

Chemical Modification of Lignite and Investigation of its Properties in Controlling Fluid Loss of Oil Well Cement Slurries

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Received: April 22, 2019; revised: May 19, 2019; accepted: July 01, 2019

Abstract

The aim of this research was to produce a convenient additive for enhancing the properties, especially the fluid loss, of oil well cement slurries. In this regard, a variety of drilling/cementing chemical additives known as fluid loss controllers were prepared through derivatization and chemical modification of lignite. Lignite-based graft copolymers were synthesized using different groups of acrylic monomers via aqueous the free radical polymerization method. Then, it was allowed to react with sulfomethylating agents to enhance its water solubility. Subsequently, a comparative sulfomethylated lignite was prepared and employed as the backbone in the free radical polymerization. ATR-FTIR and elemental analyses were performed to demonstrate the structures of the fluid loss controller and incorporated elements. The performance of these additives in improving the properties of oil well cement slurries was investigated through analyzing the quality of fluid loss controller in saline saturated slurries. Under similar desired well conditions, i.e. a compressive strength of 800-1100 psi, a thickening time of 400 minutes, and a viscosity of 25 cP, a fluid loss below 130 ml API was obtained. The best standard performance was assigned to the cement slurry which employed sulfomethylated lignite graft copolymer.

Keywords: Lignite, Sulfomethylation, Graft Copolymers, Cement Slurry, Fluid Loss Controller

1. Introduction

Drilling fluids are mixtures of synthetic and natural chemical compounds which provide the following functions in the drilling process: cleaning the borehole and successfully transferring cuttings to the surface, lubricating and cooling the drilling rig and pipes, reducing friction, providing overburden pressure on the well to prevent the well outburst, maintaining wellbore stability, preventing pore fluids from prematurely flowing into the wellbore, and so on (Caenn and Chillingar 1996; Lewis et al., 2008; Watson et al., 2012).

The process of cementing a pipe string, e.g. casing and liners, in place is commonly known as “primary drilling.” In a typical primary drilling operation, a cement mixture may be pumped into the borehole wells between the walls and the outer surface of the pipe string located therein. The cement composition is set in the annular space, so it forms a hardened impenetrable cementitious covering which positions

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and supports tubing string in the wellbore and bonds the exterior surface of the pipe string to the formations (Smith 1984; Skaggs et al., 2000). Cement hydration is a process in which anhydrous cement deforms into a slurry by reacting with water to form an amorphous paste through chemical reaction and become like a rock mass known as concrete (Nelson et al., 1990). When a cement slurry is pressurized in a permeable formation, a process called “filtration” occurs in which the slurry water phase migrates to the formation and abandons the particles behind the cement. Such a process is commonly known as “fluid loss” (Ferrell et al., 2017). The precise working mechanism of the fluid loss controllers (FLC’s) is not fully unraveled. However, some certain processes are known to occur: when fluid loss commences throughout the formation, a solid cement filter cake is deposited on the surface of the formation. In this step, FLC agents drop the filtration rate by reducing the permeability of the filter cake or increasing the aqueous phase viscosity. In a recent review, Radnia et al. studied the application of nanoparticles to chemical enhanced oil recovery. It was mentioned that when nanoparticles are injected to a porous media, four phenomena will take place: adsorption, desorption, blocking, and migration with flowing fluid. Nanoparticles are in this way capable of affecting the adsorption behavior of surfactants onto rock surface (Solaimany Nazar et al., 2018). Researchers also speculated that some fluid loss additives such as graft copolymers, mostly anionic polyelectrolytes, follow adsorptive working mechanism (Salami and Plank, 2016).

Lignite (brown coal) and leonardite, as domestic, cheap, and abundant raw hydro-carbonaceous substances, have been recognized as an economical and cost-effective oil field chemical additive so far. Their application in muds/slurries has been limited because they are less effective; in fact, they are contaminated by common salts such as sodium chloride and calcium compounds due to the coagulation and failure to exert their protective colloidal action. By combining them with biological or synthetic polymers and/or using other methods such as chemical modification through the grafting of different vinyl and acrylic monomers on their surface, the yield and application of these materials could be developed. The aforementioned methods are common approaches to manipulating and promoting the macromolecular structures of these materials and improving their performance (Salami and Plank, 2012). Various derivatization methods such as sulfonation and sulfomethylation, pre-reaction with different caustic materials, soda, etc. have been utilized not only to provide water-soluble lignite derivatives but also to produce a single material which can be manufactured under controlled conditions to be used as a single additive (Cowan 1986; Lebo and Bushar, 1997). Peripheral hydrogen atoms in the lignite molecule are replaced by sulfomethyl radicals: $\text{R.SO}_3\text{M}^-$ in which R is a substituted methylene radical derived from an aldehyde and -M^- can be a monovalent salt such as ammonium, sodium, or the same. According to the recent literature, copolymerization is an excellent method for producing specific chemical structures and achieving properties such as hydrophobicity and hydrophobicity, rigidity, solubility, polarity, etc. Meanwhile, copolymers made with acrylic monomers have reported the highest performance (Guo and Bu, 2013; Salami, 2014; Cadix et al., 2017; Cao et al., 2018; Chen et al., 2019).

