A NEW METHOD FOR ACID STIMULATION WITHOUT INCREASING WATER PRODUCTION: CASE STUDIES FROM OFFSHORE MEXICO

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ABSTRACT

Successful acid stimulation requires a method to distribute the acid between multiple hydrocarbon zones. Since almost all producing wells are inhomogeneous, containing sections of varying permeability, this can be a huge problem. In addition, the water saturation of the various zones plays an important role. Since acid is an aqueous fluid, it will tend to predominantly enter the zones with the highest water saturation. These water zones are also often the highest permeability zones, so acid stimulation will often result in large increases in water production. There are many negative aspects to increased water production, such as increased lifting and disposal costs, increased corrosion, etc. This paper describes the use of a new low viscosity system that inherently reduces formation permeability to water with little effect on hydrocarbon permeability, and also diverts acid from high permeability zones to lower permeability zones.

This new system has been used in offshore Mexico in the Chuc, Caan, and Pol fields among others over the past year. During this time, over 30 wells have been treated with the new system. Most standard acid treatments in this field result in increased hydrocarbon and water production. The new system has resulted in increased hydrocarbon production with no increase in water production, and in some cases a decrease in water production. Details from several of these jobs will be presented showing the diversion and production results.

INTRODUCTION

In matrix-acidizing treatments, the acid tends to predominantly enter the highest-permeability layers and bypass the most damaged (lower-permeability) layers. In some cases, high-permeability layers are also predominantly water-bearing, thus acid also mainly enters those zones. In some cases, the acid may also break into a nearby water-bearing zone.

In attempts to achieve uniform placement of acid across all layers, various placement techniques have been used.¹ The most reliable method uses mechanical isolation devices (such as straddle packers) that allow injection into individual zones one at a time until the entire interval is treated. However, this technique is often not practical, cost-effective, or feasible. Without a packer, some type of diverting agent must be used.

Typical diverting agents include ball sealers, degradable particulates, viscous fluids, and foams. Although these agents have been used successfully, all have potential disadvantages and none address the problem of increased water production that often follows acid treatments. Therefore, it would be a major advantage to have a material that could inherently decrease the formation permeability to water while also providing diversion.

One method of controlling water production uses dilute polymer solutions to decrease the effective permeability to water more than to oil. These treatments may be referred to as relative permeability modifiers (RPM), disproportionate-permeability modifiers, or simply, bullhead treatments. The latter name is so called because these treatments can be bullheaded into the formation without the need for zonal isolation. RPM systems are thought to perform by adsorption onto the pore walls of the formation flow paths.²⁻⁴

A previous paper has described the development of an RPM based on a hydrophobically modified, water-soluble polymer (referred to here as an associative polymer, or AP).⁵ This group of polymers was selected for study because their properties can be altered in ways that render them valuable for oilfield applications. Another paper has described a laboratory study of this polymer for use as an acid diverter.⁶

ASSOCIATIVE POLYMER PROPERTIES

The solution properties (such as rheology and viscosity) of both ionic and nonionic, water-soluble polymers are uniquely modified when hydrophobic groups are introduced into the polymer chains.⁷⁻⁸ The primary factor responsible for the property modification is the associative tendency between the hydrophobic groups when placed in aqueous medium. Previous testing has shown a unique shear thickening phenomena for the AP utilized in the current work. However, the solutions used in diversion operations show very low viscosity (<2 cp) at surface conditions.⁶

The adsorption behavior of hydrophilic water-soluble polymers can also be modified in a unique manner by the introduction of hydrophobic groups. Rather than reaching a plateau adsorption, as is common for hydrophilic polymers, hydrophobic modification appears to produce a continued growth in adsorption with increased polymer concentration. This behavior is attributed to associative adsorption of polymer chains on previously adsorbed layers of polymers.⁹ **Figure 1** illustrates the adsorption of a non-modified and a modified polymer onto a surface. In general, hydrophobic modification of water-soluble polymers adds new properties while retaining features typical for hydrophilic polymers.

