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Evaluation of a New Barite Dissolver: Lab Studies

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Proposal

Barite is a common weighting agent used for oil well applications. It is commonly used to provide adequate weight to control downhole pressures in drilling slurries. Since it is used for control of pressure, it is a common source of formation damage, especially in deep, hot formations where drilling fluid weights exceed 17 ppg. Although alternatives do exist for barite, (e.g., formate drilling fluids) they are significantly more expensive, and not available on a rapid turnaround basis as in emergency situations required by well control operations. Once damage has occurred, remediation is a very difficult proposition. Barite is not soluble in typical oilfield inorganic acids used in stimulation. The most common methods of remediation are fracture stimulation and/or deep perforations. The use of these methods can remediate the problem, but at high cost. Also, since the well productivity cannot be evaluated prior to stimulation operations, a poor quality well cannot be identified until a significant investment has been made.

The most common chemicals currently in use to address this problem are "barite dissolvers". These agents are all strong metal ion chelators. Aminopolycarboxylic acids (e.g., EDTA) and similar reagents have been used with low success rates.[1] Recently, hydroxylaminopolycarboxylic acids were introduced, but to the best of the author's knowledge was not extensively used in the field.[2]

This study investigates a new barite dissolver and compares its performance with other commercial dissolvers. The new material is a proprietary dissolver supplied in a liquid form. This study investigates the dissolving capacity, and evaluates the effectiveness of the dissolver by conducting coreflood tests. These tests were conducted using sandstone cores obtained from a deep gas well (300ºF). The effectiveness of the dissolver was followed by measuring the concentration of barium in the core effluent. Unlike other barite dissolvers, the new chemical is shown to be very effective in restoring the permeability of damaged cores. The new chemical does not require long soaking times, and does not induce fines migration due to chemical means.

Introduction

Barite, $BaSO_4$, is very difficult scale to remove. This is because it has very low solubility in water (2.5 mg/L)[3] and its low solubility product $K_{sp} = 10^{-9.99}$ at 25ºC.[4] In comparison, gypsum has a solubility of 2,080 mg/L in water at the same temperature.[5]

There are two cases where barite can cause problems in downhole environments. The first case occurs in oil fields where seawater is used for injection. Seawater has high sulfate content, whereas the formation contains high levels of barium. Barium sulfate will precipitate once these two waters mix together and the solubility product of barium sulfate is exceeded.[5,6] In the second case, the case of interest in the present study, barite is used as a weighting material in drilling mud. Barite in this case will be present in the filter cake, and will cause formation damage.

Barite can be removed from well tubulars by mechanical or chemical means. Chemicals means are not effective to remove scale present in the welbore. This is because the scale accumulates downhole, and adheres to well tubing. Chemical solvents or chelating agents are not effective in this case because the scale has very low surface area. Mechanical means including jetting or even drilling can be used to remove the scale from the wellbore. Chemical means can be used if barite invades the formation or precipitates in the formation due to mixing of incompatible waters. Traditional mechanical means cannot be used to remove barite once it is deposit or precipitate in the formation. In should be mentioned that acid and/or hydraulic fracturing can be used bypass the damaged zones, however this technique is expensive and cannot be applied in every well. Chemical means is best suited for dissolve barite that is present in the formation.

A thorough literature survey, especially the patent literature, reveals that chemical means rely on aminopolycarboxlyic acids (chelating agents).[1-15] EDTA and DTPA (**Fig. 1**) are typical barium sulfate dissolvers, however similar compounds were also proposed.[12,13,16] DTPA is one of the most effective dissolvers for barite.[1,11] It has an octodentate ligand, forms a strong 1:1 chelate in solutions at pH greater than 12. It binds to metal center with five carboxylate oxygen atoms and three nitrogen atoms to form $BaDTPA^{3-}$ complex.[4] The stability constant of the latter is 8.78.

A major concern using EDTA or DTPA is the slow dissolution rate of barite. One way to overcome this problem is to use a converter or a catalyst that enhances the dissolution rate. The patent literature is full of recommendations to use catalysts such as carbonates,[8] oxalates, and fluorides.[1,5,7] These chelants should be used at pH greater than 12 and a suitable catalyst should be included in the formulation. It is also important to prepare the chelant solution using fresh water. Seawater contains divalent cations (Ca, Mg), which will reduce the efficiency of the chelant.

As can be seen, many studies considered dissolution of barium sulfate scale. The objective of the current study is to examine dissolution of the barite that is used in drilling mud using various chelating agents.

Experimental Studies
Materials
Several barite dissolvers were studied. These dissolvers basically contained either EDTA or DTPA with a converter or a catalyst. These solvents were obtained from local service companies and were used as received or diluted with deionized water. **Table 1** gives some of the properties of the two solvents "A" and "B", including pH and density. Solvent "A" was used as received, whereas solvent "B" was diluted to 50 wt% using deionized water. Solvent "A" is based on DTPA, whereas dissolver "B" is based on EDTA. Both solvents have a pH greater than 12, which is the value recommended to chelate barium.[11]

The barite used in this study is field grade material with a specific gravity of 4.2-4.3. Sieve analysis of the barite sample indicates that the solids have a narrow distribution with a mean particle size of 0.06 mm. The mineralogy of the field material was determined by XRD, and found to contain 95.2 wt% $BaSO_4$. Elemental analysis of the sample using XRF, **Table 2**, indicates that the sample contains strontium and other impurities at small concentrations. Acid solubility (20 wt% HCl) of the barite used was found to be less than 5 wt%.

The composition and properties of the drilling mud used are given in **Tables 3 and 4**. Note that barite was extensively used in this mud.

Coreflood Experiments
Coreflood experiments were conducted using reservoir cores of 1.5 inches in diameter and 2-3 inches in length. The mineralogy of the core material was determined by XRD, **Table 5**. The sandstone cores contained quartz, kaolinite, and acid-soluble minerals including dolomite and hematite. This analysis was further confirmed by elemental analysis of core 29-4, as shown in **Table 6**. A brine that contained 7 wt% KCl was used in the pre, and post flushes. This is to minimize fines migration due to chemical means.[17] It was also used as the base fluid to prepare the drilling fluid that used to drill the target zone.

