THE USE OF A LOW-CONCENTRATION CROSSLINKED HYDROXYALKYL POLYMER SYSTEM AS A HIGHLY EFFICIENT FRACTURING FLUID

DAVID L. HOLCOMB and MIKE O. SMITH
Cardinal Chemical, Inc.

INTRODUCTION

The necessity of developing cleaner fluids for the purpose of well stimulation has been the topic of current discussion among oil company and service company personnel alike.

In fracturing, the incorporation of specific quantities and types of gelling agents and fluid-loss additives has been considered only as means by which to obtain effective viscosities for proppant transport, fracture width development, and efficiency via low leak-off of fluid away from the direction of fracture penetration.

Since it has been established by several investigators[1,2] that fluid-loss additives and natural agent gelling compounds may contribute significantly to formation damage, a need for a clean fluid encompassing the properties of effective viscosity, low fluid-loss, efficiency and comparable economics is evident. This will be shown in tabular and application history forms.

One solution to the problem is to utilize a highly efficient ultra-low residue, chemically substituted, natural polymer at low concentrations, and employ the principle of crosslinking to allow actual link-up of the molecules to provide several folds of viscosity increase over that obtainable by the *low* concentration base gel; and via the process of interlocking or connecting molecules of guar polymer, create an excellent fluid-loss control mechanism such that little or no additional fluid-loss additive is required.[3,4] This system may be batch-mixed into frac tanks unlike the predecessor high concentration crosslinked gels.

The guar used is of a relatively new type, being a highly refined (0.5% residue) chemically substituted hydroxyalkyl-type. This product's molecular structure is compared to the conventionally used guar molecule in Fig. 1.

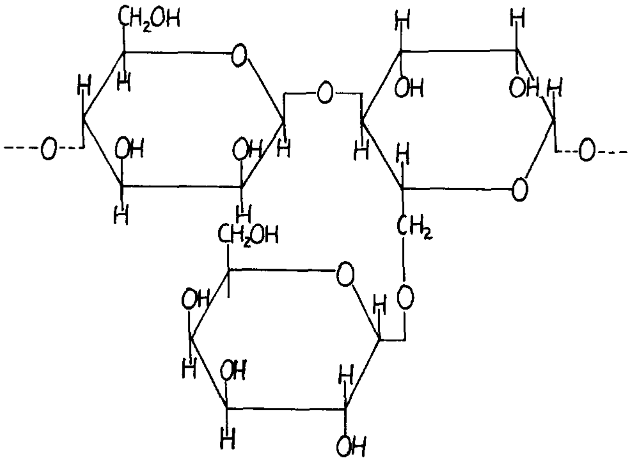

FIG. 1—GUAR MOLECULE

When crosslinked at a concentration of 15 lb/1000 gal. aqueous phased fluid, the individual hydroxyalkyl molecule, as shown in Fig. 2, is crosslinked by bonding, as shown in Fig. 3[3].

It may be stated that the use of the above-mentioned hydroxyalkyl polymer in the crosslinked state at relatively low concentrations compared to conventional oil or water-based fracturing systems is a comparably efficient or more efficient, more effective fracturing system.

The evidence for showing the low-residue hydroxyalkyl crosslinked guar system to be comparable, or better, than conventionally designed gels containing between 20 lb and 60 lb gelling agent in addition to 20-40 lb of fluid-loss control material is borne out by viscosity, fluid loss, friction loss, fluid efficiency, and cost evaluation testing. See Table 1.

