Preparation of Polymer Microemulsion Flocculant and its Application in Drilling Fluid

Xue Wang1*, Nan Xu2 and Kuisan Zhou2
1Shandong Institute of Petroleum and Chemical Technology, Dongying, Shandong, 257061, China; 2Dongying Jinmei Chemical Co., Ltd., Dongying, Shandong, 257234, China
*Corresponding author’s e-mail: 2020034@slcupc.edu.cn

Abstract. Organic macromolecular flocculants have broad application prospects in drilling fluid systems due to their strong adsorption capacity and many other advantages. At present, polyacrylamide polymer is mostly used in drilling fluid, which is difficult to dissolve, time-consuming and laborious. In this regard, this study uses acrylamide and acrylic acid as monomers, mixes acrylic acid with potassium hydroxide, adds disodium ethylenediaminetetraacetic acid solution after adsorption and filtration, and then adds acrylamide to prepare a mixed solution, using H2O2 as the initiator, polymerization reaction in microemulsion to prepare macromolecular microemulsion flocculant. It can be quickly dissolved by adding a small amount of film release agent OP-10 during application. Through the laboratory evaluation experiment of drilling fluid, it has stronger flocculation inhibition effect on the slurry formation and drill cuttings. It has strong ability to contain drill cuttings and anti-drill cuttings pollution. It is easy to absorb water to expand and can be dispersed and collapsed. The drilling roller recovery rate is high. The field application was good when carried out in Shunbei 5-14H.

1.Introduction
Organic polymer flocculant has the advantages of strong adsorption capacity, fast flocculation speed, less dosage, less influence by coexisting salts and temperature, etc., and has broad application prospects[1]. The flocculant is adsorbed on the surface of the drill cuttings and the borehole wall through the coating in the drilling fluid, which can inhibit the dispersion of the drill cuttings and maintain the stability of the borehole wall. At the same time, it has the function of regulating the flow pattern and reducing the water loss[2-3], so it is also called Coating agent. Among all the coating agents, the polymer coating agent can not only wrap the drilling cuttings, but also quickly adsorb on the well wall, block the tiny cracks in the well wall, strengthen the well wall, and prevent the filtrate in the drilling fluid from entering the well wall. The drill cuttings are put in the "ocean" of the aqueous solution of the coating agent, and the coating agent is adsorbed on the surface of the new well wall of the drill cuttings to form a coated and adsorbed hydration layer, delaying or preventing the hydration expansion and dispersion of the clay component. It has a good lubricity and elasticity, and can prevent the mechanical fragmentation and dispersion of cuttings caused by friction and collision during the upward return process. This can prevent the bonding between cuttings and/or between the cuttings and the borehole wall. The coating agents commonly used in drilling fluids are generally polyacrylamide polymers. Such solid coating agents are difficult to dissolve, easy to form "fish eyes" or agglomerates. It is time-consuming and labor-intensive. In this study, acrylic acid and acrylamide are used as...
monomers to polymerize in a microemulsion[4] to prepare a microemulsion coating agent. In the process of application, only a small amount of film release agent is added, which has the advantages of fast dissolution, high efficiency, and good performance.

2. Experiment

2.1 Materials and instruments
Acrylamide, acrylic acid, KOH, EDTA, analytically pure; white oil, Span 80, activated carbon (husk), initiator (H2O2), industrial products; film release agent (OP-10), etc. Type 101 electric heating constant temperature drying oven, Longkou Experimental Electric Furnace Factory; NGJ-2 high-speed mixer, Qingdao Tongchun Instrument; D90-A low-speed mixer, Qingdao Haitongda; GRL-BX3 roller heating furnace, Qingdao Aosite; four-necked flask (1000 ml), neutral filter paper, funnel, beaker, volumetric flask, etc.

2.2 Synthesis method
EDTA disodium salt is formulated into 2% aqueous solution; KOH is formulated into 33% aqueous solution; acrylic acid is formulated into 50% aqueous solution; acrylamide is formulated into 50% aqueous solution; initiator is formulated into 0.1% aqueous solution. The above solutions are all prepared with deionized water.

