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# Fracturing Fluids

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Additional information is available at the end of the chapter

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## Abstract

When fracturing, viscosity play a major role in providing sufficient fracture width to insure proppant entrance into the fracture, carrying the proppant from the wellbore to the fracture tip, generating a desired net pressure to control height growth and providing fluid loss control. The fluid used to generate the desired viscosity must be safe to handle, environmentally friendly, non-damaging to the fracture conductivity and to the reservoir permeability, easy to mix, inexpensive and able to control fluid loss. This is a very demanding list of requirements that has been recognized since the beginning of Hydraulic fracturing. This paper describes the history of fracturing fluids, the types of fracturing fluids used, the engineering requirement of a good fracturing fluid, how viscosity is measured and what the limitations of the engineering design parameters are.

## 1. Introduction

The selection of a proper fracturing fluid is all about choices. It begins with choosing the pad volume where one must consider what and how much pad is required to create the desired fracture geometry. This is followed by choosing how much viscosity the fluid needs to have to:

- Provide sufficient fracture width to insure proppant entrance into the fracture.
- Provide a desired net pressure to either treat some desired height growth or prevent breaking out into some undesirable zone for example water.
- Provide carrying capability to transport proppant from the wellbore to the fracture tip.

- Control fluid loss. In cases where a gel filter cake cannot form the fracturing fluid viscosity (i.e.  $C_f$ ) may be the main mechanism for fluid loss control.

This choice system continues when it comes to selecting the appropriate fluid system for a propped or acid frac treatment. The considerations include:

- Safe – The fluid should expose the on-site personnel to a minimal danger.
- Environmentally Friendly – The composition of the fluid should be as “green” as possible.
- Breaker – The fluid must “break” to a low viscosity so that it can flow back and allow clean-up of the fracture.
- Cost Effective – The fluid must be economical and not drive the treatment cost to an unacceptable level.
- Compatibility – The fluid must not interact and caused damage with the formation mineralogy and/or formation fluids.
- Clean-up – The fluid should not damage the fracture conductive of the fracture or, to prevent water blocks, change the relative permeability of the formation. This becomes very important in low pressure wells or wells that produce very dry gas.
- Easy to Mix – The fluid system must be easy to mix even under very adverse conditions.
- Fluid Loss – The fluid need to help control fluid loss. An ideal fluid should have fluid loss flexibility.

In summary an ideal fracturing fluid would be one that would have an easily measured controllable viscosity, controllable fluid loss characteristics, would not damage the fracture or interact with the formation fluid, would be completely harmless and inert and cost less the \$4.00 US/ gallon. Unfortunately this is currently not possible so compromises have to be made. Typically cost is the driving force and chooses are made which can be disastrous to the PI of the well.

Of these factors the fluid viscosity is the major fluid related parameter for fracture design. However, **how much viscosity needed is often overestimated**. Excessive viscosity increases costs, raises treating pressure which may cause undesired height growth, and can reduce fracture conductivity since many of the chemicals used to increase viscosity leave residue which damages the proppant permeability.

The need for a precise value of viscosity is also over engineered. This can be seen from the basic equations where treating pressure, and thus fracture width, is proportional to viscosity raised to the  $\frac{1}{4}$  power (for a Newtonian fluid).

$$p_{net} \propto \frac{E^{3/4}}{H} [\mu QL]^{1/4} + P_{Tip}$$

Thus a 100% error in viscosity results in an error of about 19% in calculating fracture width. This error would, of course, lead to an error in the fluid volume requirements for a particular job. However, further assuming that 1/2 of the fracturing fluid leaks off to the formation

reduces the 19% error in width to only a 9.5% error in fluid volume requirements. While such an error is not desirable it does illustrate that precise viscosity data is not a requirement for treatment design which is fortunate since the measurement of the viscosity of fracturing fluids is such a difficult task. This complexity combined with multiple methods for testing and reporting viscosity data makes the selection of precise values virtually impossible.

There are several types of fracturing fluids and a wide and confusing range of fluid additives. The types of fluids include:

- Water based fluids
- Oil based fluids
- Energized fluids
- Multi-phase emulsions
- Acid Fluids

The additives include:

- Gelling agents
- Crosslinkers
- Breakers
- Fluid loss additives
- Bactericides
- Surfactants and Non-emulsifying agents
- Clay control Additives.

## 2. History

The fracturing fluids that were used in the first experimental treatments were composed of gasoline gelled with Palm Oil and crosslinked with Naphthenic Acid. This technology was developed during the Second World War and is commonly referred to as Nalpalm. Because of the hazards associated with this fluid and its relatively high cost work was done to develop safer fluids where the base fluid was water. The vast majority of fracturing fluids used today use water as the base fluid. Generally, the components that make up crosslinked fracturing fluids include a polymer, buffer, gel stabilizer or breaker and a crosslinker. Each of these components is critical to the development of the desired fracturing fluid properties. The role of polymers in fracturing fluids is to provide fracture width, to suspend proppants, to help provide fracture width, to help control fluid loss to the formation, and to reduce friction pressure in the tubular goods. Guar gum and cellulosic derivatives are the most common types of polymers used in fracturing fluids. The first patent (US Patent 3058909) on guar crosslinked

by borate was issued to Loyd Kern with Sinclair (later ARCO) on October 16, 1962. Metal-based crosslinking agents developed by DuPont for plastic explosive applications were found to be useful for manufacturing fracturing fluids for high temperature applications<sup>2</sup>. Cellulosic derivatives are residue-free and thus help minimize fracturing fluid damage to the formation and are widely used in Frac and Pack applications. The cellulosic derivatives are difficult to disperse because of their rapid rate of hydration. Guar gum and its derivatives are easily dispersed but produce some residue when broken. Strong oxidizing agents such as Sodium or Ammonium persulfate are added to the fracturing fluids to break the polymer as it reaches temperature. The first patent (US Patent 3163219) on borate gel breakers was issued to Tom Perkins, also with Sinclair, on December 29, 1964.

Buffers are used in conjunction with polymers so that the optimal pH for polymer hydration can be attained. When the optimal pH is reached, the maximal viscosity yield from the polymer is obtained. The most common example of fracturing fluid buffers is a weak-acid/weak-base blend, whose ratios can be adjusted so that the desired pH is reached. Some of these buffers dissolve slowly allowing the crosslinking reaction to be delayed.

