Chemical Mechanism in the Fluid Loss Additive Modified Oil Well Cement System

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Abstract. Fluid loss additive (FLA) is an important chemical agent added into oil well cement to prevent cement slurry from losing water. In this work, chemical mechanism between FLA and oil well cement was investigated by multiple technologies. Compared the neat cement and the cement slurry with FLA, it is found that FLA prolongs the induction period of cement hydration, which is proved by the data of compressive strength, hydration kinetics and hydration products. The Ca^{2+} concentration, pH values and total organic carbon of cement pore solution were measured. The results show that FLA adsorbed on cement surface and the complexation occurred between Ca^{2+} and −COOH groups to build Ca^{2+} bridges between FLA and cement. Meanwhile, the fluid loss control ability of FLA is also attributed to the complexation.

Keywords: Oil well cement · Fluid loss additive · Adsorption · Complexation

1 Introduction

Polymer-based additive is one of chemical agents added into oil well cement to improve the performance of the cement slurry and to ensure cementing quality. Particularly, the polymer fluid loss additive is an important one to prevent cement slurry from losing water [1]. The most widely used for fluid loss additives are anionic copolymers synthesized by radical copolymerization of sulfonic acid and carboxylic acid monomers.

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In the past years, works in the field of cement and concrete science focused on the interactions between cement and additives. Generally, it is believed that hydration reaction made the surface of cement particles to show positively charged, once cement mixed with water. The polymer with anionic groups could adsorb on the surface of cement with the positive ions through electrostatic interaction [2]. For another, the mechanism of fluid loss additive is achieved by improving the microstructure of filter cake [3]. So far, the adsorption and improving the microstructure are the main mechanisms which have been widely accepted.

In this work, the effects of FLA on the hydration of oil well cement were analyzed by compressive strength test, isothermal calorimeter and X-ray powder diffraction (XRD). The microstructure of set cement was observed by Scanning Electron Microscope (SEM). The influence of FLA on the pore solution was analyzed via Ca^{2+} concentration, pH values and total organic carbon. These data confirmed that the complexation occurred between Ca^{2+} and –COOH groups to build Ca^{2+} bridges between the FLA and cement.

2 Experimental

2.1 Materials

Class G oil well cement in this paper was provided by Jiahua Special Cement Co., Ltd (Sichuan, China). The chemical compositions of cement were measured by X-ray fluorescence spectrometry (S4 Pioneer, Bruker, Germany), which were given in Table 1.

Fluid loss additive (FLA) was obtained by free radical polymerization according to literature [4]. FLA is the terpolymer of 2-arcylamido-2-methylpropane sulfonic acid (AMPS), itaconic acid (IA) and N, N-dimethylacrylamide (NNDMA) with a solid content of 25 wt%.

Table 1 Chemical compositions of Class G oil well cement (wt%)

CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	K_2O	SO_3	Loss on ignition
71.3	14.1	6.3	2.0	0.8	0.8	2.9	1.6

2.2 Characterization of FLA

The copolymer solution was purified by dialysis against deionized water. The purified sample was freeze-dried to be used for chemical structures and performance. The purified sample was analyzed by Bruker Vector 22 Fourier infrared spectrometer (Germany) within a spectral range from 4000 to 400 cm^{-1}. Model TGA-Q500 thermal gravimetric analyzer (Shimadz, Japan) was used to investigate the thermal stability of FLA. The heating rate is 10 °C/min and the temperature range is from room temperature to 600 °C.

2.3 Preparation and Characterization of Cement Slurry

Cement slurries were prepared according to API Recommended Practice 10B issued by American Petroleum Institute (API) [5]. The water/cement (W/C) ratio of the cement paste was fixed at 0.44 and FLA content in cement paste was 3% by weight of cement (bwoc).

High-pressure, high-temperature fluid-loss apparatus (TG-71 type, Shenyang taige oil equipment Corporation, China) was used for the static fluid loss test of oil well cement slurries. Automatic pressure testing machine (Model 4207, Chandler Engineering, USA) was used for the compressive strength test at 60 °C. An automatic cement hydration calorimeter (YT12959-08, Wuhan Yite Instrument, China) was used to record the heat evolution within 72 h. Crystal structures of hardened cement pastes were investigated by X-ray powder diffraction (X'Pert Pro, PANalytical, Holland). Morphology was observed by Field Emission Scanning Electron Microscope (Hitachi S-4800, Japan).

2.4 Characterization of Cement Pore Solution

Adsorbed amount of FLA on oil well cement surface was determined by total organic carbon analyzer (Shimadzu, Japan). The filtrate was obtained by static fluid loss test and then diluted with deionized water for TOC analysis. The amount of FLA adsorbed on oil well cement was calculated from the difference between the amount of organic carbon in liquid before and after mixing. EDTA titration is used to measure the amount of Ca^{2+} in the pore solution, which can prove the chelation of Ca^{2+} [6]. Meanwhile, the pH value of the pore solutions at different hydration time was measured by pH meter (FE20, Mettler Toledo, Switzerland) [7].

