#### FRACTURING FLUID SYSTEMS STATE OF THE ART

by John Ely, SPE-AIME, NOWSCO SERVICES

### Introduction

Since 1949 when the first fracturing treatment was conducted using a Naplam gel and a very small quantity of sand, significant advances have been made in the state of the art concerning fluids to be used in carrying proppants into fracture systems. Up until the late 1960's, the basic fracturing fluids went through a transition stage from the Napalm type gel to crude oils, condensates, and then to water based fluids. Eventually, the aqueous fluids were viscosified using starch, then finally to guar gum and cellulose derivatives. Viscous diesel and crude oils were also used. Crude oils and diesel fuel were thickened using fatty acids and caustic; creating a soap like material which adequately carried proppants. There was some use of oil external emulsions but these were limited due to high friction pressures. real variation in the type of fluids related to concentration of viscosifying agents which subsequently controlled proppant transport and viscosity of the fluids in the fracture systems. Some advances were made in degrading agents; i.e., internal breakers during these periods. But basically the fluids used up until that time were simply thickened fluids used to pump proppants back into the fracture systems which were controllably degraded and released. Some of the more obvious disadvantages of these fracturing fluids were:

- (1) High friction pressure required to pump these fluids
- (2) Low temperature stability
- (3) Vunerability to shear
- (4) Downhole viscosity dependent upon surface viscosity

If high viscosity was required downhole at elevated temperatures, an extremely viscous fluid was needed on the surface. This could cause serious problems in regards to hydraulic horsepower requirements and pressure limitations on the surface.

There were significant improvements during these years on the types and quality of thickeners, friction reducers, etc. However, basically nothing new in the art; i.e.breakthroughs yielding more temperature stability downhole or more efficient use of hydraulic horsepower were present.

# Development of New Generation Fluids

In the late 60's several significant breakthroughs were observed concerning fracturing fluids. The most significant development

during that time was the use of a Water Ring technique surrounding emulsified crudes developed by Exxon. This technique allowed the placement of large proppants at low friction pressures. However this process suffered complex problems due to the handling of viscous crudes, and a general non-acceptance in the field by both the personnel and it's problems relating to application in low pressure oil or gas reservoirs.

Perhaps of even more significance was the development of shear thinning crosslinked fracturing fluids. With this type of fluid, the ultimate dream of perfect proppant suspension in the fracture could indeed be achieved with some limitations based on temperature stability of the fluid itself $^2$ . Another development of equal importance was the use of secondary gelling agents which could be added to enhance the viscosity downhole. 3 This of course allowed stimulation of high temperature deep reservoirs by having independent surface and downhole viscosities. During this same period, significant improvements in the area of temperature stabilizing agents which further enhanced the quality of the fracturing fluids were achieved. Additionally achieved during this time, a step forward occurred in oil base fracturing fluids relating to aluminum phosphate esters. These fluids yielded high viscosity oil base fluids with excellent pumping characteristics, while at the same time having moderate to good proppant transport and suspension properties. We will attempt to discuss crosslinked water base fluids, viscous oil base fluids, and fluids containing secondary gelling agents under separate categories.

## Crosslinked Fluids

Our first area of discussion will be crosslinked water base fracturing fluids. The first and most widely used crosslinked fluids available to the industry were those which utilized a guar gum crosslinked with antimony and/or borate systems. These two crosslinked fluids had grossly different characteristics in relation to pH and temperature stability. The antimony complex created an extremely viscous fracturing fluid which generally operates in the pH range of 3 to 5. The borate crosslinked gel system operates in a pH range of 9 to 12. Both systems have inherent advantages and disadvantages. The low pH of the antimony crosslinked gel system allows for enhanced clay control in formations which have water swellable clays and also the advantage of giving relatively controlled complex times. However, it's major advantage is it's ability to be easily degraded at low temperature conditions utilizing enzymes. The high pH borate gel systems require complicated systems to degrade at low temperatures. The enzyme degrading systems presently used within the industry simply do not function at a pH in the range of the borate complexes. Techniques have been developed over the years using slow release acids and catalyzed oxidation systems thereby allowing successful use in low temperature formations. New crosslinked fluids using various new crosslinkers which consist of various metal and organic complexing agents have been introduced since the late 60's. Crosslinked fluids now being used generally consist of improved borate gels, various titaninum metal chelating

systems, and some gels utilizing chromium, zirconium, and other metals.

