A New High Temperature Polymer Fracturing Fluid

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Abstract. In this study, according to the requirement of high temperature low permeability reservoir hydraulic fracturing fluid, a novel non-residual fracturing fluid was developed through analyzing the structure of polymer 2-acrylamido-2-methylpropanesulfonic acid (AMPS). Experiment results demonstrate that synthetic polymer fracturing fluid possess good shear stability and viscosity recovery propriety. The shear viscosity of fracturing fluid for 120 min is 120 mPa.s at 170 °C, it has good resistance to high temperature and shearing performance. The residue of polymer fracturing fluid was 1.2%. Matrix and propped fracture damage test indicate that the damage to core matrix (only 15.4%) and propped fracture of synthetic polymer fracturing fluid is far less than guar gum fracturing fluid which is fit for the stimulation of high-temperature low permeability reservoir. The new fluid was tested in 120 wells in the gas and oil reservoir in China. Oil & gas production after stimulation using the new fluid increased 3 to 5 times compared with wells in similar locations.

1. Introduction

As the oil and gas exploration and exploitation continually develop, the natural environment of the reservoir is becoming increasingly harsh (abnormal high temperatures and high pressures), with correspondingly worsening physical reservoir properties (low permeability and low porosity). Given this, reservoir reconstruction based on hydraulic fracturing has evolved into a vital means for reservoir exploration and appraisal. However, hydraulic fracturing in such reservoirs raises up high performance requirements on the fracturing fluid, due to the fact that excellent tolerance to both high temperatures and shearing are required to ensure successful operation and meanwhile formation damage induced by fracturing fluids is expected to be minor for desirable stimulation results. In addition, the development of low-permeability reservoirs is mostly required to be proceeded in a low-cost way. Under such circumstances, the selection of fracturing fluids is facing tremendous challenges.

The thermal stability of the natural vegetable gum-based fracturing fluid, e.g. the boron-crosslinked guar gum fracturing fluid, which is at present the most widely-used, mainly depends on the thermal stability of the crosslink bond and the thermal tolerance of the main chain of the molecule. However, the main chain of the natural vegetable gum polymer is connected by acetal linkages (glycosidic bonds), which are prone to hydrolysis and thermal degradation under high temperatures that compromise the thermal resistance of the vegetable gum fracturing fluid. In such cases, normally in order to successfully carry out the construction, one would increase the amount of the pre-flush to cool down the formation, use more thickening agents, or choose transition metal-crosslinked fracturing fluid. But all these approaches lead to sever formation damage and reduced effectiveness of the fracturing stimulation.

Polymer fracturing fluid has good solubility to water, with minimum water-insoluble matter and no or extremely low residue after gel breaking, and thus the resultant damage to the formation and the
propped fracture is minor. The main polymer chain, in such cases, is mostly connected by covalent bonds, with no acetal linkage (the primary contributor to thermal degradation of polysaccharides), and thus possesses remarkable thermal tolerance. Therefore, the polymer fracturing fluid has a promising application potential, in terms of high-temperature low-permeability reservoirs.

2. Design of high-temperature polymer fracturing fluid

The most frequently-used synthetic polymer is the polyacrylamide type of polymers, including polyacrylamide (PAM), partially hydrolyzed polyacrylamide (HPAM), methylene polyacrylamide (PHMP) etc.\cite{1-2} The PAM-type polymer is subjected to hydrolysis of the acrylamino, and this impacts the thermal stability of the polymer molecule. Moreover, since polymers lack crosslink-able groups, the way used to increase the viscosity and thermal tolerance of the fluid is in most cases to promote the molecular weight of the polymer\cite{3}. Nevertheless, these weighted polymers are prone to chain breaking at high shear rates, which impacts the fluid property, and accordingly the molecular structure of the polymer has to be optimized. The following is the brief introduction regarding the train of thought regarding the polymer design.

(1) It is required that the main chain structure of the polymer molecule should, as far as possible, be the rigid chain, or all-carbon chain, in order to avoid hydrolysis and degradation of the main chain. Such main chains have improved thermal stability, and in addition, their pendant groups should, as far as possible, be large, and rigid, which raises up the thermal motion resistance and consequently the thermal tolerance of the polymer.

