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Research on Gel Breaking Process of Emulsion Associating Polymer Fracturing Fluid

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The associative polymer is a highly concentrated solution state in the emulsion droplets and does not need to undergo swelling in the water 10 seconds completely dissolved, as an instant-type fracturing fluid can be used for large-scale hydraulic fracturing. In this paper, the gel breaking process of this fracturing fluid is studied in detail, and it is found that ammonium persulfate can be completely hydrated in 40~120min. The surface tension is 27.5mN·m^{-1} and the interfacial tension is 0.3mN·m^{-1}, which meets the requirement of back-flow. For results of research on gel-breaking mechanism, the electron atmosphere of the C-C bond in the polymers main chain is reduced by the electron absorption effect of side -chain carbonyl. The free radical attack produced by the peroxides is broken and the amide group undergoes three stages of hydrolysis to produce the carboxyl group.

1. Introduction

Hydraulic fracturing has always been an important means to increase production and increase injection in low permeability reservoirs. The application of high performance fracturing fluid will not only make fracturing construction more smooth and safe, but also make the production capacity more ideal. In recent years, hydrophobic associates have been widely used as fracturing fluids due to their excellent properties of high temperature resistant shear resistance and low residue-free damage. In 2005, Couillet and other associative polymers with viscoelastic surfactant synergistic reduction in worm-like micelles strong sheared recovery time and thus reduced the VES fracturing fluid system loss; Luo et al., (2007), Jumari and Yusof, (2017) reported the first in the domestic successful preparation and application of the associated polymer fracturing fluid, and proved to have good shear resistance and relatively low friction, other domestic researchers also associated polymer fracturing liquid rheological properties, salt-resistant performance of the analysis and found that more excellent (Yi et al., 2010; Cheng et al., 2008; Zhou et al., 2008; Sun and Yao, 1998). The so-called associative polymer, hydrophilic main chain was the introduction of small amounts (usually less than 2%, mol/mol) hydrophobic groups (Winnik et al., 1991). Because the main chain and hydrophobic side groups in the water solubility of a certain difference, the hydrophobic side groups tended to aggregate together, form a complex three-dimensional network structure with the main chain, similar to cross-linking, and the system without the need for cross-linking agent in the case of viscosity greatly increased. However, this cross-linking was physical in nature, equivalent to the surfactant in aqueous solution. The resulting micelles had shear-reversible properties. However, the above systems were aqueous solution polymerization method for the preparation of associative polymer products for the powder state, in use with the melon glue, VES similar, and needed to be prepared in the dosing station base fluid transported to the well site, which in large Scale construction had been limited, such as "well factory" model. To this end, the Shengli Oilfield Petroleum Engineering and Technology Research Institute using reverse microemulsion polymerization prepared a high temperature emulsion associative polymer fracturing fluid. Reverse microemulsion was an isotropic,

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transparent or translucent thermodynamically stable system formed by the high dispersion of the aqueous phase in the oil phase in the presence of a surfactant. The microemulsion was prepared by reverse microemulsion method had high solid content, high dissolution speed, small particle size (1~100nm) and uniformity, and had very good stability (Barto, 1996). The preparation of hydrophobic associative polymer by inverse microemulsion polymerization could solve the drift problem of hydrophobic monomer, which was one of the research hotspots in the field of water-soluble polymer. The prepared polymer emulsion fracturing fluid had the characteristics of high temperature resistance (≤230°C), no residue, single use, low requirement on preparation water quality, and could be mixed on site. At present, it has been successfully used in Shengli Oil Field as a well plant to be applied, the total liquid volume reached 50000m^3, which achieved good results and benefits. In this paper, the gel breaking process of this fracturing fluid is studied.

2. Experimental methodology

2.1 Reagents and instruments

All chemicals were reagent grade or better. Dispersant for emulsion polymerization (DH-1, 30% wt polymer content, industrial product) was obtained from Shengli Oilfield Shengli Chemical Co. Acetone (AR) and ammonium persulfate (AR) were obtained from Shanghai Guoyao Chemical Reagent Co. Capsule gel-breaking reagent was obtained from Schlumberger Technologies Co., Ltd. A six-speed viscometer was obtained from Qingdao xin sen mechanical and electrical equipment co., LTD. Polarizing microscope was obtained from OLYMPUS and its model is BX53F. And Digital PH meter was also used.

