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Fracturing Fluid Components

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Additional information is available at the end of the chapter

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Abstract

The materials and chemistry used to manufacture hydraulic fracture fluids are often confusing and difficult for the practicing hydraulic fracturing engineer to understand and optimize. Many times the failure of a particular fracturing treatment is blamed on the fluid because that is a major unknown from the design engineer's viewpoint. Many of the components and processes used to manufacture the fluid are held proprietary by the service company which adds to the confusion and misunderstanding. This paper makes an attempt to describe the components used in fracturing fluids at a level that the practicing frac engineer can understand and use. The paper is intended as a companion paper to the Fracturing Fluids design paper which describes how to use the fluids and viscosity generated by the fluids to design a fracturing treatment.

1. Introduction

1.1. Water

The water used for hydraulic fracturing is a critical component of the fluid. It must be carefully quality controlled as describe in the Quality Control Chapter. Typically the water is filtered to 50 μ (microns) for propped fracturing treatments and to 2 μ for frac and pack treatments. Fresh water is normally used but there are gelling agents available for seawater. The main disadvantage of seawater is the presence of Sulfate which can interact with connate reservoir water causing sulphate scales to form and provides a sulfur source for Sulfate reducing bacteria. The use of post frac flowback water is becoming

common especially for slickwater fracs. When flowback water is used to manufacture crosslinked gels care must be taken because the water may contain residual breaker.

2. Clay control agents

KCl or an organic clay stabilizer is added to the base fluid to prevent the water from interacting with the reservoir mineralogy. KCl is typically added at a concentration of 2% but can be added at concentrations as high as 8% depending on laboratory testing results. Most testing on the commercially available organic clay stabilizers, which are typically some form of Quaternary Amine compound, has found them to be ineffective at the normal concentrations recommended. KCl is unique in its ability to stabilize clays and is much more effective than other inorganic salts such as NaCl, CaCl₂ etc.

3. Friction Reducers (FR)

These materials are added to water to manufacture what is called “slickwater”. They are added to reduce the friction generated as the fluid is pumped down the well tubulars. FR’s are typically added to the frac fluid at a concentration of 0.25 to 2 gal/1000 gal. Figure 1 shows a comparison of the friction when pumping water, FR “Slickwater” and Guar “Waterfrac”. There are several forms of FR which are also shown in Figure 1. They are:

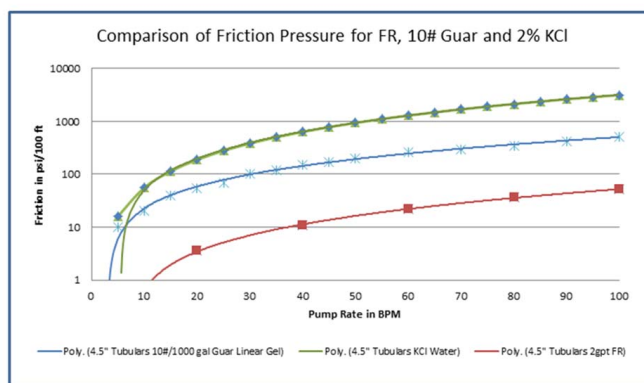
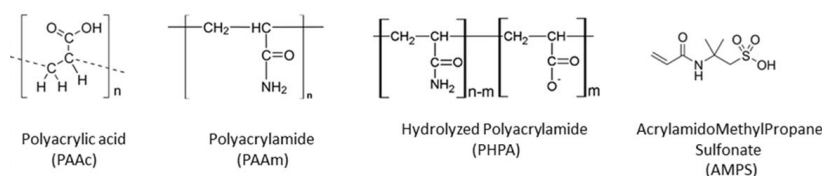


Figure 1. Chemical Structure of various Friction Reduction (FR) agents and a comparison of friction pressure for water containing only 2% KCl vs. water containing 2% KCl and 2 gallons per 1000 gallons (FR) and 10# Guar pumped down 4 1/2" 11.5# 4" ID casing.

3.1. Polyacrylic Acid (PAAc)

PAAc which is a non-toxic synthetic high molecular weight polymer of acrylic acid. The material is sold as either a white solid or as a 50% active dispersion of the solid in mineral oil which makes it easy to disperse and solublize in water. The molecule is very sensitive to divalent cationic ions (cations) such as Ca, Mg, Fe etc. and will quickly precipitate if used in hard water. Other uses for PAAc include adsorbents for disposable diapers, ion exchange resins, adhesives and as thickeners' for pharmaceuticals, cosmetics and paints.

3.2. Polyacrylamide (PAAm)

PAAm is formed from acrylamide subunits. It is non-toxic however unpolymerized acrylamide is a neurotoxin and if the PAAm is not properly manufactured it can contain some unpolymerized acrylamide. As a solid PAAm is slower to hydrate than PAAc but is less sensitive to divalent cations. It is typically delivered to the field as a 50% active suspension of PAAm emulsified in mineral oil. The PAAm polymer is quite difficult to break and is used to gel 15% HCl so is damaging to the reservoir rock and proppant pack when used. When used in Slickwater fracturing Carman and Cawiezel [19] have reported successful breaker optimization for the material. Other uses for PAAm include flocculants for wastewater treatment and papermaking, as a soil conditioner and for making soft contact lens.

3.3. Partially Hydrolyzed Polyacrylamide (PHPA)

PHPA is the most common friction reducer available. It is made by reacting sodium acrylate with acrylamide so that approximately 30 % of the acrylamide groups are in the hydrolyzed form. This improves the solubility in water, makes the polymer more compatible with cationic minerals and is commonly marketed as a 50% active dispersion in mineral oil. Because it is widely used in industry as a flocculant for water and paper manufacture it is the least expensive FR and therefore the most widely used.

3.4. AcrylamidoMethylPropane Sulfonate (AMPS)

AMPS is chemically structured so that the molecule is less susceptible to precipitation by cationic mineral salts which may be present in hard water or to high temperatures. It is also stable at a wide range of pH so that it is functional in energized fluids that contain CO₂. The Sulfonate character of the polymer also makes it active as a scale inhibitor. It is typically marketed as a 50% active emulsion. Other uses for AMPS include electrocardiogram gels, plasticizers for concrete and as coagulants in water treatment processes.

4. Gelling agents

These materials are added to the fracturing fluid to increase the viscosity. This increases the fracture width so it can accept higher concentrations of proppant, reduces the fluid loss to improve fluid efficiency, improves proppant transport and reduces the friction pressure. The

chemical structure of some gelling agents also allow for crosslinking. The viscosity of a gelling agent in solution is a function of its molecular weight. The viscosity increases with increasing chain length and concentration. Figure 2 shows how this occurs. For slick water the polymer concentration should be below the Critical Overlap Concentration C^* , for crosslinked gels the ideal range is between the C^* and the Critical Entanglement Concentration C^{**} . When the concentration exceeds the C^{**} a process called syneresis occurs in which the gel is over-crosslinked and water is “squeezed” out of the gel matrix. As water is removed from the polymer mixture as fluid loss occurs in the fracture the concentration of polymer increases dramatically causing damage to the proppant conductivity.

