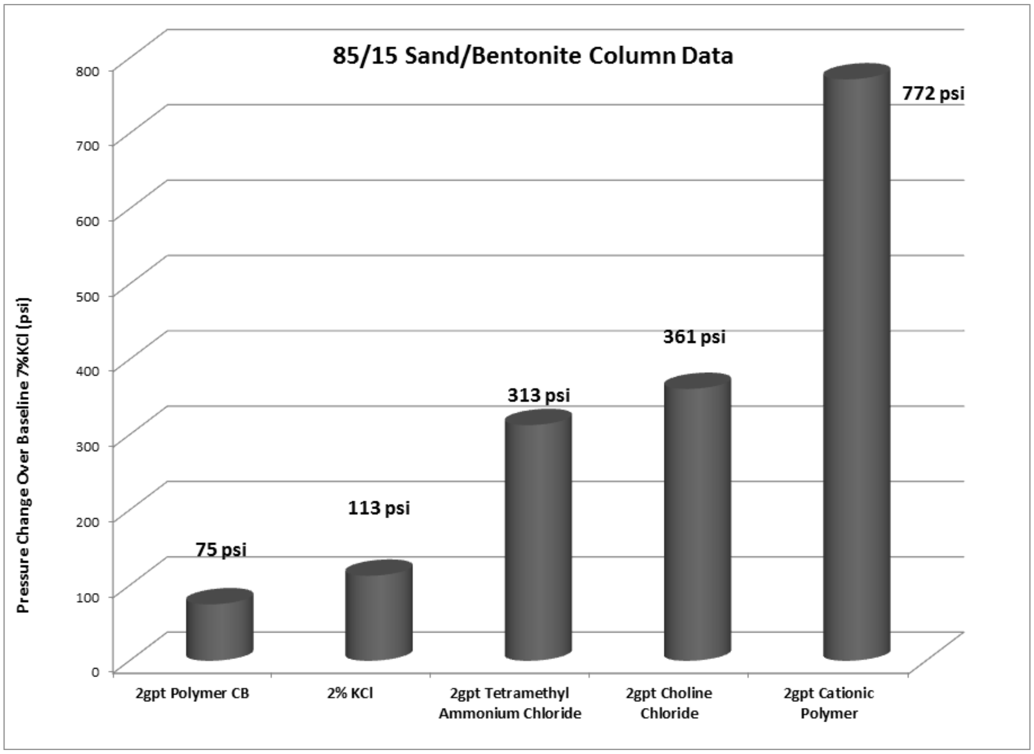
Graph 1 Capillary Suction Test (CST) on Shale of Various Clay Stabilizers at 2gpt Unless Otherwise Noted



