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#### INTRODUCTION

Stimulation results from acid treatments of carbonate reservoirs are generally limited by the extent of live acid penetration, which is determined by the rate of acid spending and fluidloss. In recent years, the effort to control acid leakoff and reduce the rate of spending has caused the industry to focus on developing gelled acid systems. Numerous gelling agents have been used, including natural gums, biopolymers, synthetic polymers and surfactants. Many of these materials have been used with only limited success, due to their inherent instability in live or spent acid, or incompatibility with common additives and contaminants.

In 1983, a polymer was introduced, which provides the desired characteristics of stable viscosity, acid retardation and compatibility with most of the common acid additives. It has since been successfully applied in more than 300 matrix and fracture acidizing treatments. This paper provides a description of this gelling agent and details of several case histories.

## DISCUSSION

A synthetic polymer has been developed for use as a viscosifying agent for hydrochloric acid, tested under extremes of field conditions (Ref. 1) and found to be successful in enhancing the results of carbonate acidizing treatments. This material (Polymer A) was originally developed as a thermally stable viscosifier for brine solutions containing calcium and magnesium ions. It's composition is designed to resist thermal degradation and hydrolysis at high temperatures. Early in it's development, it was recognized that Polymer A also resisted acid hydrolysis and could be effectively employed as an acid gelling agent. Polymer A is readily soluble in hydrochloric acid, and develops viscosity rapidly. It is effective in all commonly used hydrochloric acid systems, and the viscosity is independent of acid concentration. It's resistance to thermal degradation and acid hydrolysis provides stable viscosity and continued solubility at elevated temperatures.

Polymer A is also soluble in the calcium and magnesium brines produced by the spending of the acid in a carbonate formation. The viscosity of the brine is essentially the same as that of the original gelled acid, a feature that provides continued resistance to fluidloss. It's stability in brine solutions is demonstrated in Figure 1. A simulated spent acid (20% CaCl2 with a pH = 1) was gelled with Polymer A, at a concentration of 120 pounds per thousand gallons (PTG). The viscosity of the gelled brine at ambient temperature was

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94 cp (170 sec-1). During the 90 minute heat-up to 250 F, the viscosity declined to 30 cp, due to thermal thinning. Over the two hour period at 250 F, there was essentially no change in viscosity. Upon cooldown, the viscosity returned to 95% of the original. Figure 1 provides a comparison to another commercially available gelling agent (Polymer B), tested under identical conditions. The simulated spent acid, gelled with Polymer B, experienced a more rapid loss in viscosity during the heat-up period. The viscosity continued to decline during the test period. Figure 2 presents a closer view of the contrast in thermal stability for the two polymers at 250 F. Over the two hour period, the fluid gelled with Polymer A lost only 1% of it's initial viscosity, whereas the viscosity produced by Polymer B degraded to 46% of it's initial value. Upon cooldown, the Polymer B gelled brine regained only 14% of it's original viscosity, indicating severe thermal degradation.

Polymer A provides acid retardation by producing a stable viscosity, which restricts convection in the acid. In the application of HCl in carbonate formations, there may exist a range of conditions that define the rate of spending (Ref. 2). A minimum reaction rate is expected under completely static conditions, where the movement of ions is strictly diffusion controlled. A maximum rate would be encountered when the bulk movement of ions exceeds the rate of acid consumption, and the reaction is controlled by surface kinetics. This might be the case for acid under turbulent flow conditions. Intermediate to these extremes are conditions where the spending is determined by a combination of diffusion, convection and surface kinetics. In the development of acid systems for improving acid penetration, the objective of controlling the rate of acid spending is approached through the reduction of fluid convection, or through the maintenance of laminar flow. This is accomplished through the generation of stable viscosity in the acid.

Static spending tests were performed to demonstrate the relative effectiveness of Polymer A at increasing spending time. Figure 3 illustrates the spending behavior for the gelled acids at 100° F. Under these conditions, the gelled acid approaches a maximum retardation at a polymer concentration of between 60 and 80 PTG, with a relative spending time of 2.5 times that of the unmodified HCl. Increasing the polymer concentration to 100 PTG has no significant additional effect. This suggests that a viscosity of approximately 26 cp (170 sec-1) is sufficient at this temperature to limit the mass transfer to a diffusion mechanism, by resisting fluid convection.