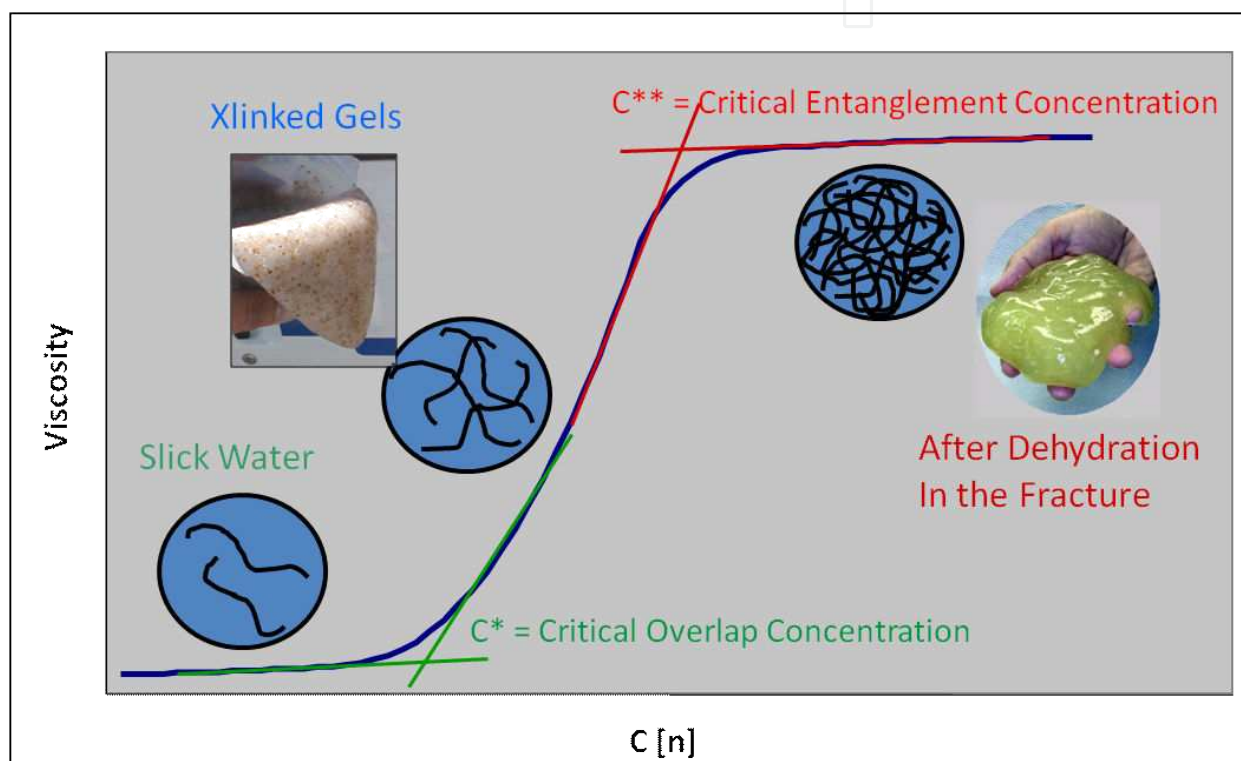


Figure 2. Intrinsic Viscosity of a Solution as a Function of the Polymer Concentration

4.1. Guar

Guar and its derivatives HydroxyPropyl Guar (HPG), CarboxyMethyl Guar (CMG) and CarboxyMethylHydroxyPropyl Guar (CMHPG) are the most common gelling agents used for fracturing. As shown in Figure 3 Guar [*Cyamopsis tetragonoloba*] is a natural galactomannan gum of the Legume family which is mostly grown in India. Beckwith[1] provides a very nice summary of guar and reports that in 2012 the industry used about 25,000 tons of guar a month at a wholesale cost of \$1,723 US/100 kg (\$7.83/lb).

After harvesting the seed coat and germ are removed to form what is called a Guar Split. This Guar Split is ground to form guar powder. This process is shown diagrammatically in Figure 4. The chemical structure of guar (See Figure 5) is unique in that it can be readily crosslinked



Figure 3. Guar

through the cis-hydroxyl functionality shown in Red and easily broken through the acetyl linkages shown in Blue. When Guar is broken it leave a 6 to 10% insoluble residue. To reduce this insoluble residue, improve the high temperature stability and improve the crosslinking performance in low pH fluids such as CO₂ the molecular structure of guar is chemically modified with Propylene Oxide to form HPG and with Monochloric Acetic Acid to form CMG or CMHPG. The chemical process is shown in Figure 6.

When using Guar or its derivatives the fluid loss control mechanism is “wall-building – i.e. C-III” in that when the base fluid leaks off the polymer is deposited on the rock face forming a filter cake. The initial leakoff is quite rapid and is called “Spurt”. Once a filter cake forms the leak-off becomes a function of the square root of time as described in the companion paper on Fracturing Fluids.

When mixing dry powered Guar, care must be taken to avoid “fisheyes by adjusting the pH of the base water to above 7 and using a high energy mixer to allow proper dispersion. Once the polymer is dispersed the pH is adjusted to just below 6 to allow hydration. Most modern commercially packaged powered Guar systems contain a buffer package that automatically adjusts the pH of the water as the powder is added to prevent fisheyes. When packaged systems are hydrated the pH of the base water needs to be near neutral and a high energy mixer used. Care must also be taken when using very cold water (<60°F) because the rate of solution for the buffer packages can be affected. Guar emulsified in mineral oil as a 50% active material is also commonly used.

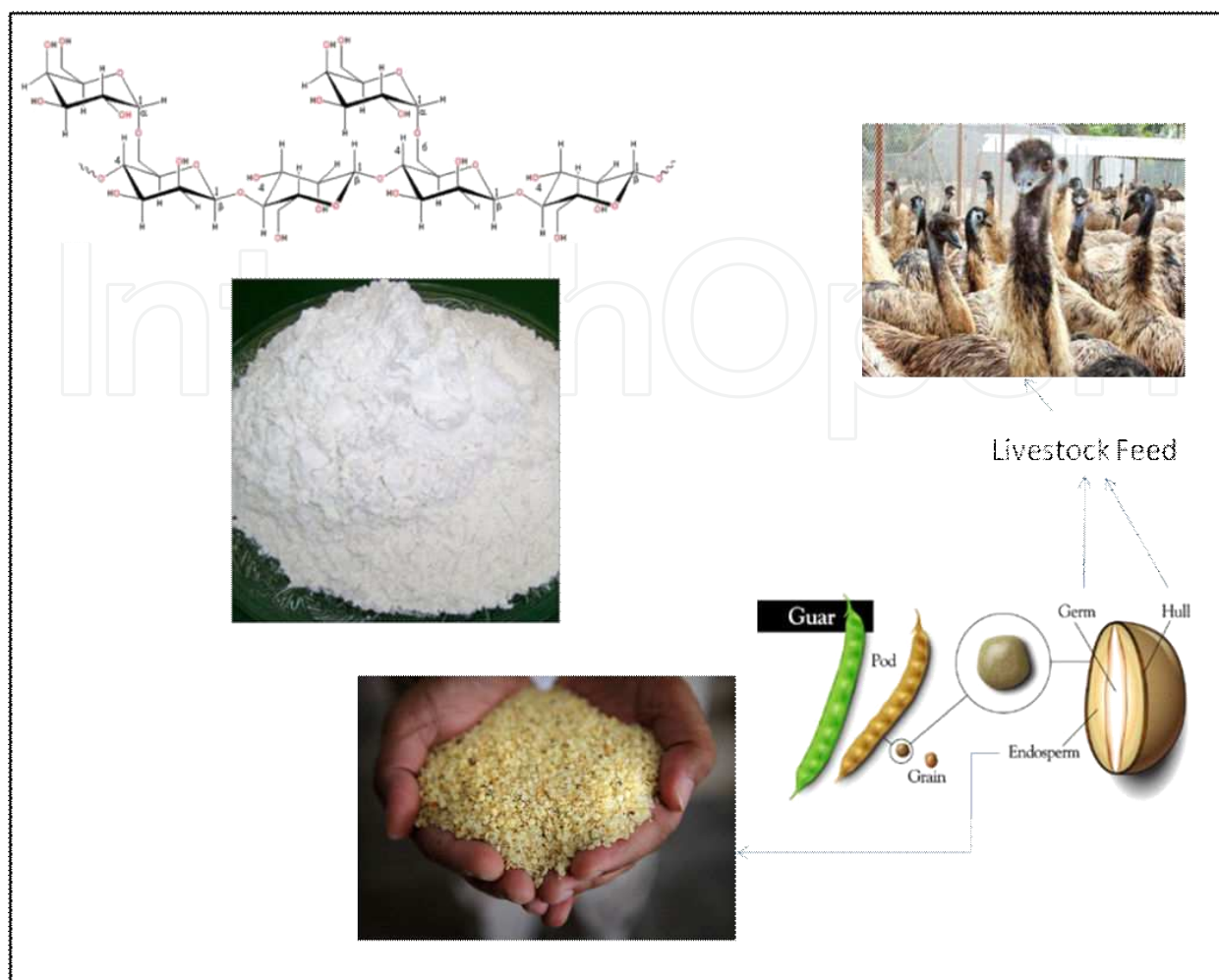


Figure 4. The process of manufacturing Guar Powder

4.2. HydroxyEthyl Cellulose (HEC)

HEC and CarboxyMethylHydroxyEthyl Cellulose (CMHEC) are derivatives of cellulose which is the most common organic compound on Earth. About 33% of all plant matter is a cellulosan organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand linked glucose units. As with Guar, Cellulose can be reacted with Propylene Oxide and/or Monochloric Acetic Acid to produce HEC or CMHEC. The chemical makeup of HEC and CMHEC is shown in Figure 9. The base cellulose used to make HEC and CMHEC comes mainly from cotton which is 90% cellulose. HEC and CMHEC are non-toxic and hypoallergenic and are widely used as a viscosifier and emulsion stabilizer in ice cream, K-Y Jelly, toothpaste, cosmetics, laxatives, diet pills, water-based paints, textile sizing and paper.