3 Results and Discussion

3.1 Structure and Property of Copolymer FLA

FTIR analysis. Figure 1 represents the FTIR spectrum of FLA. The peak observed in the spectrum of FLA at 3440 cm^{-1} is attributed to the N–H of AMPS. The peaks at 2972 and 2931 cm^{-1} are associated to the C–H stretching vibration. The peak at 1659 cm^{-1} is attributed to –C=O of amide and carboxyl, the peak at 1218 cm^{-1} is the C–N group of amide, and the peak at 1193 cm^{-1} is C–O of carboxyl. The peak at 1044 cm^{-1} is attributed to –S=O group of AMPS. It shows that the product is the copolymer of AMPS, NNDMA and IA.

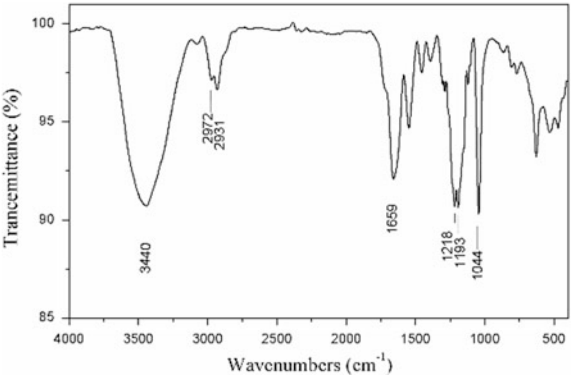

Fig. 1 FTIR spectrum of FLA

TGA analysis. Thermo Gravimetric Analysis (TGA) is widely used for characterizing the thermal stability of copolymers [8]. Figure 2 shows the TGA results of FLA which could be seen three weight loss stages. The first weight loss stage is from 60 to 153 °C with a weight loss of 3.48%, which is because the evaporation of H_2O coordinated with polymeric chain via hydrogen bonds [8]. Then, a striking weight loss occurred at the temperature up to 300 °C, this is the second weight loss stage with loss of 36.4%. The last weight loss stage with loss of 17.2% occurred from 335 to 500 °C. Thus, FLA can maintain stable structure below 300 °C and have good thermal resistance.

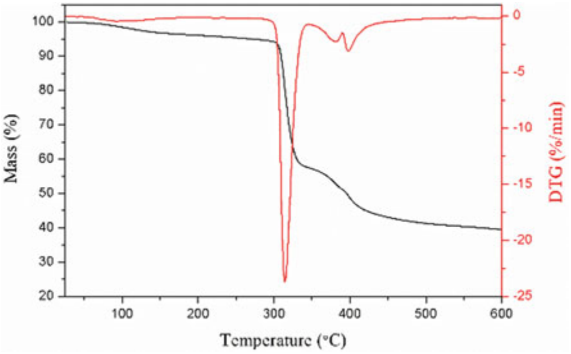

Fig. 2 TGA curves of FLA

3.2 Effects of FLA on Hydration Process

Based on the previous investigation [8] and application in oil well, the fluid loss of cement paste with FLA can be controlled within 50 ml. The static fluid loss test was repeated again to ensure the stability of the FLA. Furthermore, the compressive

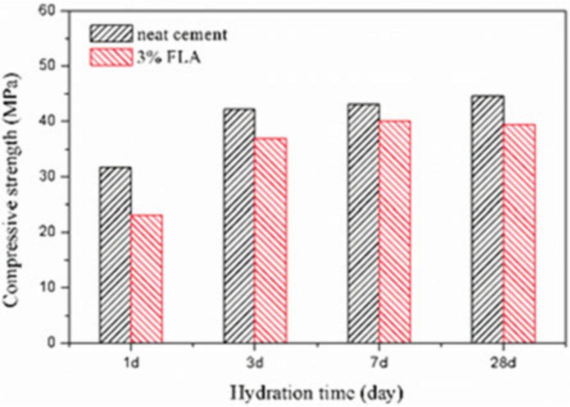

Fig. 3 Compressive strength of set cement at 60 °C

strength, hydration kinetics and hydration products were used to analyze the effects of FLA on cement hydration process.

Compressive strength. The development of compressive strength with time was measured, in order to evaluate the effect of FLA on the mechanical property of hardened cement. Figure 3 shows the compressive strength within 1, 3, 7 and 28 days at 60 °C. The oil well cement samples without FLA were treated as the neat cement. Compared with the neat cement, the compressive strength of the set cement with 3% bwoc FLA reduced due to the presence of carboxyl groups in copolymer [9].

