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Comprehensive Experiment of Recycling of Guar Gum-based Fracturing Fluid for Environmental Education

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Abstract

The comprehensive experiment of preparation of guar gum based fracturing fluid, performance evaluation, the treatment of borate in gel-breaking fluid with shielding agent and recycling of fracturing fluid was designed. The experiment focuses on the methods of shielding borate with polyhydroxy compound and preparing fracturing fluid with gel-breaking fluid. This experiment can combine theoretical knowledge and practical application of oilfield chemistry to help students grasp the chemical knowledge of fracturing fluid, deepen their understanding of the mechanism of borate shielding, improve students' innovative designing ability and practical application ability. At the same time, the waste water after fracturing is recycled, which reduces. The pollution to the environment in the process of oil and gas fracturing and saves water resources. The experiment enables students to raise awareness of environmental protection and establishes an environmental protection concept.

Keywords

Fracturing fluid; Shielding agent; Borate; Comprehensive experiment.

1. Introduction

Environmental education is a process of social practice activity with the relationship between humans and the environment as its core, with the purpose of solving environmental problems and achieving sustainable development, with the task of enhancing people's environmental awareness and effective participation ability, popularizing environmental protection knowledge and skills, and training environmental protection professionals, and with education as its means. In a word, environmental education is a kind of educational activity that focuses on the relationship between humans and the environment [1],[2]. Environmental education is divided into general environmental education and professional environmental education. General environmental education aims to help people acquire basic knowledge about the environment and environmental problems, stimulate people's enthusiasm to care for the environment, and enhance their sense of responsibility and urgency to solve environmental problems; professional environmental education aims to train professionals with the ability to analyze the environment and solve environmental problems [3][5]. Hydraulic fracturing of oil reservoirs is an important measure to increase oil and gas production and water injection [6]. When the fracturing operation is completed, the flow-back fluid is discharged to the ground with complex composition, a wide range of chemicals, and large content, the main components include suspended solids, crude oil, microorganisms, inorganic salts, inorganic acids, and some

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organic pollutants mainly benzene derivatives and polycyclic aromatic hydrocarbons[7]. If the fracturing fluid is discharged directly without treatment, it will cause serious pollution to the environment. Therefore, the efficient treatment of fracturing flow-back fluid and the use of fracturing fluid reformulation is of great significance to cost saving, environmental protection, and water conservation. For students of petroleum-related majors in higher education institutions, *Applied Chemistry in Oil and Gas Fields* is an essential subject that requires the cultivation of students' experimental and field application skills based on the teaching of theoretical knowledge, so as to combine theory and practice [8]. Oilfield chemistry experiments are characterized by large time spans, complex experimental phenomena, and diverse analytical methods. Students should be good at analyzing and solving problems during experiments, learn how to use various analytical and evaluation instruments, improve their teamwork skills, and rationalize their experimental time [9]. The department has designed a comprehensive experiment that is both environmentally friendly and resource-saving by combining the results of scientific research. The comprehensive characteristic of the experiment is reflected in the steps, which include preparation of guar gum-based fracturing fluid, gel breaking, removal of gel breaking residue, selection of boron shielding agent, amount of boron shielding agent, reformulation of fracturing fluid using treated gel breaking fluid and evaluation of fracturing fluid performance (hanging performance, rheological performance, sand suspension, residue content), secondary gel breaking and data analysis. Environmentally friendly and resource-saving characteristics are reflected in the recycling of fracturing fluid additives and water resources, avoiding the environmental pollution caused by the discharge of flow-back fluid to the ground, and the secondary use of flow-back waste fluid has important environmental significance. The experiment design not only enables students to learn about fracturing fluid and the shielding method of boron treatment but also cultivates students' awareness of environmental protection, which is conducive to the formation of good awareness of protecting the environment and promoting "green" in the future life and work [10,11].

2. Experimental Purpose

(1) To learn the preparation and breaking of fracturing fluid;

(2) To understand the mechanism of hydroxyl compounds as shielding agents to shield fluoroborate;

(3) To master the method of evaluating the performance of fracturing fluid;

(4) To learn how to analyze the effect of different shielding agents to shield boron and the reasons based on data and data query.

3. Experimental Principle

Guar gum is a kind of light yellow powder, which is easily deliquescent, insoluble in most organic solvents, and has a strong affinity for water. When guar gum powder is added to water, the particles of guar gum dissolve and hydrate, and then a viscous solution is formed. Under alkaline conditions, the aqueous solution of guar gum is cross-linked with oxyanion salt (such as borate) compounded from amphoteric metal or amphoteric non-metal to form an aqueous gel. The cross-linking reaction of guar gum and sodium tetraborate is shown in Figure 1:

Guar gum is a natural linear galactomannan gum, the main chain is D-mannose connected by -1,4 acetal bond, and the side chains are unevenly distributed with several D-galactose branch chains connected by -1,6 acetal bond, in which the ratio of galactose (G) to mannose (M) is about 1:1.6-1:1.8, and its solubility is related to the M/G ratio and the distribution of galactose in the main chain of the molecule. Add the gel breaker (e.g. ammonium persulfate) to break the cross-linked gel, and reduce the viscosity until the gel is broken. The oxidizing agent breaks the

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mannose acetal bond in the main chain and the galactose acetal bond in the side chain (as shown in Figure 2, the wavy line is the location of the oxidized broken bond). The destruction of the acetal bond in the main chain has no effect on the M/G value of the molecule, while the destruction of the acetal bond in the side chain increases the M/G value significantly, causing a decrease in the solubility of the guar gum molecule, so flocculent precipitation will appear after breaking the gel[12].

