MATEC Web of Conferences **358**, 01064 (2022) https://doi.org/10.1051/matecconf/202235801064
MSMS 2022

Synthesis of a copolymerization and the anti-high temperature property in oil well cement slurry fluid

Wenbin Wang [1, 2, *], Xiangchen Wan [1, 2], Kai Tang [1, 2]

[1] Drilling and Production Engineering Technology Research Institute of CNPC Chuanqing Drilling Engineering Co., Ltd, 710018, Xi'an, China
[2] National Engineering Laboratory for Exploration and Development of Low Permeability Oil and Gas Fields, 70018, Xi'an, China

Abstracts. Four monomers including AMPS, acrylic acid (AA), N,N-dimethylacrylamide (DMAA), and sodium allylsulfonate (AS) were used to synthesize quaternary fluid loss reducer (FRW) through copolymerization. The optimal reaction conditions were optimized by orthogonal experiment method, and the water loss reduction performance of FRW was evaluated. The results show that the optimal synthesis conditions for FRW are that the molar ratio of AMPS:AA:DMAA:AS is 4.2:1.8:3.5:0.5, the amount of initiator added is 0.3% of the total monomer mass, the monomer mass percentage is 40%, The reaction temperature was 50°C, and the pH was 7. The performance evaluation results show that FRW has good fluid loss control ability. Under the condition of adding 2%, the fluid loss is 141mL when the temperature is 220℃, which has no negative impact on the comprehensive performance of cement slurry and has strong practicability.

Key words: Fluid loss reducer; copolymer; orthogonal experiment.

1. Introduction

The main function of the oil well cement slurry fluid loss additive is to prevent or reduce the rate of the mixing water in the cement slurry from filtering to the formation[1,2]. With the gradual depletion of shallow oil and gas resources, the exploration and development targets have shifted to deeper oil and gas reservoirs[3-5]. The cementing process will not only face the problem of high temperature and high pressure, but also may encounter high salinity[6,7]. Stratum of formation water. This poses a new challenge to the performance of oil well fluid loss additives. At present, the fluid loss agent used in my country is mainly a copolymer of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and acrylamide (AM) as the main monomers [8,9,10]. This kind of fluid loss agent has low temperature resistance and salt resistance, and is easy to decompose at high temperature, causing excessive retardation of the slurry, and also reducing its ability to control fluid loss[11,12,13]. In order to solve the above problems, based on the summary of previous research results, four monomers including AMPS, acrylic acid (AA), N,N-dimethylacrylamide (DMAA) and sodium allyl sulfonate (AS) were selected. A quaternary fluid loss agent (FRW) was synthesized through copolymerization, and its structure and performance were tested.

2. Materials and methods

2.1 Materials

AMPS, AA, DMAA, AS, sodium bisulfite, ammonium persulfate, and sodium hydroxide are all analytically pure; sodium chloride is industrial grade; dispersant (SXY) and defoamer (BP-1A) are purchased from Chengdu Chuanfeng Chemical Engineering Co., Ltd.; The retarder (BXR-300L) was developed by Dagang Oilfield; Quartz sand was purchased from Henan Huarong Silica Fume Material Co., Ltd.; Jiajiang G-grade cement was purchased from Sichuan Jiajiang Weiju Feicheng Cement Co., Ltd..

2.2 Synthesis method of fluid loss agent

According to a certain molar ratio, weigh 4 kinds of monomers, AMPS, AA, DMAA, AS, etc., and dissolve them in a certain amount of distilled water, then transfer them into a 4-neck flask, and adjust the pH value with 30% sodium hydroxide solution by mass fraction. Blow in nitrogen and heat to the reaction temperature, then add initiator (ammonium persulfate: sodium bisulfite=1:1), keep the temperature constant, stir for a certain period of time, and then obtain the quaternary copolymerization fluid loss agent (FRW).