The procedure used to conduct coreflood experiments included injection of 7 wt% KCl brine and then determination of the core base permeability to brine. A synthetic drilling fluid (85 pcf) similar to the one used in the field was injected into the core until there was no fluid coming out of the cores. A solution of the barite dissolver was injected into the core to remove the damage. The solution of the scale dissolve was

injected as a neat solution (dissolver "A") or diluted to 50 wt% (dissolver "B"). The solution was injected and the pressure drop across the core was monitored. All fluids injected into the cores were filtered to 0.22 μm and were injected at 1 or 2 cm^3/min. All coreflood experiments were conducted at a temperature 300ºF (reservoir temperature), a back pressure of 500 psi and an overburden pressure of 2,500 psi.

The drilling fluid was placed in a rocker to keep the solids (barite) suspended during the injection of the drilling fluid into the cores.

Samples of the injected fluids and core effluent were collected during the coreflood experiments. The concentrations of key ions were measured. The concentration of barium, iron, silicon, calcium, magnesium, potassium, and aluminum were measured by ICP. The concentration of chloride was measured using a 0.1N silver nitrate solution; whereas the concentration of sulfate was measured using a turbidity method. More details on the analytical techniques were given by Nasr-El-Din et al.[18]

Batch Dissolution Tests
A simple experimental setup was used to measure the dissolving capacity and rate of dissolution. The solvent (250 cm^3) was placed in a glass beaker and heated up to 65°C. Agitation was provided through the use of a magnetic stirrer (350 rpm). A batch sample of field-grade barite (20 g) was added to the beaker and time was recorded. Samples were taken every five minutes from the middle of the beaker and analyzed for barium concentration.

Table 7 gives the concentration of barium in solution when dissolver "A" was used. Barium concentration rapidly increased with time and reached 23,772 mg/L after one hour. This dissolver has the ability to dissolve barite particles in a short period of time. To assess the reproducibility of these results, the same experiment was repeated and the results are given in **Table 8**. The concentration of barium increased in the same manner as was noted in the first run. The concentration of barium at any time was within 5% of that obtained in the first run.

Results and Discussion
Test #1: Core plug # 4-2, Dissolver "A"
The coreflood experiment started with the injection of 7 wt% KCl at 2 cm^3/min. Brine injection continued until a stable pressure drop across the core was achieved, **Fig. 2**. Then the barite-based drilling fluid (85 pcf) was injected into the core at the same rate, until the core was damaged and no fluids were produced from the core. The pressure drop across the core increased during the injection of the drilling mud because of its high viscosity and the fact that the mud was damaging to the core. It appears that the mud formed an external filter cake, with extremely low permeability. Dissolver "A", as received, was injected into the damaged core at a rate of 2 cm^3/min. The pressure drop across the core continued its increase until it reached a maximum of 2,050 psi, then it sharply dropped. This sudden drop indicated that the solvent removed most of the damage induced by the drilling fluid. **Photos 1 and 2** show the core inlet face before and after the experiment. Residual drilling mud can be seen on the inlet

face after the experiment. These photos show that most of the filter cake was removed by dissolver "A".

It is interesting to note that the pressure drop during brine injection was less than that before damaging the core with the drilling mud. This result may indicate that the solvent did stimulate the core to some extent.

It is important to mention that the volume of the drilling mud injected was 45 cm^3, whereas the volume of dissolver "A" was nearly 206 cm^3. It is also important to highlight that the filter cake formed by the drilling fluid contained mainly barite. The barite in this case was dispersed in the filter cake, and was coated with the water-soluble polymers used in the drilling mud. There was no diesel, condensate or oil used in the experiments. Therefore, there was no need to use mutual solvents or water-wetting surfactants. However, scale present in a typical oil well is covered with oil and other heavy hydrocarbons. In these cases, it is recommended to use xylene, mutual solvent and or surfactant to remove the oil that coats the scale before using the dissolver.

The most important conclusion that can be drawn from **Fig. 2** is that the accumulation of filter cake can adversely affect the permeability of the core. The solvent, however, was able to restore the permeability of damaged core, and even enhanced its permeability to some extent. Another important point is that this dissolver was not damaging to the core. A third important conclusion is that there was no further damage to the core due to debris generated by the dissolution processes.

Chemical analysis of the core effluent was used to determine the efficiency of the dissolver and its interactions with the sandstone core. The pH of the core effluent during the injection of the 7 wt% KCl was nearly 7.2, **Fig. 3.** It increased during the injection of drilling mud (pH 9) and the dissolver, which has a pH value of 13.5, **Table 1**. It is interesting to note the pH of the core effluent was lower than the pH of dissolver "A". Also, it took long time for the pH to decrease to its value in the 7 wt% KCl brine.

The concentration of the chloride ion is of interest because of the use of KCl brine in the preflush and overflush. High chloride concentration was noted during the injection of the drilling mud, **Fig. 4**. Chloride concentration decreased during the injection of dissolver "A", and then gradually increased during the injection of the overflush.

Figure 5 shows the concentration of barium as a function of the cumulative core effluent. The concentration of Ba in the core effluent during the injection of KCl brine and drilling mud was not significant. It sharply increased upon the injection of dissolver "A", and remained high during the injection of dissolver "A". It gradually decreased during the injection of the postflsuh brine (7 wt% KCl). It is important to mention that Ba was not detected in the core effluent, except during the injection of dissolver "A". A second important point is that dissolver "A" was able to dissolve barite even in the presence of polymers used in the drilling fluid. A third important point is that dissolver "A" was continuously injected, without soaking. In other words, this dissolver was able to dissolve barite during the injection of the dissolver. In other words, this dissolver does not require soaking time.

The concentration of sulfate ion gives another indication on the ability of the dissolver to remove barite. The sulfate was present at low concentrations in the drilling fluid. It increased during the injection of dissolver "A" in a way very similar to that noted with barium. These results further confirm than that dissolver "A" did remove barite that was present in the filter cake.

