

Self-Degrading Gel for Downhole Applications in High Temperature Reservoirs

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Abstract

The leakage of reservoir fluids into a wellbore during perforation, workover, or other completion operations is a substantial concern, especially in high temperature wells where existing fluids utilized to mitigate reservoir fluid influx offer poor performance. To maintain the hydrostatic integrity of the wellbore during these operations, a self-degrading, thermally-stable, solids-free fluid loss gel has been developed.

The gel is formulated by crosslinking a synthetic polymer with a metal cross linker. The formulation flows as a viscous liquid at ambient pressure and temperature conditions, and the cross-linking reaction can be initiated by exposing the formulation to elevated temperatures (200°F to 350°F). The cross-linked formulation forms a strong gel that can act as an appropriately-weighted, low fluid loss pill. This pill can temporarily seal the reservoir, enabling well control during the different downhole operations.

Gelled samples of the fluid loss pill have maintained integrity for up to two days under HTHP conditions in laboratory testing with minimal signs of collapse. Then after a short period (2-5 days depending on the formulation), this novel self-degrading gel degraded rapidly to a low viscous fluid. This self-degradation eliminates the need for the subsequent addition of a gel breaker.

In addition to gel stability tests, formation damage caused by the gel and the fluid loss of the pill were assessed by core flooding experiments using Berea core plugs. Average fluid loss over 3 days at 320 °F was about 70 ml. Restoration of the Berea core permeability after the treatment exceeded 85% of the initial permeability with low lift-off pressures observed. This paper presents full laboratory data on the development of the thermally-stable, solids-free self-degrading fluid loss pill including gel stability, fluid loss and rheology.

Introduction

As the world's thirst for petroleum grows, so do the challenges of extracting it from the earth. Increasing demand against a backdrop of dwindling proven reserves are pushing exploration and extraction activities into areas previously considered too difficult, too risky, or too expensive. The engineering techniques and chemical technology created to support drilling and production activities are increasingly inadequate for the new paradigm. High downhole temperature, in particular, puts a strain not only on equipment, but also on the complex chemistry of drilling muds, drill-in fluids, and

viscous pills. Some conventional materials, such as polysaccharide gums and sodium tetraborate crosslinking agents, are demonstrably unstable or simply rendered useless under high thermal loads for extended periods of time. Maintaining the performance of muds and gels at high temperatures remains an ongoing challenge in the industry. This paper describes the development of a material for one such challenge; the replacement of biopolymer-based gels for high temperature applications. The research produced a novel, workable aqueous monovalent brine-based gel derived from a synthetic water soluble polymer. The gel, which can be utilized for a variety of downhole applications including well kills, perforations, and other fluid loss applications, is thermally stable and can be applied at temperatures up to 350°F, conditions where both polysaccharides and borate crosslinking begins to fail (Shupe 1981; Rles 1988; Seright et al. 2009).

Gels are employed extensively during drilling and completions operations in specialized applications such as profile modification (Vossoughi 2000), fluid loss (Evans 2009; Dewprashad 1998; Ross et al. 1999; Cole et al. 1995), water diversion (Moradi-Araghi 2000; Kohler et al. 1991), water shut-off (Prada 2000; Moradi-Araghi et al. 2000; Kabir 2001), hydraulic fracturing (Weaver et al. 2002), insulating packers (Al-Muntasheri et al. 2007; Wang et al. 2006), perforations (Behrmann et al. 2007), and well kills (Levitt and Pope 2008) among others. Gels may be derived from inorganics, resins, monomers, highly viscous fluids, and crosslinkable bio- or synthetic polymers. Gels used for perforations and well kills are generally derived from polymer solutions of aqueous brine containing both a dissolved water soluble polymer and an organometallic crosslinking agent. Few materials (Al-Muntasheri et al. 2007; Moradi-Araghi 2000; Gamage et al. 2013) are designed specifically for use in high density brines at high bottom hole temperatures (>300°F) for extended periods.

Polysaccharides, such as guar and its derivatives, have been widely used for perforation and well kill gels due to the low cost. Typically guar-based gels are crosslinked with borates (e.g., sodium tetraborate) for low temperature application (Kesavan et al. 1993) or with organometallic titanium or zirconium-based agents for high temperature applications (Nimerick 1997). These materials have been used with great success by numerous operators in thousands of wells across the world. However, increasing bottomhole

temperatures from deeper holes are pushing these gels to the limits of their chemical and thermal stability (Moorhouse et al. 1998). The acetal linkages which make up the polymer backbone of guar are susceptible to hydrolysis at high temperatures (Weaver et al. 2003). Increasing the pH of the formulation and inclusion of stabilizers such as sodium thiosulfate, methanol, or formaldehyde (Kohler and Zaitoun 1991) can extend the thermal stability of polysaccharides (Harris 1993), to push past 300°F. However, higher temperatures require new technology based on inherently more thermally stable materials.