At higher temperatures, thermal convection of the fluid increases and greater polymer concentrations are required to provide acid retardation. Figure 4 shows the spending characteristics of the gelled acids at 150° F. The development of viscosity in the acid has led to increases in spending times of between 1.5 to 5.9 times that of the unmodified HCl. At 200° (Figure 5) and 250° F (Figure 6), similar results are obtained.

Under the dynamic conditions of fluid flow in a wormhole or fracture, the rate of acid spending will be be heavily dependent on the fluid flow regime. Being a thin, Newtonian fluid, unmodified HCl can be expected to reach turbulent flow at relatively low velocities. It's rate of spending will also be rapid. By gelling the acid with Polymer A, laminar flow can be maintained at much higher velocities, effectively increasing spending time by restricting the mass transfer to a diffusion mechanism.

#### CASE HISTORIES

## Fusselman Formation - Roosevelt County, NM

This case history demonstrates the benefit of using acid gelled with Polymer A to restimulate a well, initially completed by fracture acidizing with nongelled acid. The Fusselman zone is a 19 foot net interval of dolomitic limestone, 7830 foot depth, with a bottom hole static temperature of 155° F. It was initially treated with 18,000 gallons of 28% HCl. Initial production was 113 BOPD, 57 MCFD of gas and 55 BWPD. The production declined to 3 BOPD in less than four years, representing an annual decline rate of 70 percent.

In October of 1982, a fracturing treatment was attempted. Premature job termination due to screenout was experienced after placement of only 30% of the sand. The well was then scheduled to be abandoned, due to poor performance.

In a last attempt to revive the well, it was treated with 500 gallons of 15% HCl, and fractured with 15,000 gallons of gelled 20% HCl and 12,000 gallons of pad fluid. The acid was gelled with 80 PTG of Polymer A, which produced a viscosity of 42 cp (170 sec-1). The treatment consisted of six alternating stages of pad and gelled acid, pumped at 13 BPM. Nitrogen was added at 400 SCF/BBL.

This well was the first treated with Polymer A. The oil production history is plotted in Figure 7. Point A represents the initial completion and, Point B, the restimulation with Polymer A gelled acid. Stabilized daily production after the gelled acid treatment was 35 BOPD, 57 MCFD of gas and 5 BWPD. Four years later, the well was still producing 31 BOPD, 10.4 MCFD of gas and 3 BWPD. Due to the initiation of a more accurate well testing procedure (Point C), and a pump change (Point D), the well is currently producing 46 BOPD, 19 MCFD of gas and no water (Point E).

During the first four years of production, this well made 25,834 barrels of oil and 23.6 MMSCF of gas. Due to the success of the gelled acid treatment, the well was not abandoned, and has accumulated 38,088 barrels of oil and 29.4 MMSCF of gas in the four years since the gelled acid treatment.

Interlake Formation - McKenzie County, ND

This case history compares the significant variations in production results from identical fracture acidizing treatments, using Polymer A and Polymer C as the acid gelling agents. Two wells were recompleted with gelled 28% HCl fracturing treatments. These wells are offset by  $\frac{1}{4}$  mile. The reservoir characteristics are similar for both wells. The Interlake formation is perforated over a 110 ft. interval. The formation depth is 12,570 ft. Bottom hole static temperature (BHST) is 282 °F.

Well No. 1 (Figure 8) was initially completed (Point A) with 5,000 gallons of 15% HCl, resulting in a daily production of 590 BO, 30 BW and 927 MCF of gas. Prior to restimulation, the production was 77 BOPD, 21 BWPD and 30 MCFD of gas. The well was fracture acidized (Point B) with 17,000 gallons of gelled

28% HCl and 10,000 gallons of crosslinked pad, in four stages. The acid was gelled with 100 PTG of Polymer A, to yield a 62 cp (170 sec-1) fluid at ambient temperature. The 30 day post stimulation production was 516 BOPD, 71 BWPD and 860 MCFD of gas. Figure 8 shows an annual production decline of 24% over a  $3\frac{1}{2}$  year period.

