CHEMICAL, DESIGN AND OPERATIONAL CONSIDERATIONS IN THE USAGE OF THE NEW BORATE CROSSLINKED FRACTURING FLUIDS

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ABSTRACT

This paper discusses recent trends and advances in borate crosslinked frac fluids. The chemistry of new borate systems requires a good understanding of mixing, additives and operational considerations on the part of the operator.

The paper presents quality control, chemistry, crosslinking methods, design methods and limitations, crosslink delaying techniques, new gel breaking systems, and special additives. Additionally, the paper presents the pre-job and on location gel testing. Crosslink time and gel break time curves are also presented.

INTRODUCTION

As oil and gas fields mature most wells require hydraulic fracturing to be economically productive. Of the many fluids that can be used to fracture wells, borate crosslinked aqueous gels are the most popular at present. Borate crosslinked gels have displaced titanate, aluminate, foams and oil based gels in most applications. Borates were the first crosslinkers to be used widely and successfully to enhance proppant transport capabilities of aqueous fracturing fluids. They have been used to crosslink guar and derivatized guar since around 1967 in low to moderate temperature applications. Historically, the evolution of borate based technology was fraught with many technical problems and hurdles. These include, getting a uniform crosslinker slurry, high sensitivity to water quality, high pumping pressure, temperature limitations and occasional gel breaking and fluid recovery problems. The most significant technical problem was the rheological instability of conventional borates in applications where formation temperatures exceeded 180° F.

Consequently, early development of high temperature fracturing fluids, which was channelled towards optimizing thermal stability of rheological properties, focused on organometallic crosslinkers such as titanium, zirconium, chromium, aluminum and antimony. Chemists had known that these metal ions provided stable covalent bonding in high temperature environments. In addition, metal crosslinked guar and HPG based aqueous gels were chemically predictable, rheologically better defined and characterized. Also, organometallic crosslinked gel break times are predictable. The addition of gel preservatives such as thiosulfates and alcohols afforded organometallic crosslinked gels enhanced temperature stability.[1] Due to problems associated with borate crosslinked gels and the ease of organometallic pumpability, the use of borate systems declined precipitously between late 1970's to around 1985. Organometallic-crosslinked gels however, exhibited a high degree of irreversible gel degradation with shear. This resulted in the development of crosslink time delay technology.[2] Crosslinking time was retarded by using an organic ligand, which chelated the crosslinker metal-ion until the temperature of the reservoir released the metal-ion initiating crosslinking. In some applications, these ligands were pumped in conjunction with surface crosslinkers to provide proppant transport in the lower temperature regime.

With decline in energy prices since 1985, it has become imperative to maximize both the productivity and the cost effectiveness of fracture stimulation. Since borate salts and naturally occurring ores and minerals are low cost they addressed the need for cost reduction and thus have become primary economical choice. Separately, proppant pack or fracture conductivity which is the most important variable controlling well productivity is a function of fracture width and in-situ proppant permeability. The dimensionless conductivity C_{fd} defined in equation 1 should exceed 10 to optimize estimated production from a hydraulic fracture.[3,4]

$$C_{fd} = (K_f w) / K X_f \qquad \text{---------------} \; 1$$

Where C_{fd} = dimensionless fracture conductivity.
K_f = fracture permeability, md
K = formation permeability, md
w = fracture width, ft
X_f = fracture half length, ft

To achieve a C_{fd} value of larger than 10, the numerator of equation 1 must be maximized. Increasing fracture width by increasing proppant concentration and improving fluid rheology is eventually inefficient. A more practical and efficient approach is to retain high proppant permeability.[3,4] However, it is known that the proppant pack permeability is significantly impaired by concentration of the crosslinked gels due to leakoff of the fluid into the formation matrix along the fracture walls[5]. The proppant pack damage can be reduced by use of breakers or polymer degradants. The commonly used gel breakers are enzymes, oxidizing agents and weak acids. Enzymes are effective at low temperatures and oxidizers such as persulfates are employed in moderate to high temperature applications. The breakers reduce fracture conductivity damage by degrading the polymer and the filter cake left in the proppant pack. Studies have shown that high concentrations of persulfate can significantly reduce fracture conductivity damage.[6]

Chemically, borate crosslinked guar or HPG gel has different properties than organometallic crosslinked gels. The borate crosslinked bond is a very weak bond, but is reversible in that it reforms after being broken by shear. The reversibility of the crosslink affords improved shear stability to the borate crosslinked gels, but makes it difficult to characterize the fluid rheologically. In the late 80's several studies were conducted to develop new crosslinked gels with the purpose of better understanding their chemistry, and improving their pumping characteristics, high temperature stability and fluid rheology. By early 1990 two types of borate crosslinked systems were available, one for low temperature applications and another for moderate to high temperature applications. The low temperature application is referred to as the conventional borate and the high temperature application is termed as the new borate. This paper discusses the chemistry, design and operational considerations of the new borate crosslinked fluids in comparison with the conventional borates.

CHEMISTRY AND RHEOLOGY

Historically, boric acid or borax was used as a crosslinking agent for guar-based aqueous gels. The crosslinker was batch mixed in the guar solution and an alkaline material was injected on-the-fly to increase the fluid pH to 8.5 or higher to initiate crosslinking. The crosslinking of the fluid is controlled by the chemistry and the concentration of the borate ions in solution. Borax (sodium tetraborate) dissociates in water to form monoborate ions (MBI) in a 2 step reaction as shown. The second step (equation 3) is reversible.

$$Na_2B_4O_7 + 7\,H_2O \text{ ----> } 2\,Na^+ + 2\,B(OH)_3 + 2\,B(OH)_4^- \quad \text{---------------} \; 2$$

$$B(OH)_3 + H_2O \text{ <----> } B(OH)_4^- + H^+ \quad \text{---------------} \; 3$$

If the fluid pH is increased by addition of an alkali, the equilibrium in equation 3 is shifted to the right causing an increase in MBI concentration. Under ambient conditions, at a pH of 8.5 sufficient MBI concentration exists in solution to commence crosslinking between guar molecules cis hydroxyl groups and the MBI. The bonds formed between the polymer active sites and the MBI are very weak (hydrogen bonds) and labile. The MBI bonds are broken by shear; however, unlike the strong ogranometallic bonds, the MBI bond reforms or heals to provide high shear stability. An excess of MBI in solution causes "over crosslinking" or syneresis due to intramolecular bonding. Syneresis leads to an irreversible loss of crosslinked structure.

At a pH of 8.5 and above the MBI crosslinking is very rapid and produces gels of very high viscosity. This results in a gel with very high friction characteristics and pumping this system via small diameter tubulars necessitates the need to delay the crosslinking to reduce surface treating pressure.

A recent study has shown effects of different chemical additives by evaluating the fluid rheology. [8] Accurate and reproducible rheological measurements were made with the aid of a recirculating flow loop and a model 50 Fann viscometer. The study concluded that guar uses borate ions more efficiently than HPG, and that the fluid pH determines the crosslink rate and temperature stability. As indicated earlier MBI crosslinked fluids have been limited to low to moderate temperature applications (below 160° F). Typically, this system exhibits rapid loss of viscosity at temperatures above 160° F. Recent Stim Lab studies on conventional borate (MBI) rheology concluded that failure of proppant transport capability occurs at about 180° F.[9]

A new generation of borate crosslinked guar and HPG with rheological stability up to a temperature of 250° F was reported in 1986.[11] This temperature stability was achieved by using slow dissolving borate ores slurried in an oil phase. The new borate crosslinked gels exhibit a different crosslinking mechanism. The borate ores produce high concentration of boroxyanions with increase in temperature. The crosslinking rate is also influenced by the gelling agent and the pH of the fluid. In addition, the high concentrations of boroxyanion at elevated temperatures does not produce "syneresis". In addition the new borate chemistry lends itself to a built in crosslink delay since the production of boroxyanion is a slow and thermally initiated process. However, since the new borate crosslinked gel is thermally stable increased breaker loadings are necessary. In addition to the above mentioned new borate crosslinked system another new system exclusively developed and used by one service company employs and organo complexed borate crosslinker.[10]

DESIGN CONSIDERATION

The most important design criteria in fracture stimulation is the fluid selection. Other criteria considered in this paper are fracture conductivity, breaker applications and crosslink time.

Fluid Selection:

Due to advances in formation damage control technology and better understanding of aqueous gel chemistry, most wells today are fracture stimulated with aqueous crosslinked gels. As discussed earlier, in the mid seventies the organometallic crosslinkers became the popular choice of the industry. However, laboratory studies[12] in the late eighties showed that organometallic crosslinker cause significant damage to the proppant pack conductivity. Tests also revealed that borate gels clean up more rapidly and efficiently and have minimal fracture conductivity impairment. Consequently, borate crosslinked gels are at present widely used. This fact is amply demonstrated in Table 1 which shows that 75% of fracture treatments designed or requested from June to December 1991, were borate crosslinked gels. Borate crosslinked gels have been significantly improved since 1989. The improvements made are:

1. Better shear stability.
2. Extended thermal stability.
3. Control of crosslinking rates.
4. Improved sand suspending properties.
5. Enhanced post-treatment clean up.