DESIGN OF GEL SYSTEM AND FLUID-LOSS CONTROL

The low-concentration, low-residue, crosslinked

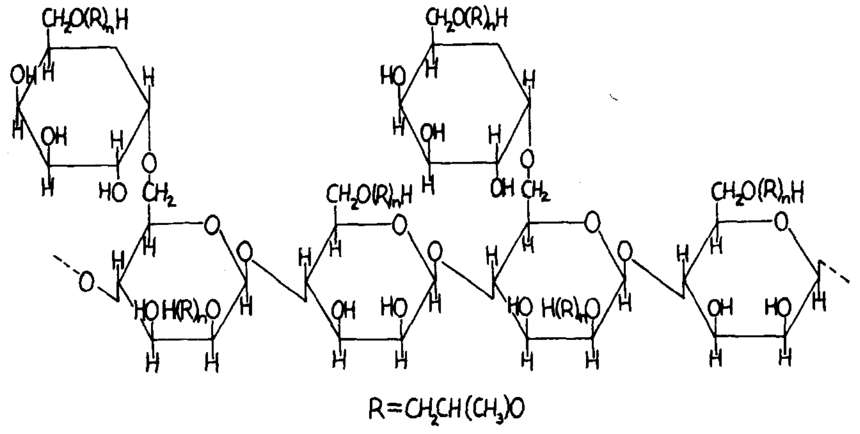

FIG. 2—HYDROXYALKYL MOLECULE OF GUAR

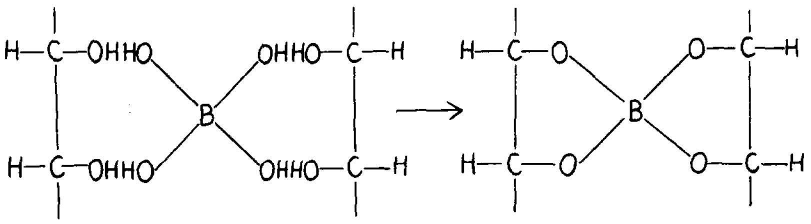

FIG. 3—EXAMPLE OF CROSSLINKING COMPLEX FORMATION

gel system is designed by first creating a base gel strength of 12-20 cp viscosity (Fann @ 300 RPM or 479 sec^{-1} shear rate). This base viscosity is indeed critical to the extent that *effective* crosslinking will not occur unless this base viscosity is achieved uniformly.[3] Water systems to be considered for the crosslinking system should be screened prior to their use either in a lab or in the field prior to gelation. Such elements as excessive water hardness, iron sulfide, pH's greater than 7.0, excessive iron, or excessive brine concentrations can cause problems with gelation if not dealt with prior to gelation. Common methods of hardness and iron chelation as well as pH control may be employed as long as they do not interfere with the process of gelation or, subsequently, crosslinking.

In a job situation where this type of fluid is being considered, it is advisable to not only check the quality of the water or brine supply, but also to check the water storage facility which is to be utilized, as it may contain a bottom sediment consisting of materials which, when circulated into the gel system, could impede gelation or crosslinking. The various means utilized to haul

TABLE 1—COMPARISON OF REGULAR AND HYDROXYALKYL GUAR

Regular Guar	Hydroxyalkyl Guar
a. Price: $1.35/lb.	a. Price: $2.20/lb.
b. Viscosity of 40 lb/1000 gals. gel in water = 36 centipoise.	b. Viscosity of 40 lb/1000 gals. gel in water = 45 centipoise.
c. Will not crosslink effectively @ 15 lb/1000 gals.	c. Crosslinks to 50-70 centipoise @ 15 lb/1000 gals.
d. Totally natural product; non-ionic guar polymer	d. Chemically substituted guar polymer non-ionic; hydroxyalkylated.
e. Fair tolerance for acid or sour water solutions; water must be buffered.	e. Good tolerance in acids. Sour water and brines must be buffered.
f. Will not gel alcohol solutions at over 20% alcohol.	f. Will gel alcohol solutions to 80% alcohol + 20% water.
g. Fluid loss control is fair due to residue control.	g. Fluid loss control is poor due to low residue, but excellent when cross linked.
h. Per cent insoluble residue: 5-12%.	h. Per cent insoluble residue: 0.5 - 2.5%.
i. Molecular weight: 220,000.	i. Molecular weight: 330,000.

water to the location, and mix the gel on location should be checked for cleanliness, particularly gel-blending units which might have some acid material trapped in the manifolds, etc. Flushing with water prior to jobs utilizing the batch-mixed crosslinking procedure should be routine for transports and blending units.

Usually, to prepare a batch-mixed or downstream crosslinked system on location requires that only 95% of the total water volume be supplied on location. This portion of the system is for the preparation of the base gel. The remaining 5% is either supplied separately, or brought to location as an already-prepared crosslinking solution consisting of a quantity of crosslinking agent (usually a boron compound and an alkaline substance for pH control).[3] The boron compound is required at a specific strength for crosslinking, and must be of an alkaline or basic pH (i.e., 8.0 or greater).

The procedure for crosslinking is to introduce the crosslinking solution to the circulating gel proportionately with the total volume circulated so that the crosslinker is distributed uniformly throughout the system. The result should be a four or five-fold viscosity increase as seen on the Fann V.G. meter at 300 RPM over the base gel viscosity.

The crosslinking effect does not allow an absolute viscosity determination, which is actually much higher than the Fann reading, but does allow a relative effective viscosity determination so as to predict fracture width, sand-carrying ability, and friction properties. The addition of 10 lb fluid-loss additive (Adomite Aqua) per 1000 gal. fluid prior to crosslinking, allows the system to approach much lower spurt loss volumes (i.e., O), and must better Cw or efficiency values. With additional amounts of fluid-loss additive, a slight viscosity increase may be noted after crosslinking, due to the presence of a percentage of organic material subject to crosslinking in the fluid-loss material. With the spurt loss approaching zero and no more significant efficiency gained, it is recommended that 5-10 lb Adomite Aqua® per 1000 gal. be the maximum amount of fluid-loss material utilized. (See Table 2 for rheological data.)

