Research Progress of High Temperature Resistant Fracturing Fluid System

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Abstract. China has made significant progress in the efficient exploration and development of deep-seated oil and gas wells. Reservoir reformation, as the core tool of high-temperature deep-seated exploration and development, puts forward a strong demand for fracturing fluids. The ultra-high temperature fracturing fluid system developed in my country is mainly divided into two types: ultra-high temperature guar gum fracturing fluid and ultra-high temperature synthetic polyacrylamide fracturing fluid. The high temperature resistant fracturing fluid system is mainly composed of high temperature resistant thickener, high temperature resistant crosslinking agent and temperature stabilizing additives and other additives. Based on indoor research and a large amount of literature, this article summarizes the research and application of high temperature resistant fracturing fluid system, high temperature resistant thickener, high temperature resistant crosslinking agent and temperature stabilizing additives in my country in recent years, and pointed out the shortcomings and limitations of the high-temperature fracturing fluid, the technical direction of the development of high-temperature resistant fracturing fluid technology is proposed.

1. Introduction

In recent years, the world economy has entered a new development cycle, and the demand for oil and gas resources in various countries has soared. Facing the huge energy demand, the world's oil and gas production capacity construction and production are relatively insufficient, so people began to pay more attention to unconventional oil and gas resources. Low permeability, deep, ocean and unconventional are the four important fields of oil and gas. Oil companies at home and abroad are very concerned about the exploration and opening of deep oil and gas. PetroChina has made great progress in deep and efficient exploration and development in Tarim, Southwest, Xinjiang, Daqing, Qinghai, Dagang, and North China. However, deep oil and gas reservoir reconstruction is facing the challenges of ultra-deep, high temperature, and high pressure. Breaking through the old and establishing the new, technologically leapfrogging development, in the aspects of material research and development, technological progress, process innovation, equipment matching, tool research and development, safety management and control, etc. still need to continue to tackle key problems, lead technological development, and solve world-class problems.

Development wells in unconventional reservoirs often require hydraulic fracturing to increase the conductivity of the fractures to increase the recovery of hydrocarbon gas. The fracturing process to improve the conductivity is to create new fractures to communicate with the existing gas holes and natural fractures in the gas reservoir rock, so that the hydrocarbon gas in the gas reservoir can flow into the wellbore to realize commercial exploitation value. Hydraulic fracturing technology has been used
for more than 60 years, and more than 1 million wells have used this technology. Reservoir reconstruction is the core "weapon" of high-temperature deep exploration and development. How to increase construction displacement, reduce liquid friction, improve sand-carrying capacity and adapt to ultra-high temperature liquids above 200°C is fracturing acidification to effectively reform reservoirs, improve construction efficiency and reduce the key problem of cost, among them, the high-temperature-resistant clean fracturing fluid above 240°C is the "stuck neck" technology of the liquid material for reservoir reconstruction.

High temperature resistant fracturing fluid system is mainly composed of high temperature resistant thickener, high temperature resistant crosslinking agent and temperature stabilizing additives. The thickener system is generally natural polymer or synthetic polymer, which is based on fracturing fluid. Liquid provides the necessary rheological and viscoelastic system structure for the suspension of sand; after adding the crosslinking agent, the polymer with linear structure can become a kind of polymer hydrogel material with linear and network structure coexisting; the addition of temperature stabilizing additives can significantly improve the temperature tolerance of the system through the mechanism of oxygen consumption or enhancement of the system's spatial network structure.

2. Research progress of high temperature resistant fracturing fluid system

At the fracturing construction site, the current status of research and application of various temperature-resistant fracturing fluids at home and abroad:

① The highest viscosity of domestic surfactant cleaning fracturing fluid system is above 200mPa.s and the highest temperature resistance is 140°C; the highest temperature resistance of foreign products is 160°C.

② Guar gum weighted fracturing fluid generally adopts 0.25% relatively mature technology in industrial applications. The domestic use of nitrate is increased to 1.5g/cm³, and the temperature resistance can reach 160°C; the foreign use of bromine salt is increased to 1.55g/cm³, and the temperature resistance is up to 160°C. The domestic technology of carboxymethyl hydroxypropyl guar gum fracturing fluid can be cross-linked with a thickening agent concentration of 0.12%, with a temperature resistance of up to 190°C, and a cost reduction of 20% to 40%. The minimum dosage of foreign guar gum can reach a temperature resistance of 186°C at a concentration of 0.18%.