(2) The molecular weight of the polymer should be retained within an appropriate range, so as to decrease the odds of mechanical shear breaking of the molecule chain. For desirable fluid viscosity, the polymer should be able to crosslink with each other (by introduction of crosslink-able groups into the polymer molecule). The fluid can be significantly thickened through crosslinking.

Given the above analysis, it is believed that introducing the high-temperature-tolerant groups, 2-acrylamide, and 2-methylenepropanesulfonic acid (AMPS), into the PAM, can improve the thermal tolerance of the system. This effect is attributed to the sulfonic acid group of AMPS, which generates sulfonate in the aqueous solution to improve the water-solubility of the polymer. Also, the steric hindrance of the polymer promoted by such rigid, large side-chain sulfonic acid groups, improves the thermal tolerance of the polymer. Moreover, the acrylic acid, introduced into the polymer molecule and providing groups capable of crosslinking (carboxyl), is able to crosslink with the multivalent transition metal ion, and this can greatly increase the effective molecular weight and thus reduce the required molecular weight of the polymer.

Taking all above into the consideration, it is concluded that with monomers of PAM, polyacrylic acid, 2-acrylamide and 2-methylenepropane sulfonic acid, the synthetic ternary random copolymer based on free radical polymerization, can meet the requirements on fracturing fluids imposed by high-temperature low-permeability reservoirs. The molecular structure of the synthetic polymer is shown in Fig. 1.

![Molecular structure of synthetic polymers](image)

3. Experimental apparatus and materials

Waring® mixer, Haake® RS6000 rheometer, the propped fracture conductivity measurement device, the core flooding tester, synthetic polymer thickening agents synthesized in the laboratory, ammonium
persulfate, the clean-up additive (BA1-5), the clay stabilizer (BA1-13), the thermal stabilizer (BA1-26), the organic zirconium crosslinking agent, etc. Composition of the fracturing fluid: 0.6% of thickening agents + 0.2% of BA1-5 + 0.3% of BA1-13 +0.3% of BA1-26. Dosage of crosslinkers: 0.3%.

4. Experimental results and discussion

4.1 Shear stability of polymers
Polymers normally have considerable molecular weights, and are subjected to shear degradation of molecule chains at higher shear rates in the wellbore, which impacts the fracturing fluid performance. Hence it is necessary to study the viscosity variation of polymers at different shear rates as well as the viscosity restoring capacity\(^\text{[4]}\). The fracturing fluid shear stability was measured at the room temperature and shear rate of 170 s\(^{-1}\).

![Figure 2. Fracturing fluid viscosity vs. shearing time (at 170 s\(^{-1}\))](image)

It is shown that the effects of shearing time on the fracturing fluid viscosity is minor. After three hours of shearing, the viscosity of the fracturing fluid only drops by 2 mPa·s and this suggests that the polymer fracturing fluid is remarkably shear-stable.

![Figure 3. Shear recovery of fracturing fluids under shearing states](image)

Figure 3 presents the shear recovery of the fracturing fluid viscosity at 70°C. At the shear rate of 170 s\(^{-1}\), the viscosity of the fracturing fluid gradually decreases. After shearing stops for five minutes, the fracturing fluid is then subjected to the shear rate of 511 s\(^{-1}\) for 15 minutes, during which the viscosity declines to 30 mPa·s. Again after five minutes of resting, the fluid is subsequently sheared at 170 s\(^{-1}\) for another 15 minutes and the viscosity presents a constant value of 55 mPa·s. The shearing at 1022 s\(^{-1}\) begins after five-minute restoring and lasts for 15 minutes, and the viscosity falls to 19 mPa·s. But the fracturing fluid viscosity grows back to above 50 mPa·s again at the shear rate of 170 s\(^{-1}\), following a five-minute resting. The data presented above indicate that the polymer fracturing fluid possesses notable shear-thinning behavior, and meanwhile excellent shear recovery capacity.
4.2 Crosslinking delay capacity of fracturing fluids

The base fluid of the fracturing fluid has excellent shear stability and shear recovery capacity. However, in cases of fracturing fluid crosslinking in the wellbore, the situation is totally different\cite{5, 6}. High shear rates have tremendous effects on the sand-carrying capacity of the fracturing fluid, and thus it is required that crosslinking should occur at locations as close as possible to the payzone, so as to minimize the duration of fracturing fluids exposed to high shear rates. In other words, the fracturing fluid should be able to delay the crosslinking.