In this study, lignite-based graft copolymers were first prepared using aqueous free radical polymerization method (FLCs 1 and 2). In the following, attempts have been made to prepare a high water soluble lignite derivative so-called “sulfomethylated lignite” (SML, FLC 3). Ultimately, a comparative SML is prepared and employed as the backbone in free radical polymerization (FLC 4). The performance of these additives in improving the properties of cement slurry was investigated through testing and analyzing FLC quality in saline saturated slurries. The FLC structures and incorporated elements were also studied using ATR-FTIR and elemental analysis (CHNS) respectively.

2. Experimental

2.1. Materials

2-Acrylamido-2-methylpropane sulfonic acid (AMPS), N,N-dimethyl acrylamide (NNDMA), acrylic acid (AA), acrylonitrile (ACN), potassium persulfate, sodium meta-bisulfite, formaldehyde, and potassium dichromate were purchased from Merck company. Lignite powder containing the following molar fraction was provided locally and utilized without further purification: 60% humic acid, 35% fulvic acid, and 5% inorganic materials.

2.2. Instruments and procedures

a. FLC quality control in saline saturated cement slurries

The experimental section in this study is generally divided into two main categories: the production of lignite derivatives as an additive in the Inorganic Chemistry Research Lab of School of Chemistry, University of Tehran, and analyzing the FLC quality of the cement slurries containing these additives as designed by National Iranian South Oil Company (NISOC) in the industrial section.

In order to investigate the effects of FLC's prepared in this study on the fluid loss of saline saturated cement slurries, the FLC quality control analyses were performed by National Iranian South Oil Company (NISOC), and the recorded results were presented in FTQE 452/14700 form.

b. API static fluid loss measurements

For API static fluid loss tests, cement slurries were prepared according to the measures listed in Table 2. To do so, fresh water was first poured into an API mixer cup (Model 9B with sine-wave impeller blades No. 9B29X, Fann Inc.), and after adjusting the mixer rate at 4000 rpm, the salt, retarders, and FLC's were added respectively. Then, the solution was mixed at 4000 rpm for one minute until complete mixing. After adding a few drops of anti-foam (TEGO ANTIFOAM MR 2123) to the solution, dry cement was introduced to it; the slurry should be thoroughly mixed and made up for a maximum of 30 seconds. Then, the slurry mixture was stirred for another one minute at 12000 rpm. In this step, the specific density of the cement slurries was assessed, and subsequently, they were placed in a low pressure apparatus already reached the desired temperature. At the final step, the prepared slurries were placed in a high temperature high pressure (HTHP) cell, and the volume of the liquid extracted/filtered from the slurries at a pressure of 1000 psi and at the desired temperature was noted and recorded as API fluid loss per 30 min.

c. Thickening time measurements

In the case of thickening time test, the cement slurries were prepared following the procedure described above (see Table 2). To evaluate the thickening time, cement slurries 1-5 were placed in a high pressure (HP) consistometer cell (Model 290 HPHT, Fann), while cement slurries 6 and 7 were placed in an atmospheric consistometer (Model 165AT Atmospheric Consistometer, Fann); the desired temperature and pressure were set as given in Table 2. Thereafter, the consistency of the cement slurries was evaluated. The slurry consistency is defined in terms of the torque exerted on the paddle enclosed in a pressure chamber by the cement slurry. The relation between torque and slurry consistency is given by:

$$Bc = \frac{\tau - 78.2}{20.02} \quad (1)$$

where, τ is the torque on the paddle in g/cm and Bc represents the slurry consistency in API consistency units. The thickening time of the slurry is defined as the time required to reach a consistency of 100 Bc .

d. Compressive strength measurements

The cement slurries were prepared in accordance with Table 1 and poured into compression strength specific molds. Then, slurries 4 and 5 were placed in a curing chamber at 210 °F and at 3000 psi for 24 hours, and the other slurries were placed in a water bath at the desired temperature and pressure as tabulated in Table 2. The molds were removed from the chamber after 24 hrs. and subsequently cooled with 80 °F water. Next, they were broken by a hydraulic press and the applied pressure was reported.

Table 1

Materials and mixing conditions used in the preparation of cement slurries.

Materials	Mixing conditions						
	1	2	3	4	5	6	7
Class D cement (g)	675.4	677.6	726	–	–	–	–
Class E cement (g)	–	–	–	733.7	731.5	–	–
Class G cement (g)	–	–	–	–	–	726	726
Salt (g)	120.34	120.7	66	113.56	113.9	66	66
FLC (g)	3.37	6.7	3.63	3.69	7.41	3.63	3.63
Low temperature retarder (LTR) (g)	–	–	0.72	-	-	-	-
High temperature retarder (HTR) (g)	–	–	–	–	–	0.72	1.45
Water (mL)	333.27	326.78	337.4	315.8	308.55	337.12	336.6
Specific weight of the slurry (pcf)	118	118	118	123	123	118	118
Temperature (°F)	170	170	170	210	210	190	190
Pressure (psi)	3000	3000	3000	4000	4000	atmospheric	atmospheric

