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Optimization of Breaker Schedules for Stimulation of Tight Gas Reservoirs

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by

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ABSTRACT

The optimal breaker selection and breaker schedule design may achieve the purpose to maximize conductivity by cleaning out most pores of the proppant bed which are filled with the fracturing fluid. However, due to many complex reasons and chemical limits, optimization of breaker selection and schedule design still remains challenging. Extensive investigations are conducted in this study. Breaker selection guidelines and breaker schedule optimization are presented at last and field cases are followed as practical examples.

Gel breakers are generally grouped into three classes: oxidizers, enzymes, and acids. All of these materials reduce the viscosity of the gel by breaking connective linkages in the guar polymer chain. Oxidizing agents decompose to produce "free radicals" which attack the polymer chains and bring about degradation. For enzymes, they will then attach to that polymer strand until it can completely degrade the polymer. The enzymes will ride to wherever the polymer travels. Acid breakers often act as a necessary component to reverse the fracturing fluid crosslinking process in matrix acidizing. They tie up the crosslinking ions and break the polymer crosslink bondings.

The performances of breakers which are influented by formation temperature, fracture fluid pH and formation mineral. These selection criteria need to be carefully concidered in fracture job design. Summarization of what needs to be taken into account for any breaker selection, and the flow chart for the entire selection process, are presented.

After selecting the proper type, determine the optimal breaker concentration is an important step for entire breaker design, no matter for the remediation treatment of fracturing wells or the producing wells. For fracturing wells, calculation method of the optimal breaker concentration is developed based on viscosity test data. As for the producing wells suffering severely gel damage, breaker selection procedures and breaker schedule optimization are also proposed.

TABLE OF CONTENTS

LIST OF FIGURESv
LIST OF TABLES
ACKNOWLEDGEMENTSix
Chapter 1 Introduction
Chapter 2 Literature Review
2.1 Low-Permeable Gas Reservoirs32.2 Fracture Fluid42.3 Oxidizer Breakers52.4 Encapsulated Breaker62.5 Enzyme Breaker72.6 Breaker Application82.7 Gel Residue10
Chapter 3 Statement of the Problem
Chapter 4 Breaking Mechanisms
4.1 Types of Breakers144.2 Oxidizing Breakers144.3 Enzyme Breakers184.4 Acid Breakers204.5 Encapsulated Breakers21
Chpter 5 Breaker Selection and Optimization
 5.1 Guidelines for Break Selection During Fracturing Treatment
Chpter 6 Case Studies
6.1 Review of Fracture Treatment Design606.2 Review of Breaker Schedule Design646.3 Production Analysis676.4 Breaker Schedule Analysis and Suggestions77
Chapter 7 Conclusions and Recommendations
References

LIST OF FIGURES

Figure 2- 1 Major gas plays in lower 48 states
Figure 2- 2 Comparison of fluid rheology with no breaker, encapsulated breaker (EB) and dissolved ammonium persulfate (APS).(Gulbis,1992)7
Figure 2- 3 Time to break the gel as a function of breaker concentration for HPG at 40lb/1000 gal and at a temperature of 266 °F and a pressure of 300 psi (Nasr-EI-Din,2007)
Figure 2- 4 Viscosity of borate-crosslinked guar gum fluid with 0.5vol% at 260 °F (H Nasr-El-Din, 2007)
Figure 2- 5 Degradation of guar gum gel and effect of breaker type at 260°F and 300 psi after two hours (Al-Aamri, 2007)
Figure 4-1 Free radical reaction sites (Brannon, H.D., 1994)
Figure 4-2 Guar Enzymatic Degradation Mechanism (Phil Rae, 1996)
Figure 4- 3 Comparison of different break profiles (Phil Rae,1996)
Figure 5-1 Decomposition of persulfate in pH 10 fluid solution (Norman, L. R., 2005)26
Figure 5-2 Magnesium peroxide activity in 30 ppt solution on temperatures after 8 hours.26
Figure 5-3 Denaturization of Hemicellulase Enzyme in pH 7 Solution (Norman ,2005) 29
Figure 5- 4 Hemicellulase Activity as a Function of pH (Laramay, S.B.1992)
Figure 5- 5 Hemicellulase Activity as a Function of Temperature at pH 4.8 (Laramay, S.B.1992)
Figure 5- 6 Effect of fluid pH on activity of a liquid hemicellulase breaker at a temperature of 77 F (R. J. Powell, 1999)
Figure 5- 7 Effect of fluid pH on activity of a liquid hemicellulase breaker at a temperature of 77 F, Fluid pH adjusted to 7 after two hours (R. J. Powell, 1999)
Figure 5-8 Viscosity Profiles of New Guar Linkage-Specific Enzyme Product at
Figure 5-9 Borate Fluid Viscosity with Various Final pH Using 30 to 35 ppt HPG at the temperatures of 125 to 175 F (Norman, 1998)

Figure 5- 11 Comparison of Fracture Conductivity for Fluids with and without using high-temperature oxidizing breakers at 350 F (R. Dusterhoft,1998)36
Figure 5-12 Breaker Selection Flow Chart for Tight Gas Reservoir
Figure 5- 13 Hydrostatic release of Encapsulated Ammonium Persulfate at 175 F (Matthew J. Miller 2002)
Figure 5-14 Hydrostatic release of Encapsulated Ammonium Persulfate at 2000psig41
Figure 5- 15 Comparative Viscosity Profile
Figure 5- 16 Effect of breaker/polymer ratio on retained permeability (Northern White Sand, 20/40-mesh, 2 lb/ft ² , 160 F; 3,000 psi; 17 hr shut-in), (H.D.Brannon, 1990)
Figure 5- 17 Viscosity profiles at 180 F and 14.7psi with different concentrations of Encapsulated Sodium Persulfate 47
Figure 5-18 Hydrostatic release rate of Encapsulated Sodium Persulfate at 180 F48
Figure 5- 19 Effect of proppant concentration and porosity on the final polymer concentration (H.D. Brannon, 1990)
Figure 5- 20 Effect of Ammonium Persulfate (APS) breaker concentration to polymer concentration ratio on the retained proppant pack permeability (Joe Small, 1991)
Figure 5- 21 Effect of proppant concentration and porosity on the final polymer concentration
Figure 5- 22 Effect of Ammonium Persulfate (APS) breaker concentration to polymer concentration ratio on the retained proppant pack permeability (H.D. Brannon, 1990)
Figure 6-1 Pumping schedule of polymer, crosslinker and buffer, for RHT #161
Figure 6- 2 Pumping schedule of surfactant and clay stabilizer, for RHT #162
Figure 6-3 Pumping schedule of polymer, crosslinker and clay stabilizer, for JCM #162
Figure 6- 4 Pumping schedule of surfactant and buffer, for JCM #163
Figure 6- 5 Proppant Concentration in Fracture Fluid of RTH #1 and JCM #163
Figure 6- 6 Breaker concentration design for RHT #1

vi

Figure 6- 7 Breaker concentration design for JCM #1 66
Figure 6-8 Comparison of Daily Gas Production Rate
Figure 6-9 Comparison of Long-term Daily Gas Production Rate
Figure 6- 10 Comparison of Long-term Daily Production Rate on Log-log Scale70
Figure 6- 11 Comparison of Average Cumulative Gas Production70
Figure 6- 12 Constant pressure log-log type curves for finite fracture conductivities (R.G. Agarwal, 1979)
Figure 6- 13 Gel damage identification for RHT #1 (PSUWELL v1.5)76
Figure 6- 14 Gel damage identification for JCM #1 (PSUWELL v1.5)77

LIST OF TABLES

Table 4- 1 Solubility of Persulfate Breakers in Water (BJ Services)	17
Table 5- 1 Static Gel Viscosity (cp) Tests for Oxidizing breaker [*]	27
Table 5- 2 Static Gel Viscosity (cp) Tests for Ensyme Breaker*	31
Table 5- 3 Summarization of Breaker Selection Guidelines	37
Table 6- 1 Reservoir Parameters	59
Table 6- 2 Fluid Specifications for RHT #1 and JCM #1	60
Table 6- 3 Fracture fluid pumping schedules	61
Table 6- 4 Breaker Selection and Specifications for RHT #1 and JCM #1	65

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Chapter 1

Introduction

Gas production from low-permeability formations has become a major source of natural gas supply in U.S. The use of hydraulic fracturing in tight gas reservoirs has unlocked natural gas resources that were not economical before. As the fracture fluid technology has improved over the past 60 years, the amount of tight gas reserves has increased dramatically.

Fracture fluids are used to create a hydraulic fracture and then to transport enough proppant into the fracture to enable production of hydrocarbon. Fracture fluid usually consists of water thickened with guar or derivatized guar polymers. After the proppant is mixed with the viscous fracture fluid and placed into the fracture, the fracture fluid needs to be flowed back from the proppant pack. It should be flowed back without moving the proppant and without damaging the conductivity of the proppant pack. To accomplish this, the operator needs to thin the viscous fracture fluid that transported the proppant to a Newtonian fluid with a viscosity of 50cp or less. Chemicals used to reduce the viscosity of fracture fluids, are called breakers.

Breakers reduce the molecular weight of guar polymer by cutting the long polymer chain. As the polymer chain is cut, the fluid's viscosity is reduced. All of these chemicals reduce the viscosity of the gel by breaking connective linkages in the guar polymer chain. Once the connective bonds in the polymer are broken, the resulting pieces of the original polymer chain are the same regardless of what type of breaker was used. For years, great efforts have been paid to understand breaking mechanisms of oxidizers, enzymes acid breakers, and their field applications. However, questions still remain to be answered include: what criterion one should follow to select the proper type of breaker, and how much breaker is needed for the complete gel degradation.

Extensive investigations are conducted in this research to critically review all types of breakers, to understand its mechanism and applications based on published and unpublished laboratory experiments and field studies, to develop an integrated and systematic guidelines for breaker selection and breaker schedule optimization, and to follow with field case studies.

Chapter 2

Literature Review

2.1 Low-Permeable Gas Reservoirs

Production from low-permeability reservoirs, including shale gas and tight gas, has become a major source of domestic natural gas supply. In 2008, low-permeability reservoirs accounted for about 40 percent of natural gas production and about 35 percent of natural gas consumption in the United States. (EIA 2008)

The use of hydraulic fracturing in conjunction with horizontal drilling in tight gas formations has opened up natural gas resources that would not be commercially viable without these technologies. As tight gas production has expanded into more basins and recovery technology has improved, the size of the tight gas resource base has increased markedly. (Figure 2-1)



Figure 2-1 Major gas plays in lower 48 states

Because the exploitation of tight gas resources is still in its initial stages, and because many shale beds have not yet been tested, there is a great deal of uncertainty over the size of the recoverable tight gas resource base. Low-permeability gas wells typically produce at high initial flow rates, which decline rapidly and then stabilize at relatively low levels for the remaining life of the wells.

2.2 Fracture Fluid

Hydraulic fracturing, as a means to improve the productivity of natural gas wells, has been applied since the late 1940s. Since then, major improvements have been made in the properties of the fluids used to initiate and propagate the fracture and to carry the proppants that deep into the fracture. Phil Rae and Gino Di Lullo (1996) reviewed the fracture fluids system since 1970s, which indicated the ideal fracture fluid should be thin and easy to handle on surface but should have sufficient viscosity to transport proppant from the surface equipment to the well tubular. Also the study pointed out that in the course of transiting the tubular, it should develop sufficient additional viscosity to transport the proppant through the tortuous near-wellbore region and to support the proppant in the relatively low shear environment of the fracture. Economides (1996) meanwhile suggested this additional viscosity is also needed to minimize fluid leak-off from the fracture so that it will remain open and able to accept proppant without the requirement for excessive volumes of fluid and unreasonably high pump rates.