In terms of the boron-crosslinked system, the crosslinking time is mainly controlled by the pH value, and that of the organic zirconium-crosslinked system by the temperature\cite{7}. Elevated temperatures decrease the bond strength between the complexing agent and the zirconium ion, in favor of the proceeding of crosslinking\cite{8}.

![Figure 4. Crosslinking time vs. temperature](image)

It is illustrated that as the temperature rises, the crosslinking time of the fracturing fluid gradually shortens. An inflection point for the crosslinking time is observed at 40°C, where massive zirconium ions are released from the complex system and join in the crosslinking reaction\cite{9}. The fracturing fluid is continuously heated, as it flows through the wellbore. Meanwhile, zirconium ions participating in crosslinking increase with the growing temperature, which equips the fluid with sufficient proppant-carrying ability. Accordingly, the breaking of the polymer molecule chain or the crosslinking bond, induced by the exposure to high shear rates after rapid crosslinking can be avoided.

4.3 High-temperature rheology of fracturing fluids

The maintaining of fracturing fluid viscosity under high temperatures is the key to a successful fracturing stimulation in high-temperature reservoirs\cite{10}. Although the all-carbon main chain of the synthetic polymer can refuse hydrolysis-induced breaking under high temperatures, it still may suffer from breaking of the molecule chain under high-temperature environments with presence of oxygen. Therefore, the thermal stabilizer should be added into the fracturing fluid, to eliminate free oxygen in the fracturing fluid and enhance the viscosity stability of the fluid under high temperatures. This paper tested the high-temperature rheological property at 170°C and 170 s$^{-1}$, using the Haake® RS6000 rheometer.
It can be seen from Fig. 5 that the gel of the polymer fracturing fluid keeps its viscosity above 300 mPa·s within the initial 20 minutes, which still holds around 100 mPa·s after 60-minute shearing. Even a minor growth of viscosity, by about 15 ~ 20 mPa·s, is seen, when the time of shearing reaches 90 minutes. At last, the gel still retains viscosity of 90 ~ 100 mPa·s, after continuous shearing for 120 minutes. During the latter part of the test, the fracturing fluid viscosity is relatively stable, which demonstrates that the fracturing fluid possesses excellent thermal and shear tolerance.

4.4 Gel breaking testing of fracturing fluids
The polymer fracturing fluid has no acetal linkage, and thus difficulties in hydrolysis-based degradation. The degradation of polymers in such cases is mainly through extra addition of gel breakers (ammonium persulfate), to break the polymer chain with the help of free radical reactions and decrease the fracturing fluid viscosity.

As is shown in Table 1, under low temperatures, gel in fracturing fluids is troubled by difficulties in breaking, and complete gel breaking of the fracturing fluid within a given period of time cannot be fulfilled unless increasing the dosage of the gel breaker. No difficulty of fracturing fluids in gel breaking is observed under high temperatures, and a small amount of gel breaks would be sufficient to ensure rapid and total gel breaking. Given this, one can absolutely use the design principle of the gel breaker for vegetable gum-based fracturing fluids for reference, to improve the gel breaking of the polymer fracturing fluid and decreasing the damage to the propped fracture.

4.5 Fracturing fluid residue testing
The residue amount is an important index to evaluate the fracturing fluid-induced damage to the reservoir and the propped fracture. The polymer fracturing is also referred to as the clean fracturing fluid, which means it should generate minimum residues.

| Test Sample               | Empty-tube Weight (g) | Total Weight after Drying (g) | Residue Weight (g) | Residue Percentage (%) |
|--------------------------|-----------------------|------------------------------|--------------------|------------------------|
| Polymer fracturing fluid | 21.7                  | 21.5                         | 0.0024             | 0                      |
| Modified guar gum        | 26.0                  | 26.1                         | 0.025              | 9.1                    |

