A Polymer-based Drilling Fluid with High Temperature, Salt and Calcium Resistance Property

Zhiwen Dai1*, Jinsheng Sun1 and Yan Wang1
1Department of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, China
daizhiwen95@163.com

Abstract. Filtrate reducer is facing higher requirements and challenges in temperature and salt resistance. A novel polymer filtrate reducer was synthesized by free radical polymerization in aqueous solution. By filtration experiments, the results show that the polymer has good filtration loss performance under high temperature and saturated salt. Through the optimization with filtrate reducer and inhibitor, the optimum components of drilling fluids are water, 4.0wt% bentonite, 0.3wt% Na2CO3, 2.0wt% DAADS, 3.0wt% SMP-II, 3.0wt% SPNH, 3.0wt% SMC, 1.0wt% SDJA and 2.0wt% RH-3. The drilling fluid system has temperature resistance up to 220℃, salt resistance to saturation and calcium resistance up to 1.0%. The API fluid loss of the drilling fluids with the addition of saturated NaCl and 1wt% CaCl2 respectively after aging at 220℃ was 6.0 mL and 4.4 mL.

1. Introduction
Drilling fluids play an important role in oil and gas exploration and development, such as carrying cuttings, cooling and lubricating drilling tools, balancing formation pressure and preventing formation collapse[1-3]. At present, there are three types of drilling fluids: water-based drilling fluids (WDFs), oil-based drilling fluids (ODFs) and synthetic-based drilling fluids (SDFs)[4]. Water-based drilling fluids are considered as the key direction of research and development of drilling fluids, because of its low cost, environmental friendliness and good cooling capacity and other advantages.

Due to the increasing demand for global oil and gas resources and the depletion of shallow oil and gas resources, the exploration target is gradually expanding to a deep complex formation with high temperature and high salinity[5,6]. Complex geological conditions lead to more difficult control of water loss and rheological properties of drilling fluids. As a key treatment agent to control fluid loss and rheology, filtrate reducer for WDFs is facing higher requirements and challenges in temperature and salt resistance[7,8]. In this study, a novel polymer filtrate reducer was synthesized in aqueous solution, which showed good salt, calcium and temperature resistance property. Through the optimization with other agents, the formula of the drilling fluid system was determined.

2. Experimental section

2.1. Materials
Acrylamide(AM,AR), 2-acrylamido-2-methylpropane sulfonic acid(AMPS,AR), N,N-dimethyl acrylamide(DMAM, AR), Dimethyl diallyl ammonium chloride(DMDAAC, 60% in water), Allyl sulfonate(SAS, AR), Ammonium persulphate(CP), Sodium Hydrogen Sulfite(CP) and NaOH(97%) were supplied from Sinopharm Chemical Reagent Co., Ltd.(Shanghai, China). KCl(Aladdin

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Biochemical Technology Co., Ltd, Shanghai, China), KCOOH(Aladdin Biochemical Technology Co., Ltd, Shanghai, China), SDJA(polyamine shale inhibitor, industrial products of China University of Petroleum (East China)) were used as shale inhibitors. SMP-II, SPNH and SMC were used as filtrate reducer and purchased from Jinsida Chemical Co., Ltd.(Kunming, China).

2.2. **Synthesis of poly(AMPS- AM-DMAM-SAS-DMDAAC)**
A certain mass of AMPS, AM, DMAM, SAS and DMDAAC were dissolved in distilled water, and then stirred until the solution was completely dissolved. The pH of the solution was adjusted by 30.0wt% NaOH. Then the initiator reaction was added in the solution, reacting under the protection of nitrogen atmosphere for 30 min. The product was purified repeatedly with acetone and dried at 103℃. Finally, a powder filtrate reducer was obtained, named as DAADS.

2.3. **Performance evaluation**

2.3.1. **Base mud preparation.** Under low-speed agitation, 16g bentonite was added into 400 mL water, then 1.2g sodium carbonate was added, and then the system was stirred at low-speed for 24 hours to fully hydrate the bentonite. 2 wt % polymer was added to the mud under low-speed stirring, and then the mud was stirred for 20 minutes at a speed of 6000 RPM.