As mentioned earlier, the dissolver is a chelating agent. It is of interest to its ability to chelate other multi-valent cations. Initial calcium concentration during the injection of dissolver A" was high and fluctuating, **Fig. 7**. It decreased during the injection of the overflush. The sources of calcium are the drilling mud, and carbonate minerals that are present in the core, e.g., calcite and dolomite. These results indicated the dissolver "A" was able to simultaneously remove calcium and barium from the filter cake and core. Similar observations were noted by Rhudy[14] and Lakatos et al.[13]

Reservoir cores contain iron containing minerals like hematite. It is of interest to examine whether dissolver "A" will dissolve any of these minerals. **Figure 8** shows that this dissolver did manage to dissolve some iron from the core. Iron concentration peaked after the release of barium.

The pH of the dissolver is greater than 13. At such high pH value, the dissolver may dissolve some silica from the core, **Fig. 9**. This indeed was the case, where the concentration of silicon increased during the injection of dissolver "A". However, the concentration of silicon was not significant. This indicates that chemical "A" did not dissolve significant amounts of silica or silicates that were present in the core. It is important to mention that aluminum concentration in the core effluent was below detection limit. Therefore, it is most likely that chemical "A" dissolved quartz from the core.

X-ray analysis of the core minerals indicates that the core contained dolomite. Chemical "A" did dissolve dolomite from the core material where Mg concentration peaked during the injection of this chemical, **Fig. 10**.

Measuring the concentration of potassium was of interest because it was used in the preflush, postflush, and drilling mud. The concentration of potassium peaked and exceeded 200,000 mg/L during the injection of dissolver "A", **Fig. 11**. This result indicates that the polyaminocarboxlic acid is present as a potassium salt.

Test #2: Core plug # 8-4, Dissolver "B"
This core flood experiment was conducted to examine dissolve "B", which is based on EDTA. The pH of this chemical is greater than 13. The coreflood experiment started with the injection of 7 wt% KCl at 2 cm^3/min. Brine injection continued until a stable pressure drop across the core was achieved, Fig. 12. Then the barite-based drilling fluid (85 pcf) was injected into the core at the same rate, until the core was damaged and no fluids were produced from the core. Dissolver "B", at 50 wt% dilution, was injected into the damaged core at a rate of 1 cm^3/min. The pressure drop across the core continued its increase until it reached a maximum of 3,000 psi. The chemical was soaked in the core for more than 15 hours, however, the pressure drop across the core remained high, with no sign of dissolving the filter cake. At this stage, it was decided to inject chemical "A". The pressure drop increased upon the injection of dissolver "A", however, it suddenly dropped. This is similar to the trend noted with core 4-1.

Samples of the core effluent were collected and analyzed for key ions. **Figures 12 to 19** show the pH and concentration of various ions. The concentration of various ions behaved in a way very similar to that noted in previous experiment. Chemical "A" was able to dissolve barium and other cations like calcium, iron and magnesium from the core.

We tried several other barite dissolvers, however all of them behaved in a manner very similar to that noted with dissolver "B". Only dissolver "A" was able to remove the damage induced by the drilling fluid.

Conclusions

1. The new dissolver is shown to be very effective in restoring permeability of damaged cores.
2. The new chemical does not require long soaking times.
3. The new chemical was able to chelate other multi-valent cations from the sandstone cores examined.

Acknowledgments

Nomenclature

DTPA = Diethlenetriaminepentaacetic acid
EDTA = Ethlenediaminetetraacetic acid

References

1. Paul, J.M. and Fieler, E.R.: "A New Solvent for Oilfield Scale," paper SPE 24847 presented at the 1992 SPE Annual Technical Conference and Exhibition held in Washington, DC, 4-7 October.
2. Frenier, W.W.: "Novel Scale Removers are Developed for Dissolving Alkaline Earth Deposits," paper SPE 65027 presented at the 2001 SPE Oilfield Scale held in Aberdeen, Scotland, 30-31 January.
3. Dunn, K. et al.: "Mechanisms of Surface Precipitation and Dissolution of Barite: A Morphology Approach," J. Colloid & Interface Science, **214** (1999) 427-437.
4. Wang, K-S., et al.: "Dissolution of the Barite (001) Surface by the Chelating Agent DTPA as Studied with Non-contact Atomic Force Microscopy," J. Colloids and Surfaces A: Physicochem. Eng. Aspects, **160** (1999) 217-227.
5. Morris, R.L. and Paul, J.M.: "Method for Removing Sulfate Scale," US patent 4,980,077 (1990).
6. Clemmits, A.F., et al.: "The Dissolution of Scales in Oilfield Systems," paper SPE 14010 presented at the 1985 SPE Offshore Conference held in Aberdeen, Scotland, 10-13 September.
7. Paul, J.M. and Morris, R.L.: "Composition for Removing an Alkaline Earth Metal Sulfate," US patent 5,282,995 (1994).
8. Quattrini, F.J.: "Aqueous Reactive Scale Solvent," US patent 3,660,287 (1972).
9. De Jong, R., et al.: "Dissolving Barium Sulfate Scale with Aqueous Solutions of Salts of Carboxymethyl Monocyclic Macrocyclic Polyamines," US patent 4,190,462 (1980).
10. Richardson, E.A. and Scheuerman, R.F.: "Economically Dissolving Barium Sulfate Scale with a Chelating Agent," US patent 4,030,548 (1977).
11. Putnis, A., Putnis, C.V., and Paul, J.M.: "The Efficiency of DTPA-Based Solvent in the Dissolution of Barium Sulfate Scale Deposits," paper SPE 29094 presented at the 1996 SPE Oilfield Chemistry held in San Antonio, TX, 14-17 February.
12. Lakatos, I. et al. "Comparative Study of Different Barite Dissolvers: Technical and Economic Aspects," paper SPE 73719 presented at the 2002 SPE International Symposium and Exhibition on Formation Damage Control held in Lafayette, LA, 20-21 February.
13. Lakatos, I. et al.: "Optimization of Barite Dissolvers by Organic Acids and pH Regulation," paper SPE 74667 presented at the 2002 SPE Oilfield Scale Symposium held in Aberdeen, Scotland, 30-31 February.
14. Rhudy, J.S.: "Removal of Mineral Scale from Reservoir Core by Scale Dissolver," paper SPE 25161 presented at the 1993 SPE Symposium on Oilfield Chemistry held in New Orleans, LA, 2-5 March.
15. Smith, C.F., Nolan, T.J, III, Crenshaw, P.L.: "Removal and Inhibition of Calcium Sulfate Scale in Waterflood Projects," *JPT* (November 1968) 1249-1256.
16. Blanco, M. et al.: "Activated Complex Theory of Barite Scale Control Processes," *Molecular Engineering* **7** (1997) 491-514.
17. Nasr-El-Din, H.A.: "Permeability Decline Due to Flow of Dilute Suspensions Through Porous Media" in Suspensions Fundamental and Applications in the Petroleum Industry, L.L. Schramm (Editor), American Chemical Society Books Series 251, Washington, DC, Chapter 6, 289-319, 1996.
18. Nasr-El-Din, H.A., S.H. Al-Mutairi, and S.M. Al-Driweesh: "Lessons Learned from Acid Pickle Treatments of Deep/Sour Gas Wells," SPE 73706 presented at the 2002 SPE Int. Symposium on Formation Damage Control, Lafayette, LA, February 20-21.