The first substantial use of titanium crosslinkers in fracturing fluid systems was in 1973. The systems were introduced in the field primarily because of improved rheological properties and enhanced temperature stability of the titanium complex compared to previous systems. Many improvements and developments concerning borate gel systems were also forthcoming during this period. One included the development of a single bag continuous mix system whereby very large treatments be conducted in a controlled manner using the borate system? As mentioned earlier, there were significant developments in the 70's relating to breaker systems for controlled degradation in the borate complexes at low temperatures. Major advantages of the borate system were those involving pumpability and, of course, its relatively inexpensive nature as compared to some of the metallic compounds. Titanium complexes consist of a titanium metal and various organic chelates which are specific for varying pH ranges. Those most commonly used can function in a pH range from approximately 5 up to fairly high pH levels. Stability of the complex and rheology of the fluid are a function of the pH at which the complex is formed. From 1968 through the middle 1970's, many assorted systems were used in complex guar gum gels. These included the use of chromium metals and reducing agents whereby the complex was formed in an intermediate state. There was some field evaluation of the xanthate gum crosslinked with chrome alum. fracturing fluids have been used fairly extensively in Canada, but have not been accepted domestically due to high cost. major advantage is excellent proppant suspension at low shear rates. As mentioned earlier, there are several titanium organic Another system presently used is a complexed fluid using another titanium complex which works at a lower pH range. This system is widely used in crosslinking of carboxymethylcellulose or carboxymethylhydroxyethylcellulose. Still another system used extensively in the industry involves a zirconium compound. This system works at a fairly low pH range and is applicable both for guar gum and cellulose derivatives. Almost any metallic material available can be made to function as a crosslinking agent either through the use of an organic chelate type reaction or an oxidation reduction reaction. To select the product to be used, consider the rheological properties of the final crosslinked fluid as well as the temperature stability if planning to use these at high temperatures. There are many patents relating to these fluids and a great deal of work has been done both by the service companies as well as the suppliers of various viscosifiers and crosslinkers.

## Clean Fracturing Fluids

Almost simultaneously to the development of titanium chelate systems, there was a push toward extremely clean fluids within the industry. For several years, there was basically only two choices of water base fluids. One being the available guar gums which yielded approximately 13% insoluble residue upon degradation or utilizing a cellulose derivative such as hydroxyethylcellulose or carboxymethylcellulose which essentially gave no residue upon

degradation by enzymes, oxidizing agents, or acids. The cost of the products was the major difference involved. The cellulose derivatives were almost twice as expensive as the guar. was some usage within the industry for the cellulose products in tighter and deeper reservoirs because of their enhanced temperature stability; however, there did seem to be a driving force toward cleaner fluids. In early 1970, the two major suppliers of guar gum in the United States developed (almost simultaneously) a derivatized guar gum, hydroxypropylguar. hydroxypropylguar gum upon complete degradation, exhibits residue values which have been reported from 4% down to 1%. Generally these values depend upon the method of quantitative determination. This product does exhibit somewhat enhanced viscosity and temperature stability over conventional guars and of course reduces the problem relating to fracture and formation damage which is created by higher residue fracturing fluids. 7,8 In fact, the product is intermediate in cost compared to that of guar gum and cellulose products exhibiting a cost essentially 25% higher than that of regular guar gum. Today, some 85% of the fracturing fluids used in industry are in fact hydroxypropylguar material. hydroxypropylguar products do constitute the vast majority of the fluids being used in the industry. There are some variations with some companies using a small amount of double derivatized guar such as carboxymethylhydroxypropylguar but these account for a very small percentage of the actual work being done in the field. There are variations upon the degree of substitution of the hydroxypropyl group for applications where high concentrations of alcohol are used but the primary system used is shown in Fig. 1. Figure 1 quickly illustrates the difference between guar, hydroxypropylguar, hydroxyethylcellulose, carboxymethylcellulose and carboxymethylhydroxyethylcellulose. These products constitute the vast majority of fracturing gelling agents being used in the field today.