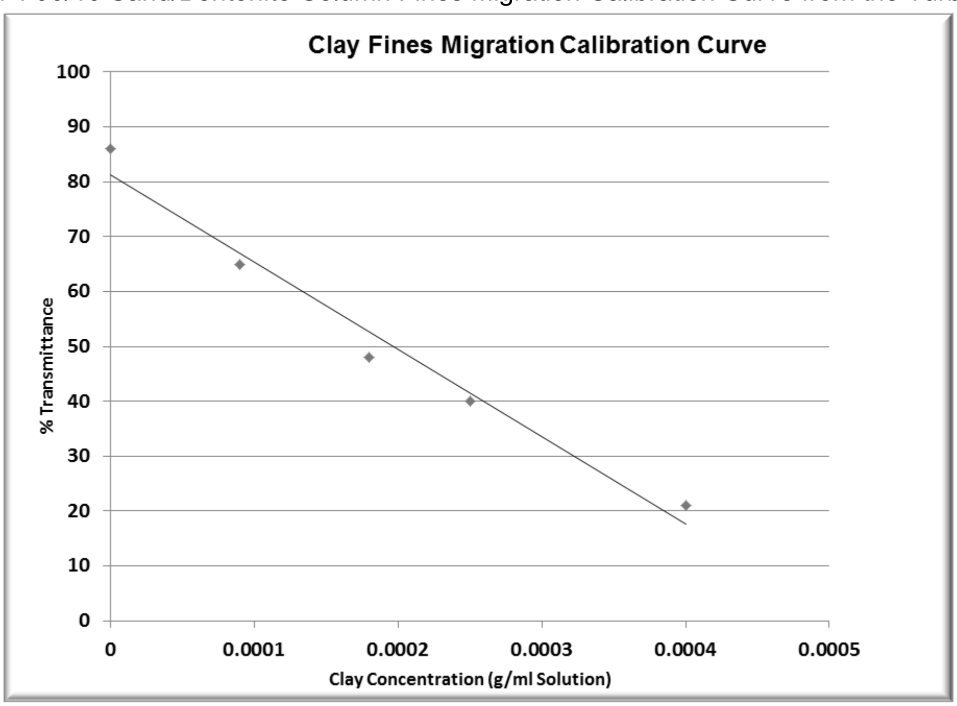
Graph 2 Clay Column Pressure Data



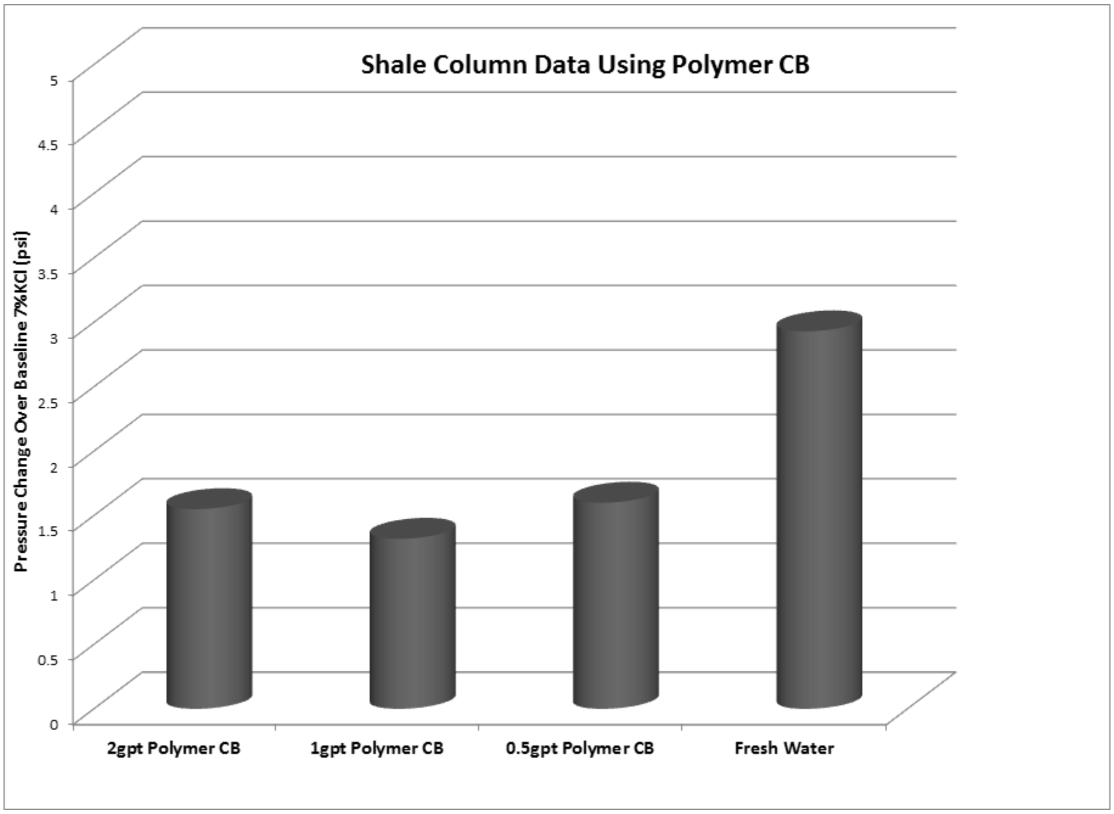
Graph 3 Clay Stabilizer Comparison



Graph 4 90/10 Sand/Bentonite Column Fines Migration Calibration Curve from the Turbiscan



Graph 5 San Juan Basin Shale Column Data Using Polymer CB at Various Concentrations



Graph 6 San Juan Basin Shale Column Data Using Choline Chloride at Various Concentrations

