Preparation and Characterization of Micron-Sized Polymer Plugging Agent

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Abstract. The experiment being made by our research is focusing on preparation and characterization of expandable plugging agent. This kind of heat resident plugging agent with spherical shape was synthesized by emulsion polymerization based on acrylamide (AM), acrylic-acid (AA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS). 2,2’-Azobis (2-methylpropionamide) dihydrochloride (AIBA) as functional catalyzer. Further separation and purification of the extracted products will be carried out to obtain the ideal products. The chemical and morphology of resin is investigated by means of thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), respectively. Moreover, compared with typical plugging agent, the expandable plugging agent we prepared should demonstrate superior properties on the aspects of temperature resistance.

1. Introduction

The issue of enhanced oil recovery from conventional and unconventional reservoirs has become increasingly important in the past decades. In order to improve oil recovery effectively, the most critical thing is increasing oil washing efficiency and sweep volume of injected fluid [1] [2]. As we all know, there are many effective methods to improve the swept volume, among which profile control technology and water plugging technology are the most widely used technology. In China, in the middle and late stage of development, most reservoirs will replenish formation energy by water injection to improve recovery [3]. Thus, after years of water flooding, researchers have found a lot of heterogeneity and favorable channels in the horizontal or vertical direction can form inside the reservoir, allowing the injected fluid to flow in and out through favorable channels and causing inefficient circulation [4] [5]. Profile control and water plugging technology can effectively block the new channel, increase the swept volume of injected fluid, and improve the recovery. However, with the deepening of exploitation, more and higher temperature and high salinity reservoirs appeared, and the performance of water blocking agent is more and more demanding [6].

At the same time, the complexity and diversity of the reservoir determine the complexity and diversity of the performance requirements of profile control agent and water plugging agent, and the rich variety of profile control agent and water plugging agent also brings more choices for enhanced oil recovery in the later stage of the reservoirs [7].
Polymer microspheres are one of the most important profile control and water shutoff technologies [8]. Microspheres synthesized by special monomers range from nanometer to micron or even millimeter in size. In addition, they have certain properties of temperature resistance, salt resistance and slow expansion, which can meet the water plugging requirements of high temperature and salinity.

2. Methodology

2.1. Materials
Acrylamide (AM), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylic-acid (AA), N, N'-methylene double acrylamide (MBA), 2,2'-Azobis(2-methylpropionamide) dihydrochloride (AIBA), sodium hydroxide (NaOH), ethanol, Span 80, Tween 60, sodium chloride (NaCl) were provided by Chengdu Kelong Chemical Co. and used as received. Kerosene was purchased from Chengdu Sidi Chemical Co., Ltd. Homogeneous core plugs were cemented quartz cores without any clays.

2.2. Synthesis and purification of polymer microspheres
The oleic phase (8.8 g of Span80 and 1.2 g of Tween60 dissolved in 70 g of kerosene) was transferred to a three-neck flask equipped with a stirrer, dropping funnel and thermometer. 10 g of AM, 4 g of AMPS, 2 g of AA, 0.8 g of MBA were dissolved to 40 g of distilled water, and then the pH was adjusted to 7 by using NaOH solution with a mass fraction of 40 percent. The blend was then added to the oleic phase with mechanical stirring at 600 r/min for 30 min. Afterwards, oxygen was eliminated by injecting pure nitrogen for 10 min. The reaction temperature was increased to 50 °C with mechanical stirring at 350 r/min, after which 0.013 g of AIBA were simultaneously dropped into the emulsion slowly. After 3 hours, the reaction was terminated and the flask was cooled down. The reactant was then washed by ethanol and pulverized. Finally the reactant was dried at 50 °C for 6 hours.

3. Result and Discussion
As shown in Figure 1 and Figure 2, the microsphere presents a good round shape. During inverse emulsion polymerization, a number of tiny droplets containing reactive substances gradually moved towards the larger droplets. Thus, some tiny clumps attached to the surface of the microsphere. Microspheres can be dispersed in water and the hydration particle size of most microspheres range from 2-10 μm. This size is ideal for blocking growls in a reservoir.

As shown in Figure 3, the microsphere lost weight at a slower rate before 270°C, which shows good heat resistance. According to the measurement, the microsphere lost half of its weight at 384°C. This means that all the water in the microsphere and some of the chemical bonds uncovered, the microsphere structure began to disintegrate. To be continued, after 480°C, the microsphere only has a mass of 80 percent. The microsphere has been almost carbonized.

In laboratory experiments, the microspheres showed good water plugging ability. Table 1 shows water plugging capacity of microspheres in cores with different permeability. When the injection pressure was stable, two PVs of microspheres solution were injected into the core gripper. The salinity of the solution is 30000 mg/L and the mass concentration of the microsphere is 0.3%. Results shows that the blocking rate is 87.30% and 77.62%, respectively.
Figure 1. SEM micrographs of microspheres.  
Figure 2. Microscope micrographs of microspheres.

Figure 3. TGA curves of microspheres.

Table 1. Water plugging experiments (80°C).

| Core Number | Permeability (μm²) | Inject PV | Blocking rate (%) |
|-------------|--------------------|-----------|-------------------|
| 1           | 0.25               | 2         | 87.30             |
| 2           | 0.61               | 2         | 77.62             |

4. Conclusion
The microspheres we prepared have good morphology, excellent temperature resistance and salt resistance. It shows outstanding potential in TGA experiment and water plugging experiment. We believe that this will be a promising polymer water plugging material.

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