2.3.2. **Rheology test.** The six-speed rotating viscometer (Qingdao Haitongda Special Instrument Co., Ltd., China) was used to measure the viscosity and yield point of Bent/polymer mud. The rheology test was conducted at fixed rates of 600 and 300 RPM using the API recommended procedure for field testing of drilling fluids, and then apparent viscosity (AV), plastic viscosity (PV), and yield point (YP) were calculated according to the following equations:

\[
AV = \frac{\theta_{600}}{2}
\]

\[
PV = \theta_{600} - \theta_{300}
\]

\[
YP = 0.5 \times (\theta_{300} - PV)
\]

2.3.3. **API filtration test.** Filtration tests were carried out in a ZNZ-D3 medium-pressure filtration apparatus (Qingdao Haitongda Special Instrument Co., Ltd., China) according to the API guidelines[9]. In each run, a volume of mud was placed in the filter press at room temperature with a filter paper under a pressure of 0.69 MPa. The filtrate volumes through the filter paper were determined at 30 min after starting each measurement.

3. **Results and discussion**

3.1. **Fluid-loss control property of DAADS**
Table 1 shows the filtrate loss of base mud after aging at 180℃ under different conditions. With the addition of saturated NaCl, the API fluid loss (FL_{API}) and high temperature and high pressure fluid loss (FL_{HTHP}) of the mud increased greatly, while the FL_{API} of the mud changed slightly and FL_{HTHP} of the mud increased with the addition of 1.0wt% CaCl₂. The results show that DAADS has good API filtration loss effect, but it has relatively more FL_{HTHP} of the mud with saturated salt and 1.0wt% CaCl₂. It needs to be compounded with other filtrate reducers to achieve better filtration loss effect.

| Type                   | FL_{API} mL | FL_{HTHP} mL |
|------------------------|-------------|--------------|
| Base mud               | 6.4         | 24           |
| Base mud+saturated NaCl| 15.6        | 38.6         |
| Base mud+1%CaCl₂       | 6.8         | 38.2         |
| Base mud+saturated NaCl+1%CaCl₂ | 16.8 | 42.8         |
3.2. Optimization of compatible filtrate reducers
Sulfonated additives (SMP-II, SPNH, SMC) were selected as compatible filtration control agents. Table 2 shows the rheological and filtration properties of mud before and after aging at 180°C with different concentration of sulfonated additives (mass ratio of SMP-II, SPNH, SMC is 1:1:1). The viscosity of the base mud increased before and after aging with the addition of sulfonated additives, and the filtrate loss before and after aging was greatly reduced. When the dosage of sulfonated additives was 9.0%, the FL_API after aging was 4.2 mL, and the FL_HTHP decreased to 18 mL. When the dosage of sulfonated additives was more than 9.0%, the viscosity of the system increased greatly and the filtrate loss decreased slightly. The results show that the DAADS has good compatibility with the sulfonated additives and the optimum dosage of sulfonated additives is 9.0%.

Table 2. Results of the rheological and filtration properties of base mud with different quality of sulfonated additives

| Concentration of sulfonated additives | Test conditions | AV mPa·s | PV mPa·s | YP Pa | FL_API mL | FL_HTHP mL |
|-------------------------------------|-----------------|----------|----------|------|-----------|------------|
| 0                                   | Before aging    | 62.75    | 39       | 23.75| 4.4       | ——         |
|                                     | After aging     | 24       | 11       | 13   | 6.4       | 25         |
| 3                                   | Before aging    | 66       | 50.5     | 15.5 | 3.2       | ——         |
|                                     | After aging     | 55       | 38.5     | 16.5 | 4.8       | 22.4       |
| 6                                   | Before aging    | 68       | 47       | 21   | 3.0       | ——         |
|                                     | After aging     | 67.5     | 50       | 17.5 | 4.4       | 20.2       |
| 9                                   | Before aging    | 73       | 51       | 22   | 2.6       | ——         |
|                                     | After aging     | 62       | 48       | 14   | 4.2       | 18         |
| 12                                  | Before aging    | 80       | 55       | 25   | 2         | ——         |
|                                     | After aging     | 61       | 50       | 11   | 3.8       | 17.8       |
| 15                                  | Before aging    | 86       | 61       | 25   | 0.8       | ——         |
|                                     | After aging     | 64.5     | 52       | 12.5 | 3.6       | 17.4       |

