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Chemical Process for Improved Oil Recovery From Bakken Shale

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Abstract

There is a new chemical improved oil recovery (IOR) process for Bakken reservoirs. In this concept a custom surfactant agent may be incorporated into standard hydraulic fracturing treatments for the Bakken to increase oil recovery. These are reservoirs from the Late Devonian to Early Mississippian age occupying about 200,000 square miles (520,000 km²) of the subsurface of the Williston Basin, covering parts of Montana, North Dakota, and Saskatchewan. The rock formation consists of three members: Lower shale, Middle dolostone/siltstone, and Upper shale. The shales were deposited in relatively deep marine conditions, and the dolostone/siltstone was deposited as a coastal carbonate during a time of shallower water. The Middle member is the principal oil reservoir, roughly two miles (3.2 km) below the surface. Both the Lower and Upper members are organic-rich marine shales.

The oil in place in the Bakken shale play is very large, with an April 2008 USGS report estimating the amount of technically recoverable oil in the Bakken Formation at 3.0 to 4.3 billion barrels. Production from the Bakken has been limited in the past, but now has become a very active area of development with the widespread advent of drilling horizontal wells and large-volume hydraulic fracturing treatments. One key to the economic production rates of oil from these formations is to create an extensive well-connected fracture system.

Laboratory experiments demonstrate that specialized surfactant formulations will interact with this mixed- to oil-wet low permeability Middle member to produce more oil. Specifically, including such a surfactant chemical formulation in an aqueous phase (e.g. hydraulic fracturing fluids) will promote the spontaneous imbibition of this fluid into the tight matrix and microfractures containing high oil saturation. This promotes expulsion of oil otherwise trapped to migrate into the fracture system and then be produced into the wellbore. Thus including an appropriate surfactant in frac fluids or in other aqueous-based treatment fluids can produce additional oil.

Introduction

The Mississippian-Devonian Bakken Formation is a restricted shallow water carbonate–clastic sequence deposited over the majority of the Williston Basin of Canada and the United States. It consists of three members: Lower (a dark marine shale with a substantial organic content), Middle (mixed carbonates and clastics) and Upper (also a dark marine shale rich in organic content). The Lower and Upper members with their highly organic dark shales serve as both the source and trap for the generated hydrocarbons. The Middle member is the main productive reservoir; it is characterized by relatively low porosity (> 10%) and permeability (typically < 10% and < 1 md) (Lever, 2002). The Bakken Formation overlies the Upper Devonian Three Forks formation, and underlies the Lower Mississippian Lodgepole formation.

Dolostones and siltstones in the Middle member typically consist of fine-grained or smaller matrix-rich rocks that exhibit permeabilities consistent with their grain size and sorting. In some portions of the basin, permeabilities and effective porosities of the Middle member can be moderate (compared to the nanodarcy ranges found in domestic oil and gas shale plays), providing a sink for reservoir fluids that can migrate to it both before and after induced propped fracturing. Most grains are well rounded to rounded, but in lower permeability reservoirs, the finer grained material is subangular or subrounded. Common lithic fragments include detrital carbonate

(limestone and dolomite) grains and deformed mudstone clasts. The matrix in the sandier portions of the Middle Bakken can also contain a variable mix of carbonate mud and allogenic clay (Dunek et. al, 2009).