Because HEC and CMHEC is 100% soluble in water and contain very little insoluble residue they are used where conductivity is the main driver for design. This is in applications such as gravel packing and Frac/Packing. The fluid loss mechanism is "Viscosity- Controlled – i.e. C-II". To control fluid loss the polymers are used to produce very viscous linear gels. However

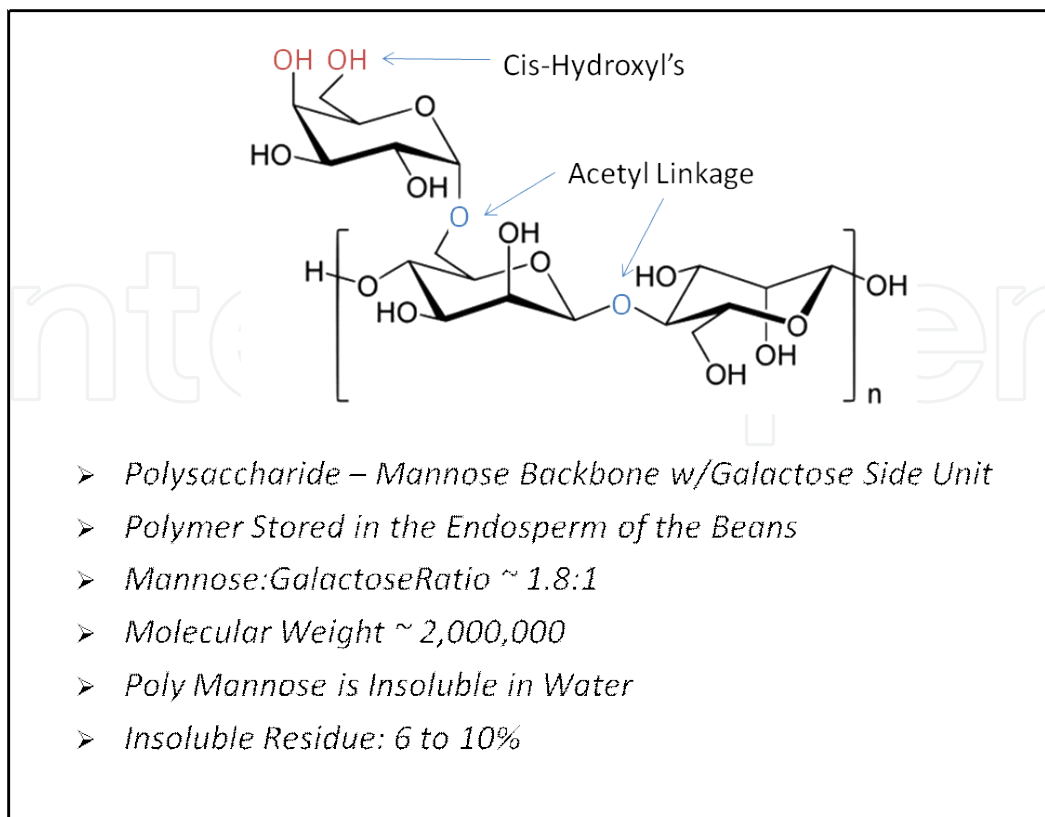


Figure 5. The chemical structure of Guar

above 60 to 80 lb of polymer/1000 gallons of water it becomes difficult to mix. Because the hydroxyls in HEC are in the trans- position (See Figure 9) it cannot be crosslinked and can only be used as a linear gel. The addition of the Carboxy Methyl group in CMHEC provides a crosslinking site so it can be crosslinked using the same mechanisms described for Guar.

4.3. ViscoElastic Surfactant (VES)

VES are polymer free aqueous based fracturing fluids that generate their viscosity through the association of surfactant molecules (Figure 10). As the concentration of surfactant is increased the molecules reach a point where they form aggregates called micelles where the hydrophobic tails form the core of the aggregate and the hydrophilic heads are in contact with the surrounding aqueous liquid. This occurs at a point called the Critical Micelle Concentration (CMC). As the concentration of micelles increase they become entangled with one another at C^* as shown in Figure 10. Typically this point is at about 4 to 6% by weight of surfactant. Anionic, cationic and zwitterionic surfactants are used to formulate VES fluids. The main advantage of these fluids is that they are non-damaging to the fracture conductivity. Fluid loss is "Viscosity- Controlled – i.e. C-II" which make the fluids particularly appropriate for Frac and Pack applications. Breaking is accomplished by overflushing with a Mutual Solvent, using an encapsulated electrolyte or by dilution. The main disadvantage these fluids have is their strong surfactant base which makes them incompatible with many reservoir fluids. The

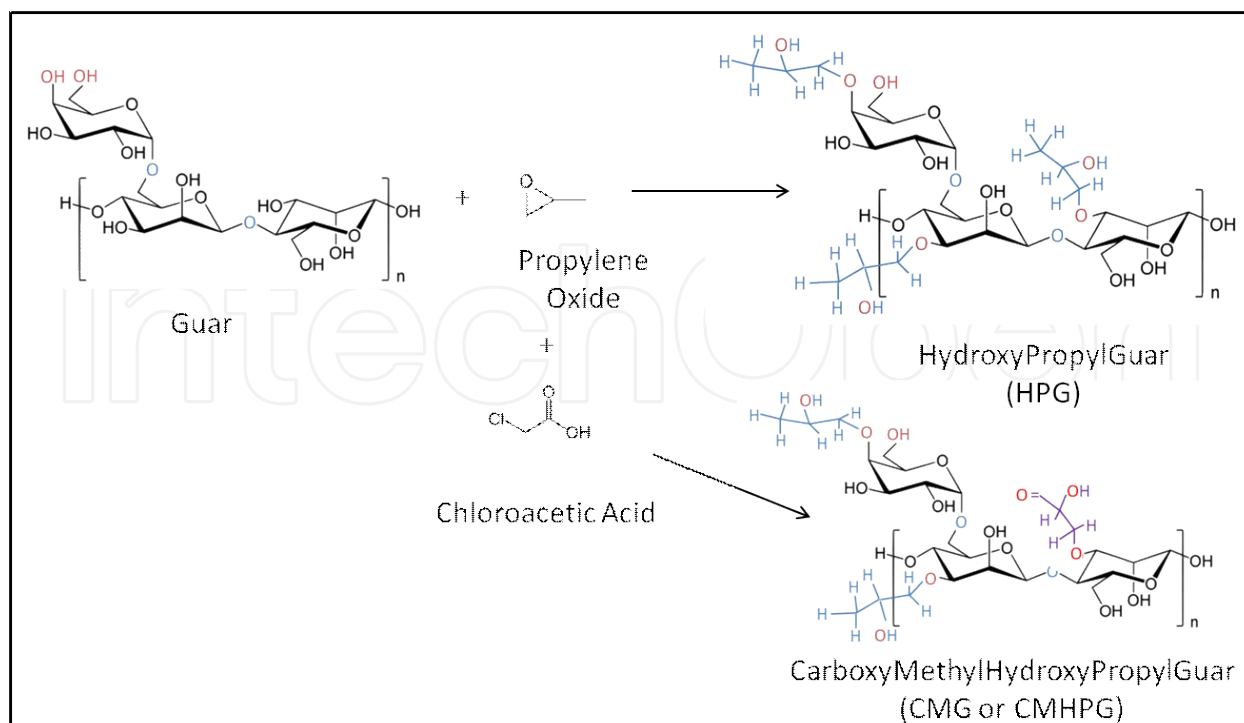


Figure 6. The formulation of HPG, CMG and CMHPG from Guar

surfactants are so strong they have been known to upset even very high API condensate type hydrocarbons.

4.4. Foam/PolyEmulsions

Foam/polyemulsions are fluids that are composed of a material that is not miscible with water. This could be Nitrogen, Carbon dioxide or a hydrocarbon such as Propane, diesel or condensate. These fluids are very clean, have very good fluid loss control, provide excellent proppant transport and break easily simply via gravity separation. PolyEmulsions are formed by emulsifying a hydrocarbon such as Condensate or Diesel with water such that the hydrocarbon is the external phase. The viscosity is controlled by varying the hydrocarbon/water ratio. Foams made with Nitrogen or Carbon dioxide is generally 65 to 80% (termed 65 to 80 quality) gas in a water carrying media which contains a surfactant based foaming agent. Sometimes N₂ or CO₂ are added at a lower concentration (20 to 30 quality) to form “Energized Fluids”. This is done to reduce the amount of water placed on the formation and to provide additional energy to aid in load recover during the post-frac flow back period. Nitrogen can dissipate into the reservoir quite quickly so fluids energized with N₂ should be flowed back as soon as the fracture is closed. CO₂, under most conditions, is in a dense phase at static down hole conditions (prior to the well being placed on production), so is less susceptible to dissipation. CO₂ does dissolve in crude oil so will act to reduce the crude viscosity which, again, improves cleanup and rapid recovery. When N₂/CO₂ are added in quantities greater than 90% the resulting mixture is termed a mist with a “0” viscosity. This quality is normally not used in fracturing. The main disadvantage of these fluids is safety i.e. pumping a gas at high pressure or in the

