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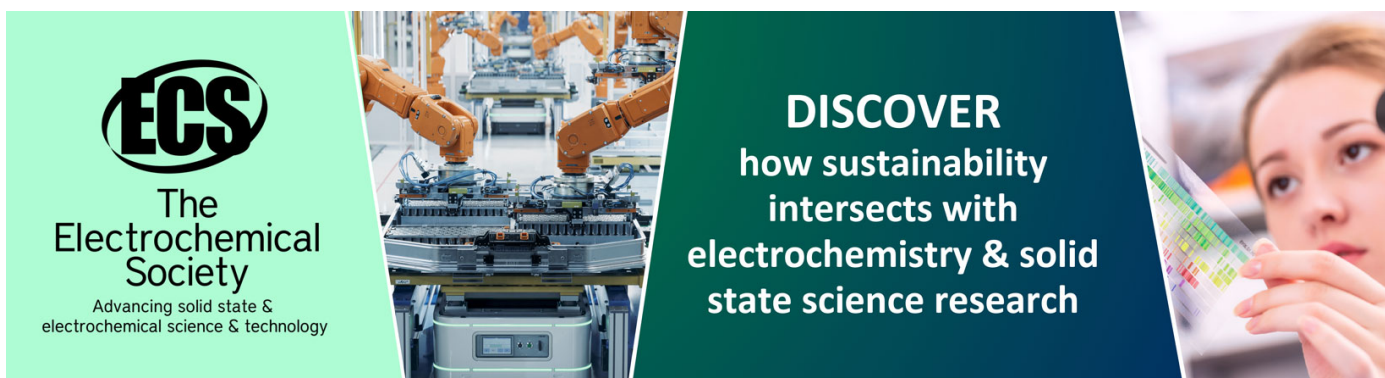
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Synthesis and application of water-soluble phenol-formaldehyde resin crosslinking agent

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Abstract. Polyacrylamide and water-soluble phenol-formaldehyde resin can produce crosslinking reaction to generate the movable gel, which can be used in deep profile control to enhance oil recovery. In this paper, the preparation process of water-soluble phenol-formaldehyde resin crosslinking agent (polyhydroxymethyl phenolic) was presented, including the raw material mixture ratio and synthesis process. The water-soluble phenol-formaldehyde resin was synthesized by the technology of two-step base catalysis with NaOH and Ba(OH)₂·8H₂O composite catalyst. The movable gel prepared with this crosslinking agent and polyacrylamide has good stability and long shelf life through the performance evaluation experiment. The above movable gel was applied to deep profile control and obtained better flooding efficiency.

1. Introduction

The deep profile control technique is an effective measure for enhancing oil recovery and improving development effect. To some extent, the movable gel is the key of the deep profile control. Therefore, the movable gel has been applied in many oilfields around the country. Polyhydroxymethyl phenol solution could crosslink with the amide group of polyacrylamide to generate gels with net structure which is widely used in deep profile control. However, the application effect of the movable gel above is not good because of some reasons, such as the short storage time, the homopolymerization, etc.

Water-soluble phenol-formaldehyde resin crosslinking agent is the A-stage product of thermosetting phenolic resin. However, its properties are affected by many factors, such as the molar ratio of phenol to formaldehyde, the type of catalyst, the pH value, as well as the reaction temperature^[1-3]. The molar ratio of phenol to formaldehyde is generally 1:2.5~3 in the synthesis, besides, the catalyst usually is NaOH. In this paper, the water-soluble phenol-formaldehyde resin crosslinking agent was synthesized by a new technology, in which NaOH and Ba(OH)₂·8H₂O was the composite catalyst^[1]. Lu36 fault block of Huabei sandstone reservoir has obtained better flooding efficiency because of the successful application of the crosslinking agent.

2. Experiment methods

2.1. Experimental materials

Phenol and formaldehyde (36% aqueous solution), industrial products, Shandong Luhua Chemical Co., Ltd.. NaOH and Ba(OH)₂·8H₂O, chemical pure reagents. Polyacrylamide (the molecular weight is



25 million and the degree of hydrolysis is 25%~30%), Beijing Hengju Chemical Co.,Ltd.. Promoting cross agent^[4], made in the laboratory by combining ammonium chloride with thiourea, etc.

2.2. Experimental equipments

Constant temperature water bath. Multi-speed mixer. Constant temperature oven, Shanghai Experimental Instrument Factory. Mars rheometer, Haake Company of Germany.

