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Evaluating the Effect of Temperature and Breaker Concentration on Degradation of Cross linked Hydroxypropyl Guar Fluid

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Abstract: *Hydraulic fracturing is a very popular and fundamental technique for stimulating petroleum and gas wells for optimum and economic recovery of hydrocarbons from formations with low permeability. The viscous and highly viscoelastic crosslinked fluids, which are often used to create fractures and transport proppants to prop opened the created fractures after pressure has been released, must be cleaned out to facilitate good retained conductivity of the proppant pack, to ensure hydrocarbon production without impairment. The action of the gel breakers used for the degradation of the polymer used in formulation the viscous fluids must be controlled. It must not act too fast to affect the quality of the fluid, making it to be unstable and affecting the fracture propagation and proppant transport capability of the fluid. An optimum amount of breaker must be used to ensure complete degradation of the viscous fluid at a specified time for a particular well condition. Several factors affect the reaction of the gel breakers, thus making it difficult to predict the break time of the fracturing fluids. Therefore, in this paper, the effect of temperature, breaker and polymer concentration on the degradation of borate crosslinked hydroxypropyl guar based fluid system was evaluated from experimental data. The test results showed that the rate of polymer degradation increases with increase in temperature and breaker concentration but decreases with increase in polymer concentration. This can serve as a guide to determine the optimum concentration of breaker that will be required for an acceptable and effective gel break, without compromising the fluid quality.*

Keywords: *Fracturing fluids, hydroxypropyl guar, sodium persulfate, gel breakers, conductivity.*

I.   INTRODUCTION

Hydrocarbons found in petroleum reservoirs are complex organic compounds mixtures that may exist in different phases over a wide range of temperature and pressure. Therefore, petroleum reservoirs can be classified as gas well containing natural gas with little or no oil, as condensate well containing natural gas as well as liquid condensate and as oil well with associated gases, depending on the bubble point and dew point pressures properties of the system [1]. After drilling oil and gas wells, the higher pressure in the formation forces the hydrocarbon to the wellbore and then to the surface. The overall productivity of the well depends on the type of natural energy or mechanism that is driving the hydrocarbon to the wellbore and this include the following: rock/liquid expansion, depletion drive, gas-cap drive, water drive, gravity drain and combination of all [1].

Low productivity from reservoirs with substantial amount of hydrocarbons may be as a result of near-well bore formation damage that may have occurred during the drilling or well completion activities or as a result of low permeability of the reservoir rock. More so, gradual build-up of scales, paraffins, asphaltenes and other residues, clogging the reservoir or tubings, may reduce the productivity of the well after operating for some time. The productivity of the well can be restored with stimulation techniques which include chemical flushing, acidizing and hydraulic fracturing. Acidizing process can be classified as matrix or fracture acidizing [2]. Matrix acidizing involves pumping acid fluid system into the hydrocarbon bearing formation through its natural existing channels to dissolve the near-well bore skin and part of the formation, creating wormholes, thereby creating free paths for the hydrocarbon to flow to the wellbore. Matrix acidizing can be grouped into carbonate (limestone) and sandstone (silica), depending on the type of rock or formation being treated. In fracture acidizing, the fluid is pumped at pressure high enough to fracture the formation or acid may simply be used to widened already created fractures [3]. In the process of hydraulic fracturing, highly conductive fractures are created by the pumping of specially formulated fluid at high rate and high pressure into the formation to crack it, paving way for the hydrocarbon to flow to the wellbore. The fractures are propped opened by pumping