The new borate crosslinked gels exhibit improved shear stability due to the fact that the crosslink junctions are not permanent covalent bonds but short lived inert temporary junctions that are not chemically altered during the process of disassociation due to increased temperature or shear. A recent paper investigating the guar borate crosslinking mechanism and reaction kinetics suggested that borate crosslinking mechanism was at least in part due to weak hydrogen or ionic bonding.[11] Studies have shown that guar crosslinks more efficiently with borate than derivatized guars such as HPG since derivatizing guar blocks off some of the active sites available for crosslinking.[11]

To achieve acceptable crosslinking, the minimum polymer concentration has to be about 18 lb/1000 gal of water.[12] Polymer loadings typically range from 30 to 50 lbs/1000 gal of water. In low to moderate temperature wells (<180° F), the polymer concentrations should range between 30 lb to 40 lb/1000 gal. In the Permian Basin, where average BHT range from 90° F to 150° F, the most commonly used formulation consists of 30 lb polymer guar per 1000 gal of water.

The quality of crosslink is also a function of the fluid pH. As shown earlier, at higher pH, MBI concentration increases due to reaction shift to the right. Increased MBI concentration increases crosslink junctions thus affording greater thermal stability to the borate crosslinked gel. Typically, new borates which are crosslinked at pH in excess of 10 are stable up to 300° F. Additionally, the new high pH borates exhibit enhanced proppant support properties as demonstrated in Figure 1 through Figure 2. It is believed, that slower crosslinking rates in conjunction with more crosslink junctions provides for a stronger and extensively improved polymer crosslink architecture. It is this improved architecture that enhances the fluid proppant support characteristics.

In the older conventional borate gels, the alkalinity was kept at or below 9 to minimize formation damage and to allow for the enzymatic degradation of the polymer backbone at temperatures below 125° F. These older borate gels therefore had lower proppant support capability.

Borate crosslinked gels are extremely pH sensitive, thus enabling rapid post frac cleanup. Formation water which usually has a pH ranging from 6 to 8 helps break the crosslink junctions thus aiding in frac fluid recovery.

Studies in mid to late eighties[13] showed that naturally occurring ores or borate salts such as colemanite and ulexite provide slow borate ion release in water. These salts are slurried and used in the new borate crosslinked guar gels. They are the calcium and sodium calcium combination salts of borate which retard or delay the crosslinking process by slowly dissolving in water and releasing boroxyanions. The solubility of these minerals is strongly influenced by the fluid environment and temperature. The dissociation of these salts into boroxyanions is substantially accelerated at higher temperatures thus improving thermal stability to around 250° F to 300° F.

Another property of these new borate salts is their inefficient dissolution in water and base gels at ambient temperatures. This allows for pumping higher loading of borate salt since crosslinking does not accelerate at the surface conditions but does so at higher temperatures in the formation. Higher concentration of the polyborate ion also improves thermal stability and proppant support characteristics.

Fracture Conductivity & Gel Breakers:

Performance of wells can significantly be improved by maximizing fracture conductivity. Several studies have been conducted to determine permeability of various proppants at differing closure stresses and temperatures. However, the actual in-situ proppant conductivity is usually an order of magnitude lower than that shown from earlier studies.[14] So, in the absence of laboratory data, engineers have compensated for fracture conductivity impairment by using correction factors.

Several researchers have studied conductivity impairment under varying conditions of temperature and pressure.[2,15-17] More importantly, a study incorporating various fracturing fluids and additives has shown their effect on in-situ conductivity.[5] A conductivity damage in the range of 50 to 75% can occur due to polymer concentration, filter cake formation and proppant embedment.

Penny[5,9] quantified various factors that effect in-situ conductivity. Factors studied were; fracturing fluids, shear rates, time and temperature. The study showed that HPG gels crosslinked with titanium yielded 43 to 70% conductivity damage at temperature ranging from 175 to 300° F. Later data published in 1987 showed that at 150° F, titanate crosslinked guar was significantly more damaging than borate crosslinked guar.[18] Titanate crosslinked HPG gel yielded a 80% proppant conductivity damage whereas the borate fluid yielded a conductivity impairment of 36%. Separately, aluminate crosslinked CMHPG yielded damage in excess of 80%. The result of this study has caused borate crosslinked guar or HPG as the frac fluid of choice since 1988.

Later study[17] concluded that even at low temperature (100° F) borate gels yielded 5 to 12% conductivity impairment whereas 40 lb HPG titanate gel yielded 81% damage. Additionally, borates in conjunction with persulfate/amine breakers yielded a 12% damage to conductivity as opposed to 32% damage yielded by borate crosslinked fluids with enzyme breakers. Low pH organometallic crosslinked HPG fluids were found to be less damaging than neutral pH titanate crosslinked HPG fluids, 40% vs 81%.

Several methods have been tried in an attempt to improve proppant conductivity. These are:

1. Use of borate vs. organometallic crosslinkers.
2. Reducing gelling agent concentration.
3. Minimizing addition of fluid-loss additives.
4. Increasing proppant concentration, and
5. Increasing breaker loading.

Among the parameters known to effect fracture conductivity damage are polymer concentration. Cooke[3] correlated the conductivity damage due to unconcentrated fracturing fluids. The study revealed that proppant-pack damage increased with increasing polymer residue concentration. Kim et al[19] reported permeability reductions from 30 to 50% for polymer concentrations ranging from 40 to 100 lb/1000 gal.

The gelling agents or polymers used in fracturing operations have particle sizes (molecular) too large to penetrate the typical low permeability formation matrix. As a result, the polymer is concentrated within the proppant pack in the fracture due to fluid loss and fracture closure. Post closure polymer concentration can be calculated using Cooke's[3] equation for concentration factor or multiplier.

Final Polymer Concentration = Initial Concentration X Cooke's Factor -------------- 4

Assuming that all the polymer remains within the proppant pack, Cooke's concentration factor varies from 6 to 50 for proppant concentrations varying from 8 to 1 lb/1000 gal. Thus, for a fluid with initial concentration of 35 lb/1000 gal. and a proppant concentration of 8 lb/1000 gals, the final polymer concentration using equation 4 will be 35 X 6 = 210 lb/1000 gal. It is evident from this study, and others that polymer concentration within the proppant-pack is generally several folds greater than the surface polymer concentration.[20]

Penny[5] and Parker[22] doing conductivity test for long term temperature and stress exposure determined that measured permeability damage was a function of the dynamically formed filter cake and the concentrated polymer in the fracture. Large reductions in the proppant conductivity were observed by Penny especially in the case of crosslinked fluids. Brannon[20] showed that at 160° F, a linear guar based fracturing fluid could damage the proppant pack permeability from 73 to 88% based on the extent of polymer concentration within the fracture. Later Brannon[6] showed that at 160° F borate crosslinked guar and HPG, induced greater proppant-pack permeability damage than non-crosslinked gels. The same study demonstrated that significant improvements in permeability could be achieved by the addition of a larger dosage of oxidizing agents such as ammonium persulfate as breaker.

The degrading of polymeric fluids or gels is at present accomplished by use of oxidative or enzymatic breakers. Rapid thermal degradation of the polymer generally starts at temperatures above 200° F. In lower temperature applications thermal degradation of the polymer is much slower, so the degradation process is enhanced by the addition of gel breakers.

Ideally, gel break time is the amount of time required for gel viscosity to drop to 10 cp (@ 511 sec^{-1}). Typically, gel break time should satisfy the following condition:

Gel Break Time > Fracturing Pump Time + 15 Minutes -------------- 5

The breaker should be added continuously to the gelled fluid during the fracturing operation and theoretically should have no effect on the gel until pumping ceases and the fracture closes. If "forced closure" is performed, the fracture normally closes in less than 15 minutes.[23]

Once the fracture closes the breaker should commence reaction with the gel. The breaker should reduce viscosity of the gel by decoupling the crosslinker and also breaking the polymer "backbone" (reducing the molecular weight of the polymer). In addition, enough breaker should be added to cause degradation of the polymer filter-cake and the final concentrated polymer remaining in the proppant pack. If all the above goals are achieved, a rapid and a maximum cleanup of the proppant pack could be achieved. Generally speaking, proppant pack conductivity impairment of less than 50% should be aimed for during design phase of the fracture treatment.

