

## New Insights of Formation Damage Caused by Borate Crosslinker Fracturing Fluids

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### Abstract

Hydraulic fracturing has substantially increased the productivity of unconventional reservoirs. The most widely used one is the cross-linked fracturing fluids. Therefore this study analyzed the formation damage issues caused by borate cross-linked fracturing fluids. Results shows that permeability of formation and proppant pack conductivity are greatly affected by residue left behind. The unbroken polymer chains may be cross-linked again if favor conditions present. The residue will ultimately reduce the conductivity of sand pack and only a small amount of guar residue can be displaced with production. To minimize the formation damage problems caused by polymer residue, the concentration of breaker needs to be the optimum value. To help analyze the degradation extent of fracturing fluids, flow-back fluids can be analyzed through various chemical analysis methods, taking into account the dilution effect of produced water.

**Keywords:** Borate cross linker; Hydraulic fracturing; Fracture conductivity; Formation damage

### Introduction

In the oil and gas industry, how to design and select the hydraulic fracturing fluids has become more and more important, especially for unconventional reservoirs, which requires minimum formation damage of fracturing fluids to reservoirs [1-5]. Gelled fracturing fluids are the most commonly used ones because of their viscosity characteristics and crosslink ability, increasing their proppant carrying capacity. More proppant and higher concentration of proppant are place in the fractures. However, gelled fracturing fluids may cause potential formation damage to the reservoirs and therefore lead to decreased productivity [6-9]. This paper presents a comprehensive analysis of the formation damage issues caused by borate fracturing fluids and various damage evaluation methods were also discussed. The formation damage issues mainly include, but not limit to, fluid loss, permeability damage, crosslink damage, and damage on fracture conductivity [10-13].

### Components

Typically, borate fracturing fluid system is composed of gelling agent, buffer agent, borate crosslinker, breaker and water as the based fluid. The most usually used gelling agents are hydroxyPropyl guar (HPG), carboxymethyl gual (CMG), carboxymethyl hydroxypropyl gual (CMHPG). The purpose of using them are to increase viscosity, to form filter cake, and to help carry proppant deep into formation. In some cases, the molecular structure of Guar chemical modified to form HPG, CMG or CMHPG to improve crosslink performance in low pH fluids. This can also increase the high temperature stability and reduce insoluble residue [14]. The addition of buffer is to adjust the pH of base fluid so that gelling agent can hydrate or crosslink time can be delayed. The most commonly used buffers are listed in Table 1. Cross linker will crosslink the backbone of polymers to substantially increase the viscosity of gelled fluids by tens of hundreds magnitude. Figure 1 shows a typical image for cross-linked polymers. High viscosity can have high proppant carrying capacity. Borate cross linker is one of the most commonly used one, including boric acid, calcium, magnesium and organic borate [15-17]. At around pH value of 8.2, borate ions will form a 3 dimensional network with the cis-hydroxyl sites in the polymer, thus further increase the viscosity of fracturing

fluids. Researchers found that pH value of 10.5 is the optimum value where cross linker is most effective. Cross linkers are in equilibrium and can be broken by shear stress [18] (Table 1 and Figure 1). There are mainly three categories of breakers: oxidizer, acid and enzyme. Breaker

Increase of pH	Decrease of pH
Sodium bicarbonate	Formic Acid
Sodium carbonate	Fumaric Acid
Sodium hydroxide	Hydrochloric Acid
Monosodium Phosphate	Magnesium Oxide

Table 1: Commonly used buffers in fracturing fluids.

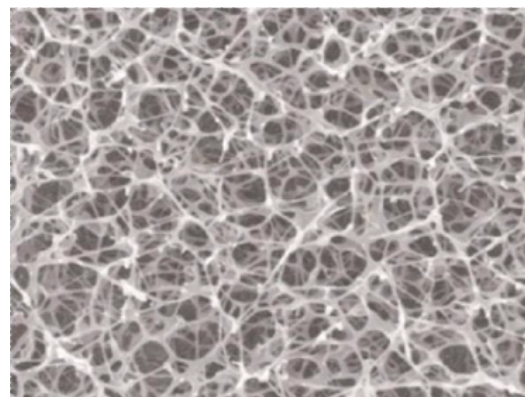


Figure 1: Cross linked polymers.

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reduces viscosity and enables flow-back of residual polymer. Flow-back of fracturing fluids should be started before the fracture closes as the residual polymers will form insoluble precipitates in the formation and result conductivity damage. Persulfate oxidizer breakers are most used in low temperature applications due to their temperature limitation. While peroxides breakers can be used at various temperature conditions. Acid is seldom used as breakers because of the formation of considerable insoluble materials [19]. Acid is mainly used to clean fractures of any residue or unbroken fluid. Enzyme is usually used in temperature below 150°F and pH value between 4 and 9. Typical enzyme breakers are hemicelluloses, cellulose, amylase, and pectinase.