However, there were studies (Elbel , 199) indicated that viscosity development cannot occur

too soon since this would produce very high friction pressures in the tubular, leading to higher surface pressure and horsepower requirements. Finally, after successfully transporting proppant into and along the fracture, the fluid must "break," reverting to a thin, water-like condition for easy clean-up from the well. This "thin-thick-thin again" behavior can today be achieved by clever chemical manipulation of a select few natural polymers and their derivatives.

2.3 Oxidizer Breakers

After proppant has been placed in the fracture, the crosslinked fluid needs to be degraded and flowed back. This is accomplished by "breakers", which are chemicals that break the crosslinked polymer molecule into smaller pieces of lower molecular weight (Phil Rae, 1996).

Many researches (Park, et al. 1996) considered the most common breakers are oxidizing agents like peroxides and persulfates. MaCabe, et al. (1998) proposed the oxidizing mechanisms that these oxidizer reactive species decompose to produce "free radicals" which attack the polymer chains and bring about degradation. Their research results showed that persulfates has much high solubility in water. Thermal decomposition of persulfates, ammonium persulfates for example, produces highly reactive sulfate radicals that attack the polymer, reducing its molecular weight and its viscosifying ability. Decomposition of persulfate, and therefore reactivity, is temperature dependent.

$$O_3S^{2-} - O:O - SO_3^{2-} \rightarrow .SO^{4-} + .SO^{4-}$$

Another alternative is presented by Mahapatra (2011), which is the use of a low volubility

peroxide, like calcium peroxide, which limits the quantity of reactive species in solution. Similarly, Misak (1975) indicated that organic peroxides can be dissolved in oil or otherwise dispersed in the fracturing fluid. With time, the peroxide slowly partitions from the oil droplets into the aqueous fluid to effect a delayed break.

At low temperatures, Hinkel (1981) indicated the rate of free radical generation may be too slow to effect a suitable break within an acceptable timeframe. In this research persulfate salts were adopted as testing samples. Below 125 F, the persulfate oxidizing process occurs very slowly, then Hinkel proposed that the reaction needs to be catalyzed to obtain acceptable break rates. In the test, persulfate salts were coupled with certain catalysts, and these chemicals which were called "initiators" could accelerate the process and leaded to a rapid reduction in fluid viscosity. Examples of such initiators are tertiary amines, some organic esters and transition metal salts.

2.4 Encapsulated Breaker

On the other hand, when temperatures are higher (usually above 180 °F), normal breakers become too active. In such cases, the fluid may degrade quickly before the treatment could finish (Burnham, 1980). This problem can be overcome by wrapping or "encapsulating" the breaker in a low permeability film. This technique was first proposed in 1964 when Wyant et al. suggested the use of water-insoluble, oil-soluble coatings, like rosin or paraffin wax to slow the release of breaker. In the early-80's, this concept was resurrected with a new generation of synthetic coating

agents to effect the encapsulation.

Irrespective of the method, the encapsulation technique works on the same principle slowing the dissolution of the breaker and its release to the fluid, thus preventing premature break (Figure 2-2). The use of reducing agents in the fluid, to "mop-up" any oxidizer that may have leaked too quickly, provides an additional element of control. Encapsulation has the added benefit of leaving highly concentrated breakers in the fracture as it does not leak-off into the aqueous phase and thus remains the inner material that is designed to break (Brannon,1992).



Figure 2- 2 Comparison of fluid rheology with no breaker, encapsulated breaker (EB) and dissolved ammonium persulfate (APS).(Gulbis,1992)

2.5 Enzyme Breaker

Enzymes have also been used for many years to break fracture fluids. Research by Cayle in 1972 specified enzymes are natural catalysts produced by living organisms and they perform very specific functions associated with the processes of cellular metabolism. Each enzyme works for only one or, at most, a very few substrates. Several different enzymes, made by certain bacteria and fungi, are capable of attacking guar and related hemicelluloses. Brannon (1994) proposed that the enzymatic breaking mechanism that these enzymes attack the guar molecule and reduce its molecular weight but, unlike oxidizing agents, they are not consumed in the process. In principle, a single enzyme molecule is capable of degrading an unlimited number of guar molecules. Brannon also pointed out that, under optimum conditions, some enzymes can degrade complex polymer, like guar and its derivatives, to simple sugar solutions (mono- and di-saccharides). Such new, improved enzymes have been developed in commercial quantities. These enzymes have exceptionally high substrate specificity, high temperature stability (up to 200 °F), activity over an extended range of pH (2 to11). This has allowed the use of enzymes in situations that were previously considered beyond their capability.

2.6 Breaker Application

The gel degradation studies for many oxidizer and enzyme breakers are well documented. The investigations on each breaker indicate the fact that, their applications are limited by the temperature, initial breaker concentration and polymer loading.

2.6.1 Temperature

Chris and Michael (1996) summarized that oxidizing breakers such as persulfate, are effective from about 120°F to about 175°F. They also indicated that application of enzyme

breakers is limited to temperatures lower than 150°F.

M.U Sarwar, et al. (2011) elevated the working temperature of persulfate breakers to a higher range, from 125 °F to 225 °F. Meanwhile, the peroxide was determined to work between the temperature from 200 °F to 240 °F. Bromate was suggested to use at the temperature above 250 °F.

2.6.2 Breaker Concentration

The study from H.A. Nasr-El-Din (2007) shows the time needed to break the gel as a function of initial breaker concentration (Figure 2-3). The gel broke after 200 minutes when the concentration of the breaker was 0.125 vol%. The time needed to break the gel was nearly 70 minutes when the concentration was doubled to 0.25 vol%. By using the recommended concentration of 0.5 vol%, the breaking time was 45 minutes and by doubling this concentration the gel breaks faster at nearly 2 minutes only.



Figure 2-3 Time to break the gel as a function of breaker concentration for HPG at 40lb/1000 gal and at a temperature of 266 °F and a pressure of 300 psi (Nasr-EI-Din,2007)

2.6.3 Polymer Loading

Tests (Al-Mohammed, 2007) were also conducted to correlate the polymer loading and breaker efficiency. Figure 4 shows the effect of increasing polymer concentration on the breaking time. The initial breaker concentration was kept constant for all gels at 0.5 vol% sodium bromate. Guar gum was used to prepare the three gels. For the gel that contained 35 lb/1000 gal, the time needed to break the gel was 45 minutes. The time needed for 40 Ib/1000 gal to break was 64 minutes where for 45 Ib/1000 gal, the breaking time was 83 minutes. These results indicated that the time need to break the gel increased at higher polymer concentration.



Figure 2- 4 Viscosity of borate-crosslinked guar gum fluid with 0.5vol% at 260 °F (H Nasr-El-Din, 2007)

2.7 Gel Residue

Al-Aamri (2007) conducted a serial of tests on oxidizer, enzyme and acid breakers. The results showed that guar and hydroxyproply guar gels produced a residue after reacting with the breaker. This residue is insoluble material present in the guar gum and can cause blockage of the

generated conductive channels and decrease in the production rate of the formation. This residue was also noted irrespective of the type and concentration of the breaker used (Photo 2-1).

Degradation of polymer in the fracturing fluids by gel breaker is accomplished via free radical mechanisms. During the oxidation reaction for example, the water-soluble broken polymer fragments that carry free radicals could become insoluble materials by reacting with each other again and/or with one polymer fragment. This will contribute to the damage of the formation. Reducing polymer concentration could be a solution and would result in less polymer residue upon polymer broken, but the insoluble polymer residue generated from the broken polymer still causes blockage of generated conductive channels and a decrease in the formation production rate.



Figure 2- 5 Degradation of guar gum gel and effect of breaker type at 260°F and 300 psi after two hours (Al-Aamri, 2007)

Chapter 3

Statement of the Problem

For each fracturing job design, breaker selection and schedule are tasks that need meticulous and all-around consideration according to their own advantages and drawbacks for different applications. The objective of this study is to develop integrated and systematic guidelines for breaker selection and breaker schedule optimization.

Extensive investigations are conducted in this study, from the breaker types and mechanisms to their own applications. Suggestions for optimization are presented at last and field cases are followed as practical examples. In Chapter 4, the breaker type and their own breaking mechanisms will be elaborated. After that in Chapter 5, the detail applications for each type of breakers are presented, through the working temperature, pressure, pH and salinity, to form the guild lines for selecting breakers for different conditions. Also, the methods for optimizing breaker schedule are discussed, followed with field case studies as practical instances.

The procedure of my research is outlined below:

- Complete a literature review of all related papers, company product reviews, laboratory experiments, and field data related to the fracture fluid breakers.
- Develop a systematic and complete understanding of breaker types and breaking mechanisms.
- 3. Develop guidelines for breaker selection and breaker schedule optimization.

- 4. Presenting the suggestions for breaker schedule optimization with field cases examples.
- 5. Document all above into a Master thesis.

Chapter 4

Breaking Mechanisms

4.1 Types of Breakers

Chemical breakers used to reduce viscosity of guar and derivatized guar polymers are generally grouped into three classes: oxidizers, enzymes, and acids. All of these materials reduce the viscosity of the gel by breaking connective linkages in the guar polymer chain. Once the connective bonds in the polymer are broken, the resulting pieces of the original polymer chain are the same regardless of what type of breaker was used.

4.2 Oxidizing Breakers

The most common oxidizing breakers are persulfate $(S_2O_8^{2-})$, peroxide $([O-O]^{2-})$ and bromate (BrO_3^{-}) . Among these oxidizing agents, Sodium, potassium, and ammonium persulfate have been used effectively as breakers for over 40 years. These reactive species decompose to produce "free radicals" which attack the polymer chains and bring about degradation. The reactive sites of a repeating unit of guar polymer are shown in Figure 4-1. There are 18 potential sites for a free radical reaction on a single repeating unit of guar (about 66,600 oxidizable sites per molecule). In this type of breaker, oxidizing-reduction chemical reactions occur as the polymer chain is broken and the resulting polymer materials may not be oxidized by themselves.



Figure 4-1 Free radical reaction sites (Brannon, H.D., 1994)

To depict the oxidizing breaking mechanism, a step-by-step procedure of the persulfate breakers degradation, as an example here, is discussed, this works as follows:

1. The persulfate ion breaks into two halves called radicals. This process is known as chain initiation.



2. Persulfate radicals oxidize water to form sulfate and two new radicals called hydroxyl radicals



3. A hydroxyl radical reacts with guar to form water and a guar radical. Many different guar radical species can be formed depending where the hydroxyl radical reacts. One guar radical can react internally or externally with guar, forming a different guar radical.



4. When a certain guar radical species is formed, it can react again with water, which removes one bond from the guar polymer chain. This reaction produces two shorter polymer chains and gives off a hydroxyl radical



5. The hydroxyl radical of step 4 continues on the path of step 3. Each time this sequence occurs, a reduction in the polymer molecular weight occurs. This entire process is the breaking chemistry.