Well No. 2 (Figure 9) was completed in 1982 with the same volume and concentration of HCl, as well No. 1. Initial production was 392 BOPD. The production spike in 1983 was the result of a proppant fracturing treatment. The well was again restimulated in 1984 (Point B) with a gelled acid treatment identical to the one described for Well No. 1, with the exception that Polymer C was used to gel the acid. The concentration of Polymer C was sufficient to produce the same acid viscosity as that for the previous well. The 30 day post stimulation production was 508 BOPD, 48 BWPD and 838 MCFD of gas. The subsequent 58% annual production decline rate was similar to that experienced after the initial completion.

Well No. 2 was produced for one year after the gelled acid treatment before being shut in because of gas curtailment. The cumulative production for this period was 118,858 BO. This is 30,612 fewer barrels of oil than was produced by well No. 1 during the same period, after restimulation with the Polymer A gelled acid. Well No. 2 was again stimulated (Point C, Fig. 9) with 28% HCl, gelled with 50 PTG of Polymer A. The response was less than expected, possibly due to the use of an insufficient polymer concentration. Later, collapsed tubing and casing problems were detected and repaired. At point D, the well was treated with HCl gelled with 100 PTG of Polymer A. The annual production decline after the last treatment was 27%, which is comparable to the 24% decline calculated for Well No. 1, indicating similarities in the final fracture geometries.

Abo Reef Formation - Lea County, NM

This case history demonstrates the benefit of using acid gelled with Polymer A, rather than non-gelled acids, to achieve a higher production rates. This 98 foot of perforated limestone interval was acidized with a total of 8500 gallons of 28% HCl, in several treatments. Due to low reservoir pressure and a relatively high permeability near the wellbore created by past acid treatments, these had either been pumped on a vaccuum, or had an instantaneous shut down pressure (ISDP) of zero psia. Oil production declined at an annual rate of 53% over an 18 month period, going from 37 BOPD to 11 BOPD.

The restimulation consisted of 9,000 gallons of 15% HCl, gelled with Polymer A, and 4,000 gallons of non-gelled acid. These volumes were divided into three stages, with ball sealers used for diversion. The gelled acid was used to control fluidloss and improve live acid penetration. The non-gelled acid was pumped behind the gelled acid to promote "fingering" of the thin fluid through the more viscous fluid, and enhance differential etching (Ref. 3). The acids were pumped at a rate of 9 BPM, down 2.875 inch tubing. The ISDP was 900 psig, indicating that fluidloss was reduced in comparison to previous acid treatments.

Initial production after restimulation was 158 BOPD, 81 MSCFD of gas and 49 BWPD. The stabilized production after 30 days was 53 BOPD, 85 MSCFD of gas and

49 BWPD. Nine months later, the production rate was 43 BOPD, 138 MSCFD of gas and 29 BWPD. The annual decline rate after the gelled acid treatment was reduced to 25%.

Smackover Formation - Washington County, AL.

This case history provides an illustration of the thermal stability of Polymer A, and it's tolerance to dissolved salts, in the spent acid. A 16,399 foot well was drilled to replace a wellbore that had been lost to corrosion. The bottom hole static temperature (BHST) of this sour gas reservoir is 293° F. Prior to abandonment, the old well produced 381 BOPD, 1.7 MMSCFD of gas and 214 BWPD. The replacement well was drilled adjacent to the old wellbore, and treated with 25,000 gallons of gelled 28% HCl. The acid was gelled with 130 PIG of Polymer A to provide 35 to 50 cp (170 sec-1) viscosity at the estimated treating temperatures of 200° to 250° F. Stabilized production, one month after treatment, was 1564 BOPD, 7.6 MMSCFD of gas and 38 BWPD. Six months later, the replacement well was producing 1466 BOPD, 8.6 MMSCFD of gas and 85 BWPD. Three and one half years later, it still produced 718 BOPD, 9.9 MMSCFD of gas and 100 BWPD, representing a 14.5% annual decline rate.