proppants to fill them in the process of fracpac. Hydraulic fracturing can be used to produce hydrocarbon from unconventional reservoirs such as tight gas reservoirs, shale and coalbed methane, which often contain large amount of natural gas but difficult to explore because of their ultralow permeability, which in some cases are in the region of micro and nanodarcy [4]. Required properties of good fracturing fluids include the ability to create good fracture width, good gravel transport capability, generate low frictional force, low fluid loss property, stable, compatible with formation fluid, low formation damage, good breaking or clean up property, safe to use and cost effective [5]. Viscous nature of fracturing fluids is important, it is needed for creating good fracture geometry, for good proppant suspension and transport into the fractures, to counteract thermal thinning and to impact necessary fluid loss property [6][7]. Various fluid systems have been used for hydraulic fracturing and this include linear gels, crosslinked gels and visco-elastic surfactants [8][9]. Also available is more thermally stable copolymer of acrylates and 2-acrymido-2-methylpropanesulfonic acid usually crosslinked with metals [10]. Guar, guar derivatives (hydroxypropyl guar and carboxymethyl hydroxypropyl guar) and cellulose (hydroxyethyl cellulose and carboxymethyl cellulose) are the most commonly used water soluble polymers used to prepare viscous fluids [11]. Very high viscosity is generated by crosslinking the polymers with crosslinkers such as boron for borate crosslinked fluids and Titanium, Zirconium, Chromium and aluminum for organometallic crosslinked fluids within a particular range of pH. Crosslinking increases the molecular weight of the linear gel to extremely high values. Most fracturing gels exhibit viscoelastic and significant shear thinning properties and this distinguish them from other fluids [12].

Guar and hydroxypropyl guar (HPG) crosslink at high pH, while carboxymethyl hydroxypropyl guar (CMHPG) crosslinks at low and high pH; CMHPG crosslinking with metals usually forms strong crosslink bonds that are nonreversible, but borate crosslinked fluids form weak crosslink bonds that are reversible and less thermal resistant[11]. Guar and its derivatives contains varying amount of solid residues of protein and cellulosic materials, capable of damaging the conductivity of the proppant pack, unlike viscoelastic surfactants (VES), a polymer free system, which uses surfactant and inorganic salt to generate viscosity [10]. However, VES exhibit thermal thinning at high temperature, lacks internal breaking mechanism and has shear degradable tendency [9]. Borate crosslinked fluids are also affected by high temperature but are shear tolerant and have the ability to reheal after exposure to high shear rates, unlike zirconate crosslinked fluids which are shear degradable but has far more thermal resistance [9]. Gel breakers are employed to degrade the polymer used in formulating the viscous fluids, to ensure good regained conductivity of the proppant pack and production without impairment. This is achieved either by breaking the polymer backbone into smaller fragments of lower molecular mass and hence lower viscosity or by simply reversing the crosslinking reaction through lowering of the pH. Available gel breakers for water based fluids include enzymes, oxidizers and acids [13][14]. Enzyme breakers are susceptible to denaturing and thermal degradation when subjected to very high or very low pH and high temperature. Therefore, they are usually used at pH between 4 and 9 and temperature below 150^oF, although a recent work as shown enzymes that function above 300^oF [14]. Oxidizer breakers include persulfates of sodium, potassium and ammonium; peroxides of calcium and magnesium; chlorites and hypochlorites [11]. Peroxides produce free oxygen radical as temperature increases, while persulfates undergo thermal decomposition to releases free sulfate radicals, which attacks the polymer backbone, reducing its molecular weight and breaking it down into its constituent sugars. Acid breakers, which include acetic acid, formic acid and hydrochloric acid, acts in similar manners as oxidizer breakers, attacking the polymer backbone to break it down [14]. Encapsulated breakers are delayed–release breakers and can be used to slow down breaker reaction rate at high temperature and also used to improve fracture or filter cake clean up without jeopardizing fluid stability [15].