A product not mentioned earlier, polyacrylamide or co-polymers of polyacrylamide, has been used for quite some time as a friction reducer and on occasion as a thickening agent for fracturing fluids. There have actually been attempts made to use these for high temperature fracturing fluids and from time to time, service companies do use them for crosslinked fracturing fluids. Basically, these fluids suffer from the fact that they are almost impossible to controllably degrade at low temperatures, and are the most expensive of all the readily available fracturing fluids; i.e., guar, hydroxyethylcellulose, or hydroxypropylguar. Polyacrylamides also suffer from another phenomenon which has led to their downfall in the field. They are extremely hard to mix without creating lumps or gel balls in the fluid itself. They are very hydrophillic by their very nature. They take on water, and tend to lump unless they are adequately dispersed. They do cause serious problems in field mixing when used at high concentrations. With the use of moderate to high concentrations of batch mix and continuous mix gels, a great deal of pressure was placed on the service companies to develop dispersible gelling agents and lump-free gel systems. Hydroxypropylguar, regular guar systems, and the hydroxyethylcellulose products lend themselves to the creation of dispersible systems. Guar and hydroxypropylguar can be chemically treated with caustic and also with a small amount of borate. This placed upon the

product will render the gum totally dispersible; i.e. insoluble in water until such time that the pH is lowered allowing hydration. Most of the batch mix guar and hydroxypropylguar systems in the field do use such a system. A continuous mix system does utilize a similar system with relatively moderate concentrations of organic acids in the bag itself. This causes the gelling agent to quickly viscosify after a short dispersion period. The polyacrylamides, carboxymethylcellulose, and carboxymethylhydroxyethylcellulose do not lend themselves well to dispersion and require complex mixing apparatus to create lump free gel in the field. Techniques such as using an empty tank on location to mix from a full tank through a properly maintained blender system into an empty tank does facilitate mixing of these gel fluids. Hydroxyethylcellulose systems through glyoxalation are easily treated and give controllable increase in the viscosity; i.e. dispersibility with virtually the same technique to be described under secondary gelling agent systems.

# Secondary Gelling Agents

Another step forward in fracturing fluid technology was the development of secondary gelling agents. These were introduced initially in the late 1960"s and early 1970's for the fracturing of high temperature formations. These secondary gelling agents basically allowed a tremendous amount of versatility in base gel; i.e., sand carrying viscosity, and at the same time independent downhole viscosity in the formation. The earlier fracturing treatments used a hydroxyethylcellulose base gel with a glyoxalated hydroxyethylcellulose secondary gel system. These products were designed such that the secondary gel starts to viscosify after the fluid temperature exceeds 140°F. This allowed a fluid to increase in viscosity with elevating temperature instead of the standard decrease in viscosity with temperature and time as seen with a conventional gel fluid. About the same time that these fluids were developed, some small developments to further enhance temperature stability of the cellulose derivatives as well as stabilizing agents for these fluids, came to the fore. 9 These techniques are still being used to some extent today combining the temperature stabilizing additives with new generation crosslinked fluids. Some interesting parts of the stabilizing systems relate to the use of methanol or other alcohols which tend to act as reducing agents and effectively change the solvent relationship of the fracturing fluid itself. Other additives used very successfully and in use today, are simple chemical reducing agents which yield enhanced temperature stability by acting as oxygen scavengers thereby reducing oxidative degradation of the polymer. Other stabilizing agents used were encapsulated or slowly hydrolyzing bases which allowed the pumping of glyoxylated hydroxethylcellulose material which requires a pH range from 2 to 6. By adding the encapsulated base, a final pH in the excess of 8 could be reached. This eliminated hydrolitic degradation from hydrogen ion attack at low pH levels. A combination of methanol, an oxygen scavenger plus an elevated pH are the primary mechanisms for stabilizing the polymers used in the oil field today wheter they be crosslinked or uncrosslinked fracturing fluids. Today common treatment of high temperature wells is accomplished using fluids which are already at a pH in excess of 8. Fairly large

treatments can be conducted using new generation crosslinking agents with stabilizers such as methanol and/or oxygen scavengers.