2.3. Synthesis of the graft copolymers

The lignite-{AMPS-NNDMA-AA} and lignite-{AMPS-NNDMA-ACN} graft copolymers were prepared by aqueous free radical polymerization using potassium persulfate as the initiator. In a typical reaction, according to the literature (Salami and Plank, 2012), 30 g lignite was first well ground and dispersed in 100 mL water followed by adding 60 mL (15% w/v) sodium hydroxide until adjusting the pH of solution to 12. Then, the whole system was placed in a 1-liter four-necked flask equipped with a stirrer, a thermometer, and an inlet for adding Ar gas. 200 g of water were added to the flask too. Afterwards, 50 g of AMPS, 35 g of NNDMA, and 1.2 g of acrylic acid were added in order. These proportions result in a theoretical molar ratio of AMPS:NNDMA:acrylic acid equal to 1:1.58:0.1, and the ratio of lignite to the graft monomers is 30:70 (wt./wt.). In the case of FLC 2, 15 g of AMPS, 2.5 g of NNDMA, and 3 g of ACN were added to obtain a molar ratio of AMPS:NNDMA:ACN equal to 1:0.34:0.73, and the ratio of lignite to the graft monomers is 60:40 (wt./wt.). Also, the amount of the added NaOH was 50 mL, (5% (w/v), i.e. mass of the added material per the whole solution volume). Moreover, 0.39 g of ethylene diamine tetra acetic acid (EDTA) was added. Then, the temperature was increased to 50 °C and the first portion of $K_2S_2O_8$ initiator (0.5 percent by the weight of monomers, i.e.

0.11g) was added. After 50 min of reaction, the second portion of the initiator (0.11g) was added. Grafting was continued for another 70 min while the temperature was increased to 60 °C. After allowing the mixture to react for an additional hour, the temperature was again increased to 80 °C to complete the reaction within an hour. Finally, prior to decreasing temperature, the reaction was quenched through adding 0.11 g sodium meta-bisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) equivalent to the amount of the initiator. The product yields a dark, odorless suspension having a pH of 7~8 which was further diluted with water and oven-dried to obtain the final product, i.e. FLC powder.

2.4. Preparation of sulfomethylated lignite (SML)

The sulfomethylation method applied in the current study was as follows (Lebo and Bushar, 1997): First, 30 g of well ground lignite was dispersed in 100 mL of water. Subsequently, 20 g of sodium meta-bisulfite was added to the reaction followed by adding 25 g of formaldehyde (37% v/v). In addition, 3 g of potassium dichromate was added dropwise, and the reaction mixture was stirred for 1 hr. The pH of the solution was adjusted to 10-11 by the addition of 25 mL of sodium hydroxide, i.e. a 12% (w/v) solution. Subsequently, the pH-adjusted solution was refluxed at 160 °C to complete the sulfomethylation reaction. The final obtained product was oven-dried to yield the FLC powder 3.

2.5. Preparation of SML graft copolymer

Initially, SML was prepared according to the method described formerly in Section 2.3. 30 g of lignite, 15 g of sodium meta-bisulfite, 20 g of formaldehyde, and 30 mL, i.e. 12% (w/v), of NaOH solution were used in the manner mentioned above. Subsequently, the SML solution with high water solubility was employed as the backbone in the aqueous free radical polymerization following the procedure for the graft copolymers which was fully described in Section 2.2 except that an excess amount of initiator was needed (a total of 0.4 g). 18 g of AMPS, 10 g of NNDMA, and 1.5 g of acrylic acid (AA) were added respectively to achieve a molar ratio of AMPS:NNDMA:AA equal to 1:0.17:0.02. In addition, the ratio of SML to the graft monomers is 50:50 (wt./wt.). The final product having enhanced water solubility is called FLC 4.

3. Results and discussion

7 samples of cement slurry were prepared according to the mixing conditions summarized in Table 1 for the four FLC's produced in this study. Due to the amount of materials used in the preparation of saline saturated slurries, in the case of cement slurries 2 and 5, the FLC content by weight of cement (BWOC) was applied twice compared to other slurries. (0.6% BWOC in cement slurries 2 and 5, while 0.3% BWOC in the other slurries).

3.1. API static filtration and other cement slurry properties

The API static properties of cement slurries 4 and 5 containing different increased dosages (0.3% and 0.6% BWOC respectively) of the FLC's produced in the current study and a fixed dosage of 10% BWOC of the salt were determined and compared in relatively high temperature (210 °F) high pressure (4000 psi) conditions (the slurry specific weight was 123 pcf). The results are shown in Figure 1.