2.3. Experimental methods

2.3.1. Synthesis of phenol-formaldehyde resin. There are two synthetic methods commonly used in water-soluble phenolic resin synthesis. One is the one-step base catalysis and the other is two-step base catalysis. The technique of two-step base catalysis synthesis was adopted in this paper.

The steel stand was used to fix the 500mL three-necked flask, which was equipped with a thermometer, a mixer and a reflux condenser. An appropriate amount of phenol was added to the flask, then heated to 50°C to melt it into a liquid. NaOH was weighted at 4% of the amount of phenol and prepared as an aqueous solution at a concentration of 40%. Then the aqueous solution was divided into two portions according to the ratio of 7:3. The heavier portion was poured into the flask and the other one reserved. Ba(OH)₂·8H₂O was weighted at 10% of the total amount of NaOH and prepared as an aqueous solution at a concentration of 2%. Start the mixer and maintain a constant temperature for 20 minutes. At the same time the formaldehyde solution was weighted according to the molar ratio of phenol to formaldehyde 1:3. After that, divide the formaldehyde solution into two parts according to the ratio of 8:2. The portion of 80% was added slowly to the flask in 30 minutes and heated to 70°C holding for 30 minutes. Then the solution of Ba(OH)₂, the remaining NaOH and formaldehyde were added into the flask. Heat the flask to 84~86°C slowly and maintain the constant temperature for 1.5~2h, then cool down. At last the tert butyl alcohol which accounted for 2% of the total solution volume was added. The final brown-red solution completely soluble in water was the water-soluble phenol-formaldehyde resin crosslinking agent and the concentration was 40%.

2.3.2. Preparation and performance detection of polyacrylamide/water-soluble phenol-formaldehyde resin gels. The polyacrylamide was firstly dissolved in a certain concentration of aqueous solution. Secondly, the right amount of water-soluble phenol-formaldehyde resin crosslinking agent and promoting cross agent were added. Then the solution was mixed evenly and filled into 100mL high temperature bottles. Place the bottles in the oven, the temperature of which was 76°C (the reservoir temperature of Lu36 fault block). The fluidity and elasticity of the gel were observed at regular intervals. The samples were taken out after 5 days and the viscosity was measured by using the Mars rheometer at a shear rate of 7.34s⁻¹.

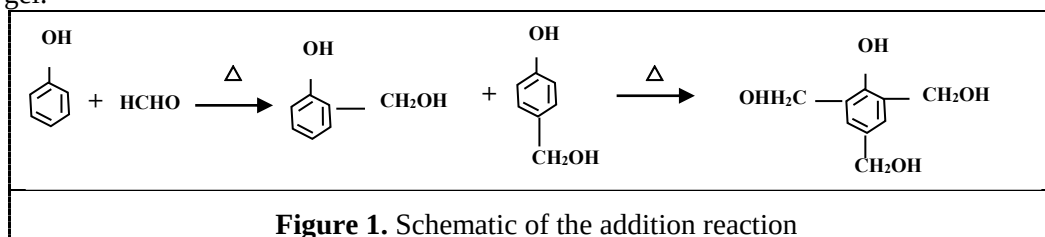
3. Experimental results and discussion

3.1. Synthesis theory of water-soluble phenol-formaldehyde resin

Phenol-formaldehyde resin is the condensation polymer synthesized from phenolic and aldehyde substances under the condition of acid or alkaline catalysis. The product is called thermosetting phenolic resin in the alkaline catalyst condition, and is called thermal shrinkage phenolic resin when the catalyst is alkaline. The properties of resin are affected significantly by the functionality, molar ratio, catalyst type and reaction temperature of raw materials. It takes two steps to synthesize water-soluble phenol-formaldehyde resin from phenol and formaldehyde.

3.1.1. Addition reaction. Phenol and formaldehyde firstly produce addition reaction to generate a mixture of polyhydroxymethyl phenol, which is the A-stage product of phenol-formaldehyde resin. The polyhydroxymethyl phenol not only has good water solubility and high reaction activity with the

amide group of polyacrylamide, but also can be used as the crosslinking agent to prepare the water-based gel.