Guar based fluids are most commonly used for hydraulic fracturing because of their excellent hydration properties, good proppant carrying capacity, abundancy, cost-effectiveness, controlled breaking and easy clean out [11]. There have been efforts to improve fracturing fluids degradation and clean out. Degradation rate of borate crosslinked fluids increases with increase in temperature and decrease in pH, because of their reversible nature [11]. Other factors that affect gel degradation include breaker type, breaker concentration, polymer type, polymer concentration, salinity and the type of salt used to prepare the base fluid [16][17][18]. The reaction of the gel breakers must be controlled; it must not act too fast to cause fluid instability but must break at the right time and effectively degrade the polymer. The success of hydraulic fracturing job is measured by successful placement of proppants in the fractures and good fluid clean out. Extensive research has led to the development of various additives and fluid systems to match different well geometries and cope with challenging well conditions. The selected fluid system for a particular well design must be validated in the laboratory for quality assurance purpose before job execution in the field to minimize likelihood of service quality issues and associated cost of poor quality. Therefore, this paper details the study of the effect of temperature, breaker concentration and polymer concentration on the break time of borate crosslinked hydroxypropyl guar fluid based on experimental data. The success of hydraulic fracturing treatment in the field relies greatly on the fluid

validation process through selection of the right additives and determination of the optimum concentrations suitable for a particular well condition and job requirement.

II.　MATERIALS AND METHODS

2.1 Gel Hydration

25lbs /1000gal (25ppt) and 40lbs/1000gal (40 ppt) borate crosslinked hydroxypropyl guar fluid system were investigated in the experiment. The additives, apart from the breaker and crosslinkers, were added to the base fluid, 2% KCl brine by weight of water (bwow), in the order as listed in Table 1, while agitating with a Waring blender without entraining air. The gel was batch mixed in 1litre. After adding the gelling agent, the pH of the mixture was adjusted to the range of 5 and 6 to aid the polymer hydration and blended for 30 minutes. pH was measured with a digital pH metal and the viscosity with viscometer model 35, equipped with R1 rotor, F1 spring and B1 bob at 300 rpm.

Table 1: HPG Borate Crosslinked Fluid Recipe

Chemical	Concentration (per 1000gal)	Amount per 1L (cc)
2% KCl Brine (bwow)	1000 gal	1000 ml
Biocide 1	0.015 lbs	0.018 g
Biocide 2	0.015 lbs	0.018 g
HPG Gelling agent	6.25 gal*	6.25 ml
Acid buffer	As required	As required
Caustic soda solution	As required	As required
Surfactant	1 gal	1 ml
SP Breaker (1ppg solution)	2.5 lbs**	2.5 ml
Delayed borate crosslinker	3 gals	3 ml
Instant borate crosslinker	1 gal	1 ml
*　Test was repeated for recipe with 10 gal/1000 gal HPG		

**Test was repeated for 2.5, 5.0 and 10 lbs/1000gal SP breaker

2.2 Crosslink Test

After full hydration, the pH of the fluid was raised to 11 with a base in preparation for crosslinking. 200cc of the base gel was measured into a glass blender jar. The blender speed was set to create a vortex while avoiding air entrainment. The required amount of breaker and crosslinker were added to the vortex. The timer was started immediately the crosslinker was added. The time it took for the vortex to close was noted as the vortex closure time (VCT). Immediately the vortex had closed, the fluid was turned into a 250cc Pyrex bottle, periodically and carefully tilted for the fluid to hang out the edge of the bottle. The time it took the fluid to hang over the edge of the container as far as possible without tearing was noted as the lip time. The time it took for the crosslinked fluid to appear dry when it touches a surface was also noted and regarded as the crosslinked time.

2.3 Static Break Test

The base gel was prepared as described in 2.1. 200cc of the base gel was crosslinked with the appropriate amount of crosslinker and breaker added, following the procedure in 2.2. The crosslinked gel with breaker was poured into 250cc Pyrex bottle, placed in a water bath preset to the test temperature and checked periodically by performing lip test as explained in 2.2. The sample is described as crosslinked (C) if it can lip and support its own weight and as weakly crosslinked (WC) if it can lip butt cannot support its own weight when the bottle container the sample is tilted. When the sample viscosity becomes low as in linear gels, its viscosity can be measured with viscometer model 35 with B1 bob and R1 rotor. Acceptable break is viscosity $\leq$ 10cP at 300rpm (511 1/s shear rate). The test was conducted at temperatures of 120°F, 150°F and 180°F and concentration of the sodium persulfate (SP) breaker was 2.5, 5.0 and 10.0ppt. A 1lb/gal solution of powder SP breaker was prepared and used for the experiment for easy and more effective metering.