It is true that one persulfate ion form only two hydroxyl radicals, but these two hydroxyl radicals may react, be regenerated, and react again hundreds or thousands of times. This reaction is a true catalytic process, which makes persulfates very effective breakers for guar-type polymers.

Below 125 F, the persulfate oxidizing process occurs very slowly, then the reaction needs to be catalyzed to obtain acceptable break rates. The entire oxidizing process is still samilar to the one discussed above, except the first reaction step becomes:



These catalyst chemicals are usually called "initiators" or "activators" which are able to accelerate the process and lead to a rapid reduction in fluid viscosity. Examples of such initiators are tertiary amines, some organic esters and transition metal salts.

Commercially available persulfate breakers nowadays are Ammonium, Potassium and Sodium persulfate salts. With the same oxidizing mechanism, these products only differ in solubility characteristics. Ammonium persulfate ranks first for its solubility in water, followed

Persulfate Salt	Solubility in H ₂ O (68 F)
Ammonium Persulfate $((NH_4)_2S_2O_8)$	79.2g/100cc
Potassium Persulfate (K ₂ S ₂ O ₈)	5.3 g/100cc
Sodium persulfate (Na ₂ S ₂ O ₈)	54.9 g/100cc

with Sodium and then Potassium persulfate salts. (Table 4-1)

 Table 4- 1 Solubility of Persulfate Breakers in Water (BJ Services)

Peroxide is a very stable and strong oxidizer which often used as an internal breaker to remove the filter cake. According to the reservoir pore size distribution and active material content, there are many different types of peroxide products available. The magnesium peroxide is one of them that widely used in industry, which acts as follow:

1. Upon contact with hydrochloric acid, the solid peroxide decomposes to form

hydrogen peroxide.



2. Hydrogen peroxide generates in situ oxygen which attach the polymers

$$2 \underbrace{H_2O_2} \underbrace{O_2} + 2 \underbrace{H_2O}$$

3. Autoxidation occurs as the polymer is exposed to the oxygen.

Other major oxidizing agents, such as sodium, potassium, and ammonium salts of bromate (BrO₃⁻), have the same mechanism to degrade the gel and lower the viscosity. However, due to their own limits upon temperature and pH working environments, these chemicals can be useful

selections for various job designs.

4.3 Enzyme Breakers

Enzymes are large, highly specialized proteins produced by living cells. They are non-toxic and can be readily broken down or absorbed back into the environment. Therefore, enzyme breakers are concidered environment friendly. The enzymatic breaking activity does not change the enzyme structure during the reaction initiation and thus, the enzyme may then initiate another breaking reaction on polymer, and so on. The initiation of reactions by enzymes is governed by a property known as the "lock and key principle". They are very specifically limited in reactivity to only those specific substrate sites to which they can match.

The structure of guar, shown in Figure 6 (a), may be most simply defined as a polymer which is a repeating unit. For enzymes, the most effective approach to engineer a structural dismantling of a guar polymer is to concentrate the attack upon the beta-1,4 linkage and alpha-1,6 linkage. Successful cleavage of these linkages will reduce the polymer to simple monosaccharide sugars which are completely soluble in water. Many different existing enzymes are specific for only guar polymer, but do not effectively reduce the polymer to simple sugars or reduce molecular weight. The enzyme must be not only polymer-specific to match up with the polymer, but also additionally, it must be polymer linkage-specific to attack the appropriate linkages to affect the desired degradation. As noted above, the most effective pathway would be the cleavage of the beta-1,4 linkages between the mannose units prior to cleavage of the alpha-1,6 linkages

between the galactose and the mannose unit as shown in Figures 4-2, which can be considered as the highest efficiency breaking mechanism of enzyme breakers.



Figure 4-2 Guar Enzymatic Degradation Mechanism (Phil Rae, 1996)

Previous studies (Tjon-Joe-Pin, 1994) indicate that upon introduction to the aqueous polymer solution, the enzyme will seek and attach to a strand of polymer until the polymer strand can be completely degraded wherever it travels; i.e., within the primary fracture, into natural fractures, or into high permeability matrices. Thus, the enzyme degradation will be distributed and concentrated homogeneously with polymer throughout the fracture, This is a major advantage for enzyme breakers, which indicates enzyme can provide long term polymer degradation anywhere in the reservoir.

4.4 Acid Breakers

Acid breakers often act as a necessary component to reverse the fracturing fluid crosslinking process in matrix acidizing. These acids are often combined with the polymer gels used in fracturing to provide an acid fracturing fluid. Once the gelled acid is formed, zirconium based crosslinking agent is added for crosslinking the polymer to form sufficient viscosity. The reason and advantage of using gelled fluids in acid fracturing is to inhibits or retards the reaction of the acid with formation, preventing the acid being depleted with very little penetration of the formation. Once the crosslinked fluid is injected into the wellbore and crack the formation, the acid then etches the fracture surfaces in a non-uniformed pattern to form conductive channels that remain open without any proppant after the fracture closure. Meanwhile, the fluoroboric acid, as the gel breaker, begin the uncrosslinking process. First, it decomposes to hydrofluoric acid. Then, the hydrafluoric acid releases fluoride ions, which ties up the zirconium ions and breaks the zirconium polymer crosslink bonding upon completion of the acid fracturing treatment. The viscosity of the acid decreases over time to allow easier recovery of the spent gelled acid solution.



Acids also are used to creat a low pH environment to break the guar polymers. The stability of a guar or derivatized guar polymer is a function of pH and oxygen concentration of the water. When oxygen effects are removed by adding the gel stabilizers, viscosity is reduced faster at lower pH. However, the applications of acid breaker in this case is limited to many factors, which will be discussed later.

4.5 Encapsulated Breakers

Any oxidizing, enzyme, or acid breaker added to the fracturing fluid and available for immediate reaction should not be considered a controlled release breaker. As noted above, for oxidizer breakers, the generation of radicals and reduction in fracturing fluid viscosity are strongly influenced by temperature. And for many cases, aggressively high breaker concentrations are needed to provide a better clean up result. Yet the fluid rheology suffers if too much active breaker is added to the fluid. The paradoxes are that breaker concentration high enough to improve proppant pack conductivity will reduce the fluid viscosity too quickly for efficient fracture creation and effective proppant placement. Additionally, chemicals like persulfates will consume themselves too soon in the fluid when temperature is higher than 200 F. These issues can not be resolved unless certain delay release method is adopoted.

Enzyme breakers, although break the gel through a different mechanism, are restricted to specific thermal and pH conditions, the fracturing fluid initial high pH will denature the enzymes forever unless the acid is used as a company to reduce the pH to the range suitable for enzyme breaking and also, uncrosslink a borate by creating low pH environments. However, the package of enzymes and acid will be significantly impaired at the early stages of treatment if no effort of delay-release is made. Thus, to avoid the issues above, it is necessary to introduce methods to delay or retard the reactions to obtain a better control.

Because of most wells located at several thousand feet depth during the fracture acidizing, acid gel breakers dispersed within these crosslinked fluids prior to pumping would react too quickly, causing the fluid to degrade before placement of the fluid within the producing area of the formation. As a result for years, breakers have been added after the fluid is in place. This, however, requires additional time and labor. It is also difficult to insure that the subsequently added breakers become adequately dispersed throughout the fluid so that the fluid becomes fully degraded.

As the factors noted above, over the decades, a wide variety of methods have been adopted in order to reduce the rate of reaction between the polymer and breaking agents. The prevalent method is encapsulation, which provides a delayed break because the reactive chemical is separated from the fracturing fluid by a water-resistant coating. Encapsulated breakers have enjoyed success relative to previous breaker technologies in many field applications. They were introduced to provide for the addition of much higher concentrations of breakers degradation to fracturing fluids and to make the breaking progress toward achieving the ideal behavior (Figure 4-3).



Figure 4-3 Comparison of different break profiles (Phil Rae, 1996)

A wide variety of coating methods can achieve the delay release effect. However, only some of them are commercially available nowadays in the industry. The major encapsulation methods are:

- Encapsulating active ingredients in impermeable membranes that release breakers when crushed.
- Encapsulating active ingredients in an impermeable membrane or coating that dissolves and releases the active ingredients.
- Encapsulating active ingredients in semipermeable membranes that rupture (and release active ingredients) by osmotic swelling.
- Encapsulating active ingredients in permeable membranes or coatings that allow slow active-ingredient release by dissolution of the active chemical through a porous membrane.
- Encapsulating the active ingredients in a material that will erode away from the active

ingredient, thereby releasing it into the environment.

• Forming a micro emulsion that contains an aqueous form of the active ingredients, which hinders the diffusion of the active ingredients throughout the fluid.

Among these proposed mechanisms of how the breaker is released from the coating, two of them are the most popular in the industry for years. Release of the payload through particle crush and rupture of the coating upon fracture closure is the predominantly one. And the second is fluidized bed coating, which usually releases breakers by diffusion or osmosis swelling. In this coating method, a particle of active breaker, such as sodium persulfate, is placed in a chamber and fluidized by air flow. This fluidized bed is then spray painted with a thin, continuous coating. The coating may vary from 10 to 50% of the particle weight depending on the desired thickness and the size of the initial breaker particle. Smaller particles of breaker require heavier coatings to obtain the same film thickness as a larger particle.

With these various coating methods, the breaking applications in field operation will also be different. For each fracturing job design, encapsulation method and breaker type selection are tasks that needs meticulous and all-around consideration according to their own breaking mechanisms, to obtain a much better clean-up result.

Chpter 5

Breaker Selection and Optimization

5.1 Guidelines for Break Selection During Fracturing Treatment

It is important to understand the general performances of breakers which are influented by fracturing fluid temperature, pH and mineral prensence. These selection criteria need to be carefully concidered in fracture job design.

5.1.1 Selection Guildelines for Oxidizing Breakers

The rate at which an oxidizing agent molecule breaks into two radicals is temperature-dependent. Numerous previous experiments have been done to investigate the temperature range for difference breaker performances. The normal working temperature for persulfate salts are usually between 120 F and 200 F. Below 120 F, the oxidizing process occurs very slowly, and the reaction must be catalyzed to obtain acceptable break rates. A variety of catalysts, including many organic amines and inorganic materials, may be used. Above approximately 200 F, persulfate decomposes very quickly. Figure 5-1 shows the data from a study of the half-life of sodium persulfate. As a function of temperature, breaker half-life is the time required for 50% of the initial breaker concentration to be decomposed. Generally, a 30-minute half-life is concidered to be the shortest value for a useful fracturing fluid breaker. The corresponding temperature for a 30-minute half-life is the maximum temperature that can be applied (E.I. Park,2001). The Figure 5-1 indicates although persulfate salts still breake the gel above 200 F, it decomposes so quickly that the breaks cannot be controlled. Peroxide, which is not as rapidly active as the persulfate in water based fracturing fluids, was better in degrading the gel between 200 $^{\circ}$ F and 250 $^{\circ}$ F, (Figure 5-2). Bromate salts, on the other hand, are advised to be considered for temperature above 250 $^{\circ}$ F (H Nasr-El-Din, 2007).