③ The domestic synthetic polymer high-temperature fracturing fluid mature technology 210°C shear 90min, the viscosity is greater than 90mPaꞏs, and it has been reported abroad that it can withstand the temperature of 260°C.

Liang Feng et al. [2, 3] proposed in their 2017 patents that they invented a new type of high temperature resistant water-based cross-linked polymer fracturing fluid. The thickener is polymerized by AA, AM, and AMPS. The linking agent adopts organic zirconium crosslinking agent. After the crosslinked polymer fracturing fluid is sheared at a high temperature of 300°F to 400°F for 40s-1 for 80 minutes, the viscosity retains at least 500cp, and the maximum operating temperature of the fracturing fluid can reach 450°F.

Du Tao et al. [4, 5] introduced a reversible physically cross-linked polymer fracturing fluid in their patents published in 2017, which can be used in the fracturing construction of reservoirs at 120°C~160°C without adding temperature stabilizers. And the viscosity of fracturing fluid after gel breaking is lower than 2mPaꞏs. The temperature resistance of the crosslinked fracturing fluid can reach 160°C, and the average retention viscosity of 170s-1 for 2 hours is 52.7mPaꞏs. The raw material of the crosslinking agent in its patent contains lower alcohol methanol.

Zhai Wen et al. [6] introduced the preparation of a new type of high temperature resistant polymer fracturing fluid system in 2012. The viscosity of 0.4%~0.7% thickener of the system after shearing at 200°C and 170s-1 for 120min is 176mPaꞏs. The cross-linking agent adopts an organic zirconium crosslinking agent with good retardation performance. Controlling the ratio and dosage of the retarding cross-linking agent can adjust the cross-linking time, which is beneficial to reduce the friction resistance of the mixed liquid and improve the liquid delivery efficiency.

Liu Ping et al. [7] introduced and prepared a polymer fracturing fluid system resistant to high temperatures of 220°C in 2018. The polymer thickener in the system is composed of AM, AMPS,
methacrylic acid (MAA) and vinyl phosphonic acid (VPA) monomer copolymerization, the apparent viscosity of the thickener base liquid is 46.5 mPa·s. The cross-linking agent is a composite cross-linking agent containing zirconium and aluminum. The cross-linking agent is a heat-induced cross-linking agent. The base solution thickens for 15 to 60 seconds at room temperature. The strength of the jelly increases when the temperature is above 50°C. Hanging, has a good delayed cross-linking effect, which is conducive to pumping. After the fracturing fluid system was sheared at 220°C and 100s⁻¹ for two hours, the viscosity was above 100 mPa·s.

In a 2018 paper, Yang Zhenzhou et al. [8] introduced the preparation of a new type of ultra-high temperature fracturing fluid system with a temperature resistance of 230°C. The fracturing fluid system contains a newly prepared ultra-high temperature thickener GAHT, high temperature resistant zirconium crosslinking agent XL2, and high temperature stabilizer TS. The new polymer thickener GAHT is prepared by inverse emulsion polymerization. The monomers used in the polymerization are AM, AMPS and VPA. Among them, the monomer vinyl phosphate (VPA) can provide cross-linked phosphonic acid groups. Its emulsion polymerization process ensures that the thickener polymer has a high molecular weight (8 million to 10 million), so the fracturing fluid has good rheology. The crosslinking agent adopts triethanolamine zirconium complex as the ultra-high temperature crosslinking agent. The fracturing fluid system has a viscosity of more than 200 mPa·s after shearing for 90 min at a high temperature of 230°C and 100s⁻¹; after shearing for 120 min, the viscosity is more than 130 mPa·s.