FRW performance test

* Corresponding author: zhangjian_gcy@cnpc.com.cn

 https://doi.org/10.1051/matecconf/202235801064

The performance evaluation of fluid loss agent is carried out in accordance with my country's oil and gas industry standard SY/T5504.2-2005 oil well cement admixture evaluation method. The cement slurry formula is: Jiajiang Grade G cement + 35% quartz sand (adding at an experimental temperature greater than or equal to 110°C) + 5% microsilica + 0.75% dispersant (SXY) + x% FRW + x% retarder (BXR-300L) + x% NaCl tap water. The x% in the formula represents the mass percentage of the additive in the cement, and the slurry is formulated according to the water-solid ratio of 0.44.

3. Results and discussion

3.1 FRW synthesis experiment

3.1.1 Effect of monomer ratio on fluid loss reduction performance

FRW performance is mainly determined by the number and ratio of functional groups, so the monomer ratio is one of the key factors that determine FRW performance. According to the literature investigation and preliminary investigation, the following synthesis conditions are used: the initiator is 0.4% of the total monomer mass, the monomer mass fraction is 40%, the experimental temperature is 50°C, the experimental pH value is 7.0, and the reaction time For 4h, 5 groups of different monomer ratio experiments were designed (Table 1). Then test its water loss performance at a FRW addition of 2% and an experimental temperature of 150°C.

Table 1 Performance table of FRW samples at 220℃ under different monomer ratios

Numbering	Monomer molar ratio				Filter loss /mL
	AMPS	AA	DMAA	AS	
1	5	1	3.5	0.5	112
2	4.5	1	4	0.5	96
3	4	1.5	4	0.5	73
4	4	2	3.5	0.5	50
5	4.2	1.8	3.5	0.5	52

It can be seen from Table 1 that the FRW samples with the proportions numbered 4 and 5 have low fluid loss and close to each other after adding cement slurry. Although the fluid loss of No. 4 is less than that of No. 5, it is considered that if the content of carboxyl groups in FRW is higher, it will cross-link with Ca^{2+} and Al^{3+} produced by cement hydration, resulting in increased slurry consistency and thickening. The "wrapped heart" phenomenon will also appear in the experiment [14]. Considering the fluid loss of cement slurry and the properties of the slurry, the optimal monomer ratio relationship is determined to be AMPS: AA: DMAA: AS=4.2: 1.8: 3.5: 0.5.

3.2 Optimization of synthesis conditions

On the basis of determining the best monomer unchanged, a set of orthogonal experiments was designed, taking the fluid loss of the cement slurry as the evaluation standard, and considering its influence on the strength and performance of the cement stone, and optimizing the synthesis conditions. The factors of the orthogonal experiment are shown in Table 2. The 24h strength test condition is 21MPa×150°C in water bath.

Table 2 Orthogonal experiment factors and level table

temperature /°C	Initiator mass fraction	pH value	Monomer mass fraction	Nitrogen gas time /min	Reaction time /h	Filter loss /mL	Cement stone strength /MPa
30	0.2%	5	20%	10	2	65.4	18.4
40	0.3%	6	25%	20	3	52.3	21.2
50	0.4%	7	30%	30	4	49.6	21.5
60	0.5%	8	40%	40	5	51.2	18.9
70	0.6%	9	45%	50	6	74.1	18.6

Through the analysis of the orthogonal experiment results, the optimal synthesis conditions were determined as follows: the initiator is 0.3% of the total monomer mass, the monomer mass percentage is 40%, the reaction temperature is 50°C, the pH value is 7, and the nitrogen flow time is 30min, the reaction time is 5h.

3.3 FRW fluid loss reduction performance evaluation

3.3.1 High temperature resistance

One of the most important performance indicators of FRW is high temperature resistance. Therefore, the above formula will be used to test the high temperature resistance of FRW. The addition amount of FRW is 1.0% and 2.0%, and the addition amount of retarder is 2.0%. The experimental results are shown in Figure 1.

