A NEW TECHNOLOGY THAT DELIVERS LONG-TERM CHEMICAL TREATMENT DURING WELL STIMULATION: ORGANIC DEPOSITS, INORGANIC SCALES, AND CORROSION CONTROL

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ABSTRACT

A new technique of delivering long-lasting treatment for damaging well conditions, such as scales, corrosion, or organic deposits, has been achieved using a novel technology. This new technology involves a viscoelastic, biopolymer-hydrogel as the matrix to incorporate and transport chemicals into the formation. When placed in the fracture length, the porous matrix controls the release of the treatment agent over long period of time. The system is environmentally safe and cost-effective, and designed to be pumped with stimulation fluids during proppant transport. This technology has proven to provide a more efficient delivery, placement, and long-term chemical treatment compared to other existing technologies, where maximum loading of the product is restricted to below 2% of the total proppant.

INTRODUCTION

Scaling and organic deposits are among the most common downhole adverse conditions encountered on a regular basis during the well production. Mixing of incompatible ions dissolved in treatment fluid, formation water, or in the mixed water can form various types of inorganic scales under favorable temperature, pH and pressure.[1, 2] On the other hand temperature and pressure drop can cause organic matters to deposit from crude oil in the near wellbore area in the form of asphaltene, paraffin or both.[3, 4] The most common inorganic scales include carbonate, sulfate, halite, and iron scales. These scale can build up anywhere from downhole perforations to the surface where it constrains production through tubing restrictions, blocked nipples, fish, gas-lift mandrels, and safety valves. Additionally, the presence of bacteria and sour gas can cause pitting and corrosion under the scales.[5] These scales are often layered up and sometimes covered with asphaltene coatings, making it harder to remove. The common remedial action for scale involves an acid treatment, which is normally effective for carbonate scales; however, does not work for barite or halite scales as those are insoluble in HCl or organic acids. On the other hand, removal of organic deposits requires either mechanical means or pumping of hot organic solvent such as xylene or crude oil, which can eventually lead to formation damage. These remedial treatments are not only ineffective sometimes; they are associated with high operational costs, production downtime, and corrosive environment for acid treatments. Therefore, preventive measures as described in this paper provide long-term solutions for inorganic scales and organic deposit problems downhole.

The short term prevention of scale, paraffin or asphaltene includes continuous injection of an inhibitor downhole or a squeeze treatment down the annulus or through coiled tubing or packers. These treatments are costly and only effective in near wellbore area without reaching deeper in the formation. Moreover, achieving the desired outcomes is more difficult in the remote locations and offshore wells. To attain a longer effective treatment period, several methods have been developed and tested over the years with decent success. These systems are mainly associated with liquid inhibitor chemicals being adsorbed or soaked on a porous solid surface, such as ceramic proppant[6] or diatomaceous earth,[7, 8] and placed in the proppant-pack along the fracture. However, due to the crush-susceptible nature, the loading of the products is low in order to minimize the conductivity damage in the proppant pack. Additionally, since these systems contain the chemicals on the surface they not only interfere with the fracturing fluid's stability, but a large amount of inhibitors also get spent during the initial placement in the formation making the effective treatment time significantly shorter.[9] To overcome these limitations in order to provide a longer treatment period, a newly developed technology has been employed, where a chemical substance can be embedded within a viscoelastic polymer hydrogel matrix for slow and controlled release.[10] The unique properties of the hydrogel enable both liquid chemicals and solid particles of different sizes to be embedded inside the porous matrix for transporting downhole. The technique makes the system completely inert preventing any early release of the chemicals incorporated inside until it is placed downhole and the well starts producing. As a result, the systems do not interact with the frac fluid or other fluid systems during the operations, even at very high loadings. The viscoelastic matrix enables the system to be crush-resistant under the normal downhole pressure. This allows pumping of higher percentage of products if necessary without affecting the proppant-pack conductivity. The current paper introduces several products developed using the aforementioned technology to address scale, organic deposits, and corrosion problems downhole as a long-term solution. The laboratory evaluation and efficacy of these treatment agents will be discussed here.

EXPERIMENTAL PROCEDURES

Standard, commercially available chemicals were used for majority of our studies. A water-based solvent package is used for all of our slurries. The commercially available chemicals and additives consists of the scale, corrosion and the paraffin/asphaltene inhibitors, borate crosslinkers, anti-foaming agent, surfactants, biocides, and clay stabilizers. Commonly used breakers in the industry were applied to break the frac fluid gels at the relevant temperatures.