Figure 5-1 Decomposition of persulfate in pH 10 fluid solution (Norman, L. R., 2005)



Figure 5- 2 Magnesium peroxide activity in 30 ppt solution on temperatures after 8 hours (Nasr-El-Din, 2007)

A number of other system components can interfere with efficiency of oxidizer agents. Although oxidizer agents are less sensitive to fluid pH value, they are sensitive to salinity, which results in premature decomposition in high salinity fluids like seawater. And also, heavy metal ions (Fe^{2+} , Cu^{2+} , Mn^{2+} , etc) can catalyze the decomposition of oxidizing agents and the generation of free radicals. Table 5-1 shows the results of the static break tests for Sodium Persulfate breaker (5lb/Mgal) at 18 hours 120 °F(E.I. Park, 2001). The Sodium Persulfate breaker appered to be consumed by the minerals presented in the fluid, demonstrating the importance of considering the mineral composition during breaker selection. Usually higher breaker concentration is concidered to avoid such issue.

BreakerKaolinite
(0.02 lb)Berea
(0.09 lb)Bentonite
(0.02 lb)Silica
(0.05 lb)Sodium
Persulfate30242427

Table 5-1 Static Gel Viscosity (cp) Tests for Oxidizing breaker*

*Usually gel viscosity less than 10cp is concidered as "broken"

Additionally, the use of resin-coated proppants can seriously impair the ability of oxidizers to break the fluid at all. This is caused by the absorption and consumption of oxidizer by the resin itself. Significant quantities of oxidizer arc consumed in this way and this requires that breaker concentrations be increased as resin-coated proppants is ramped during the job. However, the advent of enzyme breakers may bypass these limits through a completely different breaking mechanism.

5.1.2 Selection Guildelines for Enzyme breakers

For years, enzyme breaker systems appear to provide a ready solution for low-temperature
situations. A common hemicellulase type enzyme that will degrade guar polymer is active at room temperature. Hemicellulase enzyme breakers do not have the same temperature requirements that persulfate breakers do, but enzyme breakers do have specific temperature and pH requirements. Through the process of evolution, enzymes have an optimum temperature value and pH at which they will function best. Many enzymes, including hemicellulase type enzymes, will function over a fairly narrow range of temperature and pH values. When temperature is exceeded, the enzyme rotates to another shape, and its ability to catalyze gel breaking is destroyed. At this point, the enzyme is deactivated. Sometimes when the temperature is lowered, enzymes return to the required configuration for activity. At other times, however, the enzyme does not regain activity because it is permanently denatured. Research has shown that the half-life of hemicellulase enzyme is less than 30 minutes at 130 F, and become denatured at approximately 150 F (Figure 5-3). On the other hand, As pH values increase between 8 and 10, the time an enzyme can tolerate high temperatures shortens. Most enzymes, including hemicellulase, do not function above pH 10 and 11. In a word, the combination of fluid pH and fluid temperature is significant to the performance of the enzyme breaker.

A detail example of hemicellulase enzymes are discussed here (Laramay, S.B.1992). Laboratary test results indicated the optimum pH is between 4.5 and 5, and the enzyme activity drops readily as the pH increases to 9.5 where no activity exist (Figure 5-4). On the other hand, Hemicellulase is stable in solution up to 120 F, but the activity drops off readily with increasing temperature (Figure 5-5).



Figure 5-3 Denaturization of Hemicellulase Enzyme in pH 7 Solution (Norman, L. R., 2005)



Figure 5- 4 Hemicellulase Activity as a Function of pH (Laramay, S.B.1992)



Figure 5-5 Hemicellulase Activity as a Function of Temperature at pH 4.8 (Laramay, S.B.1992)

Figure 5-6 shows the activity of liquid hemicellulase enzyme on a 100 ppt HPG fluid at various fluid pH values. At elevated pH values, the enzyme has little activity at 77 $\,$ F and has become deactivated but not denatured. After 2 hours at 77 $\,$ F and a fluid pH of 10, activity of this enzyme breaker can be reinitiated by lowering fluid pH to neutral (Figure 5-7). After 2 hours at 120 $\,$ C and a fluid pH of 10, activity of this enzyme breaker cannot be reinitiated by lowering fluid pH to neutral. In this case, the enzyme breaker has been denatured and will never regain breaker activity. At lower temperatures, hemicellulase enzymes can be denatured by exposure to high pH.



Figure 5- 6 Effect of fluid pH on activity of a liquid hemicellulase breaker at a temperature of 77 F (R. J. Powell, 1999)



Figure 5-7 Effect of fluid pH on activity of a liquid hemicellulase breaker at a temperature of 77 F, Fluid pH adjusted to 7 after two hours (R. J. Powell, 1999)

It should be noted that, although not significant, certain minerals present in the fracturing fluid will affect the efficiency of enzyme breakers. There were core-flow studies indicated that enzyme solution is more effective than the oxidizing breakers in the low levels of Berea or Silica. However, enzyme activity is very sensitive to kaolinite, bentonite and high levels of Berea (Table 5-2), which is another important factor to consider during the enzyme breaker selection (E.I. Park, 2001).

	· · ·		-
Brooker	Kaolinite	Berea	Bentonite
DIEakei	(0.02 lb)	(0.09 lb)	(0.02 lb)
Ensyme	200	35	235
(Hemicellulase)	200		

 Table 5- 2 Static Gel Viscosity (cp) Tests for Ensyme Breaker*

*Usually gel viscosity less than 10cp is concidered as "broken"

New enzymes are being discovered on a routine basis. Over the past decades, new guar linkage-specific enzyme complex were extensively evaluated for their ability to degrade guar polymers in harsh environments typical of moderate to high temperature fracturing applications. Some of them were found to have extended stability for high temperature and pH situations. The preferred enzymes are called galactomannanase and, according to some study results, it has been successfully applied in several high temperature fracturing applications up to 300 F, with both low and high pH fluids, with both CMHPG and guar-based fluids (Figure 5-8).



Figure 5-8 Viscosity Profiles of New Guar Linkage-Specific Enzyme Product at Various Conditions (H.D. Brannon,1996)

Another advantage for guar linkage- specific enzyme, galactomannanase, is that it directly hits the alpha and beta linkage therefore it enhances the degradation efficiency and causes fewer residues. However, such applications for enzyme breakers are still controversial till today since others still maintain that most enzymes currently and commercially available for use in fracturing fluids have upper temperature limits for application and that oxidizing agents remain the breakers of choice for high temperature breakdown, although they do acknowledge the existence of enzymes for harsh environment survival. No matter how the industry perceives the enzyme breakers, efforts to study them are very important since their development will eventually enhance overall fracturing gel breakdown. By then, their further recognition will be earned.

5.1.3 Selection Guildelines for Acid Breakers

The stability of a guar or derivatized guar polymer is a function of pH and oxygen concentration of the water. When oxygen effects are removed by adding the gel stabilizers, viscosity is reduced faster at lower pH and at higher temperatures. Use of acid breaker with retarded release method for guar polymers and derivatives is limited to temperatures above 250 F. Between 150 F and 250 F, fluids may be adequately stable at all pH values greater than 5. To obtain an acid break, fluid pH values are reduced to below 5. Guar polymer and derivatives (HPG, CMHPG) become very unstable at all temperatures when the pH is below 5 (Figure 5-9). However, large amounts of acid are required to drop fluid pH values this low and also to overcome formation buffer effects. Commercially, delayed - release may also be useful with enzyme breakers for temperatures lower than 150 F. As noted above, at low temperatures, the use of enzymes in borate crosslinked fluids is often effective. To allow the enzyme to be effective in the pH 9 to 11 in borate fluid, delayed-release acids can be used to lower the fluid pH value to a range where the enzymes are effective. However, acid along is not used as a guar polymer breaker very often because of cost, poor break rate control, chemical compatibility difficulties, and corrosion of metal goods. What is worse, the formation may act as a buffer with acid. A small

amount of acid introduced as a breaker may be totally consumed by the formation water and minerals. This absorption could quickly change the pH of the fracturing fluid to a point where breaking may not occur. Most formation brines have a pH between 6 and 8. Fluid pH values change to the formation pH value when fracturing fluids contact the formation.



Figure 5-9 Borate Fluid Viscosity with Various Final pH Using 30 to 35 ppt HPG at the temperatures of 125 to 175 F (Norman, 1998)

As a final point, it should be also noted that dissolved oxygen in the fracturing fluid and free radicals caused by thermal degradation of the fluid components can also act as breakers at high temperature (above 275°F). While such mechanisms are inadequate to completely degrade the fluid for clean-up purposes, they may compromise its viscosity during the pumping time. Figure 5-10 shows the test results by Michael Walker, that even medium oxygen concentration in fracture fluid may cause fluid viscosity reduction to 30% within 2 hours. In order to reduce such effects, high temperature fracturing fluids normally contain stabilizers with pump times in excess of one hour. Commonly, gel stabilizers are added at 5 to 20 pptg of fracturing fluid. The most

common of these are methanol and sodium thiosulfate which act as oxygen, or free-radical scavengers. What is more, as means of remediation, there were studies (R. Dusterhoft, 1998) indicated the delay-release breakers technologies such as encapsulation combined with gel stabilizers make it possible that oxidizers can be utilized at high temperature up to 350 °F to greatly enhance the fracture conductivity (Figure5-11). However the use of high-temperature oxidizing breakers is still controversial today due to complex chemical combination and difficult reaction rate control.

All in all, for each fracturing job design, breaker selection is a task that needs meticulous and all-around consideration according to their own advantages and drawbacks for different applications. Table 5-3 is the summarization of what needs to be taken into account for any breaker selection. Figure 5-12 is the flow chart for the entire selection process.



Figure 5-10 Effect of oxygen concentration on gel viscosity (Michael Walker, 1995)



Figure 5- 11Comparison of Fracture Conductivity for Fluids with and without using high-temperature oxidizing breakers at 350 °F (R. Dusterhoft,1998)

Breaker Types	Typical Chemicals	Applications		
Oxidizers	Persulfate (S ₂ O ₈ ^{2–})	Excellent breaker below 200 F; Need activator when temp under 125 F; pH 7-12, Sensitive to high salinity and certain types of mineral. High solubility in water.		
	Peroxide ([O-O] ²⁻)	Best performance between 200 °F and 240 °F; Excellent breaker for high- permeability formations; pH 7-12, Fresh-water based fluid. Low solubility in water. Slower reaction time.		
	Bromate (BrO ₃ ⁻)	High temperature conditions (above 200 °F) ; Excellent breaker for degrading high pH borate gels at different polymer loading; Sensitive to high salinity.		
Enzymes	Hemicellulase & Cellulase	Environmental friendly; Irreversible if denatured. Sensitive to pH and Temp; Have to be below	Best performance at 90 ° and in pH 4 fluid. Mor residue due to unspecifi mixture ratio. Sensitive t minerals such as Kaolinite Bentonite and Berea.	
	Galactomannanase	150 °F and pH lower than 8.	Highly polymer linkage-specific; Less residue after break owe to directly polymer attack.	
Acid	Chlorous acid & Chlorous salts & Inorganic acid	Delay-released when use along to revert the crosslinking; Limited to temp above 250°F; Better to use with oxygen effects removed; Desirable accompany with enzymes for low-temp condition, usually large amounts are required.		

