HIGH EFFICIENCY FRACTURING FLUIDS FOR LOW TEMPERATURE RESERVOIRS

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ABSTRACT

The use of various metal salts and metal chelates as crosslinking materials for guar gum and guar gum derivatives has been investigated under low temperature conditions (≤200°F). To determine the crosslinkers of highest efficiency, these crosslinkers were evaluated using the criteria of maximum crosslinked viscosity yield per pound of polymer employed, relative shear sensitivity of each crosslinker and projected ease of application for each crosslinked fluid system in the field. Through optimization of crosslinker-polymer interaction involving development of a delayed crosslinker for low temperature conditions, improved fracturing fluids have been developed. The polymer loadings in these systems can be dropped up to 50% without losing fluid efficiency. The performance of the crosslinked fluid system which showed the highest efficiency was taken to the field and its performance evaluated on a number of wells and compared to other conventional systems.

INTRODUCTION

In the last few years, a number of papers have been presented on the development of crosslinked fracturing fluid systems for use in high temperature reservoirs.[1-8] The major emphasis in these papers has been on both the various methods of providing a stable, crosslinked fluid downhole and the rheological characterization of the crosslinked fluids. One important development that has evolved from these studies is the use of delayed crosslinkers to achieve higher fluid viscosities in the fracture.[1]

The percent of new wells with bottom hole temperatures greater than 200°F has declined to less than 25% over the last 1 1/2 years. Currently, over 75% of the wells drilled have a bottom hole temperature less than 200°F. Although the technology and field requirements involved in a successful fracturing treatment of a low temperature formation (<200°F) are not as critical as those for a deep, hot well, there is still a need to improve efficiency in fracturing fluids for use in these low temperature reservoirs.

There are several criteria which are important in the development of a new crosslinked fracturing fluid for use in low temperature reservoirs. The success with which a new fluid meets these criteria can determine whether the fluid will gain widespread use in the field or simply become another obsolete fluid system. A few of the criteria which are important in new fluid development from an application standpoint are: (1) ease in mixing of the base gel, (2) use of a buffer system which reproducibly obtains a specific fluid pH, (3) use of a crosslinker which can be metered easily and produces consistent crosslink times in a variety of waters, (4) a system which is easy to break and gives consistent break times, and (5) a fluid which is compatible with a wide range of chemicals including CO_2.

One of the criteria which has surfaced in a large number of areas as the single most important criterion and will probably remain so for at least the foreseeable future is the actual cost of the crosslinked fluid. This criterion is especially valid for the treatment of low temperature reservoirs since fewer requirements are placed on the actual fluid when compared to a fracturing treatment for a high temperature reservoir. For this reason, it is essential that any new fluid for low temperature applications must have a very high efficiency or high sand carrying capacity per dollar.

EXPERIMENTAL

Fluid Preparation

Add buffers and primary gelling agent to 750 ml of base fluid in the blender container (Waring Blendor Model 7011 with standard one quart container). Mix for 45 minutes at a speed that minimizes air entrainment in the gel but maximizes the mixing of the gel. Uncrosslinked fluids are placed onto the Model 50 Fann Viscometer without rotary vane pump shearing. For crosslinked fluids, start mixing the base gel on the rotary vane pump (Jabsco - Model 4730-0001) at its maximum rpm (1740 rpm). The fluid is circulated from the blender jar with approximately 2 feet of 3/4 inch Tygon tubing inlet and outlet hoses. The fluid volume is circulated about 60 times a minute. At the 30 second mark of the mixing time, the crosslinker is added through the intake hose over a 5 second interval. Total mixing time on the pump was 4 minutes. A sample of the crosslinked gel is placed on the Model 50 Fann Viscometer within 30 seconds after removal from the pump system.

VISCOSITY MEASUREMENT PROCEDURE

Uncrosslinked Fluids

The uncrosslinked fluid is placed on a Fann Model 35 at a shear rate of 511 sec^{-1} (300 rpm using a standard bob and sleeve) for the entire test period. An IMCO heating cup was used to heat the fluid. A viscosity reading was taken after the fluid had been allowed to equilibrate for 10 minutes at temperature.