Gel stabilizers are added to polymer solutions to inhibit chemical degradation. Examples of gel stabilizers used in fracturing fluids include methanol, TriEthanol Amine (TEA) and various inorganic sulfur compounds. Other stabilizers are useful in inhibiting the chemical degradation process, but many interfere with the mechanism of crosslinking. The TEA and sulfur containing stabilizers possess an advantage over methanol, which is flammable, toxic, expensive and can cause poisoning of reactor tower catalysts.

There has been a huge volume of work done on fracturing fluids and their components. If a search is done on One Petro (<http://www.onepetro.org>) using "Fracturing Fluids" as the search item over 15,000 hits will result. Just using one of the main gelling agents used to manufacture water based fracturing fluid "Guar" results in over 400 hits. There are several good references<sup>3,4,5,6</sup> that discuss the current state of the art for fracturing fluids if the reader is interested in a more in depth study of fracturing fluids.

Another issue that has recently come to the forefront of fracturing fluids is their threat to the environment through the contamination of the groundwater. George King put it very elegantly in his JPT article<sup>7</sup> where he says "The use of horizontal wells and hydraulic fracturing is so effective that it has been called "disruptive". That is, it threatens the profitability and continued development of other energy sources, such as wind and solar, because it is much less expensive and far more reliable." The internal Apache article<sup>8</sup> that George wrote has 204 references on the subject. Table 1,2,3 provides a summary of all the various chemicals used to make Hydraulic Fracturing fluids along with a degree of hazard rating from both the US Department of Transportation and the European Union Poison Class rating. There certainly are several of these chemicals that one must take care with when handling at their full concentrations but when used to manufacture fracturing fluids the concentrations are very dilute and pose very low hazards.

Chemical Name	CAS Number	Chemical Purpose	Product Function	Hazard Rating <sup>1</sup>
Hydrochloric Acid HCl	007647-01-0	Removes acid soluble minerals and weakens the rock to allow lower fracture initiation pressures.	Acid	4*,8**
Glutaraldehyde C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	000111-30-8	Eliminates bacteria in the water to prevent frac polymer premature breakdown and well souring	Biocide	3*,6**
Quaternary Ammonium Chloride Compounds	63393-96-4	Clay Control Agents	Biocides and Clay Stabilizers	3**
Tetrakis Hydroxymethyl-Phosphonium Sulfate C <sub>8</sub> H <sub>24</sub> O <sub>8</sub> P <sub>2</sub> ·SO <sub>4</sub>	055566-30-8	Eliminates bacteria in the water to prevent frac polymer premature breakdown and well souring	Biocide	NR
Ammonium Persulfate (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	007727-54-0	Breaks the polymer that is used to create the fracturing fluid	Breaker	4*,5**
Sodium Chloride NaCl	007647-14-5	Product Stabilizer	Breaker	NR
Magnesium Peroxide MgO <sub>2</sub>	1335-26-8	Delays the breakdown of the fracturing fluid gelling agent	Breaker	5**
Magnesium Oxide MgO	1309-48-4	Delays the cross linking of the fracturing fluid gelling agent	Buffer	4*
Calcium Chloride CaCl <sub>2</sub>	10043-52-4	Product Stabilizer and Freeze Protection	Buffer	NR
Ammonium Chloride NH <sub>4</sub> Cl	012125-02-9	Clay Stabilizer – Compatible with Mud Acid	Clay Stabilizer	4*,9**
Choline Chloride [HOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> ]C	67-48-1	Prevents clays from swelling or migrating	Clay Stabilizer	5*
Potassium chloride KCl	007447-40-7	Prevents clays from swelling or migrating	Clay Stabilizer	5*,5**
Tetramethyl ammonium chloride (CH <sub>3</sub> ) <sub>4</sub> NCl	000075-57-0	Prevents clays from swelling or migrating	Clay Stabilizer	3*,6**
Sodium Chloride NaCl	007647-14-5			NR
Isopropanol CH <sub>3</sub> CH(OH)CH <sub>3</sub>	000067-63-0	Winterizing agent	Winterizing agent and Surface Tension Reduction	3**
Methanol CH <sub>3</sub> OH	000067-56-1	Winterizing agent	Winterizing agent	3*, 3**
Formic Acid HCOOH	000064-18-6	pH adjustment	pH adjustment	4*,8**
Acetaldehyde CH <sub>3</sub> CHO	000075-07-0	Prevents the corrosion of the pipe	Corrosion Inhibitor	4*,3**

Chemical Name	CAS Number	Chemical Purpose	Product Function	Hazard Rating <sup>1</sup>
Hydrotreated Light Petroleum Distillate	064742-47-8	Carrier fluid for gelling agents, friction reducers and crosslinkers	Carrier fluid and fluid loss control	3**
Potassium Metaborate KBO <sub>2</sub>	013709-94-9	Crosslinker for borate crosslinked fluids	Crosslinker	3*
Triethanolamine (TEA) N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub>	102-71-6	Maintains fluid viscosity as temperature increases	Fluid Stabilizer	5*,3**
Sodium Tetraborate Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	001330-43-4	Crosslinker for borate crosslinked fluids	Crosslinker	4*
Boric Acid H <sub>3</sub> BO <sub>3</sub>	13343-35-3	Crosslinker for borate crosslinked fluids	Crosslinker	4*
Chelated Zirconium		Crosslinker for High Temperature or low pH Fluids	Crosslinker	
Zirconium oxychloride ZrCl <sub>2</sub> O	7699-43-6	Inorganic Clay Stabilizer	Clay Stabilizer	4*
Ethylene Glycol OCH <sub>2</sub> CH <sub>2</sub> OH	000107-21-1	Product stabilizer and / or winterizing agent.	Winterizing Agent	4*
Methanol CH <sub>3</sub> OH	000067-56-1	Surface Tension Reduction and / or winterizing agent.	Fluid Recovery and Winterizing Agent	3*,3**
Ethanol C <sub>2</sub> H <sub>5</sub> OH	000064-17-5	Product stabilizer and / or winterizing agent.	Fluid Recovery and Winterizing Agent	3**
Polyacrylamide (C <sub>3</sub> H <sub>5</sub> NO) <sub>n</sub>	009003-05-8	"Slicks" the water to minimize friction	Friction Reducer	5*
Guar Gum and its derivatives HPG, CMHPG	009000-30-0	Thickens the water in order to suspend the proppant and reduce friction	Gelling Agents	NR
Derivatives of cellulose - HEC, CMHEC R(n)OCH <sub>2</sub> COONa	9004-34-6 9004-32-4	Thickens the water in order to suspend the proppant and reduce friction	Gelling Agents	NR
Xanthan gum	11138-66-2	Thickens Acid in order to control fluid loss	Gelling Agent	NR
Citric Acid (HOOCCH <sub>2</sub> ) <sub>2</sub> C(OH)COOH	000077-92-9	Prevents precipitation of metal oxides	Iron Control	5*,8**
Acetic Acid CH <sub>3</sub> COOH	000064-19-7	Prevents precipitation of metal oxides and pH control	Iron Control and pH Adjustment	4*,8**
Thioglycolic Acid HSCH <sub>2</sub> COOH	000068-11-1	Prevents precipitation of metal oxides	Iron Control	3*,8**
Sodium Erythorbate C <sub>6</sub> H <sub>7</sub> O <sub>6</sub> . Na	006381-77-7	Prevents precipitation of metal oxides	Iron Control	NR