The production practices in the Bakken have evolved from being vertical to horizontal wells, and from no or simple fracturing methods, to now very large and sophisticated multi-fracture stimulations (Besler et. al., 2009). It is thought that hydraulically stimulating the Middle Bakken member results in the opening of microfractures or naturally occurring planes of weakness in the two shale members above and below, and that if the induced fractures are propped, then these two organically rich members may contribute substantially to production, especially when the shale is reasonably thermally mature (Dunek, et. al., 2009). In many areas of the Bakken the natural fractures that are present can influence significantly the well productivity, fluid leakoff, and pressure dependence (Olsen, et. al., 2009, and Cramer, 2008). One field study to address the role of natural fractures (Mullen et. al., 2010) performed in-situ measurements that identified the presence of “natural fracture swarms” via running an azimuthally-focused resistivity (AFR) tool and azimuthally deep-reading resistivity (ADR) tools as a final wiper trip. This procedure located natural fracture swarms and the variations of rock properties along the 10,000-ft lateral. The goal of this well measurement was to test the concept of improving production by adjusting the horizontal completion so as to connect better these natural fracture systems. The AFR image log identified more than 839 individual fractures in four clusters of fracture. Their evaluation suggests that if the well had been geosteered to remain within the sweet spots the production could have been increased by 20%.

In addition to the low porosity, tight permeability, and fractured characteristics of the Middle Bakken, another common feature is that this producing formation has very light oil (API gravity typically over 40 degrees) that resides in an oil-wet or mixed-wet condition with a high oil saturation of 75-90% (Phillips, 2009). This oil-wet condition makes it difficult for the aqueous phase to penetrate into the matrix and displace the resident oil.

This combination of features of the Bakken Middle member having a light crude oil of high saturation trapped in the matrix due to an oil-wet condition, plus natural and induced fractures suggests a surfactant technology can be employed to recover more of this oil. Specifically, existing technology designed to recover incremental oil from fractured carbonate reservoirs may be adapted for this situation in the Bakken. There have been extensive scientific studies about using surfactants for additional oil recovery in this analogous case where light crude oils are trapped in the relatively tight matrix in oil-wet carbonate fractured reservoirs (Abbasi-Asl, et. al., 2010, Berry, et. al., 2009, Chen, et. al., 2000, Hirasaki, et. al, 2004, Weiss, 2007, Wu, 2008). In fact where the Bakken Middle member lithology has substantial carbonate minerals makes it very much like carbonate cases.

In this technology, aqueous surfactant solutions designed to alter the wettability of the matrix to a water-wet condition are placed in the fracture system. This will cause spontaneous imbibition whereby the aqueous phase penetrates into the matrix by overcoming the capillary forces trapping the oil in place. The oil in the matrix moves in counter flow and goes into the fracture system. Once in the fractures, the oil can be transported easily to the production well. In addition to the theoretical and laboratory studies cited above, field applications of this surfactant technology have included “huff-puff” single well treatments and also as a pattern-wide treatment where the surfactant is added into an injection water to boost the waterflood oil recovery. (Chen et. al. 2000, Yang, et. al., 2000, Weiss et. al., 2004).

For the Bakken case the best opportunity to deploy a surfactant to promote additional oil recovery is to include this chemical in the fracture fluid package. The technical and economic advantages for this practice include:

- The fracture treatment in the Bakken involves large volumes of water, and so it is a routine means to fill the fracture system in the wellbore area with an aqueous surfactant system.
- The surfactant will capture additional oil from the matrix/microfractures; it may also promote better connectivity of the natural and induced fracture system
- These Bakken fracture treatments are expensive; the incremental cost of including an oil recovery surfactant is only that material cost. Thus adding a low dose of effective surfactant (about 0.1%) will increase the total job cost by only a small percentage.
- The oil recovery surfactant may serve as also a flow back chemical; a second surfactant may not be required in the fracture fluid. This would reduce or even eliminate the incremental cost of using this oil recovery surfactant chemical.

This paper presents the results of a laboratory investigation that demonstrates surfactant systems can be designed to penetrate Bakken Middle member rock matrix and release otherwise trapped oil. Study results also show that such surfactant products are suitable as fracture fluid additives and will not cause undesirable side effects such as incompatibility with other frac fluid components or an emulsion problem in the produced fluids.

Experimental

Materials

Crude Oils:

The laboratory testing included two Bakken crude oils. Both Oil A and Oil B are typical light oils from this area, with API gravities of 42.8 and 41.5, respectively.

