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# Potassium Formate / Manganese Tetraoxide Fluid for Ultra HPHT Drilling

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## Abstract

Potassium formate (KFo) is widely used in non-damaging drill-in & completion fluids, particularly in sensitive formations such as shale, and others containing hydratable clays. The maximum density of saturated KFo brine is 13 ppg and this is one of its limitations. Barite is soluble in KFo brine and the solubility increases with temperature. Therefore, it can't be used as a supplementary weight material to reach the desired fluid density. Manganese tetraoxide ($Mn_3O_4$) with KFo brine has been successfully used to drill many wells globally. $Mn_3O_4$ as a high density, acid soluble and micro-spherical material, is a versatile weight material for drilling & completion fluids.

Recently, intensive lab work was undertaken to formulate & test KFo/ $Mn_3O_4$ as drilling & completion fluids for ultra HPHT drilling (up to 425˚F).

This work will present the development of such fluids for ultra HPHT drilling and, as well, some of the lab testing challenges. A 16 ppg fluid was successfully tested for static heat aging for 14 days at 425˚F with a low sag factor of 0.510.

A drilling fluid with a density of 16 ppg was also tested at 425˚F with a low static fluid loss <15ml, low static sag <0.510 and low rheology (PV <30cp & YP <15Ib/100ft$^2$). The fluid has minimal formation damage potential.

In both fluids specialty additives such as viscosifier, fluid loss additive and a dispersant were used. These fluids can provide a cost effect solution for drilling & completion in ultra HPHT conditions.

## Introduction

Drilling HPHT wells is normally associated with operational challenges. A good selection of a drill-in and a completion fluid is essential for success. Low or solid free fluids such as brines or non-aqueous fluids are often used to drill reservoir sections. K and Cs formate brines, with a maximum density of 13 and 19.2 ppg, respectively, are widely used as fluids for drill-in and completion application. Cs formate brine is regarded as an excellent, but expensive fluid and its supply is limited. Therefore there is a growing need for an alternative. To increase the density of KFo above its saturation density (13 ppg) requires a combination of K/Cs formate brines or to weight up KFo with solid weight material such as $Mn_3O_4$. Barite should be avoided in weighting KFo since it dissolves and builds barium formate, which is toxic, and harmful to the environment. A sized $CaCO_3$ might be used, if a marginal increase in density is desired.

### *Manganese tetraoxide ($Mn_3O_4$)*

Manganese tetraoxide is a member of the manganese oxide family. It is produced in a thermal process by blowing air through molten manganese alloy at around 1200˚C. The $Mn_3O_4$ particle has a spherical morphology with a narrow size distribution, where the average particle size (D50) is *ca.* 1.0 µm (Figure 1). The $Mn_3O_4$ content is >96wt%, with the remaining components being associated metal oxides such as $Fe_2O_3$, CaO, $K_2O$, etc.

$Mn_3O_4$ has an iso-electric point around pH 7 and its surface is negatively charged with a zeta potential of -30 to -50mV in the pH range from 9-11, wherein most water-based drilling fluids are formulated (Figure 2).

The high density of $Mn_3O_4$ (≈ 4.8 SG / 40 ppg) and its sphericity allow the formulation of heavy fluids with low rheological properties. The high rate of solubility in many acids is another attractive feature of $Mn_3O_4$. Alternatively, at pH >8, $Mn_3O_4$ is insoluble in water and formate brine. The solubility of $Mn_3O_4$ in formate brine at 20˚C is <5ppm. This insolubility is a very useful feature for its use as a weight material in water-based fluids at HPHT.

$Mn_3O_4$ is a hard material (Mohs' number = 6) but it is not abrasive due to its small size and sphericity. This guarantees the stability and use of the fluid over a long period of time and the ability to recycle the fluid. Other softer weight materials such as barite or $CaCO_3$ tend to create fines over time, which can have undesirable effects on the fluid properties & performance.

### *$Mn_3O_4$ I KFo fluid*

Manganese tetraoxide with KFo brine has been successfully used to drill many wells globally[1-4]. Below are 3 case histories illustrating the effectiveness of this system;

Case 1: The first application for $Mn_3O_4$ in K formate as a drill-in and completion fluid was in the Gullfaks field in Norway, as reported by Svendsen *et al* (1995)[1]. It was a sandstone reservoir with high permeability (250mDarcy-10Darcy) and poor consolidation, which required an ECD managed fluid with low solids. The clay content in the formation was also about 15-40%, and this required an inhibitive fluid. The temperature was about 165˚F. A 13.7 ppg $Mn_3O_4$ /KFo fluid was successfully used. The paper reported many good practical points which were taken into account during design & use of the fluid in the field.

Case 2: Al-Saeedi *et al*[2] reported on the use of $Mn_3O_4$/KFo as a drilling fluid to drill a Jurassic well with a 6–in. hole, and a bottom hole temperature around 280°F at a depth of 16,530 ft. This fluid was selected to replace 18.5 ppg OBM weighted with API barite, which was used in previous wells with major logging issues. The $Mn_3O_4$/KFo fluid provided better quality image logs and the fluid showed excellent stability at HPHT conditions whilst being non-damaging.

Case 3: EL Bialy *et al*[3] reported on the use of $Mn_3O_4$/KFo fluid to drill a sandstone tight gas reservoir. An optimized formulation with the right bridging agent sizes provided a fluid with good filtration properties. Return permeability at a reservoir condition of 300˚F and 3000 psi was measured to almost 100%. A vertical well was completed with zero hole problems.

This work presents the further development of such fluids for ultra HPHT drilling with some of the lab testing challenges.

## Experiments

### *Chemicals*

Potassium formate brine (1.57SG/ 13 ppg) and potassium formate salt dry (PF97) were kindly supplied by Addcon, Norway. Manganese tetraoxide was used as a weight material. Various commercially available HPHT polymeric viscosifiers & fluid loss additives from various producers were used. An acrylic based HPHT dispersant was used. Sepiolite and bentonite were tested as viscosifiers.

### *Equipments*

Standard drilling fluid equipment was used: a constant speed mixer & Silverson mixer, oven for heat aging up to 450°F, static HPHT fluid loss system used at temperature of 300°F with a differential pressure of 500 psi., Fann 35 viscometer, pH meter, balance, etc were used. The solubility of $Mn_3O_4$ in potassium formate was monitored by atomic absorption spectroscopy (AAS). Bruker D8 Advance XRD instrument was used to perform phase identification. Gas measurements were conducted using Extrel's Gas Analysis (MAX300-IG™). A core flooding rig was used for return permeability measurement.