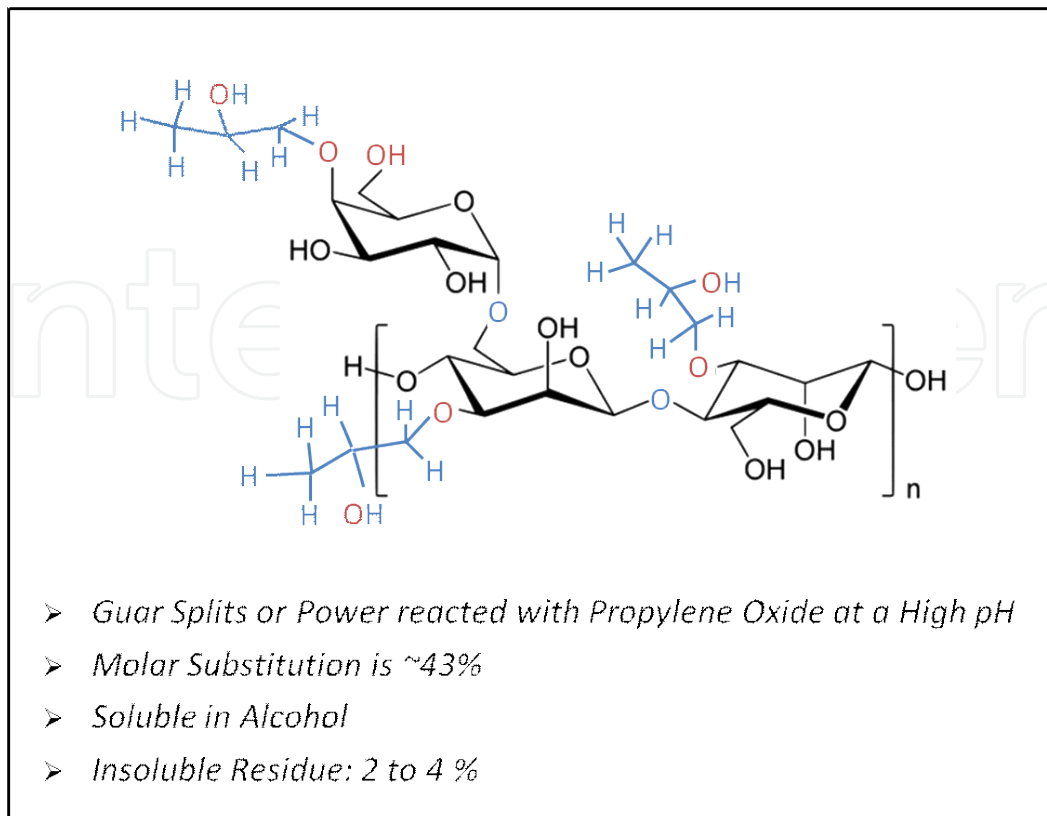


Figure 7. Chemical Structure of Hydroxypropyl Guar (HPG)

case of polyemulsions and gelled Propane, pumping a flammable fluid. CO₂ has an additional hazard in that it can cause dry ice plugs as pressure is reduced. These fluids are generally also more expensive and the gases may not be available in remote areas.

4.5. Oil based fluids

Oil based fluids are used on water-sensitive formations that may experience significant damage from contact with water based fluids. The first frac fluid used to fracture a well used Palm Oil as the gelling agent, Naphthenic Acid as the crosslinker and gasoline at the base fluid. Today most crosslinked oil based fracturing fluids use an aluminum phosphate-ester chemistry[5] that was originally developed to gel hydraulic oils. The aluminum phosphate-esters form a three dimensional structure similar to that described in the VES section. Because the aluminum will attract any polar species the presence of water in the base oil/crude will cause excess viscosity and will adversely affect the thermal stability of the fluid. Breaking of the fluid is accomplished by buffering the pH which causes the association between the base oil and the ester to break down. Although some crude oils have particulate which could build a filter cake, fluid loss is generally considered to be "Viscosity- Controlled – i.e. C-II". There are some disadvantages in using gelled oils. Gelling problems can occur when using high viscosity crude oils or crude oils which contain a lot of naturally occurring surfactants. When using refined oils such as diesel the cost is very high and the oil must be collected at the refinery before any additives such as pour point depressants, engine cleaning surfactants etc. are added. Also there

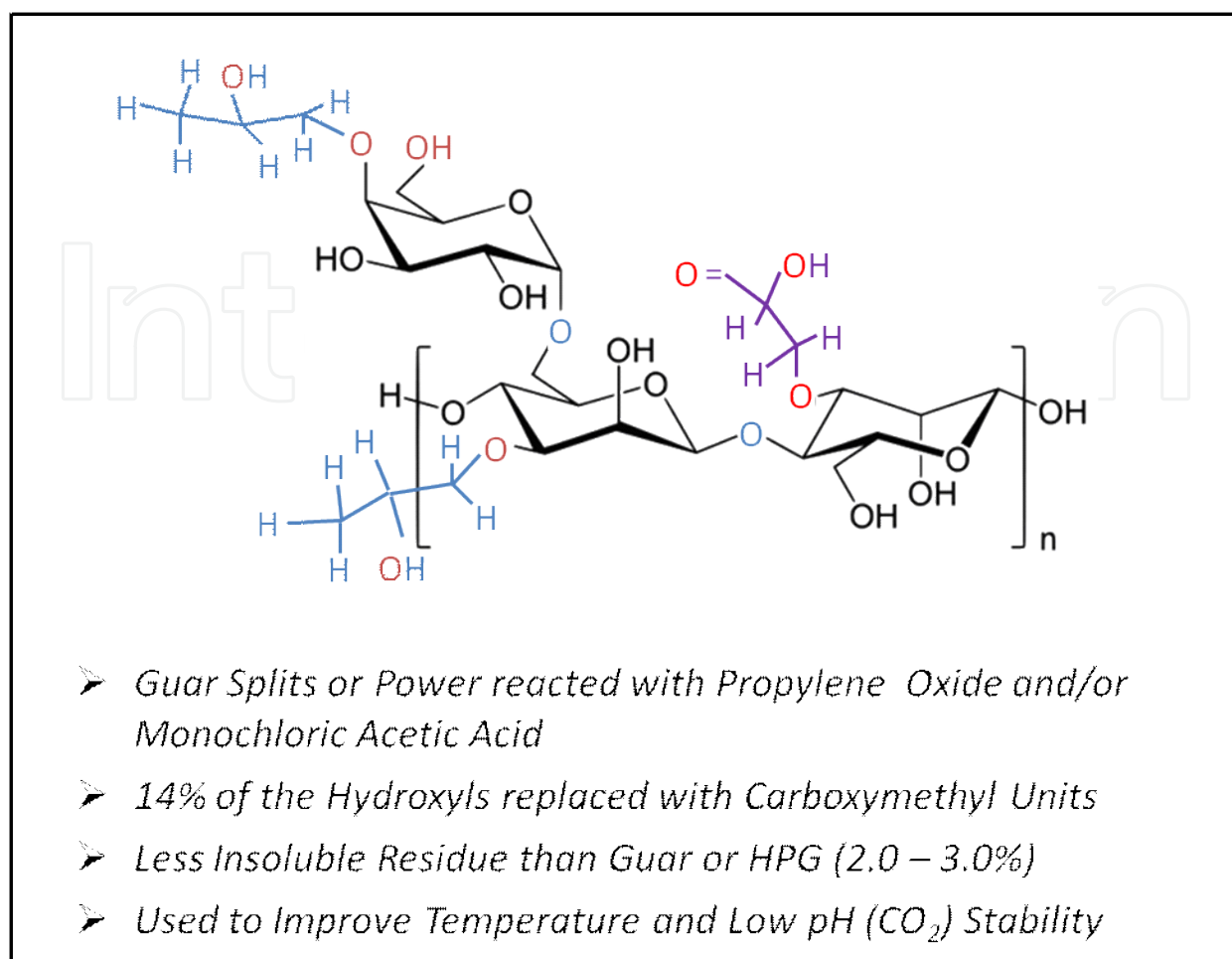


Figure 8. Chemical Structure of CarboxyMethyl Guar (CMG) and CarboxyMethylHydroxy Propyl Guar (CMHPG)

are greater concerns regarding personnel safety and environmental impact, as compared to most water-fluids.

5. Crosslinkers

Crosslinkers are used to increase the molecular weight of the polymer by crosslinking the polymer backbone into a 3D structure as shown in Figure 11. This increases the base viscosity of the linear gel from less than 50 cps into the 100's or 1000's of cps range. This crosslinking also increases the elasticity and proppant transport capability of the fluid.

For guar and CMHEC based gels, Boron and several metals including Titanium and Zirconium are used as crosslinkers. In addition to these materials Iron, Chromium and Aluminum will crosslink guar but are not commonly used. Iron is a major contaminant for fracturing fluids and is one of the metals that must be carefully controlled during the QC process to prevent premature crosslinking. Each crosslinker has a unique reaction requirement and behavior.