Viscosified, or foamed, fluids commonly used for acid diversion can result in high friction pressure and require special manifolding and/or pumping equipment. The low viscosity of the AP diverting system results in ease of mixing, low friction pressures, no special manifolding or pump requirements, etc. The diversion of aqueous fluids occurs only after the material enters the porous media, whether it is naturally fractured carbonate/dolomitic rock or sandstone matrix. It is theorized that the increased shear encountered upon entering the rock matrix, coupled with polymer adsorption, results in an apparent "viscosity" increase that may be responsible for the pressure increases seen during the treatment.

EXPERIMENTAL PROCEDURES

Acid diversion tests were run utilizing standard Hassler sleeves. For each test, one core each was taken to residual oil saturation (water core) or residual water saturation (oil core) and initial permeabilities were measured. The cores were then connected such that the treatment sequence could be bullheaded, allowing the treatment to flow through either core. An ammonium chloride spacer was pumped between the AP treatment and the acid. For the AP treatment and ammonium chloride spacer, a limit of 500 mL or 500 psi differential pressure was used, and in all tests the 500 psi limit was reached prior to pumping 500 mL. For the acid stage (5% HCl), the limit was 200 mL or 500 psi, and in each case 200 mL was pumped without reaching the 500 psi limit. In the final stage, the cores were disconnected and final permeabilities were measured.

ACID DIVERSION TESTING

Laboratory testing indicated that the modified polymer could effectively reduce permeability to water with little damage to oil.⁵ Testing was then begun to determine whether the polymer would be effective in diverting acid treatments. Parallel core testing was used; polymer and acid were bullheaded into both a water-saturated core and an oil-saturated core simultaneously. This testing has been previously described in detail,⁶ and is summarized below.

Test 1 Series: Sandstone Cores Treated Separately

The initial experiments involved a relatively high-permeability sandstone core (at residual oil saturation to represent a water-bearing stratum) and a lower-permeability Berea sandstone core (at residual water saturation to represent an oil-bearing stratum). In these control tests, 13 pore volumes (PV) of 5% HCl was pumped through each of these cores separately. Each test resulted in more than a two-fold increase in permeability, demonstrating that these cores were stimulated by the acid treatment.

Test 2 Series: Sandstone Cores Treated Simultaneously

The second test series again used a high-permeability core at residual oil saturation and a lower-permeability core at residual water saturation. However, in this case, the cores were connected in parallel so that the treatment fluid could be bullheaded into both cores simultaneously. The test temperature was 175°F. The treatment consisted of a 2,000-ppm AP solution. The volume of treatment entering the water core was 9 PV, and 0.8 PV entered the oil core before the 500-psi pressure limitation was obtained. The fluid was flushed out of the lines and a spacer of 5% ammonium chloride was pumped into the parallel core flow apparatus. All of the spacer was observed to enter the oil core (only 0.4 PV entered the core before reaching the 500-psi pressure limit). After flushing the spacer from the lines, a 5% HCl solution was pumped into the parallel treatment apparatus.

From a total 13 PV of acid, 11 PV entered the oil core and 2 PV entered the water core. The water core percent permeability reduction was 96.5% while the oil core gave over a two-fold increase in permeability (essentially the same as observed in the control test with the oil core). Thus, the AP not only effectively diverted the acid from the water core to the oil core, it also very effectively decreased the permeability of the water core while allowing stimulation of the oil core.

Test 3 Series: Berea Cores Treated Simultaneously

A third test series used two Berea cores, one at residual-oil saturation and one at residual-water saturation. Again, the cores were connected so that treatment fluids could be bullheaded and the test temperature was 175°F. A 2,000-ppm AP solution was bullheaded into the cores. The water core received 1 PV of the treatment while 0.8 PV entered the oil core before the 500-psi pressure limitation. After flushing the lines of the AP fluid, a spacer of 5% ammonium chloride followed; 0.1 PV entered the water core and 0.2 PV entered the oil core.

From a total 13 PV of 5% HCl, 10 PV entered the oil core and 3 PV entered the water core. The water core percent permeability reduction was 56% while the oil core again showed an increase in permeability.