## Preparation of $Mn_3O_4$ / KFo Completion & Drilling Fluids

An operator requested formulations of $Mn_3O_4$ / KFo for a completion fluid and a drilling fluid with a density of 16 ppg to be used at a temperature of 425°F. This fluid was intended to be an effective & cheaper replacement for Cs formate brine on HPHT completions.

## Completion Fluid

The requirements for this fluid were for a 16 ppg fluid stable to 425°F for 14 days with minimal sag.

## Viscosifier

The settling rate of $Mn_3O_4$ as a submicron material is normally very low, but to avoid settling over a long period of time, the use of a viscosifier or suspending agent is recommended. HPHT polymers such as vinyl sulphonate (AMPS) based materials and clays such as sepiolite and treated bentonite were considered. The low free water content in formate brine makes polymer or clay hydration a challenging process. Table 1 shows the tests of various viscosifiers and their effect on suspending $Mn_3O_4$. Test 1 was just $Mn_3O_4$ dispersed in KFo with soda ash as a buffer. The high volume of the supernatant liquid indicates the need for a suspending agent. A dispersant was used in Test 2 and that improved the suspension of $Mn_3O_4$ but the sag was still high. Tests 3, 4 & 5 were formulated with 3 different sepiolite grades at the same concentration of 5 lbm/bbl KFo brine. Sepiolite grade I is readily dispersible and yielded immediately without needing pre-hydration in fresh water. Sepiolite II didn't disperse well in the brine and the settling was high. Sepiolite III yielded after heating and mixing. Test 6 was conducted using treated bentonite and, as shown in Table 1, the fluid was unstable. The static sag & the supernatant liquid were quite high. In Tests 7-9 various HPHT polymeric viscosifers were used. Polymer I showed the best result but it required heat & shear to yield. To improve polymer hydration Tests 10 & 11 were conducted by first hydrating the polymer in fresh water and then, dry KFo salt was added to bring the brine up to saturation. Table 2 illustrates the fluid properties before and after heat aging at 425°F for 16h. The pre-hydration of polymer I in water improved the rheology of the fluid and also the suspension. The reason for the low rheology of Test 11 AHA was the salting out of the polymer during static aging. It is expected that under dynamic aging this salting out might be minimized. From the previous results we see the advantages of using treated sepiolite as the viscosifier over the polymeric one as follows:

1) It yields right away at room temperature. So it does not require heat to be activated.
2) It requires no free water for hydration. So it can be mixed directly into the brine phase without pre-hydration in water, unlike polymeric viscosifier.
3) Generally, it has higher thermal stability compared to the polymeric viscosifiers. It was used in geothermal applications at temperatures up to 700°F.
4) Sepiolite, which is magnesium silicate clay with a typical formula $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$, has a low charge density on its surface making its structural network in suspension easily breakable. The dominating inter-structural forces are the hydrogen bonding and the fiber entanglement.
5) Sepiolite has needle morphology with a length of *ca.* 2μm and a diameter of a few tens of nanometers and it's expected to pose less or no damage to reservoirs compared to polymeric material or bentonite.

Table 3 shows a simple completion fluid design using minimum additives and its properties after heat aging. The fluid comprises $Mn_3O_4$ in KFo brine, HPHT dispersant and treated sepiolite as viscosifier. The fluid is stable with minimal sag even after 14 days static aging at 425°F. The rheological parameters were increased slightly as the aging time increased. Such increase in rheology might be related to the sepiolite's partial thermal transformation into smectite, as described in literature[5,6]. Such increase seems to have little effect on the fluid since it is easy to stir after prolonged aging. If prolonged aging is anticipated, one can reduce the initial sepiolite concentration to offset the increase in rheology during the aging. Most previous studies on sepiolite thermal transformation were conducted on fluids such as sepiolite with $CaCl_2$ or KOH & KCl etc. No data was found regarding sepiolite thermal transformation in KFo brine, therefore 2 XRD analyses were conducted on sepiolite in KFo brine. The first test was conducted on 2% sepiolite dispersion in 10ppg KFo after heat aging at 400°F for 20h. Sepiolite was extracted using a centrifuge & dried afterward at 221°F for a few hours. Figure 3 shows the XRD spectrum. The crystalline content of this sample was estimated to be *ca.* 53%. Around 25% of sepiolite was converted into smectite (15%) & illite (9%). This is a significant transformation. The second XRD test was conducted on a fluid containing sepiolite, dispersant and fluid loss additive in 13 ppg KFo, as shown in Table 4. The fluid was heat aged at 400°F for 72h. The XRD semi-quantitative analysis as depicted in Figure 4 indicates no or small phase transformation. It is well-known in literature that potassium salts retard the sepiolite transformation. It seems the transformation in saturated KFo (13 ppg) & in the presence additives such as FLAC & dispersant is minimized drastically. This needs further investigation to confirm.

## Drilling Fluid

The requirements for the $Mn_3O_4$ in KFo brine drilling fluid were for 16 ppg @ 425°F with low, upper end rheology to provide low ECDs, minimal sag & an HPHT fluid loss of <15 ml. Whilst the formulation for a completion fluid proved quite straightforward, the creation of a robust formulation for a drilling fluid was more complex. This was due to the following reasons:

1) The drilling fluid requires fluid loss control at *ca.* 425°F. There are few additives available to successfully manage fluid loss control at this high temperature, particularly in brines.
2) The completion fluid required simple control of chemical stability & sag. There were few additives.
3) Testing formate fluids at ultra-high temperatures raises a number of issues, which are described below.

### *Selecting the right fluid loss additives*

Potassium formate is extremely soluble in water at up to 77% w/w. This results in leaving little free water to dissolve additives. Accordingly, when adding a product requiring solubilisation, such as fluid loss control polymers, sufficient time & energy is needed to allow dissolution to take place. One of the consequences of aging at high temperature may be that these polymers salt out, even if properly dissolved prior to aging. Therefore, the use of certain polymers may prove to be impossible above certain concentrations at high temperature. Non-dissolving additives such as treated sepiolite, $Mn_3O_4$, $CaCO_3$ etc, do not require pre-hydration, but do need sufficient shear to properly disperse.

It is recommended to not add the chemicals requiring dissolution to the saturated KFo directly, but rather to prehydrate them in fresh water first, then add the brine & bring up to saturation with dry KFo.