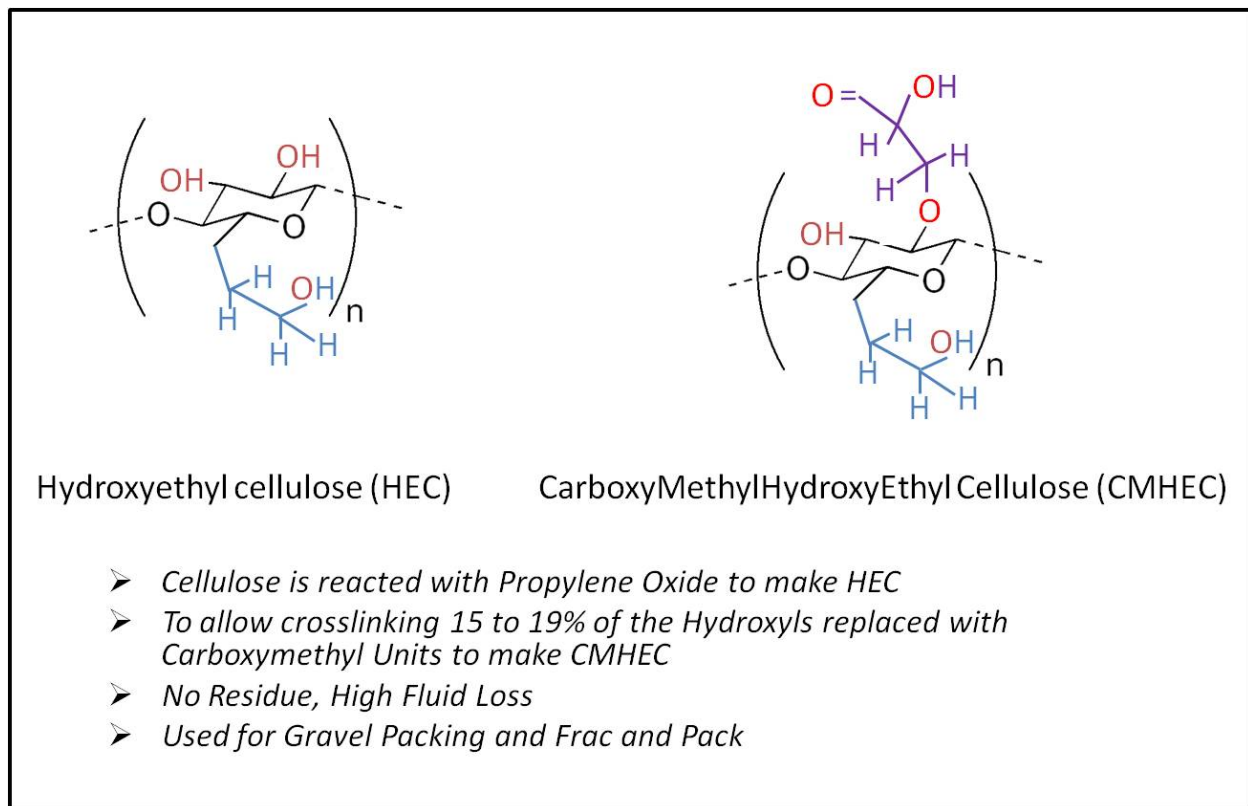


Figure 9. Chemical Structure of Hydroxyethyl Cellulose (HEC) and Carboxy Methyl Hydroxy Ethyl Cellulose (CMHEC)

5.1. Borate

Borate in the form of Boric Acid, slowly soluble salts of Ca and Mg and Organic Borate complexes is, by far, the most common crosslinker in use today. Borate crosslinked fracturing fluids can be applied across a wide range of treating conditions and are resistant to shear degradation. Figure 11 shows diagrammatically how the borate complexes with Guar. As the figure shows the Borate source forms a tetrahedral form of the borate ion when the pH of the base fluid is above about 8.2. These borate ions complexes with the hydroxyl functionality on the polymer causing a 3 dimensional network to be formed which tremendously increases the molecular weight and viscosity. Once this mechanism is understood several things become apparent.

1. The crosslinking is a function of pH which means it can be formed or reversed simply by adjusting the pH. Borate crosslinked fluids are manufactured in the field by mixing the base polymer in water at a pH above 7, adjusting the pH to below 6 and adding in the borate crosslinker and any other additives. During pumping a buffer, usually caustic, is added at the blender which brings the pH above 8 and the crosslink is formed. This also means the process can be reversed simply by dropping the pH below 8 with acid. Cement is a particularly troublesome contaminant when proppant transports are used to also transport cement because the cement raises the pH to 14 which causes premature crosslinking.

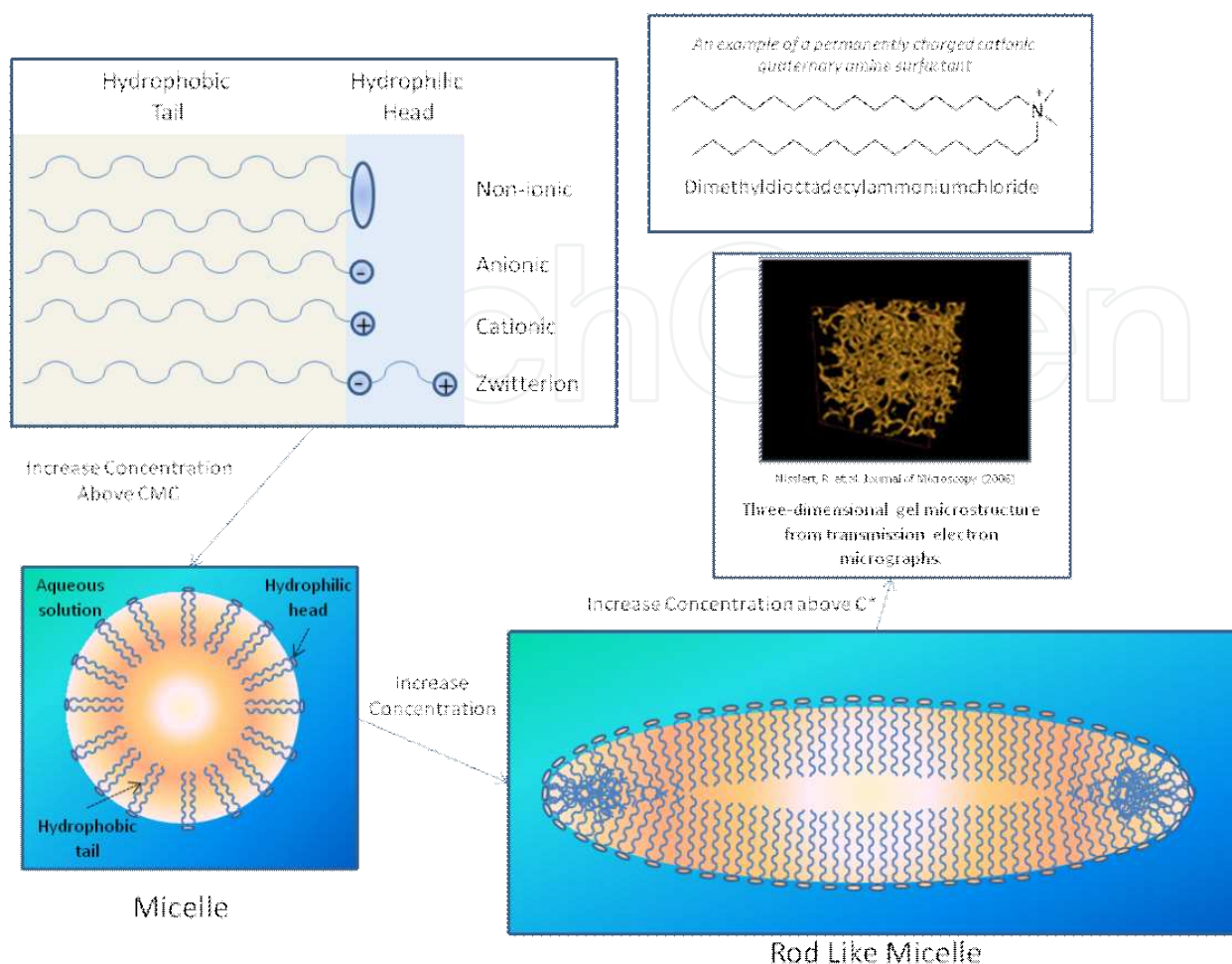


Figure 10. Structure of a Viscoelastic Surfactant Thickener

2. The optimum borate crosslinker efficiency is at a pH of about 10.5.
3. Because the crosslink is in equilibrium it can be broken by shear in the tubing and will quickly build the crosslink again once the shear is dropped.
4. Any polymer which has hydroxyls in the cis position can be crosslinked with Borate. These include Guar and all of its derivatives and CMHECellulose.