TABLE 2—RHEOLOGICAL DATA - LOW-CONCENTRATION, LOW-RESIDUE, CROSS-LINKED HYDROXYALKYL POLYMER SYSTEMS

(Temp. 85-100°F. - Fluid Loss with 2 papers @ 1000 psi)

Fann Viscosity @ 300 RPM	lbs gel/ 1000 gals.	lbs fluid loss/1000	Spurt Loss	Cw Value 10^{-3}
50	15	0	1.6	2.25
55	15	5	0.5	1.94
60	15	10	0.1	1.612
65	15	15	0.0	1.508
70	15	25	0.0	1.279
90	20	0	0.9	2.08
120	25	0	0.5	1.37
		Refined Oil		
150	0	25	2.5	0.62
150	0	0	8.0	0.78
		Non Crosslinked Gel Systems		
13	15	0	16.75	2.30
17	15	25	3.0	2.21
33	40	25	1.8	1.49

PROPPANT TRANSPORT ABILITY

Low-residue, low-concentration crosslinked gel systems allow for effective proppant transport via their superior holding power due to the physically and chemically linked polymer chains. The crosslinked effect appears to slow particle fall rates between 10% and 15% of their fall rates in conventional straight gels of equivalent viscosity.

SHEAR AND TEMPERATURE STABILITY

The hydroxyalkyl guar has the additional attribute of good viscosity stability over a wide range of shear and temperature conditions. The chemical substitution and the added crosslinking borate ions are responsible for this increased stability over conventional water gel systems. The effect is an increase in tenacity of the molecule to maintain its gel equilibrium to the extent of losing a very small percentage of that effect when confronted by shearing mechanisms and/or temperature.

FRICTION FLOW CHARACTERISTICS

Figure 4 illustrates comparative friction flow of the low-concentration crosslinked hydroxyalkyl gel system versus various other aqueous and hydrocarbon-based systems.

It can be seen that although comparable viscosities are achieved, there is a slight improvement over conventional straight guar gels of a comparable viscosity.

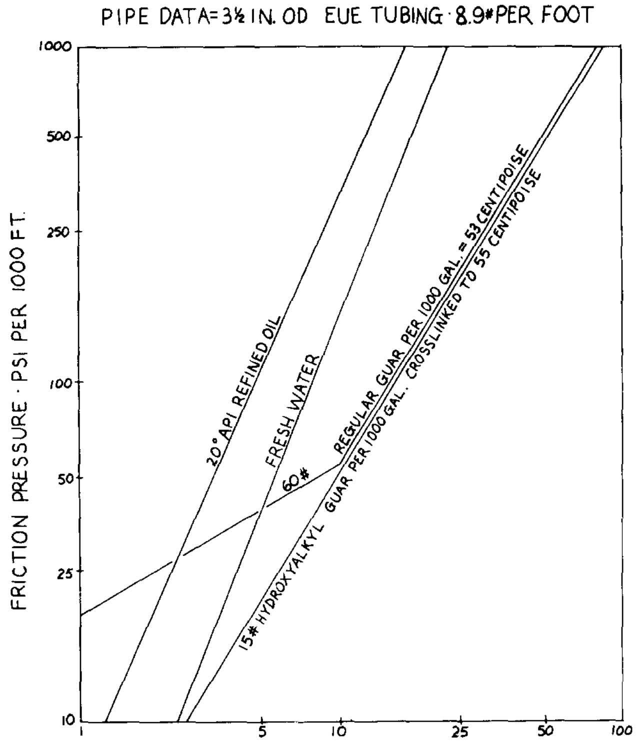

FIG. 4

BREAKER MECHANISM

The 15-lb crosslinked hydroxyalkyl system employs the use of an externally added breaker system of either an organic enzyme or inorganic chemical system. The governing factor is temperature wherein the enzyme system functions best at estimated bottomhole temperatures of 70°F to 130°F, and an inorganic chemical breaker is utilized at temperatures exceeding 130°F due to the ineffectiveness of most enzyme systems at elevated temperatures.[5] Table 3 illustrates expected break times at various temperatures and breaker concentrations for both the enzyme and chemical methods. The effectiveness of breakers is more easily realized in the low-concentration hydroxyalkyl crosslinked gels due to the small base gel concentration (15 lb per 1000 gal).