Most HPHT fluid loss additives commercially available for water based fluids are copolymers based on 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) and acrylamide monomers[7]. However, there are various modifications such as adding additional monomers such as N-vinyl-2-pyrrolidone, N-vinyl lactam, maleic anhydride, N,N-dimethylacrylamide, etc. In this work, various HPHT fluid loss additives from different producers were tested in various combinations & concentrations. Over 50 formulations were conducted until the desired fluid loss of less than 10ml at 300°F was achieved for a fluid that was aged at 400 and 425°F for 30h.

### *Decomposition of KFo under lab conditions*

Formates do decompose at high temperature, but there is a much greater degree of decomposition under lab testing than occurs in the field[8]. Essentially, lab results show more decomposition & corrosion, which have not been seen occurring in the field. This can be attributed to the following:

1) Formate decomposition to CO, $CO_2$ or $H_2$ is an equilibrium process.
2) Test cells contain headspace gas such as $N_2$, $CO_2$ or air in a much higher proportion to that experienced in a well. This larger amount of gas leads to more decomposition because the reaction gases escape into the headspace & delay equilibrium being reached.
3) Lab testing is conducted at low pressure (hundreds of PSI). HPHT wells are at high pressure (thousands of PSI) & equilibrium is reached earlier. Higher pressure restricts decomposition.

Lab test cells are made of stainless steel alloys containing e.g. nickel, which act as catalysts in the potassium formate decomposition reaction. Wells contain pipe, which has mill scale, which acts as negative catalysts in the decomposition reactions.

Because more decomposition occurs whilst testing under lab conditions, many tests can be difficult to run accurately. At elevated temperature >400°F the production of gases caused significant foaming of the mud in the test cell. Such foaming can compromise tests such as the "sag factor". For rheology or fluid testing it is better to allow the sample to be gently stirred before running the tests, to permit the removal of the entrained gases.

Gas measurements were conducted using Extrel's Gas Analysis (MAX300-IG™) on the headspace gas in the aging cell to determine the type and concentration of the gases developed during the aging of fluids. Table 7 shows the various gases developed from a formate brine & $Mn_3O_4$/KFo fluid at 392 and 420°F for 16h. The increase of $H_2$ and $CO_2$ gases at elevated temperature indicate thermal degradation of the formate. The amount of gas developed in the presence of $Mn_3O_4$ was less, compared to the KFo containing none. This indicates $Mn_3O_4$ has no catalytic effect on the decomposition of formate brine. It is worth mentioning that anionic cellulose (PAC LV) used as a supportive fluid loss additive, degrades at a temperature >300°F and definitively has contributed to the formation of $CO_2$.

Aging cells used to test formate brines are subjected to corrosion from the decomposition products. Therefore, it is recommended to use Teflon liners up to ca 400°F & Hastelloy aging cells for higher temperatures. Mud de-aeration with a vacuum pump and defoamer chemicals were used to remove the air bubbles after heat aging.

### *pH increase after heat aging*

Generally the pH of drilling fluids, particularly formate brine, decreases as a result of thermal degradation of the fluid components. Therefore it is recommended to use carbonate / bicarbonate salt as a buffer for KFo brine fluids. The opposite was observed here as the pH increased slightly after the heat aging both with & without the addition of the carbonates. Such increase in pH might be due to the formation of K carbonate / bicarbonate from the decomposed chemicals. It is worth mentioning that technical grade KFo, dry or brine, sometimes contains a low percentage of potassium acetate or KOH (<2%) and this causes pH to be >9.

The pH of the $Mn_3O_4$ / KFo fluid was adjusted to *ca.* 9, taking into consideration the slight increase during the heat aging. Formic acid was occasionally needed to adjust the pH back to 9. This was done to protect the polymers from degradation at high pH values.

This fluid can be considered as a self-buffering system and little or no carbonate / bicarbonate should be added during the fluid mixing. The increase of pH is of benefit since it will mitigate the drop in pH that can cause corrosion. Again under field conditions, the decomposition of KFo brine is very low compared to what is seen in lab testing, and probably such an increase of pH becomes insignificant.

After running more than 50 tests, a robust drilling fluid was formulated & tested at temperatures in the range 400- 425°F, as shown in Table 5&6. Beside $Mn_3O_4$ & KFo brine the fluid contains the following additives: treated sepiolite as viscosifier & fluid loss additive[6,9], HPHT terpolymer and PAC LV, as fluid loss additive, $CaCO_3$ as bridging agent and HPHT dispersant. PAC LV was used to provide early control of the filtration since the synthetic terpolymer takes longer to become fully hydrated and function properly. The drilling fluid with a density of 16 ppg was tested at 400 & 425°F. The static fluid loss of 8ml was measured at 300°F and a very thin filter cake <1mm was formed (Figure 5). The dynamic sag number (VSST) was *ca.* 0. 25ppg. The fluid exhibits a low rheology (PV <30cp & YP <10Ib/100ft$^2$).

## Core Flooding Test

Formate brine is well-known as being generally non-damaging. Byrne *et al* (2002)[10] concluded from more than 40 core flooding tests on formate brine and (supported by field data) that formate brine does not show significant or unusual formation damage potential. Also, Al-Saeedi's work[2] on $Mn_3O_4$ in KFo brine shows this fluid has no damage potential in tight sandstone. It is a common perception that a solids free system is less damaging than a fluid containing solids. This is misleading. Solid-free fluids are solids-free on surface, but acquire solids from drilling. The main damage from a fluid containing solids is from solids migration into the formation, which plugs, thus impairing the production of hydrocarbons. A well designed fluid with low fluid loss and a good filter cake greatly minimizes formation damage. The lower the filtrate volume is, the less damage there will be. However, microfine particles of $Mn_3O_4$ might migrate into the formation before the filter cake is built, but they are able to be flowed back upon production because the $Mn_3O_4$ particles are both small & spherical, possessing significantly less friction when compared to e.g. polymorphic, multi-sized barite.

It is also desirable that the materials used in drill-in fluids be easily removable. The use of acid soluble weight & bridging materials such as $Mn_3O_4$ & $CaCO_3$ allow the cleanup of internal filter cake (skin) that might occur. To assess the damage potential of this new fluid for ultra HPHT condition core flooding tests were conducted using standard Berea and Bandera sandstone cores with an initial permeability of 80 & 20µD, respectively. The drilling fluid used had a fluid loss of 8ml at 300°F. The tests were conducted according to the following procedures:

1. The core was dried at 250°F for 4 hours and weighed to obtain its dry weight. Then the core was saturated with KFo brine (10ppg) for 6 hours under vacuum and its wet weight measured. The pore volume was calculated using these measurements and the density of the brine solution.
2. The core was placed inside the core holder. KFo brine at 10ppg was flowed through the core at a rate of 2 cc/min in the production direction until it became stabilized. The pressure drop was recorded. The flow direction was reversed and the stabilized pressure drop recorded.
3. The KFo brine flow was changed to the production direction. The temperature was raised to the target value (350°F) and kept constant for the whole process. The pressure drop was monitored and recorded until it was stabilized.
4. The drilling fluid was injected at 2 cc/min, in the injection direction at 400 psi.
5. The direction of flow was then reversed to the production direction and KFo brine injected into the core until the pressure drop had stabilized. The return permeability was calculated.
6. At room temperature, the return permeability was measured again (same as step 5).