Table 5-3 Summarization of Breaker Selection Guidelines



Figure 5-12 Breaker Selection Flow Chart for Tight Gas Reservoir

*All breakers are encapsulated

1:H&C is Hemicellulase & Cellulase. 2:Galato is Galactomannanase. 3:Combine with acid to control the pH of fracturing fluid and flow back fluid

5.1.4 Application of Encapsulated Breakers

As noted in Chapter 4, Among all proposed mechanisms of how the breaker is released from the coating, release of the payload through particle crush and rupture of the coating upon fracture closure is the predominantly one. Previous studied indicated that a minimum point stress of 1000 psi is generally reported as requisite for crushing the particle. In situations such as shallow reservoirs with low overburden pressures, or soft rock susceptible to embedment, the 1000 psi point-to-point stress on the particle may not be experienced upon fracture closure (Phil Rae, 1996). Additionally, the particle size of the encapsulated particle must be greater than the median proppant particle size for crush to occur. Otherwise, the encapsulated breaker particle will be lost in the interstitial spaces between proppant particles and hence, will not experience point-to-point stress. Thus, the application of 20/40 mesh encapsulated breaker would not appear to be appropriate when using proppants sized larger than 20 mesh. The smaller 100 mesh particle is unlikely to experience release through crush unless applied with 100 mesh or smaller proppants.

Another main concern relate to the application of encapsulated breakers in hydraulic fracturing treatments is the premature release of the breaker payload. Previous investigations identified two pre-release modes: mechanic release and hydrostatic release. Mechanical release could occur due to product manufacturing imperfections or coating damage resulting from abrasion experienced in pumping the particle through surface equipment, tubulars, and perforations. Studies show that the application of encapsulated breakers has to tolerant a certain amount of premature breaker leakage from the capsule

damage no more than 5% of the whole payload in the fluid. For example, if 1ppt encapsulated ammonium persulfate breakers are used, then less than 0.05ppt breaker would leak (HD Brannon, 1994). However, with the development of technology in future, it is positive that this premature leakage concern will be healed and the application range for encapsulated breakers will be dramatically enhanced.

Hydrostatic release occurs after the breaker particles are added to water. The chemical breaker leaks through coating imperfections at low hydrostatic pressure. The release rate is a strong function of hydrostatic pressure and temperature. It decreases with increasing hydrostatic pressure, but increases with increasing temperature. Researches (Matthew J. Miller 2002) on hydrostatic release tests noted that, increasing hydrostatic pressure reduced the encapsulated ammonium persulfate release rate at 175 F and above. The ammonium persulfate releases at 175 F after 2 hours for 0 psig, is 35%. Under the hydrostatic pressure of 500 psig, the release percentage is 19%. Under 2000 psig and 8000 psig, release percentage are only 8% and 7%, respectively. After 4 hours, the releases for these pressures are 78%, 66%, 33% and 12%. At 225 F, the hydrostatic pressure impact is more significant at earlier time. The releases are 62%, 40% and 12% at 500 psig, 2000 psig and 8000 psig after 60 minutes (Figure 5-13.). On the other hand, at 2000 psig, higher temperature releases curves depart earlier than the lower ones (Figure 5-14). Both scenarios indicate the release rate release rate increases with increasing temperature and decreasing pressure. These release percentage profiles are important tools to optimize the breaker schedule. They quickly point out the breaker pre-release amount which is the key parameter to calculate the maximum allowable breaker concentration. The method for this calculation will be discussed in the coming sections.



Figure 5- 13 Hydrostatic release of Encapsulated Ammonium Persulfate at 175 F (Matthew J. Miller 2002)



Figure 5-14 Hydrostatic release of Encapsulated Ammonium Persulfate at 2000psig

5.2 Optimization of Breaker Schedule during Fracturing

In reducing the viscosity of the fracturing fluid to a near water-thin state, the breaker must maintain a critical balance. Premature reduction of viscosity during the pumping of a fracturing treatment can

jeopardize the treatment. Inadequate reduction of fluid viscosity after pumping can also reduce production if the required conductivity is not obtained. Therefore, the criteria of breaker optimization can be generally considered as:

- Breaker influence on proppant transport.
- Breaker influence on fracture conductivity.

5.2.1 Breaker Optimization on Proppant Transport

As noted above, the breaker must maintain a critical balance in reducing the viscosity of fracturing fluid, to transport enough proppant into the fracture. Viscosity profiles with related release rates data of breakers and other additives can be used to design the fluid system for a particular application. Obtaining the viscosity profile of a fluid containing breaker is desirable not only to show the fluid breaks but also to confirm that viscosity loss did not occur too rapidly. Figure 5-15 shows three hypothetical break profiles of a fracturing fluid viscosity. The ideal viscosity (curve 1) versus time profile would be if a fluid maintained 100% viscosity until the fracture closed on proppant and then immediately broke to a thin fluid. With different breaker concentration, a more realistic viscosity profile is one similar to curve 3 for fluids containing most soluble breaker chemicals. This breaker design is usually considered as unacceptable since the fluid capability of transporting proppant is jeopardized at the beginning of pumping, resulting in a less than desirable fracture length in the fracture being created. Comparatively, curve 2 is an acceptable option since at least 50% of the fluid viscosity still maintains at the end of the pumping time. This criterion may be adjusted according to job time, desired fracture length, and required fluid viscosity at reservoir temperature. For example, curve 2 would be suitable for a 2-hr pump time.



Figure 5-15 Comparative Viscosity Profile

5.2.2 Breaker Optimization on fracture conductivity

Optimally, the fracturing gel will begin to break when the pumping operations are concluded. For practical purpose, the gel should be completely broken within a specific period of time after completion of the fracturing period. However, delayed break can cause slow recovery of the fracturing fluid from the produced fracture with attendant delay in resuming the production of formation fluids. The gel residue will clog the channels of newly formed fracture and seriously impaired the fracture conductivity.

Usually, conductivity test is an important tool in laboratory for breaker design, including leaking-off fracturing fluid through two core faces and then placing proppant between these cores and applying appropriate closure stress and temperature. After the desired breaking time, the tester flows water, gas, or oil through the proppant. The regained conductivity of the proppant is measured and compared to a similar system. The amount of damage caused by the gel residue depends on the gel type, breaker type, breaker type, breaker concentration, temperature, and many other factors. Compared to clean sand, regained

conductivity may vary from 10 to 90 percent.

Dynamic and static core flow test is a tool used in the laboratory to analyze the mineral components that sensitive to breakers. As noted above, activity of some breakers is strongly dependent on the type of minerals present. To avoid the breaking efficiency reduction due to such interaction, studies (E.I. Park, 2001) indicate that additional benefit can be gained through the use of higher concentrated breakers to offset the breaker consumption by interacting with formation minerals.

Flow back test is usually performed as field results for subsequent breaker designs. When a fracturing treatment is completed, if most of the load water and gel are recovered, the breaking is considered successful. Usually, however, much less than 100% of gel and load water is recovered, and the well flowback rate or flowback efficiency may reflect a breaking problem. Recovering thick, crosslinked fluid or low flowback efficiency from a well indicates a breaking problem.

5.2.3 Optimal Breaker Concentration

Based on all the viscosity data, determine the optimal breaker concentration probably is an important step of entire breaker design. Investigations in recent years indicate that normal breaker concentration is insignificant in reducing the polymer damage in the part of the fracture near the tip to allow it to adversely affect the production. Therefore, higher breaker concentrations are needed for more thorough polymeric damage removal. Figure 5-16 illustrates how increasing the breaker concentration increases the percentage of original sand pack permeability remaining after exposure to the fracturing fluid. In the past, unfortunately, the high concentrations effective for damage removal cause fluid viscosity to decline much too rapidly during pumping. With the application of breaker encapsulation, concentrations of breaker of up to 10 lb/1,000 gal, which is three to five times the normal concentration, were added to fluids without causing premature loss of viscosity. However, as discussed previously, the coating is not perfectly impermeable. The breaker material can release through the coating under certain conditions when placed in an aqueous environment, which suggests the abnormally high concentration may still cause the premature fluid viscosity reduction. Therefore, breaker concentration optimization is needed as a critical step for the entire design procedure.



Figure 5- 16 Effect of breaker/polymer ratio on retained permeability (Northern White Sand, 20/40-mesh, 2 lb/ft², 160 F; 3,000 psi; 17 hr shut-in), (H.D. Brannon,1990)

The optimal breaker concentration is actually a compromise between the most cost effective breaker concentration and the most allowable breaker concentration. The maximum allowable breaker concentration is the concentration at which hydrostatic release reduces the fluid viscosity to the minimum allowable for successful proppant placement, which can be observed through proppant suspension test. A tester can mix the fracturing fluid and desired concentration of proppant to estimate proppant transport. If a fluid will not support proppant when static, one could predict that under shear, proppant transport will be less than ideal since most crosslinked fracturing fluids are shear-thinning, which means they are at their highest viscosity when static.

It should be noted that the test conditions are usually low-pressure environment, which do not represent the actual breaker performance under downhole conditions. As discussed in section 5.1.4, breaker designs based on room condition tests results underuse the breakers and need to be converted to the reservoir conditions. According to the correlations developed by Matthew Miller (2002), the downhole encapsulated breaker concentration, C_{DH} , can be expressed as

$$C_{DH} = C_{test} \times \frac{Hydrostatic Release at Test Pressure}{Total Release during Treatment}$$
(1)

Where C_{test} is the breaker concentration at test condition, and the *Total Release during Treatment* is the sum of the amount of encapsulated breaker downhole pressure hydrostatic release and the mechanical release which accounts for 5% on average.

5.2.4 Procedure for Optimization

To apply every criterion documented above, and to summarize the optimal breaker design, a step-by-step procedure example for the one stage of treatment is discussed here:

 Design fracture treatment. Total pump time is 55 minutes and bottomhole temperature is 180 F, with 2000psi treating pressure for this stage.

- Use the breaker selection flow chart given in 5.2 to choose the type of breaker, here we select Encapsulated Sodium Persulfate and the core flow test show there is no considerable amount of mineral from the formation rock.
- 3. Determining a minimum viscosity for the fracturing fluid necessary to maintain the proppant in suspension in the gelled fracturing fluid during an elapsed pumping time. The proppant suspension test with the given proppant and polymer concentration for this stage shows that the lowest acceptable viscosity is 100cp at 100 s⁻¹.
- 4. Perform rheology tests to obtain viscosity profiles, determine the maximum allowable concentration at test condition. Figure5-17 indicates the maximum concentration for this stage is 0.5lb/1000gal.



Figure 5- 17 Viscosity profiles at 180 F and 14.7psi with different concentrations of Encapsulated Sodium Persulfate

5. Consider the pre-release factor of encapsulated breakers. Figure 5-18 shows the hydrostatic release amount for Encapsulated Sodium Persulfate at 180 F and 14.7psi is 80% of the entire payload, while under downhole treating pressure, the hydrostatic release amount is only 8%.



Figure 5-18 Hydrostatic release rate of Encapsulated Sodium Persulfate at 180 F

Additionally, there is 5% average pre-release amount due to the manufacturing imperfection of encapsulation material that needs to be taken into consideration. Hence, the actual maximum allowable breaker concentration at the downhole condition is

$$C_{DH} = C_{test} \times \frac{Hydrostatic Release at Test Pressure}{Total Release during Treatment}$$
$$= 0.5 \times \frac{80\%}{8\% + 5\%} = 4 \text{ lb}/1000\text{ gal}$$

This process should be applied to each stage of the job to achieve the optimal breaker schedule.

