PROCEEDINGS, 50th Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 10-12, 2025
SGP-TR-229

Fracturing Fluid Additives for Very High Temperature Geothermal Well Stimulation

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Keywords: SuperHot Rock, EGS, stimulation, fracturing fluid additives, viscosifier, formation damage, polymer degradation

ABSTRACT

Oil and gas fracturing uses a suite of fluid additives to improve the outcomes of hydraulic stimulation. In addition to proppants, viscosifiers, friction reducers, surfactants, acids, scale inhibitors, gel breakers, biocides, tracers and gel stabilizers are added to water for hydraulic fracturing. The DOE Geothermal Reservoir Well Stimulation Program (GRWSP) ongoing from 1979-1984, extended petroleum industry stimulation technologies to geothermal wells. A total of ten stimulations were conducted in a range of hydrothermal resources on wells with low permeability. The methods worked to increase output for the first few geothermal stimulations done at Raft River and at East Mesa where temperatures were around 130-180C. However, none of the wells were economic after the stimulations. However, at higher temperatures like the Baca geothermal area held by UNOCAL done as Phase 2 of the GRWSP and at commercial stimulations done at the Coso geothermal area formation damage, either at the wellbore or into the fracture system, appears to have occurred, at least in part, from the use of fracturing fluid additives that were not thermally stable at the well temperatures (260C-300C). (Entingh, 2000). The high temperature well stimulation tests done at very high temperatures in the Geysers used clear water for the stimulation to avoid these issues. Fervo is having good success using methods developed for shale fracturing at temperatures up to 200C and at FORGE stimulation has been successful at up to 220C. This paper discusses fracturing fluid additives for increasing viscosity to carry proppants into tensile fractures. Testing protocols to qualify fracturing fluids for temperatures above 250C is important to reduce the risk of formation damage during very high temperature geothermal stimulation.

1. INTRODUCTION

2 VISCOSIFIERS

Viscosifiers in fracturing fluids are used to increase the carrying capacity of the fracturing fluid to emplace proppant into the fractures and also to increase the pressure applied to the rock to open the fracture wider in tensile failure. Although oil and gas fracturing may be oil based, geothermal fracturing fluids are always water based. The viscosifier therefore needs to be soluble in water and to remain soluble when encountering formation fluids and as temperature changes. Naturally derived water-soluble polymers such as guar gum, xanthan gum and cellulose are used at lower temperatures typical of oil and gas formations. Higher viscosity can be obtained by increasing the concentration of the polymer or by cross linking the polymers and by adding stabilizers to retain viscosity up to 200ºC. Cross-linking the base gel polymer, usually with a metal cation, not only increases viscosity but also changes the resulting fluid from a viscous fluid to a visco-elastic thixotropic fluid. Thixotropic fluids are lower viscosity at high shear rates such as when they are pumped through the drill string and then become more viscous when velocity and thus shear rate slows down. This reduces frictional pressure drop in the frac string where velocity can carry the proppant but allows for high viscosity at the lower shear rate in the fracture to effectively emplace the proppant. (Ely, 2019)

Most commonly used viscosifiers are polysaccharides that degrade with temperature as the bonds between the monomers break. This reduces the viscosity of the fluid and may also decrease the solubility of the remaining polymer chain. Stabilizers can be added to the fluid to prevent thermal degradation or at least slow it down. As temperature increases above the degradation temperature for the particular polymer, the carbon bonds in the polymer begin to break down as well. The resulting carbonyl and carboxyl building blocks may not only not be more viscous but may not be soluble at all. Finally at very high temperatures, different for each polymer, the only thing left will be a carbon residue.

The pH of the fluid is important to maintaining the properties of the fluid including the rate at which the viscosity increases and then decreases, the stability of the cross-linking and the rate of thermal degradation with gel breakers. Most formations fractured for EGS development have very low porosity and therefore low volumes of in situ fluid. The pH of the fracturing fluid is therefore unlikely to be altered by liquids in the rock. However, particularly in very high temperature volcanic rocks, volcanic gases such as CO_2 or H_2S can lower the pH of the treating fluid as the fluid interacts with the rock.

The behavior of the viscosifiers, gel breakers and friction reducers used for high temperature fracturing is discussed below. The emphasis is on the naturally derived polymers from xanthan gum and guar gum and their thermal behavior with different cross linkers.