A wildcat well was drilled into the Smackover formation, in an area near the previously mentioned wells. The BHST was 306° F. Although the logs indicated a good possible pay zone, the well would not produce at commercial rates. The well was fractured with 24,000 gallons of 28% HCl, gelled with 110 PTG of Polymer A, and 30,000 gallons of pad fluid. Nitrogen was added at 750 SCF/BB1. After the treatment, the fracture was allowed to close and an additional 6,000 gallons of 28% HCl was pumped at matrix injection pressures in an attempt to enhance fracture conductivity near the wellbore (Ref. 4).

The well flowed back for two days, filling all of the storrage on location. A test during flow back indicated 1580 BPD of condensate, 4.5 MMSCFD of gas and 650 BWPD. The well was shut in for a pressure buildup test, and to allow a pipe line to be built to the plant. From pressure transient analysis a skin factor of -4.0 was calculated, indicating good stimulation of the zone. Approximately 600 BBI of treating fluid remained in the formation for over 20 days of shut-in. When the well was put back on production, it flowed the remaining load water back in two days. It is noteable that the returning spent acid still had a "slickness", and a measured viscosity of 3 cp. The thermal stability of Polymer A allowed the material to stay in solution and not precipitate to plug the fracture face or damage fracture conductivity.

The initial post frac production rate was 1877 BPD of condensate, 3.6 MMSCFD of gas and 256 BWPD on an 8/64 inch choke, with a flowing tubing pressure of 2125 psi. Ninety day production was 1220 BOPD, 3.4 MMSCFD of gas and no water.

## Glorieta Formation - Gaines County, TX

This case history demonstrates the advantage of using Polymer A gelled acid in carbonate matrix acidizing treatments. The purpose of lightly gelling the acid was to enhance wormhole penetration, by reducing fluidloss and retarding the acid reaction rate, and to provide sufficient residual viscosity for fines suspension and removal. The 28% HCl was gelled with 40 PTG of Polymer A, to provide a viscosity of 18 to 20 cp (170 sec-1) at a bottom hole temperature of

## 112° F.

Two wells were treated. The first, a 6,000 foot deep Glorieta well with a net height of 83 ft., was matrix acidized with 4,000 gallons of non-gelled 15% HCl. Pump rates of 1 to 3 BPM were used to maintain a surface treating pressure below the calculated fracturing pressure. Prior to acidizing, the well produced 21 BOPD and 100 BWPD. The production for 60 days after the treatment averaged 50 BOPD. However, after 180 days, production had declined to 35 BOPD.

A similar candidate well was selected to be treated using the same procedures and fluid volumes per foot of net pay, but using the 28% gelled HCl. Prior to the treatment, this well produced 26 BOPD and 32 BWPD. Initial production after the acid treatment was 190 BOPD and 104 BWPD. The two month production rate was 105 BOPD and 60 BWPD. Six months after the matrix acid treatment, the well was producing 71 BOPD and 69 BWPD.

#### CONCLUSIONS

The use of Polymer A to produce stable viscosity in hydrochloric acid is demonstrated to produce acid retardation under static testing conditions. Under dynamic conditions, maintanence of laminar flow is important in extending spend time, requiring a stable viscosifying agent, such as Polymer A. Similarly, the thermally stable viscosity produced by Polymer A in spent acid provides consistant resistance to fluid leakoff and fine suspension capabilities..

Field studies indicate that production stimulation is enhanced by the use of acid gelling agents, due to improved acid penetration, through retardation of the acid and reduced fluidloss. In addition, the studies indicate that the stability of the gelling agent is of major importance. The use of Polymer A provided a stimulation response superior to an identical fracture acidizing treatment, using a less stable polymer. It is also apparent that production decline rates can be influenced by properly designed gelled acid treatments, using Polymer A.

#### REFERENCES

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Figure 1 - Viscosity profile during heatup and thermal exposure for Polymer A and Polymer B, in spent acid

Polymer A Concentration:

0 PTC 40 PTG 60 PTG 80 PTG 100 PTG

0 + X 4 0

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ACID CONC., wt1 



Figure 2 - Effect of time and temperature on the viscosity of spent gelled acid



Figure 4 - Spending rates for 15% HCl at 150°F



TIME (min)

TIME (min)

Figure 5 - Spending rates for 15% HCI at 200°F



Figure 6 - Spending rates for 15% HCI at 250°F