The use of secondary gelling agents has somewhat decreased in the last few years due to the enhanced temperature stability of crosslinked base gel systems at elevated pH ranges. It has been determined that 40 to 60 pounds gels which have been stabilized; i.e. have been protected from hydrolitic and oxidative degradation, can withstand temperatures within and above the 300°F range for long periods of time without benefit of secondary gelling agents. However, a new type of secondary gelling agent is being introduced by some of the service companies. This is a secondary gelling agent which is crosslinked in the dry form, disallowing viscosity increase until elevated temperatues are reached. The mechanism involves using some of the same crosslinking agents mentioned heretofore reacted with the polymers in the dry form. These crosslinking agents tie up the polymer and disallow the uncoiling and subsequent viscosity increase. Various crosslinkers can be increase in used to achieve this mechanism and a more gradual viscosity or at least maintenance of the viscosity downhole can be seen as compared to the viscosity hump seen in glyoxylated fluids. Note figure 2.

There is a great deal of work to be done in the future. There are many synergistic relationships that occur in mixtures of guar gum, cellulose derivatives, and acrylamide. There are many service companies working on either mixtures or chemical combinations of various gelling agents available. Most of these products do suffer from the basic reality that the base chain of either guar, cellulose, or polyacrylamide does fail at temperatures in excess of 350°F. Therefore, irregardless of the stabilizing agents, crosslinker, etc. used, a completely new type of fracturing fluid will have to be developed if we do indeed have the necessity for a temperature stable fluid at temperatures above 400°F. It is certainly recognized by the writer that cool down fluids, etc. can be used in the treatment of high temperature wells; but once one tries to achieve extension of fracture systems at great depths away from the well bore, cool down fluids are essentially not effective.

## Oil Base Gelling Systems

The most common oil base gel fracturing fluid available today is a combination of an aluminum phosphate ester and a base. The reaction of the ester and base creates an association reaction creating a sol which yields viscosity in a diesel or moderate to high gravity crude system. This system has been modified over the years. It's earliest use was in the early 1970's. As mentioned earlier, war surplus Napalm fluids were the very early oil gel systems used. These were followed by the soaps created by mixing fatty acids and caustic. There have been some fish oil fatty acids used in combination with aluminum phosphate esters with some success with low gravity crudes, but a system which has the disadvantage of high friction pressure is basically obtained. Quite frankly none of the fluids exhibit a great deal of enhanced temperature stability, although there has been some improvement

given by the development of a secondary gelling agent which is basically a slow dissolving aluminum phosphate ester. The inherent danger in pumping hydrocarbon fluids, as well as the high cost of diesel, crude oil, and condensates, has greatly decreased the frequency of hydrocarbon based fracturing treatments. Most service companies have had a great deal of success in the use of water external emulsions as fracturing fluids. These fracturing fluids consist of two parts hydrocarbon and one part gelled water. These fluids, due to their relatively low cost; i.e. reducing the concentration and quantity of gelling agent required to yield viscosity, did during the early 70's find a great deal of success in conventional fracture stimulation. With the advent of improved crosslinked gel fluids, as well as the vast increase in cost of hydrocarbons, their frequency of use like typical gelled oil jobs, has decreased somewhat.

These water external emulsions developed by  ${\sf Exxon}^{11}$ , have improved somewhat over the years. There has been significant developments in the surfactant used to create the emulsion. The mechanism of breaking up the water external emulsion was basically adsorption of the surfactant onto the face of the fracture. The early products were prepared using oil wetting surfactants which tend to leave the formation in oil wet state. Some developments have been made using surfactants to prepare the emulsion which do, in fact, leave the formation in a water wet It is quite obvious to those within the industry that the water wet systems are preferable. Field tests have indicated fluids so prepared, do give higher production results. Additionally, some of the service companies have developed internal breakers for the systems which negate the need for absorbtion of the surfactants as an absolute mechanism for degrading the emulsion. On the basis of cost, pumpability, and temperature stability, water external emulsions are excellent fluids to use for moderate to high temperature applications. Incidentally, the temperature stabilizing systems and secondary gel systems mentioned earlier do have application in this system and have been used to some extent in the field.