Carman et al. [9] introduced a new type of high-temperature fracturing fluid stabilizer phenothiazine preparation method in their patent published in 2014, which is used as a temperature stabilizer in combination with sodium thiosulfate for specific polymer fracturing Liquid system, which can withstand formation temperatures up to 500°F (260°C) and pumping time up to 2 hours, pumping for 4 hours at 425°F (218.3°C), and at 400°F (204.4°C) ) Can be pumped for 6 hours. The polymer thickening agent is copolymerized by acrylamide or its derivatives, vinyl phosphate and AMPS or other acrylamidosulfonates. The crosslinking agent is a compound crosslinking agent of organic zirconium titanium aluminum, and the pH buffer is made of acetic acid. Sodium acetate or formic acid to ensure that the pH of the base solution is between 4.5 and 5.25.

3. Research progress of high temperature resistant polymer thickeners

Compared with natural polymers, synthetic polyacrylamide thickeners have better temperature resistance and viscoelasticity, and have less residue after gel breaking. Oilfield polymers are mainly polyacrylamide polymers. The main difference in synthetic polymer thickeners is the type of monomers used [10].

Li Meiping [11] introduced in a 2018 paper the preparation of a new type of high temperature resistant zwitterionic polymer fracturing fluid, in which the raw material monomers of the zwitterionic polymer thickener include AA, AM and unsaturated quaternary The fracturing fluid system prepared with ammonium salt cationic monomers, etc., combined with organic zirconium crosslinking agent and polyacarbonyl compound temperature stabilizer can withstand a temperature of 200 °C, 0.6wt% thickener after crosslinking at a high temperature of 180 °C, 170s- After 1 shear for 90 minutes, the final viscosity was 71.2 mPa·s; after 1wt% thickener was cross-linked and sheared at a high temperature of 180°C and 170s-1 for 90 minutes, the final viscosity was 192.6 mPa·s.

Funkhouser Gary P of Halliburton Company [12, 13] introduced a method for preparing polymer thickener by copolymerization of AMPS, AM and AA in a patent filed in 2004. The three monomers used in the fracturing fluid system The body is also the three monomers that have been studied and applied in the industry. In 2009, it was reported in the literature that Halliburton's high-temperature polymer fracturing fluid had a maximum operating temperature of 232 °C when applied in an oil field in southern Texas.

LI Leiming et al. [15] introduced the preparation of a high-temperature polymer fracturing fluid system in a patent published in March 2019, which contains a ternary polymer thickener, a crosslinking agent and a high-temperature additive, of which three The meta-polymer is formed by copolymerization
of AMPS, acrylamide and acrylic acid monomer or its salt, and the additive contains sugar alcohol or its derivative.

Ma Yingxian et al. [16] introduced the preparation of a new type of temperature-resistant dual-network fracturing fluid thickener in the 2019 patent. The thickener is a nonionic monomer containing acrylamide and other resistant materials such as vinyl acetate. Multi-element copolymers of salt monomers. The fracturing fluid has excellent temperature resistance. The crosslinking agent is N,N-methylenebisacrylamide, and the retention viscosity is about 200 mPa·s after 2 hours at 120°C.

He Hao [17] described in detail in his 2013 paper the preparation method of a new type of high temperature resistant 200°C polymer thickener, which is obtained by solution polymerization of three acrylamide monomers. Indicates the type of raw material monomer. The fracturing fluid prepared with 0.6wt% of the pilot thickener product and 0.6wt% of the organic zirconium crosslinker was sheared at 200°C and 170s⁻¹ for 2 hours, and the final viscosity was 176 mPa·s.

Wang Yongji [18] introduced a new type of high temperature resistant fracturing fluid thickener in a 2017 paper. The quaternary polymer thickener is based on AM, AA, sodium p-styrene sulfonate PS, cationic monomer The viscosity of fracturing fluid after mixing with organic zirconium crosslinking agent is about 950 mPa·s. After the temperature and shear resistance test, the fracturing fluid has a viscosity of 265 mPa·s after shearing at 150°C for 2 hours; it has a viscosity of 114 mPa·s after shearing at 180°C for 2 hours; and it has a viscosity of 114 mPa·s after shearing at 200°C for 2 hours. The viscosity is 35 mPa·s.

Xue Junjie et al. [1] introduced in a 2018 paper the preparation of a new type of fracturing fluid thickening agent APC-30 used under ultra-high salinity and 210°C high temperature conditions. This new type of ternary polymer thickening The agent is prepared with AM, AMPS and acryloyl morpholine (ACMO) as raw materials. Among them, the innovative introduction of ACMO with a six-membered heterocyclic structure morpholine group into the monomer raw materials, the fracturing fluid system will undergo hydrolysis during the heating and shearing process to generate more cross-linking points, triggering secondary cross-linking, and then It can increase the crosslinking strength and improve the retention viscosity under high temperature shear.