Table 1. Commercial barite dissolvers tested

Dissolver	pH	Density[a] g/cm^3	Main Component
A	13.5	1.305	DTPA
B	13.1	1.32	EDTA

a. Density was measured at room temperature.

Table 2. Elemental analysis of the barite used[a]

Element	Concentration, wt%
Ba	56.01
S	11.21
Si	1.89
Sr	1.14
Fe	0.32
Ca	0.24
Al	0.18
Pb	< 0.05
K	< 0.05

a.   Determined by XRF technique

Table 3. Composition of 85 pcf drilling fluid. Chemicals were added to 66 pcf mud. All amounts were added per bbl.

Additive	Amount
Defoamer, gal	0.01
Bentonite, lb	2.0
Dextrid, lb	2.0
Drispec, lb	0.25
Lime, lb	0.25
Barite, lb	143
Sodium sulfite, lb	0.25

Table 4. Average properties of 85 pcf drilling fluid.

Parameter	Value
Density, lb/ft^3	85
Plastic viscosity, cP	20
Yield point, lb/100ft^2	18
10 sec, gel, lb/100ft^2	2
10 min, gel, lb/100ft^2	6
Filtrate, cc/30 min API	6
pH	9

Table 5. Mineralogy of reservoir cores using XRD

Mineral	Core # 8-4	Core # 29-4	Core # 35-2	Core # 52-1
Quartz	92	97	96	92
Kaolinite	2	0.5	2	1
Dolomite	4	1	1	1
Hematite	-	1	-	5
Halite	2	0.5	1	1

Table 6. Elemental analysis of core # 29-4 using XRF

Element	Concentration, wt%
Si	45
Cl	1
Ca	0.6
S	0.3
Mg	0.2
Fe	0.2
K	0.1
Ti	0.1

Table 7. Batch dissolution of barite in dissolver "A" at 65°C, run # 1.

Time, min	Ba, mg/L
0	0
5	10,163
10	11,648
15	13,443
20	15,122
25	14,481
30	16,529
35	17,307
40	18,376
45	20,272
50	21,786
55	21,238
60	23,772

Table 8. Batch dissolution of barite in dissolver "A" at 65°C, run # 2.

Time, min	Ba, mg/L
0	0
5	10,237
10	10,966
15	12,630
20	13,941
25	15,510
30	16,606
35	18,674
40	19,554
45	21,744
50	21,816
55	22,694
60	22,717

Fig. 1. Structures of EDTA and DTPA

EDTA (ethylenediaminetetraacetic acid
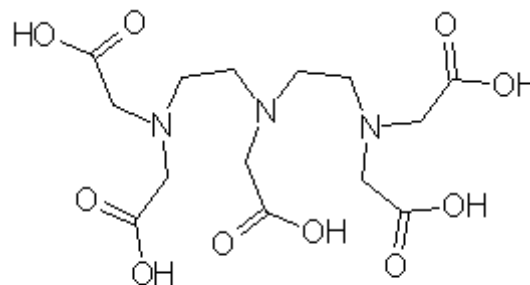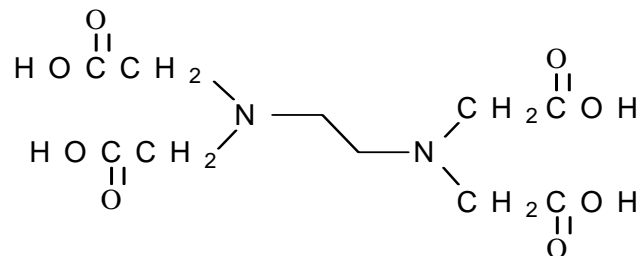
DTPA (diethylenetriaminepentaacetic acid)