2.1 Polysaccharides and Cross-linked Polysaccharides

The viscosifiers most often used in hydraulic fracturing are the naturally derived polysaccharides xanthan gum and guar gum and their cross-linked polymers. These polymers are used as thickeners not only for fracturing fluids but also for water purification, medicine, agriculture, explosives, cosmetics, textiles, paper and food. Some of these industrial uses require much higher temperatures than those seen in oil and gas. (Thakur, et.al. 2018) Published testing reports of the thermal stability of guar gum and xanthan gum and their cross-linked polymers for high temperature oil and gas uses extend up to 180ºC, still low for geothermal fracturing. Testing of thermal degradation of these polymers for other industries has been done up to 1000ºC but the cross-linkers used are not the same as those used in oil gas and the rheology is not always tested. The time that a polymer is exposed to the temperature is also very important to the degradation of the material. Some testing focuses on a range of temperatures while other studies look at the time dependance of degradation only at a set temperature.

Like any polysaccharide guar gum and xanthan gum are made up of simple sugars that are chained together. Guar gum is extracted from guar beans and is made up of the simple sugars galactose and mannose with mannose linked together and a galactose linked to every second mannose (**Error! Reference source not found.**). Guar gum can withstand a temperature of 80ºC for five minutes and doesn't gel on its own. When cross-linked with either borax or calcium it will gel and remain stable over a pH range of 5-7. At lower and higher pH, thermal degradation is accelerated.

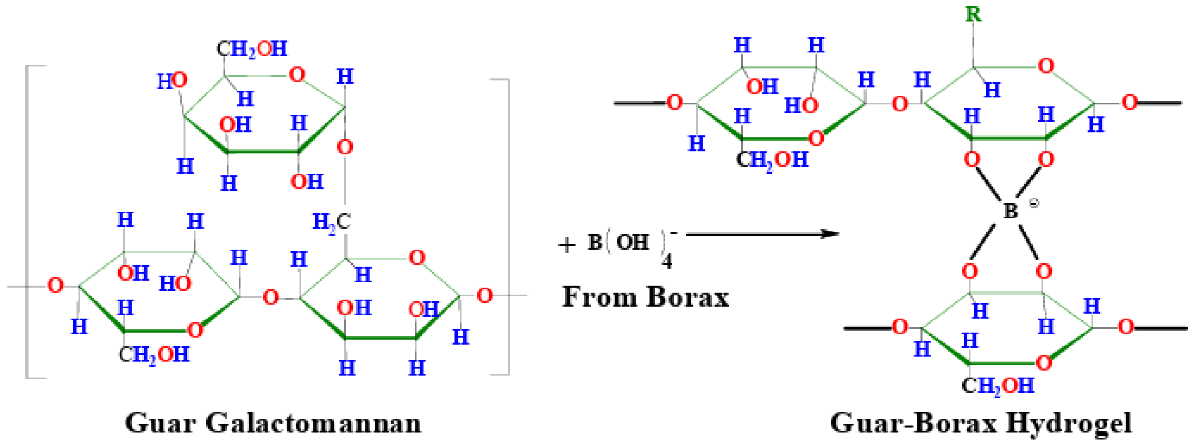


Figure 1 Schematic of synthesis of borax cross-linked guar gum hydrogel (Thakur, et.al. 2018)

Cross-linkers are used to bind the polysaccharide chains into longer polymers that develop higher viscosity with thixotropic properties. The rate at which the cross-linking occurs controls the frictional pressure drop as treatment is pumped down the frac string at high shear rates and then as the velocity slows the cross-linking takes place increasing viscosity to carry the proppant into the fracture being formed. Figure 1 shows a schematic of the cross-linking of guar chains using borax to a hydrogel. Other cross-linkers for guar gum include:

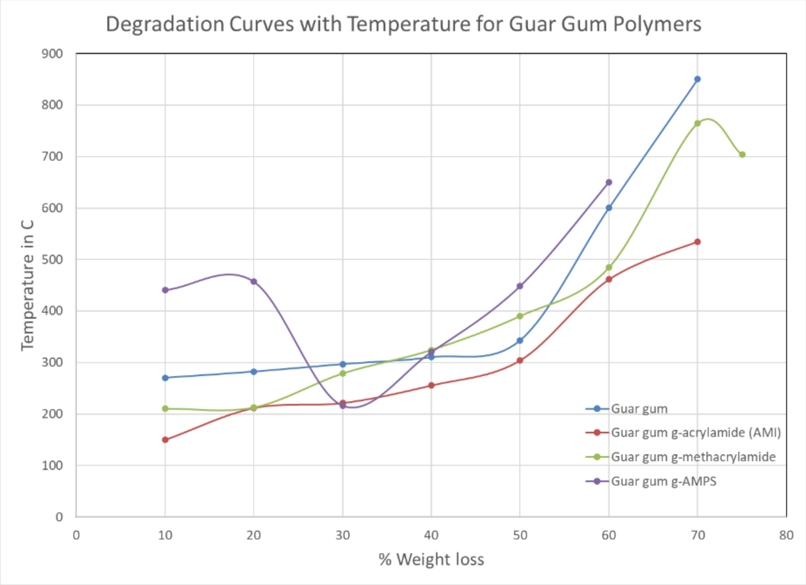
- Boron
- Zirconium
- Titanium
- Epichlorohydrin
- Dimethylacrylamide
- Sodium acrylate
- Vinyl pyridine
- Vinyl formamide
- Carboxymethyl

A cross-linker like boron increases the viscosity of guar gum but is unstable in high temperature, low-permeability reservoirs where the cross-linking is gradually ruptured with increase in temperature. Boron cross-linkers are not stable at temperatures >140 °C and the guar backbone degrades starting temperatures above 160ºC and degrades faster above 177ºC (Xiao, et.al.). The result of the rupture of the bonds is two-fold:1) the galactose bonds break reducing viscosity, 2) the reduction in galactose makes the remaining polymer less soluble in water. A zirconium cross-linker can be used instead of boron taking the temperature stability up to 260ºC, but the viscosity doesn't recover well following high shear during pumping. Using a combination of both zirconium and boron gets past this problem. (Xiao, et.al.) Guar gum cross-linked with other polymers can be more or less thermally stable. Table 2 shows that while guar gum cross-linked with acrylamide degrades at lower temperatures than the base polymer, guar gum cross-linked with acrylamido methylpropane sulfonic acid (AMPs) is initially stable at very high temperatures, greater than 441ºC, but once degradation initiates, it accelerates at lower temperatures but then slows as higher temperatures are reached. (Srivastava, 2012 Figure 2 illustrates this with degradation curves for four guar gum cross-linked polymers. One concern for using these more complex polymers of guar gum is the ability to break the rheology and solubility with temperature of the breakdown products. While the polymers may not lose mass, they may lose viscosity, or viscosity may increase due to the nature of the remaining polymer and the breakdown products. In addition, the ability to break down these high temperature stable gels needs to be investigated.

Table 2 Thermal degradation of polysaccherides with different cross-linked polymers(Srivastava, 2012)

	Tempreature in degrees C							
% Mass Loss	10	20	30	40	50	60	70	75
Guar gum	262.20	286.40	296.80	300.20	306.20	314.20	348.20	400.30
Xanthan gum	270.50	282.40	297.00	310.40	343.20	600.40	850.50	
Guar gum-*g* -acrylamide (AM1)	150.00	212.00	221.60	255.80	304.40	461.30	535.00	
Guar gum-*g* -acrylamide (AM2)	150.00	190.00	200.00	250.60	318.80	440.30	550.00	790.00
Xanthan gum-*g* -acrylamide (AM3)	220.00	280.50	320.00	390.20	540.00	850.00		
Guar gum-*g* -methacrylamide	210.40	212.70	278.80	324.50	390.30	484.50	764.50	704.00
Guar gum-*g* -acrylic acid (AA1)	215.80	280.50	340.80	410.00	460.40	640.00	870.00	836.50
Guar gum-*g* -acrylic acid (AA2)	120.00	180.40	190.30	250.80	340.60	440.60	690.00	
Xanthan gum-*g* -acrylic acid (AA3)	124.00	229.40	295.00	376.00	437.50	633.00	850.00	
Guar gum-*g* -(4-vinyl pyridine)	224.40	257.60	270.00	288.00	316.90	372.70	570.30	
Xanthan gum-*g* -(4-vinyl pyridine)	235.90	277.60	297.00	348.30	605.70	827.00	942.00	
Guar gum-*g* -AMPS	441.15	457.45	216.40	320.40	448.40	650.20		
Xanthan gum-*g* -AMPS	441.85	250.00	325.00	475.00	687.50	1031.30	1175.00	
Guar gum-*g* -*N*-vinyl formamide	231.50	300.70	311.10	372.50	600.00	800.80		
Xanthan gum-*g* -*N*-vinyl formamide	245.60	327.80	568.30	754.90	813.00			685.00
Guar gum-*g* -*N*-vinyl pyrrolidone	231.90	294.50	456.00	687.80	769.70			
Xanthan gum-*g* -methacrylic acid	216.30	258.00	310.00	382.00	478.30	718.00	942.00	