Test 4 Series: Carbonate Cores Treated Simultaneously

Previous testing focused on sandstone lithology; the fourth test series used two Bedford limestone (carbonate) cores, one at residual-oil saturation and one at residual-water saturation. Again, the cores were connected so that treatment fluids could be bullheaded and the test temperature was 175°F. In this test series, a control test was run in which acid alone was bullheaded into the two cores. In this test, 14 PV of 5% HCl entered the water core and 6 PV entered the oil core. In the next test a 2,000-ppm solution of AP was bullheaded into the two cores. Subsequently, 0.2 PV entered the water core and 1.6 PV entered the oil core. On the 5% ammonium chloride spacer, 0.5 PV entered the water core and 0.2 PV entered the oil core.

From a total 13 PV of 5% HCl, 2 PV entered the water core and 11 PV entered the oil core. The oil core had a large wormhole, while the water core appeared completely intact.

Test Results

These tests illustrate that the AP is capable of providing diversion from a water-saturated core to an oil-saturated core, and is also capable of providing significant permeability reduction to the water-saturated core.

Test series 1–4, using the dual-core setup, were the basis for establishing the capability of the AP to provide acid diversion. As mentioned, the treatment stage with the polymer ended when the differential pressure reached 500 psi. This pressure buildup is one reason that the AP was recognized as a potential acid diverter. A single-core test was used in an attempt to determine the upper temperature limit of the polymer for diversion applications. In this test, a core was treated with 3,000 ppm polymer at 350°F. The pressure reached 500 psi after pumping 9 PV of polymer, which is typical of the volume pumped for all tests in this particular rock. The initial permeability reduction was 99%. It was not determined how long the polymer would remain stable and hold this level of permeability reduction, but it does appear that acid diversion could be obtained up to at least 350°F.

JOB RESULTS

As mentioned previously, over 30 wells have been acidized utilizing the AP diversion system in the Chuc, Caan, and Pol fields. These fields are primarily dolimitic, and the acid has consisted of hydrochloric/acetic blends formulated specifically to avoid sludging problems. Results from nine of these jobs are shown in **Table 1**. The oil and water production numbers shown are the approximate values just prior to and after acid stimulation.

For comparison purposes, results from acid jobs without the AP diversion system are also shown in Table 1 and in **Figure 2**. Two acid jobs were performed on Well Caan 53. Following the first job in August 1999, the water cut eventually began to increase, followed by a decline in the oil rate. A second acid job was performed on a different interval in December 2003, again followed by an eventual increase in the water cut. So, while the acid jobs performed on this well did show increases in oil production, increases in water production were also seen.

On the well, Caan 51, the interval from 3867–3882 m began to show an increase in water cut in March 2001, with a concurrent decrease in oil production. An acid stimulation job in September 2003 did not increase the oil rate,

although the water rate continued to increase. This interval was isolated, and the interval from 3735–3756 m was perforated and acid stimulated. This did result in an increase in oil, although approximately one year later the water cut also began to increase rapidly.

On the Caan 96 well, an acid stimulation treatment was performed in March 2003 and resulted in no increase in oil production. In December 2005, the water cut on this well began a sharp increase.

In Well Pol 388, the interval from 4180–4205 m was producing 2,800 BOPD at ~50% water cut in August 1992. The well was shut in until November 2003, at which point the interval from 4080–4094 m was perforated and acid stimulated. Initial production was ~800 BOPD with ~50% water cut, and these levels were holding steady more than 2 years later.

Figure 2 shows results from Well Chuc 173. The original perforated interval began to show an oil production decline in mid-2002. In November 2005, the interval from 4273–4300 m was perforated and acidized. While there was an immediate increase in oil production, there was also an immediate onset of water production. These results are typical of acid stimulation jobs in the Caan, Pol, and Chuc fields. It should also be noted that other diverters were used in this field, such as ball sealers and foam, but with no real benefit. Also, due to the close proximity of water zones in many wells, the acid volumes were reduced in an attempt to avoid the onset of water production.

The production profile for Well Caan 73A is shown in **Figure 3**. As shown on the graph, the interval from 4020–4030 m showed a sharp increase in water production in January of 2003, along with a sharp decrease in oil production. This interval was isolated and the interval from 3992–4002 m was perforated and acidized using the AP diverter. Even with the close proximity of a water-producing zone, this interval has produced water-free for more than 2 years.