Breakers in use today consists of enzymes for low temperature application and oxidizing agents such as persulfates for moderate to high temperature application. Enzymes such as hemicellulase begin to degrade the polymer rapidly so long as the fluid environment is within a pH range of 3.5 to 8.5 and temperature is below 125° F.[21] Outside this range, the old enzyme breakers were only partially effective at best. Recently however, for the low temperature applications of the high pH borate crosslinked gels a new enzyme breaker is developed.[11,27] This new enzyme breaker is functional up to a pH of 10.5. Enzyme breakers function by digesting the polymer, very similar to the bacterial degradation of the gel.

The most commonly used oxidative breakers are persulfate ($S_2O_8^{-2}$) or peroxydisulfates. Usually salts of ammonium, sodium or potassium are used in field applications. The thermal dissociation of the persulfate radical is a slow reaction below 120° F. But above 130° F or so, the persulfate rapidly decomposes into highly reactive and acidic sulfate radicals which attack both the crosslink and the polymer back bone. The reaction can be catalyzed at low temperatures with amines

$$O_3\ S - O{:}O - SO_3^{-2} \xrightarrow[\text{Catalyst}]{\text{Amine}} 2\ SO_4^{-2} \qquad ---- \ 6$$

The free radical generation catalyst, amine, can be either batch mixed or added on-the-fly depending on its effect on the fluid pH. Some amines are alkaline and elevate the fluid pH, these have to be added continuously, especially if the source of borate ions is batch mixed. Above 160° F the free radical generation is so rapid that to satisfy equation 5 it is necessary to add very low levels of persulfate and to discontinue the addition of amine catalyst. Above 200° F, our tests have shown that addition of as little as 0.2 to .3 lb. persulfate per 1,000 gals. can cause 40 lb/1000 gal gel to break in less than 15 minutes.

Since breakers normally are extremely rapid reacting with the polymer at high temperatures, break times greater than 8 hours for long pump time treatments in high temperature wells are extremely difficult to obtain by conventional methods. To combat this problem we suggest:

1. Large "cooldown" water (or very low viscosity gel) pre-pad.
2. Very little or no breaker in the pad. (Authors do not recommend this, since it would leave a substantial filter-cake and a gel concentrate in the fracture.)
3. Use of delayed or controlled release breakers. [4,24]
4. High viscosity temperature stabilized pad.

Conventional breaker designs used today are suitable for initial surface polymer loading. However, from our previous discussion of various studies, it is evident that the fracture conductivity is impaired by the build up of a dynamic filter cake and an ultra high final polymer concentration. Therefore, a much larger breaker concentration is needed to effectively degrade the concentrated polymer. Additionally, since most breakers (water soluble salts) dissolve in water and leak off in the formation matrix, they do not accumulate with in the fracture to cause degradation of the concentrated polymer.

Studies sited earlier, have shown that fracture conductivity impairment can be significantly reduced by a combined effect of high temperature and increased breaker loading. Unfortunately, the high persulfate loading required to produce an efficient reduction in conductivity damage cannot be used without sacrificing the fluid rheological and proppant transport characteristics. Studies[4,17] have shown that persulfate concentration of 1 lb/1000 gal allows for a pump time of about one hour for a standard 30 to 40 lb borate crosslinked gel without losing proppant transport capability at 160° F. However, the same fluid would require 6 to 7 lb of persulfate per 1000 gal of gel to minimize proppant pack permeability damage.

In order to combat these problems the industry has been using delayed breakers.[4,24] The delayed breakers, which can be added in much larger concentrations are designed to activate close to or after the treatment is concluded. The delayed or the Controlled Release Breaker (CRB) consists of an oxidizer (persulfate) enclosed in an insoluble coating that allows large quantities of it to be added to the fracturing fluid without causing a rapid loss in the fluid viscosity. The coating controls the transfer of persulfate into the fracturing fluid via the relatively slow diffusion process. The CRB, which is said to be operating under a "diffusion controlled" mechanism, will be degrading the final polymer concentrate from several hours to days depending on the formation temperature (CRB's average mesh size of 80 allows it to accumulate within the fracture, see attached Table 2).

Like all manufactured products CRB may have slight manufacturing defects in the coating and along with the damage during transportation, handling and pumping, a trace amount may lose its coating either completely or partially. For design purposes between 2 to 5% of the delayed breakers may be considered to be damaged and may therefore prematurely activate.

In our study over sixty fracture treatments were conducted using the new borate crosslinked gels in conjunction with the high loadings of the CRB. The bottom hole temperature in these wells varied from 100° F to 180° F. Various methods of breaker schedule design were used as shown in Figure 3 through Figure 5. As can be seen from these figures, conventional persulfate and CRB were both used but not mixed. In addition, wells with temperatures below 125° F a small quantity of enzyme breaker was added throughout the treatment. The breaker schedule profile and the maximum amount used is based on the polymer loading, temperature, economics and the operator preference.

Crosslinking Time and Delay:

Crosslinking time which is crucial in any fracturing operation is defined as the time required for the base polymer solution to take on a rigid structure or to transform into a very highly viscous fluid. Crosslinking causes the molecular weight of the base polymer to substantially increase by joining several molecules together. The crosslink time is determined in the field usually with the help of a Waring blender at a set shear rate. The fluid is said to be partially crosslinked when the vortex in the blender (Figure 6 to Figure 9) totally disappears (at ambient temperature). The fluid is then tested for "lipping" by attempting to pour it out of a jar. When "lipping" is observed, the fluid is considered totally crosslinked (Figure 10). In rapid crosslinking fluids the time required for vortex closure and "lipping" is almost indistinguishable.

There are many advantages in delaying the crosslinking time. Recent studies have shown that delayed crosslinking allows for better dispersion of the crosslinker, yields higher viscosity and improved thermal stability. Research has shown that delayed crosslinking improves the polymer crosslink architecture by rendering it more uniform and structured. Additionally, delayed crosslinking allows for an improved dispersion of the proppant and the breaker. The most popular reason for delaying crosslink time is to reduce surface pumping pressure by lowering fluid viscosity and thus the friction in the tubulars. Lower friction pressure can substantially lower horsepower cost and also enhance safety.

Several techniques have been used in the delaying of the borate crosslinked gels. In conventional borates the rate of solubilization of the buffer or the pH elevating additive was delayed in order to lower the rate borate ion formation. This method was recently demonstrated by Cawiezel[25] by using calcined magnesium oxide slurried in oil as a buffer. In the new borate crosslinked gels the crosslinking delay is caused by a slow and thermally initiated release of polyborate ions. Typically new borate gel takes 5 to 8 minutes to crosslink based on the viscosity of the base gel, the amount of crosslinker and the pH of the fluid. In the new borate gels the crosslink time is accelerated by the addition of a buffer and a small amount of a quick dissolving source of borate ions such as boric acid (Figure 11).

With the increase in proppant concentration in the fracturing slurry, the crosslinker concentration should be reduced to account for the reduced water in the slurry. Crosslinker concentration reduction factor per gal of crosslinker is presented in Table 3. If the crosslinker is not reduced, the fracturing fluid will be over complexed and rheologically unstable. This problem is severely aggravated at proppant concentrations over 5 lb per gal (PPG).

OPERATIONAL CONSIDERATIONS:

Generally, operational factors include, quality control of water and chemical additives, mixing procedures, crosslinker adjustments and breaker scheduling. Other operational considerations such as equipment and safety are routine to every fracturing operation and will not be discussed here.

Water and Chemical Quality Control:

The new borate crosslinked gels are very sensitive and precise formulations. It is therefore very important to perform comprehensive pre-job fluid testing for successful fracturing. Water quality is critical to the proper development of base gel viscosity (figure 12 and figure 13) and subsequent crosslinked fluid stability. Since the presence of iron, reducing agents and phosphates can cause detrimental effect on the crosslinking mechanism, the water should be checked for their presence along with the pH. Additionally, iron reacts with the persulfate (added as a gel breaker) forming a precipitate and reducing the amount of persulfate available for polymer degradation.

Since guar and HPG disperse readily at high pH, the water pH should be raised with a buffer during blending of the polymer powder and then the pH should be lowered to slightly acidic to maximize gelation and achieve higher base viscosity. This method significantly reduces the formation of "fish eyes" and produces a higher quality base gel. The gel mixing process can be simplified by using a slurried polymer (slurried in diesel or any other non-solvent) instead of the polymer powder. The base gel average viscosities at different temperatures are presented in Figure 12 and Figure 13.

Since borate crosslinked gels are extremely sensitive to pH, water in all frac tanks should be checked for pH and the pH should be adjusted as necessary. Another commonly experienced problem is bacterial infestation of water. To minimize this problem all tank should be steam cleaned and dried prior to use. A bacteriacide which provides an initial kill and prevents bacteria growth should be added routinely to every tank.