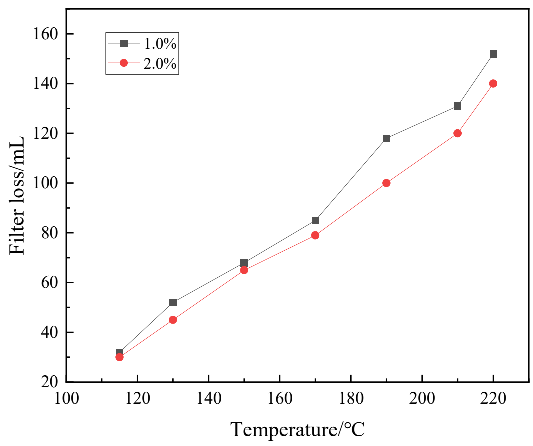

Figure 1 The relationship between the fluid loss of cement slurry and temperature

It can be seen from Figure 1 that although the fluid loss of cement slurry gradually increases as the temperature increases, the fluid loss is 152 mL when the temperature is 220°C. As the amount of FRW increases, the fluid loss of cement slurry decreases. For example, when the temperature is 220°C and the FRW increases from 1.0% to 2.0%, the fluid loss decreases by 8%.

3.3.2 Salt resistance

Stratums with high salinity often greatly reduce the effectiveness of fluid loss additives. In order to test the salt resistance of FRW, cement slurries were prepared with different concentrations of NaCl solution to investigate the salt resistance of FRW. The addition amount of FRW is 2%, the addition amount of retarder is 2%, and the curing condition of cement stone is 150°C×21MPa×48h water bath curing. The experimental results are shown in Table 4.

Table 3 Table of the influence of different salt concentrations on the performance of cement slurry

NaCl concentration	Filter loss /mL	Water separation /mL	Cement stone strength /MPa
10%	40.1	1.1	31.2
15%	42.1	1.1	32.1
20%	43.7	1.3	29.6
25%	43.9	1.4	28.3
30%	45.2	1.8	26.9
35%	45.9	2.5	25.2

It can be seen from Table 3 that with the increase of the salt content in the cement slurry, the fluid loss and water separation of the cement slurry increase slightly, but the increase is small, indicating that FRW has good salt resistance. The morphology of C-S-H gel changes, and the strength of cement stone gradually decreases. But in the case of saturated brine, the strength still reaches 20.5MPa, which is very different from the general low strength of saturated brine cement slurry.

3.3.3 The influence of FRW on cement slurry engineering performance

The fluid loss agent not only achieves the function of reducing fluid loss, but also meets other performance requirements of the cement slurry, such as rheology and mechanical properties. The effect of FRW on the engineering performance of cement slurry is studied here. The curing condition of cement stone is 150℃×21MPa×48h. The results are shown in Table 4.

Table 4 The influence table of FRW on cement slurry engineering performance

FRW increase	Liquidity /cm	Water separation /mL	Filter loss /mL	Fluidity index	Thickening factor /Pa·s^n	Thickening time /min	Cement stone strength /MPa
0	21.2	3	942	0.83	0.38	229	28.3
1%	20.3	0.8	110	0.81	0.34	235	27.6
2%	19.8	0	42	0.82	0.36	232	26.9

It can be seen from Table 4 that as the amount of FRW increases, the fluidity index (n) of the slurry decreases slightly, and the consistency coefficient (K) increases slightly, but overall the value of n is greater than 0.80 and the value of K is less than 0.40Pa•s, indicating that the cement slurry has excellent rheological properties, which is very beneficial for improving the displacement efficiency of the eccentric annulus. The water separation rate of the cement slurry is 0, and the filtration loss is less than 50mL, indicating that the slurry stability is good. The thickening time of cement slurry and the strength of cement stone did not change much with the increase of FRW, indicating that FRW would not decompose at high temperature.

