

http://pubs.acs.org/journal/acsodf

Article

# Effect of a 2-Acrylamido-2-methylpropanesulfonic Acid-Based Fluid Loss Additive on the Hydration of Oil Well Cement

Wei Chen, Chunyu Wang,\* Xiao Yao,\* Weikai Song, and Yiwei Zou

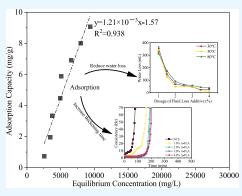
	Cite This: ACS Omeg	a 2024, 9, 9090–9097
--	---------------------	----------------------



## **ACCESS**

III Metrics & More

**ABSTRACT:** The fluid loss additive is to prevent the cement slurry from filtrating water to the formation under pressure. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS)-based fluid loss additive mainly works by adsorbing on the surface of cement particles. The adsorption affects cement hydration. In this paper, the effect of one kind of AMPS-based fluid loss additive (A-FLA) on the hydration of oil well cement was studied. The water loss, setting time, thickening time, and compressive strength of cement slurry with various amounts of FLA were measured. In addition, the hydration heat of the cement slurry, FLA adsorption isotherm on cement particles, and hydration minerals were studied. The results showed that A-FLA had a good water loss control ability. The water loss of the cement slurry decreased slowly with the increase of A-FLA dosage when the adsorption capacity exceeded 4.47 mg/g. The low adsorption capacity of A-FLA (less than 4.47 mg/g) had a significant impact on the thickening time. With an adsorption capacity greater than 4.47 mg/g,



Article Recommendations

the thickening time varied minimally. A-FLA mainly delayed the hydration of  $C_3S$  at 1 day and reduced the production amorphous phase.

## ■ INTRODUCTION

In oil wells with a depth of several thousand meters, the main function of the fluid loss additive (FLA) is to prevent the cement slurry from filtrating water into the formation under pressure and maintain the good fluidity of the slurry. There are two main types of FLAs: particulate  $FLA^{1-3}$  and 2-acrylamido-2-methylpropanesulfonic acid (AMPS)-based FLAs.<sup>4–7</sup>

Particulate FLAs rely on them to plug the pores of the filter cake to achieve the purpose of reducing water loss. Cross-linked microgels<sup>1,2</sup> and latexes<sup>8</sup> are the main representatives. The match of the filter cake pores and cross-linked microgel or latex particles is directly related to their water loss control ability. The main category of AMPS-based fluid loss additive (A-FLA) is high-molecular-weight anionic copolymers.<sup>9–11</sup> The size of the A-FLA in solution does not exceed 100 nm, which is smaller than the pore size of the cement slurry filter cake. Plugging of the pores by a single macromolecule did not occur. A-FLA is adsorbed on the surface of cement particles to reduce the diameter of the pore throat and reduce the permeability of the filter cake.<sup>9,12–14</sup> In addition, the A-FLA adsorbed on the surface of cement particles and increase the compactness of the filter cake.<sup>15</sup>

The adsorption ability of different anionic groups on cement particles is  $SO_3^- < CO_2^- < vic(CO_2^-)_2 < PO_3^{2^-}$ .<sup>10</sup> Carboxylic group-containing monomers<sup>16–18</sup> and phosphate group-containing monomers<sup>19,20</sup> are often used as anchor groups. They have strong adsorption on cement particles and can improve the

high temperature resistance of FLA.<sup>20-22</sup> The water-soluble polymer FLA containing these groups has a maximum applicable temperature of more than 200 °C.<sup>21-23</sup> The adsorption of the FLA on the surface of cement particles will affect cement hydration. However, few studies have focused on the effect of FLA on cement hydration, which is the key to affecting the thickening time of the cement slurry.

In this paper, the effect of A-FLA on the hydration of oil well cement was evaluated, compared with poly(vinyl alcohol) FLA (P-FLA). The water loss, setting time, thickening time, and compressive strength of cement slurry containing different dosages of A-FLA or P-FLA were tested. In addition, the hydration heat of the cement slurry, the adsorption isotherm of FLA on cement particles, and hydration minerals were measured. Finally, the effect of adsorption of the FLA on water loss and thickening time was comprehensively analyzed.

### MATERIALS AND METHODS

**Materials.** High sulfate-resistant Class G oil well cement was used in this paper and was obtained from Zibo Zhong Chang

Received:October 9, 2023Revised:January 22, 2024Accepted:January 25, 2024Published:February 15, 2024





ACS Omega				http://pubs.acs.org/journal/acsodf						
Table 1. Che	mical Comp	osition of the	e Cement (w	t %)						
SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	LOI <sup>a</sup>	
21.03	4.10	4.83	0.32	62.71	1.96	2.14	0.42	0.24	2.25	
<sup>a</sup> LOI: loss on	ignition.									