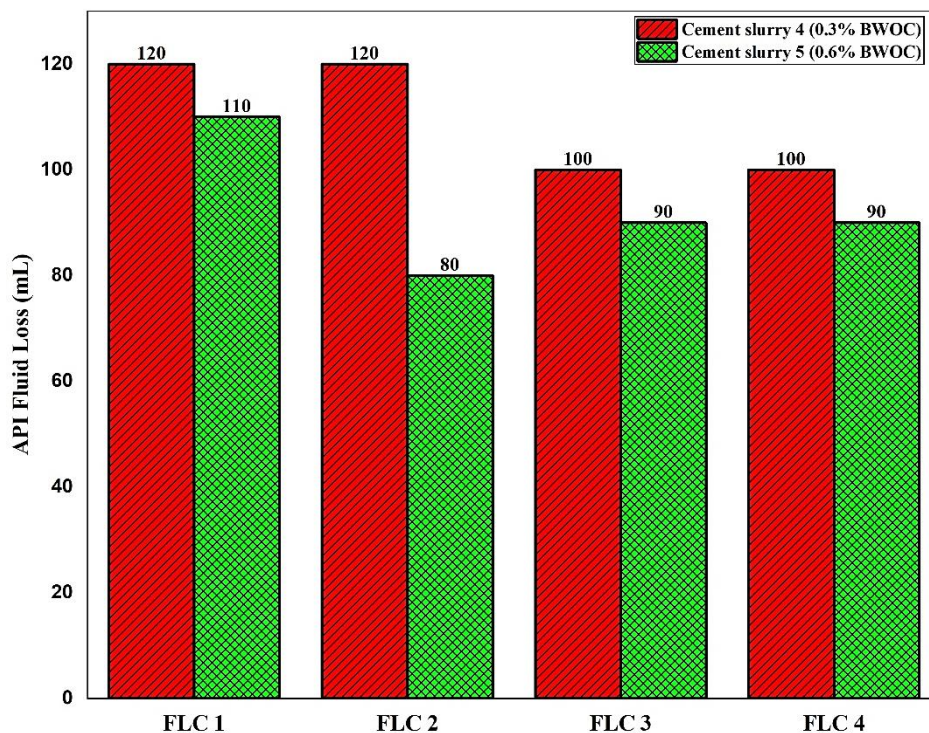


Figure 1

API static filtration properties of class E cement slurries 4 and 5 containing different increased dosages (0.3% and 0.6% BWOC respectively) of the FLC’s produced in the current study and a fixed dosage of 10% BWOC of the salt in the desired HTHP conditions.

API fluid loss has dramatically dropped in all the cement slurry mixing conditions. Notably, in cement slurries 4 and 5 which are at a high pressure (4000 psi) and temperature (210 °F), API fluid loss values have significantly been decreased to values even lower than the required minimum (the highest and lowest reported values of 120 and 80 mL respectively for FLC 1 and 2). Hereafter, a brief overlook of the definition of each measured property and the possible deduction about the reported numbers in the related tables are presented.

In all the tables, two representative numbers are demonstrated for each cement slurry mixing condition, where the number in the left column is the minimum required standard for that characteristic in terms of its unit according to the standard measure of the instrument used. The number in the right column is for the FLC sample prepared in this study and utilized in the cement slurry samples according to the mixing conditions in Table 1. A longer thickening time, a longer pumping time, a higher compressive strength, and a smaller API fluid loss value mean the better and favored cementitious properties of the oil well cement. Hence, the slurry containing FLC is required to meet the minimum standard values in the tables.

The results of using the lignite graft copolymers as FLC’s 1 and 2 are listed in Table 2 and Table 3 respectively. As could be seen, the API fluid loss values in cement slurry sample 1-3 (at a pressure of 3000 psi) have exceeded the required amount, which consequently affects the thickening time and the compressive strength of the slurries. The thickening time and compressive strength of the cement slurries containing FLC’s failed to reach the required amounts. However, under higher temperature and higher pressure conditions in slurry samples 4 and 5, they improved significantly.

Table 2
Quality control results of the cement slurries containing FLC 1.

Mixing condition	1		2		3		4		5		6		7	
Properties	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample
Maximum initial viscosity (cP)	16 ±	15	18 ±	15	15 ±	15	15 ±	15	17 ±	17	18 ±	16	18 ±	15
Viscosity at 60 min (cP)	25 ±	25	25 ±	24	25 ±	24	25 ±	22	25 ±	22	25 ±	25	25 ±	25
Minimum pumping time (min)	25 ±	330	300 ±	330	300 ±	320	400 ±	400	400 ±	400	220 ±	250	240 ±	250
Minimum thickening time (min)	310 ±	280	310 ±	280	310 ±	280	410 ±	390	410 ±	390	230 ±	250	250 ±	260
Compressive strength after 24 hrs. (psi)	800 ±	800	800 ±	800	800 ±	800	800 ±	850	800 ±	800	1200 ±	1100	1000 ±	1100
API fluid loss (mL)	130	180	130	160	130	160	130	120	130	120	130	150	130	150

Increasing the amount of FLC used in slurry 5 can also be a key factor in this process. Table 3 presents the results of quality control of the cement slurries containing FLC 2. The presence of ACN monomer in the lateral graft chains in the synthesized graft copolymer has significantly improved the rheology properties of the cement slurry samples in comparison with FLC 1 in which AA was employed as the third monomer in the graft chains. API fluid loss was dramatically reduced in all the cement slurry mixing conditions. Notably, in cement slurries 4 and 5, which are under a high pressure (4000 psi) and a high temperature (210 °F), API fluid loss values have dramatically been decreased to values even lower than the required minimum (120 and 80 mL respectively). As a result, the values of compressive strength and thickening time have also been enhanced to the required maximum values (850 psi and 410 min respectively).

Table 3
Quality control results of the cement slurries containing FLC 2.