Crosslinked Fluids

The crosslinked gel placed on the Fann Model 50 is immediately subjected to a shear rate of approximately 170 sec^{-1} (300 rpm using a modified bob with R_s/R_b = 1.4826) that is maintained throughout the test. Nitrogen (300 psi) is used to pressurize the sample cup. The fluid is raised to the test temperature at approximately 12°F per minute. Shear stress-shear rate sweeps are made when the test temperature is achieved and at predetermined times thereafter by rapidly raising the shear rate to 450 rpm and then recording the shear stress at 450 rpm, 400 rpm, 350 rpm, 325 rpm, 300 rpm, 250 rpm, 200 rpm, 150 rpm and 100 rpm shear rates. Apparent viscosities are calculated from the Power Law model:

$$T = K'(\gamma)^{n'} \qquad (1)$$

Although the use of the Power Law model for crosslinked fluids has been questioned by various investigators, the model does appear to hold for the shear rates used in this study (approximately 60-255 sec^{-1}).

RESULTS AND DISCUSSION

Laboratory Development

There is a wide variety of water soluble polymers available to the oil field from a number of suppliers. The two major types of polymers used are derivatized cellulose and guar gum or guar gum derivatives. Historically, however, the largest number of fracturing treatments in which crosslinked fluids were used have been run with guar gum or guar gum derivatives.[9] There are three factors which are believed to be responsible for the use of guar gum or guar gum derivatives. These factors are: (1) the ease of mixing of the guar materials as compared to cellulose derivatives, (2) the guar materials are easier to crosslink and crosslink with a wider variety of metals than cellulose derivatives[10,11], and (3) the guar materials have an economic advantage over the cellulose derivatives. For these factors and others, a variety of guar gum and guar gum derivatives were evaluated for use in a new high efficiency fluid.

The guar materials which were evaluated during this study are shown in Table I. There are two nonionic materials (Polymers A and B) and two anionic materials (Polymers C and D) in this series of polymers. The major differences between Polymers A and B are their relative residue content and the number of crosslinking sites available. Gelling agent residue has been shown by several researchers to cause flow impairment in both the fracture and the formation[12-18] and for years, guar gum has not been selected over derivatized guar gum in a number of applications for this reason. However, recent findings have suggested that although the relative residue content of guar gum is greater than derivatized guar when compared on a weight/weight basis, the residue volume and resultant flow impairment for the two polymers is the same.[19]

The number of crosslinking sites on guar gum and derivatized guar gum plays an important role in determining how much crosslinker will be required to achieve optimum fluid efficiency. Conway and coworkers[10] have shown that as the number of hydroxypropyl groups increases on guar gum, the amount of crosslinker required for optimum fluid efficiency also increases. A lower crosslinker concentration could be used with guar gum than with derivatized guar gum for an additional savings.

The major difference between the anionic polymers (C and D) was the actual substitution level of the anionic derivatization group. Since the crosslink will occur through the anionic group in polymers C and D, the difference in crosslinked fluid viscosities can be dramatic. This difference will be emphasized in a later section on crosslinked fluid rheology.

A temperature thinning test was run on all four polymers (Figure 1) from 60° - 200°F to determine any major differences in their thinning profiles. The crosslinked fluid viscosity has been shown to be dependent on the actual base gel viscosity at temperature[1] so any polymer with an abnormally high temperature thinning profile would be expected to produce a lower viscosity crosslinked fluid using the same crosslinker under similar conditions. Over the temperature range evaluated, the viscosities for all four polymers showed no abnormal thinning characteristics and were within a 5 cp range of each other at any given temperature.