2.2 Gel breaking liquid preparation

Experimental conditions for the implementation of China Petroleum and petrochemical industry standard were SY/T 5107-2005<water-based fracturing fluid performance evaluation methods>the relevant provisions. 15g of the stock solution was weighed and added to 485 g of tap water under stirring. 0.2g of ammonium persulfate or 0.2g of the capsule breaker was added and stirred to obtain a sample of a polymer having a polymer content of 1% by weight. The prepared fracturing fluid samples were placed in a constant temperature water bath at 90°C. When the viscosity was less than or equal to 3mPa·s, the fracturing fluid was completely broken.

2.3 Gel breaking liquid viscosity curve measurement

Samples of the fracturing fluid prepared in 2.2 were heated to 90°C. 300ml was transferred to a sample tube of a ZNN-D6 type six-speed viscometer. The viscosity was measured at 100r/s and recorded. After the recording, the samples were moved back, the operation was repeated for several minutes until the viscosity was measured three times continuously ≤3 mPa·s.

2.4 Gel breaking liquid PH curve measurement

After the fracturing fluid sample prepared in 2.2 was placed in a water bath, the probe of the pH meter was immersed in the liquid and the pH value was recorded every few minutes.

2.5 Gel breaking liquid particle morphology observation

Drop a small droplet of 2.2 prepared fracturing fluid gel in polarized light microscope, magnification 400 times, observe and take pictures.

2.6 Gel breaking liquid handling and polymer characterization

The FT-IR and ^{1}H NMR spectra were used to determine the molecular weight of the oligomer, which was prepared by the method described in 2.2, followed by drying in a vacuum oven at 40°C.

3. Results and discussion

3.1 The emulsion associating polymer instant principle

From the experimental sample preparation in the fracturing fluid, emulsion associative polymer in the water needed to be stirred more than ten seconds to achieve a stable high viscosity. Although the current water-soluble polymer industry in the crystal structure of the dissolution rate of products made great efforts, but still could not break the limits of polymer physics, in theory, the crystalline polar polymer with water hydrogen bonds. The process of enthalpy changes ΔHM<0, for the exothermic process, so the dissolution was spontaneous. This referred to the behavior of a single polymer chain, which was an aggregate of numerous polymer chains, entangled with one another, although physical, but also required a certain amount of energy to break the entanglement, so that the polymer powder by the dissolution process must first undergo the swelling process, and the water continuously infiltrated into the powder with more polymers to form hydrogen bonds, releasing heat to increase the molecular chain velocity to break the tangles, then the general polymer powder dissolution time increased 20min-60min. On the other hand, the molecular weight of water-soluble polymers, such as polyacrylamide (PAM) and anionic commercial products, had exceeded 27 million for the purpose of pursuing high tackifying performance, which made the critical solution temperature Tc higher and higher, so the dissolution rate control was more difficult. Associated polymer because of hydrophobic groups to prevent water molecules from penetrating into the powder, polar groups combined with water to produce hydrogen bonds slowing down, and more difficult to dissolve. In the emulsion, associative polymers were present in small particles, each of which was a highly concentrated solution of the polymer (Candau et al., 1984). Once the emulsification system was destroyed, these particles emitted the polymer without swelling rapidly into a highly viscous solution, which was the form of the emulsion associative polymer dissolving completely within a few seconds the principle.