### Formation Permeability Damage

Studies show that there are 4 divided regions in formation permeability damage, with region 1 being close to fracture face. Compared with the other 3 regions, region 1 has the most concentrated polymer residue and is the one that contacts with hydraulic fluids the longest time. Regions 2 and 3 have the most permeability recovery [20-22]. The original permeability of the formation also affects the results. Low permeability rock (below 1 md) allows better filter cake build-up. High permeability rock (more than 5 md) does not allow filter cake buildup for linear gel. Temperature also has a profound effect. Under high temperature conditions, it was found that more permeability gain was observed in regions 2 and 3.

### Borate Cross Liner Damage

Traditional borate crosslink fluid system maintains good proppant suspension capacity, high resistance for shear stress and temperature. However, this type of fracturing fluid system can cause significant skin damage and decrease well productivity. Borate functions when monobore ion complexes with the cis-hydroxyl sites of guar polymer [23]. Borate crosslinked fracturing fluids can damage both the formation and permeability of proppant pack. Insoluble gels residual of crosslinked fluids have been proven to have a regained conductivity of 10-12% less compared that without crosslinkers. However, the increase of breaker concentration can increase the regained conductivity. The negative effect of increase of breaker concentration can decrease proppant carrying capacity since crosslinker will be degraded faster [24]. The broken parts can become insoluble in water and will precipitate out of water. Potential damage to formation permeability and proppant pack will occur. The industry standard for gel viscosity is 10 cp after degraded by breakers. However, this standard is invalid when considerable amount of large molecule polymers still exist in the fracturing solution. Those unbroken gels can cause severe damage to formation damage and proppant pack conductivity. To be able to analyze the distribution characteristics of broken gel, gel permeation chromatography technique may be applied

to characterize the concentrations or distribution of different sizes of polymers. This technique separates different sizes of broken gels based on hydrodynamic volume of the analytes [25,26].

### Effect of Fracturing Fluids on Conductivity

Studies show that residue of fracturing fluids will reduce the proppant pack conductivity over a long period of time. Those residues, under most circumstances, will reside inside the fracture and can hardly be displaced by production and will degrade very slowly [27]. Formation stress has profound effect on the extent of fracturing residue that it affects the proppant pack conductivity, shown in Table 2. High residue of fracturing fluids would be expected in the fracture opposite permeable zone. Therefore, fracture conductivity away from the well may be lower enough to partially plug the fracture and a short effect fracture length would be expected. As discussed above, optimal breaker concentration should be designed to reduce guar residue inside the fracture [28]. On the other hand, because of the gravity effect and sand setting, the bottom of the fracture will maintain high concentration of proppant. This will increase the accumulation of guar residue in some parts of the fracture and fracture conductivity is decreased.

### Damage Evaluation Methods

As discussed above, the unbroken gel residue after fracturing can greatly damage the proppant pack permeability. Flow-back samples of fracturing fluids should be monitored to examine the extent of gel broken inside the fracture. One of the effective ways to quantify the extent of clean-up is to measure concentrations of chlorides, sulfates, and specific gravity. The difference between the source and flow-back of fracturing fluids can indicate how much gels have been broken [29,30]. Another helpful method is to continuously measure viscosity of flow-back fluids. Reduced viscosity means gel degradation. However, one should also note that the produced water will dilute the fluids, and some corrections need to be taken into account [31-33]. Carbohydrate analysis is also another helpful tool. Studies have demonstrated that guar consists of mannose backbone with galactose side chain bonded to every mannose unit. Total carbohydrate content is measured by a procedure called “Anthrone”, with the assumption that carbohydrate is dehydrated with strong acids under non-oxidizing conditions [34].

### Conclusions

Based on above discussions, the following conclusions can be drawn:

- Gel residue has a profound effect on fracture conductivity, even under low viscosity of flow-back fluids. Some unbroken polymers are enough to be crosslinked under certain circumstances. Therefore, optimum break concentration should be designed to make sure gel are degraded.

Exp	Stress, psi	Polymer Type	Polymer Concentration, 1 lb/1,000 gal	Breaker	Residue Concentration, vol/vol	Permeability darcies
1.	3000	Guar	190	Internal	0.12	115
2.	3000	Guar	480	Oxidizer	0.22	90
3.	5000	Guar	190	Internal	0.12	43
4.	5000	Guar	480	Oxidizer	0.22	29
5.	5000	Cellulose Derivative	190	Oxidizer	0.01	54
6.	7000	Guar	240	Oxidizer	0.12	12
7.	7000	Cellulose Derivative	240	Oxidizer	0.01	23
8.	8000	Guar	190	Internal	0.12	11
9.	8000	Guar	480	Oxidizer	0.22	8
10	8000	Cellulose Derivative	190	Oxidizer	0.01	16

Table 2: Permeability of 20-40 mesh sand containing fracturing fluid residue.

- Residue in pore spaces will ultimately reduce permeability of proppant pack and only a small amount of guar residue can be displaced under high pressure gradient.

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