Special Cement Co., Ltd. The chemical composition of the cement tested using an X-ray fluorescence spectrometer (ARL-9900, Thermo Scientific) is shown in Table 1. The mineral compositions were estimated using quantitative Rietveld refinement, as shown in Table 2. Even though the tricalcium

 Table 2. Mineral Composition of Cement (wt %)

C <sub>3</sub> S	$C_2S$	C <sub>3</sub> A	$C_4AF$	gypsum
53.4	23.9	4.1	13.6	5.0

aluminate ( $C_3A$ ) content is higher than 3%, all cement mineral compositions are within API specifications<sup>24</sup> while taking into account measurement uncertainties. A-FLA was obtained from China Oilfield Services Limited (COSL). It is a transparent liquid, and the solid content is 26.7%. The viscosity-average molecular weight of A-FLA is 815396, provided by the COSL. Distilled water was used throughout the slurry preparation process. The P-FLA and dispersant SAF were obtained from Weihui Chemical Co., Ltd., and they were a solid powder. The viscosity-average molecular weight of P-FLA is 1102364, provided by the company. SAF is a sulfonated aldehyde-ketone condensation polymer dispersant.

**Preparation of Cement Slurry.** The water to cement ratio was 0.44 according to API SPEC 10A: 2019,<sup>24</sup> and the slurries were prepared according to API RP 10B: 2013.<sup>25</sup> The liquid A-FLA was premixed with water, and the solid P-FLA and dispersant SAF were premixed with cement. The water was poured into a blender container. At 4000  $\pm$  250 rpm, the cement or cement/dry additive blend was added to the container in 15 s. Place the cover on the mixing container and continue mixing at 12,000  $\pm$  250 rpm for 35 s.

**Properties of Cement Slurry.** Thickening time and setting time: the thickening properties of the cement slurry were evaluated by an atmospheric consistometer. The consistency, which is expressed in Bearden units of consistency (Bc),<sup>25</sup> was measured over time. The thickening time was determined when the consistency of the cement slurry reached 70 Bc. The setting time of cement slurry was tested in accordance with the standard ISO 9597-6:2008.<sup>26</sup>

Water loss: the prepared cement slurry was poured into an atmospheric consistometer for stirring and preheating. The preheated cement slurry was poured into a fluid-loss cell to test the water loss of cement slurry, according to API RP 10B:  $2013.^{25}$ 

Compressive strength: compressive strength of hardened cement slurry was conducted based on API RP 10B: 2013.<sup>25</sup> The hardened slurry was demolded at 1 day and cured in water to the specified age.

**Hydration Heat of Cement Slurry.** To analyze the influence of the FLA on the hydration of oil well cement, an isothermal calorimeter (TAM AIR, TA) was used to measure the hydration heat. The experimental temperature was set at 50  $^{\circ}$ C, which was the maximum permissible temperature of the instrument. 5.76 g of the prepared cement slurry was accurately weighed into an ampule for measuring the cement hydration heat. The heat flow and accumulated heat were measured within 45 h. The data after 2700 s was used for analysis because the cement slurry needs time to equilibrate to 50  $^{\circ}$ C.

**Adsorption Isotherm.** The prepared cement slurry was poured into the atmospheric consistometer for stirring and preheating, with a target temperature of 80 °C and a heating time of 20 min. After the target temperature was reached, the slurry was stirred for another 20 min. Then the slurry was poured into a centrifuge tube and centrifuged at 10,000 rpm for 5 min. The supernatant was used to measure the total organic carbon (TOC) concentration of A-FLA or P-FLA using a TOC analyzer (vario TOC, ELEMENTAR). The adsorption amount of FLA on the cement particle surface was taken to be the difference between the amount initially added and the amount present in the liquid phase measured by TOC.

**Mineral Compositions.** X-ray diffraction (XRD) was used to examine the mineral composition of the hardened cement slurry. Anhydrous ethanol was used to stop the hydration of cement slurry after being cured for 1, 2, and 7 days. The mass ratio of the sample to anhydrous ethanol was about 1:20. All samples to be tested for XRD were then dried in a vacuum drying oven for 4 h at 60 °C and crushed to powder using an agate mortar before testing. NIST standard reference material SRM-676a, corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, PDF no. 01-082-1399), was used as the internal standard with a dosage of 20 wt % for estimating the mineral compositions using quantitative Rietveld refinement. The XRD test was carried out with a SmartLab diffractometer (D/MAX-RB, Rigaku Corporation) with Cu K<sub> $\alpha$ </sub> radiation at a scanning rate of 5°/min from 10 to 80°, 2 $\theta$ .

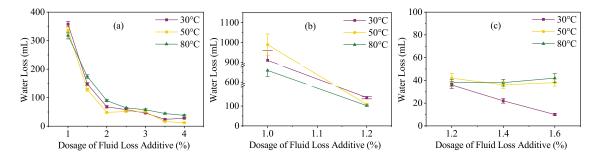


Figure 1. Water loss of cement slurry containing (a) A-FLA, (b) P-FLA, and (c) P-FLA and 0.3% SAF.