Viscosity measurements were conducted using standard Grace 5600 and Brookfield PVS Rheometers at 100 s^{-1} constant shear rate. Fluid viscosities were measured at the respective temperatures at 300 psi unless noted otherwise. The fluid was subjected to a shear ramp every 15 minutes of decreasing shear rate of respectively 75, 50, and 25 s^{-1} followed by a shear ramp of increasing shear rate of 50, 75 and 100 s^{-1}.

The compatibility tests of the spheres with different brine, crude oil and acid solutions were performed at 150 °F in a water bath over a specified time period as applicable. The static release tests were performed at 150-200 °F in an aqueous medium for the scale product, and in an organic solvent for the oil-soluble paraffin/asphaltene inhibitor. A proppant pack flow test method was used in order to simulate the release of the scale inhibitor under the dynamic downhole conditions at 150 °F.[10] The release of the inhibitors and the residual concentrations were measured using a HACH spectrophotometer.

The proppant-pack conductivity tests were done at a 3rd party lab. Tests were conducted at 150 °F for 50 hours at 2000, 4000, 6000, and 8000 psi closure stresses using Ohio Sandstone conductivity cells and 30/50 mesh ceramic proppant. In-home returned permeability measurements were obtained using a core-flow apparatus equipped with Heise PM Indicator, dual 1000 psi transducers, a Quizix pump, an Acuflow Series IV HPLC pump, and an AND GX6100 scale. The core holder was purchased from Phoenix Instruments. Sandstone cores of 3-inch length and 1.5-inch diameter were used for the experiments. An overburden pressure of 1000 psi and a back pressure of 200-500 psi were applied on the core for all tests and initial and final permeabilities of the core were measured using 6% ammonium chloride (NH_4Cl) brine.

RESULTS AND DISCUSSIONS

The current technology is applicable for fracturing, frac-packing, and gravel-pack applications where proppant is transported downhole with a gelled fluid. The inhibitor systems are designed to be delivered with proppant in the gelled fluid. During a fracturing application this process enables the treatment agent(s) to be placed in the proppant pack deep into the formation for multi-year protection. The scale inhibitor system comprises a sparingly water-soluble solid, which is highly effective against common inorganic scales, such as calcite, barite, and gypsum in a very low concentration, with MIC (minimum inhibitor concentration) of ~ 1-5 ppm. The presence of the scale inhibitor can be easily monitored by measuring residual phosphate ion concentration in the produced water.

The paraffin inhibitor system is composed of an oil-soluble, water-dispersible liquid inhibitor, which prevents both paraffin and asphaltene deposition in medium to heavy crude oils at a very low concentration (MIC ~120-240 ppm). The corrosion inhibitor system contains a high flash-point oil soluble and water dispersible product, which acts as a scavenger for carbon dioxide and hydrogen sulfide (CO_2 and H_2S). In all of these systems, the chemicals are embedded in the spherically-shaped gel matrix, which is also suitable for deep-water gravel pack and frac-pack operations. The inhibitor spheres are suspended in a water-based slurry in ~60 wt% loading for the operational simplicity. Since these systems do not interact with each other or with the frac fluid, they can be pumped at the same time at the desired volume.

Stability and Compatibility Studies

The inhibitor systems, both as solid and in the slurried form, were examined for chemical incompatibilities with the fracturing fluids and other common additives pumped during stimulation and completion of the wells. These spheres are inert in nature and do not alter the pH of a fluid. The inhibitor systems are stable and compatible with common brines, crude oil, and acids. The inhibitor spheres do not have any effect on the rheology of a frac fluid irrespective of quantity added. **Figure 1** shows that the properties of a crosslinked fracturing fluid remained unchanged, even in the presence of a high loading of the scale inhibitor spheres (SI-sphere), where as much as 7 wt% of SI to total proppant added to the fluid. Additionally, no change in the break profile was observed in presence of the SI-sphere. The paraffin (PI-sphere) and corrosion inhibitor (CI-sphere) systems exhibit similar results. As shown in **Figure 2**, they do not alter the fluid rheology when added separately or mixed together in the same fluid.

