Effects of Acrylamide Copolymer in Fluid Loss Property on Oil Well Cementing

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Abstract

The effects of varying concentration of acrylamide copolymer (an effective fluid loss control additive) and temperature on fluid loss in oil well cementing was studied. The fluid loss of neat cement, fluid loss property of cement slurry with varying concentration of acrylamide copolymer, and effects of temperature in cement slurry with acrylamide copolymer were investigated at temperature range of 120°F -180°F BHCT and pressure of 3500 psi. The concentrations of the copolymer studied were 0.25, 0.50 and 0.75% BWOC. Thickening time tests were also carried out. The fluid loss value decreased with increase in concentration of acrylamide irrespective of the temperature. At low concentration of the additive, the activity of the copolymer as a fluid loss additive was influenced by temperature. The findings from the research show that fluid loss of cement with the copolymer is a function of temperature and concentration of the copolymer.

Keywords: Acrylamide • Copolymer • Fluid loss • Cement • Oil well • Concentration • Temperature

Introduction

Cementing wells in order to ensure zonal isolation has been the adopted technology over the past decades. Throughout those years, considerable research and development efforts on both cement and admixture chemistry have led to significant improvements of that technology. Nevertheless, despite strict quality controls and API cement classification and grading, there is still a lot of variability in cement composition and reactivity. One of the most difficult to predict behaviors is the cement response to admixtures. Sometimes variability can be so dramatic such that some additives performances can completely be lost in some cement grades [1].

Conventional systems used as fluid loss control additives consist of high molecular weight sulfonated copolymers, generally comprising of 2-Acylyamido-2-Methylpropane Sulfonic acid (AMPS). The mechanism of action of these polymers was studied by Plank, et al. They reported that their performance is directly linked to adsorption of the polymer on cement surface. This adsorption is electro statically driven. Anionic sulfonate grounds from the 'AMPS' monomeric units adsorb onto the cationic sites on the cement [2].

During cementing operations on oil wells, fluid loss control additives are generally used to prevent water loss and to maintain constant water to solid ratio in cement slurries. But their mechanism of action is not yet completely understood. An experimental procedure is described to discriminate between the two predominant phenomena which are the increase of interstitial water viscosity and the decrease of cement cake permeability. The influence of polymeric additives is studied and more particularly the efficiency of fluid loss control additives is related with a threshold concentration corresponding to the overlapping concentration of macromolecular chains in solution.

Fluid Loss Additives (FLAs) are added to oil well cement to reduce uncontrolled water loss from the slurry while being pumped along porous formations in the bore hole. For polymeric FLAs, three types of working mechanisms are known [3]. First, long chain FLAs may adsorb onto hydrating cement particles and destruct filter cake pores either by polymer segments which freely protrude into the pore space or even bridge cement particles. Through this adsorptive mechanism filter cake permeability is reduced and low fluid loss is achieved [4]. Second, FLAs may plug the pores of the cement filter cake through formation of micelles or a polymer film. Third, some FLA polymers such as cellulose ethers are hydrocolloids which can bind an enormous amount of water molecules in the inner sphere of the dissolved macromolecule and their hydrate shells. This way, a large portion of the mixing water is physically bound and cannot be released during the filtration process. Besides, the uptake of water results in swelling of the hydrocolloid which then, because of its size, can obstruct the pores of the cement filter cake. Measurements by mercury intrusion porosimetry have shown that the average pore size in a cement filter cake is approx. 1 μm.