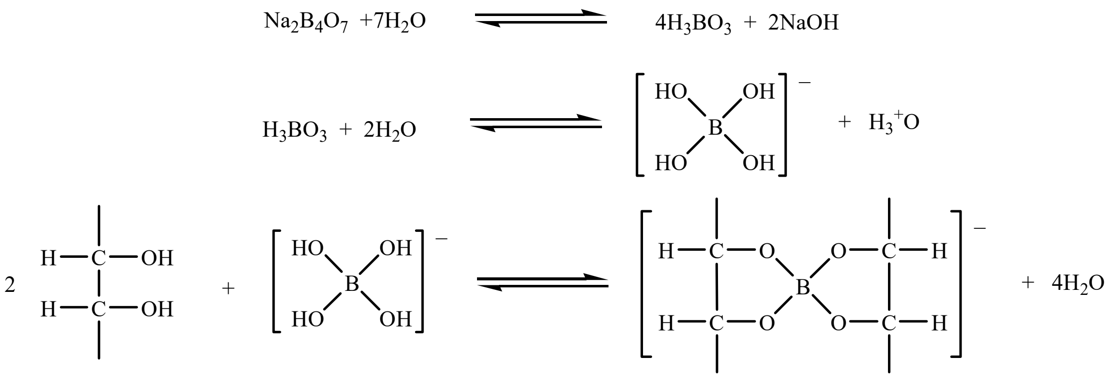

Figure 1. Cross-linking Reaction of Guar Gum and Sodium Tetraborate

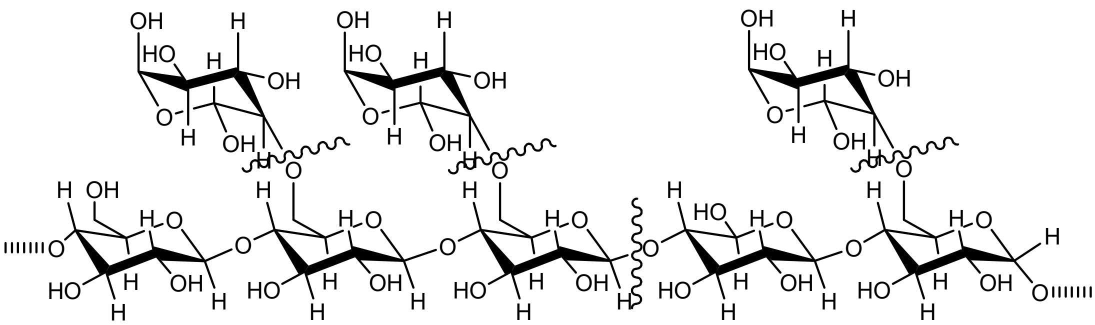

Figure 2. Molecular Structure of Guar Gum and Its Fracture Mode in Oxidative Gel Breaking

The gel breaking liquid cannot be directly mixed with guar gum powder or highly concentrated guar gum solution to prepare guar gum base solution, because the residual borate in the gel breaking liquid will cross-link with the re-added guar gum molecules, which may result in the guar gum powder not being able to swell or the viscosity of the base solution being too high to be used for fracturing operation. Therefore, it is necessary to add some kind of additive (shielding agent) to coordinate with fluoroborate before the recycling of gel breaking liquid, and its coordination ability should be stronger than that of guar gum and fluoroborate to achieve the purpose of shielding fluoroborate[13].

4. Experimental Chemicals and Instruments

Main reagents: guar gum, ceramsite, industrial grade, ChangQing Oilfield Chemistry Co., Ltd.; ammonium persulfate, propanetriol, glucose, polyvinyl alcohol, analytical purity, Xi'an Chemical Reagent Factory.

Main instruments: ZNN-D6, six-speed rotary viscometer, Qingdao Chuangmeng Instrument Co., Ltd; HAAKE MARS, HAKER torque rheometer, Thermo Fisher Scientific (China) Co., Ltd; Sartorius BSA224S, electronic analytical balance, Sartorius Group; general purpose, stirrer, water bath, benchtop centrifuge, Gongyi Yuhua Instrument Co., Ltd.