III.　RESULTS AND DISCUSSION

The 25ppt linear gel yielded lower viscosity (18cP) than the 40ppt gel (34cP) at 511 1/s as shown in Table 2. It is very essential for the polymer to fully hydrate before subjecting it to crosslink, otherwise it will affect the crosslink quality and ultimately the treatment [7]. The crosslink test result for 25ppt and 40ppt borate crosslinked HPG fluid is shown in Tables 3 and 4 respectively, using 3gpt and 1gpt delayed and instant borate crosslinkers respectively. The instant crosslinker is used to increase the rate of the crosslink reaction and shorten the crosslink time to the desired value as appropriate to match the engineering design. pH is critical to the quality of the crosslinked fluid as it influences the processes of polymer hydration, crosslinking, degradation, bacterial control and fluid stability [6]. Therefore, buffers are used to regulate and maintain the pH within a

narrow range in other to achieve the desired fluid properties. The targeted pH for HPG hydration and crosslinking by boron iron was 5 to 6 and 11 respectively. The recommended value for the crosslink pH depends on the test temperature and polymer loading [7]. The vortex closure time (VCT) indicates the progress of the crosslink reaction and the lip test informs about the extent of gel crosslinking, gel viscosity and crosslink quality. A particular concentration of crosslinker is required for crosslinking specific amount of polymer and in order to achieve the desired crosslink time and crosslink quality. From best practices, the crosslink fluid is often formulated to become fully crosslinked when it has transverse about 80% of its total expected travel time in the tubing. After full crosslinking, the fluid is usually dry when used to touch a surface and the final crosslink pH dropped slightly by magnitude of about 0.5.

Table 2: Hydration Test for Hydroxypropyl Guar

Test	HPG Concentration	
	40lbs/1000gal	25lbs/1000gal
pH of mix brine	6.07	6.07
Hydration pH	5.25	5.67
Apparent viscosity @ 511s^{-1} (cP)	34	18
Temperature (^{o}F)	80.2	80.1
Base gel pH	11.08	11.04

From the break test as shown in Tables 5 and 6, at low temperature of 120°F, it was more difficult to break the gel, especially the 40ppt gel. A good and faster break was observed at 180°F. Similarly, higher concentration of breaker provided faster and effective break, with the 40ppt gel breaking slower than the 20ppt gel. This confirmed that the rate of degradation of borate crosslinked HPG is function of temperature, breaker concentration and polymer concentration as also shown by [18].

Table 3: Crosslink Test for 25ppt HPG

SP Breaker concentration (lbs/1000gal)			
2.5	5	10	
Vortex Closure Time (min:sec)			
00:43	00:42	00:44	
Lip Time (min:sec)			
01:25	01:26	01:30	
Crosslinked Time (min:sec)			
04:20	04:15	04:18	
Crosslink pH			
10.88	10.92	10.95	

Table 4: Crosslink Test for 40ppt HPG

SP Breaker concentration (lbs/1000gal)			
2.5	5	10	
Vortex Closure Time (min:sec)			
00:11	00:10	00:09	
Lip Time (min:sec)			
00:45	00:43	00:44	
Crosslinked Time (min:sec)			
01:20	01:22	01:21	
Crosslink pH			
10.89	10.98	10.95	

Increasing the temperature and breaker concentration increases the polymer degradation rate, hence reduces the break time for the same polymer concentration. Break time increases with increasing polymer concentration for the same breaker concentration and at a particular temperature. Fig. 1 and 2 show the trend of the effect of temperature on Break Time of 25ppt and 40ppt borate crosslinked HPG fluid respectfully, while Fig. 3 and 4 show the trend for the effect of SP breaker concentration on break time. Borate crosslinked HPG fracturing fluid showed a good response to change in breaker concentration and temperature. Therefore, optimum amount of breaker must be used to degrade the polymer fluid and achieve a good hole clean out. Insufficient breaker could result to low conductivity of the proppant pack as a result of undegraded polymer or polymer filter cake. Excessively high breaker concentration can compromise the fluid quality and cause fluid instability as a result of excessively rapid polymer degradation. This can result to ineffective proppant transport, inability of the fluid to propagate fractures and general poor fluid's performance.