3.3. Optimization of shale inhibitor
Figure 1 shows the swelling increments of bentonite in water and aqueous solutions of three inhibitors (KCOOH, SDJA and KCl) as a function of time. The swelling increments of bentonite pellets immersed in water, 3 wt % KCl, 3 wt % KCOOH and 1 wt % SDJA were 6.99, 3.91, 3.6 and 3.46 mm, respectively. Compared with the swelling in water, the SDJA achieved the lowest swelling increments. Therefore, the polyamine inhibitor SDJA is selected as the inhibitor of the system and the optimum dosage is 1.0wt%.
Considering the experimental results and the properties of additives, the optimum components of drilling fluids are water, 4.0% bentonite, 0.3% Na2CO3, 2.0% DAADS, 3.0% SMP-II, 3.0% SPNH, 3.0% SMC, 1.0% SDJA and 2.0% RH-3, named as DAADS/WDF.

3.4. Performance evaluation of DAADS/WDF

3.4.1. Temperature resistance. Figure 2 shows the rheological and filtration properties of mud after aging at different temperatures. As the temperature increased from 180°C to 220°C, the apparent viscosity and plastic viscosity of the system gradually decreased, from 59 mPa·s and 45 mPa·s to 42.5 mPa·s and 34 mPa·s. And the filtration loss gradually increased, FLAPI and FLHTHP increased from 3.2 mL and 15.2 mL to 4 mL and 20.2 mL. And the increasing rate was small, and the fluid loss still maintained at a low level, which could meet the field application standard. The results indicate that the DAADS/WDF has excellent temperature resistance.

3.4.2. Salt and calcium resistance. The rheological and filtration properties of DAADS/WDF with the addition of saturated NaCl and 1% CaCl2 aging at 220°C were tested respectively. The experimental results are shown in Table 3. When NaCl was saturated, the API filtration loss of the mud before and after aging was 4.0 mL and 6.0 mL and the FLHTHP was 28.6 mL, indicating that the preferred mud had
good salt resistance. After the addition of calcium chloride, the performance of the system maintained its original performance, indicating that the system could resist CaCl₂ by more than 1.0%.

Table 3. Results of antifouling performance of DAADS/WDF

| Type          | Test conditions | AV mPa·s | PV mPa·s | YP Pa | FLAPI mL | FLHTHP mL |
|---------------|----------------|----------|----------|-------|----------|-----------|
| DAADS/WDF     | Before aging   | 70       | 54       | 16    | 2.2      | ——        |
|               | After aging    | 42.5     | 34       | 8.5   | 4.0      | 20.2      |
| DAADS/WDF + saturated NaCl | Before aging | 62       | 46       | 16    | 4.0      | ——        |
|               | After aging    | 35       | 31       | 4     | 6.0      | 28.6      |
| DAADS/WDF +1% CaCl₂ | Before aging | 43.5     | 32       | 11.5  | 2.6      | ——        |
|               | After aging    | 42       | 30       | 12    | 4.4      | 26.0      |

4. Conclusions
A novel polymer filtrate reducer called DAADS was synthesized by free radical polymerization in aqueous solution. The results show that DAADS has good API filtration performance, but it has relatively more FLHTHP of the mud with saturated salt and 1.0wt% CaCl₂. To achieve better filtration loss effect, DAADS is compounded with sulfonated additives (mass ratio of SMP-II, SPNH, SMC is 1:1:1). The results show that the DAADS has good compatibility with the sulfonated additives and the optimum dosage of sulfonated additives is 9.0%. Through the optimization with other additives of drilling fluids, the optimum components of are water, 4.0wt% bentonite, 0.3wt% Na₂CO₃, 2.0wt% DAADS, 3.0wt% SMP-II, 3.0wt% SPNH, 3.0wt% SMC, 1.0wt% SDJA and 2.0wt% RH-3. The drilling fluid system has temperature resistance up to 220℃, salt resistance to saturation and calcium resistance up to 1.0%.

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