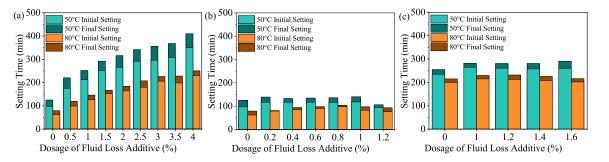
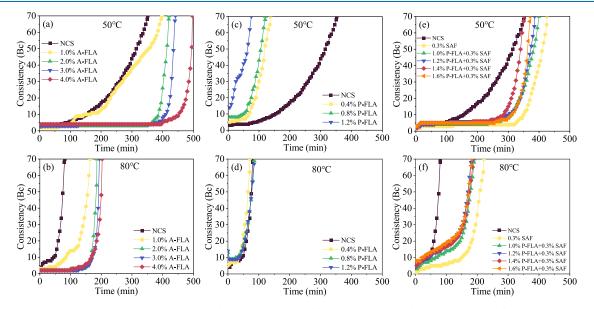


Figure 2. Setting time of cement slurry containing (a) A-FLA, (b) P-FLA, and (c) P-FLA and 0.3% SAF.



**Figure 3.** Thickening curves of cement slurry containing (a) A-FLA at 50 °C, (b) A-FLA at 80 °C, (c) P-FLA at 50 °C, (d) P-FLA at 80 °C, (e) P-FLA and 0.3% SAF at 50 °C, and (f) P-FLA and 0.3% SAF at 80 °C.

#### RESULTS

Effect of the A-FLA on the Water Loss of Cement Slurry. Figure 1 shows the water loss of oil well cement slurry containing A-FLA at 30, 50, and 80 °C, compared with that containing P-FLA and SAF. As shown in Figure 1a, at the three temperatures, the water loss of A-FLA cement slurry decreases rapidly with the increase of A-FLA dosage within 2% and decreases slowly when the dosage exceeds 2%. In addition, temperature does not affect water loss significantly.

As a comparison, the effect of P-FLA on the water loss of cement slurry is evaluated. As shown in Figure 1b, 1.0% P-FLA cannot control the water loss and the cement slurry "blows dry" (all the free water in the cement slurry was filtrated) in 30 min. 1.2% P-FLA greatly reduces the water loss of cement slurry; however, it is still higher than 100 mL. A larger dosage of P-FLA reduces the fluidity of cement slurry, and it is not conducted when the P-FLA dosage exceeds 1.2%.

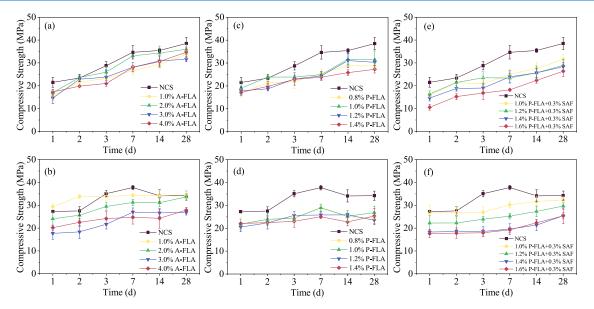
Generally, P-FLA should be used together with dispersant. These two additives have a synergistic effect on reducing the water loss of the cement slurry. As shown in Figure 1c, 0.3% SAF dispersant helps reduce the water loss of cement slurry containing 1.2% P-FLA, which is about 40 mL at the three temperatures. More P-FLA reduces the water loss at 30 °C but has little effect on the water loss at the other two temperatures.

Setting Time of Cement Slurry Containing Fluid Loss Additive. The setting time visually shows the effect of the FLA on cement hydration. The setting time of cement slurry containing A-FLA or P-FLA at 50 and 80  $^{\circ}$ C is shown in Figure 2. The initial and final setting times of cement slurry containing A-FLA increases with the dosage of A-FLA at 50 and 80  $^{\circ}$ C, as shown in Figure 2a. The final setting time of cement slurry containing 4.0% A-FLA is about 3 times that of neat cement slurry (NCS) at 80  $^{\circ}$ C. Therefore, A-FLA has a retarding effect and delays the cement hydration.

For cement slurry containing P-FLA, as shown in Figure 2b, P-FLA has little effect on the setting time of cement slurry when the P-FLA dosage is less than 1.0%, which shortens the setting time of cement slurry containing 1.2% P-FLA. The combination of P-FLA and SAF on the setting time of cement slurry is also evaluated, and the result is shown in Figure 2c. The dosage of SAF is fixed at 0.3%. P-FLA also shows little effect on the setting time of cement slurry in the case of a fixed SAF dosage. The setting time of cement slurry containing both P-FLA and SAF is longer than that containing P-FLA alone, demonstrating that SAF has a retarding effect.