A crosslinked fluid of high efficiency should contain the lowest base polymer loading required to maintain a high fluid viscosity. There is a minimum polymer loading for any polymer below which it is almost impossible to form a stable crosslinked fluid. Below this minimum loading, the crosslinked fluid will separate into regions of crosslinked fluid and regions of free water. A polymer loading of approximately 15 lb/Mgal was determined to be the minimum polymer concentration for Polymer C by using a series of crosslink tests. It is believed that in this concentration region, the gel is going from a dilute solution to a semi-dilute solution. A solution can be called dilute if the polymer molecules are on the average, so far apart that they have a negligible influence on each other or no polymer/polymer interaction[20]. A semi-dilute solution can be defined as a solution where the polymer molecules are, on the average, close enough to show an influence on each other. Figure 2 illustrates the crossover between a dilute solution and a semi-dilute solution. This crossover point can and has been measured using a Rheometric's pressure rheometer. A plot of the low shear viscosity versus concentration has shown that the crossover point for a hydroxypropyl guar (HPG) material having an MS = 0.5 was somewhere between 15 lb/Mgal and 20 lb/Mgal[21]. It appears now that the crosslinking reaction or chemical bonding pulls the individual polymer molecules together or into an interacting state in the dilute solution to produce the observed region of crosslinked fluid and free water.

The second part to a successful high efficiency fracturing fluid is the crosslinker. A wide variety of metals can be used to crosslink the guar materials[22-30] but the oil industry has narrowed its use to metal salts and chelates of titanium, zirconium, boron, aluminum, chromium and antimony. As discussed in a previous paper[10], there is an optimum pH for the crosslinking reaction of each metal with a particular polymer. This optimum pH produces the greatest viscosity increase and the highest quality gel. In the development of a low temperature crosslinked fluid, one of the more important concerns is the requirement of achieving a clean break after the treatment. Enzymes are used by most service companies as breakers in the temperature range of 60-140°F. The enzyme activity or degradation per dollar has been shown to be strongly dependent on the fluid pH[15]. Figure 3 shows that the optimum enzyme activity is achieved at a pH of 3 and the activity decreases dramatically as the fluid pH is increased. For this reason, the fluid pH for a high efficiency fluid should be on the acid side, preferably in the range of 3-5 for optimum low temperature enzyme breaks.

A considerable advancement has been made in the last 3 years with the advent of delayed crosslinkers. A number of papers have appeared recently on delayed crosslinkers and their use in crosslinked fluids for high temperature formations.[1-5] The requirement of high temperature stability has limited the number of crosslinking metals to basically two metals, zirconium and titanium, since most of the other metals do not provide a useful viscosity increase in the higher temperature ranges.[1-3] However, the advantages of using a delayed crosslinker can be easily seen when fluid viscosities are compared with a non-delayed or rapid crosslinking system. Figure 4 shows the dramatic viscosity increase obtained at 200°F using a delayed crosslink system. The actual magnitude of the enhanced viscosity obtained when comparing a delayed crosslinker to a rapid crosslinker is a function of the polymer, crosslinker and temperature.

The delayed crosslinker can produce long crosslink times at low temperatures (40-100°F). As the temperature is increased, the crosslinker is activated and the crosslink time is shortened. In many instances, however, the crosslink time of the delayed crosslinker is too long and a rapid crosslinker is added to adjust the crosslink time. This technique of using a primary crosslinker and a secondary crosslinker has been applied successfully in the field on a number of wells.[2] Figure 5 shows the effect of mixing a delayed and a rapid crosslinker. The initial viscosity of the mixed crosslinkers is higher than that of the delayed crosslinker below 130°F, however, above 130°F the straight delayed crosslinker provides the highest viscosities. In general, the use of a mixture of delayed crosslinker and rapid crosslinker provides lower viscosities at elevated temperatures than the straight delayed crosslinker. This difference can be minimized by altering the actual crosslinker or polymer.

As mentioned earlier, the major difference between polymers C and D was the actual substitution level of the derivative and actual distribution of the anionic groups. The crosslinking interaction of Metal C with polymers C and D has been shown to occur through the anionic group.[25] The optimized crosslinked fluid viscosities of polymers C and D crosslinked with metal C as a function of temperature are shown in Figure 6. Polymers which have the same derivatization groups can have significantly different crosslinked fluid rheology.