Chemical Name	CAS Number	Chemical Purpose	Product Function	Hazard Rating <sup>1</sup>
Lauryl Sulfate and its Derivatives C <sub>12</sub> H <sub>25</sub> OSO <sub>2</sub> ONa	000151-21-3	Used to prevent the formation of emulsions in the reservoir and to improve fluid recovery	Non-Emulsifier and Surfactants	4*
Sodium Hydroxide NaOH	001310-73-2	Adjusts the pH of fluid to initiate the effectiveness of other components, such as crosslinkers	pH Adjusting Agent	4*,8**
Potassium Hydroxide KOH	001310-58-3	Adjusts the pH of fluid to initiate the effectiveness of other components, such as crosslinkers	pH Adjusting Agent	2*,8**
Sodium Carbonate Na <sub>2</sub> CO <sub>3</sub>	000497-19-8	Adjusts the pH of fluid to maintains the effectiveness of other components, such as crosslinkers	pH Adjusting Agent	5*,5**
Potassium Carbonate K <sub>2</sub> CO <sub>3</sub>	000584-08-7	Adjusts the pH of fluid to maintains the effectiveness of other components, such as crosslinkers	pH Adjusting Agent	4*
Sodium Acrylate and Copolymers of Acrylamide C <sub>3</sub> H <sub>3</sub> O <sub>2</sub> . Na	007446-81-3	Prevents scale deposits in the pipe or in the fracture	Scale Inhibitor	NR
Sodium Polycarboxylate	N/A	Prevents scale deposits in the pipe	Scale Inhibitor	
Phosphonic Acid Salt	N/A	Prevents scale deposits in the pipe	Scale Inhibitor	
Naphthalene C <sub>10</sub> H <sub>8</sub>	000091-20-3	Carrier fluid for the active surfactant ingredients	Surfactant	3*,4**
Ethylene glycol monobutyl ether - EGMBE C <sub>4</sub> H <sub>9</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	000111-76-2	Surface Tension Reduction for Fluid Recovery	Surfactant	4*, 6**

1 – Hazard Rating – An attempt was made to rate the hazard associated with each of the chemicals listed. The first number with the single \* is the Poison Hazard as defined by the EU/Swiss Poison Class while the second number with the double \*\* is the transportation Hazard as defined by the US Department of Transportation (DOT). If a NR is present in the box no rating was found and the substance was normally non-hazardous.

\* EU/Swiss Poison Class

**Table 1.** A summary of the various chemicals used to make Hydraulic Fracturing fluids along with a degree of hazard rating. Modified from " [www. http://fracfocus.org/chemical-use/what-chemicals-are-used](http://fracfocus.org/chemical-use/what-chemicals-are-used)"

Class	Lethal Dose (mg/kg)
1	0 to 5
1.5	0 to 5, also teratogenic or carcinogenic
2	5 to 50

<i>Class</i>	<i>Lethal Dose (mg/kg)</i>
<b>3</b>	50 to 500
<b>4</b>	500 to 2000
<b>5</b>	2000 to 5000
<b>5S</b>	2000 to 5000, an unrestricted self-service product

\*\* DOT Transportation Hazard Classes

**Table 2.** A summary of the various chemicals used to make Hydraulic Fracturing fluids along with a degree of hazard rating. Modified from " www. <http://fracfocus.org/chemical-use/what-chemicals-are-used>"

<i>Class</i>	
<b>1</b>	Explosives
<b>2</b>	Compressed Gases
<b>3</b>	Flammable and Combustible Liquids
<b>4</b>	Flammable Solids
<b>5</b>	Oxidizers and Organic Peroxides
<b>6</b>	Poisonous/Toxic Materials
<b>7</b>	Radioactive Materials
<b>8</b>	Corrosive Materials
<b>9</b>	Miscellaneous Hazardous Materials

**Table 3.** A summary of the various chemicals used to make Hydraulic Fracturing fluids along with a degree of hazard rating. Modified from " www. <http://fracfocus.org/chemical-use/what-chemicals-are-used>"

### **Additional hazard identification resources**

<http://fracfocus.org/welcome> - The Ground Water Protection Council and the Interstate Oil and Gas Compact Commission developed this web site to provide public access to chemicals used in the hydraulic fracturing process and provides a record of the chemicals used in wells in a number of different states in the United States. At the time of this writing the site had records on over 34,000 wells.

<http://www.osha.gov/chemicaldata/> - This United States Department of Labor website provides an OSHA (Occupational Safety and Health Administration) Occupational Chemical Database



for most of the chemicals used by industry. The database can be searched by either Chemical Name or CAS Number.

<http://ull.chemistry.uakron.edu/erd/> - The Department of Chemistry at the University of Akron developed this website to provide a database composed of over 30,000 hazardous chemicals made up of information provided by a number of different published references.

<http://www.epa.gov/chemfact/> - This United States Environmental Protection Agency website provides OPPT Chemical Fact Sheets on selected chemicals that may be present in the environment in an ASCII text or Adobe PDF format along with access to other EPA databases.

### 3. Types of fracturing fluids

Table 4 provides a qualitative listing of the desirable and undesirable aspects of most fluid systems available today. As one studies the table it is interesting to note that there is “no magic bullet”. The qualitative score is close to the same for each fluid and each fluid has its advantages and disadvantages. This means that the final decision is up to the design engineer as to what is best for his reservoir. The different types of fluid systems are outlined below. A description of all the different components used to manufacture the fluids is provided in Side Bar 1.