Photo 1. Core inlet before the injection of the drilling mud
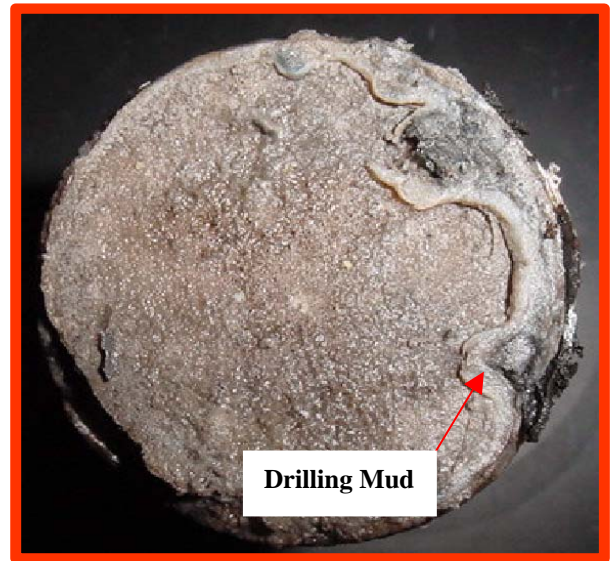
Photo 2. Core inlet at the end of the experiment
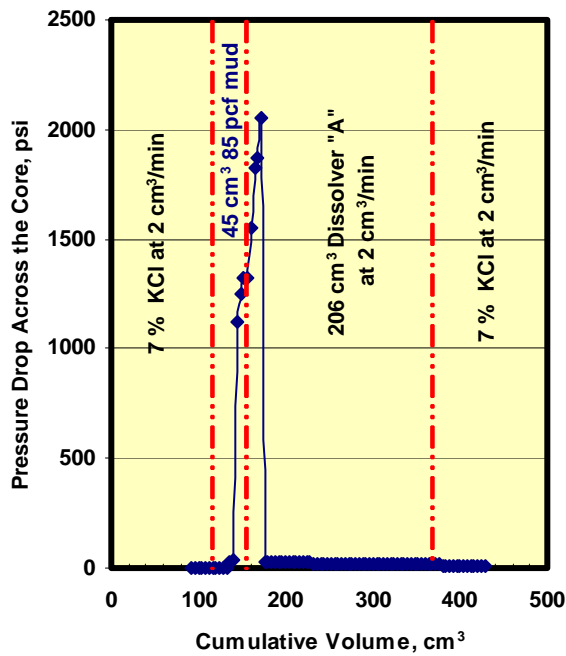
Fig. 2. Pressure drop across the core during the injection of drilling mud and dissolver "A"
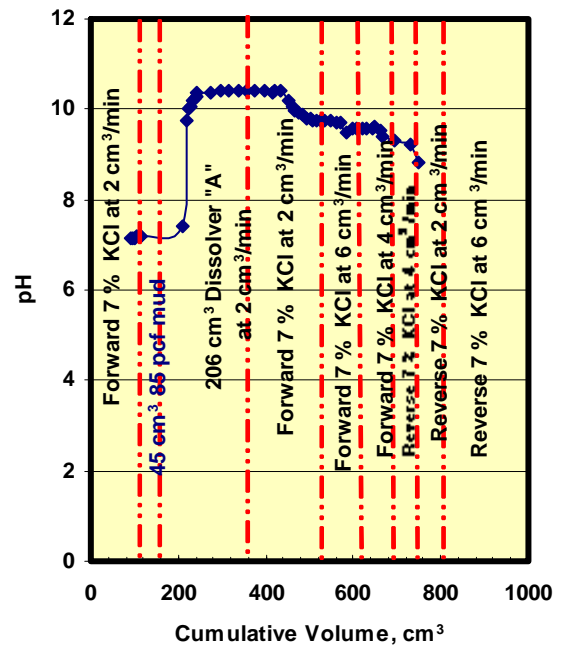
Fig. 3. pH of samples collected from a core similar to 52-1
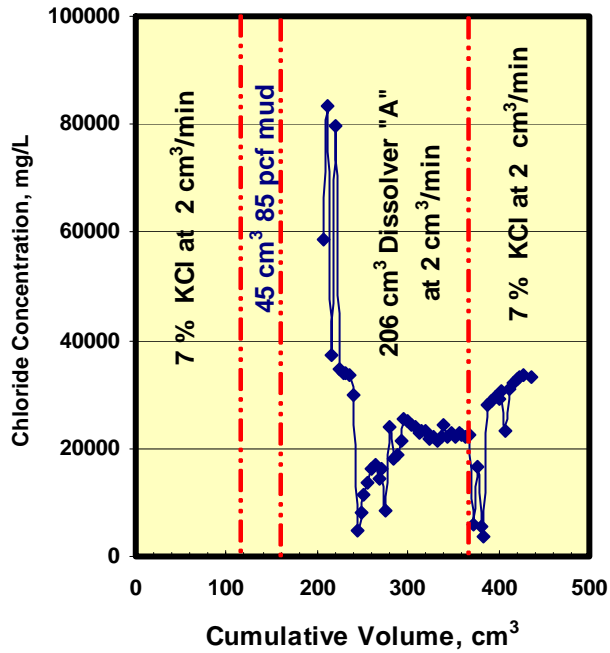
Fig. 4. Chloride concentration in samples collected from a core similar to 52-1
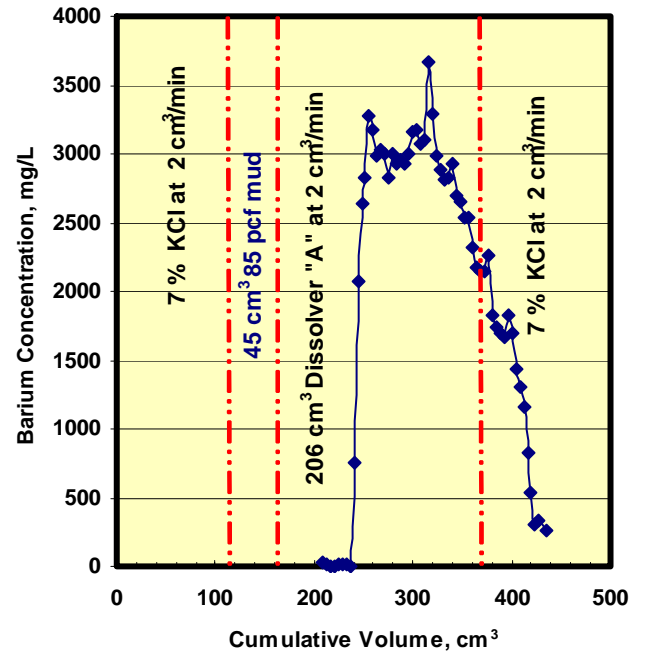