Conductivity Studies

Proppant-pack conductivity tests were performed to evaluate whether the inhibitor-spheres would adversely affect the conductive channel of the proppant pack during production. Studies were done with 2%, 5% and 7 wt% of the spheres compared to the total proppant. Tests were conducted at 150 °F for 50 hours at 2000, 4000, 6000, and 8000 psi closure stresses. The conductivity and permeability results at 6000 and 8000 psi applied pressures are summarized in **Table 1**. No noticeable damage was observed, even at the 7% loading of the inhibitor. The spheres, which were subjected to 8000 psi stress, were recovered from the conductivity cell after the test and analyzed under the microscope. No visible deformities or crushing was detected, as shown in **Figure 3**. Core-flow experiments were also conducted in the lab with the slurried SI-sphere to determine whether the product causes any formation damage when pumped with the frac fluid. In presence of up to ~60 gpt of slurry, as much as 80% returned perm was obtained using the regular breaker loadings.

Release of the Inhibitors and Treatment Life

The release of the scale inhibitor from the matrix was studied under both dynamic and static conditions. **Figure 4** displays the comparison of the release of the live vs. embedded SI-spheres under the dynamic conditions 150 °F. The release of the equivalent amount of SI placed in a proppant pack, either live or as matrix-bound form, was measured up to 6 weeks in the lab. The inhibitor concentration vs. pore volume is plotted in the graph. As evident from the results, the life of the treatment agent in the produced water samples is significantly extended, by at least 3 folds, when the SI is entrapped within the porous gel matrix. The free scale inhibitor itself has shown to be efficient for scale control up to a year at a loading of 1% of the total proppant pumped. The initial release of the inhibitor decreases considerably when bound in the matrix, thus allowing it to be active for a much longer period of time. The results clearly indicate that by adopting this technology, the initial loss of the inhibitors can be reduced significantly during the proppant transport and placement stages.

Similar results were observed when the release tests were conducted under the static conditions. Different amount of the solid scale inhibitors were suspended in water and the samples were kept at 150 °F in a water bath for the duration of the tests. The dissolved inhibitor concentration was then measured by spectrophotometry over a time period. The release rate of the inhibitor from the SI-sphere is also compared with that of a competitive product. The static release profile of the SI-sphere at different loadings compared to the current product in the market is shown in **Figure 5**. The release of the inhibitor is significantly lower at the early stage for the sphere samples and the discharge is controlled over the time period, whereas the competitive product releases most of the chemicals at the beginning of the test.

Static release profile, as shown in **Figure 6**, is obtained for the PI-spheres. The release of the oil-soluble inhibitor chemical was studied in an organic solvent and measured photometrically. Since the inhibitor is a water-insoluble chemical, no release of the active agent is expected during proppant pack placement until the well starts producing oil. This ensures long term treatment of medium to heavy crude oils with potential to deposit paraffin and asphaltene solids downhole.

Efficacy of the Products

The efficacy of the SI-spheres against various inorganic scales was examined with the produced water samples obtained in the dynamic release test. As illustrated in **Figure 7a**, the blank sample formed calcium sulfate ($CaSO_4$) scales in absence of a scale inhibitor. In comparison, the produced water samples from the proppant pack prevented any scale formation under the same conditions (**Figure 7b**). Similar efficiency was also proven against the barium sulfate ($BaSO_4$) and calcium carbonate ($CaCO_3$) scales.

The efficacy of the PI-spheres was also tested against various competitive products with a heavy Gulf-of-Mexico (GOM) crude oil (Figure 8). The data in **Figure 8** clearly shows that the PI-spheres were most effective at inhibiting paraffin solids formation in the heavy GOM crude oil by lowering the crude oil viscosity at different temperatures. The CI-spheres are designed to scavenge carbon dioxide and hydrogen sulfide gases in low-to-high temperature wells and currently under laboratory evaluation.

CONCLUSIONS

A unique, bio-degradable, biopolymer was used as a substrate to deliver long-term treatment downhole for various adverse conditions. The scope of this technology, however, is not limited to just delivering inhibitors downhole. Various type of materials, both in solid or in solution forms, can be transported into the well by this technology. Under the current scope, this paper describes the application of this technology to protect the well from different downhole conditions, including common scales, asphaltene, paraffin or corrosions for an extended period of time. Several inhibitors were developed by incorporating the chemical agents onto the polymer matrix for controlled release. The laboratory studies demonstrated that this approach extends the life of the treatment considerably, potentially providing multi-year protection against common downhole organic and inorganic deposits for flow assurance. The new inhibitor systems were shown to be completely compatible with all stimulation chemicals. The unique nature of the matrix makes it resistant to crush resulting in minimal damage to the proppant pack productivity. The matrix is completely bio-degradable and can be removed from the formation if needed. The mechanical and structural properties of the matrix allow it to shape differently, such as capsules, sheets, or strips and can be used in different applications. Development of such products is currently being researched.

