DEVELOPMENT OF ASSOCIATIVE POLYMER TECHNOLOGY FOR ACID DIVERSION

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SUMMARY

This paper describes the use of associative polymer technology (APT) to achieve fluid diversion during an acid-stimulation treatment. APT involves the use of a very low viscosity, aqueous polymer solution. It adsorbs immediately onto the formation surface and significantly reduces the capability of subsequent aqueous fluids to flow into high-permeability portions of the rock. The first stage containing the APT predominately will enter the most permeable area, diverting following acid stage(s) to other less permeable sections of the rock. APT has little or no effect on the flow of subsequent hydrocarbon production. Parallel flow data using water- and oil-saturated cores are presented, showing the capability of APT to divert acid in both sandstone and carbonate cores. In addition, case histories are presented showing the effectiveness of APT.

INTRODUCTION

Most intervals contain sections of varying permeability. In matrix-acidizing treatments, the acid tends to predominantly enter the highest-permeability portions 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 laboratory study was initiated to develop an RPM based on a hydrophobically modified (HM), water-soluble polymer.[5] This group of polymers was selected for study because their properties can be altered in ways that render them valuable for oilfield applications.

ASSOCIATIVE POLYMERS

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.[6-7] The primary factor responsible for the property modification is the associative tendency between the hydrophobic groups when placed in aqueous medium. The associative interactions of the hydrophobic groups may lead to lower or higher solution viscosities depending on the polymer concentration, which determines whether intra- or inter-molecular interactions dominate. These attractive interactions are often depicted as transient and reversible crosslinks among polymer chains that form under static or low-shear conditions, but may rupture at high shear rates. This property is useful in oilfield applications requiring particle transport, such as in fracturing or the transport of drill cuttings. Commercially, this property has also found extensive application in the coatings industry.

Another unique property of HM water-soluble polymers is their behavior in aqueous brines. The viscosity of a polyelectrolyte solution decreases with added salts because of the screening of the charges on the polymer chain by the component ions of the salt. While this phenomenon still occurs with HM ionic polymers, the reduction in viscosity caused by charge screening is more than compensated for by the increased intermolecular associations among the hydrophobic groups caused by the presence of salts. Thus, HM polymers find use as viscosifiers for brines such as those used in drill-in or drilling fluids.[8-9]

The shear-dependent rheological properties of HM water-soluble polymers can be modified without altering their behavior toward salts by the addition of surfactants. This modification has found use in polymer flooding applications for enhanced oil recovery.[10-11]

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.[12] **Fig. 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. The extent of these new properties can be controlled by the synthesis method, polymer concentration, hydrophobe type and amount, the quality of the solvent, and the monomer distribution along the polymer chain.

APT DEVELOPMENT AND TEST PROCEDURES

- ***Core flow tests for brine and oil-permeability reduction—***A previous paper has discussed the APT development.[5] As discussed in that paper, the polymer shows the capability to reduce water permeability with minimal reduction in oil permeability. All testing presented in that paper was in sandstone cores, and subsequent testing has shown similar results in carbonate cores. This testing was run in multi-tap Hassler sleeves, and Equation 1 was used to calculate the permeability reduction percentage.

$$[(\text{pretreatment perm.} - \text{post-treatment perm.})/\text{pretreatment perm.}] \times 100 \ldots\ldots (1)$$

- ***Acid diversion tests—***These tests were run using 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 so that the treatment sequence could be bullheaded, allowing the treatment to flow through either core. An ammonium chloride spacer was pumped between the APT treatment and the acid. For the APT treatment and ammonium chloride spacer, a limit of 30 PV or 500-psi differential pressure was used, and in all tests, the 500-psi limit was reached before pumping 30 PV. For the acid stage (5% HCl), the limit was 13 PV or 500 psi and in each case, 13 PV was pumped without reaching the 500-psi limit. In the final stage, the cores were disconnected and final permeabilities were measured.
- ***Rheological measurements***—Rheological measurements (shown in **Fig. 2**) were run on a Haake RS 150 rheostress rheometer, using a cone-and-plate arrangement at 73ºF. Rheological measurements (shown in **Table 1**) were run using a Brookfield LVT viscometer with a UL adapter at 60 rev/min at 74º F.