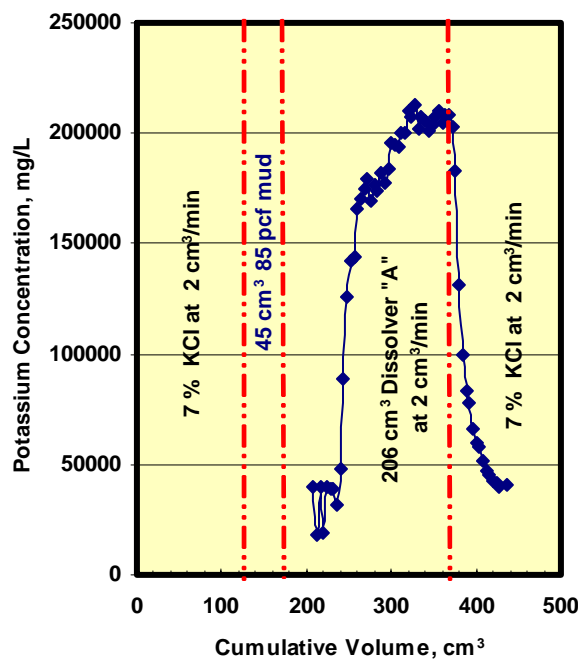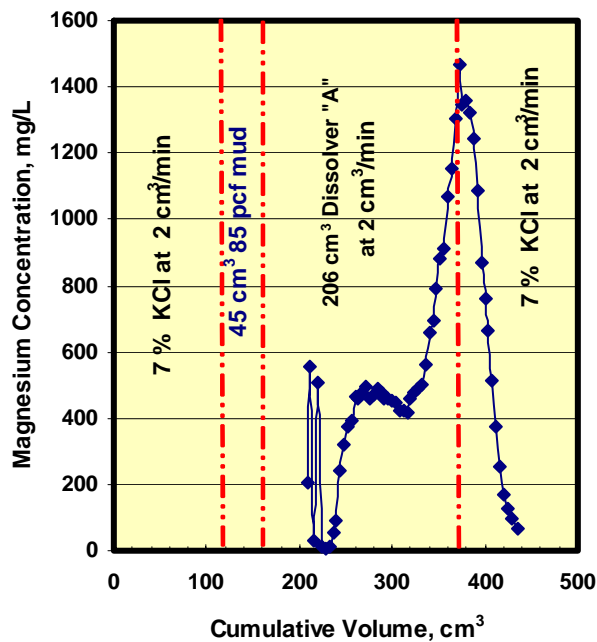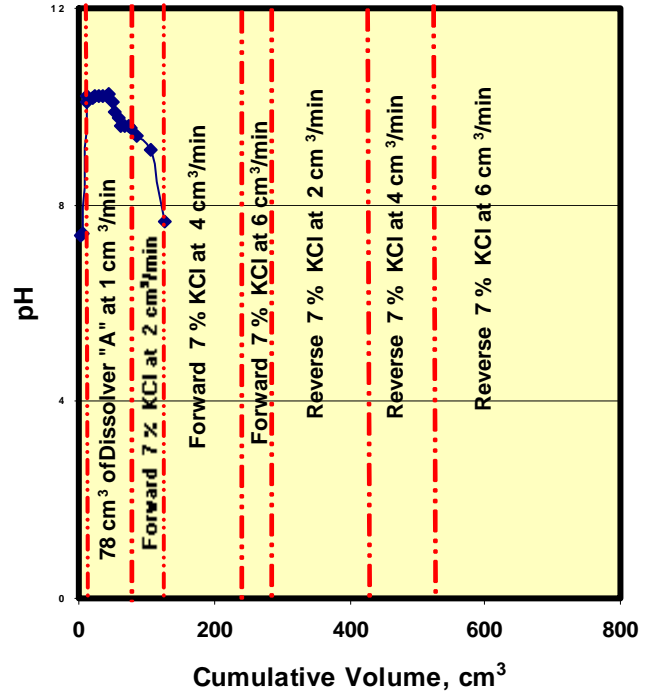**Fig. 5**. Barium concentration in samples collected from a core similar to 52-1
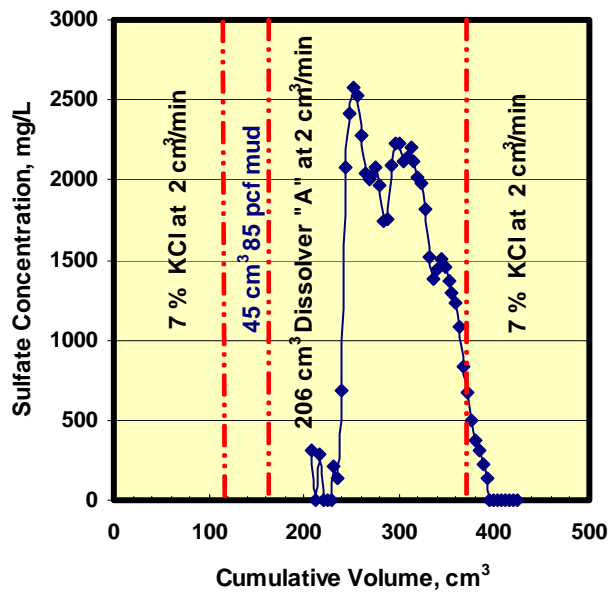
Fig. 6. Sulfate concentration in samples collected from a core similar to 52-1
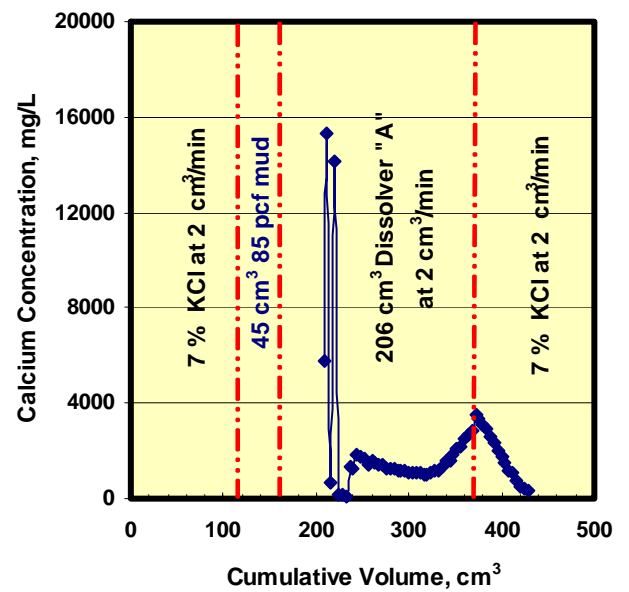
Fig. 7. Calcium concentration in samples collected from a core similar to 52-1
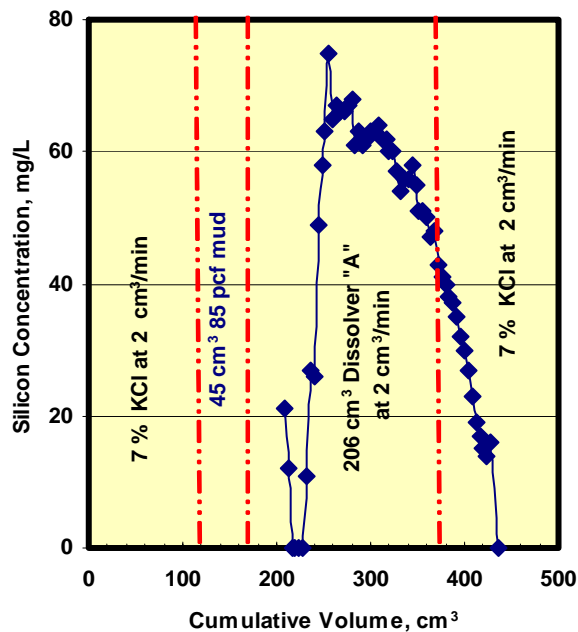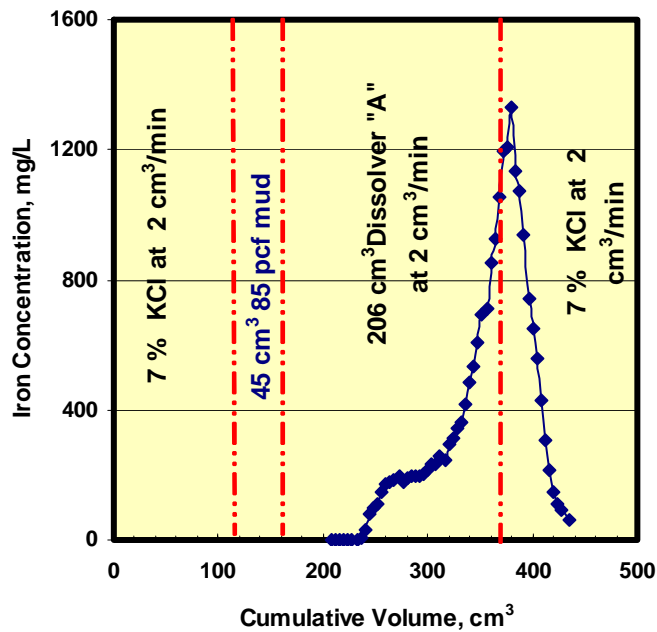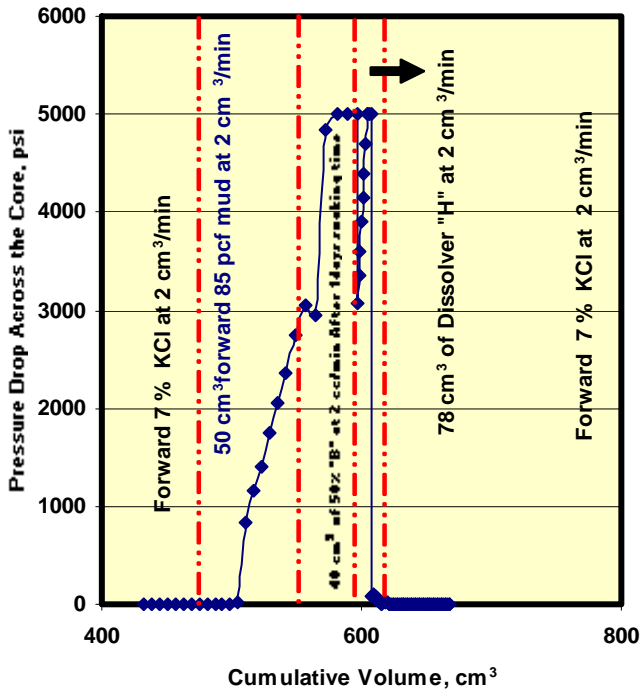
Fig. 8. Total iron concentration in samples collected from a core similar to 52-1