Fluid System	Prop Pack KW	Low Pump Pressure	VISCOSITY			Breaking	Compatibility		Fluid Loss	Ease of Mixing	Cost	Safety and Environmentally Friendly	Total
			Prop-Transport	Stable	Life		Formation Fluid	Fluid Recovery					
Water Frac <sup>1</sup>	5	5	1	3	3	5	3	4	1	5	5	4	44
Linear Gel <sup>2</sup>	3	5	3	3	3	4	3	4	2	5	4	5	44
Linear Gel <sup>3</sup>	5	5	3	3	3	4	3	4	2	5	4	5	46
Borate X-Link <sup>2</sup>	3	3	5	5	5	3	4	3	5	4	3	5	48
Delayed Borate X-Link <sup>2</sup>	3	3	5	5	5	3	4	3	5	3	3	5	47
Delayed Metallic X-Link <sup>4</sup>	3	3	5	2	2	3	4	3	5	3	3	4	40
Delayed Metallic X-Link <sup>5</sup>	3	3	5	2	2	3	4	3	5	3	3	4	40
VES <sup>6</sup>	5	3	5	4	4	2	1	3	2	2	1	5	37
Nitrogen Foam	5	2	5	3	3	5	4	4	5	2	1	3	42
CO <sub>2</sub> Foams	5	2	5	3	3	5	4	5	5	2	1	2	42
Gelled Propane	5	3	4	4	3	4	5	4	4	2	1	1	40
Poly Emulsions (K1)	4	1	5	5	5	4	4	3	5	2	3	2	43
Lease Crude	2	3	2	5	5	5	5	3	2	5	5	1	43
Gelled Oil <sup>7</sup>	2	3	4	4	4	4	3	3	3	4	3	1	38

Qualitative Rate 1 to 5 where 1 is poor, 3 is moderate and 5 is excellent

- 1 - Uses Polyacrylamide (PAA) as a Friction Reducer
- 2 - Uses Guar, HydroxyPropyl Guar (HPG) or CarboxyMethylHydroxyPropyl Guar (CMHPG) as gelling agent
- 3 - Uses HydroxyEthyl Cellulose (HEC) or CarboxyMethylHydroxyEthyl Cellulose (CMHEC) as gelling agent
- 4 - Uses Titanium or Zirconium Crosslinkers for Guar, HPG, and CMHPG gelling agents
- 5 - Uses Titanium or Zirconium Crosslinkers for CMHEC gelling agents
- 6 - Uses a ViscoElastic Surfactant system as the gelling agent
- 7 - Uses a Phosphate Ester crosslinked with an Aluminum Salt and activated with a Base

**Table 4.** Qualitative Fluid Selection Chart

**Water Frac** is composed of water, a clay control agent and a friction reducer. Sometimes a water recovery agent (WRA) is added to try and reduce any relative permeability or water block effects. The main advantage of using a “Water Frac” is the low cost, ease of mixing and ability to recover and reuse the water. The main disadvantage is the low viscosity which results in a narrow fracture width. Because the viscosity is low the main proppant transport mechanism is velocity so water fracs are typically pumped at very high rates (60 to 120 bpm). Fluid loss is controlled by the viscosity of the filtrate which is close to that of water i.e. 1.

**Linear Gel** is composed of water, a clay control agent and a gelling agent such as Guar, HPG or HEC. Because these gelling agents are susceptible to bacteria growth a bactericide or biostat is also added. Chemical breakers are also added to reduce damage to the proppant pack. WRA’s are also sometimes used. The main advantage of a liner gel is its low cost and improved viscosity characteristics. Fluid loss is controlled by a filter cake which builds on the fracture face as the fluid loses fluid to the formation. The main disadvantage is, as with waterfracs, the low viscosity which results in a narrow fracture width. The main disadvantage when compared to a waterfrac is that because the returned water has residual breaker the water is not reusable.

**Crosslinked Gels** are composed of the same materials as a linear gel with the addition of a crosslinker which increases the viscosity of the linear gel from less than 50 cps into the 100’s or 1000’s of cps range. The higher viscosity 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. This crosslinking also increases the elasticity and proppant transport capability of the fluid. Fluid loss is controlled by a filter cake which builds on the fracture face as the fluid loses fluid to the formation. A full description of the types of crosslinkers used, the chemistry and the mechanism of crosslinking is provided in the companion paper on fracturing fluid components.

**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 gasoline at the base fluid, Palm Oil as the gelling agent and Naphthenic Acid as the crosslinker i.e. Napalm. 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 are greater concerns regarding personnel safety and environmental impact, as compared to most water-fluids.

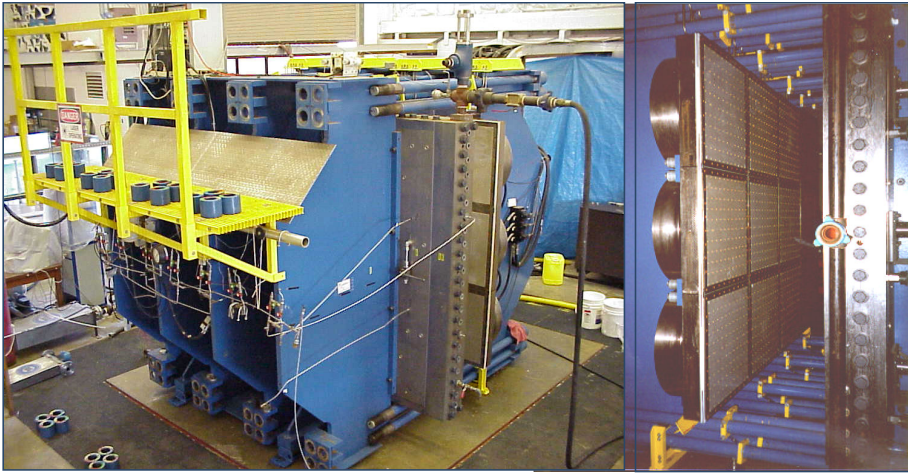
**Foam/PolyEmulsions** are fluids that are composed of a material that is not miscible with water. This could be Nitrogen, Carbon dioxide or a hydrocarbon such as Propane, diesel or condensate. These fluids are very clean, have very good fluid loss control, provide excellent proppant transport and break 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  $N_2$  or  $CO_2$  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  $N_2$  should be flowed back as soon as the fracture is closed.  $CO_2$ , 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.  $CO_2$  does dissolve in crude oil so will act to reduce the crude viscosity which, again, improves cleanup and rapid recovery. When  $N_2/CO_2$  are added in qualities greater than 80 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 case of polyemulsions and gelled Propane, pumping a flammable fluid.  $CO_2$  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. Characterization of fracturing fluids