4. Conclusions

In the experiment, a quaternary high-temperature and salt-resistant FRW sample was synthesized by the solution copolymerization method, and the best synthesis conditions were optimized: the molar ratio of AMPS:AA:DMAA:AS was 4.2:1.8:3.5:0.5, and the initiator was added as a monomer. 0.3% of the total mass, 40% of the monomer mass, reaction temperature of 50°C, and pH value of 7. At the same time, FRW has good fluid loss control ability. Under the condition of 2% addition, the fluid loss is 141mL when the temperature is 220 ℃, and it has no negative impact on the comprehensive performance of the cement slurry and is practical.

Acknowledgments

The work was supported financially by Shaanxi Provincial Key Research and Development Program (2019GY-136), Key Scientific Research Program of Shaanxi Provincial Department of Education (21JY035) and Youth Innovation Team of Shaanxi University. And we thank the work of Modern Analysis and Testing Center of Xi`an Shiyou University.

References

1. Siming Yan. Synthesis and mechanism study of temperature-resistant fluid loss reducer for oil well

cement[J]. Advances in Cement Research, 2017, 29(5): 183-193.

2. Vassilios C. Kelessidis, Christina Tsamantaki, Athanasios Michalakis, George E. Christidis, Pagona Makri, Kassiani Papanicolaou, Antonios Foscolos. Greek lignites as additives for controlling filtration properties of water–bentonite suspensions at high temperatures[J]. Fuel, 2007, 86(7): 1112-1121.
3. Knapen E and Van Gemert D. Cement hydration and microstructure formation in the presence of water-soluble polymers[J]. Cement and Concrete Research, 2009, 39(1): 6-13.
4. Lu Hongsheng. Yuan Xiap, Huang Zhiyu. Synthesis and performance evaluation of quaternary polymerization fluid loss additive AMPF[J]. Fine Chemical lndustry. 2013, 30(11)1256-1250.
5. Li Gao, Fu Qiang, Yu Hanghang, et al. Synthesis of quaternary copolymerization high temperature and saltresistantoil well ement fuid loss aditive[J]. Natural Gas lndustry, 2018, 38(12): 96-10.
6. Xiao Q, Rao P, Xiao W, Liu X and Zhang W. Preparation of a novel forpolymer as fluid loss additive for high temperature oil well cementing[J]. Russian Journal of Applied Chemistry, 2014, 87(9): 1377–1381.
7. Xu J, Hu R, Teng C, Chang L and Zhou X, The well cement technology in ultra-deep horizontal well Yuanba-103H[J]. Journal of Y angtze University (Natural Science Edition), 2013, 10(8): 64–67.
8. Song W, Wang Q, Hou Y, et al. AMPS/DMAM/FA - A Graft Copolymer Humic Acid Fluid Loss Reducer for Well Cementing[J]. Drilling Fluid and Completion Fluid. 2017, 34(1): 101-105
9. Liu JingIi, Hao Hujun, Li Xumei, et al. Study on graft modified PVA-A cement slurry fluid loss reducer[J]. Drilling Fluid & completion Fluid, 2014, 31(5): 78-80.
10. Yu Yongjin, Liu Shuoqiong, Liu Liwen, et al. Preparation and evaluation of high temperature cement slurry loss reduction additive DRF-120L[J]. Oil Drilling & Production Technology, 2011, 33(3): 24-27.
11. Xia X, Feng Y, Guo J, et al. Zwitterionic copolymer for controlling fluit loss in oilwell cementing: preparation, characterization, and working mechanism[J]. Polymer Engineering and Science, 2017, 57(1): 78-88 .
12. Liu Fei,Liu Xuepeng.Xia Chengy u,et al. Synthesis and performance evaluation of high temperature resistant cement slurry fluid loss additive SCF-1[J]. Chemistry of Petroleum and N atural Gas, 2016, 45(4): 64-67
13. Lu Jiahan, Guo Juan, Liang Haixiang. Development and application of a crosslinking agent for cementing polymer fluid loss reducer [J]. Henan Chemical Industry, 2021, 38(8): 18-21