Table 1 compares the residue amount of the polymer fracturing fluid and conventional modified guar gum. It is shown that the residue generated by the synthetic polymer is far less than that of the vegetable polymer, and thus the polymer fracturing fluid can greatly decrease the damage to low-permeability reservoir induced by residue plugging.
4.6 Formation damage of polymer fracturing fluids

4.6.1 Propped fracture conductivity damage testing
The damage to the conductivity of the propped fracture attributed to fracturing fluids shortens the effective length of the hydraulic fracture, and compromises the stimulation result of fracturing. The experiment carried out in this paper compared the damage made by two types of gel breakers to the propped fracture. The result indicates that after the gel breaker solution flows through the propped fracture, the conductivity to some extent declines in the two cases. However, in all tests with varied closure stresses, the conductivity reduction of the propped fracture induced by polymer fracturing fluids is lower than that of the modified guar gum-based fracturing fluid.

4.6.2 Rock matrix damage testing
Besides the damage to the propped fracture, the fracturing fluid-induced damage is also embodied as the reservoir damage (to the fracture surface and rock matrix). Given this, this paper used the core flooding test apparatus to compare the rock matrix damage caused by the different gel breakers of the two types of fracturing fluids. It is indicated that the rock matrix damage caused by the polymer fracturing fluid is relatively slighter, with a damage ratio of only 16.7%. This limited damage is rooted in the fact that the polymer fracturing fluid leaves no residue and hence does not lead to pore-throat plugging. In such cases, the rock matrix damage is mainly attributed to the filtrate of the fracturing fluid. As for the modified guar gum fracturing fluid, the damage is mainly solid-plugging, with a damage ratio up to 36.4%.

5. Conclusions
(1) The shear testing indicates that the base fluid of the polymer fracturing fluid has good shear stability and viscosity recovery capacity.
(2) The high-temperature rheology measurement shows that the polymer fracture fluid is rated for 170°C, and can meet the requirements of fracturing stimulation in high-temperature low-permeability reservoirs.
(3) The zirconium-crosslinked polymer fracturing fluid has difficulties in gel breaking under low temperatures, which can be solved by increasing the dosage of gel breakers to achieve rapid and complete gel breaking. In terms of high temperatures, the polymer fracturing fluid can rapidly accomplish gel breaking.
(4) The damage induced by the gel breaker of the polymer fracturing fluid to propped fractures and rock matrix is relatively low, which contributes to the improvement of the stimulation result of low-permeability reservoirs.

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References
[1] Julio Vasquez, Faruk Civan, Thomas M. Shaw. Laboratory Evaluation of High—Temperature Conformance Polymer Systems[J]. SPE80904, 2003.
[2] Mike Parris, Andrey Mirakyan, Carlos Abad. A New Shear-Tolerant High-Temperature Fracturing fluid[J]. SPE121755, 2010.
[3] Cai Bo, Zhang Yiming, Jin Fengming, et al. Research on acid fracturing system with improving stimulated reservoir volume[J]. Drilling Fluid & Completion Fluid, 2013, 30 (1): 69-72.
[4] Rusheng Zhang, Yongjun Lu, Yongli Wang 2006, Study on fracturing fluid system with low damage and high elastic polymer. Drilling fluid and completion fluid, 5-10
[5] Daneshy A A. Hydraulic fracture propagation in the presence of planes of weakness[R]. SPE 4852, 1974.

[6] Cai Bo, Wang Xiaodong, & Wang Xin 2011, Mathematical study of fracture face skin in hydraulic fractures In Chinese. Journal of China University of Mining & Technology, 938-942.

[7] Lin Li, Shuai Zhao, Hongqi Hu, 2009, Development in Solvent System of Cellulose. Journal of Cellulose Science and Technology, 69-75.

[8] Cai Bo, Ding Yunhong, & Lv Yongjun, 2014, Optimizing flow coupling in complex artificial fracture network systems In Chinese Journal of China University of Mining & Technology, 470-474.

[9] Wang Liwei, Cai Bo, Qiu Xiaohui, et al. A Case Study: Field Application of Ultra-High Temperature Fluid in Deep Well[R]. SPE 180546. 2016.

[10] Econmides M., Martin T. 2008, Modern fracturing enhancing natural gas production. Houston: Gulf Publishing Co. 116-125.