3.2 The fracturing fluid gel breaking liquid form

Figure 1 shows that the emulsion associated fracturing fluid breaking fluid has good mobility and milky white impermeable Clear appearance, consistent with the characteristics of latex. Emulsion associative polymer as a fracturing fluid application concentration is low, 140°C-160°C reservoir temperature generally 0.8%-1% of the polymer concentration conversion, so a lot of water dilution. Stable emulsion system requires the oil phase, water phase, emulsifier three precision ratio, if the balance is broken, emulsification system will be destroyed. In order to achieve rapid release of polymer with water, the HLB of the emulsifier and the hydrophobic monomer in the synthesis of the emulsion-associative polymer is 7.5, so when a large amount of water is added, the polymer dissolves in water to form a solution, phase emulsion in the form of "oil-in-water" type emulsion, and other commercial emulsion polymer emulsion, emulsion-associated polymer dissolved in water was milky white. This phenomenon continues until the polymer under the action of ammonium persulfate completely lose viscosity, that is, breaking liquid is milky white (seen in Figure 1).

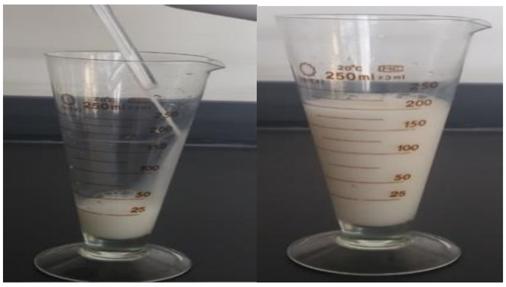


Figure 1: Emulsion type association fracturing fluid gel breaking liquid form.

However, as the emulsion, to remove the appearance characteristics, but also should have a microscopic particle structure. Figure 2 shows the results of a 400 folds magnification of the microstructure of the breaker in a laboratory using a polarizing microscope. It can be seen from the Figure 2: a large number of particles within the fluid dispersion system uniform dispersion, particle size 3~10μm. Dispersion system is the original oil in the oil phase substances in the role of emulsifiers and preparation of water to form "oil-in-water" emulsion to. This system has a surface tension of 27.5mN·m^{-1} and an interfacial tension of 0.3mN·m^{-1}, which is lower than the interfacial tension of the fracturing fluid recirculation fluid specified in the industry standard SY/T 5107-2005. Emulsion associative polymer in the use of fracturing fluid is without the addition of adjuvant agent.

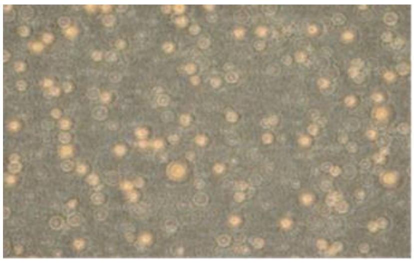


Figure 2: Emulsion type association fracturing fluid gel breaking liquid micrograph.

3.3 Gel breaking process and gel breaking mechanism

The viscosity of emulsion-associated fracturing fluid was reduced by the addition of strong oxidant such as ammonium persulfate. The gel breaking curve was tested to clarify the gel breaking behavior of this system (Figure 3). At 90°C, 0.03% ammonium persulfate was added, and the viscosity of polymer solution in 40min was almost linearly decreased to 3mPa · s. Under the same condition, the gel breaking agent was completely broken in 120min.

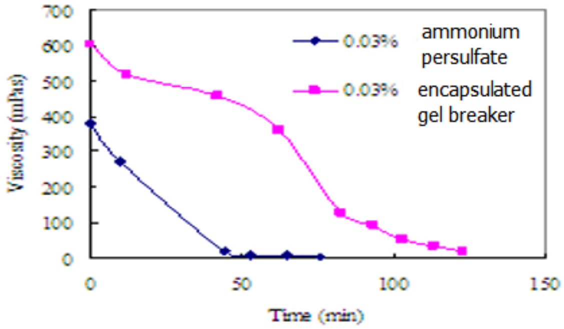


Figure 3: Emulsion type association fracturing fluid viscosity curve.