5.3 Remediation of Gel Damage in Producing Wells

The inadequate degradation of polymers used in hydraulic fracturing fluids may lead to significant decrease in well productivity from polymeric damage to proppant pack conductivity. The polymers used to create the gelled fracturing fluids are far too large to leak off into the rock matrix of most low permeability reservoir rocks. Results of various laboratory studies which evaluate the unbroken gel cause the flow impairment in porous media have been reported. Brannon observed that the polymers are first deposited on the fracture faces as a gelled filter cake. As fluid leak-off continues, the polymer concentration within the fracture steadily increases. At last during the fracture closure, all of the polymers used to viscose the fracturing fluid are concentrated to fill the pore spaces of the proppant pack. For many producing tight gas wells, reservoir conditions and hydraulic fracture design considerations often limit the addition of sufficient breakers to degrade the gel. Furthermore, the mechanical malfunction, chemical product failure and human errors can lead to insufficient breaker addition, resulting in the inadequate polymer degradation. For example, a case study was conducted on a Canyon Sand gas well in Crockett County, Texas (Brannon, 1995). The post treatment evaluation indicated that the breaker solution for original fracturing job had been mixed several days before the treatment due to a job delay and was likely self degraded already. The load recovery was significant less than normally experienced for the offset well. The stabilized production rate was 85Mcfpd, which was about half the average of 160Mcfpd observed from the offset well. The presence of highly concentrated polymer was observed through the produced water sample analysis, indicating inadequate polymer degradation due to insufficient breaker

addition.

However, one needs to understand that there are many reasons other than polymeric damage which can cause and contribute to the reduced well productivity. The success of breaker-based remedial treatment to remove the concentrated polymer damage will not be implemented if the primary impediment to production is something other than insufficient degraded polymer. Therefore, before making any decision on remediation, one should first quantify the reasonable production expectations for fractured reservoir based on the well logs, experience with similarly stimulated offset wells and establish the evaluation of pre-and-post stimulation productivity. Also, the original fracturing treatment design and execution need to be evaluated to identify any other potential causes of the inadequate well performance. Furthermore, laboratory tests of flowback sampled are important to identify if there is highly concentrated gel damage to proppant pack conductivity. Once these factors have been considered, a knowledgeable decision can be developed as to if polymeric damage is the key impediment to optimum well productivity.

5.3.1 Options for Gel Damage Remediation Treatment

If the gel damage is verified to be the primary factor that leads to fracture conductivity damage and unsatisfactory well performances, engineers must then design a remediation solution. Methods of remediation include restimulating the reservoir by refracturing, or perform a breaker injection treatment. However, depending on the reservoir characteristics, the size of the original fracture stimulation placed and the specifics of the treatment inadequacy, a refracture operation may not be applicable. Furthermore, a refracture treatment will be costly.

Another option, on the other hand, is to perform a breaker injection treatment to promote gel degradation filled in the pore space of proppant pack and improve fracture conductivity. Utilizing gel breaker typically results in fracture conductivity improvement to the range of 40% to 60% of the undamaged baseline value (Brannon, 1995). Meanwhile, the treatment is the most cost-effective method to remove the polymeric damage from the existing propped fracture and subsequently enhance the productivity. Out of these advantages, Gel breaker solution injection appears to be the most attractive remediation option.

5.3.2 Remediation Treatment Design

Successful application of the breaker injection remedial treatment is based on optimized breaker selection and breaker concentration.

Breaker selection for remedial treatment fluid is identical to the selection process for new fracture treatment design, which has been discussed in the section 5.1. Engineers should follow the given selection guidelines and flow chart according to the data such as bottom hole static temperature, pH value of both fracturing fluid and flow back fluid, and then determine the right breaker type for the job, which is the first key step of treatment design.

Determine the breaker concentration for remedial treatment fluid after breaker type selection is critical. Compared to breaker concentration design for new hydraulic fracture jobs, breaker concentration for remediation treatment needs no concern of jeopardizing fluid viscosity and proppant transportation capability since the remedial treatment fluid is simply breaker chemical solution with no polymer and crosslinking agent. Therefore, the only purpose is to guarantee that breaker concentration will be high enough to degrade the polymer left in proppant pack. Obviously, in order to quantify the breaker concentration, polymer concentration in the proppant pack is the most important parameter needs to be determined first.

The correlation of polymeric gelling agents becoming concentrated within the pore volume of proppant pack was first introduced by Cooke. Assuming that all polymer remains within the proppant pack, polymer concentration factors after fracture closure can be calculated from the pore volume.

$$\frac{1}{V_{P/L}} = \frac{\rho_s}{c_s} \times \frac{1-\phi}{\phi} \tag{2}$$

Where, $\frac{1}{V_{P/L}}$ = polymer concentration factor, dimensionless.

 ρ s = proppant density, lbs/gal.

C s = proppant concentration in fluid, lbs/gal added.

 \emptyset = proppant pack porosity, percent.

The final polymer concentration can then be calculated by multiplying the initial polymer concentration by the polymer concentration factor. Concentrations of polymer deposition can range from about 10 to greater than 25 times the surface polymer concentration according to this correlation:

$$C_{p} = \frac{1}{V_{P/L}} \times C_{pi}$$
(3)

Where, $C_p = final polymer concentration$

C_{pi} = initial polymer concentration

The plots of polymer concentration factor versus proppant concentration from the equation (1) can be obtained and used as a quick tool to estimate final polymer concentration. Figure 5-19 shows the polymer concentration factor as a function of proppant concentration for proppant pack porosity of 30%, 33.5%, and 37%. These plots points out that the polymer concentration at the end of most fracture treatments may easily approach 400 to 500 lb/1000gal and may exceed 1000 lb/1000gal.



Figure 5- 19 Effect of proppant concentration and porosity on the final polymer concentration (H.D. Brannon, 1990)

After the final polymer concentration is calculated, the retained proppant pack permeability improvement achieved through the addition of breaker at different concentration ratio with final polymer

concentration (C_{BP}) is needed for further calculation. This improvement trend can be obtained and plotted by performing fracture conductivity test (Figure 5-20). These data, used in conjecture with those in Figure 5-19, can be used to determine the breaker concentration required to achieve an improved proppant pack permeability for a given polymer concentration. A step-by-step example is discussed below to demonstrate how to quantify breaker concentration.



Figure 5- 20 Effect of Ammonium Persulfate (APS) breaker concentration to polymer concentration ratio on the retained proppant pack permeability (Joe Small, 1991)

Assume one wishes to design remedial treatment to enhance the retained proppant pack permeability percentage to 50%; the bottom hole static temperature is 160 F; the proppant pack porosity is 35%; in the original fracture design, the proppant concentration is 4 lbs/gal, the proppant density is 15.6 lbs/gal, 20/40 mesh sand; and the initial polymer concentration is 20 lbs/1000gal guar.

- Determine breaker type. According to the breaker selection guidelines and flow chart, persulfate salt is the best breaker type for the treatment.
- Determine polymer concentration factor. Using equation (2), plot the polymer concentration factor versus proppant concentration, shown in Figure 5-21, for the proppant pack porosity of 35%, polymer concentration factor is found to be 12 for proppant concentration of 4 lbs/gal.



Figure 5-21 Effect of proppant concentration and porosity on the final polymer concentration

3. Determine the final polymer concentration. Using equation (3), final polymer concentration after the fracture closure is

$$C_{p} = \frac{1}{V_{P/L}} \times C_{pi}$$

$$= 9.5 \times 20$$
 lbs/1000gal

4. Conduct fracture conductivity test, obtain the retained proppant pack permeability improvement at different breaker concentration ratio with final polymer concentration, shown in Figure 5-22, at 160 F, 1.8 lbs Ammonium Persulfate breaker per 100lbs polymer (C_{BP}) are required to achieve a 50% retained proppant pack permeability.



Figure 5- 22 Effect of Ammonium Persulfate (APS) breaker concentration to polymer concentration ratio on the retained proppant pack permeability (H.D. Brannon, 1990)

5. Calculate the breaker concentration for remedial treatment fluid. Here, Ammonium Persulfate

breaker concentration can be calculated as

$$C_{APS} = C_{BP} \times C_{p}$$

= 1.8 lbs/100lbs × 190 lbs/1000gal
= 3.4 lbs/1000gal

Therefore, an Ammonium Persulfate breaker concentration of 3.4 lbs/1000gal would need to enhance the permeability percentage to 50%.

5.3.3 Other Remediation Treatment Design Considerations

Apart from the breaker selection and quantify breaker concentration, there are several other points need to be considered for the treatment design to reach the maximum remediation result.

A treatment volume of at least twice the proppant pack pore volume is recommended to achieve maximum coverage of the fracture area and contact as much of the offending damage as possible. Less treatment volume is unlikely to contact damage in the distant regions of the fracture due to fluid loss to the formation. The proppant pack pore volume can be calculated by multiplying the bulk proppant volume placed by the estimated proppant pack porosity \emptyset .

Encapsulation is also needed to control the gel degradation rate so as to achieve maximum remediation fluid penetration and contact as much of polymers as possible. If no delay release method adopted, breaker will first directly contact and degrade the near wellbore polymeric filter cake on the formation and therefore, uncontrolled fluid leakoff may arise, resulting in less treatment volume for remediation.

Furthermore, the injection pressure should not exceed the fracture opening pressure. Otherwise the proppant could be displaced out of well bore. However, the injection rate should be the maximum within the pressure limitations to facilitate fluid penetration down the length of the fracture.

Last but not least, The addition of fluid additives including surfactants, non-emulsifies and pH adjusting buffers should be considered to facilitate load recovery if necessary. Especially a surfactant preflush is recommended to remove oil from the surface of polymeric filter cake and the gel left in the proppant pack, to allow better contact with the remedial treatment fluid.

Chpter 6

Case Studies

The most important results often can be observed from analysis of treatment case histories. Two Hosston formation gas wells which were drilled in northern Louisiana are studied and compared with various breaker selection and schedule design. Through a series of analysis, the impact of breaker performances is found to be quite obvious on the gas production and proppant pack conductivity. Table 6-1 lists the reservoir parameters used in this study, which were partially provided by engineers and geologists at Sklar Exploration Company.

Well Name	RHT #1	JCM #1
Formation Name	Hosston	Hosston
Well Type	Gas	Gas
Rock Type	Sandstone	Sandstone
Formation Permeability, k, md	0.105	0.105
Formation Porosity, ø, f	0.19	0.17
Formation Thickness, h, ft	18	15
Reservoir Temperature, T, $^{\circ}F$	204	210
Reservoir Pressure, p, psi	2,685	3,126
Total System Compressibility, c, psi ⁻¹	2.48×10^{-4}	2.1×10 ⁻⁴
Initial Gas Viscosity, µ, cp	0.0172	0.0179

Table 6-	1	Reservoir	Parameters
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6.1 Review of Fracture Treatment Design

Initial comparisons are made on the fracture treatment of these two wells. Although the polymer, crosslinking agent, proppant and other additives utilized are basically same since both stimulation jobs were conducted by one services company, the concentrations for each of them are quite different. RHT #1 was stimulated with 145,656 gallons of a CMHPG-borate fracturing fluid, with perforated interval from 7272 to 7576. 275,000 pounds of 20/40 White sand were placed into fracture under 3300 psi average treating pressure. On the other hand, JCM #1 was treated with the same fracturing fluid as RHT #1, perforated interval from 7212 to 7277. 166,700 pounds of 20/40 White sand blended in 64,000 gallons fluid were pumped into the fracture under 2930 psi treating pressure. Specific fluid data and components for both wells are listed in Table 6-2, and their schedules with different job stages are shown in Table 6-3 and Figure 6-1 through 6-2, from which it is easy to find that only on polymer schedule RHT #1 is more aggressive than JCM #1.