Synthetic water soluble polymers, in general, and specifically polyacrylamide, offer a path to more thermally stable aqueous gels. The backbone of acrylamide polymers, in contrast to polysaccharides, consists of carbon-carbon bonds which are stable in the presence of water at elevated temperatures. However, there are still formidable challenges at high temperatures; polyacrylamides are susceptible to amide hydrolysis and free radical decomposition reactions. Hydrolysis can be greatly minimized by copolymerization with monomers such as 2-acrylamido-2-methylpropanesulfonic acid (AMPS) which protects the amide functionality through a neighboring group effect (Heiwell and Hoskin 1989). Oxygen and $\text{Fe}^{2+}/\text{O}_2$ redox catalyzed free radical chain scission of the polymer backbone is problematic with all water soluble materials at elevated temperatures. However, that can be solved by adding appropriate free radical stabilizers and oxygen and/or iron scavengers. Nevertheless, synthetic AMPS-acrylamide copolymers are far more stable under the harsh targeted application environment than either poly(acrylamide) homopolymer or polysaccharides.

A novel fluid loss pill has been developed by Gamage et al. (Gamage 2013) to be used in high temperature reservoirs. However, the gel was designed to remain stable for more than 3 weeks. With this robust pill, breakers would potentially be necessary in different applications. This paper describes a novel self-degrading solids-free fluid loss gel based on synthetic polymers designed for use in high temperature reservoirs. As detailed in subsequent sections, the novel pill combines excellent thermal stability for up to 72 hours and low fluid loss.

Experimental Section

Gel Formulation

Five different gels (A, B, C, D and E) were formulated using a high-density brine solution of a synthetic water-soluble polymer and a metal-based cross-linker. Further additives include pH buffers to lower the pH to an appropriate range for crosslinking to occur (pH = 4-5) and thermal stabilizers to mitigate gel decomposition by radical reactions or other processes. The concentration of polymer, the polymer to cross-linker ratio, and the formulation pH were carefully tuned to provide optimized gelling and fluid loss properties. Different stabilizer concentrations were used in the formulations to control the self-degradation time. The brine choice is determined by the desired density for the specific

application. The formulations presented in this paper were based on 10.0 lb/gal brine prepared from dilution of stock 12.5 lb/gal NaBr brine with water. Gels have been successfully prepared in other brines, including divalents, and will be presented at a later date. Different types of testing on the novel pill were performed to evaluate the pumpability, static fluid loss, gelling time, gel breakage by an external breaker, and regained permeability.

Gel Formation Kinetics

To ensure the rate of cure is sufficiently slow to allow spotting under reasonable rig conditions, a series of experiments was conducted to evaluate gelling times of different formulations at different temperatures. Number of samples derived from the different formulations (A-E) were placed in aging cells and pressurized to 500 psi. Next, the samples were placed individually in ovens at 350°F, 320°F, 300°F, 275°F, and 225°F, and were removed at predetermined time intervals. These samples were qualitatively assessed for cure which is indicated by the resistance of the fluid to flow when held at a 45° angle. Minimum gelling times at different aging temperatures and 500 psi pressure obtained by the experiments are listed in **Table 1**.

Gel Degradation

To monitor the gel degradation over time at elevated temperature, samples were subjected to long-term static aging. Again, a number of samples derived from the different formulations (A-E) were placed in aging cells and pressurized to 500 psi. These samples were then placed in ovens at 320°F and 350°F. Samples were removed after 3, 7, 14, 21, 28, and 35 days. Gel degradation at each time interval was measured with respect to the initial gel volume. Gel degradation at 320°F and 350°F temperatures can be seen in **Fig. 1** and **Fig. 2**.

Rheology Testing

Viscosity of the fully formulated gels A and E was used to assess their pumpability into the well. Shear stress and shear rate were measured using concentric cylinder geometry on an Anton Paar MCR 501 advanced rheometer at room temperature. Viscosity at different shear rates was measured and depicted in **Fig. 3**. Furthermore, Fann 35 equivalent rheology data has been generated from the Anton Paar readings and is listed in **Table 2**. These data can be utilized to simulate the behavior of the pill while it is being placed in the wellbore.