Chemicals:

Over 15 different chemical formulations were prepared and screened for their ability to recover the subject crude oils from porous media via spontaneous imbibition. The formulations are predominantly different combinations of non-ionic and/or anionic surfactants. The candidate surfactant products are winterized in order to be suitable for the cold climate associated with the Bakken area.

Core Material:

Initial testing for oil recovery focused on outcrop samples of limestone (Texas Crème). These outcrop cores measure 1-inch diameter and 2-inches in length. These may be purchased from service company suppliers. The air permeability of these limestone cores average near 5 md and range from 2 – 10 md.

The study included two small cores from the Middle member of a Bakken shale reservoir (size approximately 1.5-inch diameter by ½ inch thickness). Both of these are from a depth in excess of 10,000 feet. The properties of these cores are not reported, but are taken from a productive part of the Middle member and would be expected to have permeability less than 1 md.

--- Core 1 Depth 10319.75
--- Core 2 Depth 10451.85

The make-up brine used for these tests is 2 wt% KCl, a common choice for the stimulation fluids.

Screening Chemicals for Solution Properties:

Oil Recovery by Spontaneous Imbibition:

The stepwise procedure to test for oil recovery by spontaneous imbibitions from a core is:

- Prepare a 2 wt% KCl brine solution as a blank sample solution
- Prepare a 2 wt% KCl solutions where add different 0.1 wt% Surfactant Product
- Dry the test cores overnight near 200 °F.
- Measure the dry weight of each core
- Place cores into a vacuum flask
- Have a tube going into the top of the container. Have a separatory funnel connected to this tube leading into the top of the container. Close the stopcock of the funnel.
- Pull a high vacuum on the cores for 3 – 4 hours
- Load crude oil into the funnel
- Stop the vacuum pump
- Slowly open the stopcock of the funnel and introduce enough crude oil to cover the sample cores completely. Close the stopcock.
- Allow the cores to soak in crude oil for 16 – 24 hours. Release the vacuum.
- Remove cores one at a time and allow the surface oil to drain off and reweigh the cores to determine mass of oil loaded into that core
- Load each Amott cell with the oil-saturated core and fill with the aqueous test solution. . .
- NOTE: perform this soaking test in an oven at 185 F.
- Monitor the volume of oil expelled by the core versus time. .

The photographs below (Figure 1 and 2) show an Amott cell with a limestone core. One can see the oil is extracted to the surface of the core, released, and then floats into the burette above to be collected and counted.

The oil recovery experiments are performed at 185 F so as to avoid the necessity of using elevated pressure. The actual reservoir temperature which can be bit higher than the boiling point for water.

Emulsion Tendency and Chemical Compatibility:

Three grams of Oil A was put into a test tube, and 4 grams of 0.1% or 0.5% solution of Surf 1 or Surf 2 also was added. The test tubes were capped and shaken on a shaker machine at high speed (180 strokes/min). After a half hour of shaking, the test tubes are removed from the shaker and the appearance of the fluids was observed versus time.

Chemical Properties:

Surface tensions measurements were performed using the capillary rise method. Interfacial tension (IFT) was measured using a spinning drop tensiometer. The oil/surface interaction is examined by a spot test whereby a drop of diluted chemical solution is placed on a smear of Oil A on a plate. The penetrating power of different chemical solutions may be compared by the resulting appearance of the treated oil area.

Results and Discussion

Oil Recovery Tests

Figure 4 presents the oil recovery response by spontaneous imbibition for 7 of the surfactant systems considered during the screening process. All of the candidates show almost an immediate response, reaching almost the maximum response occurs within one hour of soaking time. There is some spread of results, with oil recovery ranging from about 15% to 60%. In contrast, for the blank sample of 2% KCl brine the oil recovery is seen to be only 3%. Figure 5 demonstrates a similar oil recovery for the best two candidates, Surf 1 and Surf 2, when the limestone cores are loaded with the other crude oil sample, Oil B. The Surf 2 has a slightly better oil response than the Surf 1, the oil recovery curve is very much like that observed for the Oil A in Figure 4.