Hydration kinetics. Figure 4 shows the heat evolution rates curves and cumulative heat curves of neat cement slurry and cement slurry with 3% bwoc FLA at 40 °C. From Fig. 4a, it can be seen that FLA prolonged the induction period of cement hydration and reduced the hydration rate in the acceleration stage [10]. At the same time, FLA decreased the total heat during curing ages, which is shown in Fig. 4b. These phenomena exactly explained why FLA reduced the compressive strength of the set cement. The anionic groups on FLA combined with Ca^{2+} from cement to prolong the cement hydration process.

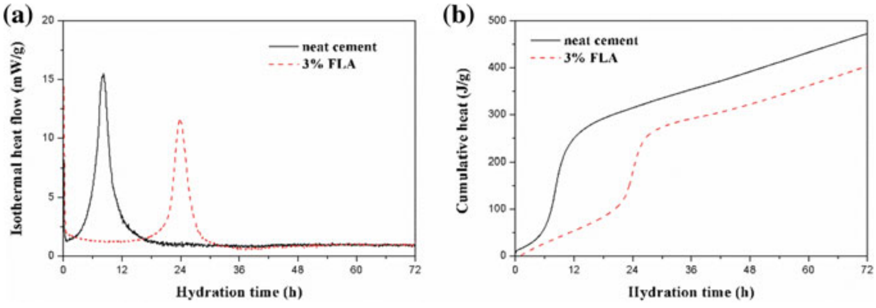

Fig. 4 The heat evolution rates (**a**) and cumulative heat (**b**) of the neat cement slurry and cement slurry with 3% bwoc FLA

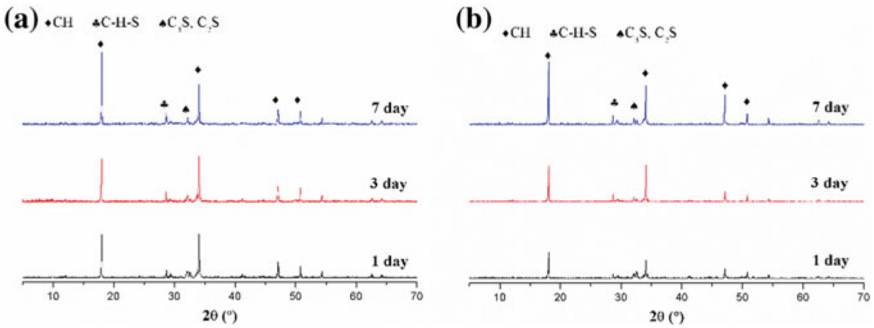

Fig. 5 XRD patterns of set cement for 1, 3 and 7 days at 60 °C, **a** neat cement, **b** set cement with 3% bwoc FLA

Hydration products. Figure 5 gives the mineral composition of set cement with 1, 3 and 7 days at 60 °C to analyze the hydration process. The mainly mineral compositions include portlandite (CH) with the peaks at 18.06°, 34.10° and 47.12°, calcium silicate hydrate (C–S–H) and unhydrated minerals (C_3S and C_2S) [11]. The precipitates of portlandite (CH) formed at the acceleration stage of cement hydration [8]. From the intensity of CH in Fig. 5a and b, the FLA put off the form of CH crystals due to the chelation with Ca^{2+}. This result is in accordance with hydration kinetics in Fig. 4.

3.3 Microstructure Analysis by SEM

SEM is a direct technology to investigate the microstructure of materials. In this section, SEM was used to observe the pore structure of set cement. As shown in Fig. 6a, lots of pores existed in the neat cement. However, the set cement with 3% bwoc FLA in Fig. 6b shows less pore structure. The hydration product CH could be clearly observed from the image. CH is scattered distributed in cement which is marked by red regions in Fig. 6a. However, it can be seen a large area of CH in the field of vision in Fig. 6b. The large area of CH is more likely to break the cement stone due to poor continuity of the C–S–H structure. Thus, FLA is of benefit to the formation of CH, but not good for compressive strength.

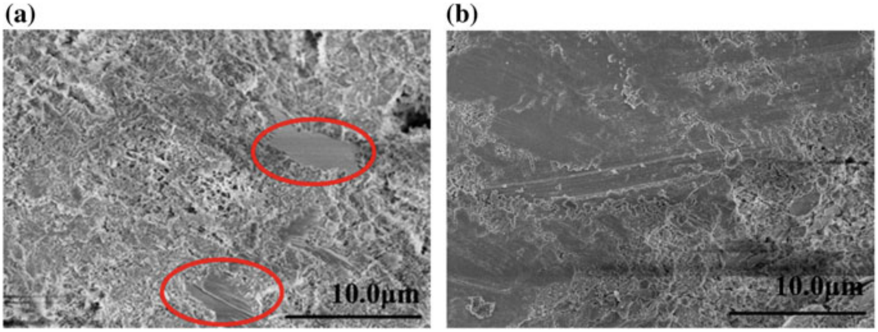

Fig. 6 SEM images of hydration cement cured for 3 days at 60 °C, **a** neat cement, **b** set cement with 3% bwoc FLA

