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Optimization of breaker schedules for stimulation of tight gas reservoirs

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ABSTRACT

Breakers are a small portion of the total fracture fluids, but could be very critical in determining the fracture treatment effectiveness. Wrong selection of breaker may result in extended fracture cleanup in weeks or months. An optimized selection and design of breaker schedules help maximize fracture conductivity by cleaning up the proppant pack after a treatment. However, breaker selection and design still remains as a challenge.

We conducted an extensive and complete investigation of breakers through a systematic and critical review of relevant publications in this area. We first presented the major breaker types and their own breaking mechanisms, then built guidelines in a flow chart for selection of breakers based on formation temperature, pressure, PH, salinity, and mineral compositions. We then developed a step-by-step procedure for optimizing breaker schedules and finally demonstrated with field case studies of two tight gas wells in Louisiana. The new knowledge helps one optimize breaker design and improve fracture treatments in tight gas wells.

1. Introduction

Fracture fluid is used to break the formation rock and then to transport enough proppants to prop open the fracture that enables flow of oil and gas. Fracture fluid usually consists of water thickened with guar or derivative guar polymers to increase its viscosity. After a fracture treatment, the fracture fluid needs to be flowed back without moving the proppant and without damaging the conductivity of the proppant pack. To accomplish this, one needs to break the viscous fracture fluid to a Newtonian fluid with a viscosity of 50 cp or less (Voneiff et al., 1996). Breakers reduce the molecular weight of guar polymer by cutting the long polymer chains into smaller chains. As the polymer chain is cut, its viscosity is reduced. All of these chemicals reduce the viscosity of the gel by breaking connective linkages in the guar polymer chain. 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 sufficient gel degradation.

Oxidizing breakers include 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 and degrade the polymer chains. The reactive sites of a repeating unit of guar polymer are shown in Fig. 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). Breaking mechanism of persulfate breakers could be summarized as: 1) The persulfate ion breaks into two halves called radicals (SO_4^-). This process is known as chain initiation; 2) Persulfate radicals oxidize water to form sulfate and two new radicals called hydroxyl radicals (OH^-); 3) A hydroxyl radical reacts with guar to form water and a guar radical. 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 ($guar^-$); 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 by following the process in 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 many times. This reaction is a true catalytic process,

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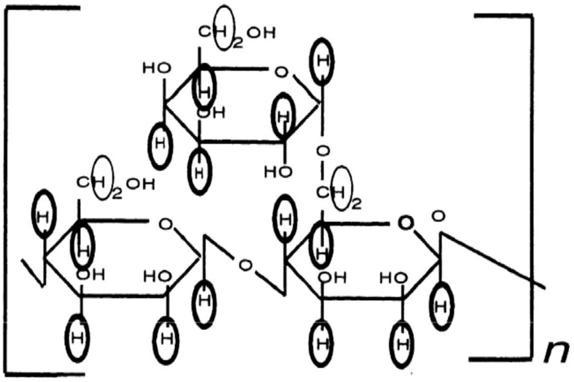

Fig. 1. Free radical reaction sites (Brannon and Tjon-Joe-Pin, 1994).

which makes persulfates very effective breakers for guar-type polymers. However, below 125 °F, the persulfate oxidizing process occurs very slowly, and the reaction needs to be catalyzed to obtain acceptable break rates. 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 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 with sodium and then potassium persulfate salts as shown in Table 1. Peroxide is a stable and strong oxidizer which often used as an internal breaker to remove the filter cake. According to the reservoir pore size distribution and rock minerals, there are different types of peroxide products available. The magnesium peroxide is one of widely used in the industry. The third category of oxidizing agents, such as sodium, potassium, and ammonium salts of bromate (BrO_3^-) have the same mechanism to degrade the gel and lower the viscosity, but has its own limits of temperature and pH environments.

Enzyme Breakers are 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 considered environmentally friendly. The enzymatic breaking activity does not change the enzyme structure and thus, the enzyme may initiate another breaking reaction on polymer. The initiation of reactions by enzymes is governed by a property known as the ‘lock and key principle’. They are limited to only those specific substrate to which they can match. The structure of guar, shown in Fig. 2, may be most simply defined as a polymer which is a repeating unit. For enzymes, the most effective approach is to 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 soluble in water. The enzyme should be not only polymer-specific to match up with the polymer, but also it should be polymer linkage-specific to attack the appropriate linkages to achieve the desired degradation. Most effective way 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. Previous studies (Brannon and Tjon-Joe-Pin, 1994) indicated 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 within the primary fracture, into natural fractures, or into high permeability matrix. Thus, the enzyme degradation will be distributed and concentrated homogeneously with polymer throughout the fracture. This is a major advantage for enzyme breakers, which provides long-term polymer degradation.

Table 1
Solubility of persulfate breakers in water (BJ services).

Persulfate salt	Solubility in H_2O (68 °F)
Ammonium Persulfate ($(NH_4)_2S_2O_8$)	79.2 g/100cc
Potassium Persulfate ($K_2S_2O_8$)	5.3 g/100cc
Sodium persulfate ($Na_2S_2O_8$)	54.9 g/100cc

Acid breakers often act as a necessary component to reverse the fracture fluid crosslinking process. These acids are used in fracturing to provide an acid fracturing. 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 inhibit or retard the reaction of the acid with formation and to prevent the acid from being consumed. Once the crosslinked fluid is injected into the wellbore and formation, acid then etches the fracture surfaces to form conductive channels that remain open without any proppant after the fracture closure. Meanwhile, the fluoroboric acid, as the gel breaker, begins the uncrosslinking process. It first decomposes to hydrofluoric acid and releases fluoride ions, which ties up the zirconium ions and breaks the zirconium polymer crosslink bonding. The viscosity of the acid decreases over time to allow easier recovery. Acids are also used to create a suitable 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 are limited to many factors, which will be discussed later.

For oxidizer breakers, the generation of radicals and reduction in fracturing fluid viscosity are strongly influenced by temperature. In many cases, aggressively high breaker concentrations are needed to provide a better cleanup result, but it may reduce the fluid viscosity too quickly for 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 delayed release method is adopted. This also applies to enzyme breakers. Encapsulated breakers were introduced to allow for much higher concentrations of breakers and to make the breaking progress closer to the ideal behavior as shown in Fig. 3. A wide variety of coating methods can achieve the delayed release effect, which include impermeable membranes that release breakers when crushed and an impermeable membrane or coating that dissolves and releases the active ingredients.

2. Breaker selection and optimization

Breaker performances are influenced by temperature, pH, salinity, and minerals. The selection criteria for each breaker type will be discussed in this section.

2.1. Selection guidelines for oxidizing breakers

The rate at which an oxidizing agent breaks into two radicals is temperature dependent. Previous experiments showed that 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 200 °F, persulfate decomposes very quickly. Breaker half-life is the time required for 50% of the initial breaker concentration to be decomposed.