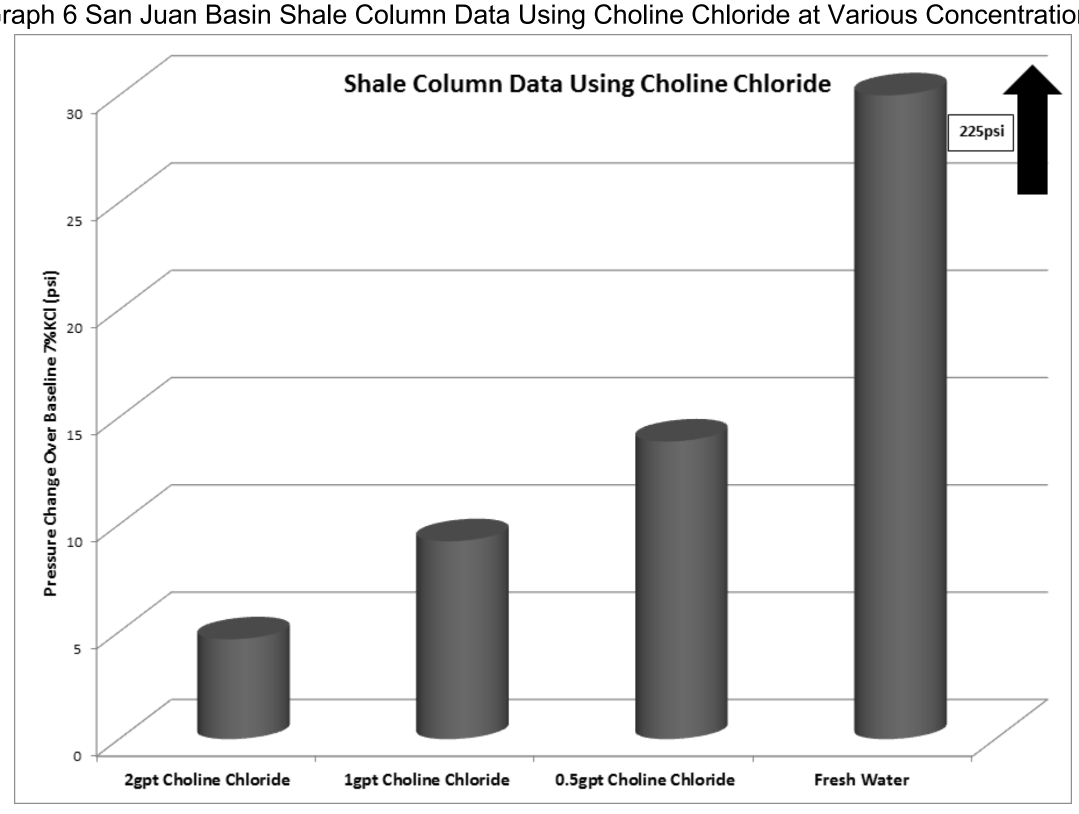


Table 1 X-Ray Diffraction (XRD) of Shale Cuttings from San Juan Basin

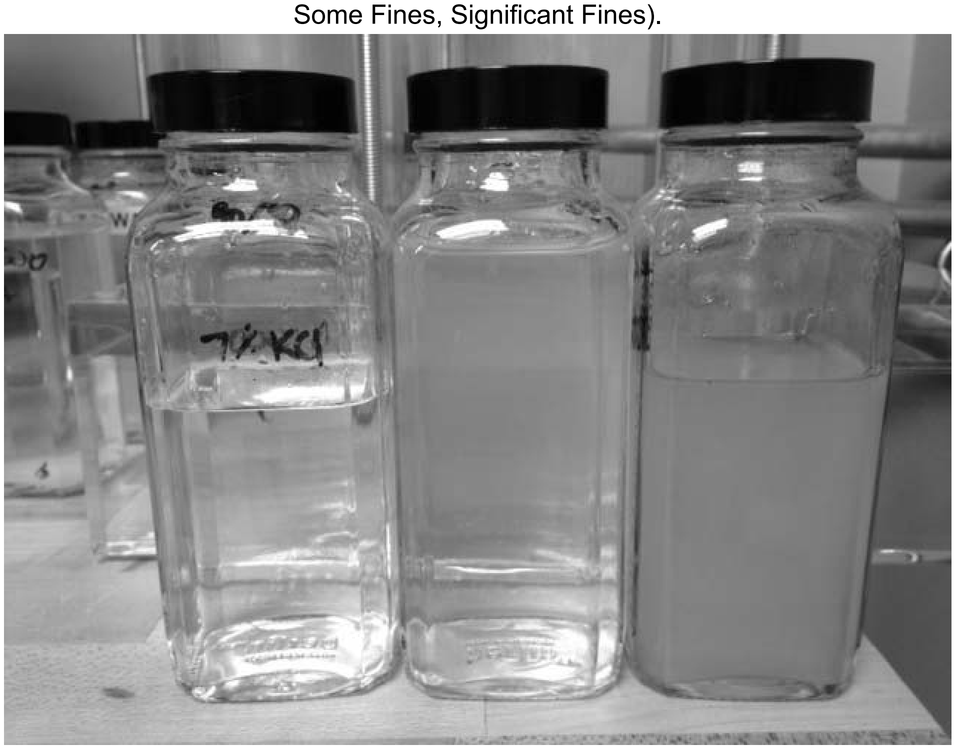
Phase	Composition (%)
Sample Name	Drill Cuttings
Quartz (SiO_2)	55
Muscovite $KAl_2(AlSi_3O_{10})(F,OH)$	3
Calcite ($CaCO_3$)	5
Dolomite ($CaMg(CO_3)_2$)	20
Microcline ($KaAlSi_3O_8$)	4
Albite ($NaAlSi_3O_8$)	8
Kaolinite ($Al_2Si_2O_5(OH)_4$)	3
Pyrite (FeS_2)	2