TEST RESULTS

Rheological Measurements

As discussed, hydrophobically modified polymers show unique rheological properties. Fig. 2 shows viscosity measurements over a 30-minute period for 1% active solutions of an unmodified polymer and two hydrophobically modified polymers. The unmodified polymer revealed essentially constant viscosity for 30 min at shear rates ranging from 20 to 1,000 sec^{-1}. The hydrophobically modified polymer samples initially showed constant viscosity, but a rapid increase in viscosity was seen after a period. For the 5 mole % C_{16} modified polymer, the viscosity increase was observed at a shear rate of 200 sec-1. For the 7 mole % C_{16} modified polymer, the increase occurred at 50 sec-1. While more extensive investigation of the rheological properties is not presented here, the hypothesis is that this viscosity increase is due to a change from intra- to inter-molecular hydrophobic associations. Under low-shear conditions, intramolecular associations dominate. However, under higher shear conditions, these associations break, allowing the polymer chains to stretch and experience intermolecular associations. These intermolecular associations are believed to result in the rapid increase in viscosity observed. It should be noted that similar shear-thickening phenomena were not seen with solutions less than 1% active (which covers typical treating solutions).

This rheological phenomenon could have implications in the use of this polymer system. In some core flow tests at low treatment rates, no pressure increase was seen even after 30 PV of treatment had been flowed into the core.[5] One test has been run to investigate the effect of treatment flow rate. In this test, 16 PV of treatment was pumped at 2 mL/min, with no pressure increase. The flow rate was then increased to 4 mL/min, and after pumping only 3 additional PVs of treatment, the pressure had increased to 400 psi (in this case the treatment was stopped at 400 psi rather than 500 psi). This phenomenon is not new, and a recently published paper discusses a “flow induced adsorption” of polymers at various treatment flow rates.[13]

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 APT diverting system (shown in Table 3) results in ease of mixing, low friction pressures, no special manifolding or pump requirement, 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.

Acid Diversion Testing

Testing to this point indicated that the modified polymer could effectively reduce permeability to water with little damage to oil. 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.

- ***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 Table 2, Cores 1 and 2 show the results of control tests in which 13 PV of 5% HCl was pumped through each of these cores separately. As shown, 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 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 175ºF. The treatment consisted of a 2,000-ppm polymer 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. As shown in Cores 3 and 4 (Table 2), 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 APT 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 175ºF. A 2,000-ppm polymer 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 APT 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. As shown in Cores 5 and 6 (Table 2), 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 175ºF. 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. The results are tabulated in Table 2, Cores 7 and 8. In the next test a 2,000-ppm solution of APT was bullheaded into 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 of 13 PV of 5% HCl, 2 PV entered the water core and 11 PV entered the oil core. These results are tabulated in Table 2, Cores 9 and 10. The oil core had a large wormhole, while the water core appeared completely intact (see **Fig. 3**).

Test series 1-4 using the dual-core setup were the basis for establishing the capability of APT to provide acid diversion. As mentioned earlier, the treatment stage with the polymer ended when the differential pressure reached 500 psi. This pressure buildup is one reason that APT was recognized as a potential acid divertor. 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 (see Core 11 in Table 2).

JOB RESULTS

As of this writing, approximately 105 APT jobs have been performed, and over 50 of these have been in one geographical region. In this region, acid jobs typically result in increased water production. With the use of APT, water production has typically not changed following the acid job, and in some cases has decreased. In addition, in almost all cases, APT has resulted in increased wellhead pressures when the polymer solution reaches the formation, which has not typically been seen with other acid-diverting agents.

In particular, one job was performed in a well producing from a cretaceous, naturally fractured carbonate reservoir with a bottomhole temperature of 250ºF. The operator's previous experience stimulating wells in this area had shown that after acid stimulation, water production increased more than oil production and water continued to increase until production from the well was killed by hydrostatic pressure from the long hydrostatic column. Based on treating-pressure response, the treatment using several stages of APT and acid appeared to divert the acid into sections of lower permeability (assumed to be the hydrocarbon-bearing portions of the zone). Following the job, oil production increased by 34% and the water cut was reduced from 21% to 17%.

A second job was also performed in a cretaceous formation at 17,400 ft with a bottomhole temperature of 320°F, 1-md permeability, and 7% porosity. The well was perforated in a new zone and was not producing before the stimulation. An acid frac was proposed to stimulate the well but due to problems with the completion, a high-rate job was not feasible. The operator agreed to perform a matrix stimulation in three stages, using a combination of organic and inorganic acid using APT for diversion. The production after the stimulation showed 2,480 BOPD, 4.0 MMSCF/D, with only 0.3% water cut. Pressure response during the job indicated diversion was occurring when APT reached the formaton.

CONCLUSIONS

Based on the laboratory investigation and subsequent field trials, the following conclusions can be drawn:

- Laboratory and field tests have shown that APT can divert acid from predominantly water-saturated zones to predominantly oil-saturated zones in both sandstone and carbonate lithology.
- In sandstone and carbonate, APT can provide acid diversion and permanent water-permeability reduction.