	Component			
Additive	RHT #1	JCM #1		
Polymer	CMHPG	CMHPG		
Fracture fluid Volume, gal	145,656	64,000		
Crosslinker	Borate	Borate		
Proppant	White Sand, 20/40	White Sand, 20/40		
Proppant total amount, lbs	275,000	166,700		
Clay Stabilizer	7.5% KCl at at 1 gpt	2% KCl at 1 gpt		
Surfactant	Nonionic Fluoro-Surface	Nonionic Fluoro-Surface		
	Tension Reducer	Tension Reducer		
Duffor	Potassium Carbonate	Potassium Carbonate		
Duller	(pH 9.5-11.5)	(pH 9.5-11.5)		

Table 6-2 Fluid Specifications for RHT #1 and JCM #1

Additive	Pumping Schedule			
	Stage	RHT #1	JCM #1	
Polymer	Prepad	6 gpt	N/A	
	Pad	14 gpt	7.5 gpt	
	Proppant Laden	11 gpt	6.5 gpt	
	Flush	10 gpt	17 gpt	
Crosslinker	Pad	1.25 gpt	1.5 gpt	
	Proppant Laden	1.25 gpt	1.7 gpt	
Proppant	Proppant Laden	2.8 ppg	3.2 ppg	
Clay Stabilizer	All	1 gpt	1 gpt	
Surfactant	Pad	1 gpt	4.9 gpt	
	Proppant Laden	1 gpt	0.5 gpt	
Buffer	Pad	1 gpt	3.8 gpt	
	Proppant Laden	1.5 gpt	1.4 gpt	

 Table 6- 3 Fracture fluid pumping schedules



Figure 6-1 Pumping schedule of polymer, crosslinker and buffer, for RHT #1



Figure 6-2 Pumping schedule of surfactant and clay stabilizer, for RHT #1



Figure 6- 3 Pumping schedule of polymer, crosslinker and clay stabilizer, for JCM #1



Figure 6- 4 Pumping schedule of surfactant and buffer, for JCM #1



Figure 6- 5 Proppant Concentration in Fracture Fluid of RTH #1 and JCM #1
6.2 Review of Breaker Schedule Design

Various breakers were selected with different concentrations for RHT #1 and JCM #1, which became the primary reason for breaker performances discrepancy and correspondingly, led to difference in production performances.

RHT #1 selected the encapsulated calcium peroxide and pumped 320 pounds into the fracture under 204°F BHT, combined with 62 pounds of non-encapsulated guar-derivative specific enzyme. Fracture fluid sample analysis showed that the pH of the fluid was maintained between 7.22 and 8 throughout the entire treatment. Clay control agent and 7.5% KCl and HCl solution were prepared and added into the fluid. Surfactant and buffer were both added with different concentrations (Table 6-3)

JCM #1 utilized non-encapsulated guar-derivative specific enzyme as main breaker under 210°F BHT, and ammonium persulfate was also pumped 10 minutes before the flush stage. Fracture fluid pH was maintained as 11 throughout the entire job. 2% KCl solution was also added into the fluid. The detailed comparison for breaker selection and fluid preparation of RHT #1 and JCM #1 are listed in Table 6-4.

Various breaker concentrations were scheduled throughout the entire fracture job of RHT #1 to achieve breaker homogeneous distribution. 0.25 lbs/1000gal breaker were pumped in the prepad stage, then started from 0.5 lbs/1000 gal in pad stage. When the proppant laden began, breaker concentration proportionally increased to 4 lbs/1000gal, and then reached to peak of 6 lbs/1000gal before flush stage started. Enzyme agents were added at 15 gal/1000gal in average at the very beginning of prepad stage to

let them work afterwards (Figure 6-6).

Relatively low and constant breaker concentration schedule was adopted for JCM #1 to insure the fracture fluid did not prematurely lose integrity. Enzyme was added during all stages, which started pumping at 2 gal/1000gal in pad, then fell down to 0.5 gal/1000gal for slurry. In the last portion of slurry, enzyme concentration increased to 1 gal/1000gal and eventually reached to 2 gal/1000gal. Ammonium persulfate breaker was also added at 2 lbs/1000gal at the same time to enhance the fluid cleanup ability (Figure 6-7).

Well Name	RHT #1	JCM #1	
	Encapsulated Oxidative	Non-encapsulated Enzyme	
Breaker Type	(main)	(main)	
	&	&	
	Non-encapsulated Enzyme	Encapsulated Oxidative	
Essential Chemical	Calcium Peroxide (main)	CMHPG Specific Enzyme	
	&	&	
	CMHPG Specific Enzyme	Ammonium Persulfate	
Bottom Hole Temperature, °F	204	210	
Fracture Fluid pH	7.22-8	10.3-11	
Other Additives	7.5% HCl at 1 gpt	None	

 Table 6- 4 Breaker Selection and Specifications for RHT #1 and JCM #1



Elapsed Time (min)

Figure 6-6 Breaker concentration design for RHT #1



Figure 6-7 Breaker concentration design for JCM #1

6.3 Production Analysis

6.3.1 Review of production data

Figure 6-8 shows the post-fracture production rates of RHT #1 and JCM #1 in one year. During initial 60 days, performance discrepancy of two wells were slight, however, after 100 days wellhead compressor was put on RHT #1 to boost the production. Usually the wellhead compressor is used to reduce the hydrostatic pressure, by removing the casing-head gas and compressing that gas into a higher pressure flow line. The result is temporary "jump" of gas production of RHT #1, stabilized long term gas production and increased long term gas flow. Therefore the production rate of RHT #1 is pushed back to 2300 Mcf/d peak while JCM #1 still continued to decline to 580 Mcf/d after 100 days. Figure 6-9 shows the production performances over four years as of June 2012, and the difference between both wells is still obvious. This can be considered as the contribution provided by enzyme breakers, whose long term proppant pack clean-up effect demonstrated great production improvement for RHT#1. Figure 6-10 demonstrates the daily water production for both wells, which shows the RHT #1 produced more water than the JCM #1 based on daily bases. Figure 6-11 shows the Gas Water Ratio (GWR) for both wells, the JCM #1 displayed more steep decrease of GWR than RHT #1. Figure 6-12 shows the production rate vs time on log-log scale, which indicates that both RHT #1 and JCM #1 are still in transient flow regime.

The total cumulative gas production for both wells are shown in Figure 6-13. The first year cumulative production of RHT #1 has reached 433 MMcf, which was 78% higher than JCM #1, 243 MMcf. After 4years, the total cumulative production of RHT #1 peaked to 724 MMcf while JCM #1 averaged 310 MMcf. The impact of breaker designs, no matter in short or long term, demonstrated a



remarkable 134% increase in production over 4 years.

Figure 6-8 Comparison of Daily Gas Production Rate



Figure 6-9 Comparison of Long-term Daily Gas Production Rate



Figure 6-10 Comparison of Daily Water Production Rate



Figure 6- 11 Comparison of GWR



Figure 6-12 Comparison of Long-term Daily Production Rate on Log-log Scale



Figure 6-13 Comparison of Average Cumulative Gas Production

6.3.2 Type Curve Analysis

Fracture conductivity may directly reflect the long term well performances and gel degradation for RHT #1 and JCM #1. Since the variations in bottomhole flowing pressure were small, the two wells could be assumed to produce at a constant flowing bottomhole pressure for the period studied. The constant wellbore pressure type curves, developed by R.G. Agarwal (1979) for finite fracture conductivity, are used in this study (Figure6-14).



Figure 6-14 Constant pressure log-log type curves for finite fracture conductivities (R.G. Agarwal, 1979)

The reciprocal of dimensionless rate, $1/q_D$, was plotted as a function of dimensionless time, t_{Dxf} , on log-log paper with dimensionless fracture conductivity, F_{CD} , as a parameter which is defined as follows.

$$\frac{1}{q_D} = \frac{kh\Delta[m(p)]}{1424 qT}$$

It should be noted that $\Delta[m(p)]$ is the difference between the initial and flowing real gas pseudopressure, which is defined as

$$\Delta[m(p)] = \frac{\Delta(p^2)}{\mu z}$$

Where $\Delta(p^2) = \text{Reservoir Pressure}^2 - \text{Bottom Hole Flowing Pressure}^2$. The Bottom Hole Flowing

Pressure, P_{BHF}, is defined as

$$p_{BHF} = p_t + p_{hydro} + p_{fric}$$

Where pt is the tubing pressure, phydro is the hydrostatic head and pfric is tubing friction losses.

Based on the fracture half-length, x_f , the dimensionless time, t_{Dxf} is defined as follows.

$$t_{Dxf} = \frac{2.634 \times 10^{-4} kt}{\emptyset(\mu c) x_f^2}$$

Also the dimensionless fracture conductivity, F_{CD} is defined as follows.

$$F_{CD} = \frac{k_f w}{k x_f}$$

In which k_f is the fracture permeability and w is the fracture width.

To apply the type curve matching technique, 1/q vs time data are plotted on tracing paper using the log-log scale of the type curves. Main x and y axes also are drawn on the tracing paper. Such plots for RHT #1 and JCM #1, according to their performance data, are shown in Figure 6-15 and 6-16.







Figure 6- 16 Reciprocal rate vs time for JCM #1

Since the formation conductivity, kh, is known, the matching procedure is simpler and much more reliable. The tracing paper is only shifted horizontally to find a suitable match point. For RHT #1, for a value of $1/q = 10^{-3}$, the corresponding value of $1/q_D$ can be calculated:

$$\frac{1}{q_D} = \frac{kh\Delta[m(p)]}{1424\,qT} = \frac{(0.105)(18)(4.5 \times 10^8)}{(1424)(1000)(664)} = 0.9$$

Thus, the position of $1/q = 10^{-3}$ on the y axis of the tracing paper is fixed in relation to $1/q_D = 9 \times 10^{-1}$ on the y axis of the type curve graph paper. Then a match point is obtained: t = 50 days = 1200 hours, and $t_{Dxf} = 5 \times 10^{-2}$ and $F_{CD} = 5$. Fracture half length then is

$$x_f = \sqrt{\frac{(2.634 \times 10^{-4})kt}{\emptyset \mu c t_{Dxf}}}$$
$$= \sqrt{\frac{(2.634 \times 10^{-4})(0.105)(1200)}{(0.19)(0.0172)(2.48 \times 10^{-4})(5 \times 10^{-2})}}$$
$$= 905 \text{ ft}$$

Therefore the fracture conductivity can be calculated as

$$(k_f w) = F_{CD}(kx_f) = (5)(0.105)(905) = 425$$
 ft-md

The same procedures are repeated for calculating the fracture conductivity for JCM #1, for a value of

 $1/q = 10^{-3}$, the corresponding value of $1/q_D$ can be calculated:

$$\frac{1}{q_D} = \frac{kh\Delta[m(p)]}{1424\ qT} = \frac{(0.105)(15)(4.53 \times 10^8)}{(1424)(1000)(670)} = 0.8$$

Thus, the position of $1/q = 10^{-3}$ on the y axis of the tracing paper is fixed in relation to $1/q_D = 8 \times 10^{-1}$ on the y axis of the type curve graph paper. Then a match point is obtained: t = 50 days = 1200 hours, and $t_{Dxf} = 9 \times 10^{-2}$ and $F_{CD} = 1$. Fracture half length then is

$$x_f = \sqrt{\frac{(2.634 \times 10^{-4})kt}{\emptyset \mu ct_{Dxf}}} = \sqrt{\frac{(2.634 \times 10^{-4})(0.105)(1200)}{(0.17)(0.0179)(2.1 \times 10^{-4})(9 \times 10^{-2})}}$$

=898 ft

Therefore the fracture conductivity can be calculated as

$$(k_f w) = F_{CD}(kx_f) = (1)(0.105)(898) = 96$$
 ft-md

To summarize, the fracture half length of RH T #1 is 905 ft with 425 ft-md fracture conductivity, while fracture half length of JCM #1 it is 898 ft with 96 ft-md fracture conductivity. It is quite obvious that RHT #1 is much more satisfied than JCM #1 in fracture propagation and gel degradation.