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Table 1**-** Summary of the conductivity results at 6000 and 8000 psi closure stress

Loading	Time (Hrs)	Stress (psi)	Conductivity (mD-ft) % Regain	Perm (D) % Regain	Stress (psi)	Conductivity (mD-ft) % Regain	Perm (D) % Regain
Blank	50	6000	**95.94**	**96.24**	8000	**89.36**	**89.91**
2% SI	50	6000	**96.47**	**96.30**	8000	**87.51**	**88.89**
5% SI	50	6000	**91.51**	**92.37**	8000	**85.78**	**88.31**
7% SI	50	6000	**92.11**	**93.64**	8000	**85.85**	**87.50**

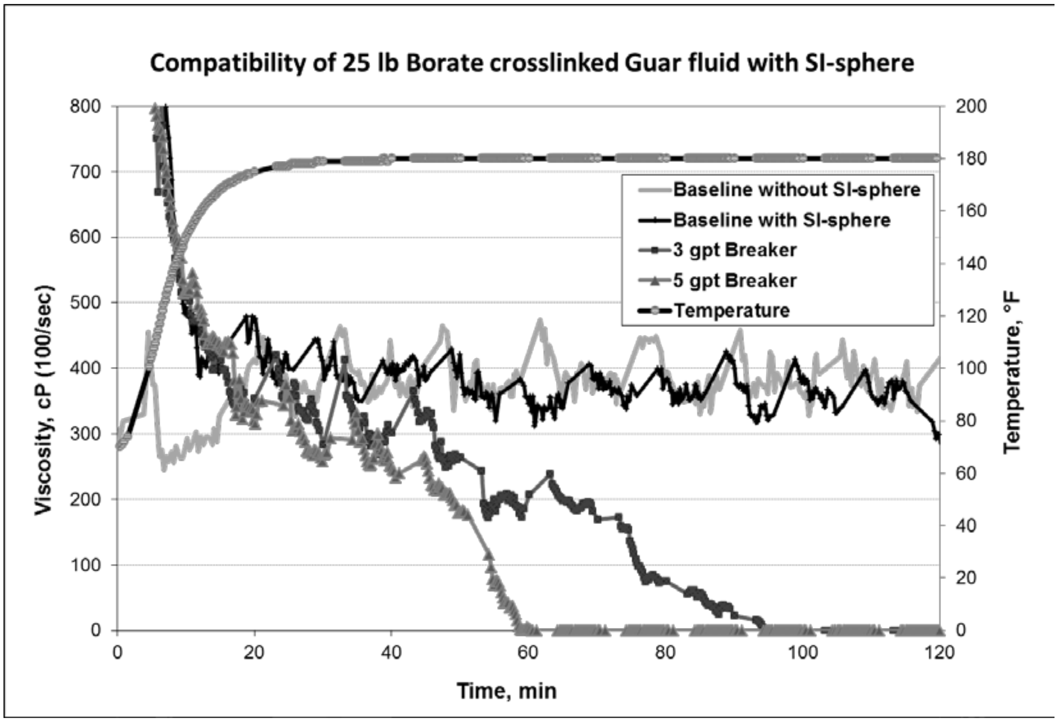

Figure 1- Compatibility studies of the SI-sphere with cross-linked guar fluid

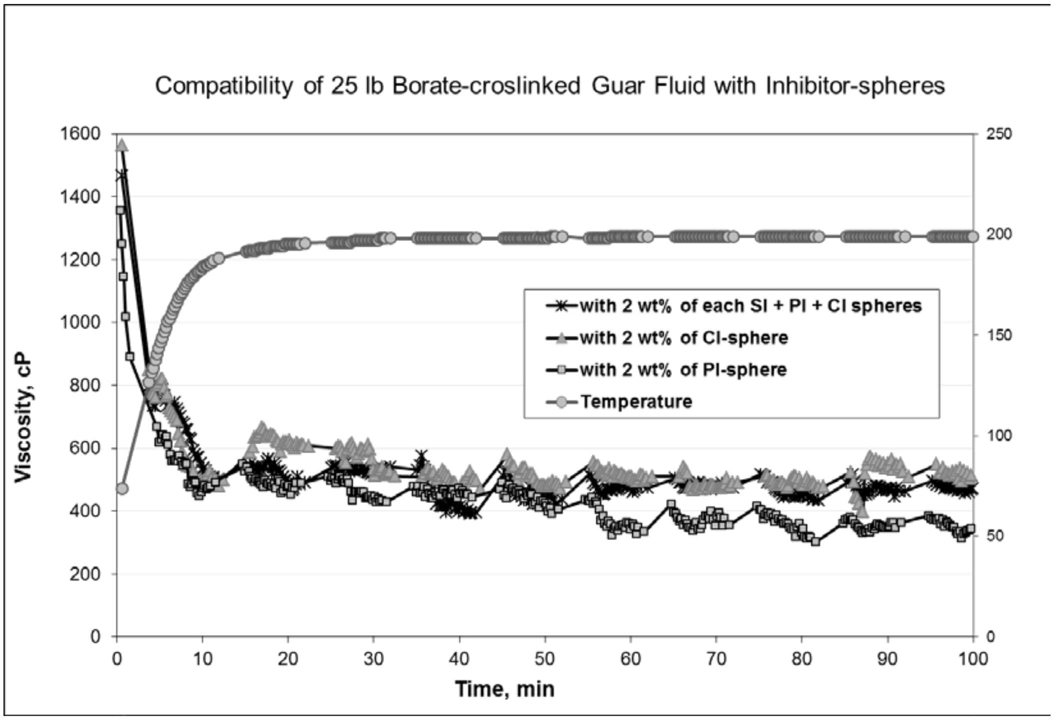

Figure 2- Compatibility studies of the inhibitor-sphere with cross-linked guar fluid

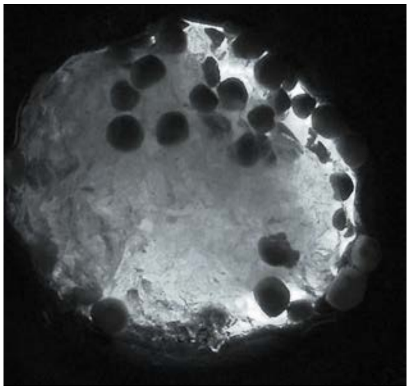

Figure 3- Photomicrograph of an SI-sphere (20x) post-conductivity test at 8000 psi closure stress