5.2. Titanium and zirconium

Titanium and zirconium crosslinkers were originally developed for manufacturing explosive gels[14]. Because Borate crosslinked systems were limited to temperatures below 250°F and pH's above 8 metallic crosslinked fluids were developed to broaden that range. The crosslinkers are manufactured in the form of a metal ligand or chelant using various complexing agents including TEA (Triethanol Amine), LA (Lactic Acid) and AA (Acetylacetone) [15]. When the chelant complex is exposed to water the metal becomes active and crosslinking can occur. Once exposed to water the ionic metal starts to oxidize and if left will become inactive. Both Zirconium and Titanium have coordination num-

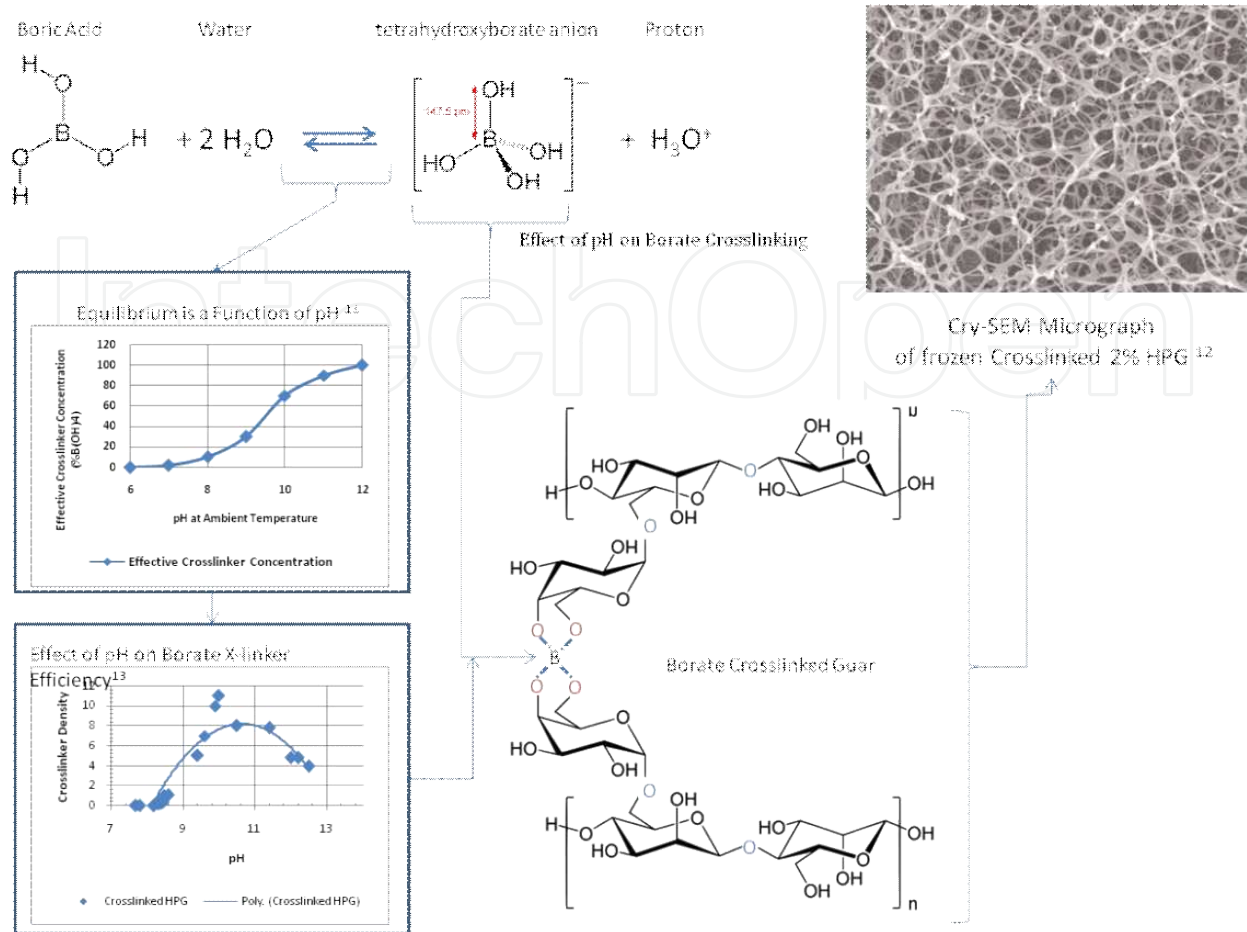


Figure 11. Crosslinking Mechanism of Borate onto Guar

bers of +4 so they form a strong covalent rigid bond with the polymers cis hydroxyls as shown in Figure 12. The various complexing agents allow the crosslinker to become active under a range of time, temperature and pH conditions. Titanium and Zirconium crosslinked fluids can be manufactured that are stable at pH levels from 3.5 to 10.5 and up to temperatures of 350°F. When compared to Borate crosslinked fluids metallic crosslinked fluids have several advantages/disadvantages.

1. The metallic crosslink is a strong covalent bond which makes the crosslink susceptible to high shear rates. Once the bond is broken it will not heal as a Borate crosslink will. To prevent shear degradation the crosslink time should always be delayed to about 2/3 of the pipe time.
2. Because it takes time for the metal to interact with the polymer the crosslink time can be delayed. The type of ligand used to complex the metal controls the delay time. Sometimes it is quite difficult to achieve any delay particularly at a pH < 5.
3. Metallic crosslinked polymer systems can be built that cover a broad range of pH conditions so they can be used in CO₂ based fracturing fluids. They are also much more stable at high temperatures.

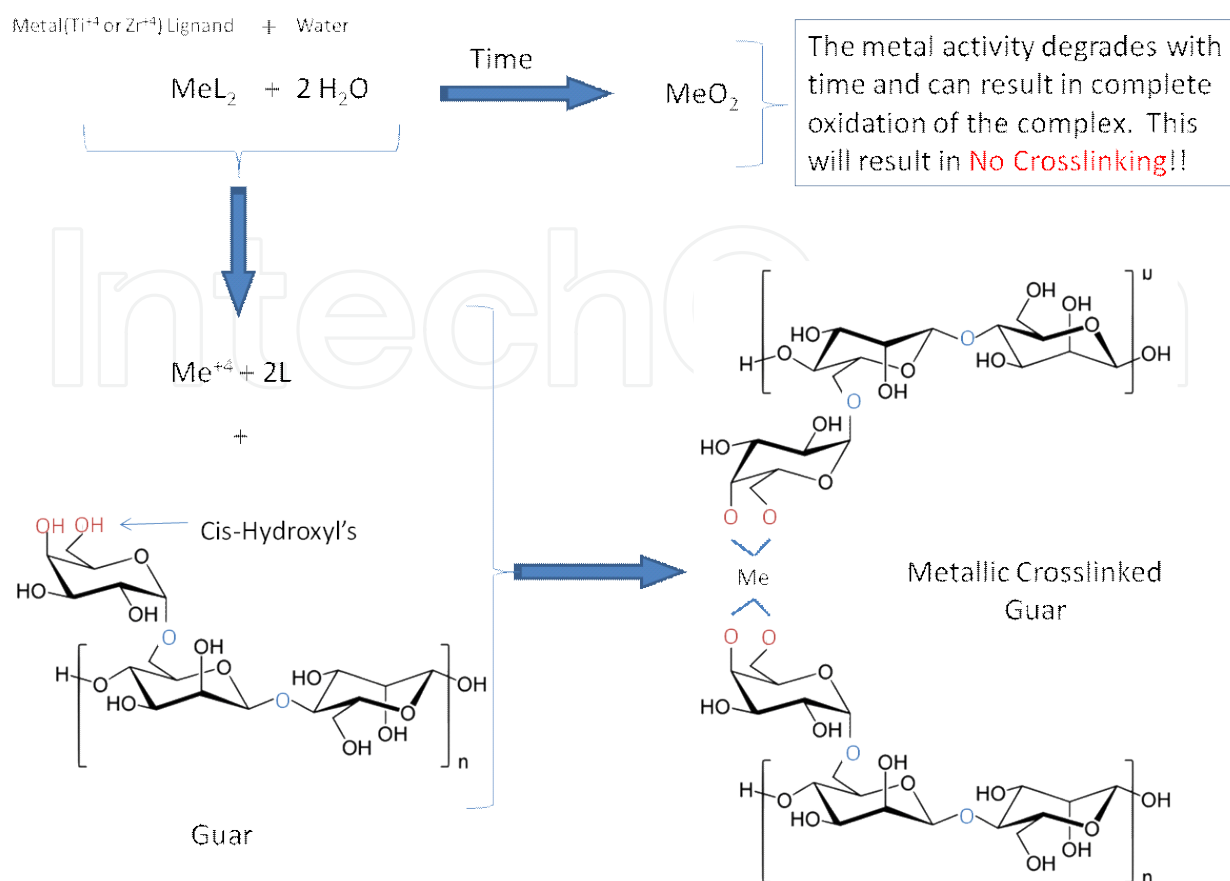


Figure 12. Crosslinking Mechanism for Metallic (Ti^{+4} and Zr^{+4}) Crosslinkers onto Guar

- Because of the permanent nature of the metallic crosslink, the molecular weight of the broken gel residue is much greater than that formed from linear or borate crosslinked gels. This causes a greater degree of proppant pack damage and conductivity loss.
- Any polymer which has hydroxyls in the cis position can be crosslinked with Metallic crosslinkers. These include Guar and all of its derivatives and CMHECellulose.