Mixing condition	1		2		3		4		5		6		7	
Properties	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample
Maximum initial viscosity (cP)	16 ±	16	18 ±	16	15 ±	16	15 ±	15	17 ±	18	18 ±	16	18 ±	16
Minimum viscosity at 60 min (cP)	25 ±	25	25 ±	25	25 ±	26	25 ±	25	25 ±	24	25 ±	23	25 ±	25
Minimum	300 ±	300	300 ±	300	300 ±	300	400 ±	410	400 ±	410	220 ±	250	240 ±	230

Mixing condition	1		2		3		4		5		6		7	
Properties	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample
pumping time (min)														
Minimum thickening time (min)	310 ±	300	310 ±	300	310 ±	300	410 ±	400	410 ±	420	230 ±	210	250 ±	220
Compressive strength after 24 hrs. (psi)	800 ±	800	800 ±	820	800 ±	820	800 ±	850	800 ±	850	1200 ±	1100	1000 ±	1100
API fluid loss (mL)	130	110	130	110	130	90	130	120	130	90	130	130	130	130

According to Table 4, the properties of the cement slurry employing FLC 3 additive were significantly improved in all the mixing conditions, especially in slurry samples 4 and 5 (high temperature, high pressure, and salinity). Significantly, the API fluid loss values of cement slurries 1-3 were obtained 70, 80, and 90 mL respectively. Their compressive strength was 900 psi and their thickening time was 410 minutes. More importantly, in the case of cement slurries 4 and 5, the API fluid loss of 100 and 90 mL respectively, the thickening time of 420 minutes, and the compressive strength of 900 psi indicate the superior performance of these FLC samples in controlling the properties of cement slurries. One justification could be that the reaction of lignite with sulfomethylating agents and increasing its solubility can improve its filtration properties in oil well cement slurries as a result of better interaction with clinker cement slurry phases, thereby reducing its dehydration.

Table 4
Quality control results of the cement slurries containing FLC 3.

Mixing condition	1		2		3		4		5		6		7	
Properties	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample
Maximum initial viscosity (cP)	16 ±	10	18 ±	10	15 ±	11	15 ±	10	17 ±	9	18 ±	9	18 ±	8
Minimum viscosity at 60 min (cP)	16 ±	32	25 ±	32	25 ±	30	25 ±	28	25 ±	28	25 ±	29	25 ±	28
Minimum pumping time (min)	30 ±	320	300 ±	320	300 ±	310	400 ±	450	400 ±	440	220 ±	280	240 ±	280
Minimum thickening time (min)	310 ±	400	310 ±	410	310 ±	410	410 ±	420	410 ±	420	230 ±	400	250 ±	400
Compressive strength after 24 hrs. (psi)	800 ±	900	800 ±	900	800 ±	880	800 ±	900	800 ±	900	1200 ±	1000	1000 ±	1000
API fluid loss (mL)	130	70	130	80	130	80	130	100	130	90	130	90	130	90

The results of the quality control of the slurry containing FLC 4, the SML graft copolymer, are tabulated

in Table 5. API fluid loss in all the slurry samples was significantly reduced compared to the FLC samples, in which the grafting reaction was performed on the lignite backbone dispersed in water. In the case of slurries 1 to 3 (under the same temperature and pressure conditions), API fluid loss values were 90, 90, and 80 respectively; a compressive strength of around 890 psi and a thickening time of about 400 minutes were also reported. In slurry samples 4 and 5, which are under more severe conditions (temperature, pressure, and salinity), it is obvious that the amount of fluid loss reported, i.e. 100 mL, was higher than that of slurries 1-3. Significantly, a compressive strength of 900 psi was also reported, and the thickening time increased up to 470 minutes.

This is ascribed to the synergistic effect of increasing the solubility of lignite backbone in water and the presence of acrylic monomers in the grafted copolymer structure. Both its interaction with the soluble clinker phase in the cement and the high temperature-brine tolerance of acrylic sulfonate copolymers (AMPS), as well as the presence of NNDMA as a crosslinking agent and the enhancement of the molecular weight of the grafting copolymer, have improved the properties of cement slurry in oil well conditions.

Briefly analyzing the rheological properties of the cement slurries based on the quality control tests reported in the above tables reveals that the viscosity of the prepared cement slurries is quite smaller than the required scales. In all the cement slurries, the viscosity does not exceed 160 cP, and the minimum value reported in Table 5 is 80 cP. Specifically, FLC 4 is by no means a viscosifying agent for the cement slurries. Hence, the synthesized FLC's behave more advantageous in high-density cement slurries regardless of the dosage applied. This could hopefully help prevent the coagulation of the cement slurries through the cement pipes in severe (HTHP) conditions and promise a successful cementing operation.

Table 5

Quality control results of the cement slurries containing FLC 4.

Mixing condition	1		2		3		4		5		6		7	
	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample	Required	Sample
Maximum initial viscosity (cP)	16 ±	14	18 ±	14	15 ±	14	15 ±	11	17 ±	11	18 ±	11	18 ±	9
Minimum viscosity at 60 min (cP)	25 ±	30	25 ±	31	25 ±	31	25 ±	28	25 ±	28	25 ±	22	25 ±	21
Minimum pumping time (min)	300 ±	320	300 ±	320	300 ±	310	400 ±	450	400 ±	450	220 ±	280	240 ±	280
Minimum thickening time (min)	310 ±	280	310 ±	370	310 ±	370	410 ±	450	410 ±	470	230 ±	280	250 ±	290
Compressive strength after 24 hrs. (psi)	800 ±	890	800 ±	890	800 ±	800	800 ±	900	800 ±	910	1200 ±	1000	1000 ±	1100
API fluid loss (mL)	130	90	130	90	130	80	130	100	130	100	130	90	130	80