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The goal of the investigation presented here was to study and compare the working mechanisms of three chemically different FLAs. Their chemical structures are shown in Figure 1. At first Polyvinyl Alcohol (PVA), a low temperature and highly economical FLA, was investigated. It is commonly cross-linked with boric acid to enhance its performance [5]. However, non-cross-linked PVA is effective up to a temperature of approx. 40°C only and has the reputation of giving unreliable performances in the field. Understanding its working mechanism may stimulate ideas for improvement of its fluid loss performance. Second, Polyethylene Imine (PEI), a cationic FLA with an entirely different chemical structure in comparison to PVA, was studied. When PEI is combined with anionic additives such as ammonium lignosulfonate and naphthalene sulfonic acid formaldehyde or Acetone-Formaldehyde-Sulfite polycondensate (AFS), its performance increases dramatically. Yet, the mechanism behind this improvement was not known. Third, poly (Ca acrylamide tert-butylsulfonate-N, N-dimethylacrylamide) (CaATBS-co-NNDMA), a sulfonated copolymer possessing a weight average molecular weight of approx. 1.8 mio. g/mol, was studied. This statistical copolymer contains both hydrophilic and hydrophobic segments along the polymer chain. When dissolved in water, it assumes a stretched conformation, like a cigar. It possesses sulfonate functionalities which represent good anchor groups for adsorption onto cement hydrates [6].
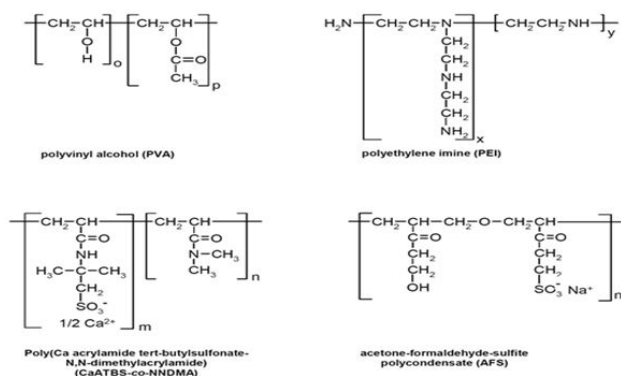

Figure 1. Chemical structures of some fluid loss additives.

Fluid loss additives

Fluid loss additives work by reacting with the water (gelling) to tie up the water molecule [7]. This gelation causes an increase in viscosity which aids in controlling fluid loss, restricting the loss of water from the cement system slurry. Percent by volume changes of water in the slurry system can be induced by interaction [8]. This can result in detrimental changes to the mechanical properties of the cement system including. Compressive strength, viscosity, transition time, and density. If this fluid loss occurs when the slurry is static in the annulus and when gel strength is forming, the unset cement is more vulnerable to formation gas/fluids percolating into unset cement [9].

Fluid loss control is the measure of how well a cement slurry system can retain the mix fluids with which the system is blended. Any permeability encountered down hole can rob the slurry system of fluid, causing an increase in viscosity that makes the slurry more difficult to respond to pump pressure to obtain the flow required for complete placement [10]. Ensuring that cement slurry performs

according to design parameters is essential to the success of a cement job. To limit potentially detrimental effects to both cement slurry and formation, and to help ensure successful cement placement, fluid loss additives are commonly added to cement compositions where there is a suspected likelihood for cement slurry dehydration, e.g., cementing across high permeability formations.

Advantages of fluid loss additives

Fluid losses additives help maintain an ideal water to cement ratio to help:

- Prevent cement bridging in the annulus,
- Protect sensitive formations from cement filtrate invasion, and
- Maintain cement slurry density.

The fluid loss additive is a copolymer which has been engineered to be salt tolerant, water soluble, and thermally stable. Fluid loss additive is thermally stable and compatible with high temperature cement retarders. Therefore, it has been used primarily under high temperature conditions [11].

This study was carried out to investigate fluid loss control using different acrylamide copolymer concentration at temperature on the fluid loss control. The use of acrylamide/acrylic acid copolymers has generally been restricted to wells below 60 °C BHCT. Above that temperature chemical changes in the copolymer often lead to retardation of the cement.

Materials and Methods

The following materials were used for the study: Weighing balance, blender jar, viscometer, pycnometer, fluid loss tester (Fann Instrument Company USA), atmospheric and High-Pressure High Temperature (HPHT). Consistometers and Waring blender are all products of fann instrument company, USA. Thickening time cup and deformer (Fann Instrument Company, USA).

Reagents

Acrylamide copolymer samples, Dyckerhoff class G cement and fresh water were obtained locally. D-air 3000 L (HES USA) (Figure 2).

Figure 2. Equipments.

Method for determination of fluid loss

This test determines the effectiveness of a cement slurry composition in preventing the loss of water from the slurry to a formation in the wellbore. A standardized mesh screen is used in the procedure to simulate the permeability of an average formation as described in API, (2004) (Figure 3).

Procedure

- After conditioning the slurry, stir it with a spatula to ensure uniformity, and then pour the cement slurry into the static fluid loss cell preheated to test temperature.
- Close the valve in the bottom cap in the closed position.
- Leave a 1 (± 1/4) inch void at the top of the 5 inch or 2 (± 1/4) inches at the top of a 10 inch cell to allow for expansion of the slurry during heating.
- Place the cell in the heating jacket with the end containing the filter screen at the bottom.
- Raise cell/heat jacket into place and tighten securely using the hand nut.
- Insert the thermocouple into the side of the cell.
- Position a graduated cylinder under the fluid loss cell to capture the filtrate.
- Ensure the pressure vent valve and manifold supply valve are closed.
- Turn the pressure regulator knob clockwise until 1,000 psi is reached.