Figures 6 & 7 show a core flooding test of 16 ppg drilling fluid measured at 350°F with Berea & Bandera sandstone cores, respectively. The results shown in Table 8 indicate the fluid has an excellent return permeability of 97% with Berea sandstone core and 99% with Bandera core. There was no need to use a clean-up fluid.

## Conclusions

In this work, robust & non-damaging drilling & completion fluids based on $Mn_3O_4$ / KFo brine suitable for ultra HPHT drilling, were successfully formulated & tested. These fluids had a density of 16 ppg and were tested at temperatures up to 425˚F. The fluids exhibited excellent properties such as low fluid loss and rheology. An easily dispersible treated sepiolite was used as the viscosifier. Also, an effective HPHT dispersant developed specifically for $Mn_3O_4$ was used. A combination of a well-selected HPHT terpolymer together with $CaCO_3$ and PAC LV, were used as fluid loss additives. These fluids have minimal formation damage potential. These fluids can provide a cost effective solution for drilling & completion in ultra HPHT conditions.

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## Nomenclature

$Mn_3O_4$ = *Manganese tetraoxide*
*KFo* = *Potassium formate*
*HPHT* = *High pressure high temperature*
*ECD* = *equivalent circulation density*
*PAC LV* = *Polyanionic cellulose low viscosity*
*VSST* = *The viscometer sag shoe test*
*AHA* = *After Heat Aging*

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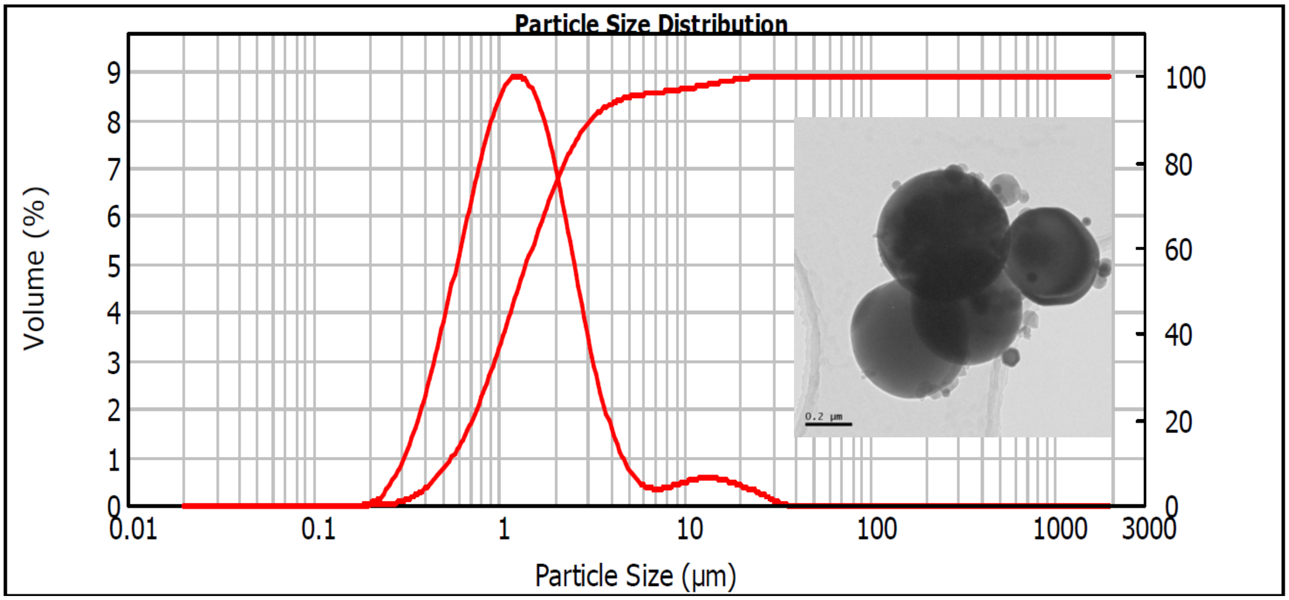

Figure 1. Particle size distribution of manganese tetraoxide.

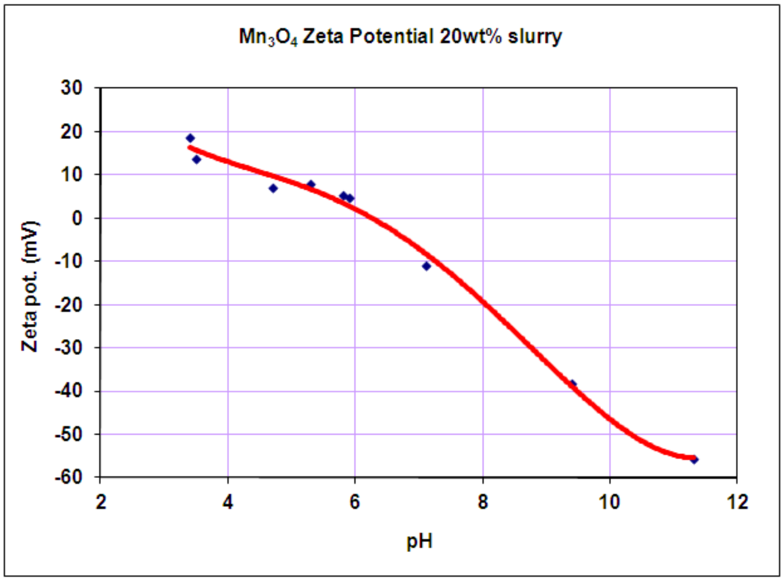

Figure 2. Zeta potential of manganese tetraoxide.