A variety of crosslinkers and polymers were evaluated together as crosslinked fluid systems. The results of this study are shown in Figure 7 and indicate that the crosslinked fluid formed with metal F and polymer C produced the fluid with the highest viscosity and efficiency. At a polymer loading of only 25 lb/Mgal, this polymer-crosslinker combination produced viscosities equivalent or superior to all of the other crosslinked fluids which used a 40 lb/Mgal polymer loading and offers the greatest economic incentive. For this reason, the combination of polymer C and metal F were evaluated further.

To achieve consistent performance in the field, a buffer system had to be developed which provided consistent pH control at the optimized crosslinking pH of the polymer C - metal F system. The importance of pH control as opposed to pH adjustment is illustrated in Figure 8. A solution which has a controlled pH (buffered) is resistant to pH change through the addition of a strong acid or a strong base. A fluid which has been adjusted to a certain pH (unbuffered) can be altered dramatically through addition of traces of acid or base. The ideal buffer moves the pH to the desired value with a low concentration, controls the fluid pH when traces of acid and base are introduced and is not subject to over-treatment. Figure 9 shows the effect of adding an ideal buffer to a typical field water and emphasizes the above requirements. This buffer system was used in conjunction with the crosslinked fluid system of polymer C and metal F.

The use of CO_2 in conjunction with various fluid systems has been shown to be an advantage in the treatment of a variety of low temperature/low pressure reservoirs.[31-33] The effect of CO_2 addition (20% v/v) on the viscosity of the crosslinked fluid using polymer C and metal F was determined by placing a mixture of the hydrated polymer and crosslinker into the flow system described by Harris, et al.[34] The fluid pH had been adjusted so that no crosslinking could take place prior to CO_2 addition. An initial rheogram was obtained on the base gel and then liquid CO_2 was pumped into the system until a concentration of 20% CO_2 was achieved. As shown in Figure 10, the addition of CO_2 produced a dramatic viscosity increase and the fluid appeared complexed through the sight glass. Heating the fluid, which was kept in a dynamic mode (500 sec^{-1}), produced a slight temperature thinning but the fluid appeared to remain in a complexed state.

In addition to rheological data at various temperatures, fluid loss data, friction data and break data were also developed for the new system. After this data had been gathered and placed into an organized format, the fluid was used in field operations.

Field Testing

The crosslinked fluid system comprised of polymer C and metal F has been used on over a hundred wells to date in the last sixteen months. Results from a variety of formations in which the fluid has been used as a fracturing fluid with and without the addition of CO_2 are shown in Tables II and III, respectively. The production increase on these example wells was on the average equivalent to those obtained for a conventional fracturing fluid which used a 40-50 lb/Mgal polymer loading. However, for a 100,000 gallon treatment, the average gelling charge for the conventional treatments was $17,800 and $11,100 or a 37% reduction in the gelling cost with the new fluid. The overall results from wells too numerous to list have agreed with the previous findings and indicate that a new fluid which is developed in the lab can be successfully applied to the field.

SUMMARY

(1) The minimum polymer concentration for both the nonionic guar gum derivative and the anionic guar gum derivative required for formation of a stable crosslinked fluid was determined to be between 15 lb/Mgal and 20 lb/Mgal.

(2) Use of a delayed crosslinker can be used in formations with low temperatures if a rapid crosslinker is used in conjunction with the delayed crosslinker.

(3) The use of a mixture of delayed crosslinker and rapid crosslinker reduces the viscosity increase at elevated temperatures obtained with a delayed crosslinker only.

(4) The optimum pH for crosslinked fluids which are to be broken using an enzyme breaker is in the range of 3-5. The enzyme activity falls off drastically at higher pH's.

(5) Optimization of the polymer-crosslinker interaction can reduce the amount of base polymer required to achieve a specific viscosity and has reduced the cost of gelling by up to 37%.