- Ensure the cell inlet valve is open, and then slowly open the manifold supply valve to charge the test cell.
- Open the valve in the bottom cap and simultaneously start a timer.
- A test is over after 30 minutes, or when nitrogen blows through the slurry prior to the 30 minute mark.
- Close the cell outlet valve on the bottom cap.
- Measure and record the amount of filtrate collected during the test period. Filtrate should be measured in milliliters to a precision of 1 ml. If nitrogen blows through less than 30 minutes, also note the time at which the blowout occurred.
- Record filtrate volume at 30 seconds, and 1, 5, 10, 15, 20, and 30 minutes after the test begins.
- Calculate the API Fluid Loss with the following formulas: Test duration=Full 30 minutes; Vol filtrate (mL) × 2=API fluid loss.
- Where "Vol filtrate" is volume (mL) of filtrate collected
  test duration <30 minutes
  Calculated API fluid loss=Vol filtrate (mL) × 2$\sqrt{(30/t(min))}$
- Where "Vol filtrate" is volume (mL) of filtrate collected at the time "t (min)" of the blowout.

Results

From Tables 1 and 2 it shows that the acrylamide copolymer has the ability to enhance the flow rate of the cement slurry during oil well cementing (Figures 3-7).

Conc. of acrylamide copolymer (% BWOC)	Temperature (°F)		
	120	140	160
	Fluid loss of acrylamide copolymer		
0.25	219	219	207
0.5	88	96	96
0.75	54	56	81

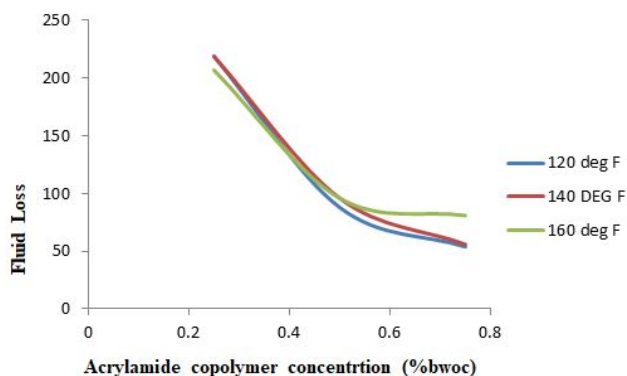**Table 1.** Fluid loss properties of acrylamide copolymer

Figure 3. Fluid loss versus acrylamide concentrations at varying temperatures
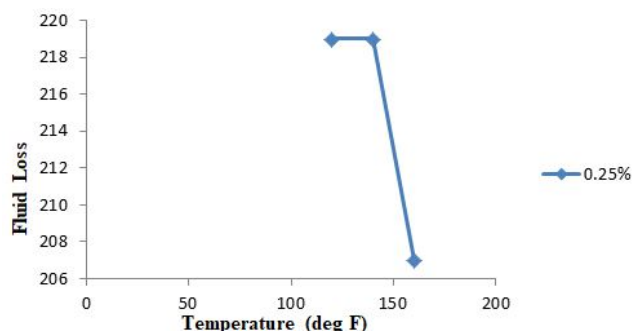

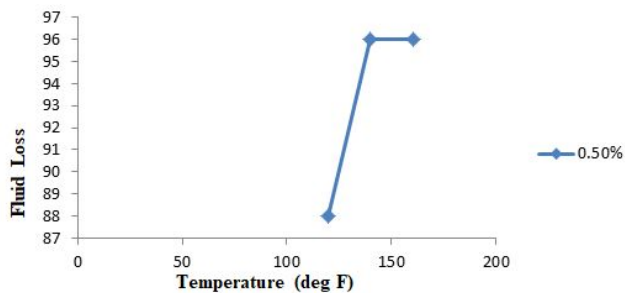**Figure 4.** Plots of fluid loss versus temperatures at 0.25% acrylamide concentration.