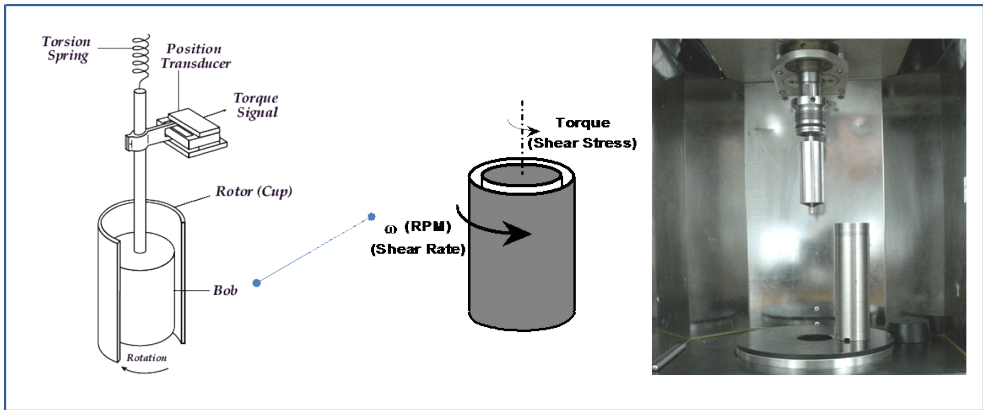
Fluid viscosity for treatment design is determined from laboratory tests and is reported in service company literature. The ideal experiment for describing fluid flow in a fracture would be to shear a fluid between two plates which are moving parallel and relative to one another. The shear stress on the fluid equals the drag force on the plates divided by the area of the plates, and has units of stress or pressure (e.g., psi). The shear rate (or velocity gradient) is the relative velocity of the two plates divided by the separation distance between the plates. Shear rate has the units of 1/time (e.g.,  $sec^{-1}$ ). A vertical 7 ft high by 10 1/3 ft long high pressure parallel-plate flow cell, shown in Figure 1, capable of operating to temperatures of 250°F and pressures of 1200 psi is available at the University of Oklahoma<sup>11</sup>. Termed the "Fracturing Fluid Characterization Facility (FFCF)" the laboratory simulator is a very sophisticated; one of a kind unit that utilizes 12 servo-controlled 28" by 28" platens that can dynamically adjust the width of the slot from 0 to 1.25 inches.

Such an ideal test is not feasible for day to day applications so a rotating "cup and bob" viscometer known as a "Couette" viscometer is used. API standard RP39<sup>12</sup> and ISO 13503-1<sup>13</sup> fully describe the current testing procedures used by the industry. The viscometer uses a rotating cup and a stationary bob with a gap between the two that simulates the fracture. As shown in Figure 2 the rotational speed of the cup imparts a shear rate and the bob measures the shear stress or drag force exerted on the walls of the cup and bob. This is sensed by measuring the torque on the bob. The shear rate is the relative velocity between the stationary bob and the rotating cup divided by the separation gap. Figure 3 shows several commercial rheometers and how they are set up in the field. For a Fann 35 (See Figure 3) equipped with a R1 rotor and a B1 bob and the appropriate spring a rotational speed of 100 RPM represents a shear rate of  $170 sec^{-1}$  and a speed of 300 RPM gives a shear rate of  $511 sec^{-1}$ . The Fann 35, which is manufactured by the Fann Instrument Company <http://www.fann.com/>, the Model 3530,

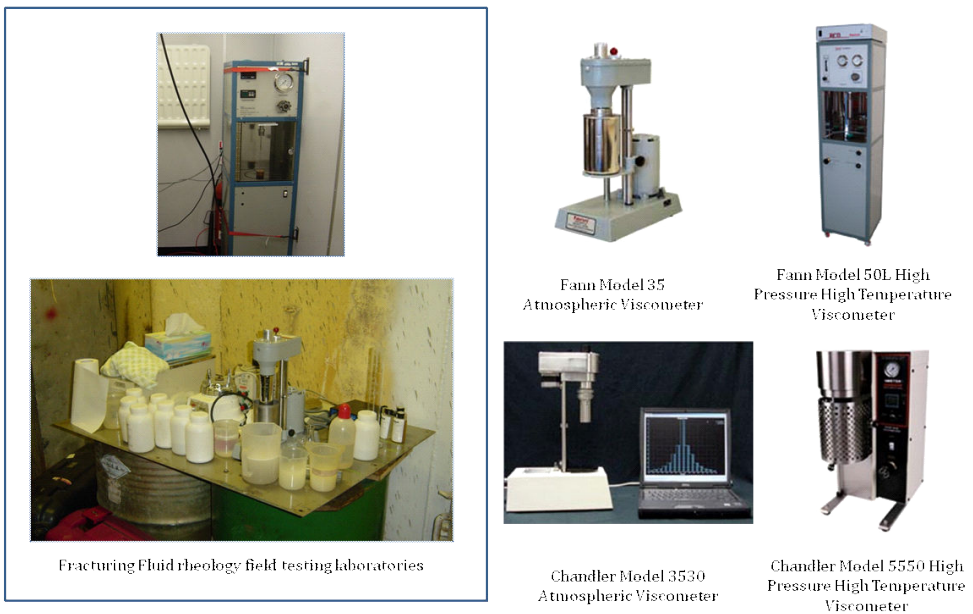


**Figure 1.** University of Oklahoma Parallel Plate Fracturing Fluid Characterization Facility (Courtesy of the University of Oklahoma).