TABLE 3—GEL BREAK TIMES FOR 15 LB/1000 GAL. CROSSLINKED HYDROXYALKYL GUAR SYSTEM

A. Enzyme Breaker System

Temp. °F	lbs Breaker/1000 gal	Gel Break Time
70 -90	2.0	12-15 hrs.
90 -120	1.5	12-15 hrs.
120 -130	1.0	12-15 hrs.
70 -90	3.0	10 hrs.
90 -120	2.0	10 hrs.
120 -130	1.0	10 hrs.
70 -90	4.0	8 hrs.
90 -120	3.0	8 hrs.
120 -130	2.0	8 hrs.

B. Chemical Breaker System

Temp. °F	lbs Breaker/1000 gal	Gel Break Time
120 -150	5.0	24 hrs.
150 -180	5.0	20 hrs.
180 -210	5.0	18 hrs.
210 -250	5.0	16 hrs.
120 -150	10.0	18 hrs.
150 -180	10.0	15 hrs.
180 -210	10.0	10 hrs.
210 -250	10.0	8 hrs.
120 -150	15.0	[illegible] hrs.
150 -180	15.0	12 hrs.
180 -210	15.0	8 hrs.
210 -250	15.0	6 hrs.

Should any breaking problem be encountered upon load recovery, which has been rare with this system, the simple addition of a small acid clean-up treatment (3-5% HCl) will alter the pH-controlled crosslinking effect, and return the gel at a viscosity less than 5 cp. This has only been necessary on less than one percent of the jobs performed. Thus, the breaker mechanism is much improved over the older type high-concentration, often high-residue type crosslinked systems where breaker systems were often very inefficient, to the extent that recovery operations were often hampered.

Tuttle and Barkman[1] have established that conventional guar gum solution viscosity is based on the large size of the concentrated (>30 lb/1000 gal.) and collected molecules; and although the techniques of enzyme and chemical breakers reduce the sizes of these molecules by the process of hydrolysis, the broken solutions still caused an irreversible 52% permeability reduction when injected into cores with permeabilities as high as 450 md.[1] Pye and Smith have conducted similar investigations to establish that fluid-loss additives seriously reduce fracture proppant conductivity and formation permeability.[2]

The low-residue, low-concentration,

hydroxyalkyl crosslinked systems do not lend either particulate fluid-loss material to any great degree, or excessive residue content such that the conditions described by the above-mentioned investigators are realized.

The low-concentration crosslinked hydroxyalkyl systems stay well below the damage parameters existent in conventional guar and fluid-loss combinations.

Comparable gel concentrations and particulate fluid-loss concentrations are seen on Table 2, where crosslinked systems with and without fluid-loss control are compared to the rheological properties of refined oil and non-crosslinked aqueous fluids. Note the necessary quantities of fluid-loss and gelling agent required to match the properties of the 15-lb crosslinked system.

DISCUSSION OF APPLICATIONS AND RESULTS

The low-concentration, crosslinked hydroxyalkyl systems which have been emphasized herein have been applied in more than a dozen counties in the Permian Basin. Table 4 lists several areas and formations where this system has been used with at least comparable or more effective stimulation results than treatments which were in vogue for that area.

To compare results of this system with specific oil-base fluids is difficult because new oil and water will be produced immediately, whereas oil-base loads are distinguishable only by API gravity changes.

It is evident that no noticeable damage has occurred in areas where oil-base fluids are frequently used, such as the Spraberry Trend in the Midland Basin, which has long been a suspected area of high sensitivity to aqueous-base fracturing fluids. Cost and the lack of economical, nondamaging, aqueous-phase treatments have dictated the use of oil-base fluids in many areas. In many of these areas, the low-concentration, low-residue crosslinked hydroxyalkyl gels have remedied this need, and have provided a more efficient, more easily handled, and cleaner stimulation system than either the oil/fluid-loss systems, or the higher concentration aqueous gels and their fluid-loss systems.