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5. Experimental Steps

5.1. Fracturing Fluid Preparation and Gel Breaking

(1) Weigh 0.9 g of guar gum, slowly add 300 mL of stirred water, stir well and leave it for more than 4 h to make it fully swell, and measure the viscosity (apparent viscosity) of the solution at 600 r/min with a six-speed rotary viscometer.

(2) Weigh 1 g of sodium tetraborate, add it to 20 mL of water, and heat it to dissolve. Take 3 mL of sodium tetraborate solution, add it to 300 mL of guar gum solution, stir it with a glass rod, observe its pick hanging performance after fully cross-linking (about 15 min), and then measure its viscosity at 60 °C with a HAKER viscometer.

(3) Pour the cross-linked fracturing fluid into a 100 mL measuring cylinder, place it in a thermostatic water bath at 60 °C, measure the liquid surface height h with a ruler, gently place the selected 10 ceramsites into the liquid surface, press the stopwatch, and record the average time t to reach the bottom of the cylinder. Calculation method of sinking speed: sinking speed v = liquid surface height/sinking time = h/t.

(4) Weigh 0.25 g of ammonium persulfate and dissolve it in 25 mL of water. Measure 5 mL of ammonium persulfate, add it into the aqueous gel and put it into the water bath, heat it at constant temperature for 30 min and then use the rotary viscometer to measure its viscosity at 600 r/min; if the viscosity value is higher than 5 mPa·s, then add 5 mL of ammonium persulfate into the aqueous gel, heat it, measure its viscosity, repeat until the viscosity of the gel breaking liquid is lower than 5 mPa·s, observe and record the experimental phenomenon.

(5) Measure a quantitative volume V0 of secondary cross-linked fracturing fluid, add a certain amount of ammonium persulfate solution, heat it at constant temperature to make it completely broken, transfer all the gel breaking liquid to a dry centrifuge tube (the mass is m0), centrifuge at 3,000 r/min for 30 min, slowly pour out the clear liquid, repeat washing and centrifugation twice, then put the centrifuge tube into a constant temperature oven, dry it at 105 °C to a constant weight, and weigh it as m1. The fracturing fluid residue contentis expressed as:

$$\eta = \frac{m_1 - m_0}{V_0} \times 1000$$

Where: η- is the fracturing fluid residue content, mg/L; m0- is the mass of centrifuge tube, mg; m1- is the total mass of centrifuge tube and residue, mg; V0- is the fracturing fluid dosage, mL.

5.2. Treatment of Gel Breaking Liquid

(1) Filter the gel breaking liquid through a 100 mesh filter and take the filtrate. Measure 150 mL of the filtrate, add it into 3 beakers, number them as 1, 2 and 3, and stir well.

(2) Measure 5 mL of propanetriol, dissolve it in 100 mL of water, then measure 2, 4, 6 mL of propanetriol solution, add into beakers 1, 2, 3 respectively, and stir wel.

5.3. Recycling and Performance Evaluation of Fracturing Flow-back Fluid

(1) Weigh 1.8 g of guar gum, slowly add it into 300 mL of stirred water, stirred well, and left it for more than 4 h to make it fully swell.

(2) Add 150 mL of guar gum solution in 5.3 (1) to beakers 1, 2 and 3 respectively, stir well, measure its viscosity at 170 s-1 and compare it with that of 0.3% guar gum solution (prepared by water).

(3) Add 3 mL of sodium tetraborate solution to the above mixture, fully cross-link it and observe its hanging performance, and use HAKER viscometer to measure its viscosity at 60 °C.

(4) Measure the sinking speed of ceramsite in cross-linked fracturing fluid as in 5.1.

(5) Conduct gel breaking and measure residue content in cross-linked fracturing fluid as in 5.1.

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(6) The operation of boron shielding agent, glucose and polyvinyl alcohol is the same as that of propanetriol (the experiment can be conducted separately in groups, and the results will be compared after the experiment).

6. Questions

Compare the shielding effect of several shielding agents on boron, and explain the reasons. Analyze the effect of excessive amount of shielding agent on the secondary use performance of fracturing fluid. What are the other additives that can be used as boron shielding agents by reviewing relevant literature?

7. Conclusion

Oilfield applied chemistry experiments focus on the feasibility of experiments applied in the oilfield, which should not only have a theoretical basis, but also focus on the convenient implementation and environmental protection. This experiment involves the preparation of fracturing fluid, gel breaking, simple treatment of flow-back fluid, recycling of fracturing fluid, determination of rheological properties, etc. It can enable students to master the use of HAKER viscometer and rotary viscometer, improve their experimental operation ability in professional courses, have a general understanding of knowledge in fracturing fluid, and lay a solid foundation for future work. At the same time, this experiment focuses on the recycling of flow-back waste fluid to solve the problem of oilfield pollutant treatment and improve students' awareness of environmental protection. There are many kinds of boron shielding agents, students should have the ability to search the literature, be good at analysis, and draw inferences about other cases from one instance, which is conducive to exert strengths in future research. This experiment has a large time span and is comprehensive, requiring multiple people to complete.

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