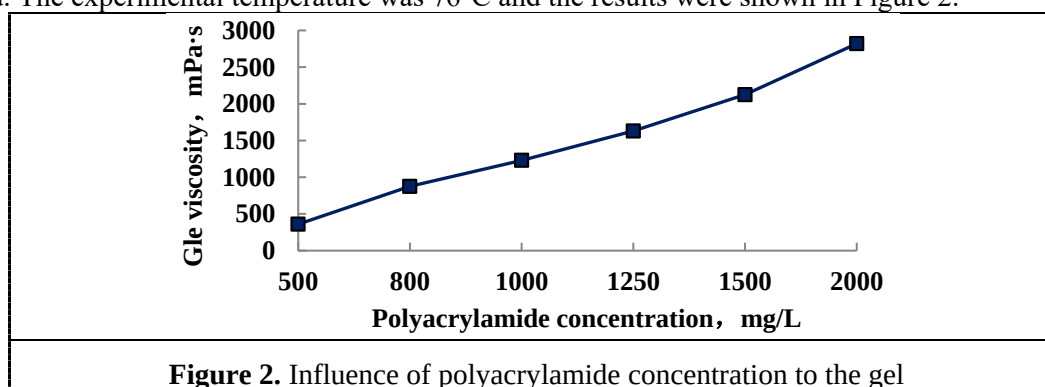
3.1.2. Condensation reaction. Hydroxymethyl phenol can be further polycondensation resulting in resin viscosity increases and generating viscous or solid phenolic resin, which is water-insoluble.

The reaction rate of addition is faster than that of the polycondensation under the alkaline catalyst condition. In general, the polycondensation rarely occurs, and the addition reaction rate is about 5 times of the polycondensation^[1] when pH is high and the temperature is below 60°C. In addition, the reaction of formaldehyde with hydroxymethyl phenol is easier than that with phenol. The phenomenon will continue until 50% of formaldehyde is reacted. Therefore, the maximum reaction temperature must be strictly controlled below 90°C in order to obtain the A-stage phenol-formaldehyde resin solution (polyhydroxymethyl phenol), which has excellent water-solubility and crosslinking property. NaOH is the commonly used alkaline catalyst and Ba(OH)₂·8H₂O is added in this study. The composite catalyst can increase the content of dihydroxymethyl phenol and trihydroxymethyl phenol^[5]. The technique of two-step base catalysis synthesis to synthesize water-soluble phenol-formaldehyde resin crosslinking agent is studied in this paper. The molar ratio of phenol to formaldehyde is chosen to be 1:3 in order to facilitate the hydroxymethylation reaction occurring both in ortho-position and polarization of benzene ring.

The synthesized crosslinking agent has some advantages such as good solubility in water, no precipitation and flocculation, etc. Therefore this product can be further used for gelling experiments^[6].

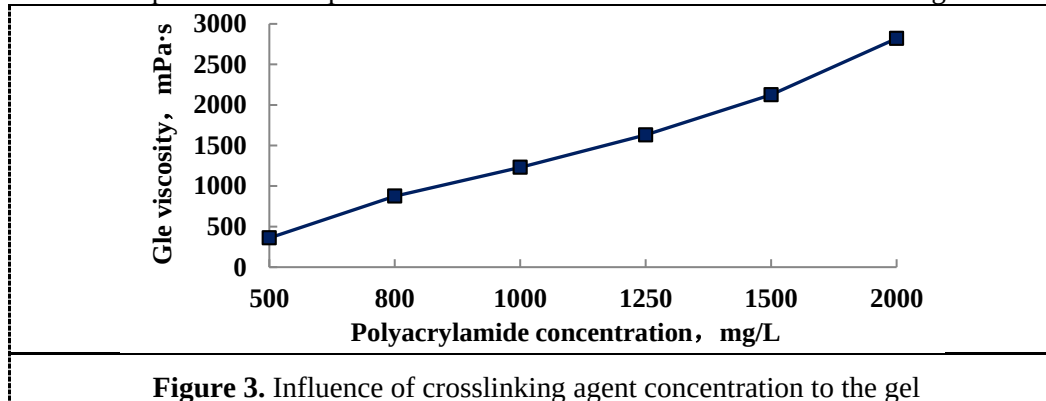
3.2. Polyacrylamide/water-soluble phenol-formaldehyde resin gelling experiments

3.2.1. Influence of polyacrylamide concentration to the gel. The concentration of crosslinking agent was 1500mg/L, the promoting cross agent was 750mg/L, and the concentration of polyacrylamide was varied. The experimental temperature was 76°C and the results were shown in Figure 2.