From a comparative point of view, the results of the API fluid loss of the cement slurries employing the

additives produced in this work were compared with the ones in the literature in which their applied method was analogous to that introduced herein (Salami and Plank, 2012). The mixing conditions of cement slurries 6 and 7 are similar to those in the reference work; both use the same dosage of graft copolymer (0.3% BWOC), class G cement, and the same amount of retarder (1.2% BWOC). The demonstrated API fluid loss of the reference work in the mentioned conditions was 160 mL, while that of the cement slurries containing FLC's 1 and 2 was 130 mL, and that of the cement slurries containing FLC 4 was 80-90 mL. Furthermore, the performance of the additives of this research was compared with that of HTF-200C produced elsewhere (Guo and Bu, 2013). They prepared 10 different cement slurries using HTF-200C additive. The overall comparison between the highest values of cement slurries reported herein and that of the mentioned counterpart additive (HTF-200C) is represented in Figure 2.

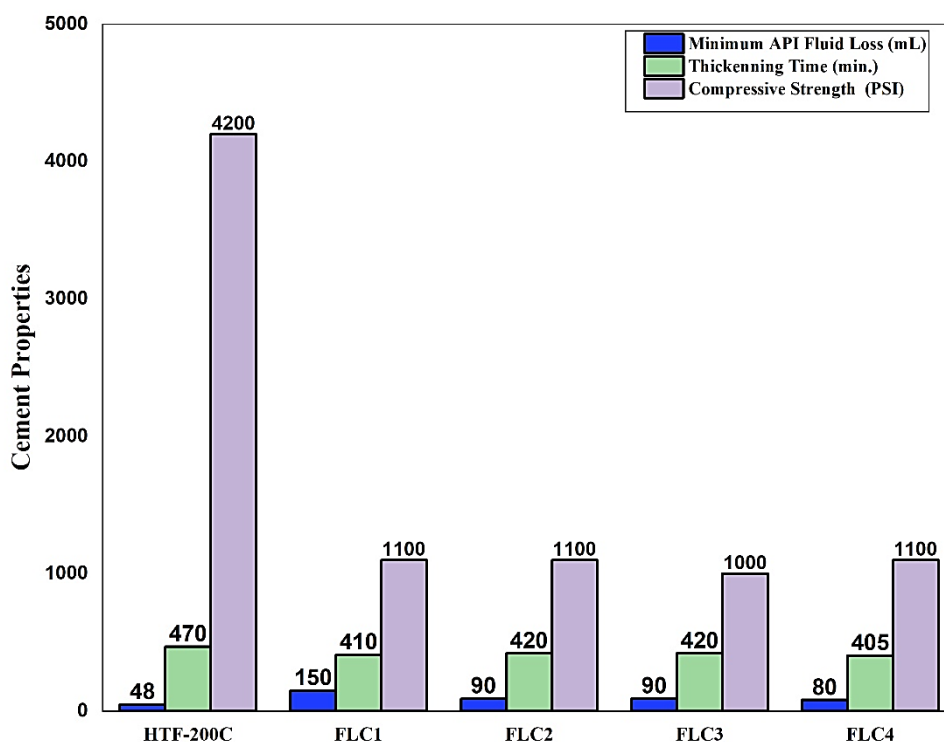


Figure 2

Comparison between the highest records of the cement slurries containing FLC's in the present work and those of another high quality additive HTF-200C reported in the literature (Guo and Bu, 2013).

Although the lower limit of thickening time reported herein, i.e. 280 minutes, was not comparable to that of HTF-200C, its higher limit in the case of the cement slurry containing FLC 4, i.e. 470 minutes, was comparable to that of HTF-200C (407 minutes). However, the compressive strength of HTF-200C was almost four times higher than that of the cement slurries containing FLC's in our work (4200 vs. 1100).

3.2. ATR-FTIR spectra

Determining the molecular structure of humic substances is so complicated. However, attenuated total reflectance infrared (ATR-IR) by using a Nicolet 560 Fourier transform infrared spectrometer was employed to characterize lignite-co-AMPS-NNDMA-ACN and the SML copolymer (SML-co-AMPS-NNDMA-AA). To this end, ATR-FTIR spectra were obtained from the raw lignite surface prior to

chemical modification and after grafting/sulfomethylation on its surface (FLCs 2-4).

As depicted in Figure 3, the characteristic bands for raw lignite are the stretching vibrations attributed to the R-COOH carboxylic group as well as Ar-OH phenolic groups at approximate frequencies ranging from 3500 to 3000 cm^{-1} , the stretching vibrations of the carbonyl group (amide groups and peptide groups on the surface of the humic acid structure) at 1615 cm^{-1} , highly intense peaks attributed to CO stretching at 1010 cm^{-1} . Specific absorption bands of grafted copolymers include symmetrical and asymmetrical stretching vibrations attributed to single and double sulfur-oxygen bonding (S=O and S-O due to sulfonic acid groups in the AMPS structure grafted on the lignite surface (as twin frequencies at approximately 1180 cm^{-1} , 1400 cm^{-1} and 1650 cm^{-1} respectively). The latter could be attributed to the RSO_3 formation as a product of sulfomethylating reaction in FLC's 3 and 4. Nitrile ($\text{C}\equiv\text{N}$) group is hydrolyzed in alkaline medium and converted to carboxylic acid or carboxylate salts. Thus, the absorbent bands of carboxylic acid (1010 cm^{-1} , 1615 cm^{-1} , and in the 3000-3500 cm^{-1} range) would have been observed instead.