NOMENCLATURE

R_b = radius of bob
R_s = radius of sleeve
n' = flow behavior index
K' = consistency index - lb_f-sec n'/ft^2
HPG = hydroxypropyl guar
T = shear stress
γ = shear rate - sec^{-1}

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Table 1

Polymer	Polymer Type	Charge	Residue Content (% w/w)
A	Guar Gum	nonionic	8-10
B	Derivatized Guar Gum	nonionic	1-3
C	Derivatized Guar Gum	anionic	1-3
D	Derivatized Guar Gum	anionic	1-3

Table 2
Field Results Obtained with Polymer C Crosslinked with Metal F Without CO_2

			Proppant		Production	
Formation	Gel Concentration (lb/Mgal)	Total Treatment Volume (gal)	Type	Total (sks)	Before	After
Cleveland	30	80,000	20/40	1500	New Well	14 bopd
Cleveland	25	80,000	20/40	1425	New Well	14 bopd
Cleveland	25	60,000	20/40	1050	New Well	12 bopd
Cleveland	25	80,000	20/40	1650	New Well	101 mcfd 20 bopd
Cleveland	25	80,000	20/40	1500	New Well	12 bopd 223 mcfd
Granite Wash	30	20,000	20/40	240	New Well	1.5 mmcfd
ABO Sand	20	61,860	20/40 10/20	630 350	70 mcfd	700 mcfd
Upper Spraberry	25	100,000	20/40	2650	3 bopd	25 bopd

Table 3
Field Results Obtained with Polymer C Crosslinked with Metal F With CO_2

				Proppant		Production	
Formation	Gel Concentration (lb/Mgal)	Total Treatment Volume (gal)	CO2 (% v/v)	Type	Total (sks)	Before	After
Atoka	30	20,000	30	20/40	225	200 mcfd	3400 mcfd
Yates	25	40,000	50	20/40	600	1 bopd 1 bwpd 69 mcfd	1 bopd 1 bwpd 600 mcfd
Douglas	30	55,000	30	20/40	1000	New Well	50 bopd 0.5 mmcfd
Strawn Sand	25	37,000	25	20/40	315	New Well	750 mcfd
Penn Wildcat	25	42,000	30	20/40	690	0	70 mcfd

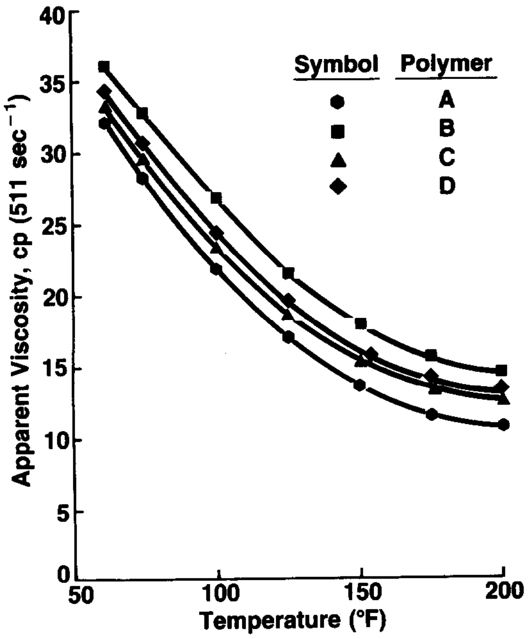

Figure 1 - Base gel viscosity as a function of temperature for 40 lb/mgal polymer loadings

C < C° (a)

C = C° (b)

C > C° (c)

Figure 2- Crossover between dilute and semi-dilute solutions: (a)dilute, (b)onset of overlap, and (c)semi-dilute solution where C⁰ is crossover point.