All the chemical additives should be checked both visually and by pilot testing prior to the job. The additives should also be tested for compatibility with each other and for their effects, if any, on crosslink and gel-break times. The new borate crosslinkers are generally slurried mixtures and therefore each drum should be tested to determine ore settling and or extreme thickening due to either lower ambient temperature or concentration variations from drum to drum. If the crosslinker is too viscous and cannot be easily pumped, it should be diluted with a non-solvent liquid such as diesel and properly blended. Based on the amount of dilution the crosslinker required for crosslinking should be changed. Since this is a time consuming process it should be done a day or two before the actual job. Excellent quality control methods are shown by Ely.[26]

Mixing Operations:

Since 1985 the onshore oil industry has started using polymer slurries on large fracturing operations. Generally, when a fracturing operation entails more than 2 frac tanks of gel it is advantageous to use slurried polymers as opposed to the polymer powder. The slurried polymer which contains a small amount of viscosifier and a surfactant to keep the polymer in suspension can be either batch mixed or continuously mixed. The advantages of this process are:

1. A more uniform base gel with higher viscosity and fewer "fish eyes".
2. A reduced amount of gelling time on location.
3. When continuously mixed it eliminates fluid wasted due to "tank bottoms".
4. In case of premature job termination, only the fluid gelled continuously is lost, as opposed to all unused the gel wasted in case of batch mixing.

The continuous mix process consists of two specialized units. The first is a transport with 2 very accurate pumps. The unit carries the slurried polymer concentrate and the pumps are used to add the concentrate and another additive such as a liquid KCl substitute or a surfactant. The unit also has high volume suction and discharge pumps to move large quantities of water from the frac tanks to a holding tank. The holding tank provides time for polymer gelation or hydration. Different service companies use different schemes to achieve the same goals. The commonly used scheme is shown in Figure 14.

The residence time within the hydration tank is critical to the overall result of the fracturing operation. This residence time (equation 7) provides for polymer gelation, mixing of the chemical additives and the monitoring of gel properties. The design of the gelation tank includes several baffles which enhance the mixing operation by generating turbulence and providing path tortuosity to eliminate pockets of fluid stagnation.

$$\text{Hydration Tank Residence Time} = \frac{\text{Hydration Tank Capacity (bbl)}}{\text{Injection Rate (BPM)}} \quad \text{-----------------}7$$

The hydration time or the time required to reach between 85 to 90% of maximum possible base gel viscosity varies from about 2 minutes to 10 minutes depending on the polymer and the slurried concentrate used. Typically from a design stand point the following relationship should be satisfied:

$$\text{Hyd. Tank Residence Time} > \text{Polymer Hydration Time} + 2\ \text{Minutes} \quad \text{--------------}\ 8$$

The 2 minutes is provided as a safety factor and can be eliminated where job parameters do not afford the availability of extra time. The rate of addition of the slurried polymer to the hydration tank should be adjusted based on the injection rate as shown in equation 9.

$$\text{Concentrate Rate (GPM)} = \frac{\text{Injection Rate (BPM)} \times C}{24\ bbl\ /\ 1000\ gal} \qquad \text{----}9$$

Where C = Slurried polymer required per 1,000 gals. of water

Chemicals added at the discharge side of the blender have to be continuously adjusted based on the proppant concentration pumped (see Table 3).

Crosslink Adjustments:

Of all the chemicals added continuously during fracturing, the crosslinker and the associated activators (buffers) and modifiers (delayers and accelerators) are the most critical to the success of the operation. The new borate crosslinker should never be batch mixed since, in most instances, depending on the base gel pH, the crosslinking may commence in the frac tanks. Most companies add the crosslinker on-the-fly, between the discharge side of the blender and the suction side of the high pressure triplex frac pumps. The amount of crosslinker will change by a factor shown in Table 3, as proppant is added to the frac fluid. It is very important to reduce the crosslinker concentration by this factor, since a failure to do so will significantly over crosslink the gel especially at high proppant concentrations. The same factor should be applied to all the additives introduced in the discharge stream of the blender. The alteration of the crosslinker rate gets more complex with the introduction of the ramping method of proppant delivery as opposed to the conventional stair-step method.

The crosslink activator or the buffer should be added on-the-fly or batch mixed to the base gel after the polymer is hydrated. When slurried polymer continuous mix fracturing is being conducted the activator should always be added on-the-fly. The high pH activators hinder and retard the hydration or the gelation of the polymer making it necessary to run them on-the-fly.

The activator or the buffer loading depends on the pH of the base gel and the bottom hole temperature of the formation being fractured. The new borate gels are formulated in a pH range of 10 to 11.5. For high BHST wells the pH is maintained closer to 11 or higher. Since, in high temperature wells the buffering capacity of the activator is more important than the pH itself, the prescribed buffer loading should be added even though the fluid has attained the desired pH.

The new borate gels, by design, are delayed with respect to crosslink time, Figure 11 shows effect of temperature on crosslink time. It can be seen that the crosslink time is approximately seven minutes at an ambient temperature of 70° F. No adequate method is available to additionally delay the new borate crosslinked gels as yet. However, the crosslinker can be accelerated to the desired time by the addition of a small amount of an additive that accelerates the formation of borate ions as shown in Figure 11.

Generally, dry chunky and brittle crosslinked gel that easily breaks apart is indicative of over-crosslinking, on the other hand overly wet and low viscosity crosslinked gel is indicative of under-crosslinking. Most service companies have specially equipped vans to test the fluids and run the necessary tests to execute successful fracture treatments. During critical treatments a special quality control unit is placed between the hydration tank and the blender (suction side of the blender). This unit continuously monitors and records the base gel viscosity, temperature and pH on a strip chart (see Figure 15). The quality control unit output data is continuously monitored and corrective action is taken as necessary. In addition, the pH is usually monitored on the discharge side of the blender, and activator concentration is changed based on the fluid pH.

The laboratory van should have a Fann 35 and Fann 34 rheometers for measuring base gel and crosslinked viscosity. A temperature bath should be available to run gel break tests and based on these tests the breaker concentration should be modified. It should be emphasized however, that the gel break tests are time consuming and they can be very easily replaced by statistically reliable breaker test data that is generated by service companies.

Breaker Schedule Design:

For the commonly pumped new borate crosslinked gels, most service companies have developed precise gel break time vs. temperature curves. These curves are sufficiently accurate for design purposes and no additional prejob testing is necessary. However, for critical jobs where special products and non-standard polymer loadings are used, it is recommended that both prejob and on site gel break time tests be run. It should be remembered, that since the breakers are added on-the-fly to the proppant slurry, in most instances, the breaker loading should be reduced by the factor shown in the Table 3. In large treatments, where substantial formation cool down is suspected, a computer simulated fracture temperature profile is generated and used to increase breaker loading.

As mentioned earlier, the high final polymer concentration in the fracture and the build up of filter cake on the fracture walls has been shown to cause substantial fracture conductivity impairment. To alleviate this problem, since 1990 many operators have been using a very aggressive breaker schedule, especially in shallow and low BHT wells.[4] The heavy loadings (above 4 lb/1000 gals) require the use of a delayed or controlled release breaker.

Prior to 1990, breakers (both enzyme and persulfates) were run at relatively low concentrations so as not to destroy the rheological integrity of the fracturing fluid. Generally, the persulfate concentrations varied from 0.25 lb/1000 gal in the pad to about 2 lb/1000 gal in the final stages of the fracture treatment. The breaker increments and maximum loading are based on BHT. Similarly, when an enzyme breaker is used the concentrations are varied from 0.1 to 1.5 lb/1000 depending on BHT and the stage of the frac treatment. From an operational standpoint, it is easier to change breaker concentration during the changing of proppant concentration or the water storage tank. In the Permian Basin, where most wells are shallow and BHT average around 130° F, the average persulfate breaker pumped is 2.5 to 4.0 lb/1000 and the average enzyme breaker run is 0.5 to 1.5 lb/1000 gal.

With the advent of the delayed controlled release breaker in 1990 the gel breaker loading has been varied from 2 lb/1000 gal in the pad to 8 lb/gal in the final stages, producing an overall average delayed breaker concentration of around 5 to 6 lb/1000 gal throughout the treatment. Since late 1990, many fracturing treatments routinely use a combination of delayed (CRB) and conventional persulfate breakers. This technique improves the economics of the treatment while optimizing the breaker concentration in the filter cake and in the very highly concentrated polymer towards the tip of the fracture. The most cost effective (delayed breakers cost an average of 10 times the cost of conventional breaker) breaker schedule being pumped is shown in Figure 16. The fracture treatment starts of with a very high CRB concentration (about 5 to 8 lb/1000 gal) and then the CRB concentration is tapered off to zero at about 70 to 80% of the treatment. In the last 30% or so off the treatment the CRB is replaced with a conventional breaker whose concentration is tapered up from zero to around 3 lb/1000 gal at the tail end of the treatment. The tapering up and down can be done in a stair-step fashion or a linear or curvilinear ramp fashion. In very low BHT wells some operators have even combined CRB, a conventional breaker and an enzyme breaker.