**Thickening Time of Cement Slurry Containing Fluid Loss Additive.** Thickening time is a key measure of cement slurry pumpability. The thickening curves of cement slurry containing A-FLA or P-FLA at 50 and 80 °C are shown in Figure 3. As shown in Figure 3a, the thickening time of the cement slurry increases with the dosage of A-FLA at 50 °C. The thickening time of the NCS is 352 min, while the thickening time of the cement slurry containing 4.0% A-FLA is 497 min. When the dosage of A-FLA exceeds 2.0%, cement slurry containing A-

Article



**Figure 4.** Compressive strength of hardened cement slurry containing (a) A-FLA at 50 °C, (b) A-FLA at 80 °C, (c) P-FLA at 50 °C, (d) P-FLA at 80 °C, (e) P-FLA and 0.3% SAF at 50 °C, and (f) P-FLA and 0.3% SAF at 80 °C.

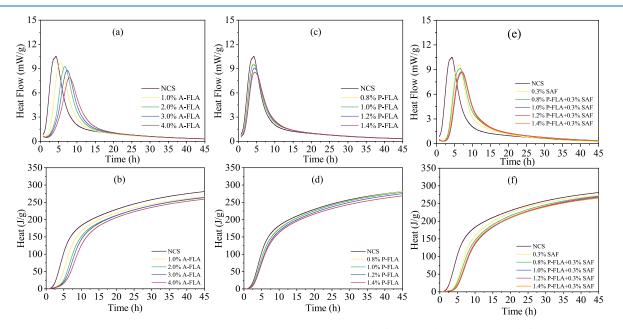


Figure 5. Heat flow and accumulated heat of cement slurry containing FLA at 50 °C, (a,b) A-FLA; (c,d) P-FLA; and (e,f) P-FLA and 0.3% SAF.

FLA exhibits excellent right-angle thickening properties compared with the NCS. Figure 3b shows the thickening time of cement slurry containing A-FLA at 80 °C. The thickening time of cement slurry containing A-FLA is longer than that of NCS and also exhibits excellent right-angle thickening property. The thickening time of NCS is only 81 min, while the thickening time of cement slurry containing 4.0% A-FLA is 203 min. However, the thickening time increases a little when the dosage of A-FLA increases from 2.0% to 4.0%. It demonstrates that the effect of A-FLA on the thickening time of cement slurry becomes limited after exceeding a certain amount at 80 °C.

P-FLA shortens the thickening time of the cement slurry at 50 °C, as shown in Figure 3c, and increases the initial consistency. The thickening time of cement slurry containing 1.2% P-FLA is only 75 min and the starting consistency increases to 14 Bc. This is possibly due to the fact that P-FLA thickens the cement slurry

at 50 °C. P-FLA's thickening effect becomes weak at 80 °C, and the thickening time of cement slurry varies little with P-FLA dosage, as shown in Figure 3d. The starting consistency is still affected by the P-FLA's thickening effect. The starting consistency of the cement slurry containing 1.2% P-FLA is also 14 Bc. However, it decreases after heating to the target temperature. The combination of P-FLA and SAF on the thickening time of cement slurry is also evaluated, and the result is shown in Figure 3e,f. It also demonstrates the retarding effect of SAF on cement hydration. The thickening time of cement slurry containing 0.3% SAF is 426 min at 50 °C and 222 min at 80 °C, which is longer than that of the NCS. The P-FLA's thickening effect is not very significant. The thickening time of the cement slurry containing both P-FLA and SAF is shorter than that containing only SAF but varies little with the P-FLA dosage at 80 °C. The right-angle thickening property of the

Tab	le 3.	Summar	y of the	Hy	dration	Heat	Results	of	Cement Slurries	
-----	-------	--------	----------	----	---------	------	---------	----	-----------------	--

notation			accele	accumulated heat (J/g)			
	duration (h)	minimum heat flow $(mW/g)$	begin (h)	end (h)	maximum heat flow $(mW/g)$	24 h	45 h
NCS	0.61	0.90	1.33	4.23	10.52	242.49	281.15
1.0% A-FLA	1.33	0.57	2.56	5.57	9.73	231.13	266.23
2.0% A-FLA	2.28	0.52	3.65	6.65	9.24	225.32	263.20
3.0% A-FLA	2.50	0.48	3.96	7.34	8.78	225.27	264.28
4.0% A-FLA	2.70	0.46	4.24	7.89	7.88	219.82	259.07
0.8% P-FLA	0.79	0.62	1.54	4.07	9.56	239.40	281.05
1.0% P-FLA	0.81	0.50	1.53	4.15	9.50	238.73	278.87
1.2% P-FLA	1.14	0.62	1.76	4.38	9.07	234.07	274.90
1.4% P-FLA	1.03	0.68	1.78	4.46	8.57	228.99	268.64
0.3% SAF	1.33	0.32	3.06	6.39	9.67	237.95	273.30
0.8% P-FLA + 0.3% SAF	1.43	0.30	3.13	6.44	9.13	230.08	271.27
1.0% P-FLA + 0.3% SAF	1.67	0.26	3.52	7.09	8.65	224.24	267.57
1.2% P-FLA + 0.3% SAF	1.25	0.28	3.05	6.96	8.75	225.73	269.80
1.4% P-FLA + 0.3% SAF	1.41	0.32	3.06	6.88	8.71	224.34	265.40

cement slurry containing P-FLA and SAF is not as good as that containing A-FLA.