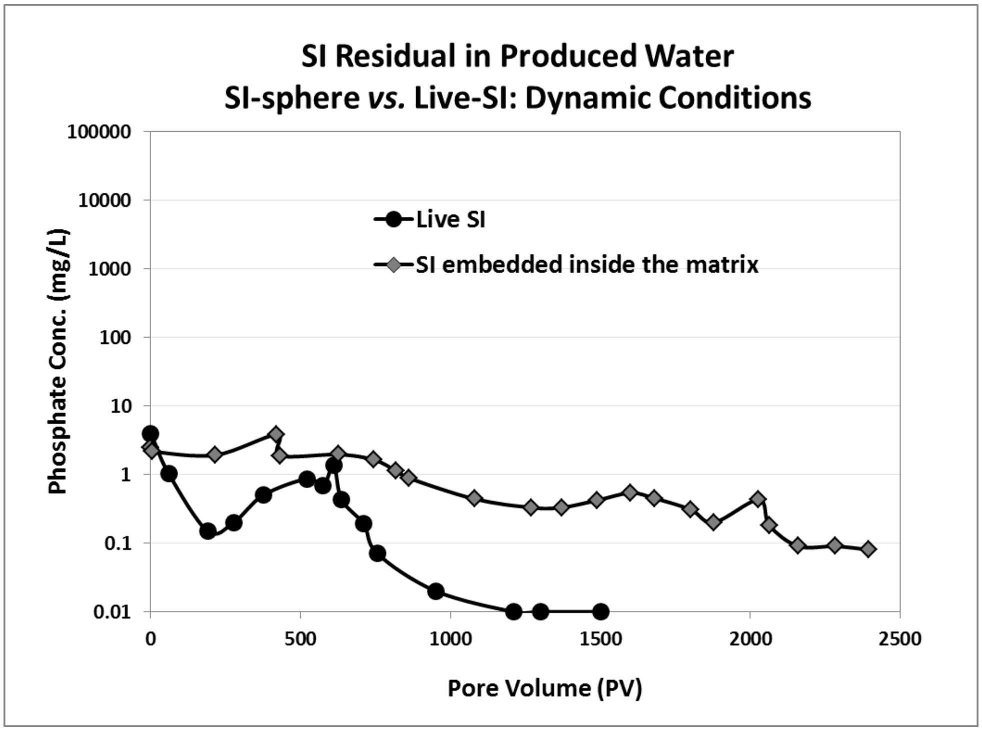

Figure 4- Residual inhibitor concentration in the produced water during the dynamic test-setup