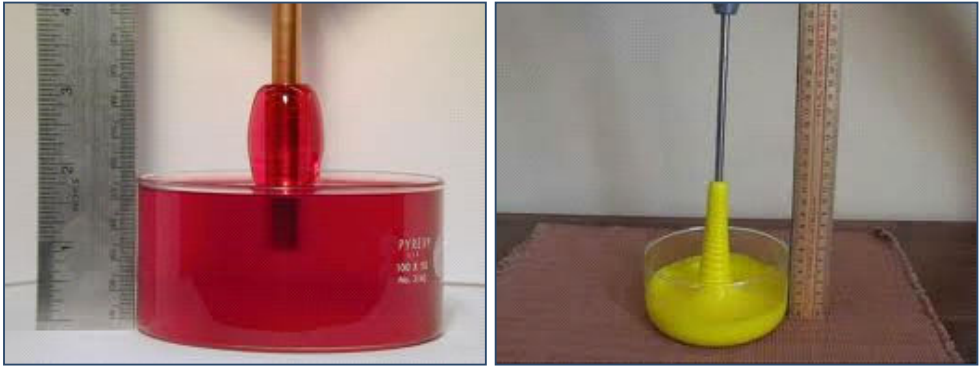
which is manufactured by Chandler Engineering <http://www.chandlerengineering.com/> and the Model 800 8 speed viscometer manufactured by OFI Testing Equipment, Inc. <http://www.ofite.com/> are atmospheric rheometers which limits their use to the boiling point of water. The Fann 50, Chandler 5550 and OFI 130-77 viscometer's are equipped with a pressurized cup and bob which can be placed into an oil bath for higher temperature measurements. Fluids, including foam, can be dynamically flowed into the cells so that the fluid can be measured under the shear conditions that it would experience in the well. These rheometers are very rugged reliable instruments but suffer from a phenomenon called the Weissenberg effect when trying to measure crosslinked viscoelastic fluids. It occurs when a spinning rod, like the rotor, is placed into a solution of polymer. Instead of being thrown outward the polymer chains entangle on the rod supporting the bob causing the polymer solution to be drawn up the rod. Figure 4 shows what the Weissenberg effect looks like. As temperature increases and the gel thins the issue goes away to a certain extent and modern rheometers try to control the effect. Overall the effect can result in some very misleading data and care must be taken when very odd looking, unusual data is presented. The testing problem is compounded in that, as illustrated in Figure 5, many fracturing fluids (particularly crosslinked gels) are not truly fluids. Trying to characterize these materials with a "viscosity" can be very difficult. Fortunately, even for these fluids, temperatures above about 120°F make the behavior more predictable.



**Figure 2.** The geometry of a curette “Cup & Bob” Viscometer



**Figure 3.** Rheometer’s for testing fracturing fluids.



**Figure 4.** The Weissenberg Effect



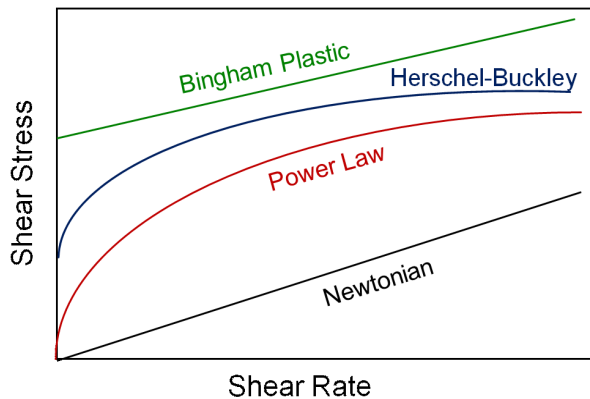
**Figure 5.** Example of a Complex Dehydrated Cross-linked gel

## 5. Rheological models

The tests described above measure the shear stress generated by specific increasing shear rates (called a ramp), and this data is converted to a "viscosity" value by using a rheological model to describe fluid behavior. Figure 6 shows the three models that are in common use by the oil industry and these are:



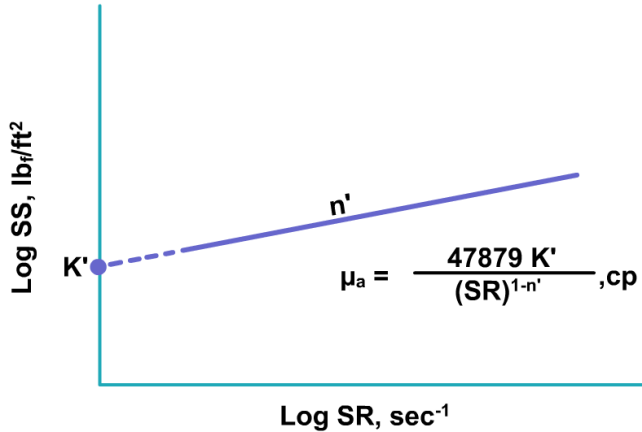
1. Newtonian Fluid - A Newtonian fluid has a linear relation between shear rate and shear stress and fluid viscosity is the slope of the shear rate versus shear rate data.
2. Bingham Plastic - A Bingham Plastic differs from a Newtonian fluid in that a non-zero shear stress called the Plastic Yield Value is required to initiate fluid flow. The slope of the shear rate/shear stress data is labeled Plastic Viscosity and this model is routinely used for cements and many drilling muds.
3. Power Law Fluid - This is the most common fluid model used for current fracturing fluids and for this rheological model the shear stress/shear rate data give a linear relation on log-log scales. The slope of this log-log line is denoted by  $n'$ , and this is labeled the Flow Behavior Index.  $n'=1$  implies a Newtonian fluid;  $n'>1$  is called a shear stiffening fluid; and  $n'<1$  is a shear softening fluid.  $n'$  is generally less than 1 for fracturing fluids. The shear stress at a shear rate of "1" is labeled the Consistency Index and is denoted by  $K'$ . For real fluids  $K'$  and  $n'$  change with temperature and time with  $K'$  generally decreasing and  $n'$  tending toward unity.



**Figure 6.** Rheological Models

For non-Newtonian fluids (a Power Law fluid being one example) the "apparent viscosity - ( $\mu_a$ )" is used as a shorthand way of characterizing the fluid. Apparent viscosity ( $\mu_a$ ) is illustrated in Fig. 7 and is the ratio of shear stress to shear rate - at a particular value of shear

rate. Thus a fluids apparent viscosity depends on the shear rate at which the viscosity is measured (or calculated). For a Power Law Fluid with  $n' < 1$ , the apparent viscosity will decrease with increasing shear rate.



**Figure 7.** Apparent viscosity using a Power Law Equation

To determine  $n'$  and  $K'$  a fluid is placed in a rheometer and sheared at a constant rate while the temperature is brought to equilibrium. Periodically the fluid  $n'$  and  $K'$  is measured by bringing the shear rate up, holding the rate for a few seconds then increasing the rate again typically over a range of at least 4 shear rates. This is termed a ramp and is typically done every 30 minutes during the fluid test. Figure 8 shows an example of a shear stress vs shear rate set of ramps that was provided by C&A Inc. - <http://www.candalab.com/>. Note that for each ramp four shear rates were used. The slope of the line is the  $n'$  and the intercept at a 0 shear rate is the  $K'$ . Using this information an apparent viscosity for any shear rate can be calculated with the following equation.