The commonly run breaker schedules are presented in Figure 16 to Figure 18. The breaker profiles shown are as follows:

1. Constant CRB concentration up to about 80% of the treatment followed by a constant conventional breaker in the last 20% of the treatment (Figure 3).

2. High initial concentration of CRB tapered down to zero at about 70% of the treatment, followed by increasing amount of conventional breaker in the last 40% of the treatment (Figure 4).

3. Constant CRB concentration throughout the treatment combined with an increasing amount of conventional breaker in the last 30% of the treatment (Figure 5).

The amount of breaker added is equal to the area under the curve. For example the amount of breaker used in Figure 17 using a linear (triangular) profile is:

$$\text{Amount of CRB used} = 70{,}000 \times (6/1000) \times 1/2 = 210 \text{ lb}$$

$$\text{Amount of Conventional Breaker} = 40{,}000 \times (2/1000) \times 1/2 = 40 \text{ lb}$$

It should be noted that most delayed breakers, due to manufacturing defects and handling problems have about 5% active oxidizer available for quick dissolution into the gel. Hence it is not necessary to introduce the conventional persulfate until the last 30 to 40% of the treatment. The tail end of the treatment is pumped without any delayed breaker since in most cases the last part of the treatment is either flowed back immediately during "forced closure" or within 2 to 3 hours of the treatment completion. This procedure will cause a significant portion of the delayed breaker to be lost in the load fluid and thus be unavailable for long term polymer degradation.

Lab Van Testing and Equipment:

Of the several tests that lab vans perform, the water, chemicals and base gel quality, the breaker tests and crosslink time tests are most important. Sound rheological data is generated by using a Fann 50 viscometer and its use is highly recommended. However, the expense, the maintenance and the limited number of these being available make their use on location prohibitive. A Fann 35 viscometer is adequate for most day to day fracturing operations.

The following equipment should be available for use on location. A Waring blender with a variable speed transformer, or a Talboy stirrer with 4 blades, a high accuracy electronic balance (0.01g accuracy), constant temperature water bath, a power generator, a mercury thermometer, several beakers and sample cups, long handle proppant sampler, Fann 35 viscometer (R1/B1 & R1/B2 & #1 torsion spring) and sampling apparatus.

Gel Break Time Measurement:

Until recently most rheological data was generated without the inclusion of breakers. Since about 1988 breaker added gels are tested for rheology with respect to time with the aid of a Fann 35 viscometer. The Fann 35 viscometer which was initially used to measure base gel viscosity, is low cost, portable and easy to maintain.

The gel break time is obtained as follows. The crosslink gels are hard to measure rheologically at high shear rates, but lend themselves to rheological measurement at low shear rates using a Fann 35 viscometer. Since shear rates typically experienced in a fracture are relatively low, about 30 to 50 sec.$^{-1}$, a lower shear rate was recommended for a standard on site gel rheology test. A number 2 bob used with number 1 torsion spring at 100 RPM was selected. This combination provides a realistic shear rate of 37.72 Sec^{-1} as shown by equation

$$\text{Shear Rate} = A.N \quad \text{--------------------} \quad 8$$

Where A = R1 - B2 Nominal Shear Rate
= 0.37723 sec^{-1} / RPM

N = Rotor RPM
= 100 RPM Selected

Shear Rate = 0.37723 sec^{-1} / RPM X 100 RPM
= 37.72 sec^{-1}

To convert the dial reading to viscosity in centipoise use equation 9 as shown by Fann Instrument Corp.

$$Nn = (S)(D)(F)(C) \text{ ----------------------- } 9$$

Where S = Speed Factor = 3 at R/B2 - 100 RPM
D = Dial Reading
F = Spring Factor = 1.0 at R/B2 - 100 RPM
C = Rotor-bob Factor = 8.915
Nn = Newtonian viscosity, centipoise

Substituting these values in the above equation we obtain :

$$Nn = 26.85 D$$

The viscosity obtained this way at low shear rates is realistic, although actual fracture shear rates will vary with fracture geometry and fluid viscosity. The viscosity measured at a constant shear rate of 37.72 sec^{-1} plotted as a function of time provides quantification of gel degradation. Similarly, for field standardization and quantitative definition, a viscosity of 1,000 cp or more at the above shear rate is considered to be crosslinked. Below 1,000 cp at 37.72 sec^{-1}, which is not always a clearly defined point but is more determined by experienced visual inspetion rather than a numberical measured value, the rheological properties are measured in the conventional manner using a R1-B1 combination and number 1 torsion spring at 300 RPM, that is at a shear rate of 511 sec^{-1}. When the fluid is degraded to exhibit a viscosity of 10 cp or less at a shear of 511 sec^{-1} the gel is considered to be "broken" and the time taken to reach a viscosity of 10 cp at 511 sec^{-1} is defined as gel break time. The results of gel break tests conducted have been presented in Figure 16 through Figure 18.

Crosslink Time Measurement:

The new borate crosslinked gels are inherently delayed and pose a special problem with respect to measurement of crosslink time. Since late sixties a Talboy type stirrer has been used to mix the crosslinker in the base gel. This method is adequate when the conventional borate gel was being tested since the crosslinker is readily soluble. However, with the advent of the new borate crosslinked gels, the crosslinker is too viscous and not readily soluble at the low shear rate produced by the Talboy stirrer. Consequently, the crosslink times measured using a Talboy stirrer are consistently higher than those measured using the actual crosslinker added base gel obtained on site from the discharge side of the blender. In order to get a close match with the actual field crosslink times a Waring blender with a variable speed transformer (to adjust the shear rate) was used to provide agitation to mix the viscous crosslinker in the base gel. Using this method and carefully controlling the shear rate, crosslink times comparable to the actual crosslink times of blender discharge fluid are obtained. These tests as a standard field practice are run at ambient temperature and help determine the injection rate and the amount of crosslink accelerator required.

Measuring crosslink time on site consists of two steps. The first step is to establish a definite vortex in the Waring blender at a constant shear and then measuring the time taken to build up enough viscosity to produce a "vortex closure". This time is defined as time = T_1. The second step is to let enough viscosity develop to observe the "lip" effect. This is considered as fully crosslinked fluid and the time is defined as time = T_2.

Most service companies use T_2 as the crosslink time and T_1 is considered as partial crosslink time. Some companies that use Talboy stirrer define T_2 as the time taken to get "vortex inversion" i.e. time taken for the gel to finger and climb on the stem of the stirrer.

The new borate crosslinkers should be tested for viscosity, especially in colder winter months, as high viscosity of this slurry can dramatically impair pump efficiency. Prejob or regular calibration of crosslinker pumps is recommend. When the crosslinker is diluted with organic nonsolvents to reduce viscosity the crosslinker loading should be increased to compensate for the decrease in the active ingredient.

Other Chemical Additives:

Liquid KCl substitutes, surfactants and clay stabilizers presently used are usually compatible with the new borate crosslinked gels and can be batch mixed with water. Some amines used as catalysts to enhance persulfate breaker rates at temperatures below 120° F tend to raise the fluid pH, therefore they should not be batch mixed. When amines are used gel break tests should include amine in the fluid being tested, since they significantly change the amount of breaker required.

All gel breakers should be added on-the-fly to prevent settling and also premature gel breaks. Care should be exercised when oxidizer breakers are used since they are inflammable. Gel breakers should be introduced in the feed stream with accurate low volume dry chemical feeders. While using the new borate crosslinked gel in low temperature application the use of high pH enzyme breaker is recommended.[27]

CONCLUSIONS

The new borate crosslinked gels offer an economical, clean and rheologically sound choice for fracturing fluids. However, these fluids are precise formulations and sensitive to water quality and mixing procedures. The success of hydraulic fracturing will depend on prejob planning and testing. The following check list may help ensure the success of the job.

1. Make absolutely sure the frac tanks are clean and treated with bactericide as required.
2. Check water quality.
3. Check all chemical additives for quality and pumpability a day before the job and on location.
4. Crosslinker, buffers and activators should be added on-the-fly. Only buffers needed to improve polymer hydration should be batch mixed.
5. Base gel viscosity should be checked and adjusted if viscosity is off by 10% or more.
6. Crosslink time and crosslink quality should be checked at regular intervals.
7. Crosslinker, activator and breaker concentration should be adjusted to compensate for the proppant.
8. Higher concentrations of delayed breaker is recommended to improve proppant pack conductivity.

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Special thanks go to Lisa Worthan who spend many hours deciphering our written notes and typing them.