Figures 6 and 7 show the oil recovery response for the Bakken Middle member core material. For both the case of Oil A in Core 1 (Figure 6) and Oil B in Core 2 (Figure 7) the oil recovery plateaus at approximately 40% recovery and this is attained after roughly 10 hours of soaking time. The somewhat slower response and total oil recovery is most easily explained by the lower permeability of the Bakken material than the outcrop limestone.

Emulsion Tendency and Chemical Compatibility:

The photographs in Figure 8 show the surfactant solution and oil in the test tubes just after removing from the shaker and after standing for 3 minutes of time. The four samples shown side-by-side includes:

1. 0.1% Surf 1 in 2% KCl -- Oil A
2. 0.5% Surf 1 in 2% KCl -- Oil A
3. 0.5% Surf 2 in 2% KCl -- Oil A
4. 0.1% Surf 2 in 2% KCl -- Oil A

As expected, the oil-separation is rapid for both of these very light crude oils and the Surfactant A solutions, even with an excessive surfactant product concentration of 0.5 wt%.

Other companion tests conducted in a service company laboratory demonstrated no significant impact of the best surfactant formulations on the gelation or breaking performance of a common fracture fluid recipe. Also there was observed no noticeable chemical compatibility problems with the other frac fluid additives used for the Bakken.

Chemical Properties:

The results of the surface tension and interfacial tension measurements are summarized in Table 1. The best surfactant formulations Surf 1 and Surf 2 show reduced IFT with the Oil A at the oil recovery experimental conditions. Two other formulations that had somewhat less oil recovery in the imbibition tests, Surf 5 and Surf 7 have a relatively high IFT. The IFT for Oil A and 2% KCl brine is approximately 35 dyne/cm.

The oil spot test indicates good oil penetration and interaction between the best surfactant formulations and the Oil A. Figure 9 indicates the formulation Surf 1 is slightly better than Surf 2. In contrast the 2% KCl alone shows no effect on the film of Oil A.

:

Applications and Implications:

The laboratory results of this investigation indicate that including a customized surfactant product in the fracture fluids can provide spontaneous imbibition and oil expulsion as an additional mechanism for oil recovery. This general concept of improved oil production via combining surfactant and stimulation technology has been proposed before (Tang, 2009a, Tang 2009b). A related topic of flow behavior and imbibition of brines and

surfactant solutions in the Bakken shales is receiving increased interest (Wang, et. al., 2010).

The concept for improved stimulations in unconventional fractured oil reservoirs by increasing imbibition have been recognized previously (Cramer, 2008). For example, for the Austin Chalk it is suggested that water imbibition into that fracture system is one key to success, and further that pump and soak treatments should be effective (Mehan, 1995). Other examples include an interest in this approach for the Niobrara formation (Johnson, 1993).

And as demonstrated here, this oil displacement and recovery by imbibition can be enhanced by the selection of a surfactant system matched to the local reservoir conditions. So the general approach suggested for including surfactants for Bakken fracture treatments should be considered also for other unconventional oil resources.

Conclusions:

- 1.. Customized surfactant formulations developed as oil recovery agents have promising laboratory results for two different Bakken crude oils tested in low permeability limestone and Bakken core material.
- 2., Fast and significant oil recovery by spontaneous imbibition is observed in both outcrop Texas Crème limestone cores and from Bakken reservoir cores.
3. The best surfactant formulations found in this laboratory study are compatible with a common fracture fluid system, Also these chemicals do not exhibit any significant emulsion tendency when mixed with Bakken oil.
4. The literature indicates adding surfactant systems tuned to conditions representative of the Bakken should increase oil recovery of fracture stimulations performed in the Middle member..