## Foam Fracturing

Probably the fluid which is gaining widest acceptance, other than crosslinked water based fluids in the industry, is either foamed aqueous fluids or foamed hydrocarbons. One of the greatest desires of most oil company representatives is to pump the least quantity of fluid possible into the formation to negate possible formation damage. The foam fracturing system has the advantage in that the quantity of water to be pumped into a reservoir can be greatly reduced. For the most part, foam fluids have found excellent success in shallow to moderately deep reservoirs and have been found particularly applicable in formations that are water sensitive and at low pressure. Ease in clean-up has proven this fluid to be not only a successful one, but one that can compete economically with conventional or crosslinked fluids. This is mainly due to the presence of very high concentrations of Nitrogen. One fluid very new to the industry, is foamed hydrocarbons which are also finding much success in water sensitive

formations. At the present time, the quality of foams produced with oil suffer somewhat due to the newness of the technology in producing stable hydrocarbon foams. Particularly on early treatments, there were numerous screenouts due to inadequate foam preparation.

Foam also has a distinct advantage in that it is an excellent fluid in relationship to fluid loss control. Treatments have been conducted in relatively deep reservoirs carrying up to a million pounds of sand. Presently the major disadvantage of foamed fractring fluids are the mechanical problems incorporating high concentrations of sand since foam fluids by definition contain anywhere from 55% to 95% nitrogen by volume. All the sand laden fluid must be added into the gelled water at a very high concentration to achieve moderate downhole concentrations. To achieve a downhole concentration of 3 pounds per gallon in a 75 quality foam, approximately 12 pounds per gallon must be added into the blender tub. To achieve a downhole concentration of 4 pounds per gallon, a slurry approaching 16 pounds per gallon must be achieved for a 75 quality foam. Great strides have been made by the service companies in relationship to development of equipment. Devices which have been used are sand intensifers which concentrate the sand in the fluid while running clean fluid back into the blender system. Another technique is the use of special valves in the pumps for handling high sand concentration. Some service companies recirculate the blender tub allowing higher concentrations to be pumped.

Without further significant developments in mechanical technology, it appears that the maximum downhole sand concentration in foamed fracturing fluids will be something slightly in excess of 4 pounds per gallon. At 16 pounds per gallon and higher, the sand becomes virtually dry. This concentration is virtually all that can be mixed either using sand intensifiers or special valving or recirculation. Downstream injection may be the wave of the future if it is felt that higher concentrations other than 4 pounds per gallon are required. It should be noted that with the exception of some areas in West Texas, 4 pounds per gallon downhole concentration is virtually equivalent to any fluid being pumped throughout the United States.

Most of the foamed fracturing fluids used today have been complicated greatly by the addition of viscosifiers, foam stabilizers, fluid loss components, and other additives. These agents do greatly change rheological properties in these fluids and grossly complicate properties of these fluids at bottom hole temperature and fracture shear rates. A great deal of work needs to be done in the area of development of equipment to evaluate what in fact we do have with foamed fracturing fluids. The foamed systems indeed do show a great deal of promise in the future of truly clean fluids which do have inherent enhanced flow back properties.

A great deal of work is presently being conducted in relationship to research and development towards stabilizing foams and understanding the fluid loss and rheological properties of foam per se.