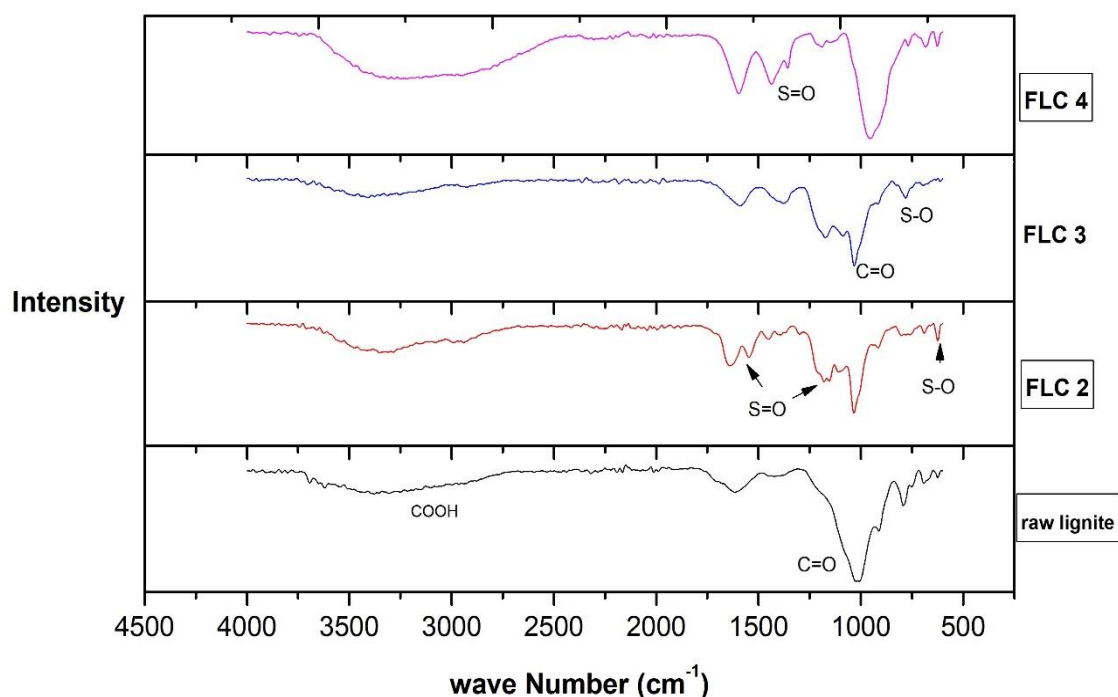


Figure 3

ATR-FTIR spectra of the FLC samples prepared in this study.

According to the literature (Assmann and Reichenbach-Klinke, 2014; Salami and Plank, 2016), the phenolic group present in humic acid, as the main constituent of lignite, allows the grafting of monomers through a hydrogen abstraction mechanism initiated by strong oxidants such as peroxydisulfates or Ce^{4+} , which is schematically depicted in Figure 4.

3.3. Elemental analysis (CHNS) of SML

The elemental analysis apparatus (Elementar-Germany) was employed to determine the amounts of elements in SML and in raw lignite. According to the data presented in Table 6, the weight percentage of sulfur in the raw lignite sample was 3.77% of the total sample weight, but it increased to 12.39% of the total sample in the SML. The weight percentage of carbon has also decreased from 21.44% to

15.99% of the total sample weight. This confirms the successful participation of the sulfone functional group (SO₃) in the lignite structure and the replacement of CH₂SO₃.Na with CH₂OH in the grafted chains, which could be verified through the ATR-FTIR spectrum of the SML as portrayed in Figure 1.