3.4 Effects of FLA on the Pore Solution

Adsorption behavior of FLA on cement surface. The filtrate was obtained by static fluid loss test to use for TOC analysis. The adsorbed amount was calculated from the difference between the amount of organic carbon in liquid before and after mixing. Figure 7 illustrates the adsorbed amount of FLA on the surface of cement with time. It can be clearly seen that the equilibrium adsorbed amount decreases with the temperature, but the equilibrium rate increases. The molecular motion of FLA increased at higher temperature, which leads to desorption, as well as accelerating reaction rate. Usually, the surface of cement particles shows positively charged, and polymers have anionic groups. The adsorption of polymer onto cement surface occurred by electrostatic interaction [2]. Thus, the adsorption behavior is due to the chelation with Ca^{2+}.

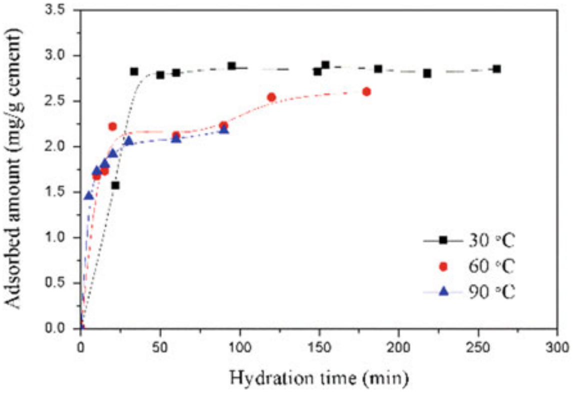

Fig. 7 The adsorbed amount of FLA on the surface of cement with time

Ca^{2+} concentration and pH values of pore solutions. The effect of copolymer on Ca^{2+} concentration in pore solutions was investigated in this section. The filtrate of cement slurry was obtained by centrifugation and used for Ca^{2+} concentration test. Figure 8a illustrates the effect of copolymer on Ca^{2+} concentrations in cement pore solutions at 30 °C. FLA makes the Ca^{2+} concentrations in cement pore solutions increase rapidly. The copolymer complexes calcium ions and inhibits the formation of CH. The nucleus formation of CH is dependent on the calcium ion concentration in the pore solution [8]. Thus, it is considered that –COOH groups on FLA are complexed with Ca^{2+} from cement and retained Ca^{2+} in the solution.

Figure 8b shows the effect of copolymer on pH values of cement pore solutions at 30 °C. Whatever the cement pore solution with and without FLA, the pH value increased during the time from 0 to 30 min. The pore solutions become alkali-rich due to the fast dissolving of some mineral components when the water mixed with cement [12]. At the same time, an intense heat is quickly released [10], which can be observed in Fig. 4a. Then, the pH value of the solution reduces and is close to equilibrium. However, it is shown that FLA makes the pH value of the solution reduces from

Fig. 8b. FLA containing the –COOH and $–SO_3H$ would lead the pH value to decrease. For another, –COOH groups are complexed with Ca^{2+} to produce $Ca(HCOO)_2$ which is slightly alkaline, while the production of $Ca(OH)_2$ in the neat cement shows a higher pH value [12].

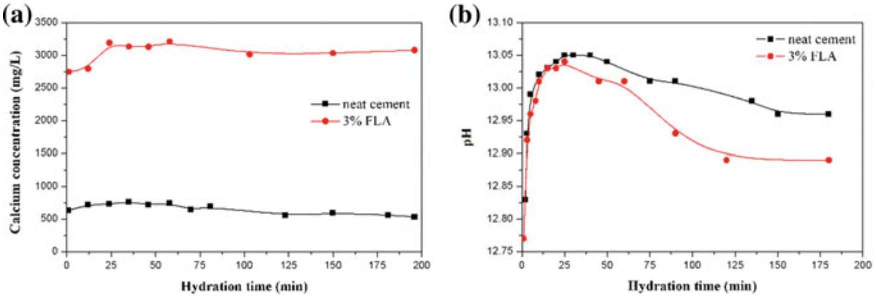

Fig. 8 The effect of copolymer on **a** Ca^{2+} concentrations and **b** pH values of cement pore solutions

4 Conclusions

In this work, the interactions between FLA and oil well cement were investigated through different testing methods. FLA containing –COOH groups could prolong the induction period of cement hydration, which is induced by the complexation of Ca^{2+} and –COOH groups. Meanwhile, the water loss control ability of FLA is also attributed to the complexation. FLA adsorbed on cement surface and the complexation occurred between Ca^{2+} and –COOH groups to build Ca^{2+} bridges between FLA and cement.

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