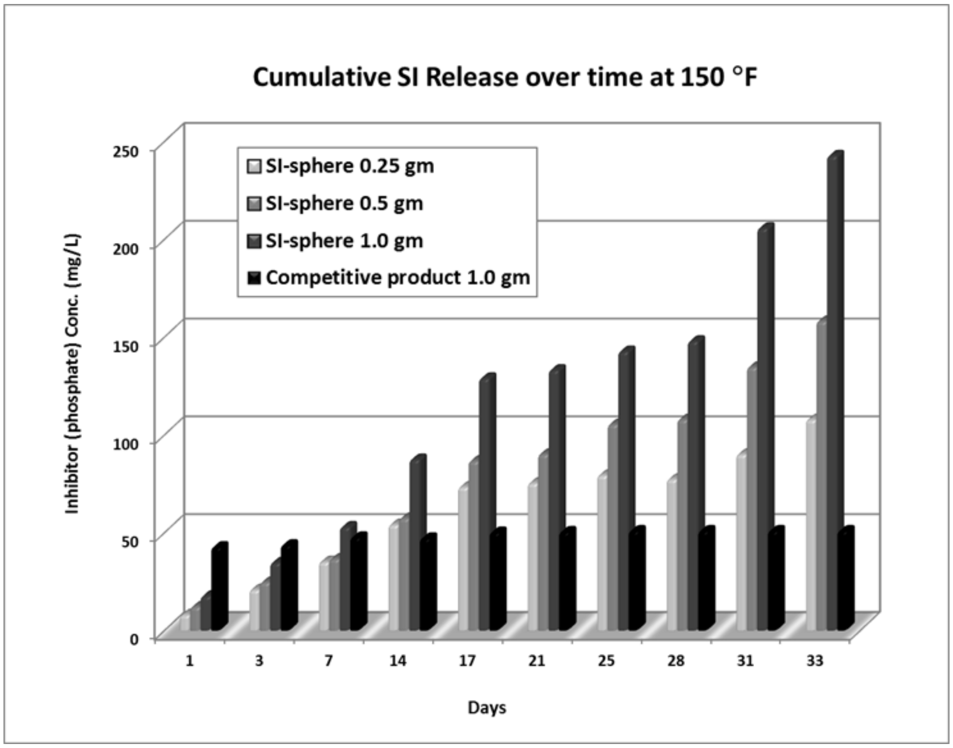

Figure 5- Scale inhibitor release over time under static conditions

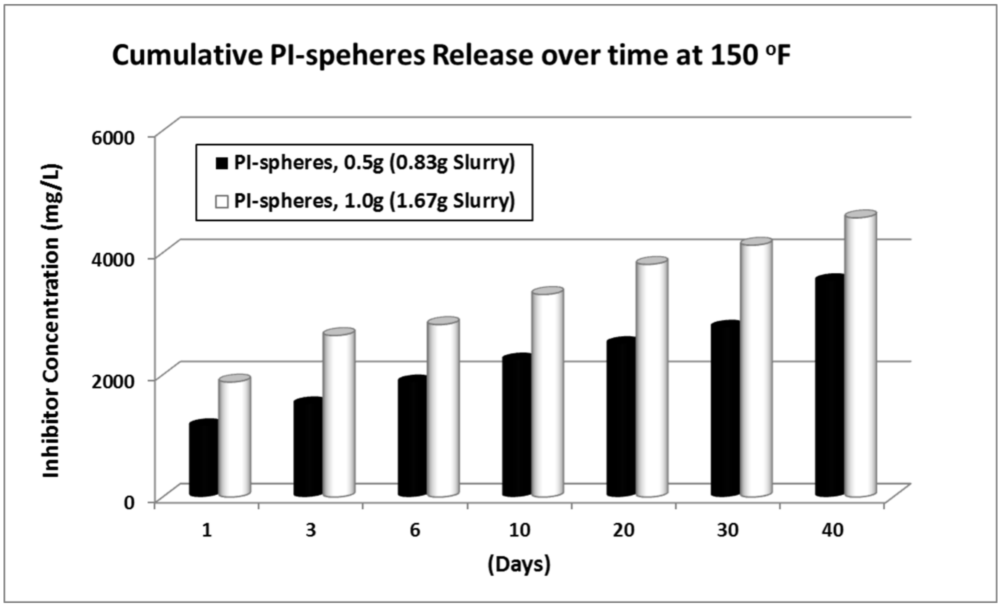

Figure 6- Paraffin inhibitor release over time under static conditions

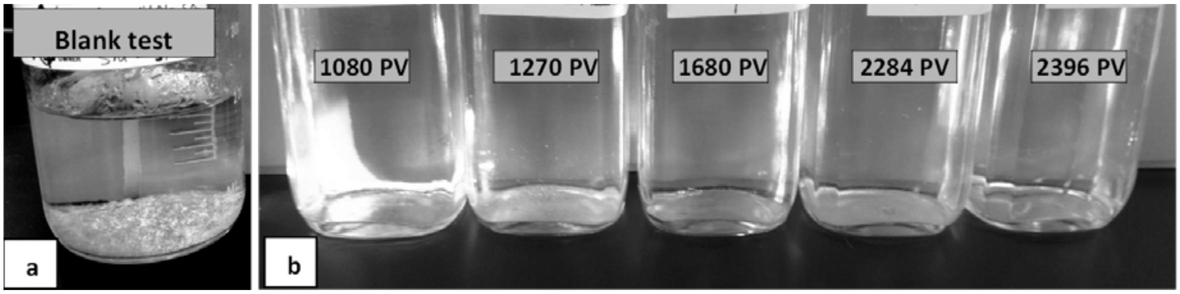