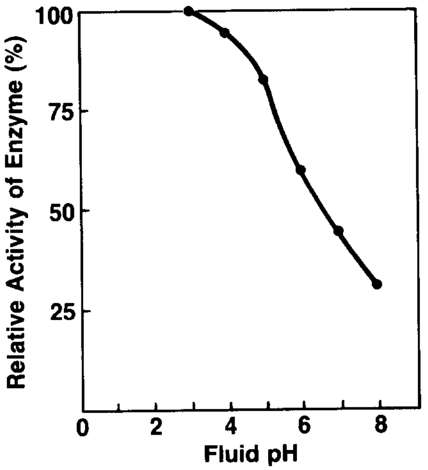

Figure 3 - Effect of pH on enzyme activity

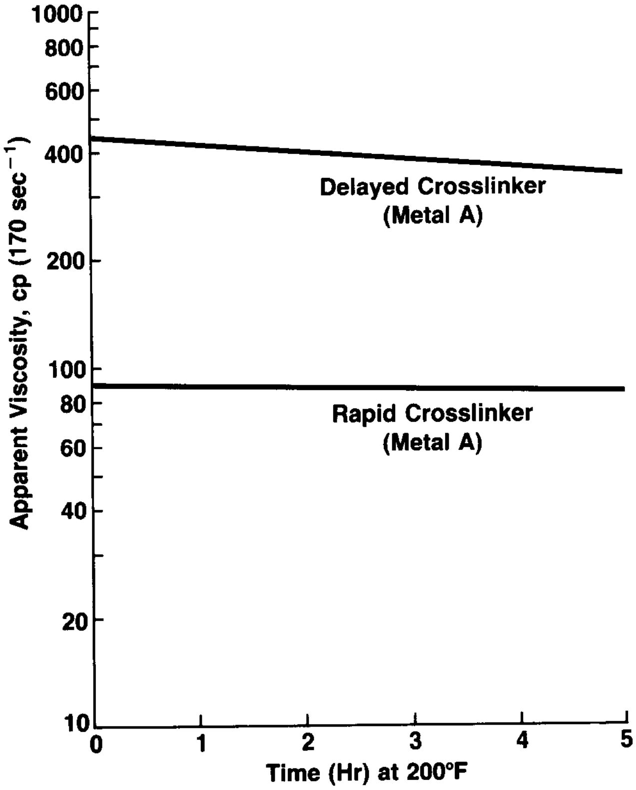

Figure 4 - Apparent viscosity versus time for polymer B (40 lb/mgal) crosslinked with a rapid crosslinker and delayed crosslinker

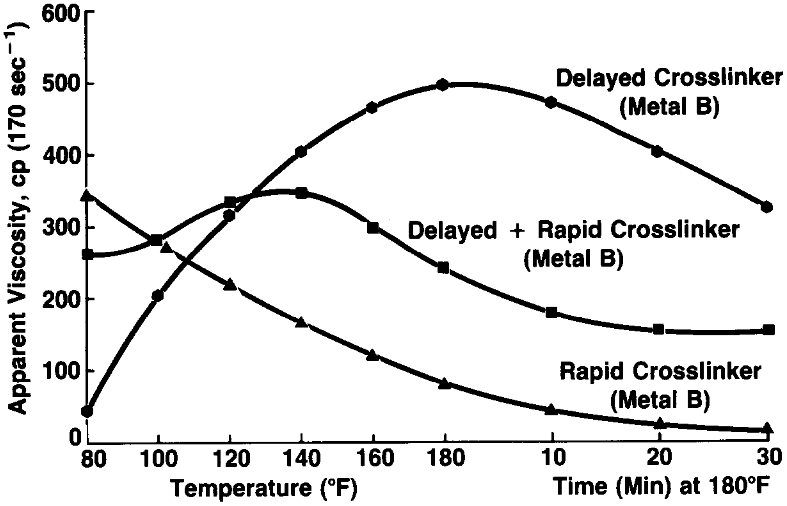

Figure 5 - Apparent viscosity versus temperature and time at temperature for polymer C using crosslinking metal B