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Table 1
Fracture Treatments Designed in the Permian Basin from June 1 - December 31, 1991

FLUID TYPE	NO OF TREATMENTS	%
BORATE	445	75
ORG METALLIC	25	4
OIL BASE	1	*
POLY-EMULSION	4	1
LINEAR	27	5
OTHERS	90	15
TOTAL	592	100

* LESS THAN 1%

Table 2
Typical Size and Weight Distribution of Delayed Breaker

SIEVE SIZE U.S. SERIES	WEIGHT ON SIEVE/g	WT %
< = 40	< = .10	< = .5
50	3	2
60	22	18.5
80	73	61
100	18	14.8
200	4	3
> = 400	< = .02	< = .2

Table 3
Crosslinker Correction Factor Per Gal Crosslinker

PROPPANT ADDED LB/GAL OF LIQUID	PROPPANT ADDED LB/GAL SLURRY	CORRECTION FACTOR
0	0	1.000
1	.96	.978
2	1.83	.936
3	2.64	.881
4	3.39	.847
5	4.08	.816
6	4.72	.786
7	5.32	.759
8	5.87	.734
9	6.40	.711
10	6.89	.686
11	7.35	.668
12	7.77	.648
13	8.18	.630
14	8.57	.612
15	8.94	.596
16	9.28	.580
17	9.61	.565
18	9.92	.551
19	10.22	.538
20	10.50	.525

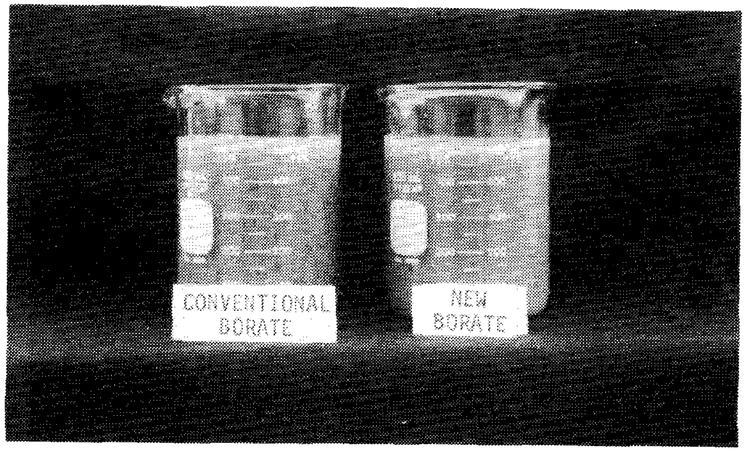


Figure 1 - 35 ppt conventional and new borate crosslinked gels
Time = 0 at 72°F
(Sand concentration = 4 lb/gal)

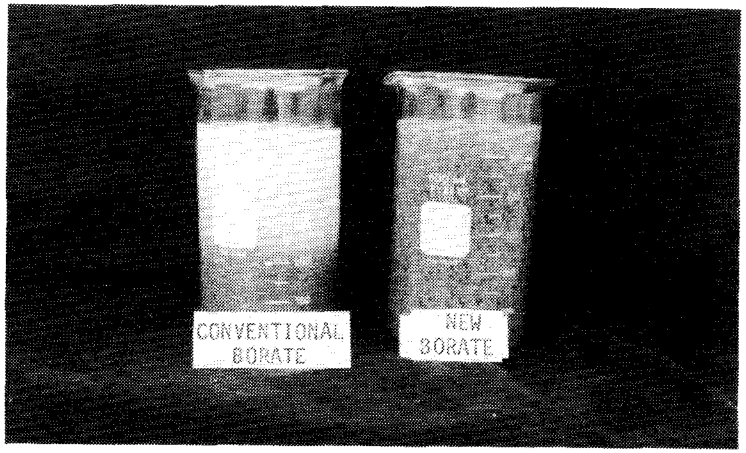


Figure 2 - 35 ppt conventional and new borate crosslinked gels
Time = 2 hours at 72°F
(Sand concentration = 4 lb/gal)