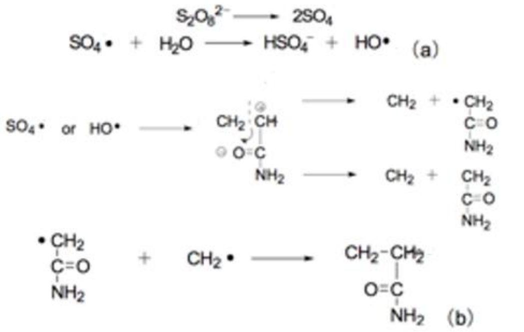


Figure 4: Emulsion type association fracturing fluid gel breaking mechanism.

Cliff-type viscosity decreased, and the viscosity does not return, belonging to the molecular chain under the action of free radicals in the form of broken gel, the mechanism can be seen in Figure 4. (1) Free radical formation: ammonium persulfate heated decomposition in aqueous solution, releasing SO4- and HO·free radicals (Figure 4a) (Cipriano et al., 2014; Carlsson et al., 2016); (2) Chain and chain growth: polyacrylamide backbone of the C-C bond by the carbonyl electron-withdrawing electron cloud density is low, so the free radical attack main chain fracture, the formation of new macromolecular free radicals, and then continue to attack other main chain C-C bond, generating more free radicals, while the two macromolecules with free radicals collide and annihilate each other to form new C-C bonds, and the two processes coexist (Figure 4b); (3) Free radicals perish: when the number of free radicals is very high, the probability of collisions with each other increased, the annihilation accounted for the main body, while the free radicals of the main body, can break the molecular chain, free radicals hit the wall and other substances will be self-annihilation, broken gel end.

3.4 Gel breaking process of the change of PH value and its mechanism

In contrast to the crosslinking system and viscoelastic surfactant (VES), the PH value of the emulsion associating fracturing fluid changes during the gel breaking process. The PH value of 1%wt polymer concentration solution is from 6.8 to 3.8-4.2, in order to study the changes in the law and mechanism, the process of breaking the PH value of the curve (Figure 5).

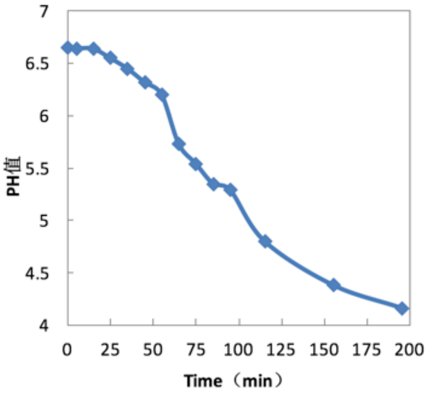
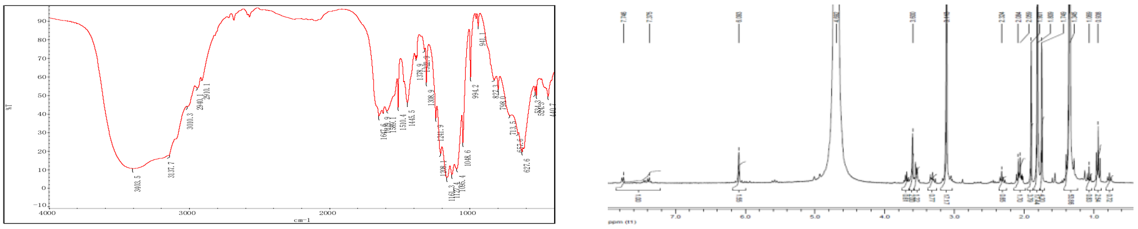


Figure 5: Emulsion type association fracturing fluid gel breaking process of PH change curve.

Figure 5 shows a continuous decrease in PH during gel breaking, resulting from the hydrolysis of amide groups (-CONH3) of acrylamide in the backbone of the associative polymer to form carboxylic acid Figure 7 (a). The presence of carboxyl groups was also confirmed by infrared (FT-IR) figure 6 (a) and ^{1}H NMR figure 6 (b) analyzes of the precipitate. It can be seen in Figure 6 that the broad peak at 2800cm^{-1} to 3700cm^{-1} should be the sum of the stretching vibration peaks of the amide group and the hydrogen carboxylate, because if the amide stretching vibration band of the amide is 3200cm^{-1}, 1647.6cm^{-1} is the stretching vibration peak of the carbon-oxygen-carbon double bond which forms hydrogen bond to low-frequency, but 1619.9cm-1 is the stretching vibration peak of amide carbon-oxygen double bond, while 1589.1cm^{-1} and 1378.9cm^{-1} are the antisymmetric and symmetric attraction peaks of the carboxylic acid, respectively. In the ^{1}H NMR spectrum figure 6 (b), the multiple d=2.3 ppm is likely due to C-H on the backbone CHCOOH structure.