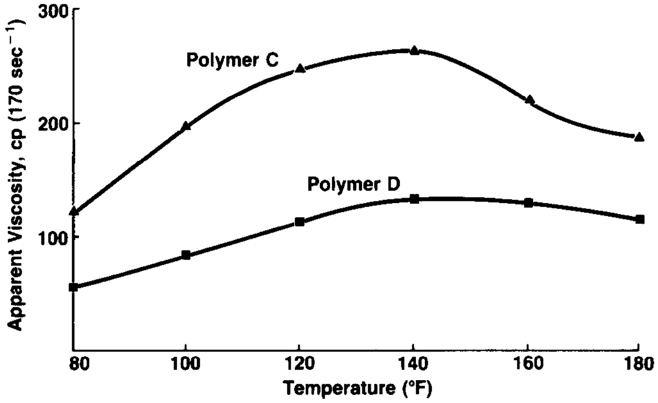

Figure 6 - The effect of derivative substitution distribution on apparent viscosity for polymers C and D which are chemically equivalent and crosslinked identically with metal C

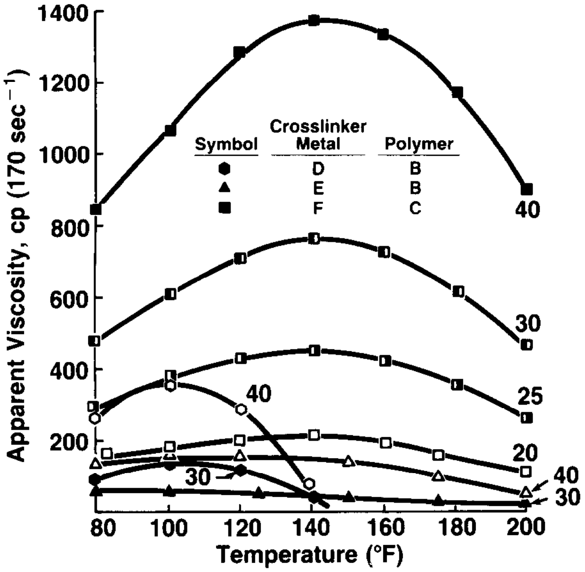

Figure 7 - Apparent viscosity versus temperature for a variety of polymer/crosslinker combinations

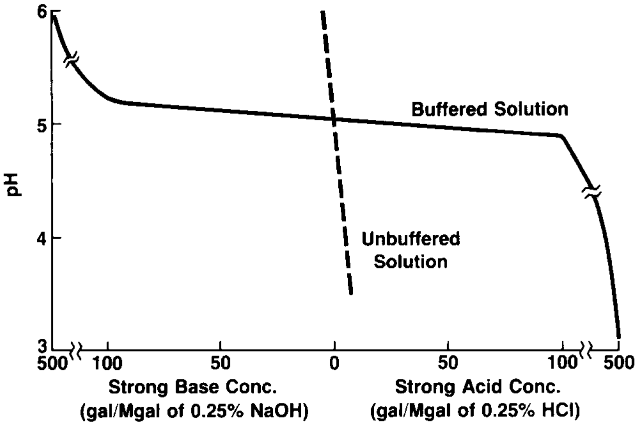

Figure 8 - Effect of strong acid and strong base addition to a water buffered with sodium dihydrogenphosphate (1% W/W)

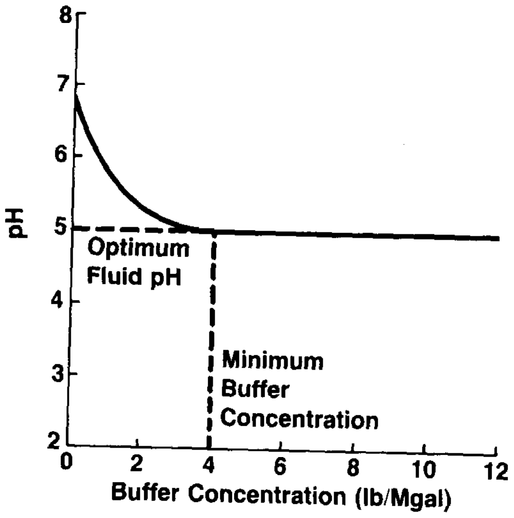

Figure 9 - Fluid pH versus buffer concentration for an ideal crosslinked fluid buffer