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Unit Conversions

| | | | | | | | |
|-----|--------------------|---------------------|-------------------|-------|-------|------------------|------------------|
| API | 141.5/(131.5 + AI) | = g/cm ³ | bbl | 1.589 | E-01 | = m ³ | |
| ft | 3.048 | E-01 | = m | gal | 3.785 | E-03 | = m ³ |
| md | 9.869 | E-04 | = μm ² | | | | |

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Table 1. Surface Tension and Interfacial Tension of Surfactant Solutions

| Surfactant ⁽¹⁾ | Make-Up Water | Surface Tension (dyne/cm) | Oil | Interfacial Tension (dyne/cm) |
|----------------------------------|----------------------|--------------------------------------|------------|--|
| 1 | Distilled | 33.2 | | |
| 1 | 2% KCl | 32.8 | A | 0.12 |
| 2 | Distilled | 35.6 | | |
| 2 | 2% KCl | 34.1 | A | 0.012 |
| 3 | 2% KCl | 35.2 | A | > 5 |
| 7 | 2% KCl | 33.5 | A | > 5 |

(1) Surfactant concentration 0.1 wt%

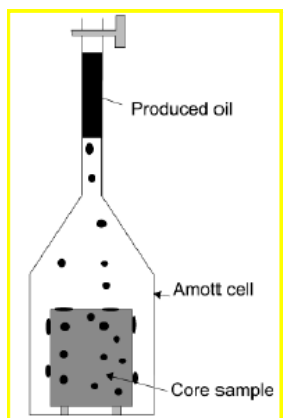


Figure 1. Diagram of Amott Cell



Figure 2. Close up of a core in an Amott Cell. Oil drops are seen on core surface.



Figure 3. Comparison of response of oil produced by different surfactant solutions

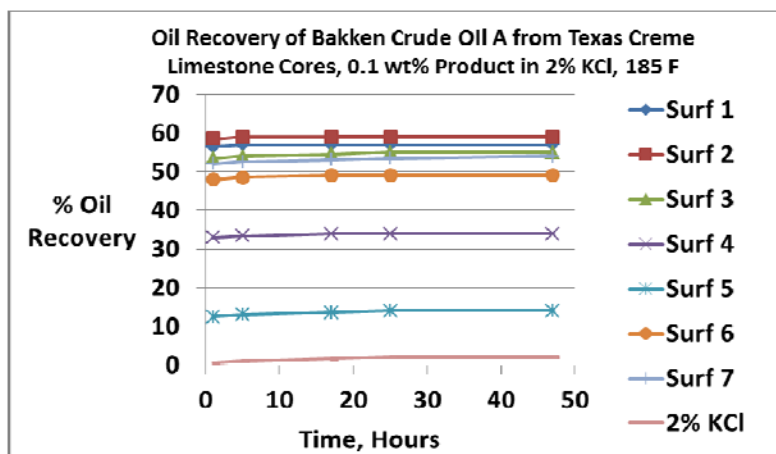


Figure 4. Imbibition recovery of Oil A by different surfactant solutions from limestone cores

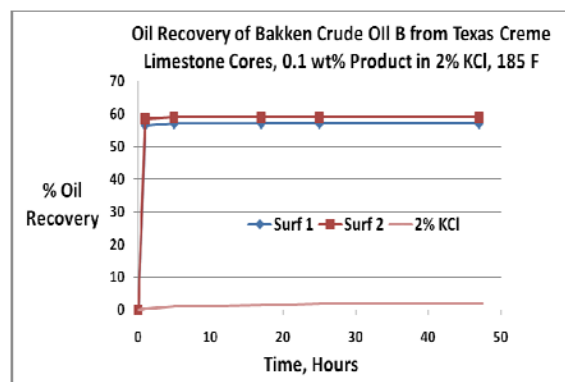


Figure 5. Imbibition recovery of Oil B by different surfactant solutions from limestone cores.