TABLE 4—AREAS OF ACTUAL APPLICATION OF LOW CONCENTRATION CROSSLINKED HYDROXYALKYL SYSTEMS

County	Field	Formation
Crane	Dune	San Andres
Crockett	Noelke	Soma Sand
Ector	Goldsmith	San Andres, 5600 & L. Clearfork
	Notrees TXL	Clearfork
	N. & S. Cowden	San Andres
Edwards	Undesignated	Canyon
Glasscock	Spraberry Trend, N. Calvin and Undesignated	Dean, Upper and Lower Spraberry
Lea	Vacuum, Wantz, Eunice Area	San Andres, Abo, Drinkard, Blinebry, Tubb, Granite Wash &
	Monument Area	Eumont Gas
Martin	Flower Grove, Hill Ranch, Ackerly, Lenorah Area, N. & S. Stanton Area and Undesignated	Dean and Spraberry
Midland	S. Stanton & Spraberry Trend	Dean, Upper and Lower Spraberry
Nolan	Lake Trammell	Canyon
Reagan	Calvin & Undesignated	Dean, Upper and Lower Spraberry
Upton	Spraberry Trend	Dean, Upper and Lower Spraberry
	Spraberry Trend	Re-frac in Spraberry
Yoakum	Wasson	San Andres & Clearfork

Table 5 provides an indicative cost comparison

TABLE 5—COST COMPARISON

Products/Services	Refined Oil	Emulsion Frac	Crosslinked Gel
80,000 gal.	$ 24,000.00	$ 4,800.00	$ 5,600.00
109,500 lb. sand	3,098.85	3,098.85	3,098.85
HHP (25 BPM - 4-1/2″ csg. to 8500′)	5,390.40	3,675.00	2,296.50
Blender for 25 BPM	375.00	375.00	375.00
Fluid-loss additive	1,700.00	408.00	0
KCl - 1% to fresh water	0	249.60	832.00
Breaker	0	0	336.00
2,500 gal. 15% HCl	926.00	926.00	926.00
80 gal. emulsion control	880.00	0	760.00
56,000 gal. crude oil	0	16,800	0
Totals	$ 36,370.25	$ 30,332.45	$ 14,224.35

of comparable systems together with a partial payback analysis.

CONCLUSIONS

The utilization of low-concentration. low-residue, crosslinked, hydroxyalkyl guar gelling systems for fracturing and gel-pad acidizing systems is a successfully applied approach to providing cleaner and more efficient fracturing fluid systems to the oil and gas industry.

The increase in efficiency, stability, and tenacity of the chemically substituted guars is truly an improvement in natural polymer gel technology, and is already being utilized extensively as an approach to designing stimulation fluids with less material required for obtaining the desired viscosity and fluid-loss properties.

If a fluid-loss control mechanism is required for the crosslinked system, it is shown that a minimum quantity of the least damaging variety, Adomite Aqua ®, is required, at only 5-10 lb/1000 gal.

The theory behind the use of 15 lb of the hydroxyalkyl guar per 1000 gal. water in a crosslinked state provides an optimum method for obtaining comparable rheological properties to systems containing considerably higher gelling agent and fluid-loss concentrations.

The advantages lie in the ultra-low residue content ($<0.5\%$) for more easily broken gels with less damaging effects, as well as easier mixing under field conditions, owing to the small amount of actual material required to be added in the performance of the job as compared to the problems involved in the uniform mixing of high concentrations of gel and fluid-loss material. High concentrations are defined as any amount over 15 lb of either gel and/or fluid-loss additive per 1000 gal.

The emphasis on the cleanliness of the system can not be overstated. This system can only be as effective as the preparation undertaken for its use, that is, such requirements as clean frac tanks, clean blenders, and clean water or brine, with adequate hardness and pH control.

With this consideration, the hydroxyalkyl crosslinked gel systems provide a practical and economic approach to efficient and clean fracturing fluid development, and successful application.

REFERENCES

1. Tuttle, R.N., and Barkman, J.H.: New Non-damaging and Acid-Degradable Drilling and Completion Fluids, *Jour. Petr. Tech.*, Nov. 1974, SPE of AIME, pp. 1221-1226.
2. Pye, D.S., and Smith, W.A.: Fluid Loss Additive Seriously Reduces Fracture Proppant Conductivity and Formation Permeability, SPE 4680, presented at the 48th Ann. Fall Mtg., SPE of AIME, Las Vegas, Nev., Sept. 30-Oct. 3, 1973.
3. Kern, Loyd R.: Method and Composition for Formation Fracturing, U.S. Patent 3,058,909, Oct. 16, 1962.
4. Wyant, R.E.: Method and Composition for Reducing Fluid Loss, U.S. Patent 3,079,332, Jul. 23, 1957.
5. Wyant, R.E., Perkins, T.K., and Moore, T.F.: Borate-Gum Gel Breakers, U.S. Patent 3,163,219, Dec. 29, 1964.

ACKNOWLEDGMENTS

Laboratory rheological data reported in this paper was obtained from the fracturing section of the Cardinal Chemical, Inc. Analytical Service Laboratory. The drafting for the figures was done by Steve Wilson of Cardinal Chemical's Analytical Service Laboratory.