The production profile for the Chuc 63 well is shown in **Figure 4**. As shown, the initial production from this well was ~1,000 BOPD, with a 16% water cut. After one month, production was ~1,800 BOPD with the same water cut. However, less than one month later, oil production had dropped dramatically. The well was acid stimulated in February 2005 using the AP diverter. The response in increased oil production was excellent; one year later the oil production remained steady at almost 3,600 BOPD. In addition, rather than increasing water production, the water cut fell to zero from the initial level of 16%, and was holding steady at zero almost two years later.

The production profile for Well Chuc 192 is shown in **Figure 5**. As shown, oil production began to drop rapidly with a concurrent increase in water production in February 2005. This interval was isolated and a new interval perforated and acid stimulated with the AP diverter. An increased level of oil production was seen, along with approximately a 2% water cut, which fell to zero within a few months. The increased oil production with no water has held steady for almost one year.

Results of the other wells acid stimulated with the AP diverter are shown in Table 1. Of nine wells acidized with the AP diverter, the average percent increase in oil production was 231%. In addition, 22% showed a decrease in water cut following the job and 67% showed no change in water cut following the job.

For the five wells acidized without the AP diverter, four showed substantial increases in water cut following the jobs. In fact, one well went from producing no water to producing 3,273 barrels per day. Also, three of the wells showed decreased oil production following the jobs.

CONCLUSIONS

- Laboratory tests have shown that the AP diverter can divert acid from predominantly water-saturated zones to predominantly oil-saturated zones in both sandstone and carbonate lithology.
- In sandstone and carbonate, the AP diverter can provide acid diversion and permanent water-permeability reduction.
- Results from the Chuc, Caan, and Pol fields show that the use of the AP diverter results in lower water production and increased oil production as compared to control wells acidized without the AP diverter.

NOMENCLATURE

- BOPD = barrels of oil per day
- BWPD = barrels of water per day
- in. = inches
- Kw = water permeability, millidarcies
- m = meters
- MBD = thousand barrels per day
- mL = milliliters
- min = minutes
- psi = pounds per square inch
- ppm = parts per million
- PV = pore volumes

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Well	Temperature, °F	Initial Oil, BOPD	Initial Water, BWPD	Initial Water Cut, %	Final Oil, BOPD	Final Water, BWPD	Final Water Cut, %	Elapsed Time after Acid Job, yr ¹
Without AP Diverter								
Caan 51	309	2,000	667	25	1,800	2700	60	2
Caan 53	311	1,100	179	14	4,000	1195	23	2
Caan 96	302	7,000	0	0	4,000	3273	45	3
Chuc 173	282	4,000	0	0	7,000	300	4	0.3
Pol 388	297	2,800	3,000	52	900	1100	55	2.4
With AP Diverter								
Caan 73A	309	1,515	0	0	3,650	0	0	2
Caan 11	303	1,900	29	1.5	2,740	175	6	0.8
Caan 55	301	4,518	0	0	6,138	0	0	0.5
Chuc 63	284	245	47	16	3,591	169	4.5	1.8
Chuc 171	280	2,321	0	0	2,497	0	0	0.25
Chuc 192	271	2,820	67	3	4,925	0	0	0.8
KU 87D	253	1,000	0	0	4,500	0	0	_
Pol 79A	275	727	255	35	735	396	35	2
Pol 93B	275	530	0	0	850	0	0	0.25

 Table 1

 Production Results from Acid Stimulation Treatments

¹Amount of time elapsed since the acid job and point at which final production numbers were taken.



Figure 1—(a) Non-modified polymer adsorption, (b) hydrophobically modified polymer adsorption, and (c) hydrophobic interactions.

CHUC 173 Historical Production



Figure 2—Production results from Well Chuc 173, acid job without AP diverter.



CAAN 73A, Historical Production

Figure 3—Production results from Well Caan 73A, acid job with AP diverter.

CHUC 63 Historical Production



Figure 4—Production results from Well Chuc 63, acid job with AP diverter.



CHUC 192, Historical Production

Figure 5—Production results from Well Chuc 192, acid job with AP diverter.