## Surfactants and Clay Stabilizing Agents

Almost no water base or oil base fracturing fluids are pumped without the presence of some form of surfactant. These surfactants are added to reduce surface tension of the fracturing fluids and allow them to produce back. Primarily, they are added such that potential emulsion problems with the hydrocarbons in the formation do not develop . Surfactants typically used over the years have been anionic non-emulsifiers for use in sandstone reservoirs and cationics where the fracturing fluids were used in limestone or dolomite. The charged species were used such that the formation is left in a water wet state. For dry gas reservoirs or formations where emulsion problems did not exist. some form of fluorocarbon surfactants has been used. Fluorocarbon surfactants do typically reduce surface tension drastically as compared to conventional products but have not shown particularly good performance in reducing emulsion problems. The most common surfactants used today are preferably nonionic products. The extensive use of nonionics has come about for basically two reasons. First of all, the nonionics have less of a tendency to adsorb on the face of the fracture; i.e. they can be pumped far back into the fracture system without adsorbing onto the face of the rock. The secondary reason relates to the very common use today of relatively high molecular weight cationic clay stabilizer materials. It is quite obvious that anionic surfactants are not applicable in the presence of these oppositely charged clay stabilizers. There have been some significant breakthroughs in the past year or so in the development of nonionic surfactants. These new generation nonionics have allowed both the use of cationic clay stabilizers and have in fact very economically competed with state of the art commonly used anionic non-emulsifiers. There is a considerable amount of argument within the industry concerning clay stabilizers. Clay stabilizers are basically high molecular weight cationic compounds which do function by tenaciously adsorbing on the face of the clay, thereby tieing the potentially swelling or migrating clays down disallowing their potential damage to the formation. These additives have been tremendously successful and were used in their early stages in non viscous portions of the fracturing treatments, i.e. breakdown fluids. Because of their success, they have been incorporated in viscous portions of the fluid with reports from the field of improved clay stabilization. This particular report is open of course, to some argumentation, with very little the laboratory backing up their advantages in the presence of a viscosifier.

# Breakers or Degrading Agents

One of the most important things to be incorporated in a successful fracturing fluid is a device whereby the viscous fracturing fluid, be it crosslinked or uncrosslinked, water or oil base, can be controllably degraded such that the fluid is produced back out of the fracture and out of the formation pore spaces. In the early days, attempts were made to overflush the fracturing fluid with breaker solution. In most cases these attempts failed as it was very difficult to recontact all the viscous fluid. It was very obvious that an internal breaker systems must be added. The first internal breaker systems used in viscous fluids were

slowly dissolving acids which were incorporated into the Napalm gels. Also used, were slowly dissolving bases, surfactants, or other materials. Most of these breakers suffered from a chemical relationship in that they were on a threshold level; i.e., up to a certain quantity they did not function and above a certain concentration, they degraded the product very rapidly. It was indeed an interesting experience to conduct a fracture treatment trying to get it completed prior to the gel breaking. With the development of guar gum viscosifying agents for water base fluids, it was found that enzyme breakers function very well as long as the gelling agents are buffered within the operating range of the enzymes. Enzyme breakers generally used in bottom hole temperatures approaching 140°F, do function very well in a pH range from approximately  $2\frac{1}{2}$  up to 8, with an optimum range of about 5. Below a pH range of 2, or above a pH range of  $8\frac{1}{2}$ , enzyme breakers do not function at all. This is why the borate or high pH crosslinked gels require special systems other than enzymes. As mentioned earlier, new techniques involving slow release of acid or catalyzed oxidizing agents, have found some success in degrading high pH gells at low temperatures. Above 140°F, enzymes rapidly deactivate and a new breaker mechanism must be utilized. Breakers generally used in the range of 1400 to 2000 are commonly sodium or ammonium persulfate. These oxidizing agents do function very well as breakers. They function adequately at pH ranges of 2½ up to very basic pH's. They do not function whatsoever at low pH's and essentially are deactivated in acid media. There have been a large number of wells which have been temporarily plugged because an acid system was used with the customer or service company counting on the oxidizer breaker to degrade the gel. Above 200°F, two separate mechanisms can be used. Perhaps the most common is the use of weak organic acids. These acids when properly selected, can controllably degrade the crosslinked or uncrosslinked gel reducing it back close to the viscosity of water. Of course, these systems cannot be used in limestone reservoirs or reservoirs with high acid solubility. Acid systems will react with the formation and neutralize themselves instead of degrading the gel systems.

Another alternative to the acid degrading mechanisms at temperatures above 200°F, are some special proprietary oxidizing agents. These are used generally from 180° to 260°-270°. For the hydroxypropylguar gums there is no breaker required above 270°F. Hydroxyethylcellulose or carboxymethylcellulose products do require some breaker up to temperatures of 300°F. It is extremely important for the service company personnel to know the bottom hole temperature and the length of the job to adequately design breaker concentrations. This will allow for the fluid to be designed to last for the period of the job, and at the same time allow controllable degradation, so that the fracturing fluid can be pumped back or produced back after a specified closed-in period. times, many of the problems in the field relating to fracture damage do relate to unbroken fracturing fluids which are left in the fracture matrix plugging the flow capacity of the sand pack in the fracture.