(a) (b)

Figure 6: (a) Emulsion type association fracturing fluid sediment FT-IR spectra and (b) Emulsion type association fracturing fluid sediment 1H NMR spectra

The curve in Figure 5 can be divided into three stages: (1) 0~55min, PH value from 6.65 to 6.20, belonging to the slow reduction zone, contacting the viscosity curve in Figure 3, we found that this time period has not fracturing fluid breaking the gel completely, the viscosity of the system is very large, and hydrophobic groups make the polymer solution to form a three-dimensional network structure of the form of aggregates in the focusing body. Due to hydrophobic group concentration, water space is small, and amide incomplete contacting with water may be one of the reasons for the low hydrolysis rate. In addition, it is possible that the steric hindrance of the hydrophobic monomer cannot hydrolyze the adjacent amide groups. (2) At 55 to 115min, the PH value decreases to 4.80, which belongs to the fast decreasing region. Of the viscosity is less than 3mPa·s, the polymer chain was completely broken into fragments, amide from the focus of the liberation of the body, while water-soluble monomer from the hydrophobic far, so full access to water, thus hydrolysis rate. (3) 115195min, PH value of the final reduction to 4.16, the PH value of the amide group in the amide group, the reaction time, but also tended to slow down. This stage because the system of hydrogen ion concentration was high enough, hydrolysis has reached a balance, so PH value gradually became a certain value.

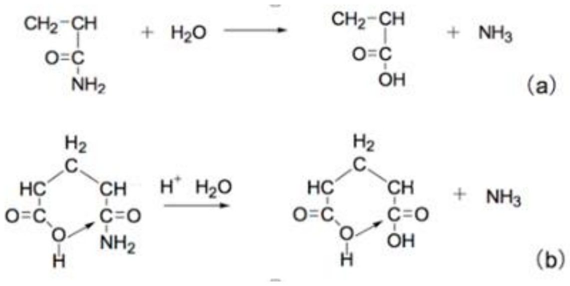


Figure 7: Amide hydrolysis

What can react with Ca^{2+}, Mg^{2+} and Al^{3+} ions in clay minerals to form water-soluble organic acid salt is dissolved in the re-drainage solution again, thereby reducing the damage to the core Matrix damage.

4. Conclusions

By analyzing the process of dissolving the emulsion associative polymer into a fracturing fluid and breaking the fracturing fluid systematically, the following conclusions are obtained:

(1) Associative polymer in the emulsion droplet is a high concentration of solution, so it does not need to go through the swelling process of dissolution, and this is the emulsion associating polymer fracturing fluid to the principle of instant solution.

(2) Emulsion associative polymer fracturing fluid breaking fluid is still latex, milky appearance, good liquidity, and the interfacial tension is $0.3 mN\cdot m^{-1}$, which is lower than the interfacial tension of the re-drainage liquid table. It is not necessary to carry out the construction of the oil-in-water system by adding auxiliary agent.

(3) Gel breaking time is about 40~120min, the breaking principle of free radical scission chain: amide group has a strong of the electron-withdrawing effect, so that the electron atmosphere of the C-C bond in the polymers main chain is reduced by the electron absorption effect of side -chain carbonyl, and bond energy becomes smaller in the ammonium sulfate produced by the free radicals produced under fracture.

(4) The amide group of the polymer undergoes three stages: slow hydrolysis, rapid hydrolysis and slow hydrolysis. Hydrolysis to carboxylic acid leads the final PH value to be 4.1, which may be such fracturing fluid core matrix damage rate of a factor.

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