Fig. 9. Silicon concentration in samples collected from a core similar to 52-1

Fig. 10. Magnesium concentration in samples collected from a core similar to 52-1

Fig. 11. Potassium concentration in samples collected from a core similar to 52-1

Fig. 12. Pressure drop across the core during the injection of drilling mud, dissolver "B", then dissolver "A", core 8-4

Fig. 13. pH of samples collected from the core 8-4
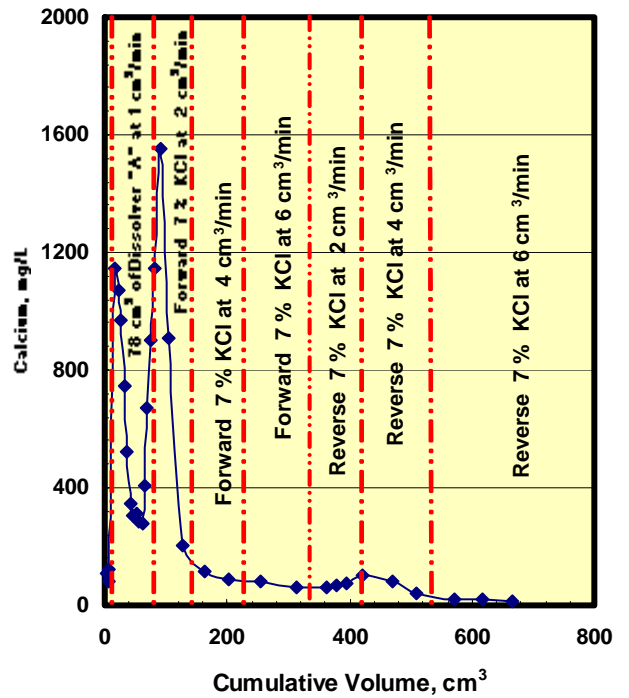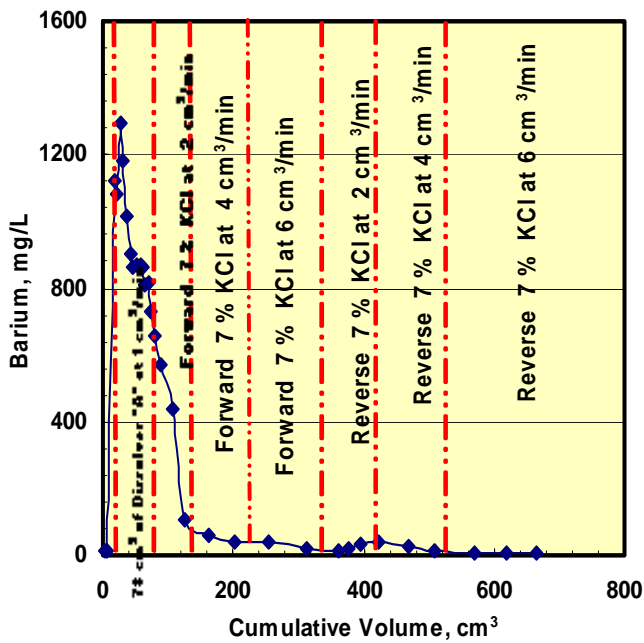
Fig. 14 Barium concentration in samples collected from the core 8-4