## Fluid Loss Additives

One of the most interesting and perhaps confusing areas relating to hydraulic fracturing concerns fluid loss additives for fracturing fluids. In the early days using oil base fluids, an excellent fluid loss additive was developed which has been sold for many years under the code name "ADOMITE MARK II". ADOMITE MARK II does give excellent fluid loss control when used with soap type fluids or simply oil without viscosifier. be used in Napalm type gells. For these systems common non oil soluble water fluid loss agents are used. One of the water base fluid loss additives used in the field consists of very finely ground silica flour over a wide particle range which tends to plug off the pore spaces of the formation. Another product widely used consists of non swelling clays, silica flour and guar gum. Still another product available on the market today is a mixture of oil soluble resin and a swellable gum. Other products used in the industry consist of mixtures of vegetable compounds, talc, silica flour, and again, more guar gum. Most of the products described involve plugging materials to some degree or another. These products tend to plug off the face of the fracture, hopefully without too much penetration back into the matrix, allowing a much more efficient fracturing fluid. Quite frankly, the fluids which had the best fluid loss control were those early guar gums which had high residual content combined with silica flour. Also used successfully, were combinations of talc and swellable gums with guar. Generally an excellent Cw and spurt loss value almost independent of permeability, could be obtained. Clean fluids, hydroxyethylcellulose products or carboxymethylcellulose products can not be treated adequately to give excellent fluid loss control in high permeability. In fact many formations of moderate permeability would be damaged when trying to treat with clean fluids. To achieve excellent fluid loss control, it is generally agreed across the industry that one must not only have a bridging material, but must have wall building property. Non-residual fracturing fluids do not have a wall building property.

Another new development along these lines has been the addition of either diesel fuel at concentrations up to 5%, or aromatic hydrocarbons using surfactants which yield a micro-emulsion, thereby giving fluid loss control. This technique does appear to give better Cw and spurt loss values for fracturing fluids used in formations with permeability ranges less than 1/10 of a millidarcy. The fluid loss control achieved by micro-emulsion using diesel or aromatic hydrocarbons is not usually efficient at permeabilities exceeding 1 millidarcy.

It is indeed interesting, if not ironic, that many of the oil companies using these very clean fluids; i.e., the hydroxypropyl-guar or cellulose derivatives, are forced to add large concentrations of fluid loss additives to achieve even moderate fluid loss control. It appears to be somewhat self defeating when one has gone to the trouble to reduce the residue in a fracturing fluid to a low degree by paying a higher price for fracturing fluids, and then add high concentrations of solids containing fluid loss additives to the fluid itself to make it applicable in moderate permeability

formations. It becomes apparent that for many applications conventional guar gum systems with inexpensive silica flour fluid loss additives might be the most cost effective method to follow. Most of the crosslinking agents mentioned are applicable with the "dirty fluids" used in the past.

### Conclusion

Perhaps the most difficult thing today to define in our industry is an objective realistic comparison of two competing crosslinked fracturing fluids. One must not only be aware of the type of gelling agent used, but also the type of substitution on the gelling agent itself. One should certainly compare the products at comparable pH level. Comparing an acid base or low pH crosslinked gel system to a high pH gel system for temperature stability is simply not being realistic. Hydrolitic degradation is one of the best means of degradation of products at elevated temperatures. One should ascertain if the two products have comparable stabilizing agents. Vitally important in comparing two fracturing fluids, is to be assured that the viscosity data that you're investigating, does contain the breakers required for complete break-down of the gel system. Quite typically, most of the data printed in the industry is on fracturing fluids without breakers. Some of the most perplexing problems involving service companies today relate to viscosity comparisions relating to shear history. Because of the complex nature of crosslinked fluids, the shear history of the fluid can alter viscosity development drastically. One must typically compare the fracturing fluids as to what type of shear mechanism was used in their development prior to placing on a viscometer.