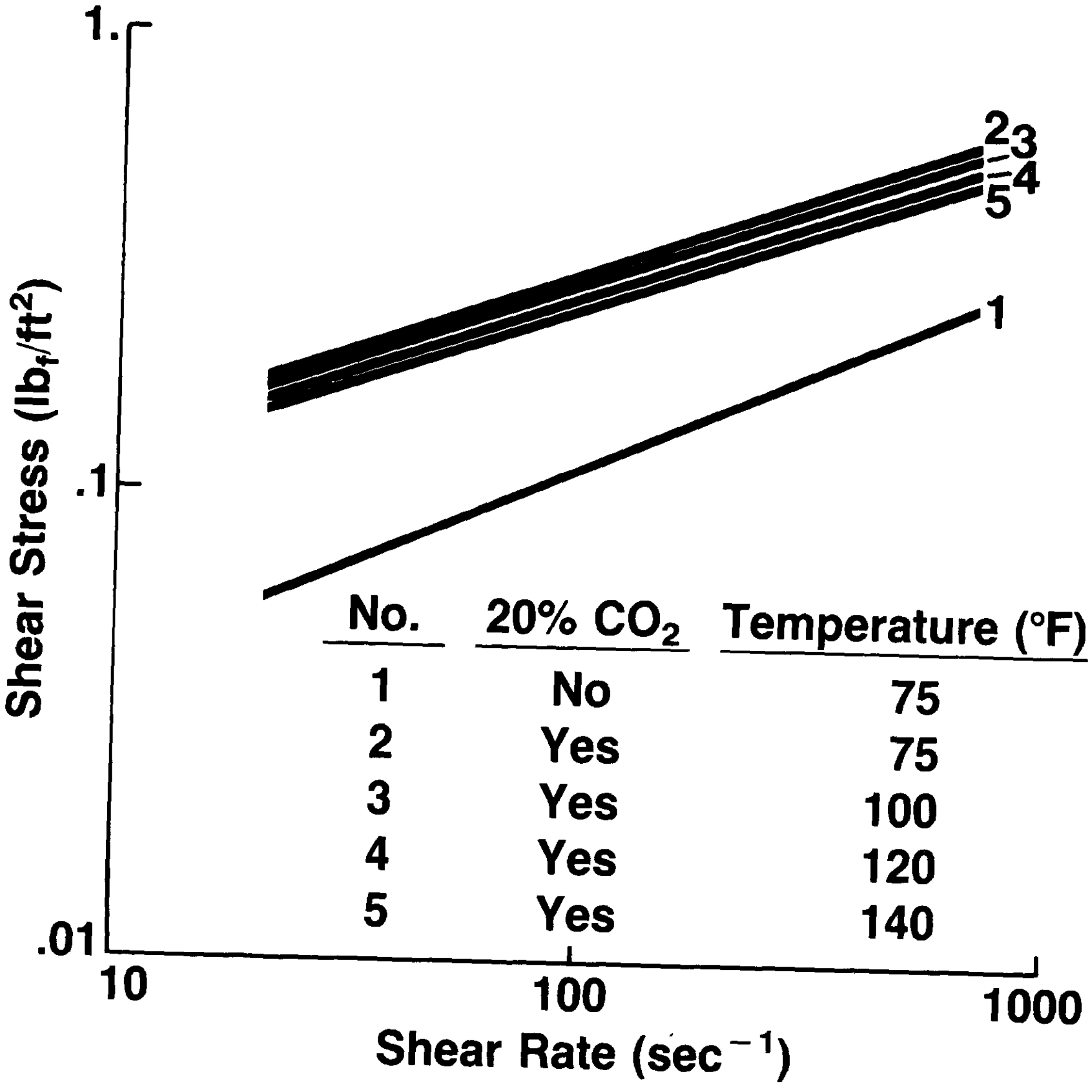

Figure 10 - Effect of CO_2 addition on the viscosity of polymer C (30 lb/mgal) crosslinked with metal F