Table 2 Clay Fines Migration (90/10 Sand/Bentonite Column)

Sample	%Transmittance	Total Clay Fines in Effluent (g)	% Clay Collected as Fines in Effluent
7%KCl	83	0	0
2gpt Polymer CB	79	0.003	0.03
2gpt Choline Chloride	45	0.046	.46
2gpt Choline Chloride then Switch to Fresh Water	38 (20:1 dilution needed)	1.09	10.9

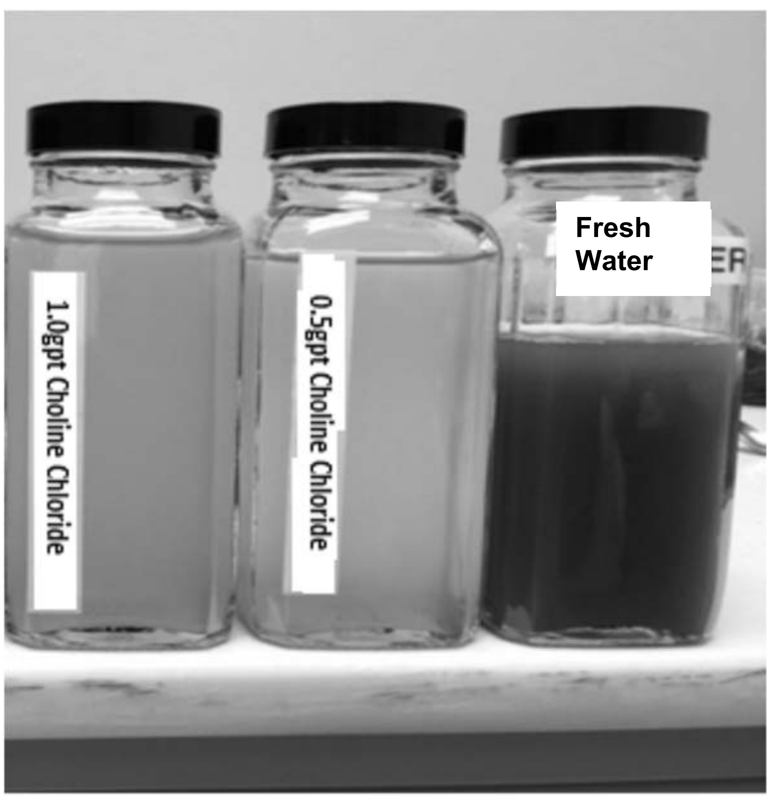
Picture 1 Clay Column Test Station

Picture 2 Effluent from a Sand/Clay Column Test Showing Clay Fines (From Left to Right, Minute Fines, Some Fines, Significant Fines).



Picture 3 Formulaction Turbiscan

Picture 4 Effluent from a San Juan Basin Shale Column Test Using Choline Chloride Showing Fines (Some Fines at 1gpt and 0.5gpt Loadings, Significant Fines When Switch to Fresh Water).



Picture 5 Effluent from a San Juan Basin Shale Column Test Using Polymer CB. Minimal Fines at 1gpt and 0.5gpt Loadings. An Increase in Fines is Seen When Switch to Fresh Water.