Figure 2 Degradation curves with temperature for cross-linked guar gum polymers



Xanthan gum is another frequently used polysaccharide with slightly better temperature stability than guar gum for the base polymer. Xanthan gum consists of pentasaccharide repeat units of glucose, mannose and glucuronic acid in the ratio 2:2:1 and is derived from fermentation of sucrose and glucose by bacteria. Figure 3 shows the chemical structure of xanthan gum with two possible cross-linked polymers (Patel, et.al.2020). Unlike guar gum, xanthan gum gels on its own at fairly low concentrations in water. However, its viscosity can collapse very suddenly at 70-120°C influenced by the ions in the fracturing fluid. For geothermal applications this can be very problematic, but it does act as a self-breaking polymer if the temperature can be held at a low enough temperature while high viscosity is needed. Adding formates to the fracturing fluid can aid in thermal stability increasing the degradation temperature of the fluid to over 200ºC and also increasing the time for significant mass loss.by up to 16 hours. Anti-oxidants, free radical scavengers and other thermal stabilizers can improve this performance. The pH of the fluid needs to be slightly alkaline so the presence of volcanic gases in the formation fractures may reduce pH and cause sudden loss of viscosity. Cross linking xanthan gum with other polymers can further improve the thermal stability and stabilize the rheologic properties as shown in Table 2. The degradation curves for some of these xanthan gum polymers are shown in Figure 4. While this testing was focused on the mass loss for the polymers tested and no testing of the viscosity was done, the degradation curves do give us a clue to what might happen with viscosity. For the most part, longer chain polymers are going to result in higher viscosity fluids. If the bonds linking together the xanthan gum with the other polymer such as acrylamide or **2-**

Acrylamido-2-methylpropane sulfonic acid (AMPS) are severed as part of the degradation process as the polymer heats up, then the remaining polymers will be the xanthan gum and the AMPS or what ever.polymer was linked the xanthan gum. The xanthan gum is then subject to the temperature and may experience the sudden collapse of viscosity.

Figure 3 Chemical structure of xanthan gum and some cross-linked polymers (Patel, 2020)