Static Fluid Loss

Static fluid loss testing was performed on gels using an HPHT filter press. First, the uncured gels were added to fill a standard HPHT cell with a 20µm disc. The filter press was sealed, pressurized to 500 psi, and heated to 320°F for a previously determined time duration to set the gel. Next, flow was initiated through the gel with a 200 psi differential pressure and the volume of fluid was collected and recorded as a function of time at 320°F. Fluid loss tests were run for 6 hours for gels A and E. The same experimental procedure was

used to measure the fluid loss at, 350°F. Another set of static fluid loss testing was performed on guar-based gels similarly to that described above, however the gels did not require initial heating as the guar sets at room temperature. Static fluid loss test results are depicted shown in **Fig. 4** and **Fig. 5**.

Regained Permeability Testing

Regained permeability testing was performed to assess the formation damage that would result in using this novel perforation pill in downhole applications. Berea sandstone core plugs (1.5 in diameter and 2.5 in length) were used in the core flooding experiments. Experiments were run at 320°F and 500 psi back pressure. First, air permeability of the cores was measured at 320°F after mounting the cores in a Hassler-type core holder. Next, the pill was injected to the core from the borehole side of the core under 500 psi constant pressure. The 500 psi pressure on the pill was kept constant for three days. Fluid released from the other end of the core (reservoir side) was collected and the total volume was measured. Lift off pressure was measured by injecting gas into the core from the reservoir side. Finally, regained permeability at 320°F was measured by injecting gas into the core.

Results and Discussion

All the gels demonstrated very good stability in the two-day static aging testing at temperatures up to 350°F. These results can be contrasted with results seen with cross-linked guar gels where complete destruction of the gel was noted after only a few hours at the test temperature of 320°F.

Viscosity of the gel formulations will increase as the downhole temperature increases due to the polymer crosslinking at elevated temperatures. The formulation will be gelled completely when the crosslinking of the polymer reaches a certain value. Table 2 shows the minimum time required to convert the formulations into a gel at different temperatures. At relatively lower temperatures, the formulations require a longer period of time to form the gel due to the lower kinetics of the crosslinking reaction. Furthermore, at 225°F formulations D and E take longer time to form gel compared to formulations A, B, and C. As the temperature increases, time required to form the gel decreases. These formulations were specifically designed for wells with about 320°F bottomhole temperature. The results listed in Table 2 show that all the formulations can be pumped downhole within a reasonable time period before it converts to a gel.

Gel degradation results at 320°F and 350°F are depicted in **Fig. 1** and **Fig. 2**, respectively. At both temperatures Gel E exhibits a higher degradation rate after the initial time period. Gel A remains stable for excess of 30 days at 320°F. Among the gels used in this study, Gel A can be considered as the most stable gel while the Gel E shows the highest degradation rates at both temperatures.

Table 1. Gelling Times of Different Formulations at Different Temperatures

Temperature	Gelling Time (A)	Gelling Time (B)	Gelling Time (C)	Gelling Time (D)	Gelling Time (E)
225°F	5 hrs	5 hrs	5 hrs	6 hrs	7 hrs
275°F	2 hrs	2 hrs	2 hrs	2 hrs	2.5 hrs
300°F	1.5 hrs				
320°F	1 hr				
350°F	1 hr				

At 320°F, more than 80% of Gel E was degraded within the first ten days. Furthermore, at 350°F more than 90% of Gel E was degraded within the first ten days. Gels B, C, and D show very similar degradation curves at both temperatures and those degradation curves lies between the curves for Gel A and Gel E. Gel A and E were used in further studies to compare fluid loss performance and rheology.