Table 5: Break Test for 25ppt HPG Borate Crosslinked Fluid

Time (mins)	SP Breaker concentration (lbs/1000gal)								
	2.5	5	10	2.5	5	10	2.5	5	10
	Temperature (ºF)								
	180	180	180	150	150	150	120	120	120
	Gel Texture / Viscosity (cP) at 511 1/s								
0	C	C	C	C	C	C	C	C	C
10	C	WC	7	C	C	C	C	C	C
20	WC	6		C	C	WC	C	C	C
30	7	2		C	C	7	C	C	C
40	2			C	WC	4	C	C	C
50				WC	7		C	C	C
60				14	4		C	C	C
70				8			C	C	C
80				3			C	C	C
90							C	C	WC
100							C	C	WC
110							C	WC	18
120							WC	WC	15
130							WC	WC	12
140							WC	21	10
150							WC	18	7
160							22	14	
170							20	12	
180							18	10	
190							17		
200							16		
210							14		
220							13		
230							12		
240							10		
Break Time (mins)	**30**	**20**	**10**	**60**	**50**	**30**	**240**	**180**	**140**

Table 6: Break Test for 40ppt HPG Borate Crosslinked Fluid

| Time (mins)	SP Breaker concentration (lbs/1000gal)								
	2.5	5	10	2.5	5	10	2.5	5	10
	Temperature (ºF)								
	180	180	180	150	150	150	150	120	120
	Gel Texture / Viscosity (cP) at 511 1/s								
0	C	C	C	C	C	C	C	C	C
10	C	C	WC	C	C	C	C	C	C
20	C	WC	9	C	C	C	C	C	C
30	WC	10	2	C	C	C	C	C	C
40	8	8		C	C	WC	C	C	C
50	4	3		C	C	9	C	C	C
60				C	WC	4	C	C	C
70				C	WC		C	C	C
80				WC	15		C	C	C
90				WC	9		C	C	WC
100				WC	5		C	WC	WC
110				WC			C	WC	WC
120				27			WC	WC	WC
130				18			WC	WC	WC
140				11			WC	WC	WC
150				7			WC	WC	WC
160							WC	WC	27
170							WC	WC	24
180							WC	27	20
200							WC	21	15
210							WC	18	14
220							WC	15	12
230							WC	13	10
240							WC	12	
270							WC	10	
Break Time (mins)	**40**	**30**	**20**	**150**	**90**	**50**	**NA**	**270**	**230**
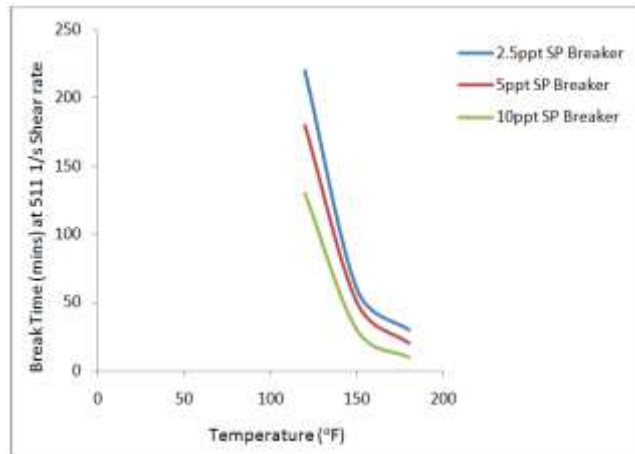
Figure 1: Effect of temperature on break time of 25ppt HPG borate crosslinked fluid
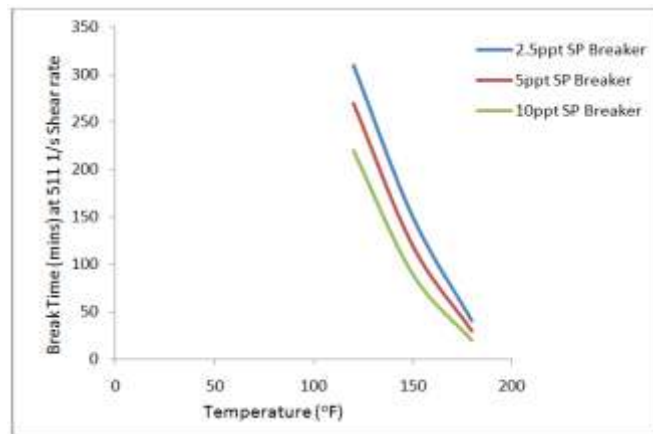