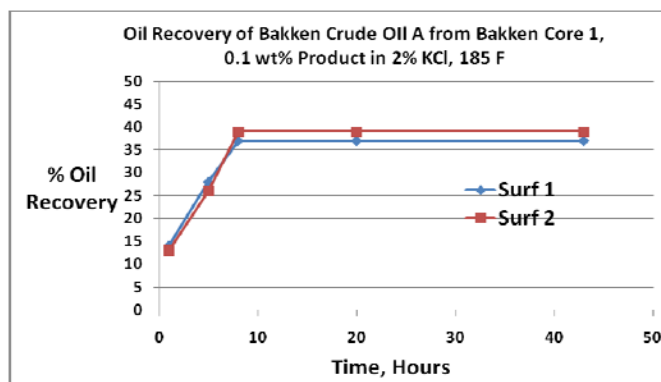


Figure 6. Imbibition recovery of Oil A by different surfactant systems from Bakken core.

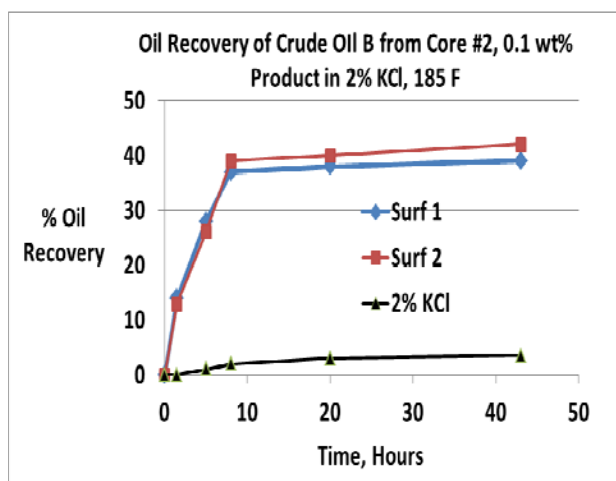


Figure 7. Imbibition recovery of Oil B by different

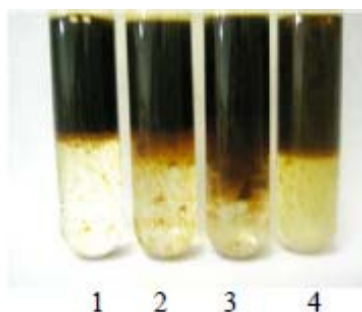


Figure 8a. Fluid separation. Test tubes immediately after shaking.

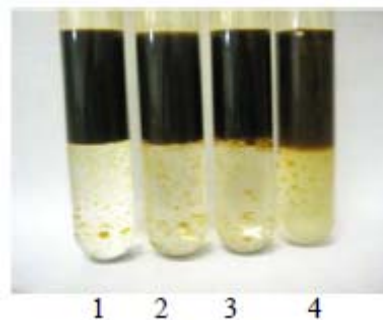


Figure 8b. Fluid separation. Three minutes settling after shaking.

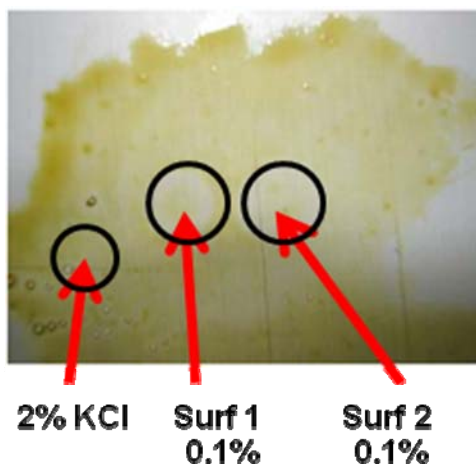


Figure 9. Comparison of interaction of a 2% KCl solution and 0.1% Surf 1 and 0.1% Surf 2 solutions in 2% KCl with an Oil A film on a plate