Table 1. Dispersion of $Mn_3O_4$ in potassium formate brine.

| Test | Mixing time (min) | #1 | | # 2 | | # 3 | | # 4 | | # 5 | | # 6 | | # 7 | | # 8 | | # 9 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Additives | 4000 rpm | Concentration in (gm) | | | | | | | | | | | | | | | | | |
| Kfo brine (SG1.57) | | 650 | | 650 | | 650 | | 650 | | 650 | | 650 | | 650 | | 650 | | 650 | |
| Soda Ash | 5 | 0,35 | | 0,35 | | 0,35 | | 0,35 | | 0,35 | | 0,35 | | 0,35 | | 0,35 | | 0,35 | |
| Sepiolite I | 5 | 0 | | 0 | | 6 | | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | |
| Sepiolite II | 5 | 0 | | 0 | | 0 | | 6 | | 0 | | 0 | | 0 | | 0 | | 0 | |
| Sepiolite III | 5 | 0 | | 0 | | 0 | | 0 | | 6 | | 0 | | 0 | | 0 | | 0 | |
| Modified bentonite | 5 | 0 | | 0 | | 0 | | 0 | | 0 | | 4 | | 0 | | 0 | | 0 | |
| HPHT polymer I | 5 | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | | 3 | | 0 | | 0 | |
| HPHT polymer II | 5 | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | | 3 | | 0 | |
| HPHT polymer III | 5 | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | | 3 | |
| HPHT dispersant | 5 | 0 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | |
| $Mn_3O_4$ | 10 | 235 | | 235 | | 235 | | 235 | | 235 | | 235 | | 235 | | 235 | | 235 | |
| Static heat aged at 218°C for 16h | | BHR | AHR | BHR | AHR | BHR | AHR | BHR | AHR | BSHA | AHR | BHR | AHR | BSHA | AHR | BHR | AHR | BHR | AHR |
| 600 rpm | | 35 | 35 | 29 | 24 | 56 | 54 | 37 | 47 | 55 | 81 | 49 | 62 | 36 | 57 | 34 | 41 | 20 | 21 |
| 300 rpm | | 21 | 21 | 15 | 12 | 35 | 34 | 21 | 24 | 34 | 52 | 30 | 43 | 20 | 34 | 18 | 19 | 10 | 11 |
| 200 rpm | | 15 | 15 | 10 | 8 | 27 | 26 | 15 | 16 | 26 | 40 | 24 | 35 | 14 | 25 | 13 | 13 | 7 | 7 |
| 100 rpm | | 10 | 10 | 5 | 4 | 19 | 18 | 10 | 8 | 19 | 27 | 16 | 27 | 8 | 17 | 7 | 6 | 4 | 3 |
| 6 rpm | | 3 | 3 | 0 | 0 | 9 | 8,5 | 3 | 1 | 10 | 12 | 6 | 15 | 3 | 8 | 1 | 1 | 0 | 0 |
| 3 rpm | | 2 | 2 | 0 | 0 | 9 | 8 | 3 | 1 | 10 | 12 | 5 | 14 | 3 | 8 | 1 | 1 | 0 | 0 |
| PV @ 120˚F, cP ( 50 C ) | | 14 | 14 | 14 | 12 | 21 | 20 | 16 | 23 | 21 | 29 | 19 | 19 | 16 | 23 | 16 | 22 | 10 | 10 |
| YP, lb/100ft2 | | 7 | 6 | 5 | 4 | 14 | 14 | 6 | 8 | 8 | 12 | 11 | 24 | 6 | 9 | 5 | 6 | 3 | 4 |
| 10 sec Gel, lb/100ft2 | | 3 | 4 | 2 | 1 | 11 | 9 | 7 | 1 | 14 | 18 | 6 | 14 | 5 | 7 | 3 | 1 | 1 | 1 |
| 10 min Gel, lb/100ft2 | | 3 | 4 | 6 | 2 | 19 | 10 | 13 | 5 | 15 | 20 | 7 | 14 | 10 | 13 | 7 | 2 | | 1 |
| pH | | 11,05 | 11,7 | 8,97 | 11,3 | 9 | 11,84 | 9,05 | 11,75 | 8,96 | 12,08 | 10,8 | 11,9 | 9,04 | 11,7 | 8,95 | 11,95 | 9,5 | 11,38 |
| Supernantant liquid ( ml ) | | | 160 | | 0 | | 1 | | 60 | | 27 | | 150 | | 127 | | 72 | | 35 |
| Density Top | | | 2,08 | | 1,65 | | 1,97 | | 1,94 | | 1,90 | | 1,84 | | 2,27 | | 1,89 | | 1,614 |
| Density Bottom | | | 2,08 | | 2,33 | | 1,99 | | 2,03 | | 1,94 | | 2,22 | | 2,29 | | 1,96 | | 2,278 |
| Sag Factor | | | 0,500 | | 0,585 | | 0,503 | | 0,511 | | 0,505 | | 0,547 | | 0,502 | | 0,509 | | 0,585 |

Table 2. Dispersion of $Mn_3O_4$ in potassium formate brine in presence of polymeric viscosifier.

| Test | Mixing time (min) | # 10 | | # 11 | |
|---|---|---|---|---|---|
| Additives | 4000 rpm | Concentration in (gm) | | | |
| Water | | 110 | | 110 | |
| Soda Ash | 5 | 0,35 | | 0,35 | |
| KFo dry | 5 | 250 | | 250 | |
| KFo brine (SG1.57) | 5 | 280 | | 280 | |
| Soda Ash | 5 | 0,35 | | 0,35 | |
| HPHT polymer I | 5 | 2,4 | | 4 | |
| HPHT dispersant | 5 | 4 | | 4 | |
| $Mn_3O_4$ | 10 | 235 | | 235 | |
| Static heat aged at 218°C for 16h | | BHR | AHR | BHR | AHR |
| 600 rpm | | 35 | 32 | 90 | 50 |
| 300 rpm | | 22 | 19 | 64 | 29 |
| 200 rpm | | 17 | 14 | 50 | 21 |
| 100 rpm | | 11 | 9 | 32 | 13 |
| 6 rpm | | 4 | 4 | 11 | 4 |
| 3 rpm | | 3 | 3 | 9 | 3 |
| PV @ 120˚F, cP ( 50 C ) | | 13 | 13 | 26 | 21 |
| YP, lb/100ft2 | | 9 | 6 | 38 | 8 |
| 10 sec Gel, lb/100ft2 | | 4 | 4 | 9 | 6 |
| 10 min Gel, lb/100ft2 | | 4 | 3 | 11 | 20 |
| pH | | 9,06 | 11,75 | 11,87 | 12,06 |
| Supernantant liquid ( ml ) | | | 20 | | trace |
| Density Top | | | 1,68 | | 1,75 |
| Density Bottom | | | 1,99 | | 1,9 |
| Sag Factor | | | 0,542 | | 0,521 |