(1) 100~200 g of KOH solution was added to 100~150 g of acrylic acid solution until the PH value of the solution is in the range of 8-9. During the addition, ensure that the reaction temperature is below 40°C. After the addition is complete, add activated carbon to fully absorb impurities. Filter out the activated carbon; add 1%~2% EDTA solution, 250~300 g acrylamide solution, and pass in N2 gas protection, stir well to obtain a mixed solution.

(2) 150~200 g of white oil was added to a four-necked flask, stir 10~20 g of Span 80 for 30 minutes and mix uniformly, add dropwise the mixture in step (1) under the protection of nitrogen, and stir while adding dropwise to control the reaction The temperature is 25-35°C. After the dripping is completed, stir it fully, and then increase the temperature to 48-51°C to check whether the mixture will be drawn. If not, you can continue to increase the temperature and continuously check its drawing condition until the temperature rises to 52-54°C.

(3) When the wire drawing is started, the initiator is added dropwise to the reaction system to start the polymerization reaction. After the reaction starts, the temperature of the reaction system will increase by 1-2°C. Wait for the temperature of the reaction system to drop to the initial temperature at the beginning of the reaction After that, continue to add the initiator dropwise, add the initiator dropwise every 5-10 minutes, and keep the temperature of the reaction system at 45-60°C until the temperature of the reaction system no longer continues to rise, the reaction is complete, stop adding initiator and raise the temperature of the reaction system to 65-75°C. After it is fully stabilized, cool to room temperature to obtain a polymer microemulsion flocculant (LWW-1). 100 ppm of film release agent OP-10 was added before use.

3. Evaluation on the polymer microemulsion flocculant

3.1 Base slurry preparation
According to the formula [6]: fresh water 2000 ml + soda ash (8 g) + caustic soda (8 g) + 5% bentonite (100 g), was added in order, stir at high speed (3000 r/min) for 20 minutes, then stir at low speed (300 r/min) for two hours, and let stand tightly closed Curing for 24 hours standby.

3.2 Flocculation capacity
Two portions of the base slurry prepared by the above method for each 400 ml was used. 2 g KPAM weighed in advance in one portion of the base slurry under high-speed stirring (3000 r/min) was added; the other portion of the base slurry is stirred at high speed (3000 r/min) 1). 2 ml of polymer
microemulsion flocculant (LWW-1) which has been drawn in advance (injection syringe without needle) under the conditions was added. The above two samples are stirred at high speed for 20 min.

After stirring, pour the above two base slurries into a 100 ml graduated cylinder with stopper, and let stand for 8 hours to observe the free water precipitation volume. The result is that the volume of free water precipitated by adding KPAM base slurry is 3 ml; the volume of free water precipitated by adding organic polymer flocculant base slurry is 10 ml.

Experimental conclusion: The flocculation ability of macromolecular microemulsion flocculant (LWW-1) on bentonite colloidal particles is better than that of KPAM products commonly used in drilling fluid construction. It can be predicted that the use of polymer microemulsion flocculant (LWW-1) has stronger flocculation inhibition effect on the slurry formation and drill cuttings when drilling in the formations that are prone to hydration, swelling and slurry making.

3.3 Drill cuttings capacity

The base slurry prepared by the above method is divided into two parts. Under the condition of low-speed stirring (300 r/min), one part is added with 5 g KPAM; the other part is added with 5 ml of polymer microemulsion flocculant (LWW-1), and stirring is continued for two hours. After that, dry 120 g Minghuazhen drill cuttings (100 mesh) were added separately, and the stirring was continued for 2 hours before the funnel viscosity was tested. Measured separately: the base slurry with KPAM added has a funnel viscosity of 74 s; the base slurry with organic polymer flocculant has a funnel viscosity of 49 s.

Put the two groups of base slurries into airtight aging tanks, heat-roll at 120°C for 16 hours, cool to room temperature and open the tank for observation. It is found that the base slurry added with KPAM produces gelation, which cannot be stirred with a glass rod and loses fluidity. The base slurry added with polymer microemulsion flocculant (LWW-1) has a thickening phenomenon. After stirring it with a glass rod for several times, it restores its fluidity.