Figure 2: Effect of temperature on break time of 40ppt HPG borate crosslinked fluid
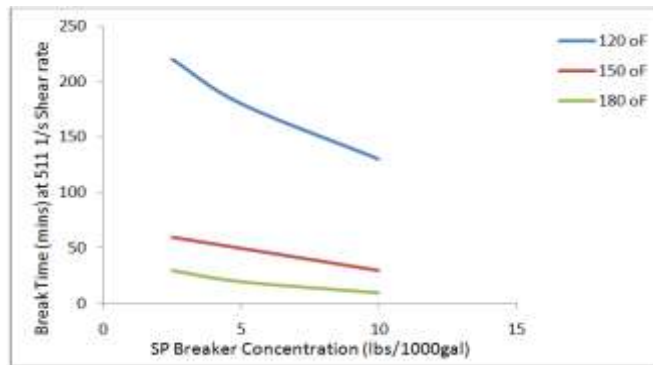

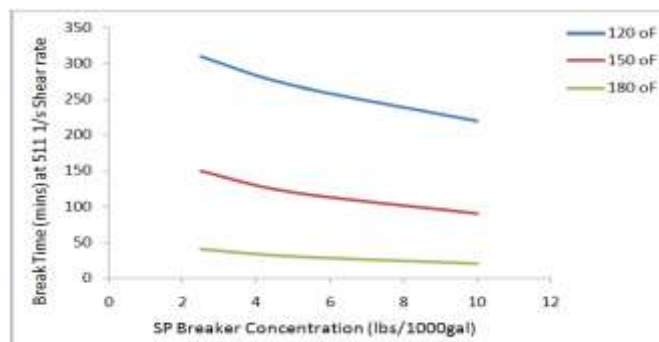**Figure 3:** Effect of breaker concentration on break time of 25ppt HPG borate crosslink fluid

Figure 4: Effect of breaker concentration on break time of 25ppt HPG borate crosslink fluid

IV.   CONCLUSION

pH is critical in determining the quality of borate crosslinked HPG fluids as it affects the fluid stability and gel hydration, crosslinking and degradation processes. The HPG polymer degradation is function of temperature, breaker concentration and polymer concentration. HPG polymer degradation rate increases with increase in temperature and breaker concentration and decreases with increase in polymer concentration. It is recommended to use, as much as possible, low polymer concentration to minimized formation damage. It is essential to allow full hydration of the polymer before initiating the crosslinking reaction, especially for low polymer concentration. This is necessary to achieve successful treatment. Using inadequate amount of breaker could result to undegraded or partially degraded polymer, capable of causing low regained conductivity of the proppant pack. Excessively high breaker concentration could result to unstable fluid with poor quality. Therefore, optimum breaker concentration required to achieve an affective polymer degradation without causing fluid instability, within a specific time frame, for a particular temperature and for a specific job requirement, must be determined through laboratory testing. Fluids validation is very essential prior to field deployment.

ACKNOWLEDGEMENT

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