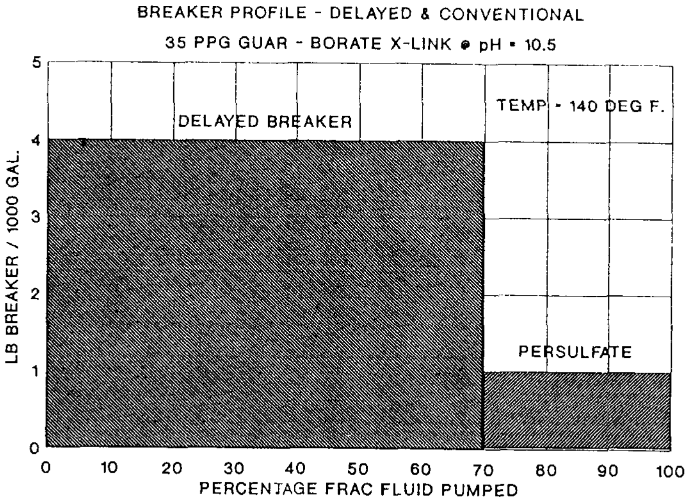


Figure 3 - Delayed and conventional breaker schedule - 1

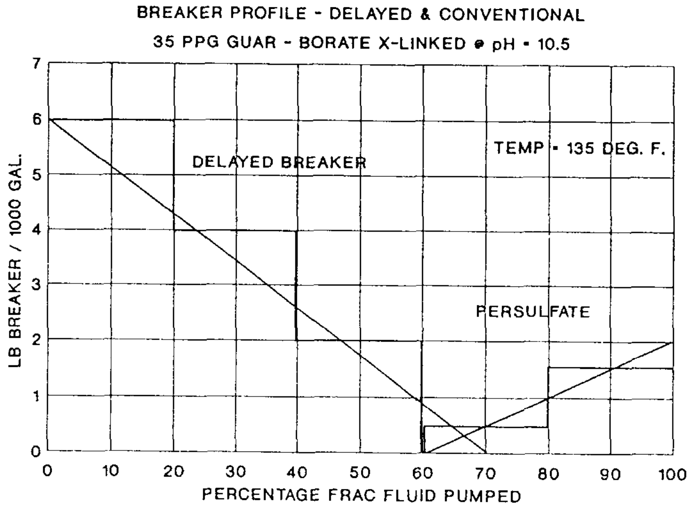


Figure 4 - Delayed and conventional breaker schedule - 2

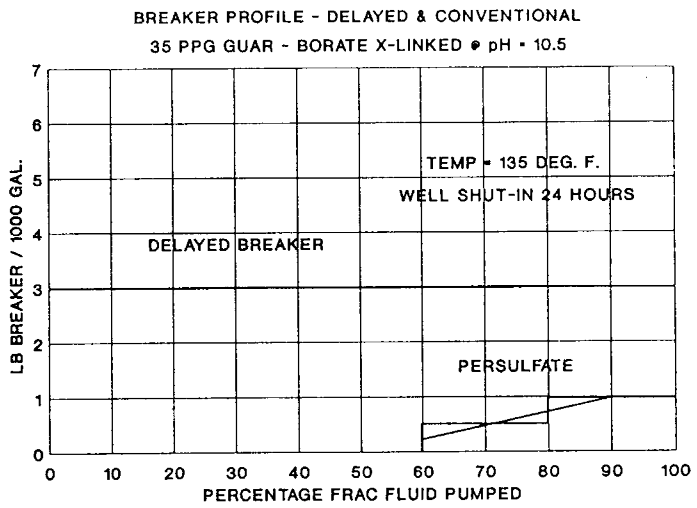


Figure 5 - Delayed and conventional breaker schedule - 3

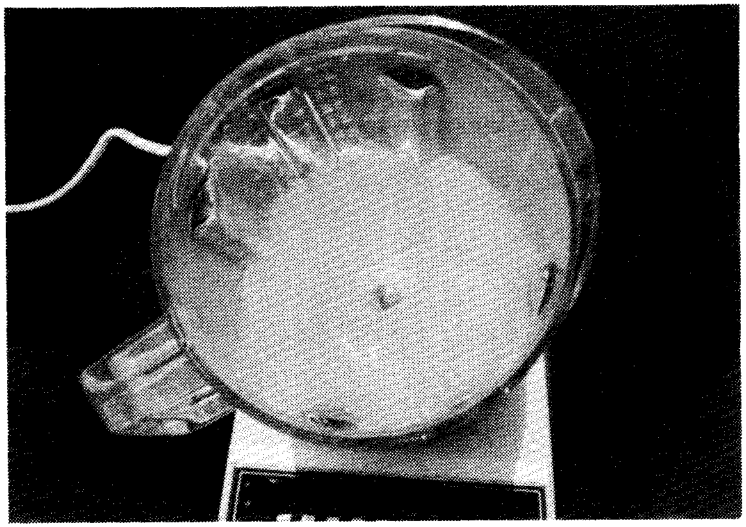


Figure 6 - Fully developed vortex in 35 ppt HPG gel
Time = 0 at 72°F

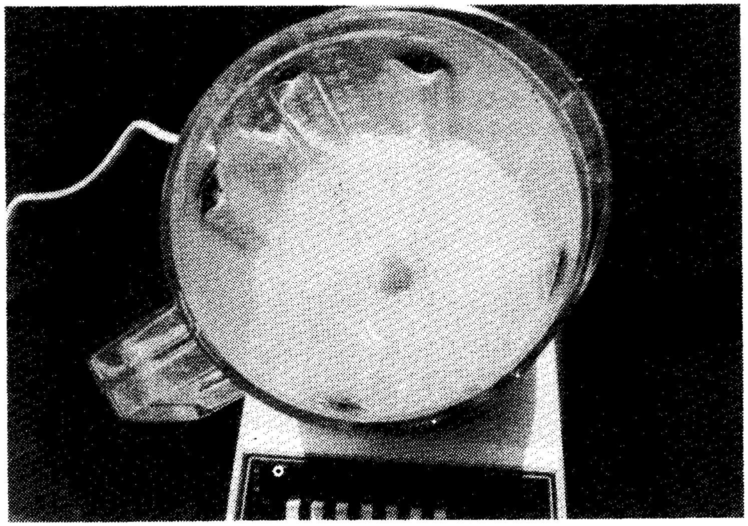


Figure 7 - Partially closed vortex in 35 ppt HPG gel
Time = 80 seconds at 72°F

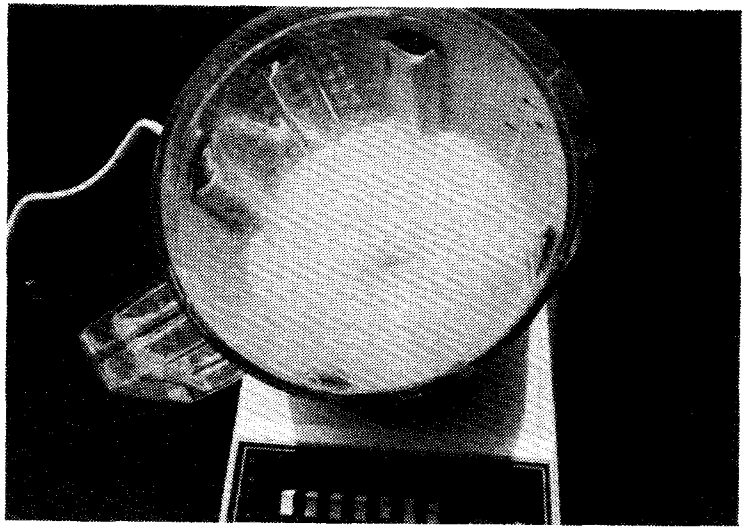


Figure 8 - Partially closed vortex in 35 ppt HPG gel
Time = 300 seconds at 72°F

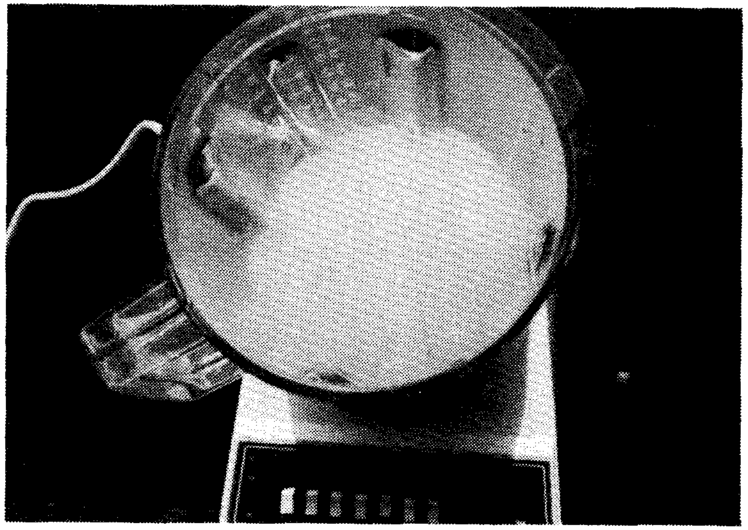


Figure 9 - Fully closed vortex in 35 ppt HPG gel
Time = 328 seconds at 72°F
(Vortex closure time = T1 = 328 seconds)

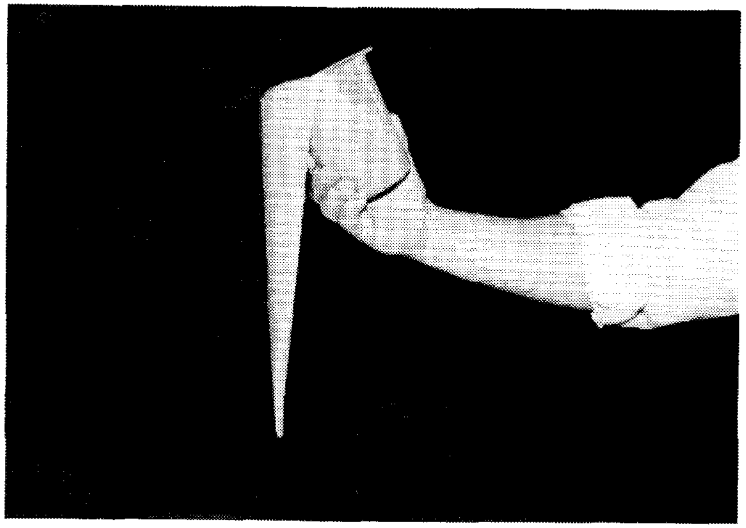


Figure 10 - 35 ppt HPG crosslinked with the borate technology
"Fully lipped"
Time = 8 minutes at 72°F