Experimental conclusion: The base slurry treated with polymer microemulsion flocculant (LWW-1) has a stronger ability to contain drill cuttings, that is, the ability to resist drill cuttings pollution is stronger than that of KPAM.

3.4 Ability to restrain drill cuttings dispersion

Two portions of the base slurry prepared by the above method for each 400 ml was used. 2 g KPAM weighed in advance in one portion of the base slurry under high-speed stirring (3000 r/min) was added; the other portion of the base slurry is stirred at high speed (3000 r/min). 2 ml of polymer microemulsion flocculant (LWW-1) which has been drawn in advance (injection syringe without needle) under the conditions was added. The above two samples are stirred at high speed for 20 min.

40 g of dry Shahejie drill cuttings (40 mesh) was added to the above two base slurries, respectively. They were put into airtight aging tanks, heated at 120°C for 16 hours, and cooled to room temperature via opening the tank. The above two base slurries were poured on a 40-mesh sieve. The mud was rinsed on the surface of the drill cuttings with water. For the next step, the collected drill cuttings were poured on the watch glass (weighed), and then put in the drying box. It was dried for 16 hours at 105°C (±1°C), then weighed after cooling to room temperature. The recovery rate was calculated[5].

Experimental conclusion: The base slurry treated with organic polymer flocculant has stronger anti-dispersion and anti-collapse ability on hard and brittle shale than KPAM treatment agent.

4. Application in oil field

The organic polymer microemulsion flocculant (LWW-1) has been applied in many domestic oil fields. The application technology in Shunbei 5-14H well 1st, 2nd and 3rd opening will now be briefly summarized.

4.1 Conduit and the first spud (0–1499.5 m, bentonite-polymer system)

The organic polymer microemulsion flocculant (LWW-1) has been applied in many domestic oil fields.
The application technology in Shunbei 5-14H well 1st, 2nd and 3rd opening will now be briefly summarized.

Before drilling, prepare 350 m$^3$ bentonite slurry and pre-hydrate for at least 24 hours. The formula is: desalinated water + 0.1% Na$_2$CO$_3$ + 0.06% NaOH + 10% bentonite, and the viscosity of the tube shoe is maintained for more than 80 s. The initial displacement is 30 L/s, and the drilling pressure is 1~2 t. After drilling to 100m, the normal drilling parameters are gradually restored. Enhance the function of drilling fluid wall protection, prevent the formation from collapsing, and control the loss of water at the same time, so as to solve the problem of jamming caused by the reduction of the diameter.

4.2 Upper section of second spud (1499.5 m~2350 m, polymer drilling fluid system)
The first spud well fluid from a drilling well is used to drill the cement plug, and all the mixed slurry and contaminated drilling fluid in the well are discharged during the plug sweeping process.

This well section will encounter the lower part of the Neogene Kangcun Formation, Jidike Formation; Paleogene, Cretaceous, Triassic, Permian, and will end 10 m after entering the Carboniferous Karasayi Formation.

Drilling to a depth of 2350 m according to the design will convert the drilling fluid system into a KCl polymer system. On the basis of small experiments, 8% KCl is added at one time by mixing KCl solution, and the system conversion is completed.

| Table 1 Mud performance before transformation |
|-------------------------------|----------------|----------------|-------------|----------------|-----------------|---|---|
| density /g cm$^{-3}$ | Plastic glue /mPa s | gel strength /Pa | Api fluid loss /ml | funnel viscosity /s | yield value /Pa | PH | Cl/mg L$^{-1}$ |
| 1.14 | 13 | 2/5 | 9.2 | 47 | 4 | 9 | 9690 |

Table 2. Mud performance after transformation

| density /g cm$^{-3}$ | Plastic glue /mPa s | gel strength /Pa | Api fluid loss /ml | funnel viscosity /s | yield value /Pa | PH | Cl/mg L$^{-1}$ |
|---------------------|--------------------|-----------------|-------------------|-------------------|----------------|---|---------------|
| 1.7 | 8 | 0.5/2 | 9.8 | 41 | 2 | 9 | 29800 |