$$\mu_a = \frac{448000 K'}{(SR)^{1-n'}}$$

Where  $\mu_a$  = Apparent viscosity in cps

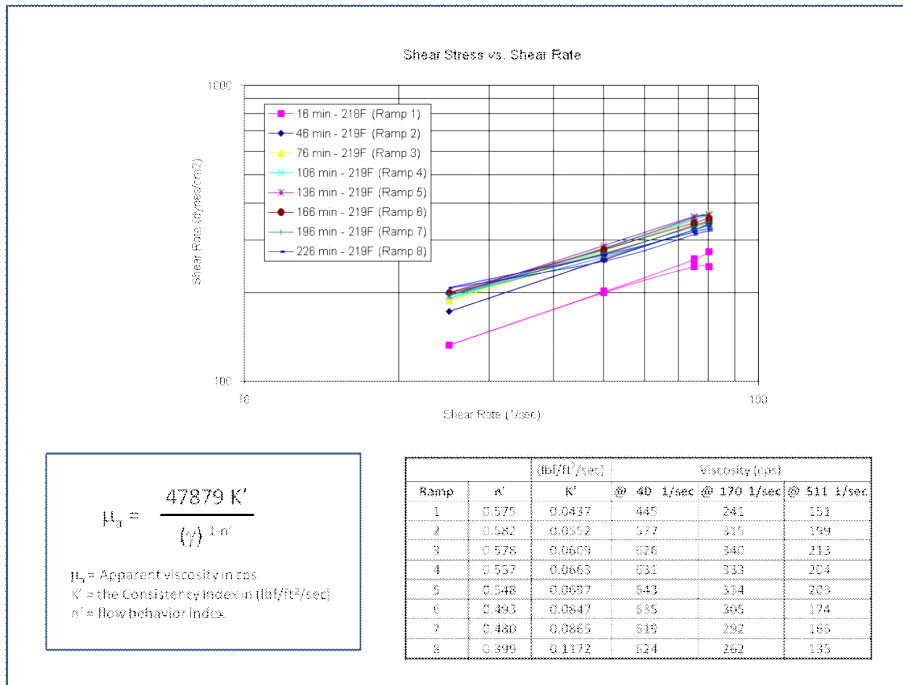
$K'$  = the Consistency Index in (lb/ft<sup>2</sup>/sec)

$n'$  = flow behavior index

SR = Shear Rate in Sec<sup>-1</sup>

Service company literature reports viscosity at different shear rates (usually 170 or 511 sec<sup>-1</sup>) and the shear rate in a fracture can be as low as 30 to 40 sec<sup>-1</sup>. The example shows that the identical fluid might be reported by one company to have a viscosity of 300 cp (170 sec<sup>-1</sup>), by another to have 200 cp (511 sec<sup>-1</sup>), and the fluid may actually have in excess of 600 cp in the fracture (at 40 sec<sup>-1</sup>). In selecting a fluid it is important to know at what shear rate the viscosity





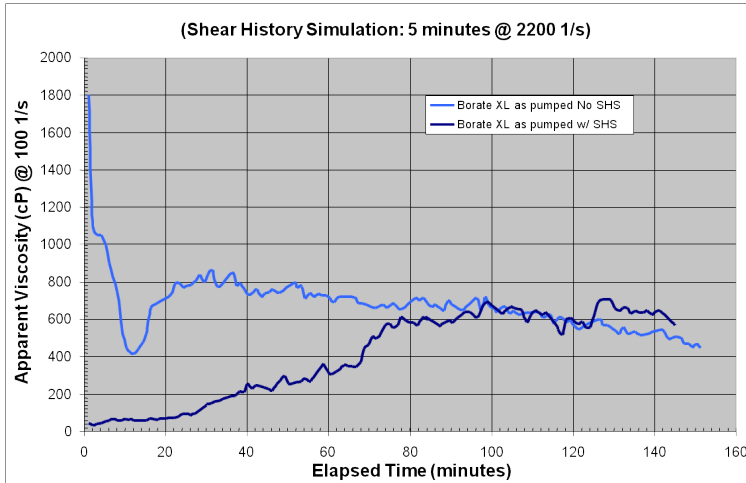
**Figure 8.** A set of shear stress vs shear rate set of ramps along with the calculation of apparent viscosity at three shear rates.

data was measured. In addition, **during the testing the fluid should be sheared at a shear rate somewhat representative of the behavior expected in the fracture.** This is typically on the order of 50 sec<sup>-1</sup>, but for some soft rock treatments the shear rate may be much lower than this, and in some hard rock treatments, the shear rate may be much greater.

## 6. Shear history simulation

As the fluid is pumped through the surface equipment, well tubular, perforations and fracture it is subjected to a range of shear rates that may have a detrimental effect on the fluid rheology. For example Figure 9 shows the apparent viscosity for a borate crosslinked HPG that was used to fracture a well in China. A series of premature screenouts had occurred and an evaluation was conducted to determine why. The well was completed with an open annulus and a tubing string and the treatments were being pumped down the annulus. The shear rate was calculated to be 2200 s<sup>-1</sup> and the time in the tubing/casing annulus was 5 minutes. As the figure shows the apparent viscosity without the 5 minutes of high shear was 800 cps but if subjected to shear was about 20 cps. The fluid did recover its viscosity but it took 80 minutes. The higher proppant

concentrations were settling out near the wellbore and causing the screenouts. The buffer package was adjusted by the service provider and that cured the problem.



**Figure 9.** Viscosity Profile for a Borate Crosslinked HPG with and without shear history simulation.

Reference 13 provides a detailed procedure on how to do shear history simulation. The equipment needed is shown in Figure 10. Because the flow in the tubulars is in pipe flow rather than slot flow using a curette “Cup & Bob” viscometer at high shear rate can be misleading. The shear rate in the tubular is a function of pump rate and tubing size. The equations for determining shear rate are included in reference 13.

## 7. Slurry viscosity

Another factor affecting viscosity is the addition of proppant to the fracturing fluid to form slurry. For a Newtonian fluid the increase in viscosity due to proppant can be calculated from an equation originally developed by Albert Einstein<sup>14</sup>. The chart shown in Figure 11 demonstrates this effect. The figure shows that an 8 ppg slurry has an effective viscosity about 3 times that for the fracturing fluid alone. This increased viscosity will increase net treating pressure and may significantly impact treatment design. This increase in slurry viscosity also retards proppant fall as discussed below.