6. Breakers

Breakers are added to the fracturing fluid to reduce the molecular weight of the various polymers used. This reduces the viscosity and facilitates the blowback of residual polymer which allows for cleanup of the proppant pack. The inappropriate use or ineffective breakers can cause significant damage in the proppant pack and a reduced PI. Ideally these materials would be totally inactive during the treatment and then instantly “spring to action” when pumping stops, rapidly breaking the fluid back to a low viscosity preparing the fracture and formation for flow. This is very difficult to achieve as the breaker activity is very dependent

on fluid temperature which varies with time. The three general types of breakers are Oxidizers, Acid and Enzymes.

6.1. Oxidizer

Oxidizer breakers include Ammonium persulfate, Sodium persulfate, and Calcium and Magnesium peroxides. They work by cleaving the acetyl linkages in the polymer backbone as shown in Figure 13[6]. Ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ and Sodium persulfate $(\text{Na}_2\text{S}_2\text{O}_8)$ are very strong oxidizers which forms a free Oxygen radical when the temperature exceeds 125°F. These free radicals attach the backbone of the polymer strand and break it down into its constitutive sugars. If left in the fracture these residual sugars will cook and form insoluble precipitates resulting in conductivity damage[7]. This is the reason flow back of the fractured well is suggested as soon as the fracture is known to be closed. Both Calcium and Magnesium peroxide (CaO_2 and MgO_2) release Oxygen when they come in contact with water. The breaking action is controlled by the solution rate of the peroxide into the water. They are not affected by temperature as much as the persulfates and are used for low temperature applications. The free radical oxidation is not specific to the polymer backbones and the materials will spend on any available free radical acceptor such as a gel stabilizer. All of these materials are strong oxidizing agents and will produce a very active fire when exposed to organic material. They are used in industry for applications such as a water disinfectant, bleach and pickling agents for metals.

The main disadvantage of oxidizing breakers is both how well they work and how fast they work is a function of the amount of chemical added. Figure 14 shows that a concentration of 0.5 lb/1000 gal of persulfate breaker will break the polymer viscosity back to the viscosity of water but will damage the proppant pack so that only 20% of the original conductivity remains. If we want to get the maximum retained permeability we need to go to concentrations of 10 to 12 lb/1000 gallons which will break the fluid viscosity instantly. To counteract this and retard the release of the persulfate encapsulated breakers were developed. There are two types of encapsulated breakers available. The release rate of the breaker in the first type is controlled by hydrostatic pressure, elevated temperatures and the pH of the fracturing fluid[10]. The second method of release is by crushing the capsule coating as the fracture closes. Because these encapsulated breakers require conditions similar to those in the fracture i.e. closure or hydrostatic pressure they are difficult to test for QC purposes in the field and to date no field test has been developed to quantify their activity in the field.

6.2. Acids

Acids such as HCl or Acetic acid will attach the polymer back bone and break the gel similar to oxidizing breakers but they are much less selective and can cause considerable amount of insoluble material to be formed. They are generally used to try and clean fractures that are believed to be damaged by a job where sufficient breaker was not used or the gel is believed to not be broken. They also work by reversing the crosslink in Borate crosslinked systems. They are typically used after a job has been completed and placement becomes the main issue.

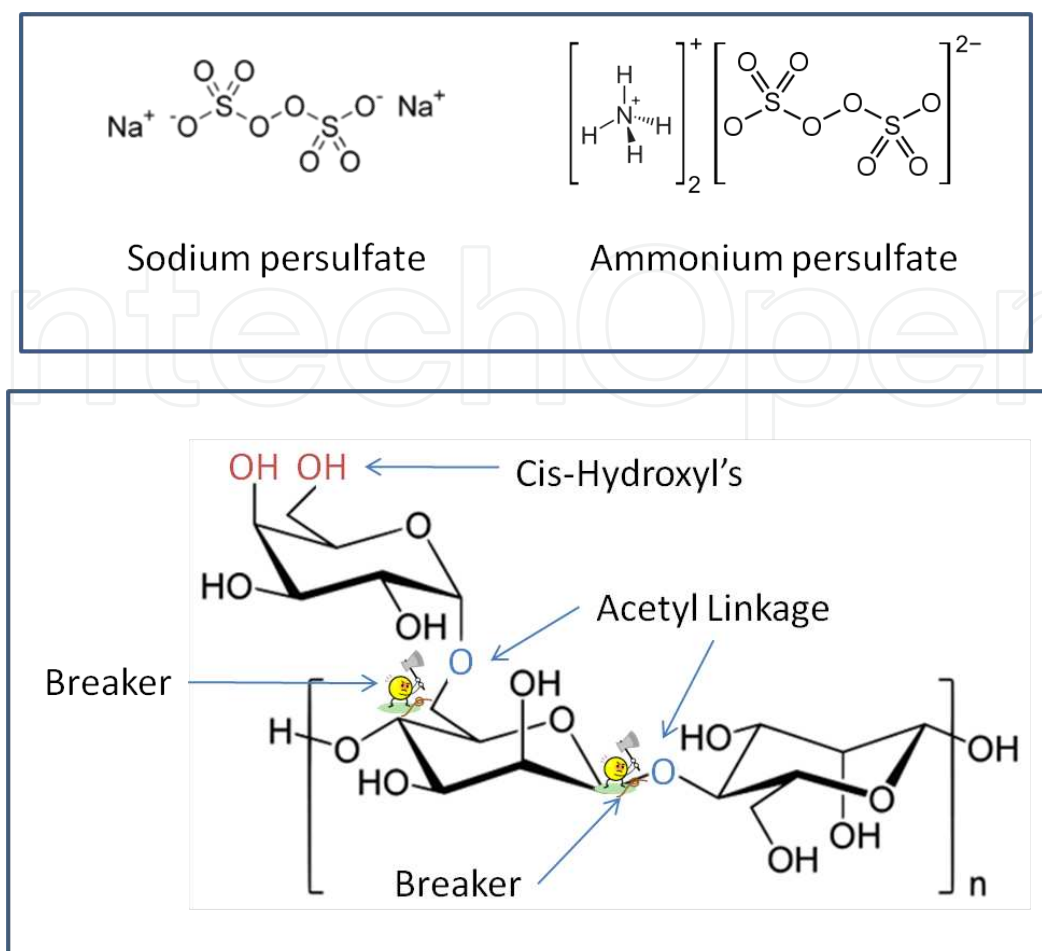


Figure 13. Oxidative Breakers and their action on Guar

6.3. Enzymes

Enzymes are protein molecules that act as organic catalysts that attach and digest the polymer at specific sites along the polymer backbone. Because they are catalysts they are not “used up” during the breaking process and persist until there is no polymer present to digest. Typical enzymes that are used include hemicellulase, cellulose, amylase and pectinase. These enzymes are susceptible to thermal degradation and denaturing when exposed to very high or very low pH so are limited to mild temperatures below 150°F (66°C) and fluid pH's between 4 and 9. Recent work by Brannon and Tjon-Joe-pin have developed proprietary GLSE (Guar Linkage Specific Enzymes) that are reported to work at temperatures more than 300°F[8]. Figure 15 shows diagrammatically how enzymes work and the degradation of the molecular weight of HPG with time as it is digested by Hemicellulase.

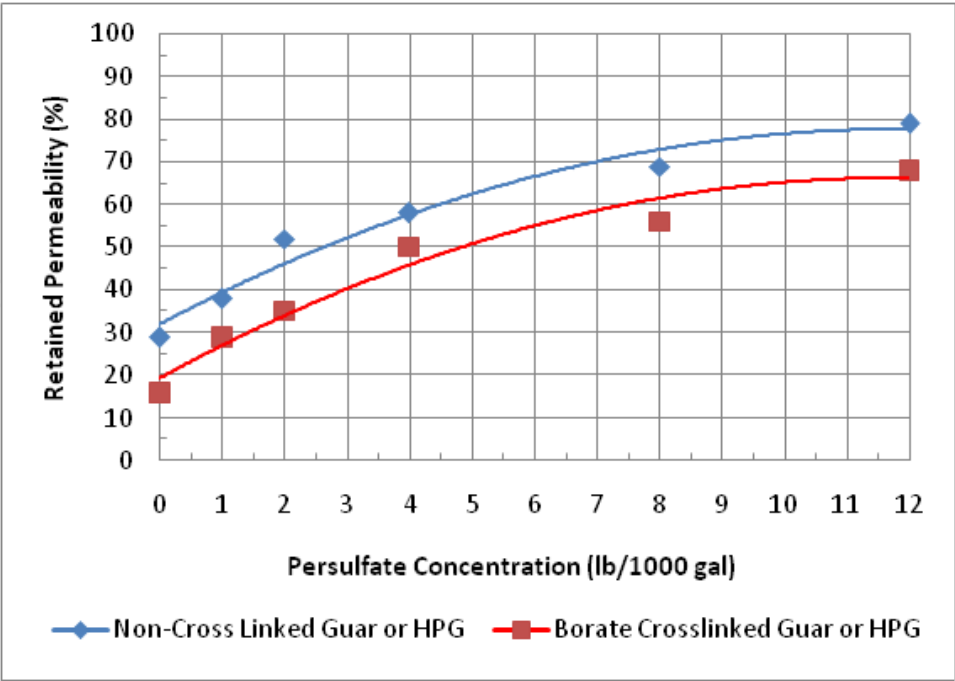


Figure 14. Gel Cleanup vs Breaker Loading (after [9])