Daily colloidal solution maintenance formula: 40 m$^3$ water + NaOH: 0.1 t + LWW-1: 0.25 t + CMC-LV: 0.2 t + CMC-HV: 0.1 t. And by supplementing KCL to maintain K$^+>15000$ mg/L. The stratum in the lower part of the Kucun Formation is loosely cemented and prone to leakage. TRS-DF is added to the mud during drilling to improve the plugging and wall-building capabilities of the drilling fluid and reduce the amount of leakage. By supplementing the polymer colloid solution, the inhibition ability of the drilling fluid is ensured, and the supplement of ultrafine calcium improves the plugging ability of the drilling fluid. After the system is converted, mix with 10% bentonite slurry in time (using CMC-LV protective glue on site) to appropriately increase the shear force of the slurry.

4.3 Third spud (5122 m~7630 m, potassium amine-based polysulfon drilling fluid system)
When drilling, prepare potassium amine-based polysulfonate fluid to supplement the consumption and adjust the performance of the drilling fluid. The basic formula of glue is: wellsite water+0.6% caustic soda+0.3~0.5%LWW-1+3-4%SMP-2+3~4%SPNH+3.5%KCl+0.3~0.5%polyamine+0.5~1%
Polyalcohol + 1~2% High Softening Point Emulsified Asphalt +0.5%PAC-LV +0.5%DSP-1. Due to the large difference in density between colloidal solution and well slurry, the replenishment rate should be strictly controlled when replenishing the colloidal solution. According to the daily consumption, it will be uniformly added to the drilling fluid in a long flow of water in a cycle time.

After the three-opening of this well was drilled, the electrical survey operation went smoothly, and the calculated average caliper expansion rate was 11%, which was better than the design requirement.
The electrical survey curve showed that the three-opening borehole diameter was relatively regular and smooth as a whole, which also ensured smooth casing operation.

5. Conclusion
In this study, acrylic acid and acrylamide were used as monomers to polymerize in a microemulsion to prepare a microemulsion coating agent. Adding a small amount of film release agent during application has many advantages such as fast dissolution. Some conclusions are as follows:

1. The flocculation ability of macromolecular microemulsion flocculant (LWW-1) for bentonite colloidal particles is better than that of KPAM products commonly used in drilling fluid construction. The use of macromolecular microemulsion flocculant (LWW-1) shows a stronger flocculation inhibitory effect on the mud making formation and drill cuttings.

2. The base slurry treated with macromolecular microemulsion flocculant (LWW-1) presents a stronger ability to contain drill cuttings, that is, the ability to resist drill cuttings pollution is stronger than that of KPAM.

3. The base slurry treated with organic polymer flocculant illustrates a stronger anti-dispersion and anti-collapse ability on hard and brittle shale than KPAM treatment agent.

The base slurry is various in different kinds of oil field. The performance of the polymer microemulsion flocculant is significant during application. Further evaluation will be conducted.

References
[1] Zhao, J., Ren, J.P., Zhou, J.K., Ma, X.Y. (2021) Research process of polymer flocculant. Technol. Dev. Chem. Industry, 50: 35-37.
[2] Li, H.K., Luo, J.S., Li, Z.L., Geng, T., Jing, P., Huang, X.Q. (2013) Research and evacuation of a low molecular encapsulator PF-UCAP for deep-water. Petrochem. Appl., 32:91-93.
[3] Jiang, G.C., Shi, Y.W., He, Y.B., Yang, L.L., Cui, W.G., Yang, X. (2018) Preparation and characteristic of amphoteric polymer as a high temperature resistant coating agent. Oilfield Chemistry, 35: 197-202.
[4] Chen, L.W., Gan, L.H., Li, G.M., Sha, H.X, Yue, T.Y. (1999) Preparation of ultrafine poly(methyl methacrylate) particles by microemulsion reaction. Appl. Chem., 16: 25-28.
[5] China National Petroleum Corporation (1995) SY / T 5696-95 zwitterionic polymer strong coating agent FA367 for drilling fluid.
[6] Suter, J. L., Coveney, P.V., Anderson, R.L., Greenwell, H.C., Cliffè, S. (2011) Rule based design of clay-swelling inhibitors. Energy & Enviro. Sci. 4: 4572-4586.