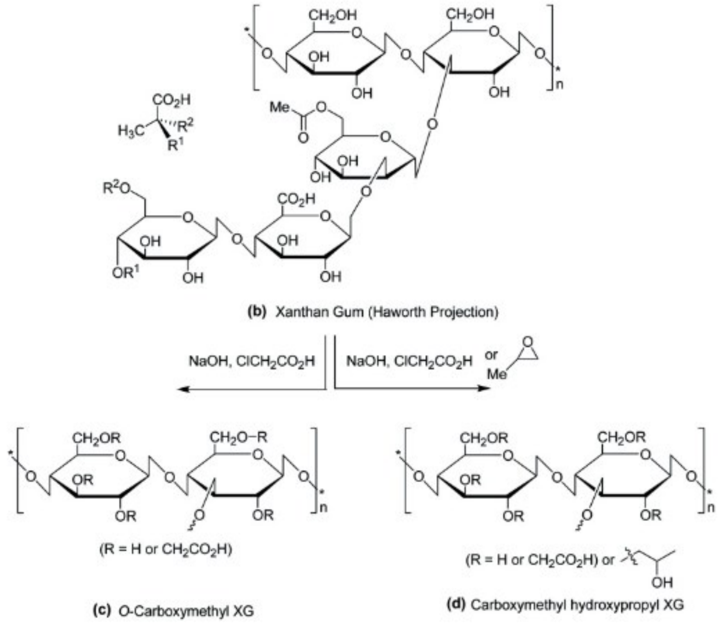
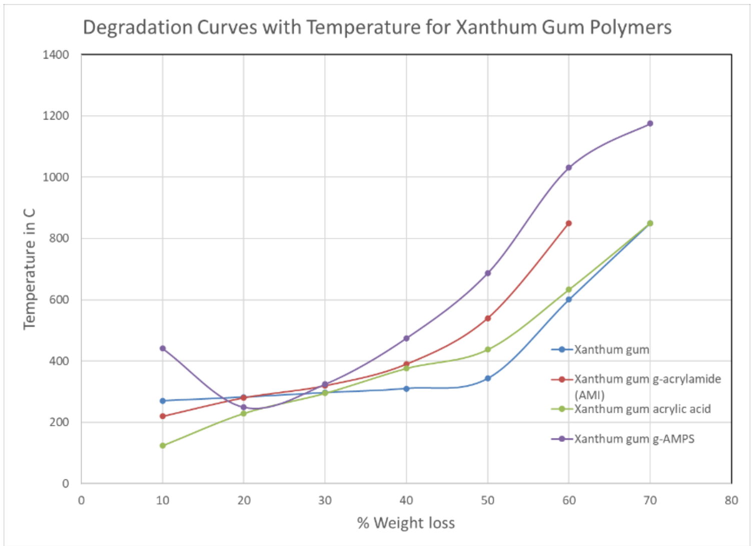


Figure 4 Degradation Curves for xanthan gum and cross-linked polymers



2.2 Polyacrylamides

Polyacrylamides alone or cross-linked to guar or xanthan gum can perform as thermally stable viscosifiers as seen in Table 2. However, they can exhibit incomplete gel breaking and cause formation damage. The polymer can also break down leaving insoluble residue in the fractures and in the proppant pack. The blockages consist of inorganic and organic components, with the inorganic portion composed of 63.5 % quartz and 35.0 % siderite dissolved from the rock, while the organic portion is mainly composed of a complex of polyacrylamide and Fe ion. Polyacrylamide is often used as a high viscosity friction reducer since it has interesting rheologic properties that allow it to provide low frictional pressure drop while retaining high viscosity at low shear rates.

2.3 Silica gel

silica gel-based fracturing fluids have achieved good production enhancement effects in practical field applications, there is relatively limited literature available on the fundamental performance of silica gel-based fracturing fluids. Conclusions regarding the performance of silica gel-based fracturing fluids have mainly been drawn from field application cases, and there is still a lack of systematic performance evaluation through experimental research. For example, in geothermal well fracturing cases, the reservoir temperature reached as high as 260ºC. Experimental data is only available for temperatures up to 90ºC so more work is needed to determine if silica gels will be useful for geothermal situations.

3 GEL BREAKERS

Gel breakers are used to remove the viscosifier from the wellbore, proppant pack and the formation and created fractures. Several different gel breakers are available that are stable at high temperatures:

- Strong acid solutions – since many of the cross-linking agents aren't stable at high temperatures, lower the pH can break the bonds and reduce viscosity. Strong acids don't work for metal-cross-linked polymer gels like metal-acrylamide polymer gels. Temperature accelerates the action of the acid so larger volumes of lower strength acid may work better at geothermal temperatures.
- Hydrogen peroxide – this strong oxidizer can break down many of the most strongly bonded visosifiers such as metal-cross-linked acrylamide polymer gels that don't break down with strong acids. However, peroxide can react with rust on the tubulars and many other substances in the fracturing fluid.so that not enough is left to break apart the bonds. Temperature also accelerates the action of hydrogen peroxide so that it may have all reacted by the time it gets out into the fracture.
- Bleach – Sodium hypochlorite or sodium chlorite. These work well for acrylamide polymer gels. It survives downhole conditions better than hydrogen peroxide but it can cause polymer cross-linked with chromium (III) to convert to toxic chromium(IV). Since most geothermal reservoirs are reducing environments the Cr(IV) probably converts back to Cr(III) but it is important to contain any flow back fluids if a chromium cross-linker is used.
- Some gels are designed to reverse in viscosity using chemicals that break down on their own. This reversing ability is likely affected by temperature, but no easily found published data is available on this.