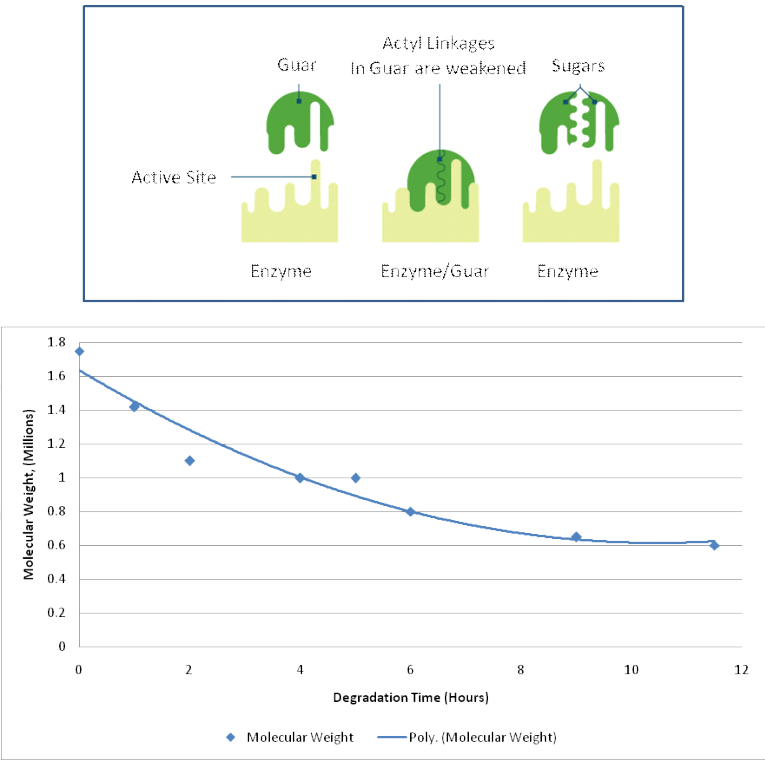


Figure 15. Degradation of Guar by Hemicellulase Enzymes

6.4. Viscosity stabilizers

Viscosity stabilizers are added to the fracturing fluids to reduce the loss of viscosity at high reservoir temperatures. The two most common stabilizers are methanol (used at 5 to 10% of the fluid volume) and Sodium thiosulfate[16]. These materials will extend the temperature range of guar based fluids to over 350°F. Thiosulfate is the more effective of the two and is less hazardous to handle. These materials act as free radical scavengers that are present in the base water. An example would be free oxygen. Without the stabilizers these free radicals can naturally oxidize the polymer as described in the breakers section. Because breakers are free radical generators and these materials are free radical scavengers they should not be run at the same time.

7. Buffers

Buffers adjust the pH of the base fluid so that dispersion, hydration and crosslinking of the fracturing fluid polymers can be engineered. Because some buffers dissolve slowly they can be used to delay crosslinking for a set period of time to reduce friction in the tubing. Typically this delay time is adjusted so that crosslinking occurs at about 2/3 of the pipe time i.e. when the fluid is about 2/3 of the way to the top perforation. The use of the proper buffer package also improves the high temperature capability of Borate crosslinked fluids and reduces the amount of polymer need to get good viscosity[17]. Table 1 shows some commonly used buffer components.

Sodium Bicarbonate	Formic Acid
Sodium Carbonate	Fumaric Acid
Sodium Hydroxide	Hydrochloric Acid
Monosodium Phosphate	Magnesium Oxide

Table 1. Commonly Used Fracturing Fluid pH buffering chemicals.

8. Surfactants/Mutual solvents

Surfactants/Mutual solvents are added to the fracturing fluids to reduce the surface tension of the fracturing fluid to improve fluid recovery and compatibility between the fracturing fluid and the formation matrix or formation fluids. Lab tests are used to determine the type and loading level of surfactant to be used. The primary goals of a surfactant are to leave the rock surface water wet, act as an emulsion preventer or as a defoamer and reduce the surface tension. In very dry gas wells the water in the frac fluid can shift the relative permeability to the water side and form a “water block” that reduces gas flow. An example of how a proper formulation can reduce this effect is shown in Figure 16. Typically if a well is producing any

water this “water block” effect is minimal. EGMBE (ethylene glycol monobutyl ether) used at 10 gal/1000 and BGMBE (butylene glycol monobutyl ether) used at 5 gal/1000 are common mutual solvents.

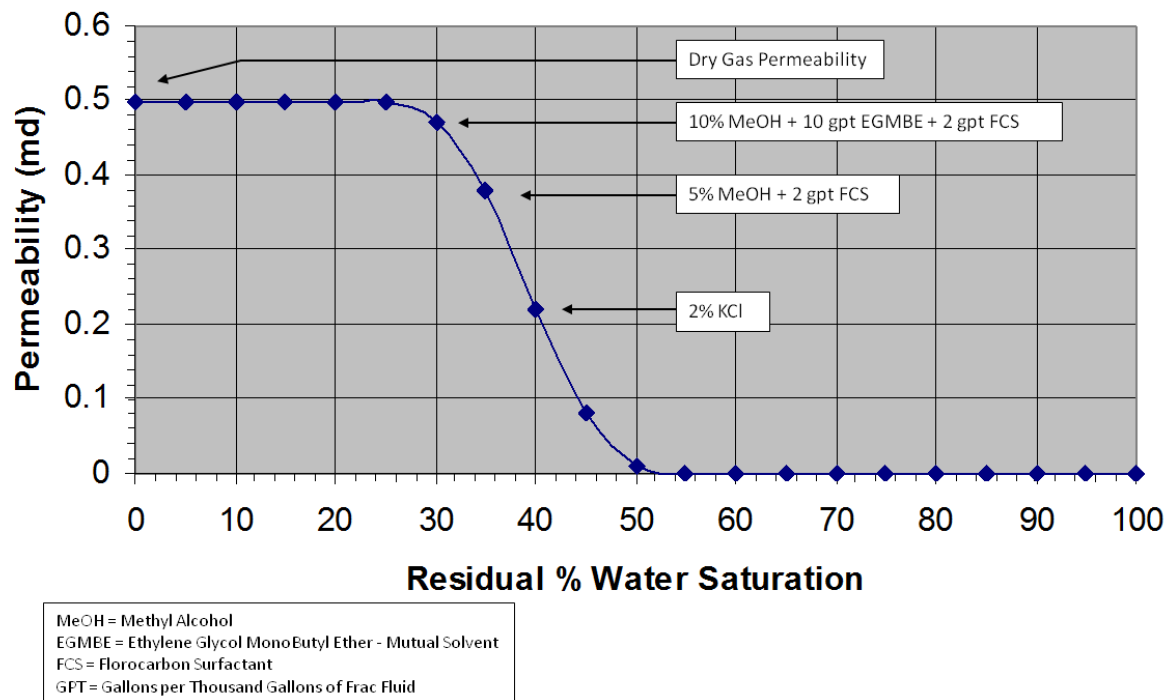


Figure 16. Residual Permeability to Dry Gas of a 0.5 md Berea Sandstone Core

9. Biocides/Bactericides

Biocides/Bactericides are added to minimize the enzymatic attack of the polymers used to gel the fracturing fluid by aerobic bacteria present in the base water. If not controlled the growth of micro-organisms will quickly degrade the polymer to a non-functional level. In addition biocides and bactericides are added to fracturing fluids to prevent the introduction of anaerobic sulfate reducing bacteria (SRB) into the reservoir. These bacteria can “sour” a well and produce corrosive hydrogen sulfide gas. They can also produce a black, slimy “biofilm” in wells that produce water which will block production. Quaternary amines, amides, aldehydes and Chlorine dioxide are effective biocides used in the industry[12]. The use of ultraviolet (UV) light as a disinfectant for fracturing water is also used[18]. A good functional bactericide not only kills the bacteria but also inactivates the enzymes that the bacteria release. Bacteria also mutate so can become resistant to a particular bactericide if used continuously i.e. use a variety of bactericides to provide protection.

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