It becomes readily apparent that an oil company representative involved in designing a critical fracturing treatment, need not only be aware of the chemical nature of the fracturing fluids, but also of how the fluids were prepared. This can be a very long and complicated procedure which quite frankly is not followed on most treatments in the field. It is the opinion of the writer that not enough studies or data is developed in relationship to optimizing both cost and utility of fracturing fluids today.

There have indeed been advances in the state of the art concerning fracturing fluids, particularly in the 70's. Fluids are becoming more and more complex, and do require intensive quality control and design before conducting large long term fracturing treatments. It has always been ironic within the industry, that extensive long term testing is conducted prior to a relatively inexpensive cementing job and then large massive fracturing treatments are conducted with little or no quality control testing of the fluids actually used on the treatment itself. We've come a long ways in the last 10 to 15 years in the industry, but it is imperative that oil companies as well as service companies, work together in developing either laboratory or at least field testing and quality control, to optimize and produce more efficient fracturing fluids for the 80's.

### REFERENCES

- 1. Kiel, Orthar M."A New Hydraulic Fracturing Process", J. Pet. Tech., Jan. 1970, 89-96
- Hopemeyer, M.C. and Githens, C.J. "Field Performance of a New Viscosity Water Base Fracturing Fluid", <u>API Paper 875-24-E</u>, presented at the Spring Meeting of Rocky Mountain District, Division of Production, Denver, Colorado, April 27-29, 1970
- 3. Sidel, W. R. and Stahl, E.J. "Gas Wells Stimulation with a New Viscous Water Base Fracturing Fluid", J.Pet.Tech, August 1973, 959-964
- 5. Kucera, C.H., Smith, C.F. and Brualich, F.H., "New Oil Gelling Systems to Prevent Damage in Water Sensitive Sands", SPE 3503, presented at SPE 46th Annual Meeting, New Orleans, October 3-6, 1971.
- 6. Free, D.L., Frederick, A.F., and Thompson, J.E., "Formation Fracturing with High Viscosity Crosslinked Gel: Continuous Fracturing Technique" J.Pet. Tech., January 1978, 119-122
- 7. White, J.L., and Means, J.O., "Polysaccharide Derivatives Provide High Viscosity and Low Friction at Low Surface Fluid Temperatures", J. Pet. Tech. Sept 1975, 1067-1973
- 8. Cook, C.E., Jr., "Effects of Fracturing Fluids on Fracture Conductivity", J.Pet.Tech., Oct. 1975, 1273-1982
- 9. Ely, J.W. et al, Methods for High Temperture Well Formulations Patent 37685766, October 3, 1973
- 10. Brunham, J.W., Harris, L.E., and McDaniel, B.W. "Developments in Hydrocarbons Fluids for High Temperature Fracturing", J.Pet. Tech. Feb. 1980, 217-220
- 11. Sinclair, R.A., Kiel, O.M., and Terry, W.M. "A Polymer Emulsifing Fluid" J.Pet.Tech., July 1974, 731-738
- 12. Holditch, Stephen A. PhD and Plummer, Ray, "The Design of Stable Foam Fracturing Treatments", Proceedings of the Twenty Third Annual Meeting, Southwestern Petroleum Short Course, Texas Tech Univer., Lubbock, Texas, April 1976.
- 13. King, George. "Factors Affecting Dynamic Fluid Leak-off with Foam Fracturing Fluids", paper SPE 6817presented at SPE 52 Annual Meeting, Denver, Colorado, October 9-12, 1977.

**GUAR** 

HYDROXYPROPYL GUAR

HYDROXYETHYL CELLULOSE

CARBOXYMETHYL CELLULOSE

CARBOXYMETHYLHYDROXYETHYL CELLULOSE

$$\begin{array}{c|cccc} CH_2 & CH & CH_2 & CH_2 & CH_2 \\ \hline & C=0 & C=0 \\ & NH_2 & x & O \\ \hline & NH_2 & x & Na^{+} & y \\ \hline & Hydrolyzed & Polyacry lamide \\ \end{array}$$

Amps Polymer

#### TYPICAL POLYACRYLAMIDE