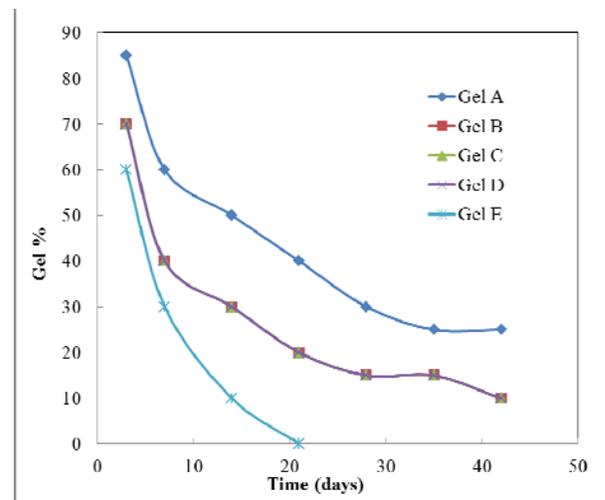


Fig. 1 Gel degradation curves of gels A-E at 320°F

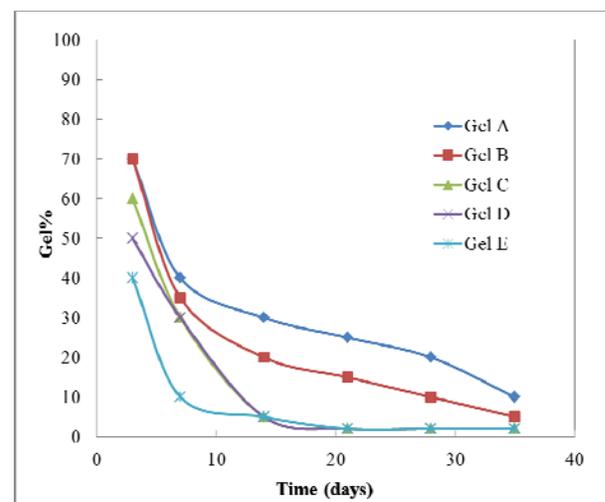


Fig. 2 Gel degradation curves of gels A-E at 350°F

The viscosity reading of formulations A and E obtained from the Anton Paar rheometer shows lower viscosity at the

higher shear rates (**Fig. 3**) in both formulations. However, viscosity increases rapidly at lower shear rates. Fann® 35 viscometer equivalent viscosity data generated by the Anton Paar viscosity readings are listed in **Table 2**.

The viscosity of Gel E is higher than that of Gel A at lower shear rates. At higher shear rates the viscosity of both formulations was very similar. These values suggested that both formulations can be pumped downhole with normal pumping pressures. In addition, both pills have very good suspension properties. This property could potentially be utilized to transport particles to the well to be used for different applications.

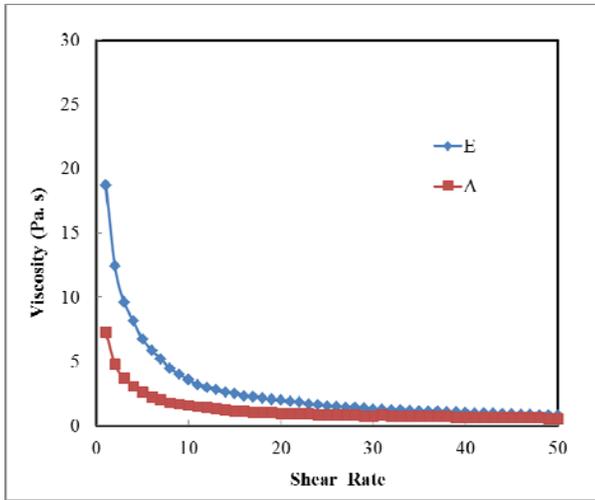


Fig.3 Effect of shear rate on the viscosity of the formulation at 25°C

Table 2. Simulated FANN 35 Viscometer Readings

FANN 35 RPM	FANN 35 Reading (Gel A)	FANN 35 Reading (Gel E)
600	192	210
300	145	160
200	123	133
100	94	98
6	30	66
3	25	60

Fluid loss in these gels (A and E) at different temperatures shows a better performance compared to cross-linked guar gum (**Fig. 4** and **Fig. 5**). This can be attributed to the higher thermal stability of the AMPS-acrylamide copolymer backbone in the formulations. At 320°F (targeted reservoir temperature) with Gel A, 8.3 ml of fluid loss was observed in the first 30 minutes. About 7.9 ml of fluid loss was observed with Gel E at the same conditions after 30 minutes. After six hours, about 34 ml of fluid loss was observed in Gel A compared to 35 ml of fluid loss in Gel E at 320°F. In summary, the fluid loss curves of both Gel A and E are similar. In general, an increase in fluid loss volume was observed with an increase in experimental temperature. This can be explained by the reduction in gel stability with

increasing temperature. At both experimental temperatures, performance of the novel self-degrading fluid loss pill (Gel E) is much superior to the cross-linked guar gum.