Nomenclature

in. = inches
mL = milliliters
min = minutes
psi = pounds per square inch
Kw = water permeability, millidarcies
ppm = parts per million
PV = pore volumes

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Table 1
Polymer Treatment Viscosities

Polymer Concentration (ppm)	Viscosity (centipoise)
2000	1.4
4000	1.9

Table 2
Results of Core Flow Tests

Core No.	Lithology	Treatment Concentration (ppm)	Temperature (°F)	Fluid	Initial Permeability (md)	Treatment Volume (Pore Volumes)	Total Reduction (%)
1	Brown sandstone	5 % HCl	175	API brine	840 (Sor)	13	-138
2	Berea sandstone	5% HCl	175	Kerosene	300 (Swr)	13	-114
3	Brown sandstone	2,000 ahead of 5% HCl	175	API brine	623 (Sor)	2 (acid)	96.5
4	Berea sandstone	2,000 ahead of 5% HCl	175	Kerosene	340 (Swr)	11 (acid)	-120
5	Berea sandstone	2,000 ahead of 5% HCl	175	API brine	266 (Sor)	3 (acid)	56
6	Berea sandstone	2,000 ahead of 5% HCl	175	Kerosene	274 (Swr)	10 (acid)	-34
7	Bedford limestone	5% HCl	175	API brine	10 (Sor)	14 (acid)	-310
8	Bedford limestone	5% HCl	175	Kerosene	51 (Swr)	6 (acid)	-10
9	Bedford limestone	2,000 ahead of 5% HCl	175	API brine	10 (Sor)	2	ND
10	Bedford limestone	2,000 ahead of 5% HCl	175	Kerosene	28 (Swr)	11	ND
11	Brown sandstone	3,000	350	API brine	670 (Sor)	9	99