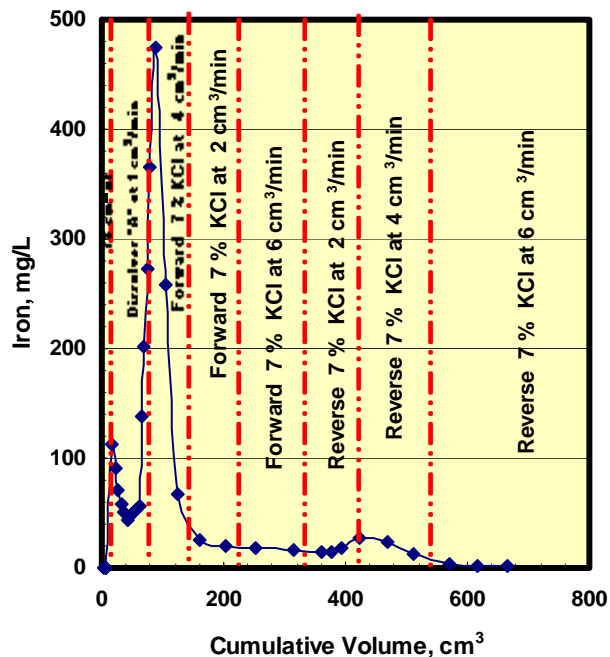**Fig. 15** Calcium concentration in samples collected from the core 8-4

Fig. 16 Iron concentration in samples collected from the core 8-4
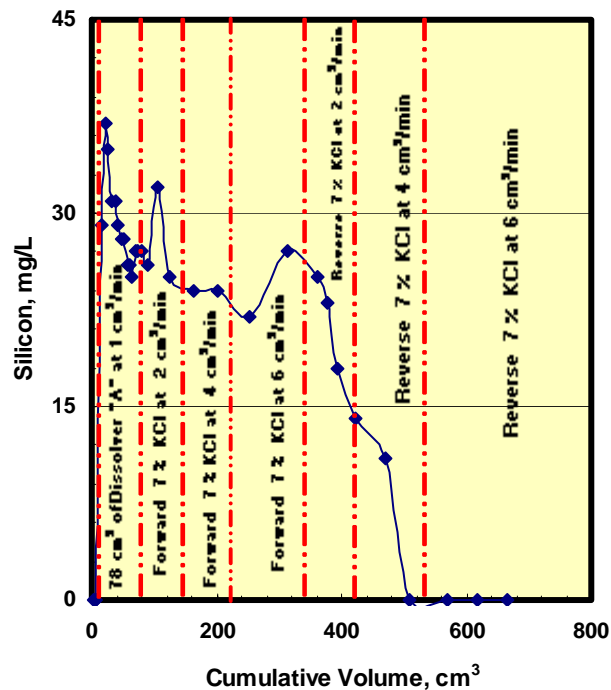

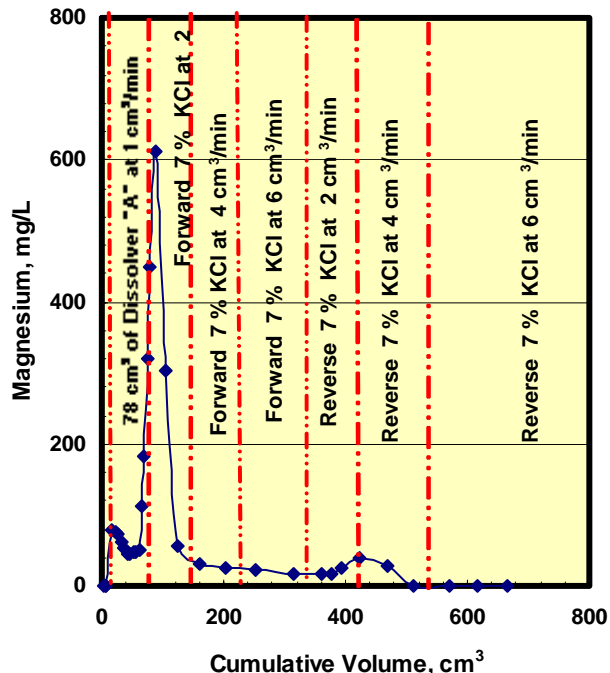**Fig. 17** Silicon concentration in samples collected from the core 8-4

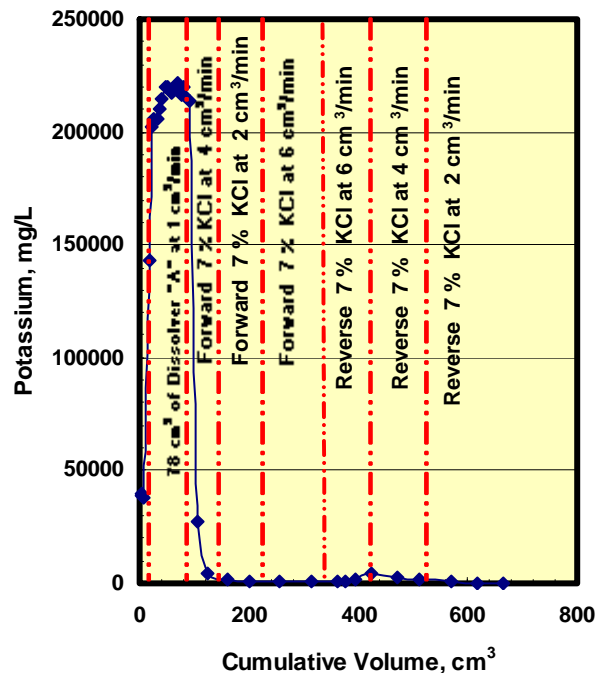**Fig. 18** Magnesium concentration in samples collected from the core 8-4

Fig. 19 Potassium concentration in samples collected from the core 8-4