Figure 7- $CaSO_4$ scale inhibition studies with the effluent samples from the proppant pack flow test

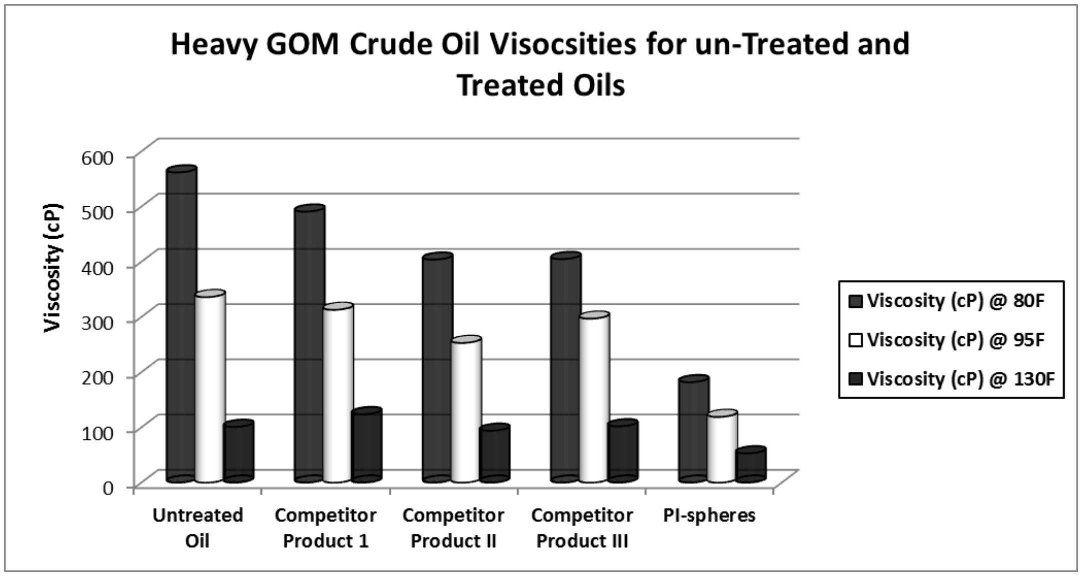

Figure 8- Efficacy of the PI-sphere in lowering the viscosity of crude oil vs. other commercial products