Compressive Strength of Hardened Cement Slurry Containing Fluid Loss Additive. Figure 4 presents the compressive strength of a hardened cement slurry containing a FLA. At a temperature of 50 °C, the compressive strength of hardened NCS increases with curing age. It starts at 21.52 MPa at 1 day and steadily rises to 38.51 MPa at 28 days. A-FLA, however, reduces the compressive strength of cement at the same curing age and exhibits a substantial decrease in compressive strength at a 4% A-FLA dosage, as illustrated in Figure 4a. P-FLA also reduces the compressive strength of cement at 50 °C, but the P-FLA dosage does not significantly impact the compressive strength, as seen in Figure 4c. The addition of SAF further decreases the compressive strength of the P-FLA cement, as indicated in Figure 4e. Notably, when 0.3% SAF is added, the compressive strength of cement decreases with an increase in P-FLA dosage.

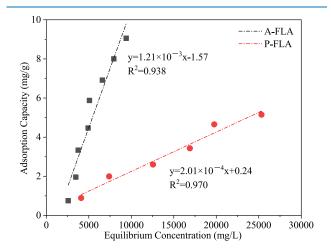
At 80 °C, the compressive strength increases with curing age within the first 7 days but decreases at 14 and 28 days. A high dosage of A-FLA considerably reduces the compressive strength of cement at the same curing age, particularly at 3 and 4% A-FLA, as demonstrated in Figure 4b. The impact of P-FLA on the compressive strength of cement at 80 °C is similar to that at 50 °C. P-FLA reduces the compressive strength of cement, but the P-FLA dosage does not significantly affect the compressive strength, as shown in Figure 4d. The introduction of SAF further diminishes the compressive strength of the P-FLA cement, as depicted in Figure 4f. When 0.3% SAF is added, the compressive strength of cement declines with an increase in P-FLA dosage.

Hydration Heat of Cement Slurry Containing Fluid Loss Additive. Heat is generated during the process of cement hydration. The study involved measuring the hydration heat of cement slurries, and the results can be observed in Figure 5 and summarized in Table 3. In Figure 5a,b and Table 3, it is evident that an increase in A-FLA dosage leads to a prolonged induction period, a delayed onset of the acceleration period, and a reduction in the maximum heat released during the acceleration period. The 24 h accumulated heat decreases as the A-FLA dosage increases from 1.0 to 4.0%, while the 45 h accumulated heat remains relatively stable. These results align with the setting time and thickening time of cement slurry containing A-FLA.

In Figure 5c,d and Table 3, it is observed that P-FLA has minimal impact on the heat flow and accumulated heat of the

cement slurry. When compared to A-FLA cement slurry, the induction period of P-FLA cement slurry extends slightly, indicating that P-FLA has little influence on the hydration of oil well cement. However, when 0.3% SAF is added to the P-FLA cement slurry, the induction period further extends, the onset of the acceleration period is delayed, and the maximum heat during the acceleration period decreases, as demonstrated in Figure 5e,f and Table 3. This clearly illustrates that SAF retards the cement hydration process.

Adsorption Isotherm Curves. Figure 6 illustrates the adsorption isotherm curves of a cement slurry containing A-FLA



**Figure 6.** Adsorption isotherm of cement slurry containing A-FLA or P-FLA at 80 °C.

or P-FLA at 80 °C. The adsorption of A-FLA or P-FLA on the surface of cement particles follows a linear isotherm pattern. These two curves were fitted separately, and the results are presented in Figure 6. Notably, the adsorption isotherm curve of A-FLA on cement particles displays a steeper slope compared to that of P-FLA. This suggests that A-FLA exhibits a higher adsorption capacity on the surface of cement particles, while the adsorption of P-FLA is minimal.

The adsorption of A-FLA onto the cement particle surfaces begins at an initial equilibrium concentration. As per the fitted equation, this initial equilibrium concentration is measured at 1296 mg/L.

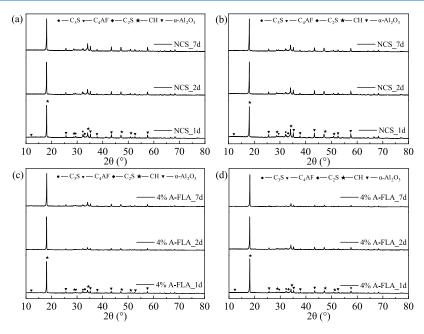


Figure 7. XRD patterns of cement slurries with and without A-FLA cured for 1, 2, and 7 days (a) NCS at 50 °C, (b) NCS at 80 °C, (c) 4% A-FLA cement slurry at 50 °C, and (d) 4% A-FLA cement slurry at 80 °C.