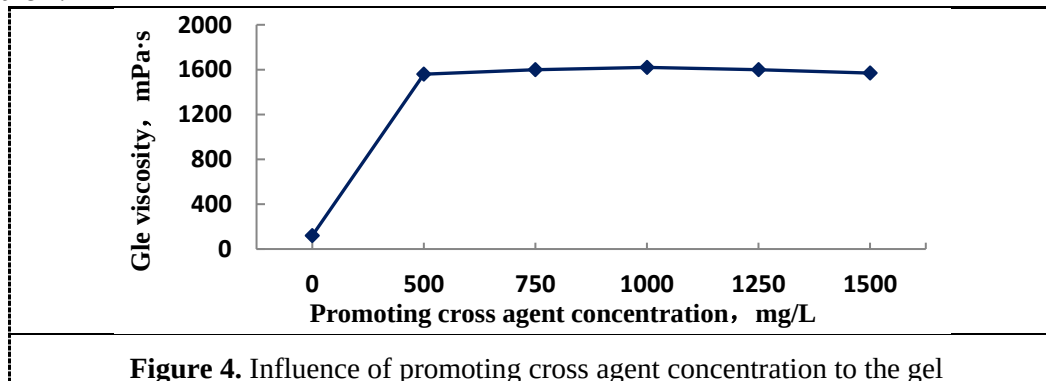
The experimental results indicated that the gel viscosity increased with the increase of polyacrylamide concentration. Based on the experience of deep profile control, the gel stability is good when the gel viscosity is above 1000mPa·s. Therefore, the polyacrylamide concentration was preferred 1000mg/L~2000mg/L.

3.2.2. Influence of crosslinking agent concentration to the gel. The concentration of polyacrylamide was 1250mg/L, the promoting cross agent was 750mg/L, and the concentration of crosslinking agent was varied. The experimental temperature was 76°C and the results were shown in Figure 3.



The gel viscosity increased with the increase of crosslinking agent concentration. However, the increasing speed slowed down when the concentration reached 1500mg/L. Therefore, the crosslinking agent concentration was preferred 1500mg/L~2000mg/L.

3.2.3. Influence of promoting cross agent concentration to the gel. The concentration of polyacrylamide was 1250mg/L, the crosslinking agent was 1500mg/L, and the concentration of promoting cross agent was varied. The experimental temperature was 76°C and the results were shown in Figure 4.



The crosslinking reaction would not occur without promoting cross agent. The viscosity value was stable after the promoting agent concentration reached 500mg/L. Therefore, the promoting cross agent concentration was preferred 500mg/L~1000mg/L.

4. Field application

Water-soluble phenol-formaldehyde resin crosslinking agent was industrially produced on the foundation of this synthetic process. It was used in deep profile control^[6] in Lu36 fault block of Huabei Oilfield and the corresponding wells obtained desirable stimulation result. During the field application, the crosslinking agent was stored for 3 months and still maintained good water-solubility, cross-linking property with polyacrylamide.

There are 4 injection wells and 5 production wells in NgII of North Lu36 fault block. The fault block is a high porosity and high permeability reservoir, and the reservoir connectivity is good. The water is injected by horizontal wells and the oil is produced by vertical wells. Based on the above experiment results, the polyacrylamide concentration applied in the field was 1200mg/L~1500mg/L, the crosslinking agent concentration was 1500mg/L, and the promoting cross agent was 750mg/L. The movable gel was injected in 4 injection wells simultaneously. The diurnal injection and formulation concentration were adjusted to keep the pressure of 4 wells as same as possible. The cumulative gel

injection was 51200m³ from June 17, 2014 to July 23, 2015. The production of the 5 oil wells increased significantly by October 2014, and the daily production increased from 5.2t to 17.1t, the composite water cut declined from 94.6% to 85.8%. The cumulative increase of oil production was up to 6483t and the term of validity was more than two years.

5. Conclusions

- i. Water-soluble phenol-formaldehyde resin was synthesized by two-step base catalysis technology using composite catalyst. It has excellent water-solubility and crosslinking property. It can crosslink with polyacrylamide to generate the gel with good stability even if the polyacrylamide concentration is lower.
- ii. The synthesized crosslinking agent has good stability which is conducive to massive injection. Polyacrylamide/water-soluble phenol-formaldehyde resin gels obtained better stimulation results in Lu36 fault block and can be introduced to similar reservoirs.
- iii. It is feasible to use the technique of deep profile control in the reservoir, in which the water is injected by horizontal wells and the oil is produced by vertical wells. The study provides an effective way to increase the oil production in this type of reservoirs.

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