Table 3. 16 ppg $Mn_3O_4$ / KFo completion fluid heat aged statically at 425°F for 7, 10 and 14 days, respectively.

| Test | Mixing time (min) | # 12 | | # 13 | | # 14 | |
|---|---|---|---|---|---|---|---|
| Additives | 4000 rpm | Concentration in (gm) | | | | | |
| KFo Brine (SG1.57) | | 650 | | 650 | | 650 | |
| Soda Ash | 5 | 0.35 | | 0.35 | | 0,35 | |
| Sepiolite I Viscosifier | 5 | 8 | | 8 | | 8 | |
| HPHT dispersant | 5 | 4 | | 4 | | 4 | |
| $Mn_3O_4$ | 10 | 268 | | 268 | | 268 | |
| Mud Weight, ppg | | 16.0 | | 16.0 | | 16.0 | |
| Static heat aged at 218°C | | BSHA | ASHA 7 days | BSHA | ASHA 10 days | BSHA | ASHA 14 days |
| 600 rpm | | 62 | 93 | 62 | 124 | 62 | 130 |
| 300 rpm | | 39 | 68 | 39 | 94 | 39 | 92 |
| 200 rpm | | 31 | 58 | 31 | 81 | 31 | 79 |
| 100 rpm | | 23 | 45 | 23 | 67 | 23 | 63 |
| 6 rpm | | 12 | 25 | 12 | 45 | 12 | 37 |
| 3 rpm | | 11 | 23 | 11 | 40 | 11 | 34 |
| PV @ 120˚F, cP ( 50 C ) | | 23 | 25 | 23 | 30 | 23 | 38 |
| YP, lb/100ft2 | | 16 | 43 | 16 | 64 | 16 | 54 |
| 10 sec Gel, lb/100ft2 | | 18 | 20 | 18 | 25 | 18 | 26 |
| 10 min Gel, lb/100ft2 | | 21 | 21 | 21 | 26 | 21 | 26 |
| pH | | 9,00 | 12,88 | 9,00 | 13,00 | 9,00 | 12,20 |
| Supernatant liquid ( ml ) | | | 0,00 | | 0,00 | | 0,00 |
| Density Top | | | 2,15 | | 1,91 | | 19,80 |
| Density Bottom | | | 2,20 | | 1,95 | | 2,08 |
| Sag Factor | | | 0.506 | | 0.505 | | 0,51 |

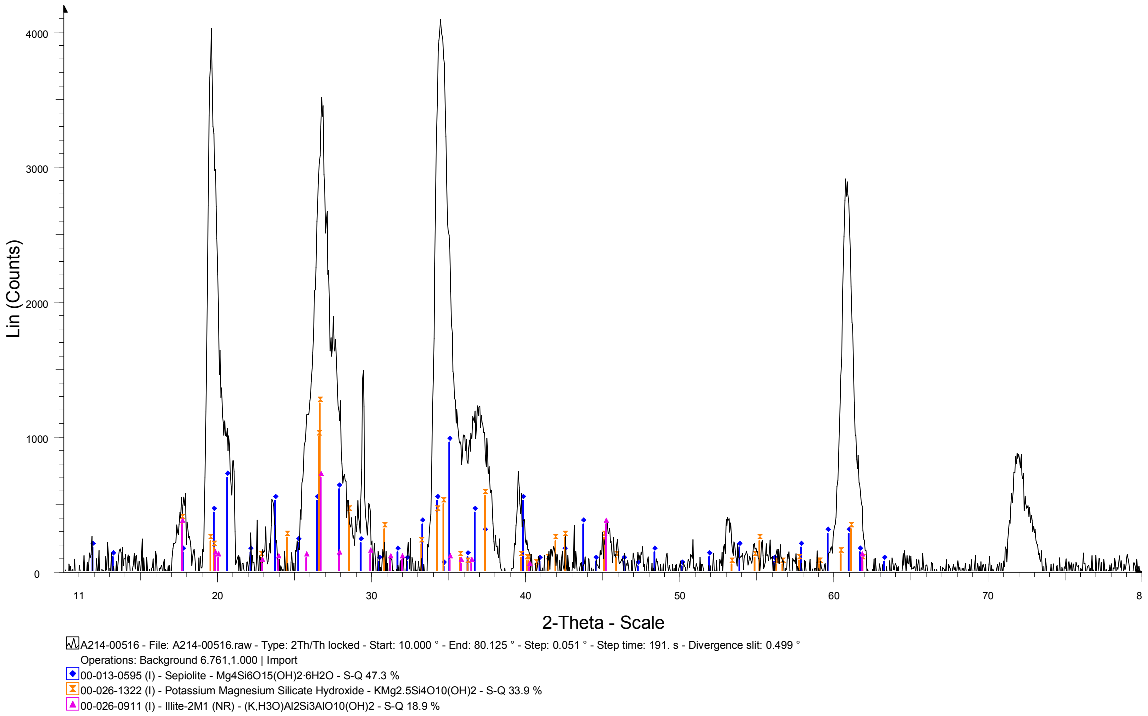

Figure 3. XRD spectrum of 2% sepiolite dispersion in 10 ppg KFo brine. The sample was heat aged at 400°F for 20h.