Table 4. Minerals of Hardened Cement Slurry Cured for at 50 and 80 °C (wt %)

	minerals	C <sub>3</sub> S	$C_4AF$	$C_2S$	СН	amorphous phase
50 °C	NCS_1day	15.00	8.88	9.88	17.63	48.61
	NCS_2days	12.38	7.38	8.88	18.88	52.48
	NCS_7days	5.13	6.63	6.50	18.75	62.99
	4% A-FLA_1day	18.25	7.88	10.50	18.50	44.87
	4% A-FLA_2days	13.75	7.38	8.13	18.25	52.49
	4% A-FLA_7days	7.50	6.33	6.38	18.76	61.03
80 °C	NCS_1day	7.13	7.00	6.63	19.63	59.61
	NCS_2days	6.88	6.75	6.88	21.25	58.24
	NCS_7days	4.00	5.00	4.75	25.25	61.00
	4% A-FLA_1day	8.74	7.13	7.25	18.25	58.63
	4% A-FLA_2days	7.18	6.68	7.13	21.50	57.51
	4% A-FLA_7days	4.86	5.75	4.74	23.63	61.02

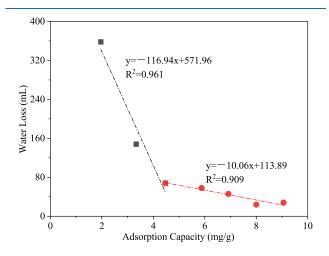
Early Hydration Minerals. Figure 7 depicts the XRD patterns of cement slurries, both with and without A-FLA, cured for 1, 2, and 7 days. In the NCS samples at both 50 and 80 °C, only portlandite (CH, PDF no. 01-076-0570) is observed as a crystallized product, as shown in Figure 7a,b. Weak unreacted minerals C<sub>3</sub>S (PDF 01-085-1378), C<sub>4</sub>AF (PDF 01-070-1498), and C<sub>2</sub>S (PDF no. 01-070-0388) are detected at all three time points. Importantly, the presence of A-FLA does not alter the hydration products, as evidenced in Figure 7c,d. Table 4 provides a summary of the minerals present in hardened cement slurry cured at 50 and 80 °C, determined through Rietveld refinement. Notably, the 4% A-FLA cement exhibits a higher remaining C<sub>3</sub>S content than NCS at 1 day, both at 50 and 80 °C. However, this difference diminishes with increasing curing time. A-FLA has a minimal impact on the  $C_4AF$  and  $C_2S$  content. Furthermore, A-FLA has a minor influence on the formation of CH, although it does reduce the presence of amorphous phases at 1 day.

#### DISCUSSION

A-FLAs are effective due to their ability to adsorb onto the surface of cement particles. The correlation between the water

loss of the cement slurry and the adsorption capacity of A-FLA

on cement particles at 80 °C is illustrated in Figure 8. Notably, as



**Figure 8.** Relationship between the water loss of cement slurry and the adsorption capacity of A-FLA at 80 °C.

the adsorption capacity of A-FLA increases from 1.96 to 4.47 mg/g, the water loss of the cement slurry experiences a rapid reduction. However, when the adsorption capacity of A-FLA surpasses 4.47 mg/g, the decrease in water loss becomes less pronounced. This relationship between water loss and adsorption capacity forms two distinct lines, with 4.47 mg/g serving as the inflection point. These two lines are separately fitted, and the results are displayed in Figure 8. Furthermore, the slope of the fitting lines indicates that the water loss remains relatively stable after reaching the inflection point.

The adsorption of A-FLA onto the surface of cement particles has a retarding effect on cement hydration. This is mainly because the adsorption of FLA on the surface of cement particles delays the hydration of cement particles.<sup>27,28</sup> The stronger the adsorption capacity, the stronger the impact on cement hydration. As depicted in Figure 6, A-FLA exhibits a notably higher adsorption capacity on cement particles when compared with P-FLA. This difference is mainly affected by the functional groups of the two FLAs. The main functional group of A-FLA is a sulfonic acid group, while the main functional group of P-FLA is a hydroxyl group. The sulfonic acid group has a stronger adsorption energy than the hydroxyl group. Therefore, the adsorption capacity of P-FLA is less. Concurrently, A-FLA extends both the hydration induction period and the thickening time of cement slurry. In contrast, P-FLA does not have a significant impact on either the hydration induction period or the thickening time (as observed in Figures 2 and 5 and Table 3).

The correlation between the thickening time of the cement slurry and the adsorption capacity of A-FLA on cement particles at 80  $^{\circ}$ C is presented in Figure 9. It is evident that the thickening

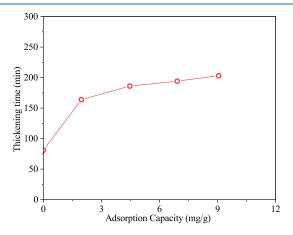


Figure 9. Relationship between the thickening time of cement slurry and the adsorption capacity of A-FLA at 80  $^\circ$ C.

time of cement slurry increases as the adsorption capacity of A-FLA rises from 0 to 4.47 mg/g. However, when the adsorption capacity of A-FLA surpasses 4.47 mg/g, the increase in thickening time becomes marginal. This behavior is analogous to its impact on the water loss of cement slurry. The substantial adsorption capacity of A-FLA on cement particles does not significantly reduce water loss or significantly extend the thickening time of cement slurry. This phenomenon can likely be attributed to the multilayer adsorption of A-FLA onto cement particles.