Zhai Wen et al. [19] introduced in a patent published in 2015 that he invented a new type of high temperature resistant quaternary anionic polymer thickener with a molecular weight of about 4 to 8.5 million. The polymer thickener is prepared with AMPS, AM, DAM, methacycloxyethyl trimethylammonium chloride (DMC) as raw materials, and 0.6wt% of the thickener is cross-linked at 230°C, 170s⁻¹ After 1 shearing for 2 hours, the final viscosity is 60.31 mPa·s.

Li Yongming et al. [20] introduced in the patent published in 2019 that he invented a cationic polymer thickener and detailed the preparation method of cationic monomers. They used acryloyl chloride raw materials as the polymerization unit to prepare N- Benzyl-N-(3-(dimethylamino)propyl)acrylamide is added to alkyl bromide for reaction to obtain the target cationic monomer. The cationic polymer thickener is obtained by photo-initiating the cationic monomer and acrylamide, and the viscosity average molecular weight of the thickener is 1 to 6 million.

Lu Yongjun et al. [21] introduced in their patents published in 2014 that they prepared a new type of high-temperature resistant anionic terpolymer thickener and a long-chain chelated organic zirconium crosslinker. The polymer thickener DMAM, AMPS, NVP are used as monomers to be prepared by solution polymerization. The fracturing fluid system has been tested for temperature and shear resistance, and can withstand shear and temperature above 210°C.

Mao Jincheng et al. [22] mentioned in his patent published in 2018 that he invented a self-healing low-damage and ultra-high temperature resistant fracturing fluid. The polymer thickener is composed of AM, acrylic, AMPS, rigid monomers and cationic hydrophobic fracturing fluids. It is formed by polymerization of monomers, etc. The thickener solution is cross-linked with non-metallic cross-linking agent polyethyleneimine to make fracturing fluid gel, which can form a new substance for viscosity repair at high temperature, and shear at 170s⁻¹ The maximum temperature is as high as 220°C; the
temperature resistance is as high as 260°C at a shear rate of 100s⁻¹, and the final viscosity is stable at 30~35mPa·s.

4. Conclusion
As China has made great progress in the high-efficiency exploration and development of deep oil and gas wells, the "three super" challenges of ultra-deep, high temperature and high pressure have also followed. Among them, high temperature resistant and clean fracturing fluids above 240°C are the liquid materials for reservoir reconstruction. "Snake neck" technology, high temperature resistant fracturing fluid system is mainly composed of high temperature resistant thickener, high temperature resistant crosslinking agent and temperature stabilizing additives. The thickener system provides the necessary sand suspension for the fracturing fluid base fluid. The system structure with rheological viscoelasticity, the cross-linking agent turns the polymer with linear structure into a kind of polymer hydrogel material with linear and network structure coexisting, and the temperature stabilizing additive can consume oxygen or enhance the system. The mechanism of the spatial network structure can significantly improve the temperature resistance of the system. This article reviews the research and application progress of the main high temperature fracturing fluid systems, high temperature resistant thickeners, high temperature resistant crosslinkers and temperature stabilizing additives in recent years. Reservoir reconstruction fracturing fluid researchers still need to work hard to continue to study the mechanism of ultra-high temperature synthetic polymer fracturing fluid, and develop ultra-high temperature fracturing fluid technology with performance comparable to foreign countries to meet the needs of China’s ultra-high temperature deep well fracturing demand.

5. Suggestions
(1) Continue to carry out research on ultra-high temperature guar gum fracturing fluid technology, develop modified guar gum with low base fluid viscosity at high concentration and supporting high temperature crosslinking agent;
(2) In-depth study of the matching relationship between organic cross-linking agents and inorganic cross-linking agents, development of composite cross-linking and step-by-step cross-linking technology;
(3) Research and develop ultra-high temperature synthetic polymer fracturing fluid system, analyze its temperature resistance and shear rheological properties, and establish the molecular structure-activity relationship of high temperature fracturing fluid system.

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