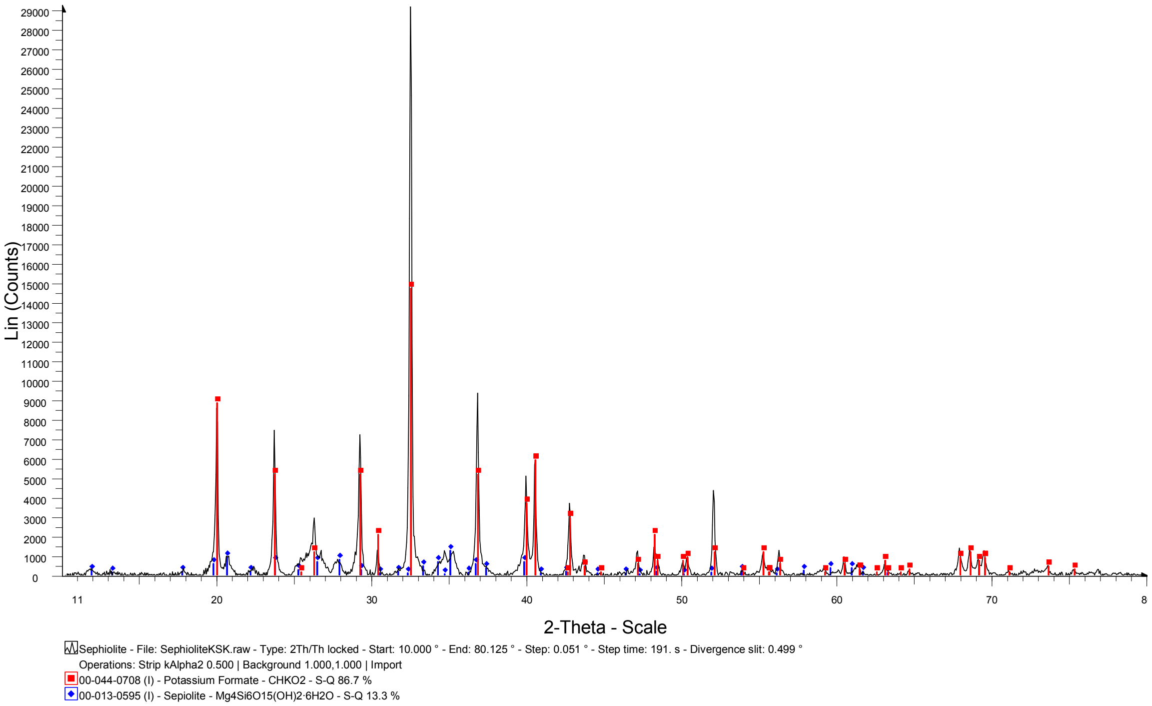

Figure 4. XRD spectrum of 1.6% sepiolite dispersion in 13 ppg KFo brine. The sample was heat aged at 400°F for 72h.

Table 4. Simple fluid to test sepiolite thermal stability in KFo brine after heat aged for 72h at 400°F.

| Chemicals | Conc in gram |
|---|---|
| KFo brine (13ppg) | 600 |
| Sepiolite | 10 |
| Fluid loss additive | 4 |
| Dispersant | 4 |

Table 5. 16 ppg $Mn_3O_4$ / KFo drilling fluid heat aged statically at 425°F for 7, 10 and 14 days, respectively.

| Test | Mixing time (min) | # 15 | | # 16 | | | # 17 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Additives | mass (gm) | Concentration in (gm) | | | | | | | | |
| Water | 0 | 187,5 | | 187,5 | | | 187,5 | | | |
| PAC LV | 5 | 4,0 | | 3,0 | | | 3,0 | | | |
| HPHT terpolymer | 5 | 16,0 | | 16,0 | | | 16,0 | | | |
| Sepiolite | 5 | 6,0 | | 5,0 | | | 5,0 | | | |
| KFo brine 1.57 sg | 5 | 480,0 | | 480,0 | | | 480,0 | | | |
| KFo Powder | 10 | 427,5 | | 427,5 | | | 427,5 | | | |
| $CaCO_3$ (medium, 20µm ) | 5 | 18,8 | | 18,8 | | | 18,8 | | | |
| Soda ash | 5 | 0,0 | | 0,5 | | | 0,5 | | | |
| HPHT dispersant | 2 | 6,0 | | 6,0 | | | 6,0 | | | |
| Mn3O4 | 15 | 437,5 | | 437,5 | | | 437,5 | | | |
| Static heat aging | | BSHA | ASHA 20HRS @ 392 F | BSHA | ASHA 20HRS @ 392 F | ASHA 20HRS @ 420 F | BSHA | ASHA 16HRS @ 392 F | ASHA 30HRS @ 392 F | ASHA 30HRS @ 420 F |
| 600 rpm | | 71 | 59 | 71 | 68 | 53 | 75 | 88 | 117 | 85 |
| 300 rpm | | 41 | 35 | 42 | 40 | 30 | 45 | 50 | 70 | 48 |
| 200 rpm | | 31 | 26 | 33 | 38 | 21 | 32 | 35 | 48 | 35 |
| 100 rpm | | 20 | 16 | 20 | 20 | 12 | 20 | 18 | 24 | 20 |
| 6 rpm | | 6 | 3 | 7 | 5 | 3 | 7 | 4 | 3 | 3 |
| 3 rpm | | 6 | 2 | 6 | 4 | 3 | 6 | 3 | 2 | 2 |
| PV @ 120˚F, cP ( 50 C ) | | 30 | 24 | 29 | 28 | 23 | 30 | 38 | 47 | 37 |
| YP, lb/100ft2 | | 11 | 11 | 13 | 12 | 7 | 15 | 12 | 23 | 11 |
| 10 sec Gel, lb/100ft2 | | 9 | 3 | 5 | 4 | 3 | 6 | 3 | 2 | 3 |
| 10 min Gel, lb/100ft2 | | 15 | 4 | 7 | 7 | 3 | 7 | 4 | 6 | 7 |
| Fluid loss at 150 C (ml) | | 54,0 | 6,0 | 46,0 | 14,0 | 10,0 | 44,0 | 20,0 | 8,0 | 12,0 |
| Filter cake (mm) | | 4,5 | 1,0 | 1,0 | <1 | <1 | 3,0 | <1 | <1 | <1 |
| pH | | 10,3 | 10,9 | 9,3 | 11,5 | 11,9 | 9,1 | 11,3 | 11,4 | 11,5 |

Table 6. 16 ppg $Mn_3O_4$ / KFo drilling fluid heat aged statically at 400°F 40hrs.

| Additives in order of addition | Mixing Time | Concentration | |
|---|---|---|---|
| | min | gm | |
| Water | | 187,5 | 187,5 ml |
| PAC LV | 5 | 3,0 | 1,26 lbm/bbl |
| HPHT terpolymer | 5 | 14,0 | 5,89 lbm/bbl |
| Sepiolite | 5 | 5,0 | 2,1 lbm/bbl |
| KFo brine 1.57 sg | 5 | 480,0 | 306ml |
| KFo Powder | 15 | 427,5 | 179,8 lbm/bbl |
| $CaCO_3$ (medium, 20µm ) | 5 | 18,8 | 7,9 lbm/bbl |
| HPHT dispersant | 5 | 6,0 | 2,5 lbm/bbl |
| $Mn_3O_4$ | 30 | 437,5 | 184 lbm/bbl |
| | | BHR | AHR |
| Heat aging | | Hot rolling 400 F - 40 h | |
| 600 rpm | | 55 | 66 |
| 300 rpm | | 34 | 36 |
| 200 rpm | | 26 | 26 |
| 100 rpm | | 18 | 16 |
| 6 rpm | | 7 | 5 |
| 3 rpm | | 6 | 4 |
| PV @ 120˚F, cP | | 21 | 30 |
| YP, lb/100ft$^2$ | | 13 | 6 |
| 10 sec Gel, lb/100ft$^2$ | | 8 | 5 |
| 10 min Gel, lb/100ft$^2$ | | 10 | 10 |
| Fluid loss at 300F ; ml | | | 8 |
| Filter cake (mm) | | | <1 |
| Density g/ml | | 1,75 | 1,9 |
| pH | | 9,1 | 12,27 |
| Sag number (VSST); ppg | | | 0,25 |