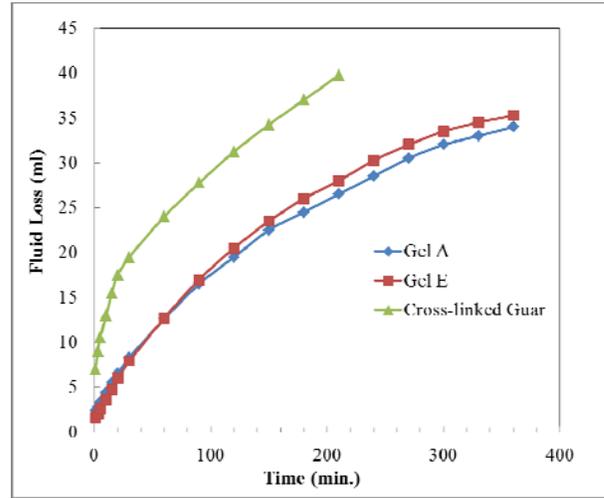


Fig. 4 Static fluid loss results at 320°F

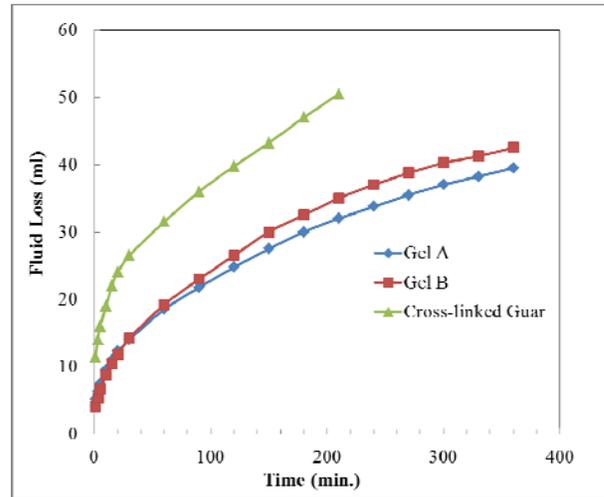


Fig. 5 Static fluid loss results at 350°F

Less than 50 ml of fluid loss was observed over a 72-hour core flooding experiments at 320°F and 500 psi using a Berea core and Gel A. About 70 ml of fluid loss was measured during the similar core flooding experiment with Gel E. Differences in fluid loss in static aging and core flooding experiments can be explained by the permeability difference in the disc used in the fluid loss test and the Berea core. Berea cores used in the core flooding experiments have about 200 mD permeability compared to the 20 µm pore throat size in the discs used in the HT fluid loss experiments. The average pore size in the Berea rock is much smaller than the 20 µm in the discs. Both static aging and core flooding experiments show similar performance with both Gels A and E. However Gel A performs slightly better than Gel E under similar conditions. Both gels perform much better than cross-linked guar at elevated temperatures.

Lift-off pressure measured for both gels ranged between 2-3 psi. The regained permeability values measured by the core flooding experiments after the treatment with both gels were more than 85% of the original values without the use of an external breaker.

Conclusions

A novel solids-free self-degrading fluid loss pill for higher temperature reservoirs has been formulated. This gel can be effectively used in reservoirs with temperatures up to 350°F. Static fluid loss testing proved that the new self-degrading gel (Gel E) shows similar performance compared to the previously developed fluid loss gel (Gel A, Gamage et al. 2013). The synthetic polymer-based gel outperforms the thermal stability and fluid loss of guar/borate based gels tested under similar conditions. In addition, the novel gel has low lift-off pressures, generally ranging between 2-3 psi. This pill can be used in short-term downhole applications (2-5 days, depending on the formulation). After that time, the gel will degrade rapidly. Moreover due to the lower lift-off pressure, reservoir pore pressure can easily remove the pill upon completion of the well. Most importantly this gel can be utilized in downhole applications without any external breakers.

Fluid loss observed during the three day core flooding experiment at 320°F and 500 psi differential pressure was about 75 ml. The solids-free nature of the formulation minimizes the formation damage caused by the novel high temperature fluid loss pill. Regain permeability experiments confirm that the restoration of the Berea core permeability after the treatment is more than 85% of the original permeability. The formulated pill is shelf-stable at room temperature for more than three months without curing or losing its subsequent gel performance. The newly developed gel should provide an excellent alternative to biopolymer-based gels for perforations, workovers, well kills, or other completion operations.

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