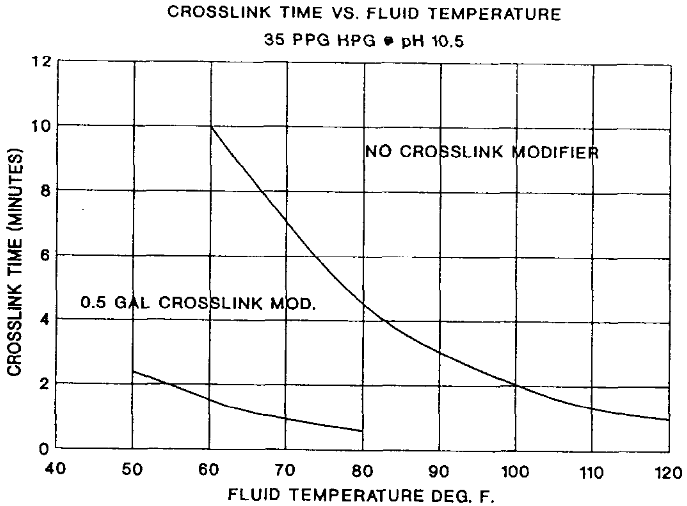


Figure 11 - Effect of temperature and modifier
on crosslink time

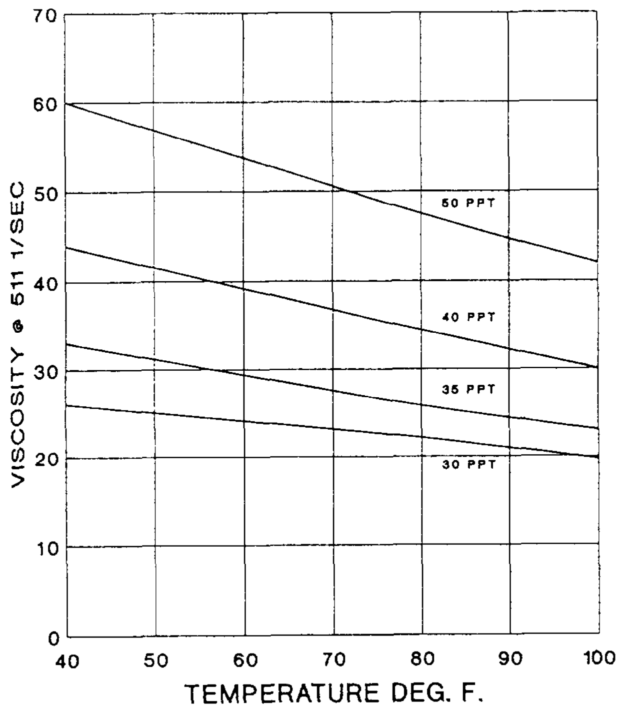


Figure 12 - Guar base gel viscosity vs. temperature

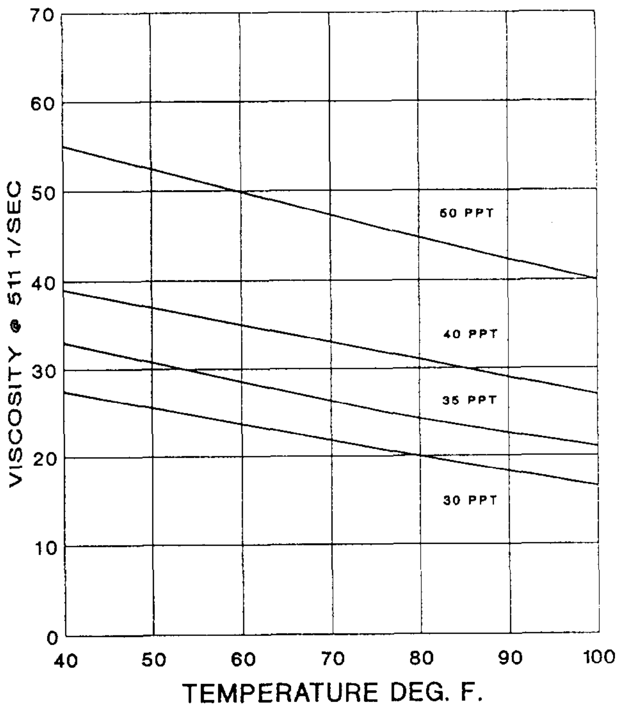


Figure 13 - HPG base gel viscosity vs. temperature

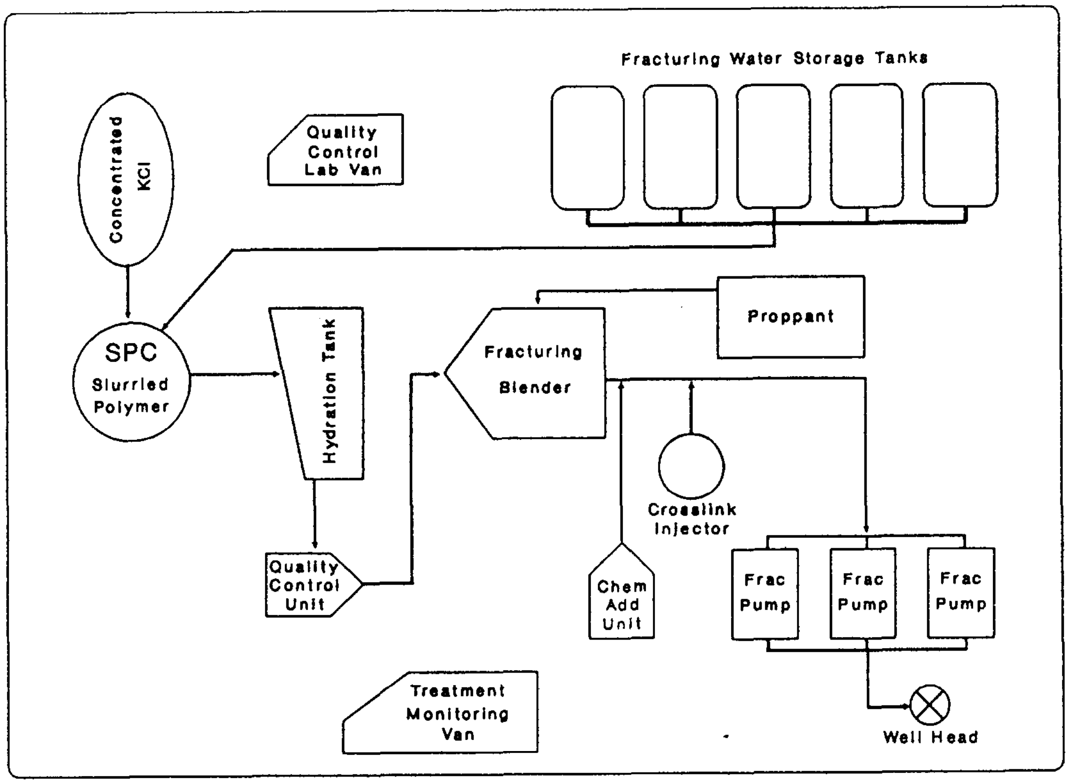
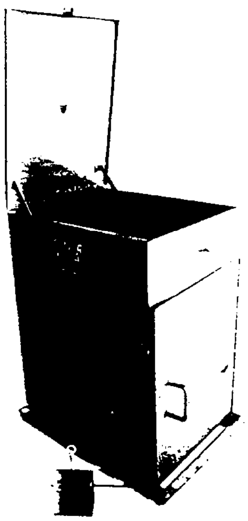


Figure 14 - New borate crosslinked gel fracturing layout (equipment)

To make sure the treatment is being run as designed, the Western Quality Assurance Skid continuously measures fluid properties from lines sampling from the clean and the proppant-laden sides of the blender.

The unit transmits measurements to Western Treatment Monitoring Vehicles where they can be displayed and permanently recorded.



Monitored Characteristics

Clean Side	
Base Gel Temperature	0 - 150°F
Base Gel Viscosity	0 - 100 cp at 5-11 sec.$^{-1}$
Base Gel pH	0 - 14
Proppant Side	
pH	0 - 14

Figure 15 - Quality assurance skid continuously provides key fluid data for treatments pumped on the fly

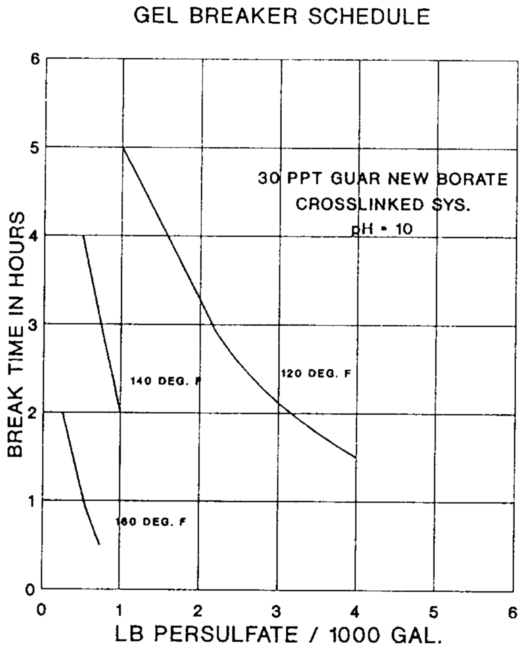


Figure 16 - Persulfate loadings in new borate crosslinked gels

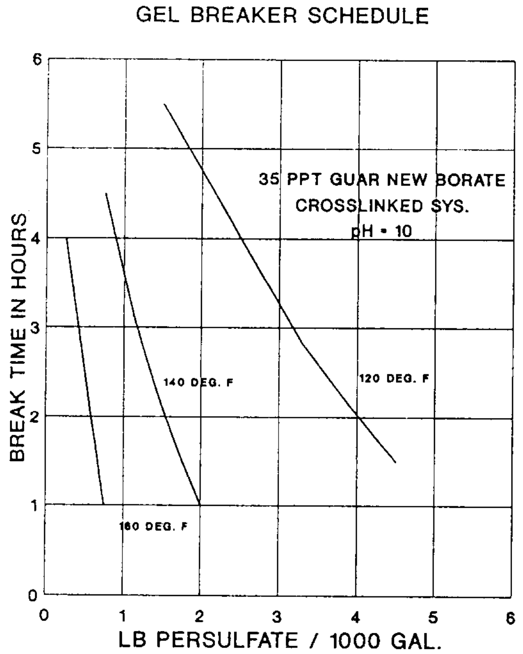


Figure 17 - Persulfate loadings in new borate crosslinked gels

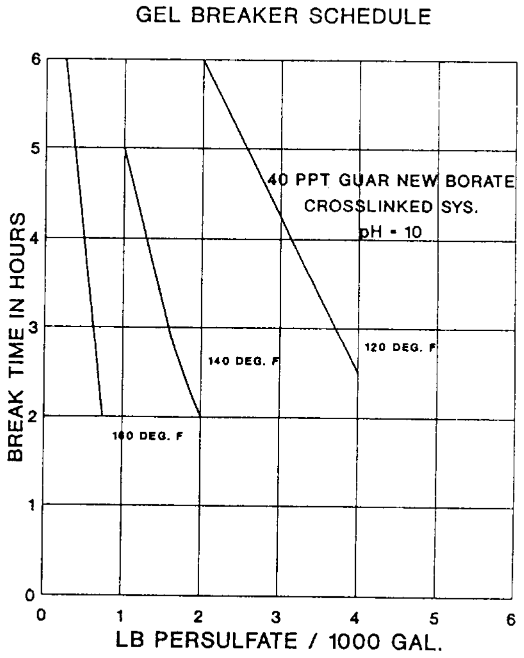


Figure 18 - Persulfate loadings in new borate crosslinked gels