6.3.3 Quantification of gel damage

Gel damage type curves are generated to identify and quantify the gel damage of both wells well using a fracture damage analysis model. Reservoir, fracture treatment, and production data of RHT #1 and JCM #1 are inputted to generate their own dimensionless cumulative production curves, which are compared to the type curves of gel damage, from no damage to severe damage. Figure 6-16 shows that the damage level of RHT #1 is between no damage and slight damage for a long time owe to proper breaker schedule and relatively complete gel degradation. RHT #1 becomes a slightly damaged well at 1200 days, and is still just a slight damage well at the end of production period (Figure 6-17). On the other hand, JCM #1 begins with very clean proppant pack, however, as fracture fluid begin to leak off to formation, and the non encapsulated enzyme breaker are unable to perform normally due to high fluid temperature, unbroken gel residue accumulate in fracture and fill the pore space and channels in the proppant pack. Therefore the fracture damage on proppant pack conductivity starts soon and aggravate swiftly. After 350 days, JCM #1 becomes a slightly damaged well, and after 570 days it is a medium damaged well. Finally, after 1360 days, at the end of the production period, JCM #1 becomes a severely damaged well (Figure 6-18).



Figure 6- 17 Gel damage identification for RHT #1(PSUWELL v1.5)



Figure 6- 18 Gel damage identification for JCM #1 (PSUWELL v1.5)

6.4 Breaker Schedule Analysis and Suggestions

Based on the breaker selection flow chart developed in Chapter 4, the calcium peroxide is a good choice for RHT #1 since the formation temperature is 204 °F. The encapsulation prevents the pre-mature fracture fluid viscosity degradation from happening. Plus the 7.5% HCl solution were added, not only to maintain proper fluid pH at 8 in average, but also to react with peroxide, which may be decomposed to form hydrogen peroxide to initiate the oxidizing process. All of these considerations maximize breaker

performances. Additionally, the combination with non-encapsulated enzyme is a thoughtful patch, which may provide long-term cleanup after the stimulation treatment since wherever the polymer particle travels, enzymatic agent will seek to attach to it until the polymer particle can be completely degraded. During pumping, the enzyme activities will be dropped off due to the high formation temperature of 204 °F. However, as production goes on for years, enzyme beakers can still degrade the gel gradually. The breaker concentration designs were turned out to be very successful. The concentration increased proportionally to the proppant and gel concentration achieved further breaker penetration throughout the proppant pack. 74% of fracture fluid recovered indicated high proppant pack permeability and thorough gel degradation.

It is worth suggesting certain practices that may improve the breaker performance for RHT #1. First, the polymer specific enzyme should be designed as encapsulated breakers, because enzymes are expected to provide long-term clean up in the proppant pack after the stimulation job. However, both of the 210 °F formation temperature and initial fluid pH are not only too high to activate any enzyme particle, it may permanently damage the enzyme as well. The coating materials are able to delay the release time, which protects the enzyme from being exposed to high temperature and pH environment for quite a while during the treatment. Secondly, the concentration of encapsulated calcium peroxide is another important factor that needs to be paid attention. As discussed in Chapter 5, the main concern relate to the application of encapsulated breakers in hydraulic fracturing treatments is premature release of the breaker payload. Usually no more than 5% of the whole payload in the fluid is damaged due to product manufacturing

imperfections or abrasion experienced in pumping the particle through surface equipment, tubulars, and perforations, causing the premature release. What is more, the hydrostatic release also occurs after the breaker particles are added to water. Therefore, the concentration of encapsulated calcium peroxide should increase to tolerant pre-released breaker payload. Based on the calculation method introduced in Chapter 5, concentration for each stage can be calculated. For example, during the pad stage, with 205 °F formation and 3300 psi treating pressure, total pre-release amount consists of 15% hydrostatic pre-release and 5% mechanical pre-release, and under 14.7 psi the release percentage is 95%. Therefore, the concentration of encapsulated calcium peroxide C_{cp} , can be calculated by using Matthew Miller's equation,

$$C_{cp} = C_{old} \times \frac{Hydrostatic Release at 14.7 PSI}{Total Release during Treatment}$$
$$= 0.5 \times \frac{95\%}{15\% + 5\%} = 2.4 \text{ lb}/1000\text{ gal}$$

Concentrations recalculated by taking the pre-released breaker payload into account are believed more accurate and higher enough to achieve better gel degradation. Generally, in spite of miner omission, breaker design for RHT #1 did a good job and led to the satisfied production.

On the contrary, a series of flaws can be found from the breaker design of JCM #1. First of all, defective breaker selection directly caused the chemical underperformance during the job. According to breaker selection flow chart, the best performance temperature for polymer specific enzyme should be lower than 120 °F and fluid pH also needs to be maintained below 8. However, within the environment of 210°F BHT and pH of 11 for approximately 120 minutes, these enzymatic agents could denatured shortly

and cannot be reactivated due to permanent molecular structure damage. Secondly, the non-encapsulation made everything even worse. It accelerated enzyme damage process since the enzyme particles contacted reservoir environment immediately when they were pumped into the well bore and, the enzyme concentration had to be low in order to protect the fluid viscosity for proppants transportation. Thirdly, although the addition of ammonium persulfate during the last portion of slurry stage appeared to be a wise patch, the half-life of persulfate usually only lasts 10 minutes at 210 °F, which means the persulfate can only provide short breaking effort to entire job. According to the selection chart, the proper breaker selection should resemble RHT #1 since peroxide are designed to work best between the temperatures of 200°F to 250°F. Meanwhile, the bromate breaker is also an option if the peroxide is unavailable, with fracture fluid pH maintained between 6 and 8 for best performance. Also, breaker schedule of JCM #1 should follow the good example of RHT #1. With different concentration design for each stage, breaker should be added at the very beginning of the job, in order to fully blend the breaker and polymer. Thus, all breakers can be homogeneously distributed within the fracture and proppant pack. Again, if any encapsulated breakers are selected and applied, concentration arrangements have to consider the premature release factor and used the method proposed previously to calculate for each stage. Last but not least, use of gel stabilizers should also be considered, since the dissolved oxygen in the fracturing fluid will be very active at the temperature of 210 °F. The dissolved oxygen can oxidize and decompose the polymer. While such "gel breaking" is inadequate to completely degrade the fluid for clean-up purposes, they may compromise its viscosity during the pumping time. Therefore, gel stabilizers which act as

oxygen scavengers, are usually added at 5 to 20 pptg into fracture fluid to eliminate the issue. To sum up, all these factors that lead to breaker underperformances of JCM #1 result in incomplete gel degradation and are needed taking into consideration for correction, in order to obtain great gel degradation improvements.

Chapter 7

Conclusions and Recommendations

Complete investigations of breaker types and breaking mechanisms are conducted, and guidelines for breaker selection and breaker schedule optimization for tight gas reservoirs have been developed and evaluated with case studies, which will serve as a valuable reference of breaker design for any type of stimulation treatment. The following conclusions are summarized from this research:

- Gel breakers are generally grouped into three classes: oxidizers, enzymes, and acids. Oxidizers decompose to free radicals, and then attack reactive sites of polymer units. Enzymes disconnect critical linkages in the guar polymer chain, cutting repeated polymer units to simple pieces. Acid may reduce fluid viscosity by reversing the fracturing fluid crosslinking process in matrix acidizing.
- Breaker selection depends upon breaker types. However, they are generally influenced by The performances of breakers which are influented by formation temperature, fracture fluid pH and formation mineral. The specific breaker selection criteria and an integrated selection flow chart have been developed, which can be a useful tool for any breaker job design.
- The method of estmating the optimum breaker concentration for each stage of the entire treatment has been proposed, which is another critical step to optimize breaker schedule. Especially when encapsulated breakers are applied, breaker concentrations need to be recalculated by taking the pre-released payload into account.

- A step-by-step procedure for breaker injection remedial treatment design has been proposed to solve gel damages in producing wells. This remedial treatment is able to degrade the highly concentrated gel inside the proppant pack and therefore, to improve effective fracture length and conductivity.
- Field studies of RHT #1 and JCM #1 validated the theories established above. The production and the fracture conductivity of RHT #1 turned out to be more satisfied and only slightly damaged, since the entire breaker design including breaker selection, fluid preparation and breaker concentration arrangement, complied with the breaker selection chart and proposals on breaker schedule optimization to a considerable degree. JCM #1 on the other hand, did not follow proper breaker design procedures, which led to the less agreeable production and fracture conductivity, and eventually identified as a severely damaged well.

A great deal of work still needs to be done for this study in the future. With the development of polymer chemical technology, a number of emerging types of breaker and breaking mechanisms are being introduced into industry and the gel degradation efficiency will be greatly enhanced. Therefore, the study of breaker schedule optimization will always be an important task that requires constant improvement with updated information.

NOMENCLATURE

C _{APS}	Ammonium Persulfate breaker concentration	[lbs/1000gal]
C_{cp}	Concentration of encapsulated calcium peroxide	[lbs/1000gal]
C_{DH}	Downhole encapsulated breaker concentration	[lbs/1000gal]
C _{test}	Maximum allowable breaker concentration at test condition	[lbs/1000gal]
C _s	Proppant concentration in fluid	[lbs/gal]
C _p	Final polymer concentration	[lbs/1000gal]
C_{pi}	Initial polymer concentration	[lbs/1000gal]
C_{BP}	Breaker concentration to polymer concentration ratio	[lbs/100lbs]
с	Total System Compressibility	[psi ⁻¹]
F_{CD}	Dimensionless fracture conductivity	[md-ft]
h	Formation Thickness	[ft]
р	Reservoir Pressure	[psi]
$p_{\rm BHF}$	Bottom hole flowing pressure	[psi]
p_{fric}	Tubing friction losses	[psi]
p _{hydro}	Hydrostatic head	[psi]
p_t	Tubing pressure	[psi]
k	Formation Permeability	[md]
\mathbf{k}_{f}	Fracture permeability	

q	Production rate	[Mcf/D]
$1/q_D$	Reciprocal of dimensionless production rate	[-]
t	Production time	[hours]
t _{Dxf}	Dimensionless time	[-]
Т	Reservoir Temperature	[°F]
$\frac{1}{V_{P/L}}$	Dimensionless polymer concentration factor	[-]
W	Fracture width	[ft]
X _f	Fracture half-length	[ft]
Z	Gas compressibility factor	[-]
Ø	Formation Porosity	[-]
μ	Initial Gas Viscosity	[cp]
\triangle [m(p)]	Real gas pseudopressure difference	[psi]

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