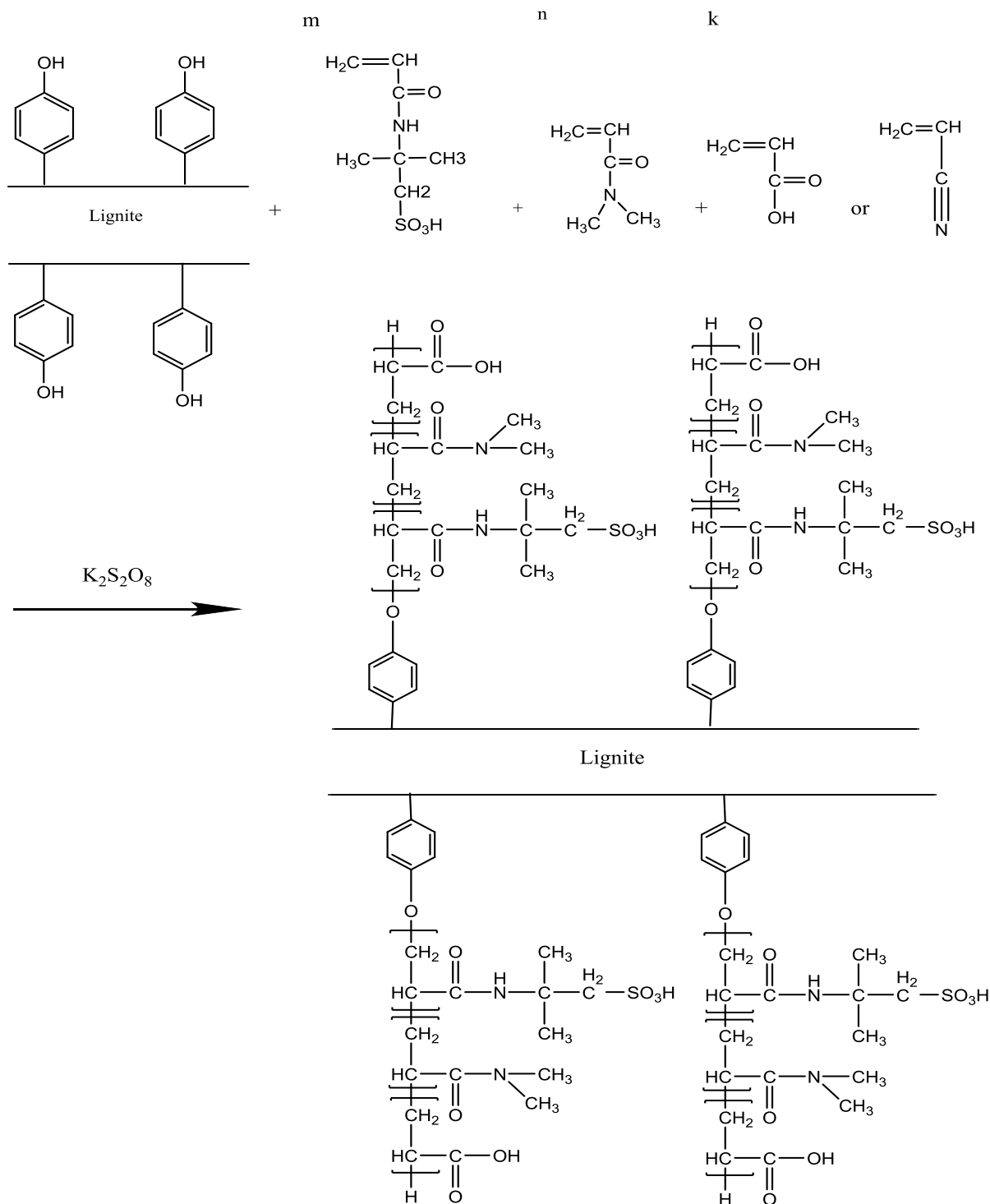


Figure 4

A schematic representation of the grafting reaction that produces the graft copolymers of lignite-co-AMPS-NNDMA-AA [adapted from Ilg, M. and Plank, J., 2016].

Table 6

Elemental analyses data of raw lignite and SML (FLC 3).

Element	Raw lignite found (mg)	SML-FLC 3 found (mg)	Raw lignite found (%)	SML-FLC 3 found (%)
N	0.031	0.032	0.18	0.1
C	3.603	4.955	21.44	15.9
H	0.045	0.087	0.27	0.28
S	0.634	3.861	3.77	12.39
Total (sample weight)	16.808	31.168	25.66	28.67

4. Conclusions

The highest performance of the cement slurries in order belonged to the graft copolymer of SML (FLC 4), the water soluble SML in sample 3, and the lignite graft copolymer in FLC sample 2. The way in which graft copolymers work is likely through adsorption on the cement particles and filter-cake permeability reduction according to the literature. As noted, the highest performance of the synthesized FLC's was attributed to FLC 4, which is probably due to the synergistic effect of lignite solubility enhancement and grafting side chains on its backbone simultaneously.

The study demonstrates that lignite and its analogues due to the presence of side hydroxyl groups can be engineered to become a suitable additive for high-density cement slurries capable of functioning in HTHP conditions. Moreover, the non-viscosifying behaviors of the FLC's in the slurries make them a suitable candidate for the successful applications in harsh conditions of cementing operations and prevent them from coagulation during cementing. Comparing the results of the current work with another FLC additive demonstrated that the FLC's in this study provided convenient fluid loss values under the same mixing conditions. Likewise, the API fluid loss of 80-90 mL in the case of FLC 4, containing enhanced soluble lignite graft copolymers, might indicate the effect of water solubility in the effectiveness of oil well cement additives.

Nomenclature

AA	Acrylic acid
AMPS	2-acrylamido-2-methyl propane sulfonic acid
ACN	Acrylonitrile
ATR-IR	Attenuated total reflectance infrared
<i>B_c</i>	Bearden units of consistency
BWOC	By weight of cement
BHCTP	Bottom-hole circulating temperature and pressures
cP	centipoise = 0.1 kg.m ⁻¹ .s ⁻¹
EDTA	Ethylene diamine tetra acetic acid
FLC	Fluid loss controller
HTHP	High temperature and high pressure
HTR	High temperature retarder
LTR	Low temperature retarder

NNDMA	N, N-dimethyl acrylamide
pcf	lb per cubic ft = 9.807 kN/m ³
psi	lb _f /in ² = 6895 N/m = 6.894757 kPa
SML	Sulfomethylated lignite
WOC	Weight on cement

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