Table 7. Gas measurement of $Mn_3O_4$ / KFo drilling fluid after heat aging for 30hrs at 392 and 420°F.

| Gas | Mn3O4 / KFo Fluid | | | KFo Fluid |
|---|---|---|---|---|
| Vol.% | Ref | 392 °F | 420°F | 420°F |
| N2 | 97 | 95,3 | 94,4 | 89,1 |
| O2 | 1 | 0,5 | 0,7 | 0,9 |
| CO2 | 0 | 0,2 | 0,2 | 1 |
| Ar | 0,1 | 0,1 | 0,1 | 0,1 |
| H2 | 0,5 | 2,5 | 3,3 | 6,2 |
| H2O | 1,5 | 1,5 | 1,4 | 2,4 |

Table 8. Core flooding test of $Mn_3O_4$ / KFo drilling fluid after heat aging for 30hrs at 392 and 420°F at 350°F.

| | Berea sandstone | | Bandera sandstone | |
|---|---|---|---|---|
| | Pressure drop, psi | Permeability, md | Pressure drop, psi | Permeability, md |
| Initial | 31,9 | 82,1 | 71,3 | 22,9 |
| After fluid | 32,8 | 79,9 | 72,2 | 22,7 |
| Return permiability (%) | 97 % | **97 %** | 99 % | **99 %** |

Figure 5. Filter cake (<1mm) of $Mn_3O_4$ in KFo fluid that was heat aged for 30h at 400°F and filtrated statically at 300°F and 500psi.

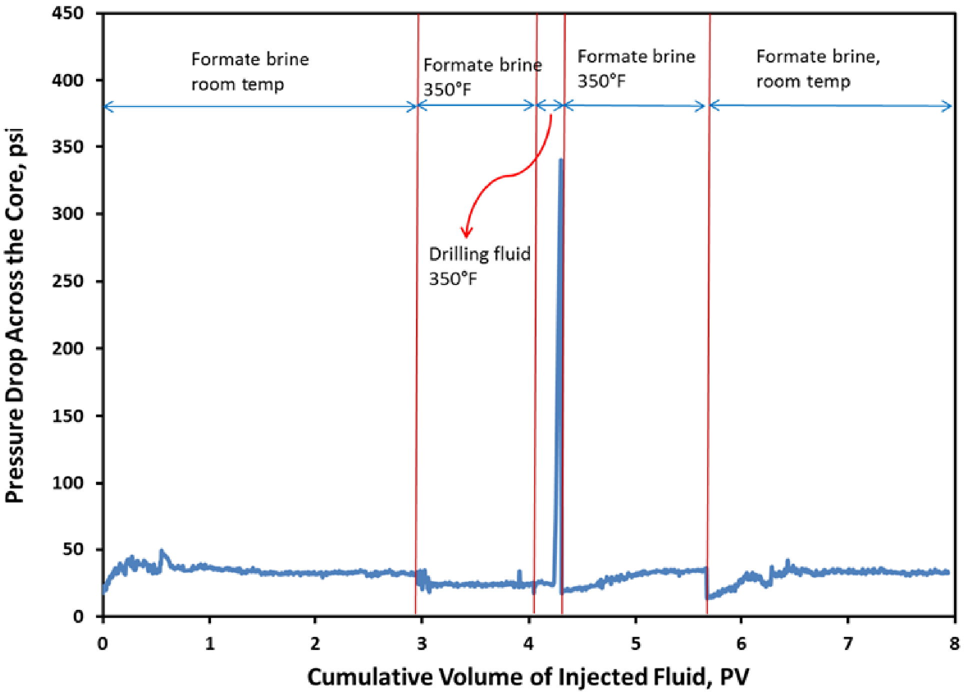

Figure 6. Pressure drop across the Berea sandstone core during core flooding test at 350°F.

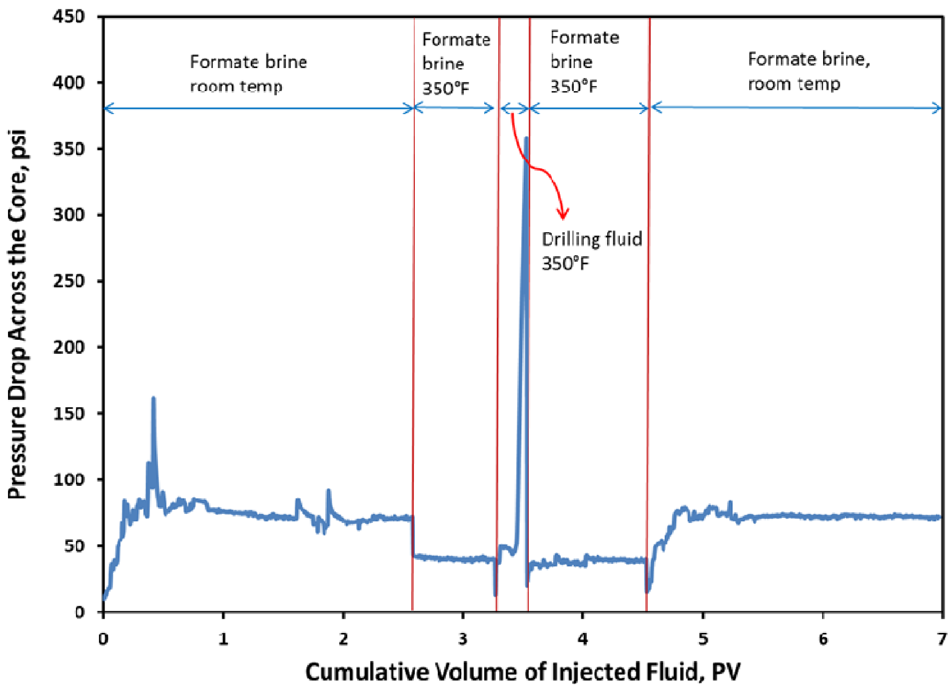

Figure 7. Pressure drop across the Bandrea sandstone core during core flooding test at 350°F.