The XRD results in Table 4 further reveal that A-FLA primarily delays the hydration of  $C_3S$  at 1 day and reduces the formation of the amorphous phase. This is mainly because the

adsorption of A-FLA on the surface of cement particles is significant, which slows the hydration of cement.

#### CONCLUSIONS

This study investigates the influence of the A-FLA on the hydration of oil well cement. The following conclusions are drawn from the analysis:

- A-FLA effectively manages the water loss of cement slurry when used in dosages exceeding 2%. The water loss decreases significantly as the adsorption capacity of A-FLA increases from 1.96 to 4.47 mg/g. However, once the adsorption capacity surpasses 4.47 mg/g, the reduction in water loss becomes marginal.
- The setting time of cement slurry containing A-FLA increases with higher A-FLA dosages at both 50 and 80 °C. In contrast, P-FLA has a minimal impact on the setting time of cement slurry. A-FLA added cement slurry exhibits excellent right-angle thickening properties.
- At 50 °C, the thickening time of cement slurry increases with increasing A-FLA dosage. At 80 °C, the thickening time of cement slurry containing 4.0% A-FLA extends to 203 min, but it experiences only a slight increase when the A-FLA dosage goes from 2.0 to 4.0%. The thickening time of cement slurry correlates with the adsorption capacity of A-FLA, increasing from 0 to 4.47 mg/g. Beyond an adsorption capacity of 4.47 mg/g, the thickening time experiences a slight rise, similar to the trend observed in water loss due to A-FLA.

#### AUTHOR INFORMATION

#### **Corresponding Authors**

- Chunyu Wang College of Materials Science & Engineering, Nanjing Tech University, Nanjing 211816, China; orcid.org/0000-0001-9071-117X; Email: wangchunyu@ njtech.edu.cn
- Xiao Yao College of Materials Science & Engineering, Nanjing Tech University, Nanjing 211816, China; Email: yaoxiao@ njtech.edu.cn

#### Authors

- Wei Chen College of Materials Science & Engineering, Nanjing Tech University, Nanjing 211816, China
- Weikai Song COSL Oilfield Chemicals R&D Institute, Sanhe 065200, China
- **Yiwei Zou** COSL Oilfield Chemicals R&D Institute, Sanhe 065200, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c07890

#### Notes

The authors declare no competing financial interest.

#### REFERENCES

(1) Plank, J.; Dugonjić-Bilić, F.; Lummer, N. R.; Taye, S. Working mechanism of poly (vinyl alcohol) cement fluid loss additive. *J. Appl. Polym. Sci.* **2010**, *117*, 2290–2298.

(2) Wang, H.; Li, M.; Zheng, Y.; Gu, T. Function synergy of crosslinked cationic PVA polymer to AMPS-type fluid loss additive used for cement-based material. *Int. J. Polym. Sci.* **2020**, 2020, 1–15.

(3) Bülichen, D.; Plank, J. Mechanistic study on carboxymethyl hydroxyethyl cellulose as fluid loss control additive in oil well cement. *J. Appl. Polym. Sci.* **2012**, *124*, 2340–2347.

(4) Lummer, N. R.; Dugonjić-Bilić, F.; Plank, J. Effect of high temperature and the role of sulfate on adsorption behavior and effectiveness of AMPS®-based cement fluid loss polymers. *J. Appl. Polym. Sci.* **2011**, *121*, 1086–1095.

(5) Tiemeyer, C.; Plank, J. Impact of Temperature on the Solution Conformation and Performance of AMPS<sup>®</sup>- and AHPS-based Fluid Loss Polymers in Oil Well Cement. *Z. Naturforsch. B.* **2014**, *69*, 1131–1140.

(6) Plank, J.; Dugonjić-Bilić, F.; Lummer, N. R. Modification of the molar anionic charge density of acetone–formaldehyde–sulfite dispersant to improve adsorption behavior and effectiveness in the presence of CaAMPS®-co-NNDMA cement fluid loss polymer. J. Appl. Polym. Sci. 2009, 111, 2018–2024.

(7) Tiemeyer, C.; Plank, J. Working mechanism of a high temperature (200°C) synthetic cement retarder and its interaction with an AMPS®-based fluid loss polymer in oil well cement. *J. Appl. Polym. Sci.* 2012, 124, 4772–4781.

(8) Guo, J.; Pan, W.; Fan, J.; Yu, Y. Improving the performance of oilwell cement by graft-modified PB latex. *Trans. Tianjin Univ.* **2018**, *24*, 434–441.