There are several reasons why a chemical breaker doesn't work to fully degrade a gel that has been placed deeply in either a matrix-rock or a fractured reservoir. First, successfully delivering the chemically reactive gel-breaker solution deeply in an oil reservoir is a daunting task. Second, and more fundamentally problematic, even if a chemical breaker solution could be 100% effective in the reservoir during its entire gel-breaking life, once injected into the reservoir, the gel-breaker solution would tend to wormhole through the emplaced gel. Thus, the chemical breaker would only be able to regain a small fraction of the pre-gel-treatment fluid-flow capacity within the gel-treated reservoir volume. (Petrowiki, 2015) Another issue is that once the gel breaker works to break apart the cross-linked bonds, the increasing temperature near the wellbore after the cooling from the treatment degrades the base polymer leaving insoluble breakdown products that sometimes even strong acids can't remove. (Personal experience)

4 CONCLUSIONS AND RECOMMENDATIONS

Guar gum and xanthan gum have potential when cross-linked with appropriate metal anions and with other polymers to maintain viscosity at very high temperatures. However, there are risks associated with the break down products of guar gum and with the thermal stability of xanthan gum that can cause serious formation damage. The sudden loss of viscosity in xanthan gum based fluids can result in dropping the proppant before it has fully penetrated the fracture. High temperature stable polymers of both polysaccharides have been developed but whether gel breakers can be developed to remove them from the formation is not yet know.

Test data for rheologic properties of the polysaccharide based fracturing fluids at high temperatures above 230ºC are needed prior to using these polymers at in EGS stimulation. An API procedure for qualifying high temperature viscosifiers and gel breakers for EGS use is needed.

REFERENCES

Ely, J. W., Herndon, R. A. "Fracturing Fluids and Additives", Hydraulic Fracturing: Fundamentals and Advancements, Jennifer L. Miskimins, Society of Petroleum Engineers, 2019.

Arti Srivastava, Vivek Mishra, Pooja Singh, Ambika Srivastava & Rajesh Kumar, Comparative study of thermal degradation behavior of graft copolymers of polysaccharides and vinyl monomers, Journal of Thermal Analysis and Calorimetry, (2012) 107-1:211-223.

D. W. Brown, P. R. F'ranke, M. C. Smith, and M. G. Wilson Hot Dry Rock Geothermal Energy Development Program Annual Report Fiscal Year 1985

Sourbh Thakura, Bhawna Sharmab, Ankit Vermab, Jyoti Chaudharyb Sigitas Tamuleviciusa, Vijay Kumar Thakurc* International Journal of Polymer Analysis and Characterization, Volume 23, 2018 - Issue 7, pp. 621-632

Bo XIAO, Shicheng ZHANG, Jian ZHANG, Tengfei HOU, Tiankui GUO, Experimental Investigation Of A High Temperature Resistant And Low Friction Fracturing Fluid, Physicochem. Probl. Miner. Process. 51(1), 2015, 37−47

PetroWiki. 2015. Gel breakers. https://petrowiki.spe.org/Gel_breakers (2024).

Patel J, Maji B, Moorthy NSHN, Maiti S, Xanthan gum derivatives: review of synthesis, properties and diverse applications, RSC Advances, 21 Jul 2020, 10(45):27103-27136

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Siv Howard, Cabot; Lauren Kaminski, formerly Cabot; John Downs, Xanthan Stability in Formate Brines - Formulating Non-damaging Fluids for High Temperature Applications, SPE European Formation Damage Conference and Exhibition held in Budapest, Hungary, 3–5 June 2015.

Zhongzheng Xu a b, Mingwei Zhao a b, Jiawei Liu c, Yiming Zhang a b, Mingwei Gao a b, Xuguang Song d, Ning Sun a b, Lin Li a b, Yining Wu a b, Caili Dai, Study on formation process and reservoir damage mechanism of blockages caused by polyacrylamide fracturing fluid in production wells, Fuel, February, 2024, Volume 358, Part A.