Figure 5. Plots of fluid loss versus temperatures at 0.50% acrylamide concentration.
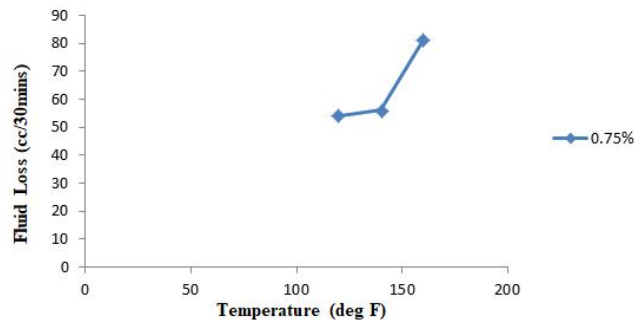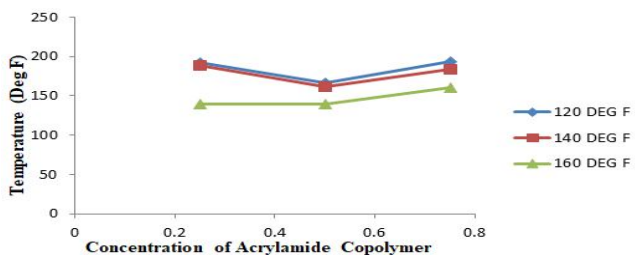

Figure 6. Plots of fluid loss versus temperatures at 0.75% acrylamide concentration.

Concentration of acrylamide copolymer (% BWOC)	120 °F	140 °F	160 °F
0.25	192	188	140
0.5	166	161	140
0.75	193	183	160

Table 2. Results of thickening time tests.

Figure 7. Plots of temperature versus concentration acrylamide copolymer.

The results show that the addition of acrylamide copolymer did not significantly increase the cement consistency but did substantially increase Apparent Viscosity (AV) JREAC-23-97474 (Tables 3-6 and Figures 8-11).

RPM	80 °F	120 °F	140 °F	160 °F
300 RPM	90	130	130	124
200 RPM	64	104	104	101
100 RPM	36	74	74	70
6 RPM	8	26	26	21
3 RPM	6	20	20	14
	PV=81	PV=84	PV=84	PV=81
	YP=9	YP=46	YP=46	YP=43

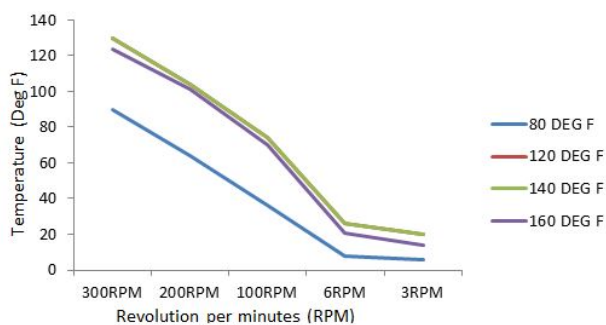**Table 3.** Rheological values of the 0.25% BWOC acrylamide copolymer.

Figure 8. Plots of temperatures versus revolution per minute of the 0.25% BWOC acrylamide copolymer.

RPM	80 °F	120 °F	140 °F	160 °F
300 RPM	146	236	244	210
200 RPM	110	182	184	163
100 RPM	66	114	130	114
6 RPM	7	30	34	33
3 RPM	4	22	25	25
	PV=120	PV=183	PV=171	PV=144
	YP=26	YP=33	YP=73	YP=66

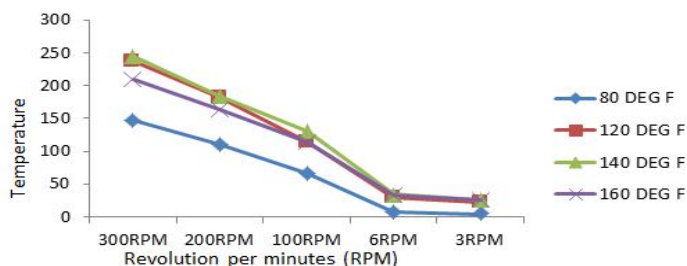**Table 4.** Rheological values of the 0.50% BWOC acrylamide copolymer.

Figure 9. Plots of temperatures versus revolution per minute of the 0.50% BWOC acrylamide copolymer.