(9) Plank, J.; Brandl, A.; Zhai, Y.; Franke, A. Adsorption behavior and effectiveness of poly (N, N-dimethylacrylamide-co-Ca 2-acrylamido-2-methylpropanesulfonate) as cement fluid loss additive in the presence of acetone-formaldehyde-sulfite dispersant. *J. Appl. Polym. Sci.* **2006**, *102*, 4341–4347.

(10) Plank, J.; Brandl, A.; Lummer, N. R. Effect of different anchor groups on adsorption behavior and effectiveness of poly (N, Ndimethylacrylamide-co-Ca 2-acrylamido-2-methylpropanesulfonate) as cement fluid loss additive in presence of acetone–formaldehyde– sulfite dispersant. J. Appl. Polym. Sci. **200**7, 106, 3889–3894.

(11) Guo, S.; Lu, Y.; Bu, Y.; Li, B. Effect of carboxylic group on the compatibility with retarder and the retarding side effect of the fluid loss control additive used in oil well cement. *R. Soc. Open Sci.* **2018**, *5*, 180490.

(12) Chen, D.; Guo, J.; Xu, Y.; Hu, M.; Li, P.; Jin, J.; Yu, Y. Adsorption behavior and mechanism of a copolymer used as fluid loss additive in oil well cement. *Constr. Build. Mater.* **2019**, *198*, 650–661.

(13) Cao, L.; Liu, C.; Tian, H.; Jia, D.; Wang, D.; Xu, Y.; Guo, J. Adsorption interaction between cement hydrates minerals with fluid loss additive investigated by fluorescence technique. *Constr. Build. Mater.* **2019**, 223, 1106–1111.

(14) Plank, J.; Lummer, N. R.; Dugonjić-Bilić, F. Competitive adsorption between an AMPS®-based fluid loss polymer and Welan gum biopolymer in oil well cement. *J. Appl. Polym. Sci.* 2010, *116*, 2913–2919.

(15) Cadix, A.; James, S. Fluid Chemistry, Drilling and Completion; Elsevier, 2022; pp 187–254.

(16) Xia, X.; Feng, Y.; Guo, J.; Liu, S.; Jin, J.; Yu, Y. Zwitterionic copolymer for controlling fluid loss in Oilwell cementing: Preparation, characterization, and working mechanism. *Polym. Eng. Sci.* **2017**, *57*, 78–88.

(17) Guo, J.; Lu, H.; Liu, S.; Jin, J.; Yu, Y. The novel fluid loss additive HTF-200C for oil field cementing. *Pet. Explor. Dev.* **2012**, *39*, 385–390. (18) Salami, O. T.; Plank, J. Synthesis, effectiveness, and working mechanism of humic acid-{sodium 2-acrylamido-2-methylpropane sulfonate-co-N, N-dimethyl acrylamide-co-acrylic acid} graft copolymer as high-temperature fluid loss additive in oil well cementing. *J. Appl. Polym. Sci.* **2012**, *126*, 1449–1460.

(19) Hurnaus, T.; Plank, J. Synthesis, characterization and performance of a novel phosphate-modified fluid loss additive useful in oil well cementing. *J. Nat. Gas Sci. Eng.* **2016**, *36*, 165–174.

(20) Hurnaus, T.; Echt, T.; Plank, J. Synthesis, Properties and HT Performance of a Novel Cement Fluid Loss Polymer Modified with Phosphate Groups. In SPE International Symposium on Oilfield Chemistry, 2017.

(21) Tiemeyer, C.; Plank, J. Synthesis, characterization, and working mechanism of a synthetic high temperature (200°C) fluid loss polymer for oil well cementing containing allyloxy-2-hydroxy propane sulfonic (AHPS) acid monomer. *J. Appl. Polym. Sci.* **2013**, *128*, 851–860.

(22) Salami, O. T.; Plank, J. Preparation and properties of a dispersing fluid loss additive based on humic acid graft copolymer suitable for cementing high temperature (200 °C) oil wells. *J. Appl. Polym. Sci.* **2013**, *129*, 2544–2553.

(23) Cadix, A.; Wilson, J.; Barthet, C.; Phan, C.; Poix, C.; Dupuis, P.; Harrisson, S. Diblock Copolymers: A New Class of Fluid Loss Control Additive for Oilfield Cementing. In *SPE International Symposium on Oilfield Chemistry*, 2015.

(24) Cements and Materials for Well Cementing. American Petroleum Institute, 2019. API SPEC 10A.

(25) Recommended Practice for Testing Well Cements. American Petroleum Institute, 2013. API RP 10B-2.

(26) Cementing—Test methods—Determination of setting time and soundness. International Organization for Standardization, 2008. ISO 9597:2008.

(27) Zhang, Y.; Kong, X. Correlations of the dispersing capability of NSF and PCE types of superplasticizer and their impacts on cement hydration with the adsorption in fresh cement pastes. *Cem. Concr. Res.* **2015**, *69*, 1–9.

(28) Thomas, N.; Birchall, J. The retarding action of sugars on cement hydration. *Cem. Concr. Res.* **1983**, *13*, 830–842.