ND = Not Determined

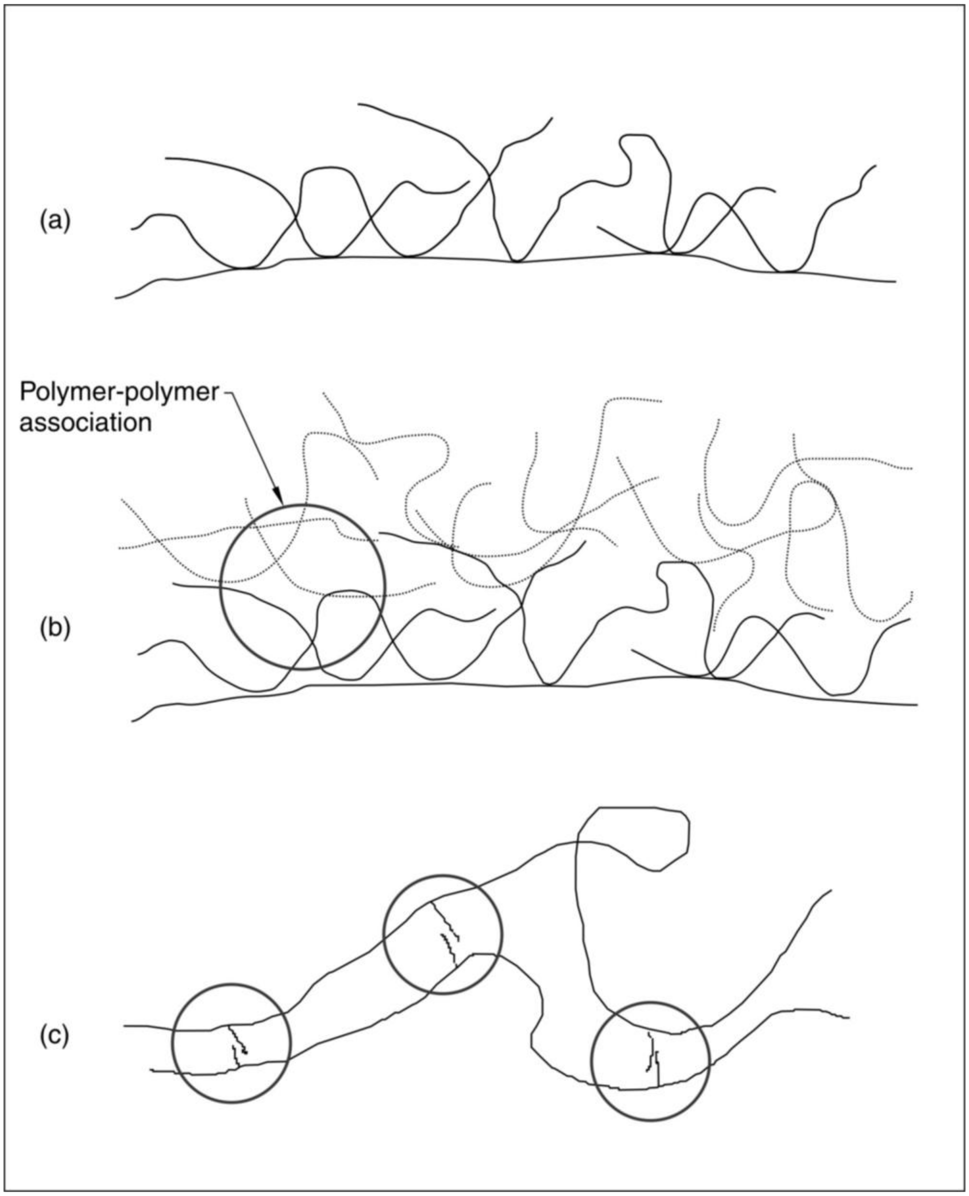

Figure 1 — (a) Non-modified Polymer Adsorption, and (b) Hydrophobically Modified Polymer Adsorption, and (c) Hydrophobic Interactions

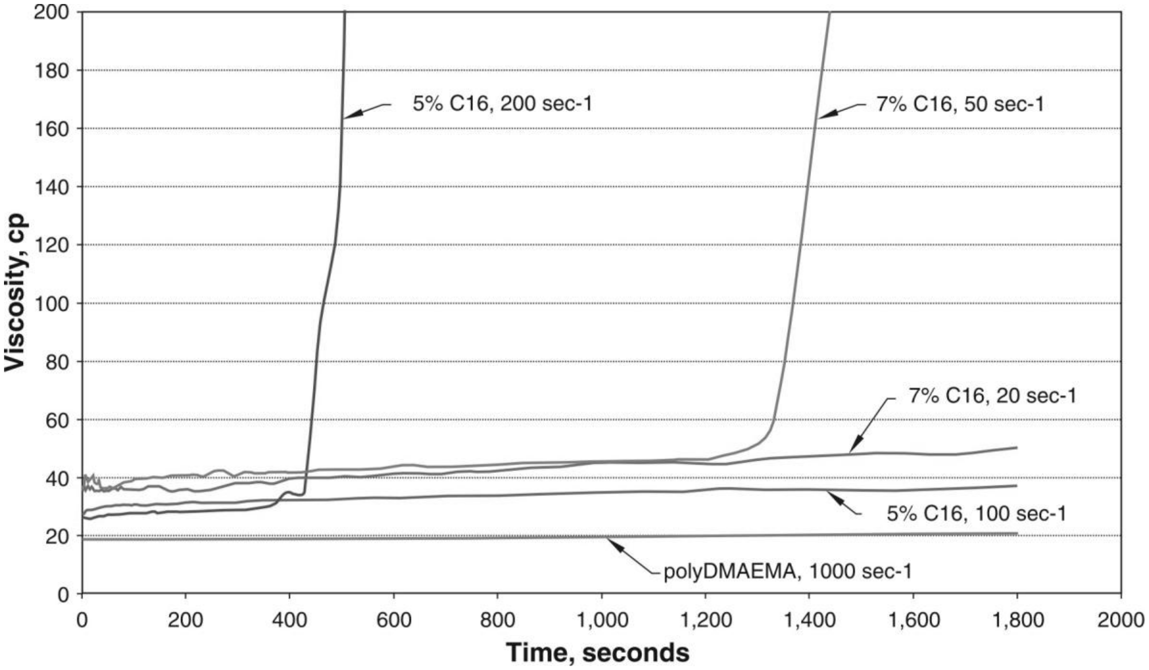

Figure 2 — 1% Solution Viscosities of PolyDMAEMA, 5 Mole % C_{16} and 7 Mole % C_{16} Modified PolyDMAEMA

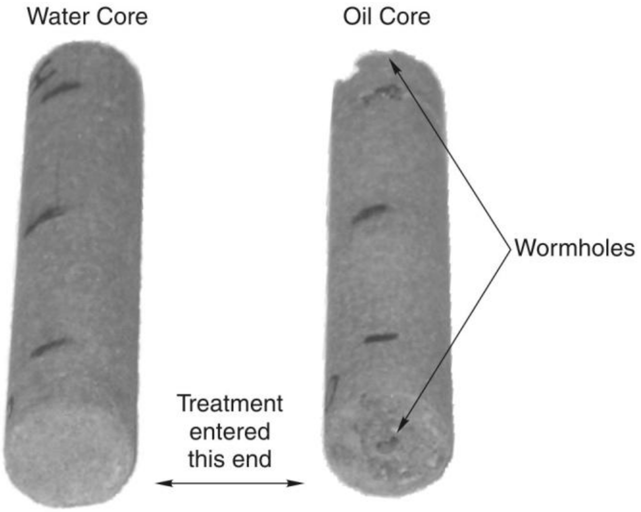

Figure 3 — Oil and Water Bedford Limestone Cores After APT Preflush/Acid Diversion Test in Parallel Core Flow Test