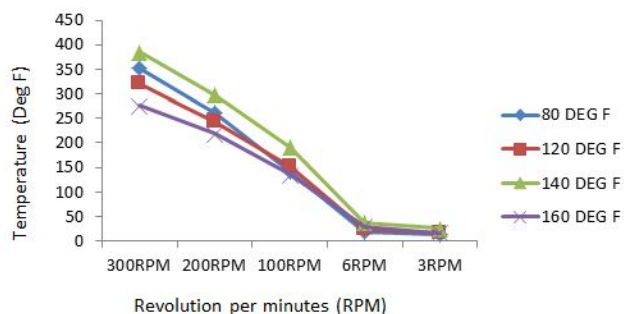| RPM	80 °F	120 °F	140 °F	160°F
300 RPM	352	320	386	276
200 RPM	262	243	298	219
100 RPM	140	152	191	135
6 RPM	19	25	36	28
3 RPM	13	17	26	15
	PV=318	PV=252	PV=293	PV=212
	YP=34	YP=68	YP=94	YP=65

Table 5. Rheological values of the 0.75% BWOC acrylamide copolymer.

Figure 10. Plots of temperatures versus revolution per minute of the 0.75% BWOC acrylamide copolymer.

RPM	80 °F	160 °F
300 RPM	234	254

200 RPM	215	212
100 RPM	144	146
6 RPM	28	46
3 RPM	16	37

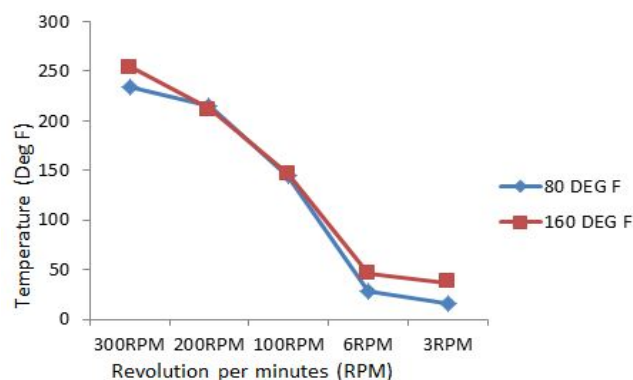**Table 6.** Rheological values of the 0.75% BWOC acrylamide copolymer with salt.

Figure 11. Plots of temperatures versus revolution per minute of the 0.75% BWOC acrylamide copolymer with salt.

Discussion

Table 1 shows the results of fluid loss at different concentrations. The fluid loss was less at 0.75% BWOC concentration and more at 0.25% BWOC concentration. This may be as a result of the increased level of the acrylamide copolymer in the slurry which utilizes the water content but for the low concentration of the acrylamide copolymer there was more fluid coming out of the slurry. The results show that the higher the concentration of the polymer the lower the fluid loss irrespective of the temperature. Liu, made similar observation in their research.

At low polymer concentration of 0.25% BWOC acrylamide copolymer, slight increase in temperature from 120°F to 140°F did not affect the fluid loss (Figure 4). However, increasing the temperature to 160°F gave a decrease in fluid loss. This may be attributed to the effect of heat that breaks the bonding of the polymer with the cement slurry. At 0.5% BWOC acrylamide copolymer (Figure 5), a decrease in fluid loss was observed when the temperature was increased from 120°F to 140°F and then stabilized with further increase in temperature. This shows that at 0.5% BWC fluid loss stabilizes at 140°F.

At 0.75% BWOC acrylamide copolymer (Figure 6), the fluid loss increased slowly and then very fast as temperature increased from 120°F to 160°F. These synthetic anionic copolymers achieve fluid loss control by reducing filter cake permeability through polymer adsorption onto the positively charged surfaces of cement hydrates (adsorptive working mechanism) as reported by Desbrieres and Plank, et al. Earlier researchers observed that while this Fluid Loss Additive (FLA) works excellent when being the sole admixture, its effectiveness may be impeded when other polymers are present in the cement slurry. As a result of this competitive adsorption, increased fluid loss was observed (Figures 7-11).

From Tables 3-6, it shows that the acrylamide copolymer has the ability to enhance the flow rate of the cement slurry during oil well cementing.

The results show that the addition of Acrylamide copolymer did not significantly increase the cement consistency but did substantially increase Apparent Viscosity (AV).

Conclusion

Acrylamide Copolymer is an effective fluid loss control additive for cementing class G cements. Fluid loss of cement slurry with acrylamide copolymer is a function of temperature and concentration of acrylamide copolymer.

The fluid loss value of the slurry with acrylamide copolymer decreased with increase in concentration of acrylamide copolymer irrespective of the temperature; therefore, the activity of acrylamide copolymer as a fluid loss additive is influenced by temperature especially at low concentration of the additive.

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fluid loss additive in the presence of acetone-formaldehyde-sulfite dispersant." *J Appl Polym Sci* 102 (2006): 4341-4347.

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