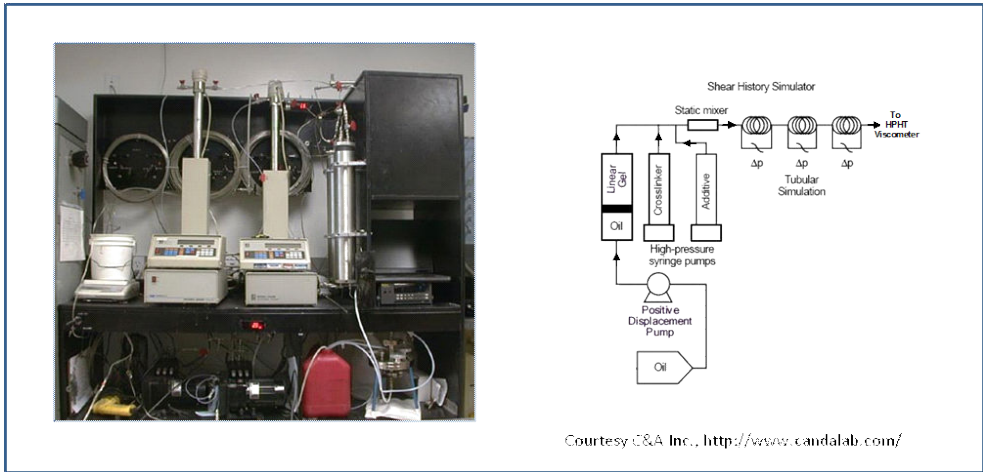


Figure 10. Shear History Simulation Laboratory Equipment

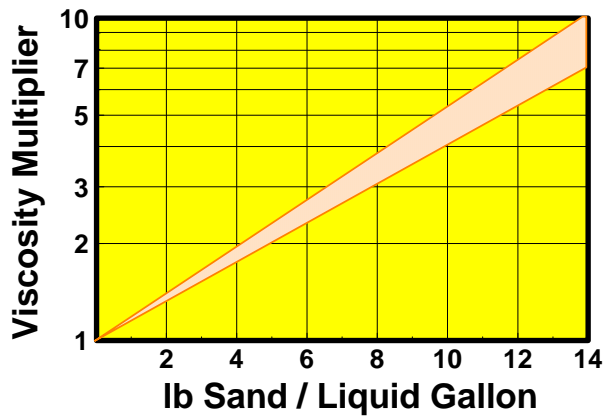


Figure 11. Slurry Viscosity Multiplier as a function of proppant concentration.<sup>14</sup>

## 8. Proppant fall rates

The rate of fall for proppant is normally calculated using Stoke's Law which can be written as:

$$\text{Fall Rate} = V \text{ (ft/sec)} = 1.66 \times 10^5 D^2 / \mu_f [SG_{\text{prop}} - SG_{\text{fluid}}]$$

Where:

$D$  = the average proppant diameter in feet

$\mu_f$  = the apparent viscosity of the fluid in Cps

$SG_{\text{prop}}$  = the specific gravity of the proppant (i.e. 2.65 for sand)

$SG_{\text{fluid}}$  = the specific gravity of the fluid (i.e. 1 for water)

Stokes's Law is generally not valid for Reynolds numbers much in excess of unity<sup>15</sup> or for hindered settling due to proppant clustering in static fluids<sup>16</sup>. For crosslinked fluid the actual fall rate may be much less than Stokes Law. Hannah and Harrington<sup>17</sup> present lab data that shows that proppant in crosslinked fluids falls at a rate which is reduced by about 80% when compared to non-crosslinked linear gels with the same apparent viscosity. The rate of proppant fall in foams and emulsions is also much less than would be indicated by using the apparent viscosity in Stoke's Law<sup>18</sup>. Another factor affecting proppant fall is the particle concentration which increases slurry viscosity (Figure 11). This retards or hinders the proppant fall because of clustered settling<sup>16</sup> in static fluids. Finally the slurry flowing down a fracture is generally much lower than the shear rate of 170 or 511  $\text{sec}^{-1}$  used to report the fluid apparent viscosity.

When all of these factors are put together they can significantly affect the viscosity. To provide an example consider a crosslinked gel which has a reference apparent viscosity at 170  $\text{sec}^{-1}$  of 50 cps after four hours at reservoir temperature.

1. Shear Rate Correction – If the fluid has an  $n'$  of 0.6 and the shear rate in the fracture is 50  $\text{sec}^{-1}$ , the effective apparent viscosity in the fracture would be  $(170/50)^{1-n'}$  times the measured viscosity or  $(1.63 \times 50 = 81 \text{ cps})$ .
2. Slurry Correction – If the slurry enters the fracture at a concentration of 1 PPG (pounds of sand per liquid gallon) and concentrates to 10 PPG after four because of fluid loss, the average concentration of 5 PPG gives a viscosity multiple of 2 from Figure 11. This would give an effective average apparent viscosity of  $(2 \times 81 = 162 \text{ cps})$ .
3. Fall Rate Correction – Harrington and Hannah<sup>17</sup> state that for a crosslinked fluid the rate of fall is reduced by up to 80%. For this example assume that the fall rate is reduced by 50%. This effectively doubles the viscosity to  $(2 \times 162 = 324 \text{ cps})$ .
4. Temperature Correction – The fluid enters the fracture at a relatively low temperature and thus a higher viscosity. If the fluid viscosity reduces by a factor 10 over the 4 hour exposure time (down to the originally referenced 50 cps) with a log viscosity versus time relationship (typical for most crosslinked fluids) the average fluid viscosity over the four hour period would be a factor of 4.3 times the final viscosity. This gives an effective average apparent viscosity of  $(4.3 \times 324 = 1393 \text{ cps})$ .

Using a value of 1393 cps of apparent viscosity in Stoke's Law gives a total proppant fall of 15 feet during the four hour period. Almost perfect transport is achieved by a fluid system having a final reference apparent viscosity of only 50 cps.

This example may appear to be extreme but it is actually conservative. The Fall Rate Correction was reduced from 80% to 50% and the time it takes to heat up to reservoir temperature was ignored. The main point to be taken from this is that the viscosity requirements for a frac fluid can be overestimated by an order of magnitude and sufficient proppant transport can be achieved with a fluid having a reference apparent viscosity of 50 to 100 cps.

## 9. Viscosity and fracture treating pressure

Treating pressure is fairly insensitive to viscosity as the pressure is proportional to viscosity raised to the  $\frac{1}{4}$  power. However as discussed above the viscosity estimate can easily be off by an order of magnitude which can have a drastic impact on treatment behavior. An order of magnitude would be ( $10^{0.25} = 1.8$ ) so the treating pressure would be 80% greater than anticipated. This could cause undesired height growth and result in treatment failure. For jobs where the control of net pressure to prevent height growth is important, fluid viscosity is a critical parameter.

### Author details

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